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The vibrational spectra of alkyl isocyanates, isothiocyanates and thiocyanates

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THE VIBRATIONAL SPECTRA OF ALKYL ISOCYANATES, ISOTHIOCYANATES AND THIOCYANATES

by

Robert Paul Hirschmann

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In Charge of Major Work

Head of Major Department

Dean of Graduate College

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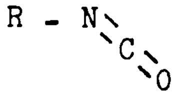
INTRODUCTION

The infrared spectra of organic isocyanates (I), isothiocyanates (II) and thiocyanates (III) have not been studied in detail. This is rather surprising in view of the extensive occurrence of these functional groups in compounds employed as fungicides, insecticides and in the preparation of urethane polymers. Isothiocyanates and the isomeric thiocyanates provide an interesting example of isomerism and permit a comparison of the effect of restricted rotation upon two distinct but still closely related functional groups. Isocyanates and isothiocyanates also offer a unique opportunity to compare very similar functional groups.

(I)



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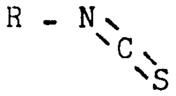

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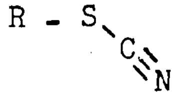


By far the major portion of the publications dealing with alkyl isocyanates, isothiocyanates and thiocyanates have been concerned with the respective methyl derivatives. However, there is considerable disagreement among the several vibrational analyses published for methyl isothiocyanate (15, 27, 28, 58). This is true also, but to a lesser extent, for the vibrational analyses on methyl thiocyanate (28, 58, 88). The sole paper (22) describing the vibrational spectrum of methyl isocyanate suffers considerably in accuracy from an inappropriate choice of optics. Only incomplete spectral information is available on the other alkyl derivatives.

In the present study complete vibrational analyses are presented for methyl, ethyl and isopropyl esters of isocyanic, isothiocyanic and thiocyanic acids. A vibrational analysis is also presented for tert-butyl isothiocyanate. Individual vibrational analyses result from consideration of the spectral characteristics found in a series of alkyl derivatives containing the same functional group. This is in sharp contrast to the usual literature presentation in which the vibrational analysis of a single compound is termed as representative for all of its homologues. Furthermore, this approach has necessitated consideration of restricted rotation about single bonds and its effect on group vibrations. In the study of rotational isomerism resulting from restricted rotation the comparison of spectra obtained from different physical states of a molecule has proven to be of great value.

GROUP FREQUENCIES

There are two distinct approaches to the study of the vibrational spectra of polyatomic molecules. Observed spectra, infrared and Raman, may be interpreted, through mathematical analysis, in terms of internal structural parameters and force constants relating the interactions between bonded and nonbonded pairs of atoms. An alternate and extremely useful approach involves the interpretation of the vibrational spectra in terms of group frequencies. In other words, assignment of specific vibrational frequencies to localized subgroups within the molecule. While the concept of group frequencies is a simplification, it does have a basis in theory (30). This investigation is primarily concerned with the group frequency approach. Accordingly, a clear insight is necessary concerning the origin and limitations of group frequencies.

Vibrational transitions in a molecule are discussed most simply by assuming that the atomic masses undergo only small amplitudes of vibration. Consequently, the potential energy, V, may be expanded in terms of a Taylor series in powers of the displacement coordinates q_i

$$V = V_o + \sum_i (\partial V/\partial q_i)_o q_i + \tfrac{1}{2} \sum_i\sum_j (\partial^2 V/\partial q_i \, \partial q_j)_o q_i q_j$$

$$1/3! \sum_i\sum_j\sum_k (\partial^3 V/\partial q_i \, \partial q_j \, \partial q_k)_o q_i q_j q_k \cdots$$

where the subscript zero indicates the derivatives are evaluated at the equilibrium position. Since the equilibrium position is characterized by a minimum for the potential energy, all the first derivatives are equal to zero. By convention, V_o, the potential energy in the equilibrium position is also equated to zero. Third and higher order terms represent anharmonicity corrections and in a first approximation need not be considered. As a result the expression for the potential energy then reduces to

$$2V = \sum_{ij} b_{ij} q_i q_j \qquad \text{where } b_{ij} = (\partial^2 V/\partial q_i \, \partial q_j)_o$$

A quadratic form

$$2T = \sum_{ij} a_{ij} \dot{q}_i \dot{q}_j \qquad \text{with } \dot{q}_i = (\partial q_i/\partial t)$$

is also found for the kinetic energy, T. Substitution of the relationships for the kinetic and potential energy of a vibrating molecule into the Lagrangian equations of motion

$$\frac{d}{dt}(\partial L/\partial \dot{q}_i) - (\partial L/\partial q_i) = 0 \qquad i = 1,2,3 \ldots 3n-6$$

where L=T-V, results in a set of 3n-6 simultaneous, homogeneous linear equations (see Appendix A). Nontrivial solutions of the resulting secular determinate

$$\left| b_{ij} - \lambda a_{ij} \right| = 0 \qquad \text{where } \lambda = 4\pi^2 \nu^2$$

yields frequencies ν_i corresponding to the normal modes of vibration. Solutions of the secular determinate will be functions of atomic masses, internal bond angles and force constants.

Only in an extremely few cases is it possible to directly calculate the value of the potential constants in a purely theoretical manner. In most molecules the potential constants b_{ij} must be found from experimental data. However, if the most general expression for V is assumed, the number of force constants to be determined exceeds the number of observed frequencies. Consequently some assumption must be made as to the form of force field model used to describe the molecule.

In the central force field the only force acting on a given atom in a molecule is the resultant of the attractions and repulsions by all the other atoms. This is equivalent to assuming that the potential energy is purely a quadratic function of the displacement coordinates, q_i, associated with the internuclear distances without cross products.

$$2V = \sum_i b_{ii} q_i q_i$$

it should be noted that this force field is inadequate for an accurate description of the vibrational frequencies of a linear triatomic molecule. For example, in carbon dioxide there will be restoring forces against stretching the individual C-O bonds and expansion of the O-O distance. Taking into account symmetry, $b_{11} = b_{22}$, the potential energy is given by

$$2V = b_{11}\,(q_1^{\,2} + q_2^{\,2}) + b_{33}\,q_3^{\,2}$$

where q_1 and q_2 are associated with the C-O bonds and q_3 is the displacement coordinate associated with the O-O distance. Solution of the secular determinant will then yield a null frequency for the doubly degenerate bending vibrations since this force field does not include a restoring force perpendicular to the O-C-O axis. Likewise, the central force field model is unable to predict the out-of-plane vibrations of a planar polyatomic molecule.

A more successful model is the valence force field. In its simplest form the valence force field assumes restoring forces opposing changes in valence bonds and also changes in the angle between two valence bonds connecting one atom with two others. With respect to carbon dioxide the potential energy is

$$2V = a_{11}(q_1^{\,2} + q_2^{\,2}) + a_{33}\,\delta^2$$

where q_1 and q_2 are defined as above and δ is the valence coordinate related to a change in the O-C-O bond angle. More refined applications of the valence force field include cross terms between the angle deformation and bond stretching displacement coordinates.

Another basic force field was proposed by Urey and Bradley and contains not only the restoring forces found in the basic valence force field but also terms corresponding to repulsive forces between nonbonded atoms. Frequently the Urey-Bradley force model will contain more constants than observable frequencies and additional assumptions must be made.

As indicated above, the force field model that is chosen to represent the molecule will determine the number and form of force constants b_{ij}. However, within the assumption of a specific force field it has been conclusively shown that there exists a transferability of force constants between molecules having similar structures (16, 30, 60).

A given diatomic unit, X-Y, will thus be associated with an invariant bond stretching force constant in related molecules. From this invariance in force constant the normal modes primarily associated with the stretching of the X-Y bond should then exhibit the same or very similar frequencies in related compounds. Likewise, the transferability of force constants opposing changes in angles between two valence bonds leads directly to a group frequency concept for bending or deformation modes.

The invariance of force constants does not imply a complete invariance of group frequencies. If this were the case much of the usefulness of infrared and Raman spectroscopy as an interpretive tool in molecular structure work would be lost. The sensitivity of group frequencies to changes in state, crystal form, solvent-solute interactions and inter and intra molecular hydrogen bonding has been discussed thoroughly (7). Of greater interest in this investigation is the sensitivity of group frequencies to internal structural changes. It has been shown (30) that if all bonds were mutually orthogonal, vibrational coupling would not occur between adjacent bonds. However, in practice orthogonality of bonds is rare and some coupling will always occur. Subtle differences in internal structure due to restricted rotation about single bonds will thus be reflected in variations of group frequencies. A case of special interest, which will be discussed at length later, is the sensitivity of the C_α -X[1] vibration to internal rotation about the C_β -C_α bond. Vibrational coupling will increase as the similarity between adjacent bonds increases, being greatest for exactly equivalent bonds. Hence, in long chain alkanes there will not be one characteristic CC stretching frequency but as many frequencies as CC bonds, and these will be distributed over a rather wide frequency range. The general criterion for a minimum of coupling and consequently the greatest adherence to the group frequency concept is summarized in the following rule: Either the

---

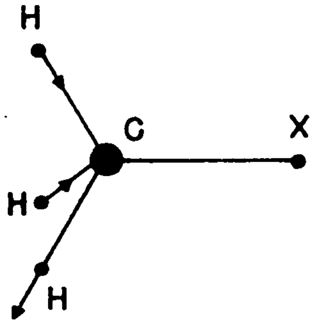
[1] Since the discussion of restricted rotation will involve primary, secondary and tertiary substitution of the functional group X, the notation alpha rather than one is preferred for the carbon atom directly bonded to X. Successive carbon atoms are then denoted beta, gamma, etc.

force constants in successive bonds or the masses of adjacent atoms in a chain like molecule must differ considerably in magnitude for truly localized group frequencies to occur.

The discussion of group frequencies has been thus far limited to valence stretching and angle deformation vibrations. A useful extension of this concept has been made for adjacent C-H bonds. Adjacent CH groups will of course produce several normal frequencies. In the case of methyl and methylene units the resulting vibrations have been thoroughly studied and assigned to specific couplings, permitted by symmetry, of the individual C-H bonds. Figures 1 and 2 present schematic versions of the highly characteristic methyl and methylene vibrations. The notation system employed in later discussions is also indicated. Analogous forms have been proposed for NH_2, NH_3 and similar polyatomic groups containing hydrogen. Also the literature contains reference to skeletal stretching modes for highly branched systems of heavier atoms. For example, symmetric and asymmetric N-C stretching vibrations in trimethylamine are of the same form as the corresponding stretching vibrations in the methyl group.

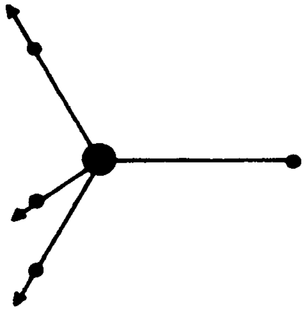
As previously stated the discussion and assignments of the spectra of alkyl isocyanates, isothiocyanates and thiocyanates will be in terms of group frequencies. Valence stretching vibrations will be denoted by the Greek symbol ν

Figure 1. Normal vibrations of the methyl group



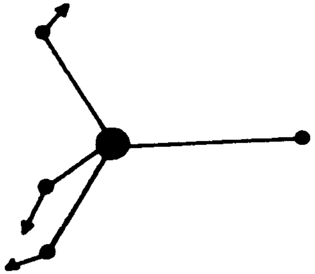
ν_{as} CH$_3$

A.



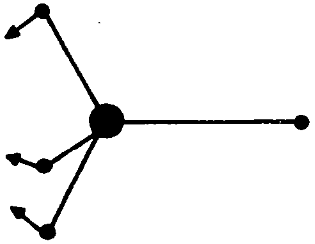
ν_s CH$_3$

B.



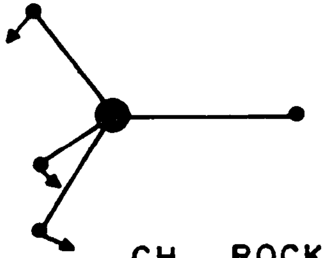
δ_{as} CH$_3$

C.



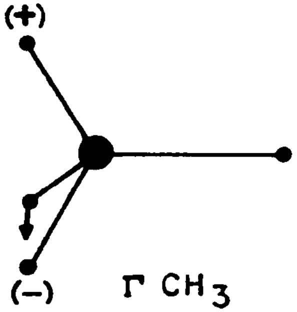
δ_s CH$_3$

D.



CH$_3$ ROCK

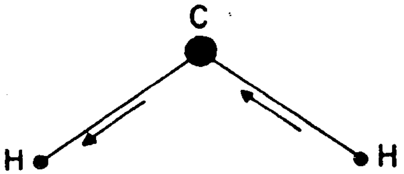
E.



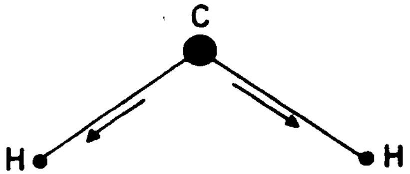
Γ CH$_3$

F.

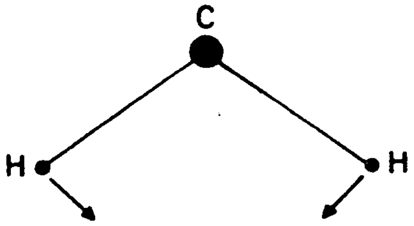
Figure 2. Normal vibrations of the methylene group



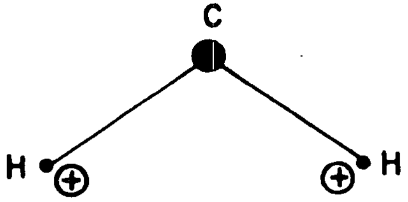
A. ν_{as} CH_2



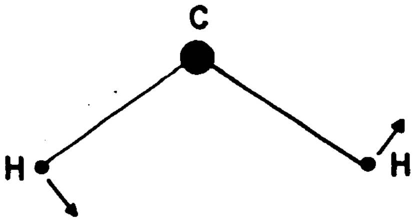
B. ν_s CH_2



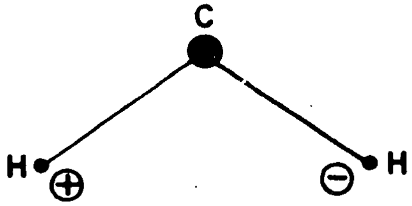
C. CH_2 BEND



D. CH_2 WAG



E. CH_2 ROCK



F. CH_2 TWIST

and angle deformation vibrations by δ . The symbols employed to designate methyl or methylene vibrations are indicated in Figures 1 and 2. In-plane and out-of-plane deformation vibrations, with respect to a plane of symmetry, will have an additional subscript $\parallel$ or $\perp$, respectively.

Symmetry classes for normal modes of vibration and combinations of normal modes shall be denoted in the manner proposed by Herzberg (30). Capital case letters shall be employed to specify the symmetry of a combination or overtone energy level and small case letters shall be employed to specify the symmetry class of a fundamental.

INTERNAL ROTATION

The principle of free rotation about single bonds was founded upon a lack of separable isomeric species for molecules such as 1,2-dichloroethane. Free rotation does not imply either a continuous rotation or that all orientations are of equal a priori probability. It does imply that transitions between any preferred orientations are both rapid and reversible. Early studies on restricted rotation were concerned with sterically hindered molecular systems, a case in point being the separation by Kenner and Turner (44) of the rotational isomers of 2,2'-dimethyl-6,6'-dicarboxydiphenyl.

Kemp and Pitzer (42, 43) observed that a serious discrepancy of 1.57 E. U. occurred between the entropy of ethane as determined calorimetrically (90) and the calculated value (41, 56), based upon a statistical thermodynamic model with freely rotating methyl groups. In addition they noted that a significant difference was present between the experimental (45) and theoretical (82, 84) values for the heat of hydrogenation of ethylene. The theoretical calculations were again based upon a model for ethane which included freely rotating methyl groups. Since the experimental values seemed reliable, the statistical model employed in the theoretical calculations was altered to include an internal barrier. From the difference in entropy, Kemp and Pitzer found an internal barrier of 3.15 kcal. per mole.

The spectroscopic detection of chemically inseparable rotational isomers occurred somewhat earlier than the thermodynamic investigations on ethane. Kohlrausch (47) interpreted the unexpectedly complex Raman spectra of n-propyl halides as indicative of discrete rotational isomers in the liquid state. Mizushima, Morino and Nojiri (62) showed that a simplification in the infrared spectra occurs during the transition from liquid to solid state as a result of preferential stability of one isomeric form. Hornig (34) has pointed out that a similar simplification may occur as a result of a change in selection rules since the symmetry of the unit cell, not of the isolated molecule, determines the nature of these rules. Mizushima's observation still form the basis for most spectroscopic investigations on rotational isomerism.

Internal barriers against free rotation about single bonds are defined by their symmetry properties, barrier heights and differences in potential energy between successive minima. The origin of these barriers are at best only imperfectly understood and will not be discussed here. Barrier symmetry reflects the rotational symmetry about the axis of internal rotation. Molecules such as ethane, methyl alcohol and ethyl chloride have threefold symmetric barriers. This reflects the equivalence between the eclipsed forms and similarly between the three low energy staggered forms.

This is also reflected in the lack of rotational isomers for these molecules. 1,2-dichloroethane also has a three-fold internal barrier. However, the eclipsed configurations are not equivalent, and even more important, neither are the staggered configurations. Consequently, two distinct minima are observed in the potential barrier. This results in two rotationally isomeric configurations. In molecules with some symmetry the two configurations can often be denoted as gauche or trans.

Raman and infrared spectoscopy have been employed in the determination of the energy differences between rotationally isomeric species. Consider the equilibrium between two such species

$$C \rightleftharpoons D$$

where C is the more stable isomer. Integration of the Gibbs-Helmholtz equation yields

$$K_{eq} = N_D/N_C = (\text{constant}) \exp(-\Delta H^o/RT)$$

with the standard enthalpy difference, ΔH^o, being positive and measured with respect to the more stable isomer. Langseth and Bernstein (50) have shown that the integrated intensity, A, of an absorption band is given by

$$A = \int \ln(I_o/I)\, d\nu = 8\pi^3 N\nu |M|^2/3hc$$

with $|M|^2$ being the transition moment. The ratio of integrated intensities for absorption bands originating in species A and B can therefore be directly related to ΔH^o.

$$\ln (A_D/A_C) = -\Delta H^o/RT + \text{constant}$$

The usual method of determining ΔH^o is to measure the ratio A_D/A_C at various temperatures. The resulting data is either graphically analyzed or a least squares method is employed.

Application of standard statistical thermodynamic methods to the vapor state results in a similar equation for ΔE_o^o, the energy difference at zero degrees Kelvin.

$$N_D/N_C = (f_D/f_C) \exp (-\Delta E_o^o/RT)$$

f_C and f_D are the partition functions for the isomeric species. The Langseth-Bernstein relationship for A is equally valid for the vapor state. However, it should be noted that the harmonic oscillator contribution to the partition function is temperature dependent and results in a slightly smaller value for ΔE_o^o as compared to ΔH^o.

Calculation of ΔH^o was possible for ethyl and isopropyl thiocyanate in the liquid state. Mizushima (61) has interpreted similar ΔH^o values as equivalent to ΔE^o. This assumes that the ΔPV term is relatively small and is probably a valid assumption for the liquid state.

THE C_α -X STRETCHING VIBRATION

The sensitivity of group frequencies to subtle changes in internal structure is especially apparent in the case of the C_α -X stretching vibration, $\nu(C_\alpha$ -X). Extensive studies have been published on the dependence of ν (C_α -X) in alkyl halides and thiols upon the restricted rotation about the C_α -C_β bond (10, 78) and on substitution of the alpha carbon (73, 74, 75, 76). Mizushima and his colleagues (63) have employed these observations as an interpretive tool in polymer structure investigations. Several important assignments in the vibrational spectra of alkyl isothiocyanates and thiocyanates are made as a consequence of the dependence of ν (C_α -X) on internal structural changes. Hence, a review is necessary on the spectral characteristics of (C_α -X) in order that these key assignments be understood and accepted.

Sheppard has presented vibrational analyses for ethyl, isopropyl and tert-butyl halides and thiols in a series of papers (73, 75, 76). As is readily seen in Table 1, there is a consistant decrease in frequency for ν (C_α -X) corresponding to successive substitution of methyl groups on the alpha carbon. If these shifts in frequency result from a weakening of the restoring force in the C_α -X bond, a simultaneous increase in the C_α -X bond distance should be observed in going from a methyl to a tert-butyl derivative.

Table 1. Characteristic Cα -X stretching frequencies in alkyl halides and thiols

Compound	Frequency (cm^{-1}) [a] $\nu(C_\alpha$ -Cl)	$\nu(C_\alpha$ -Br)	$\nu(C_\alpha$ -I)	$\nu(C_\alpha$ -S)
CH_3X	712	594	522	704
CH_3CH_2X	656	560	500	660
$(CH_3)_2CHX$	615	536	495	630
$(CH_3)_3CX$	570	514	490	587

[a] Data for ethyl, isopropyl and tertiary butyl derivatives were obtained from Sheppard's papers (73, 75, 76) while that for the methyl derivatives from Kohlrausch (46).

However, microwave and electron diffraction data (59) for methyl, ethyl, isopropyl and tert-butyl chlorides and bromides do not show the expected increase in bond length. Hence, the shift in frequency is more probably explained in terms of an increase in the effective mass of the alpha carbon.

Brown and Sheppard (10) have conclusively shown that the different isomeric configurations of alkyl halides resulting from restricted rotation about the C_α -C_β bond can be characterized by their C_α -X stretching frequency. Shipman, Folt and Krimm (78) recently extended these observations in an very comprehensive manner for alkyl chlorides. Previous to discussion of their assignments it is advisable to restate the nomenclature proposed by Mizushima (63) to distinguish the various configurations about the C_α -C_β bond. Although the terminology is quite general in application it will be discussed as it applies to alkyl chlorides. According to this system P, S and T specify the chemical type of chloride; primary, secondary and tertiary, respectively. The subscript H indicates that the chlorine is trans to a hydrogen atom and the subscript C specifies that the chlorine atom is trans to a "gamma" carbon atom.

For primary chlorides it is desirable to denote, by use of primes, the number of carbon atoms gauche to the chlorine atom. Therefore, the only structure possible for ethyl chloride is denoted by P_H and the two structures possible for n-propyl chloride are P_C and $P_{H'}$. The two structural

Table 2. Characteristic C_α -Cl stretching frequencies in primary alkyl chloride configurations

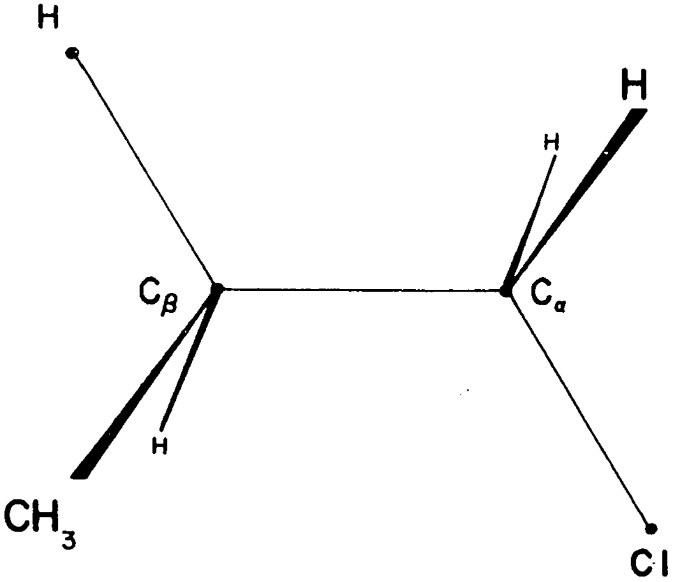
Configuration Term	Average Frequency (cm^{-1})[a]	Number of Compounds Studied
$P_{C''}$	723	1
$P_{C'}$	728 ± 1	3
P_C	728 ± 3	10
$P_{H''}$	682 ± 3	3
$P_{H'}$	651 ± 3	10
P_H	657	1

[a] Data from Shipman, Folt and Krimm (78).

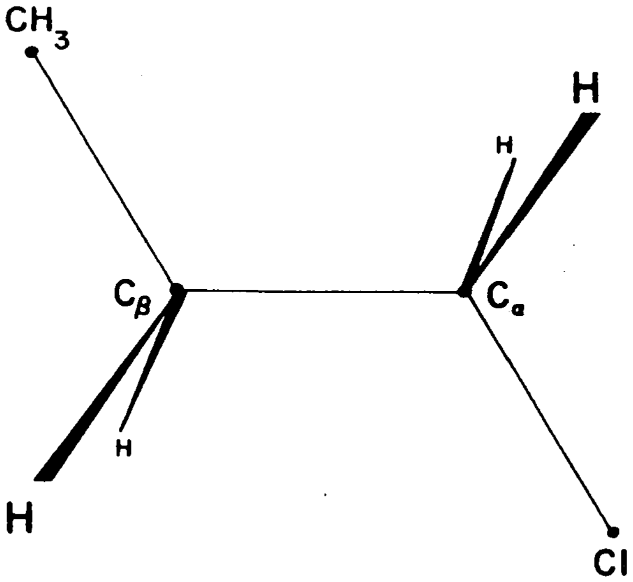
forms of n-propyl chloride are shown in Figure 3. A summary of the C_α-Cl frequencies found by Shipman, Folt and Krimm for the various primary chloride configurations is given in Table 2. The P_C configuration is characterized by a frequency about 725 cm^{-1} irrespective of the presence of gauche carbon atoms. In contrast the P_H configurations do show a marked, albeit nonuniform, sensitivity to gauche carbon atoms. It is difficult to explain the absence of a significant difference between the P_H and $P_{H'}$ configurations in face of a 30 cm^{-1} difference between $P_{H'}$ and $P_{H''}$.

Secondary alkyl chlorides can be described in an analogous manner except that two subscripts are required to specify the trans atoms. For example, the sole configurations permitted for isopropyl chloride and 3-chloro-2,2,4,4-tetramethyl pentane are S_{HH} and S_{CC} respectively. In addition it is necessary to alter the use of primes in the notation scheme as applied to secondary derivatives. Two distinct S_{HH} configurations are possible for 2-chlorobutane and higher homologues. In one isomeric form the first four carbon atoms are planar while in the other they are bent. The planar and bent configurations are designated as S_{HH} and $S_{HH'}$, respectively. Table 3 contains a summary of the characteristic frequencies found (78) for secondary alkyl chlorides. As seen previously for primary chlorides the replacement of a trans hydrogen with a carbon atom will

Figure 3. Isomeric configurations of n-propyl chloride



TRANS P'_H



TRANS P_C

Table 3. Characteristic C_α-Cl stretching frequencies in secondary alkyl chlorides

Configuration Term	Average Frequency $(cm^{-1})^a$	Number of Compounds Studied
S_{CC}	754 ± 5	2^b
S_{CH}	668 ± 5	11
$S_{HH'}$	631 ± 4	6
S_{HH}	610 ± 2	11

[a] Data from Shipman, Folt and Krimm (78).

[b] Only the first ten compounds listed in Table 2 of reference 78 have unambigous assignments for the S_{CC} configuration.

cause an upward shift in frequency of 50 to 70 cm^{-1}. Comparison of the values obtained for S_{CC} and S_{CH} configurations indicates that the effect is almost additive.

Tertiary chlorides require three subscripts to completely define the configuration about the three C_α -C_β bonds. Neglecting chain bending and branching at sites removed from the carbon chlorine bond, the existence of four rotationally isomeric forms might be expected for tertiary chlorides. Of the four configurations, T_{CCC}, T_{CCH}, T_{CHH} and T_{HHH}, the first two seem improbable due to steric hinderence. Tertiary butyl chloride has a single isomeric configuration, namely T_{HHH}. Again in Table 4 the replacement of a trans hydrogen with a carbon elevates the C_α -X stretching frequency approximately 53 cm^{-1}.

Table 4. Characteristic C_α-Cl stretching frequencies in tertiary alkyl chlorides

Configuration Term	Average Frequency (cm^{-1})[a]	Number of Compounds Studied
T_{CCC}		0
T_{CCH}		0
T_{CHH}	620 ± 5	6[b]
T_{HHH}	567 ± 6	7[b]

[a] Data from Shipman, Folt and Krimm (78).

[b] The eighth compound listed in Table 3 of reference 78 has only tentative assignments for the C_α-Cl vibrations.

Sheppard's findings on the decrease in frequency of ν (C_α-X) with substitution of successive methyl groups on the alpha carbon can be extended to cover configurations with the same number of carbon atoms trans to the chlorine atom. The following sequences can be derived from Tables 2, 3 and 4:

1. $P_C > S_{CH} > T_{CHH}$
2. $P_H > S_{HH}$ or $S_{HH'} > T_{HHH}$

Within a given chemical type of chloride there is an increase in frequency in going from a trans hydrogen to a trans carbon configuration. A special effect is observed for P_H forms where the number of gauche carbon atoms effects the C_α-Cl stretching frequency. A similar effect is not observed for secondary, tertiary or even P_C chlorides. While the most extensive work has been published on alkyl chlorides analogous results have been recorded for alkyl bromides (11, 65), iodides (10) and thiols (1,2). However, it is interesting to note that this line of investigation has not been pursued with respect to C_α-N and C_α-O bonds. Perhaps, of even greater interest is the absence in the literature of a quantitative explanation for the observed frequency variation of $\nu(C_\alpha\text{-}X)$.

BAND SHAPE AND PHYSICAL STATE

Vapor State

As a result of the free rotation by molecules in the vapor state, fine structure is introduced into vibrational absorption bands reflecting changes in rotational energy accompanying vibrational transitions. Since the contours of the rotation-vibration band system vary considerably with molecular structure the observed bands represent an important indication of the molecular structure. Most often the rotation-vibration band system is made up of P, Q and R branches corresponding, in addition to a change in vibrational energy level, to a change in rotational quantum number of -1, 0 or +1, respectively. The relative intensity of the P, Q and R branches are determined by selection rules based upon the symmetry of the vibration and the ratio of the moments of inertia, I_A, I_B and I_C, about the three principal axes of the molecule.

Inasmuch as the occurrence of discrete rotational fine structure depends on small moments of inertia it is only useful to study the vapor state spectra of relatively small molecules. Consequently, only the vapor state spectra of methyl isocyanate, isothiocyanate and thiocyanate will be interpreted. All three methyl derivatives are asymmetric tops since $I_A \neq I_B \neq I_C$.

Since two of the moments of inertia are almost equal and much larger than the third, these molecules may also be considered as pseudo-symmetric tops. It is thus appropriate to discuss in detail the band shapes characteristic of symmetric and asymmetric tops.

Symmetric top

A true symmetric top has two equal moments of inertia, denoted I_B, and a third and somewhat different moment of inertia I_A. The vibrational and rotational energy for such a molecule is given by (30)

$$T(v_i, J, K) = G(v_i) + F(J, K)$$

where G and F are the term values for the vibrational and rotational energies and v_i, J and K are the corresponding quantum numbers. More specifically, the rotational energy is

$$F_v(J, K) = B_v J(J + 1) + (A_v - B_v)K^2$$

with the rotational constants being the average values for an entire vibrational cycle of a given normal mode. The constants A_v and B_v differ slightly from the values A_e and B_e calculated from the equilibrium configuration.

It can be shown (30) that the shape of an individual rotation-vibration band system depends upon the direction of the change of dipole moment (transition moment) for the vibrational transition with respect to the figure or symmetry axis. Each of the three possible orientations between the transition moment and figure axis gives rise to a highly specific shape for the rotation-vibration band system. The terms parallel, perpendicular and hybrid which are used to denote the three band systems, originate from the description of the orientation of the transition moment with respect to the figure axis.

As a result of the selection rules

$$\Delta K = 0; \quad \Delta J = 0, \pm 1; \qquad K \neq 0$$
$$\Delta K = 0; \quad \Delta J = \pm 1 \qquad K = 0$$

for a parallel type band, three distinct series of lines occur giving rise to discrete P, Q and R branches. The most distinctive feature of a parallel type band is the prominent needle like central maxima of the Q branch, either at or very close to the median between the broader P and R branches.

If the transition moment is perpendicular to the figure axis a different set of selection rules are in effect, namely

$$\Delta K = \pm 1; \quad \Delta J = 0, \pm 1.$$

Even neglecting rotation-vibration interactions, the subbands, arising from transitions between levels with the same J but different in ΔK being +1 or -1, do not coincide. As a result the P and R branches form a continuous unresolved broad band envelope. The Q branch forms a series of equidistant "lines" separated by $2(A_v - B_v)$ and superimposed on the P-R envelope. If the moment of inertia about the figure axis is considerably smaller than the moments about the other two axes the separation between the Q "lines" becomes quite distinct.

Rotation-vibration interactions cannot be ignored if the vibrational transition involves a degenerate level. Then the effect of Coriolis coupling must be included in the expression for the rotational energy. The rotational energy is given by (30)

$$F_v(J, K) = B_v\, J(J + 1) + (A_v - B_v)K^2 \pm 2A_v\, \xi K$$

where ξ is the eigenvalue for the angular momentum due to Coriolis coupling between the degenerate levels. A brief description of this type of coupling is given in Appendix C. As a result of Coriolis coupling the separation between individual Q branches will be $2(A_v(1-\xi) - B_v)$. ξ can range between -1 and +1 and while it is a constant for any given vibrational mode it will vary considerably for different vibrations in the same molecule. Table 5 shows the Coriolis coupling constants for the degenerate vibrations in the vapor spectra of the methyl halides. Examples of the parallel and perpendicular band systems of a symmetric top (methyl iodide) are shown in Figure 4.

In a manner quite analogous to the formation of ortho and para hydrogen, the methyl halides and similar molecules consist of two modifications, A and E. While for these

Figure 4. Parallel and perpendicular bands of a symmetric top (methyl iodide)

(A) parallel band

(B) perpendicular band

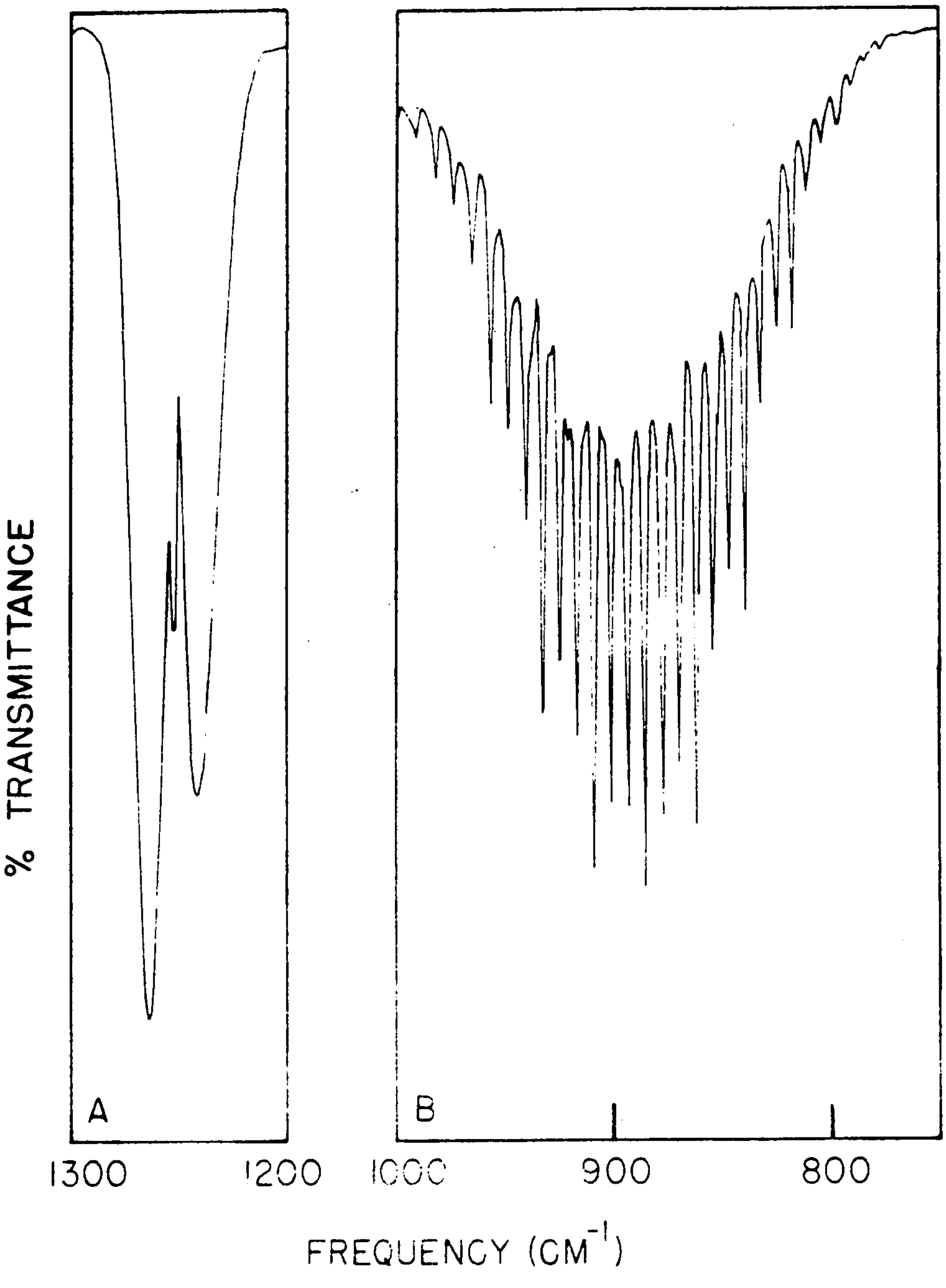

% TRANSMITTANCE
A
B
1300
1200
1000
900
800
FREQUENCY (CM^{-1})

Table 5. Coriolis coupling constants for the degenerate modes of the methyl halides (30)

Compound	Vibration $\nu_{as}CH_3$	$\delta_{as}CH_3$	CH_3 rock
CH_3-F	-0.099	-0.294	0.280
CH_3-Cl	0.100	-0.273	0.222
CH_3-Br	0.053	-0.232	0.208
CH_3-I	0.058	-0.216	0.187

modifications all possible rotational levels can occur, different statistical weights accrue to the levels. Consequently a characteristic intensity pattern of strong, weak, weak, strong occurs for the Q "lines" in a perpendicular band. This intensity pattern is observable in Figure 4.

The third type of band is a hybrid between the first two. Frequently this type of band system does not exhibit any P, Q or R structure, only a broad band envelope.

Asymmetric top

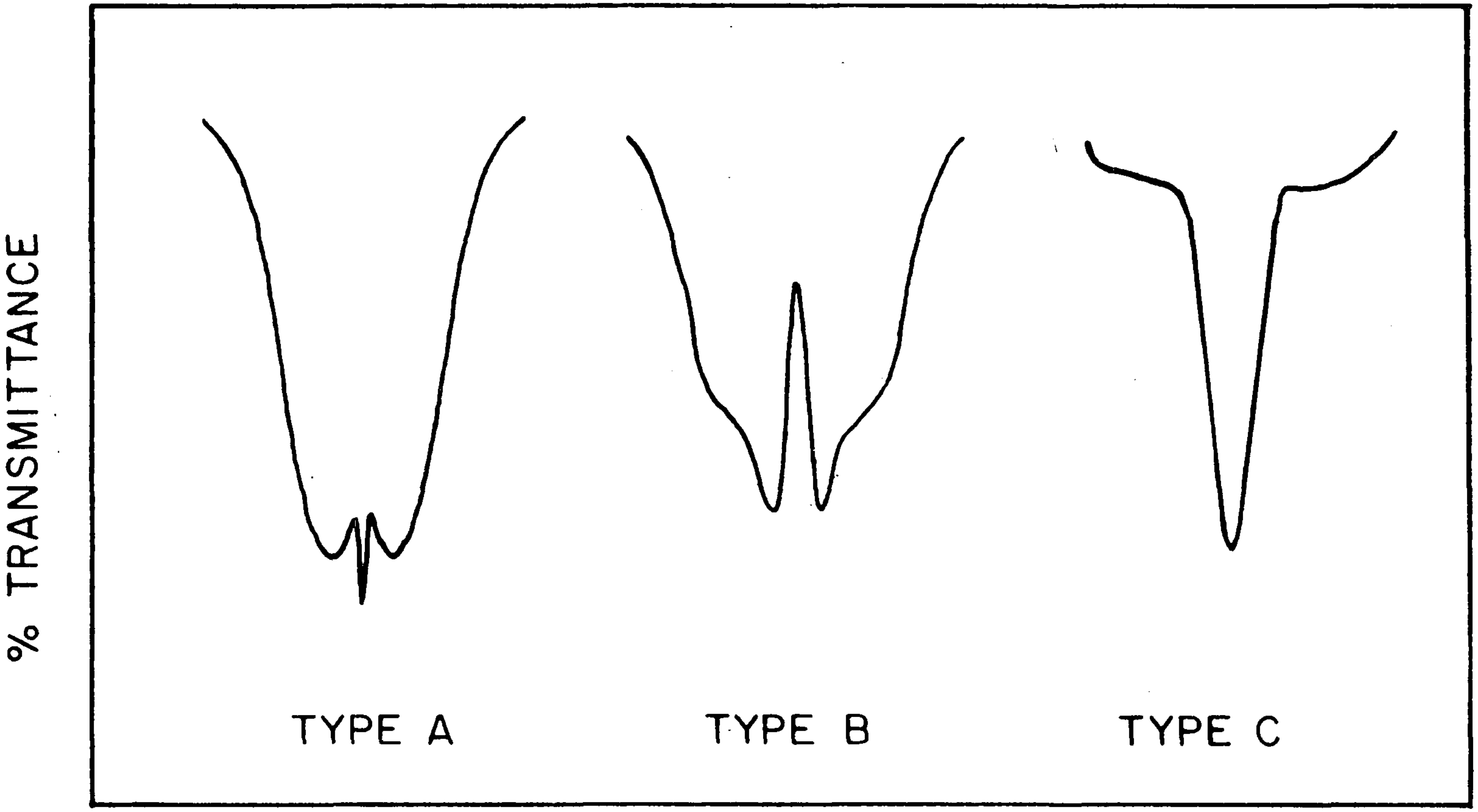
The three moments of inertia are assumed to be such that $A_e > B_e > C_e$. As with a symmetric top the ratio of the moments of inertia determine the band shape. The band types are classified with respect to the axis parallel to the transition moment. Therefore the band systems are denoted A, B and C. Actual band shapes for the three band types must be discussed in terms of ρ, the ratio of the moments of inertia I_A and I_B. For small values of ρ type A bands are similar in form to the parallel bands of the symmetric top with well defined P and R branches and a needle like central Q branch. The similarity holds even for moderate values of ρ. At the limiting values of ρ, i.e., 0 and 1, type B bands generate into the perpendicular bands of a linear molecule and a symmetric top respectively. Therefore unlike type A bands, type B bands do not exhibit a central maxima for any value of ρ. For very small values of ρ type C bands are quite similar to type B. However, even for small values of ρ, a Q branch begins to dominate the rotation-vibration band system. Schematic representation of typical band shapes found for an asymmetric top appear in Figure 5.

It will be shown later that both methyl isocyanate and methyl isothiocyanate exhibit a vapor state spectrum characteristic of a symmetric top. In contrast methyl thiocyanate seems to be a asymmetric top.

Liquid State

Considerable spectroscopic evidence has been obtained supporting the hypothesis that certain molecules conserve essentially free rotation in condensed states. While almost all of the investigations to date have been concerned with small molecules and free rotation of the entire molecule,

Figure 5. Type A, B and C bands of an asymmetric top


% TRANSMITTANCE
TYPE A
TYPE B
TYPE C

Jones and Sheppard (39) have interpreted the liquid state spectra of nitromethane and toluene in terms of free rotation of the methyl group.

Lascombe, Huong, and Josien (51) studied the infrared spectra of a large number of diatomic molecules in nonpolar and polar solvents. They concluded that in these solutions there are effectively two types of solute molecules. One type has essentially retained its freedom of rotation and absorption bands originating from this species will have broad wings closely analogous to the entire vibration-rotation band system of the vapor state. The second species of solute molecule has its rotation completely inhibited and gives rise to sharp "Q" like absorption bands. As a result the observed absorption bands will be a superposition of the bands originating in each species. They found that in polar solvents, in which free rotation would be most effectively quenched, that the observed bands generally acquired a simpler form, consisting of a central maximum without shoulders on either side.

With respect to free rotation in solution the methyl halides offer a unique series of compounds. Since the moment of inertia about their symmetry axis is rather small, e.g., the order of magnitude found for diatomic molecules, free rotation about this axis might well remain largely unaffected in solution. In addition, it is highly improbable that free rotation about the other axes can exist in solution. The fundamental vibrations of the methyl halides are of two types, nondegenerate modes with a transition moment parallel to the figure axis and doubly degenerate modes with their transition moment perpendicular to the figure axis. In the vapor state spectra these vibrations give rise to parallel and perpendicular type bands of the symmetric top. As stated above the perpendicular bands show considerable Coriolis coupling. If free rotation is conserved only about the figure axis it is expected that the degenerate vibrations should produce absorption bands that are considerably broader than those arising from the vibrations whose transition moment is parallelwith the figure axis. In addition the absorption bands from the degenerate modes should exhibit different band widths at half-peak height as a result of Coriolis coupling. The observed band widths for the methyl halides in a carbon tetrachloride solution are given in Table 6. It is readily observable that the absorption bands from the degenerate modes, $\nu_{as}CH_3$, $\nu_{as}CH_3$ and CH_3 rock, are considerably broader than those from the nondegenerate modes. Jones and Sheppard (39) plotted the separation for the Q "lines" in the perpendicular bands of a given fundamental in the vapor state spectrum versus the half-peak height and quarter-peak height band widths for the same fundamental in carbon tetrachloride solution. In each case a linear relationship was obtained. It should be remembered that the spacings

Table 6. Half-peak heigth band widths (cm^{-1}) for the absorption bands of the fundamental modes in the methyl halides (39)

Vibration	Degeneracy	CH_3Cl	CH_3Br	CH_3I
$\nu_s CH_3$	1	17[a]	18[a]	15[a]
$\delta_s CH_3$	1	12	10	10
νC_α -X	1	22	--	--
$\nu_{as} CH_3$	2	--	--	--
$\delta_{as} CH_3$	2	50	44	45
CH_3 rock	2	32	28	30.5

[a] These values were obtained in a region where the effective slit width is comparable to the band width.

between the "Q" lines includes a Coriolis coupling factor. Thus not only is free rotation about the figure axis perserved but also the Coriolis interaction. Jones and Sheppard (39) also observed that the degenerate asymmetric methyl deformation vibration is comparable in band width, at -195°C in a carbon tetrachloride matrix, to that found for the symmetric methyl deformation vibration. They interpreted this as indicative of complete inhabition of all rotatory motion.

Jones and Sheppard (39) employed their observations as an interpretive tool in the detection of free internal rotation of methyl groups. In the solution spectrum of nitromethane, which has a very small barrier to internal rotation, the symmetric vibrations of the methyl group were readily identified by half-peak height band widths of 10 cm^{-1}. The perpendicular bands, primarily the asymmetric methyl deformation and methyl rock, were much broader. These differences were also apparent for the methyl vibrations in toluene and provide strong support for the free internal rotation of the methyl group. As shall be discussed later these observations also provide an insight into the problem of internal rotation of the methyl group in methyl isocyanate, isothiocyanate and thiocyanate.

Solid State

The interpretation of vibrational spectra obtained from solid state samples is fraught with difficulties. Mizushima and his colleagues (63) were the first to observe that for molecules with discrete, although not chemically separable, rotational isomers a simplification of the vibrational spectrum is usually concurrent with the transition from liquid to solid state. The simplification results from a preferential stability of one isomeric form. This observation has been the basis for numerous spectroscopic investigations of rotational isomerism. However, Hornig (34) has warned that a mere simplification of the solid state spectrum is not sufficient evidence to prove the existence of rotational isomerism. Several other perturbations in the solid state can cause either an increase or decrease in complexity of the solid state spectrum.

In a crystalline solid the selection rules are not determined by the symmetry of the isolated molecule but by the symmetry of the unit cell. A change in the selection rules also alters the infrared activity of the various vibrational symmetry types. An example of this is found in benzene where one fundamental and four combination bands (34) disappear in the spectrum of solid benzene because of the operation of selection rules in the crystal which do not exist in the liquid state. Another example of this may be the disappearance of the CH stretching vibration in solid bromoform (53).

Molecular vibrations in a crystalline solid can be most readily discussed in terms of the perturbations acting upon the potential field of an isolated molecule. Vibrational selection rules for a truly isolated molecule, e.g., one in the vapor state, reflects the internal potential field of the molecule. Built into the potential field is the molecular symmetry. For a molecule in a crystal lattice site, a first order perturbation interaction occurs between the internal potential field of the molecule and the crystal field. Inherent within this potential field is the symmetry of the crystal. Selection rules operative in the solid state must then also reflect the symmetry of the crystal. As a result, both genuine and accidental degeneracies can be split by 5 to 25 cm^{-1} (21, 34). This splitting of degeneracies is often referred to as site splitting since it is caused by the anisotropy of the crystal.

A second order perturbation arises from the interaction of equivalent molecules in the unit cell. Through this perturbation the same vibrations in equivalent molecules will be coupled. Although the number of components for a given normal mode will be equal to the number of equivalent molecules per unit cell, selection rules can reduce the number actually observed. Usually this type of crystal field splitting is of the order of magnitude of 3 to 5 cm^{-1}.

If the crystal structure is known the selection rules can be readily derived. Theoretically the number of components having infrared activity for each unperturbed fundamental can then be calculated. In actual practice the interpretation is not nearly so quantitative. For example, Hornig (34) was unable to reconcile the numerous differences between the number of observed and expected frequencies for solid carbon dioxide. Dows (21) had similar difficulties with the methyl halides. Therefore, at best, only a qualitative interpretation is generally possible for the vibrational spectra of crystalline materials.

Dows has made several observations of additional interest. He found that the fundamental modes were very narrow, the half-peak heigth band widths ranging from 2 to 5 cm^{-1}.

In contrast, combination bands, especially those involving lattice modes, were considerably broader. There also seemed to be a selective preference for combination bands between the lattice modes and the methyl rock and the asymmetric methyl deformation vibration.

The observations made for the vapor and liquid state spectra of methyl isocyanate, isothiocyanate and thiocyanate are reinforced by spectra from solid samples of these compounds. There is a considerable difference between the spectra from methyl isocyanate and methyl isothiocyanate on the one hand and that from methyl thiocyanate on the other.

FERMI RESONANCE

Frequently in polyatomic molecules two different vibrational levels belonging to different normal modes may have the same or nearly the same energy. Such accidentally degenerate levels interact with each other causing a mixing of their respective eigenfunctions. Corresponding to this reasonance is a mutual repulsion of the unperturbed levels. This type of resonance interaction between vibrational levels was first observed by Fermi in the spectrum of carbon dioxide.

The magnitude of the perturbation depends upon the value of the matrix element W_{ni} of the perturbation function W:

$$W_{ni} = \int \phi_n^o \, W \, \phi_i^o \, d\tau$$

where ϕ_n^o and ϕ_i^o are the eigenfunctions of the unperturbed energy levels E_n^o and E_i^o. W is primarily the anharmonicity term of the potential energy. Nonzero values for the matrix element W_{ni} will occur only when ϕ_n^o and ϕ_i^o are of the same symmetry class (30). Otherwise the matrix element would change sign for at least one symmetry operation permitted by the molecule. However, since W has the full symmetry of the molecule, W must be invariant to all permitted symmetry operations. As a result, Fermi resonance can occur only between levels of the same symmetry species.

As shown in Appendix B, relationships between the observed energy levels E_a and E_b and the unperturbed energy levels can be obtained through perturbation theory. The simplest forms being

$$E_a + E_b = E_n^o + E_i^o \text{ and } E_a - E_b = (4W_{ni}^2 + \delta^2)^{\frac{1}{2}}$$

with δ being the difference between the unperturbed energies.

The resultant vibrational levels are observed through transitions from the ground state. It can easily be shown that the eigenfunctions associated with these levels are linear combinations of the eigenfunctions for the unperturbed levels. Thus the dipole moment change for transitions from the ground state to each resultant level will include contributions from hypothetical transitions involving the unperturbed levels. A net result is that the observed transitions are more nearly equal in intensity than would be the case if there were no resonance interaction.

Two strong absorption bands are found about 2150 cm^{-1} in the infrared spectra of methyl and ethyl isothiocyanate. Both bands are far more intense than any other band in the respective spectra. However, only a single fundamental mode is expected in this region. Badger (5) has proposed an explanation involving a Fermi resonance interaction between the expected normal mode and the first overtone of a second mode at 1088 cm^{-1}. This explanation has received both favorable and unfavorable criticism and will be discussed in detail later.

EXPERIMENTAL

Preparation of Materials

Almost all of the alkyl derivatives studied in this investigation were obtained from commercial sources. Unfortunately several alkyl isothiocyanates and thiocyanates were necessarily synthesized by the author.

Shriner's procedure (79) was used in the preparation of n-propyl and sec-butyl thiocyanate. Using this procedure several unsuccessful attempts were made to synthesize tert-butyl thiocyanate. The synthesis product was usually impure tert-butyl isothiocyanate. A slight modification of the procedure lead to excellent yields of tert-butyl isothiocyanate. Samples of tert-butyl isothiocyanate used in this investigation were obtained in this manner. As in Shriner's procedure an alcoholic solution of sodium thiocyanate was added to tert-butyl bromide. Immediately upon stirring, a copious white precipitate of sodium bromide formed. However, instead of warming the reaction mixture, sufficient water was added to triple the volume of the reaction mixture. The resultant solution was extracted with ether. The ether extracts were in turn washed with very dilute solutions of sodium hydroxide and hydrochloric acid. Finally, tert-butyl isothiocyanate was purified by vacuum distillation. Warming the reaction mixture in the presence of ethanol sharply reduces the yield through formation of a thiourethane.

The procedure of Moore and Crossley (64) was used to synthesize n-propyl and isopropyl isothiocyanate. In both cases ethyl carbonate was a major side product. Distillation techniques were able to easily separate n-propyl isothiocyanate from ethyl carbonate. Unfortunately only a partial purification was possible for isopropyl isothiocyanate. A sample of this material obtained from commercial sources also contained considerable amounts of ethyl carbonate. The infrared spectrum of isopropyl isothiocyanate, Figure 22, contains several spurious bands resulting from traces of ethyl carbonate.

Spectroscopic Procedures

The infrared spectra were obtained using a Beckman IR-7 prism-grating spectrophotometer. By means of sodium chloride and cesium iodide prism interchanges the spectral region from 4000 to 200 cm^{-1} was made available to observation. Atmospheric water and carbon dioxide were used to "spot check" the factory calibration. The spectrum of indene, proposed by Jones and coworkers (37, 38) as a liquid phase calibrant material, was utilized in more comprehensive calibration checks. For most general purposes, the frequencies are given to the nearest wavenumber and are estimated to be accurate to ±3 cm^{-1} above 2000 cm^{-1} and ±2 cm^{-1} below 2000 cm^{-1}.

With the exception of methyl isothiocyanate, m.p. 35.5°C, all the compounds included in this investigation are liquids at room temperature. Previous to procurement of their spectra all samples were vacuum distilled. This is especially necessary for alkyl isocyanates as they have a marked tendency to polymerize. Standard techniques and cells were used to obtain the spectra of liquid and solid state samples. Spectra acquired using 0.01 mm potassium bromide cells are shown in Figures 6 through 13 for alkyl thiocyanates, Figures 19 through 25 for alkyl isothiocyanates and Figures 30 through 34 for alkyl isocyanates. Methyl and ethyl esters of isocyanic and isothiocyanic acids have sufficient vapor pressure at room temperature to permit recording their spectra in an unheated gas cell. In contrast, even using a heated gas cell, type GH-5 from Limit Research Corporation, only a weak and incomplete spectrum was obtained for methyl thiocyanate. A cryostat very similar in design to one proposed by Lord, McDonald and Miller (54) was used in obtaining spectra of solid state samples at liquid nitrogen temperature.

Calculation of standard enthalpy differences between rotationally isomeric configurations requires quantitative values for the integrated intensity ratio between bands originating in the different isomers. A commercial heated infrared cell and low temperature unit, J-1 and LTJ-1 available from Limit Research Corporation, fitted with a 0.02 mm potassium bromide cell were employed for this purpose. Temperature measurements were made with an iron-constantan thermocouple. Integrated intensity ratios were calculated by weighing the absorption bands.

A Lane-Wells 40-A Raman spectrograph equipped with a Toronto excitation lamp and a Schmidt photographic camera was used to photograph the Raman spectrum of methyl isocyanate. The instrument was calibrated with the spectra of benzene, carbon tetrachloride, chloroform, cyclohexane and toluene.

ALKYL THIOCYANATES

Historical Background

It is interesting to note that the first published spectra for an alkyl thiocyanate appeared in 1905 when Coblentz (14) reported the infrared spectra of methyl and ethyl thiocyanate. Even though the spectra were quite crude, Coblentz was able to observe distinct differences about 2100 cm^{-1} between spectra obtained from the isomeric isothiocyanates and thiocyanates. Gordy and Williams (25, 26) assigned the strong and extremely sharp infrared absorption band at 4.635 μ(2158 cm^{-1}) in the spectra of methyl and ethyl thiocyanate to the C≡N stretching vibration, ν (CN).

Petrikaln and Hochberg (69) were the first to record the Raman spectrum of methyl thiocyanate. However, since their spectrum was quite incomplete, the first significant compilation of Raman data was published by Kahovec and Kohlrausch (40). Independently, Goubeau and Gott (27) reported the Raman spectra of methyl and ethyl thiocyanate. They also performed a force constant calculation for methyl thiocyanate using as a model a linear system of four point masses. Since their calculation involved two rather unrealistic assumptions, i.e., reduction of the methyl group to a point mass and a linear CSCN chain, the force constants and bond distances cannot be considered reliable. Interestingly, they did distinguish between the two carbon-sulfur stretching vibrations. Employing a spectrograph with a higher resolution than was available to earlier investigators, Vogel-Högler (88) remeasured the Raman spectra of both alkyl thiocyanates. In addition she reported polarization data for the principal Raman lines and a partial assignment scheme for both compounds.

Perhaps the most confusing information in the literature is the 2140 cm^{-1} frequency erroneously ascribed to ν (CN) by Lieber, Rao and Ramachandran (52). It is difficult to reconcile this frequency, low by 16 cm^{-1}, with values obtained by other investigators. Undoubtedly this paper was the source of the same erroneous frequency in Nakaniski's (66) infrared text.

Two recent papers (28, 58) have dealt rather thoroughly with the vibrational spectrum of methyl thiocyanate. The only significant disagreement between them arises in the characterization of the carbon-sulfur stretching vibrations. In contrast to Goubeau and Gott (27), Miller and White (58) proposed assignments in terms of symmetric and asymmetric CSC stretching vibrations. Ham and Willis (28) did not specify their assignments further than denoting that two absorption bands originated from carbon-sulfur stretching vibrations. Fateley and Miller (24), from their observation of the torsional mode in methyl thiocyanate at 131 cm^{-1}, were able to calculate an internal barrier against rotation about the C_{α} -S bond of 1 kcal. per mole.

The observed infrared frequencies for methyl, ethyl, n-propyl, isopropyl, n-butyl and sec-butyl thiocyanate appear in Appendix E, Table 41 through 46. Spectra of these compounds appear in Figures 6 through 13. Raman data for methyl and ethyl thiocyanate are presented in Appendix H, Table 60.

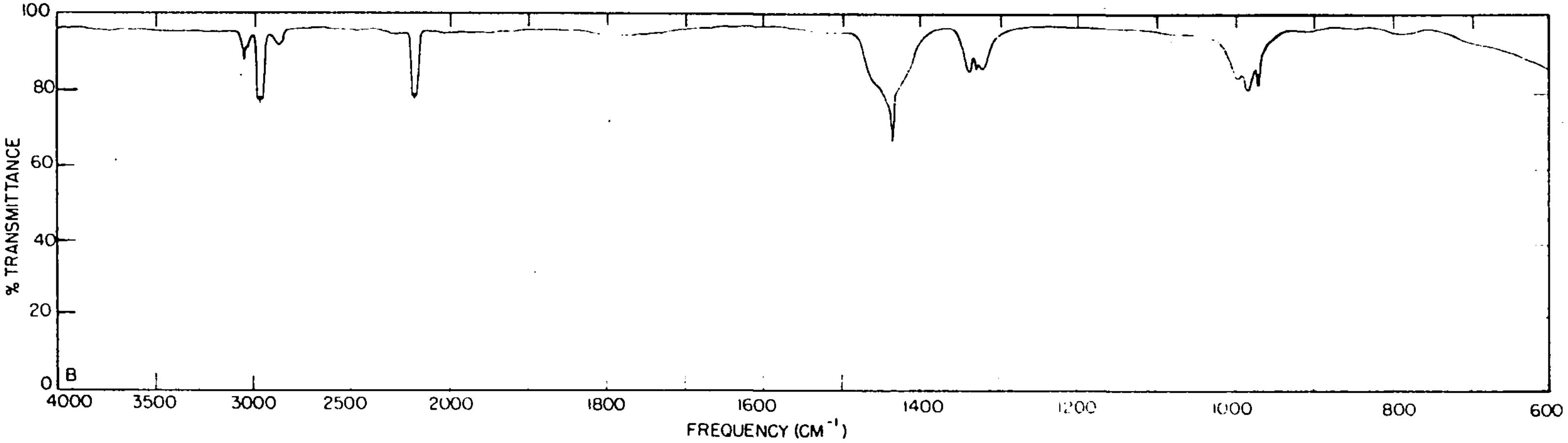
Carbon-Sulfur Spectral Region (725 to 550 cm^{-1})

In the interpretation of the spectra of alkyl thiocyanates the principal problem occurs in assignment of the 725 to 550 cm^{-1} region, in which the carbon-sulfur stretching vibrations occur. The problem originates in the multiplicity of absorption bands found in this region. An insight into the complexity of this spectral region may be gained from Table 7. Since the region between 725 to 550 cm^{-1} is too low for carbon-hydrogen vibrations and too high for skeletal vibrations of the alkyl or thiocyanate groups, the absorption bands must originate from either combination or carbon-sulfur stretching vibrations. While one or two of the observed bands can be possibly assigned as combination bands the regularities apparent in Table 7 and the phase transition phenomena observed for ethyl and isopropyl thiocyanate require a more subtle answer in terms of carbon-sulfur vibrations.

Figure 6. Infrared spectra of methyl thiocyanate

(A) liquid state

(B) vapor state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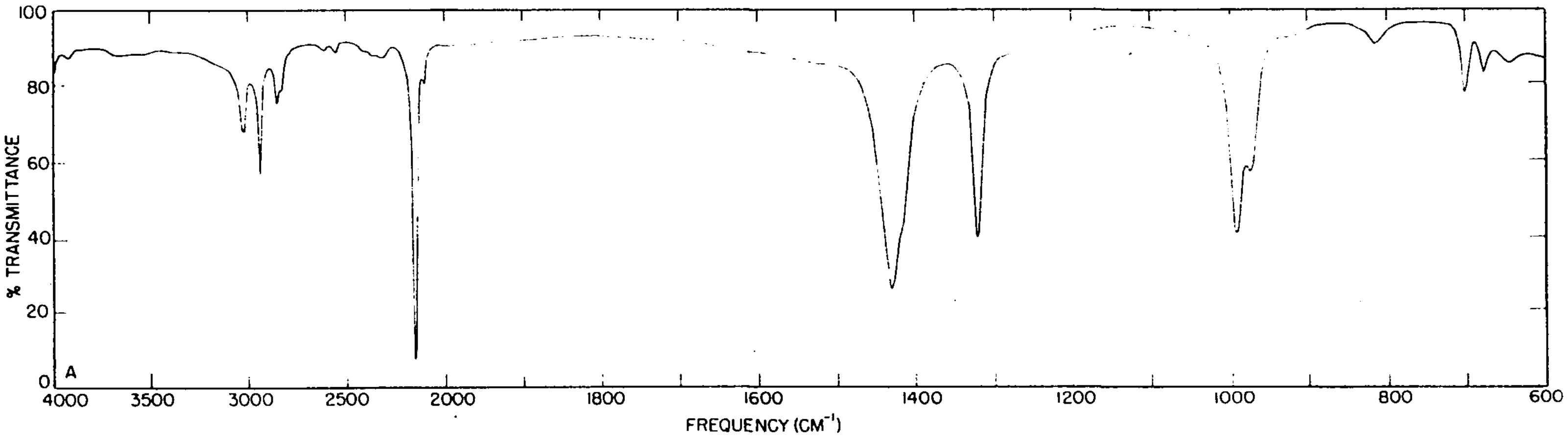
FREQUENCY (CM⁻¹)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% TRANSMITTANCE
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3500
3000
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2000
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1600
1400
1200
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800
600
FREQUENCY (CM⁻¹)

Figure 7. Infrared spectrum of ethyl thiocyanate

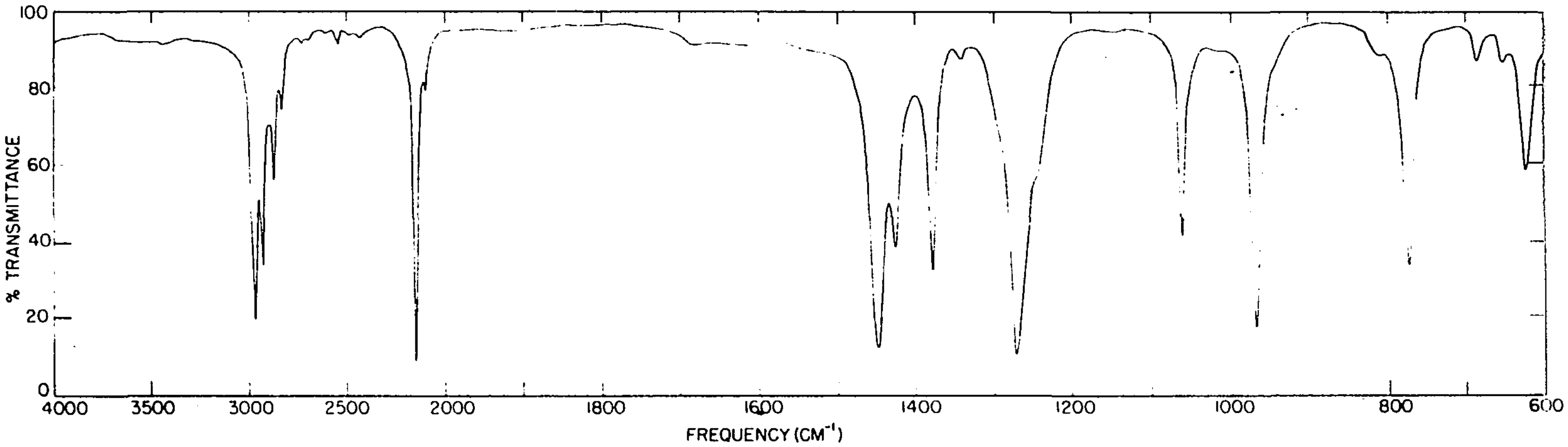

100
80
60
40
20
0
% TRANSMITTANCE
4000
3500
3000
2500
2000
1800
1600
1400
1200
1000
800
600
FREQUENCY (CM⁻¹)

Figure 8. Infrared spectrum of n-propyl thiocyanate

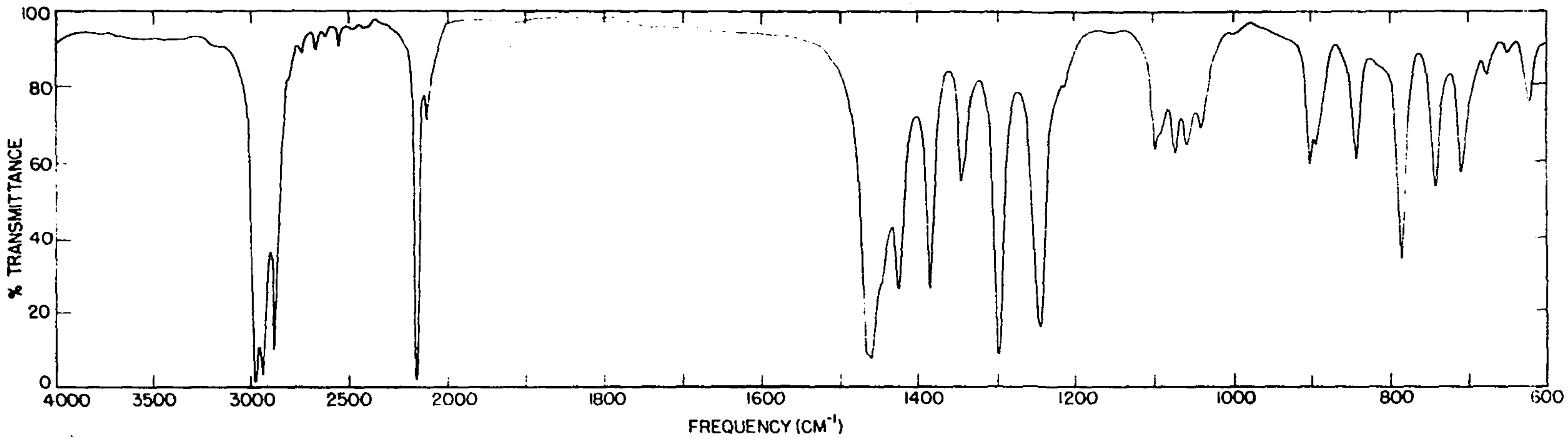

100
80
60
40
20
0
% TRANSMITTANCE
4000
3500
3000
2500
2000
1800
1600
1400
1200
1000
800
600
FREQUENCY (CM^{-1})

Figure 9. Infrared spectrum of isopropyl thiocyanate

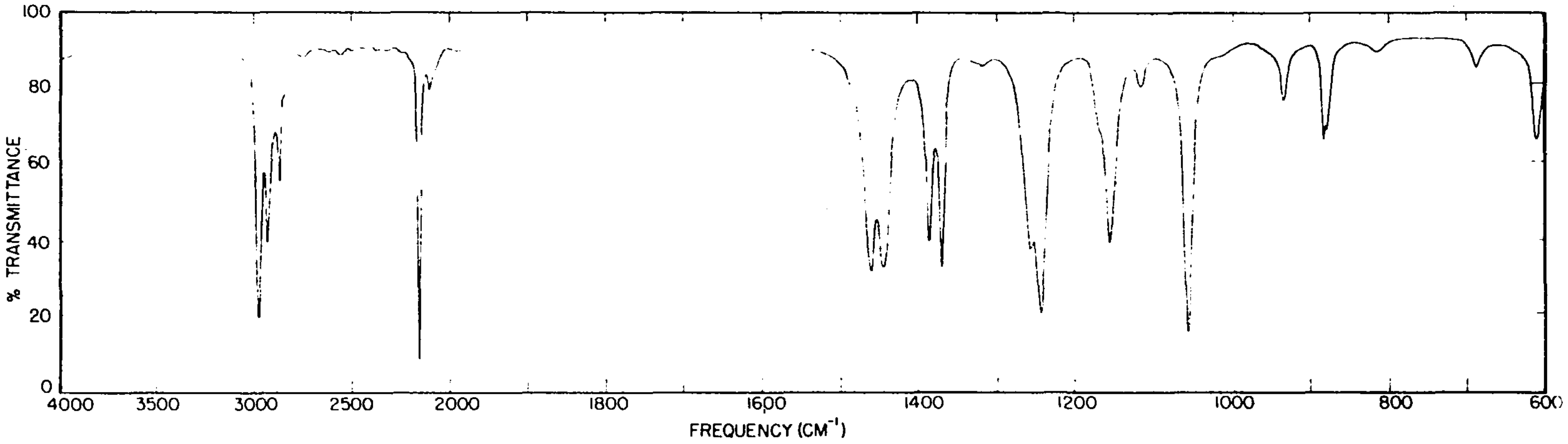

100
80
60
40
20
0
% TRANSMITTANCE
4000
3500
3000
2500
2000
1800
1600
1400
1200
1000
800
600
FREQUENCY (CM⁻¹)

Figure 10. Infrared spectrum of n-butyl thiocyanate

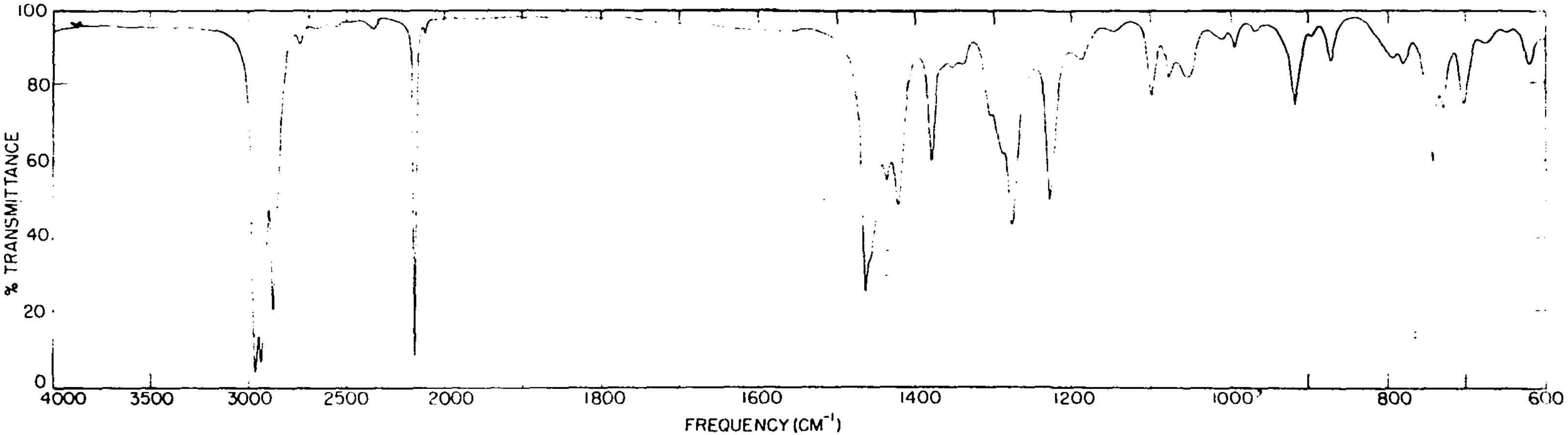

100
80
60
40
20
0
% TRANSMITTANCE
4000
3500
3000
2500
2000
1800
1600
1400
1200
1000
800
600
FREQUENCY (CM⁻¹)

Figure 11. Infrared spectrum of sec-butyl thiocyanate

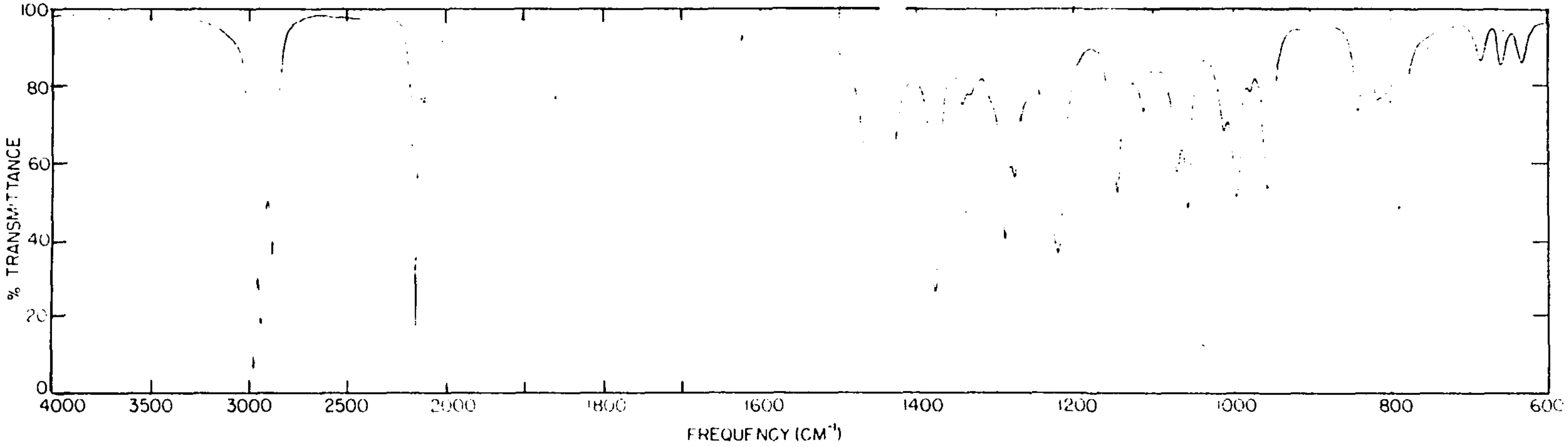

100
80
60
40
20
0
% TRANSMITTANCE
4000
3500
3000
2500
2000
1800
1600
1400
1200
1000
800
600
FREQUENCY (CM^{-1})

Figure 12. Infrared spectrum of n-heptyl thiocyanate

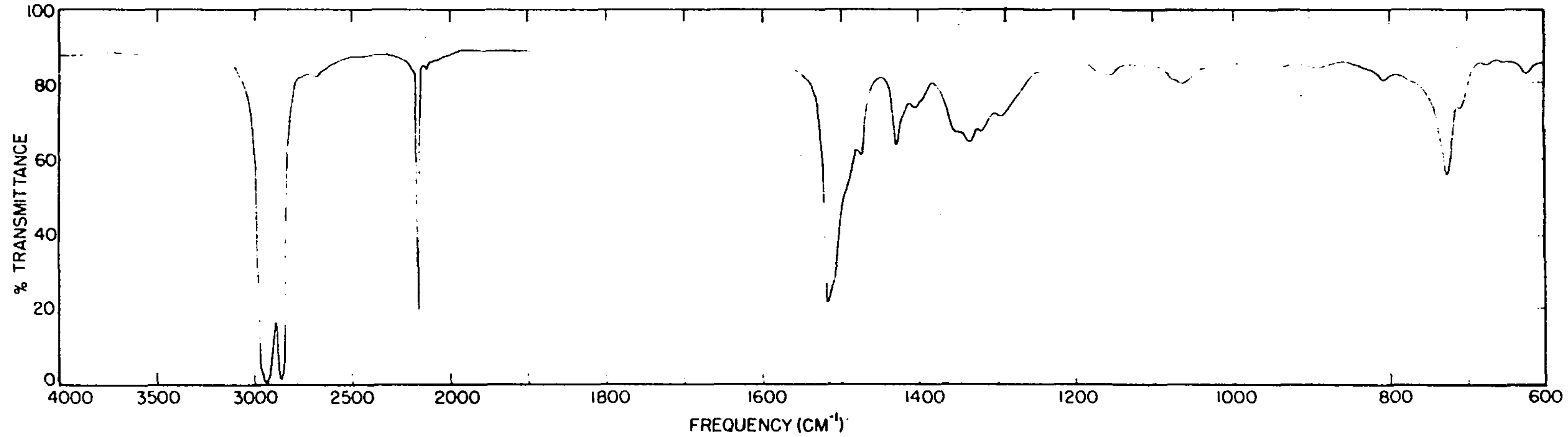

100
80
60
40
20
0
% TRANSMITTANCE
4000
3500
3000
2500
2000
1800
1600
1400
1200
1000
800
600
FREQUENCY (CM⁻¹)

Figure 13. Infrared spectrum of n-dodecyl thiocyanate

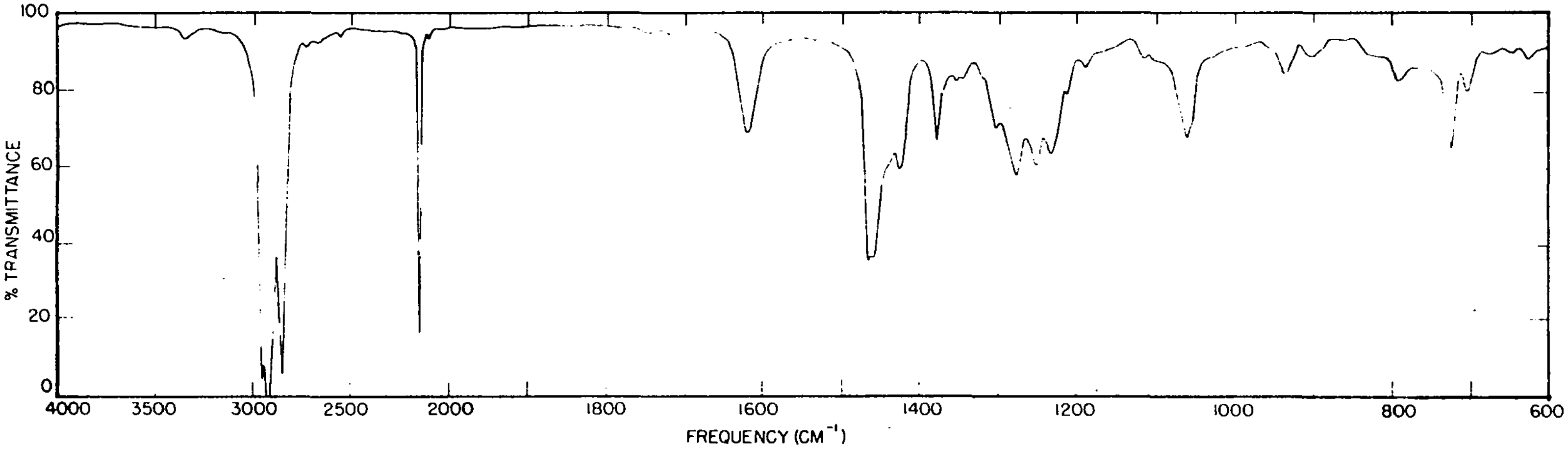

100
80
60
40
20
0
% TRANSMITTANCE
4000
3500
3000
2500
2000
1800
1600
1400
1200
1000
800
600
FREQUENCY (CM⁻¹)

Table 7. Observed absorption frequencies for the alkyl thiocyanates in the 725 to 550 cm^{-1} region

Alkyl thiocyanate	Frequency (cm^{-1})[a]				
Methyl	699	675	645		
Ethyl		686	654	624	
n-Propyl	706	674	647	619	
n-Butyl	702	678	653	622	
n-Heptyl	703	678	654	624	
n-Dodecyl	702	679	652	624	
Isopropyl	688			613	586
sec-Butyl	687	663	636	606	576

[a] Data from the liquid state.

For purposes of clarity the two carbon-sulfur bonds in alkyl thiocyanates are differentiated as follows: The bond between the alkyl group and the thiocyante group is denoted as C_α -S. The other carbon-sulfur linkage, completely within the thiocyanate group, is denoted as S-C. As a consequence the respective stretching vibrations are denoted ν (C_α -S) and ν (S-C). Miller and White's (58) proposed alternate descriptive notation will be discussed later.

Initially the discussion must be limited to the spectra of methyl, ethyl and isopropyl thiocyanate. Spectra obtained from the liquid and solid states of these compounds

Figure 14. The infrared spectra of alkyl thiocyanates for the 725-550 cm^{-1} region

For each compound the upper spectrum is of the solid state at liquid nitrogen temperature and the lower spectrum is of the liquid state at room temperature.

(A) methyl thiocyanate

(B) ethyl thiocyanate

(C) isopropyl thiocyanate

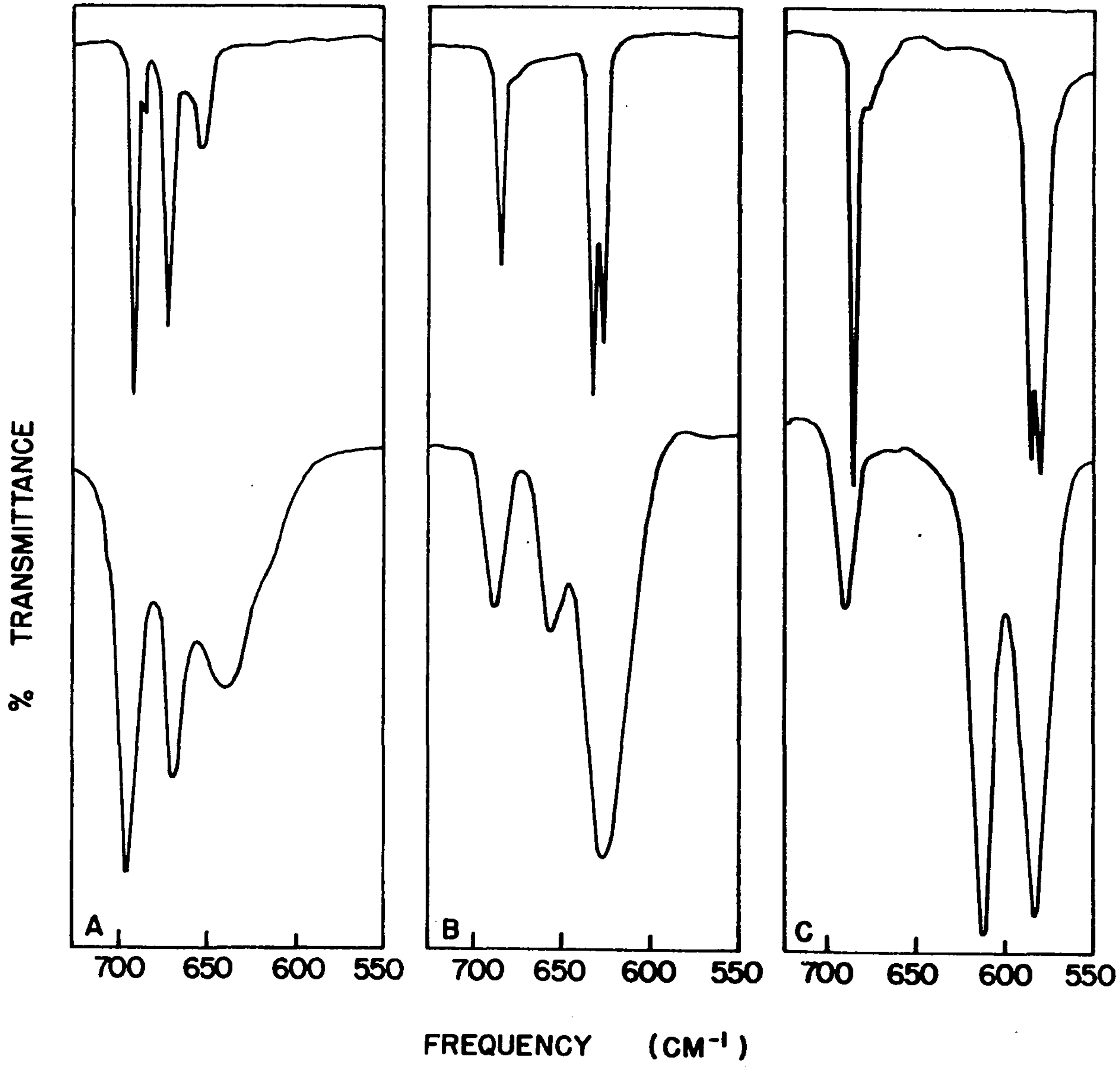
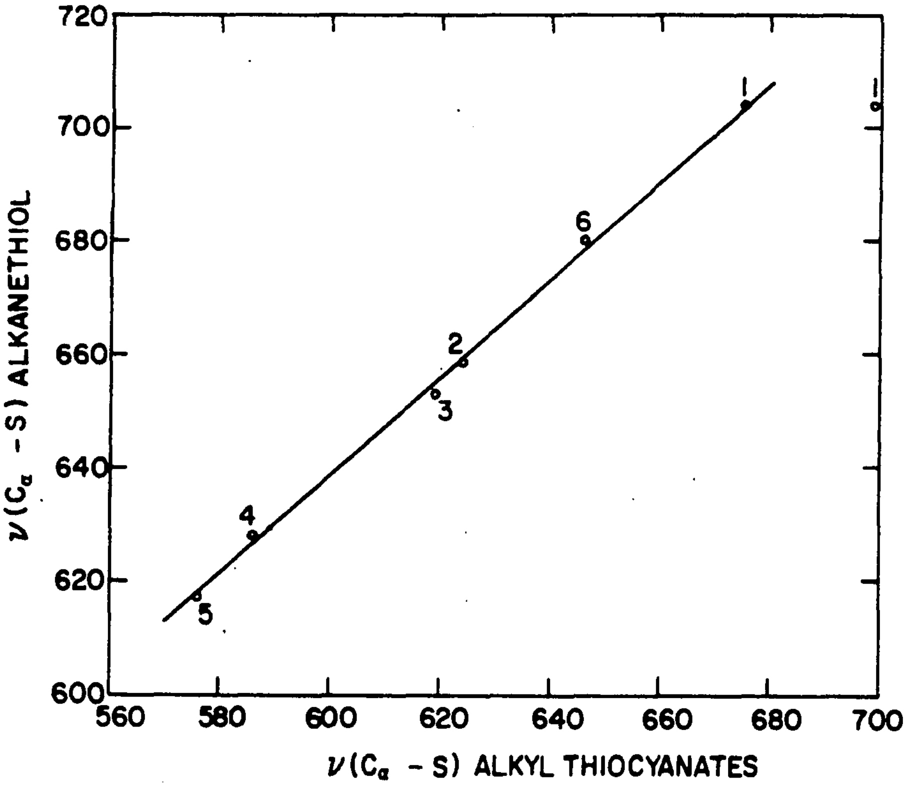

% TRANSMITTANCE
A
B
C
700
650
600
550
FREQUENCY (CM^{-1})

Figure 15. Relationship of $\nu(C_\alpha-X)$ in corresponding alkyl thiocyanates and alkanethiols

The points represent (1) methyl; (2) ethyl; (3) n-propyl; (4) isopropyl; (5) sec-butyl; (6) benzyl derivatives. Data for the thiols were obtained from (29, 74).


720
700
680
660
640
620
600
560
580
600
620
640
660
680
700
1
1
6
2
3
4
5
$\nu(C_\alpha - S)$ ALKANETHIOL
$\nu(C_\alpha - S)$ ALKYL THIOCYANATES

are shown in Figure 14. Referring to the findings of Sheppard (73, 74, 75, 76) for alkanethiols, see Table 1, a marked decrease in frequency is expected for $\nu(C_\alpha -S)$ in comparing isopropyl thiocyanate to methyl thiocyanate. In contrast $\nu(S-C)$ should exhibit a reduced or even negligible effect. As indicated by Figure 15 a strong correlation does exist between the lowest observed frequency listed in Table 7, with the exception of methyl thiocyanate where the 675 cm^{-1} frequency was used, and the $C_\alpha -S$ frequency for the corresponding alkanethiol. On this basis these frequencies are assigned to $\nu(C_\alpha -S)$. The assignment for methyl thiocyanate is anomalous because the lowest frequency originates from a combination mode (58). This assignment is in agreement with the relatively large half-peak height band-width observed for this band as compared to the adjacent fundamental modes.

To assign the remaining bands in the liquid state spectra of these compounds it is necessary to refer to the solid state spectra. As shown in Figure 14, the solid state spectra of ethyl and isopropyl thiocyanate have only two distinct bands in this region, with the lower band exhibiting crystal splitting. In both spectra the intermediate frequency is absent. The difference between the liquid and solid state spectra can be readily interpreted in terms of restricted rotation about the $C_\alpha -S$ bond.

Methyl thiocyanate has an internal barrier against rotation about the C_α -X bond of approximately 1 kcal. per mole (24). This is in agreement with a barrier of 1.3 kcal. per mole in methanethiol (48, 72). A barrier of this magnitude is sufficient to restrict the free rotation of the thiocyanate group at room temperature. Consequently the two isomeric configurations of both ethyl and isopropyl thiocyanate, schematically drawn in Figure 16, should be spectroscopically detectable although chemically inseparable. To facilitate the discussion of assignments in the various isomeric species the following notation is employed:

H_α denotes the (S-C) bond is trans to a (C_α -H) bond
C_β denotes the (S-C) bond is trans to a (C_α -C_β)bond
' denotes the (S-C) bond is gauche to a (C_α -C_β) bond
" denotes the (S-C) bond is gauche to two (C_α -C_β) bonds.

Thus the only configuration possible for methyl thiocyanate would be H_α . Likewise, referring again to Figure 16, the isomers of ethyl thiocyanate are H_α' and C_β while those of isopropyl thiocyanate are H_α'' and C_β' .

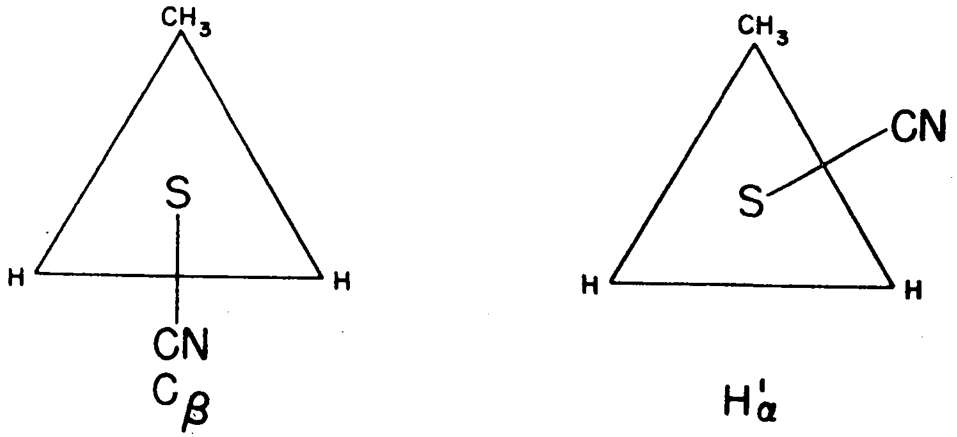
The interpretation of the spectra is now straightforward. The absorption bands that remain in the spectra of the solid state originate from the most stable form, i.e., C_β for ethyl thiocyanate and C_β' for isopropyl thiocyanate. The assignment of the bands at 624 (ethyl thiocyanate) and 586 cm^{-1} (isopropyl thiocyanate) to $\nu(C_\alpha$ -S) is not affected.

Figure 16. Schematic representation of the isomeric forms of

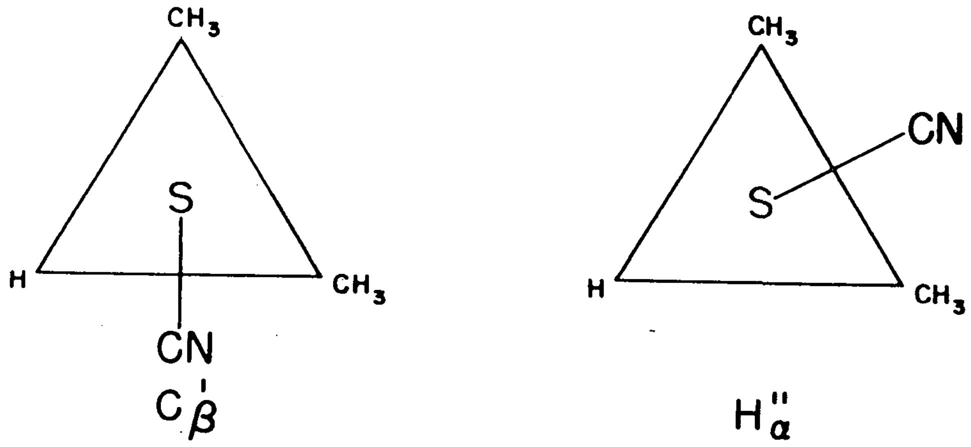
(A) ethyl thiocyanate

(B) isopropyl thiocyanate

(A)


CH$_3$
S
H
H
CN
C$_\beta$
CH$_3$
CN
S
H
H
H$'_\alpha$

(B)


CH$_3$
S
H
CH$_3$
CN
C$'_\beta$
CH$_3$
CN
S
H
CH$_3$
H$''_\alpha$

The remaining bands, in the solid state spectra, at 686 (ethyl thiocyanate) and 688 cm^{-1} (isopropyl thiocyanate) are assigned to ν(S-C) in the more stable isomeric species. The bands at 654 cm^{-1} (ethyl thiocyanate) and 613 cm^{-1} (isopropyl thiocyanate), which appear only in spectra obtained from the liquid state, are then assigned to ν(S-C) in the less stable isomer.

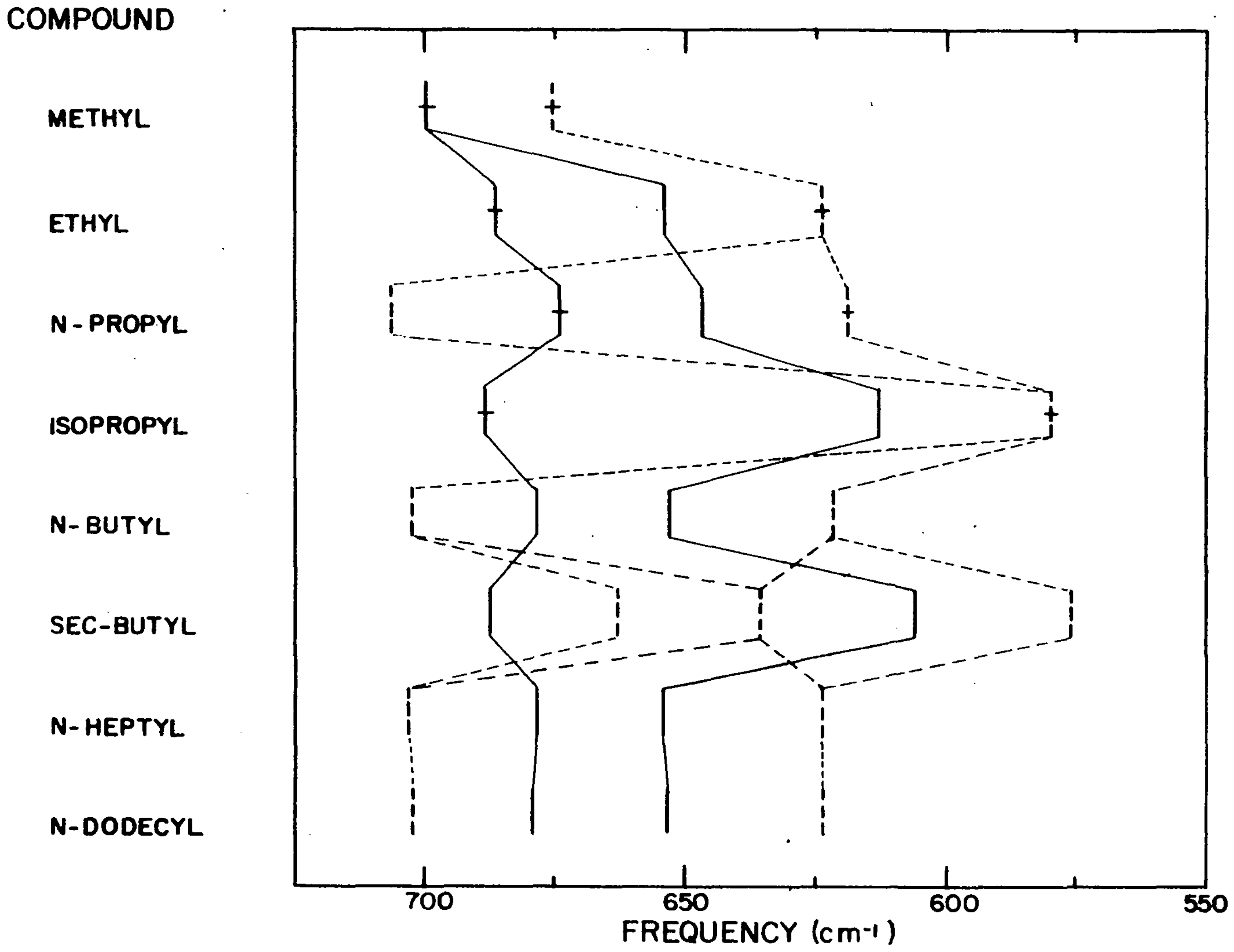
There is a close analogy between the "splitting" observed for $\nu(C_\alpha$ -Cl) in primary alkyl chlorides as a result of restricted rotation about the $C_\alpha - C_\beta$ bond and that observed for ν(S-C) as a result of restricted rotation about the C_α -S bond. The relative constancy of the bands about 685 cm^{-1} is consistent with the observations, see Table 2, of Shipman, Folt and Krimm (78) on the uniformity of $\nu(C_\alpha$ -Cl) in isomers of primary alkyl chlorides having a trans configuration with respect to a C_β -C bond. Likewise, the decrease in frequency for ν(S-C) in the H''_α configuration of isopropyl thiocyanate as compared to its value in the H'_α isomer of ethyl thiocyanate is also in agreement with their observations.

The assignments for ethyl and isopropyl thiocyanate serve as a basis for the interpretation of the spectra for the remaining alkyl thiocyanates listed in Table 7. The absorption bands at 677± 3, 651± 4 and 622± 3 cm^{-1} in the spectra of all the n-alkyl thiocyanates are direct analogues to the three absorption bands in the spectrum of ethyl thiocyanate. Consequently the series at 677 and 651 cm^{-1} are assigned to ν(S-C) in the isomeric configurations C_β and H'_α . The series of bands at 622 cm^{-1} is assigned to $\nu(C_\alpha$ -S) as is the new series at 703± 3 cm^{-1}. The last series of bands originates from restricted rotation about the C_α -C_β bond and are the <u>exact</u> analogues to the 728 cm^{-1} bands in primary alkyl chlorides. Similarly, the absorption bands at 663, 636 and 576 cm^{-1} in the spectrum of sec-butyl thiocyanate arise from restricted rotation about the C_α -C_β bond and are direct counterparts to the bands listed in Table 3 for secondary alkyl chlorides. The remaining two bands in the spectrum of sec-butyl thiocyanate are assigned in agreement with isopropyl thiocyanate. The preceding assignments are summarized in Figure 17.

Miller and White (58) have proposed assignment of the carbon-sulfur vibrations in methyl thiocyanate in terms of symmetric and asymmetric CSC vibrations. These assignments indicate a strong coupling between the two individual carbon-sulfur bonds. While there is certainly some coupling, the spectral characteristics observed in this region are best explained by assignment of the absorption bands as ν (C_α -S) and ν(S-C). Strong coupling should result in a quartet of bands appearing in the spectra of ethyl and isopropyl thiocyanate. This was not observed. Furthermore, as the unperturbed energy levels for $\nu(C_\alpha$ -S) and ν(S-C) approach one another an increase in coupling should occur.

Figure 17. Correlation of the CS stretching vibrations in the spectra of alkyl thiocyanates in the liquid state

Solid lines represent bands associated with ν(S-C) and dashed lines correspond to $\nu(C_{\alpha}-S)$. A horizontal bar indicates the band persists in the solid state spectra. Solid state spectra were obtained only for methyl, ethyl, n-propyl and isopropyl thiocyanate.


COMPOUND
METHYL
ETHYL
N-PROPYL
ISOPROPYL
N-BUTYL
SEC-BUTYL
N-HEPTYL
N-DODECYL
700
650
600
550
FREQUENCY (cm⁻¹)

As a consequence a marked deviation from linearity should be observed in Figure 15 since the coupling is operative only in alkyl thiocyanates.

The assignment of the 725 to 550 cm^{-1} spectral region permits the discussion of the spectra of specific compounds. Since the carbon-hydrogen vibrations in alkyl derivatives with two or more methylene groups becomes prohibitively complex only the spectra of methyl, ethyl and isopropyl thiocyanate will be discussed in detail.

Thiocyanate Group Vibrations

To avoid duplication in the discussion of specific molecules, the remaining vibrations internal to the thiocyanate group will be assigned separately. Linear triatomic units such as the thiocyanate group have four vibrational degrees of freedom. For the thiocyanate group this results in two stretching vibrations, ν(CN) and ν(S-C), and a doubly degenerate deformation vibration. The first unambiguous assignment of a thiocyanate vibration was made by Gordy and Williams (25, 26) for ν(CN) at 2156 cm^{-1}. This band is practically invariant to changes in the alkyl group and solvent effects. Caldow and Thompson (12) have observed that in aromatic thiocyanates, ν(CN) is relatively insensitive to substitution on the benzene ring. A result of the off axis position for the alkyl group in an alkyl thiocyanate is a splitting in the degeneracy of the SCN deformation. The resultant in and out-of-plane deformation vibrations occur about 455 and 407 cm^{-1}. However, specific assignment of the vibrations must be considered as tentative since neither vapor state spectra nor Raman polarization data offers supporting evidence. A summary of the frequency ranges observed for the thiocyanate group is presented in Table 8. Only the (S-C) stretching vibration exhibits a significant variation in frequency.

Table 8. Frequency ranges for the characteristic vibrations of the thiocyanate group

Vibration	Frequency (cm^{-1})	Intensity
ν(CN)	2156± 3	strong
ν(S-C)	700 to 600	weak
$\delta_\perp$(SCN)	460 to 450	very weak
$\delta_\parallel$(SCN)	407± 2	moderate

Methyl Thiocyanate

Methyl thiocyanate has C_s symmetry with ten fundamental vibrations belonging to class a' and five to class a". All the vibrations are infrared active and in addition those of symmetry species a' are polarized in the Raman effect. A schematic description of the normal vibrations is given in Appendix I. Vibrational assignments for the fundamental and combination modes appear in Tables 9 and 10. In general they agree with the assignments tentatively proposed by Miller and White (58) with the exception of the previously discussed carbon-sulfur vibrations, a band at 813 cm^{-1} which they did not observe and the grouping of band maxima in the vapor state spectrum about 981 cm^{-1}.

Before discussing the assignments of specific vibrations and the differences with Miller and White, the assignments of Ham and Willis (28) and Vogel-Högler (88) deserve comment. Neither Ham and Willis nor Vogel-Högler had access to absorption data in the far infrared and consequently their assignments were beset by the same basic difficulty, i.e., lack of two reasonable low frequency assignments for the CSC angle deformation and the methyl torsional vibration. Vogel-Högler (88) avoided the problem by not assigning the CSC angle deformation. In contrast, Ham and Willis (28) compounded the problem by assuming that the SCN deformation vibrations are doubly degenerate and assigned the CSC angle deformation to the rather high Raman frequency at 397 cm^{-1}. The observation by Fateley and Miller (24) of an absorption band at 131 cm^{-1} eliminated the difficulties that faced these authors.

The stretching and deformation vibrations of the methyl group are readily assigned to the absorption bands at 3027, 2943, 1431 and 1320 cm^{-1}. In the vapor state spectrum,

Table 9. Assignments for the fundamental modes of methyl thiocyanate

Vibration	Frequency (cm^{-1})[a]	Degeneracy
$\nu_{as}CH_3$	3027	2
ν_sCH_3	2943	1
$\nu(CN)$	2158	1
$\delta_{as}CH_3$	1431	2
δ_sCH_3	1320	1
$\gamma_{\parallel}CH_3$	989	1
$\gamma_{\perp}CH_3$	973	1
$\nu(S-C)$	699	1
$\nu(C_\alpha-S)$	675	1
$\delta_{\parallel}(SCN)$	460	1
$\delta_{\perp}(SCN)$	407	1
$\delta(CSC)$	190[b]	1
ΓCH_3	131[c]	1

[a] All frequencies are from the liquid state unless otherwise indicated.

[b] Frequency from (58).

[c] Solid state frequency (24).

Table 10. Assignments for the combination bands of methyl thiocyanate

Frequency (cm^{-1})[a]	Assignment (cm^{-1})	Symmetry Class
3999	3027 + 973 = 4000	A'
3923	2943 + 989 = 3932	A'
2853	2158 + 699 = 2857	A'
2833	2158 + 675 = 2833	A'
2615	2158 + 460 = 2618	A'
2558	2158 + 407 = 2565	A"
2411	1431 + 973 = 2404	A'
2308	1320 + 989 = 2309	A'
2109	1431 + 699 = 2130	A"
927[b]	466[b] + 466[b] = 932	A'
813	407 + 407 = 814	A'
645	460 + 190 = 650	A'

[a] All frequencies are from the liquid state unless otherwise indicated.

[b] Solid state frequency.

these vibrations produce absorption bands which are very characteristic of an asymmetric top. Most striking are the C type bands of the a" vibrations, $\nu_{as}CH_3$ and $\delta_{as}CH_3$. Pronounced P, Q and R branches are observed for the a' vibrations, ν_sCH_3, δ_sCH_3 and $\nu(CN)$. The methyl rocking vibrations are assigned at 989 and 973 cm^{-1}. Miller and White (58) have indicated some displeasure in assigning the out-of-plane methyl rock to the band at 973 cm^{-1}. However, the vapor state spectrum in this region confirms the assignment. Miller and White grouped the band maxima at 996, 981 and 958 cm^{-1} into a single band envelope. An alternate grouping, indicated in Table 41, is preferred. In the previous assignment the P-R separation is 28 cm^{-1}, in strong contrast to the 18 cm^{-1} found for the other bands. Assignment of the band at 968 cm^{-1} to the out-of-plane methyl rock is consistent with the C type bands found for the other a" vibrations. The band maxima at 996 and 981 are assigned to the in-plane methyl rock. As expected the band structure is of type B.

Miller and White (58) did not report an absorption band at 813 cm^{-1}. This band remained after repeated distillation and was also reported by Ham and Willis (28). It is easily assigned as an overtone of the SCN deformation at 407 cm^{-1} and has counterparts in the spectra of ethyl and isopropyl thiocyanate.

As mentioned previously, Fateley and Miller (24) have calculated a barrier against rotation about the C_α-S bond from their observation of the torsional frequency at 131 cm^{-1}. Their calculations were also based upon the structural data for methyl thiocyanate reported by Beard and Dailey (6). The latter authors observed two rotational transitions in the microwave region which they assigned to $\Delta J \; 3 \rightarrow 4$, $\Delta K = 0$ and $\Delta J \; 4 \rightarrow 5$, $\Delta K = 0$. Employing Mecke's formula (30),

$$F(J, K) = \tfrac{1}{2}(B + C)J(J + 1) + (A - \tfrac{1}{2}(B + C))K^2$$

for the rotational energy levels of a slightly asymmetric top, they were able to calculate a mean value for the rotational constants $\tfrac{1}{2}(B + C)$. Beard and Dailey assumed the bond distances and bond angles shown below:

C-H bond	1.09 Å	HCH	angle	109°
C_α-S bond	1.81 Å			
S-C bond	1.61 Å			
C≡N bond	1.21 Å			

From these assumptions they calculated a CSC angle of 142° as being consistent with the observed rotational constants. Pauling (67) has observed that the assumption of a 1.61 Å distance for the S-C bond implies a 70% contribution of resonance form A and only a 30% contribution of form B. This is not reflected in the vibrational spectrum of methyl

A. $H_3C - \underset{\cdot\cdot}{S}^{+} = C = \underset{\cdot\cdot}{N}\overset{-}{\colon}$ B. $H_3C - \underset{\cdot\cdot}{\overset{\cdot\cdot}{S}} - C \equiv N\colon$

thiocyanate. The two carbon-sulfur stretching frequencies in methyl thiocyanate are almost identical, 699 and 675 cm^{-1}. Furthermore, they are quite close to the normal single bond carbon-sulfur frequency of 704 cm^{-1} found in methanethiol.

Hence, both the C_α -S and S-C bonds should have equal or nearly equal internuclear distances. A more consistent assumption for both would be the 1.81 A found for C_α -S in methanethiol.

Using this bond distance the calculations of Beard and Dailey were repeated with the result that the optimum CSC angle was found to be 128°. This is still somewhat larger than the 113° expected by Pauling (67). However, it is in agreement with the 127° angle found by Bergmann, Sandor and Engel (9) for aromatic thiocyanates. The principal moments of inertia for these bond distances and a CSC angle of 128° are

$$I_A = 29.46 \times 10^{-40} \text{ gm-cm}^2$$
$$I_B = 284.12 \times 10^{-40} \text{ gm-cm}^2$$
$$I_C = 308.37 \times 10^{-40} \text{ gm-cm}^2.$$

Another result of the change in the S-C bond distance is a small increase in the calculated internal barrier against rotation about the C_α -S bond. Fateley and Miller (24) calculated the barrier to be 1.00 kcal. per mole. The recalculated barrier is 1.09 kcal. per mole.

Standard procedures were used to calculate the thermodynamic values listed in Table 11. The vibrational contributions to the thermodynamic functions, with the exception of the torsional mode, were evaluated with the aid of

Table 11. Thermodynamic properties of methyl thiocyanate[a]

Temperature ^{o}K	$-(F^{o}-H_{o}^{o})/T$		S^{o}		C	
	Tr+R	Vib	Tr+R	Vib	Tr+R	Vib
273.16	54.89	3.03	62.84	7.17	7.95	8.35
298.16	55.59	3.39	63.54	7.93	7.95	9.03
300	55.64	3.42	63.59	7.98	7.95	9.08
400	57.93	4.92	65.88	10.94	7.95	11.55
600	61.15	7.86	69.10	16.44	7.95	15.50

[a] Values listed in table are in units of calories per degree per mole.

Torkington's (87) tables. Pitzer's method (70) was employed to calculate the contribution of internal rotation. Frequencies obtained from condensed states were used for several of the normal vibrations. Fateley and Miller (24) have shown that there is only a small shift in frequency from the vapor state to the liquid state for the torsional mode in several compounds. The uncertainty in the assumed structural parameters does render the rotational contribution to the thermodynamic functions tentative.

Ethyl Thiocyanate

Symmetry classes ascribed in Appendix I to the normal vibrations of ethyl thiocyanate are based upon the C_s

molecular symmetry of the more stable isomer, C_β. Group theory calculations for C_s symmetry yields 15 normal vibrations of type a' and nine vibrations of type a". Vogel-Högler (88) has published the complete Raman spectrum of ethyl thiocyanate with polarization data for the more prominent Raman lines. Relatively high polarization ratios are reported for several vibrations of the a' symmetry class. This reflects the coexistence of the two isomers, of which only one has vibrations exhibiting polarization in the Raman effect.

Vibrational assignments for the fundamental and combination modes of ethyl thiocyanate are presented in Tables 12 and 13. The stretching vibrations of the methyl and methylene groups are readily assigned to the bands at 2976, 2935 and 2875 cm^{-1}. Methyl or methylene groups adjacent to a sulfur atom characteristically have relatively low frequencies for their deformation vibrations (8). Hence, the assignment of the absorption band at 1428 cm^{-1} to the CH_2 bend is preferred over the alternate assignment to $\delta_{as}CH_3$. Furthermore, the splitting found in the solid state spectrum about 1450 cm^{-1} can be readily explained as site splitting of the degenerate $\delta_{as}CH_3$.

In addition to a decrease in frequency for the deformation vibrations of a methyl or methylene group adjacent to a sulfur atom there is a simultaneous enhancement in intensity. An excellent illustration of this enhancement can be

Table 12. Assignments for the fundamental modes of ethyl thiocyanate[a]

Vibration	Frequency (cm^{-1})[b]	Degeneracy
$\nu_{as}CH_3$	2976	2
$\nu_{as}CH_2$	2935	1
$\nu_{s}CH_3$, $\nu_{s}CH_2$	2875	2
ν (CN)	2155	1
$\delta_{as}CH_3$	1451	2
CH_2 bend	1428	1
$\delta_{s}CH_3$	1381	1
CH_2 wag	1273	1
$\gamma_{\parallel}CH_3$	1062	1
CH_2 twist	1047[c]	1
ν (CC)	969	1
$\gamma\ CH_3$	960[d]	1
CH_2 rock	774	1

---

[a] The assignments are for the more stable isomeric form Γ_{β}.

[b] All frequencies are from the liquid state unless otherwise indicated.

[c] Raman line from liquid state sample (88).

[d] Solid state frequency.

Table 12. (Continued)

Vibration	Frequency (cm^{-1})	Degeneracy
ν(S-C)	686[e]	1
ν(C_α-S)	624	1
$\delta_{\parallel}$(SCN)	453	1
$\delta_{\perp}$(SCN)	407	1
$\delta_{\perp}$(CCS)	330	1
$\delta_{\parallel}$(CCS)	311	1
ΓCH_3	230[f]	1
δ(CSC)	161[c]	1

[e] ν(S-C) in the less stable isomer is assigned to 654 cm^{-1}.

[f] Band implied from a combination frequency at 388 cm^{-1} in the Raman spectrum (88) and an overtone at 468 cm^{-1} in the infrared.

seen in the spectra of methyl isothiocyanate and methyl thiocyanate, Figures 6 and 19. Three of the methylene deformation vibrations, CH_2 bend (1428 cm^{-1}), CH_2 wag (1273 cm^{-1}) and CH_2 rock (774 cm^{-1}), are indeed quite strong. On this basis it is quite tempting to assign the CH_2 twist to the strong band at 1062 cm^{-1}. However, the in-plane methyl rock should also occur in this region. Strong support for the assignment of the latter vibration

Table 13. Assignments for the combination bands of ethyl thiocyanate

Frequency (cm^{-1})[a]	Assignment (cm^{-1})	Symmetry Class
2900	1451 + 1451 = 2902	A'
2835	2155 + 686 = 2841	A'
2699	1428 + 1273 = 2701	A'
2614	2155 + 453 = 2608	A'
2553	2155 + 407 = 2562	A"
2486	1428 + 1062 = 2490	A'
2438	1381 + 1062 = 2443	A'
2349	1381 + 969 = 2350	A'
2103	1428 + 686 = 2114	A'
1305[b]	685 + 630 = 1315[b]	A'
1250	624 + 624 = 1248	A'
1047[b]	630 + 418 = 1048[b]	A"
810	407 + 407 = 814	A'
468	230 + 230 = 460	A'
388[c]	230 + 161 = 391[c]	A"

[a] All frequencies are from the liquid state unless otherwise indicated.

[b] Solid state frequency.

[c] Raman frequency (88).

arises from the distinct polarization of the coincident Raman line (88). Since even in the more symmetrical C_β isomer the CH_2 twist is an a" type vibration it cannot be polarized. Therefore the in-plane methyl rock is assigned to the band at 1062 cm^{-1} and the CH_2 twist is assigned to the Raman line at 1047 cm^{-1}. Either of the weak absorption bands seen in the spectrum of the solid state may originate from the CH_2 twist.

The out-of-plane methyl rock is assigned, in full agreement with Sheppard's assumption (73), as being degenerate with ν(CC) in the liquid state spectrum. Site splitting removes the degeneracy in the solid state.

Skeletal vibrations frequently lose their identity through mixing. However, both the SCN deformation vibrations are almost identical in frequency with the values observed in methyl thiocyanate. Discrete SCN deformation vibrations are possible because of the significant difference in frequency between them and the lower frequency CCS deformation vibrations. The in-plane CCS deformation is assigned to the absorption band at 311 cm^{-1} on the basis of the polarization found for the coincident Raman line. Both CCS deformation vibrations exhibit similar frequencies to the 331 cm^{-1} value found in ethanethiol (73). Only one normal vibration, the methyl torsional mode, was not directly observed either in the infrared or Raman spectrum. However, it is possible to assign the methyl torsional vibration to a 230 cm^{-1} frequency on the basis of combination bands at 388 and 468 cm^{-1}. A similar frequency is directly observed for the same vibration in ethyl chloride (24). Likewise, similar combination bands appear in the spectrum of ethanethiol and predict a methyl torsional frequency of 220 cm^{-1}.

The spectrum of solid ethyl thiocyanate exhibits both site and second order crystal field splitting. Site splitting of the accidental degeneracies of $\nu_{as}CH_3$ and $\delta_{as}CH_3$ are quite apparent. In addition almost every fundamental internal to the ethyl group shows a second order splitting of 3 to 5 cm^{-1}. Anomalously, not one vibration internal to the thiocyanate group exhibits a similar effect. Dows (21) has stated that such field effects indicate a high degree of crystallinity.

As previously discussed, it is possible to calculate the standard enthalpy difference between two isomers by measuring the integrated intensity ratio for two absorption bands, one originating in each of the discrete isomers, at several different temperatures. The integrated intensity ratio for the S-C stretches, A_{654}/A_{686}, in the liquid state are given in Table 14. A plot of (1/T) versus $\ln(A_{654}/A_{686})$ results in a ΔH^o of 490 cal. per mole. Some experimental difficulty was encounted in measuring the integrated intensity of the absorption band at 654 cm^{-1} because of the

Table 14. Integrated intensities for the S-C stretches in liquid phase ethyl thiocyanate

Temperature	A_{654}/A_{686}	Number of Observations
238.1°K	0.893±.003	2
305.5°K	1.124±.008	2
345.8°K	1.59 ±.05	2

proximity of the strong $\nu(C_\alpha$ -S) at 624 cm^{-1}. This was especially true for the measurement at 345°K where both bands tended to broaden considerably.

Isopropyl Thiocyanate

Neither the infrared nor the Raman spectrum of isopropyl thiocyanate has been reported in the literature. As discussed previously, rotationally isomeric configurations C'_β and H''_α coexist at room temperature. Unlike ethyl thiocyanate, the more stable isomer of isopropyl thiocyanate, C'_β, does not have any symmetry elements other than the identity operation. Consequently, all 33 normal vibrations are of the same vibrational symmetry type. Inasmuch as both isomers have basically the same normal vibrations, the character of these vibrations can be illustrated by a vibrational analysis for the less stable isomer H_{α}''. Such an analysis is presented in Appendix I, Table 66. Most of the vibrations internal to the isopropyl group are described in terms of localized methyl vibrations. In the H_{α}'' configuration the methyl groups occupy equivalent positions on opposite sides of the symmetry plane. As illustrated in Figure 1, each methyl group has its own characteristic group vibrations. The normal vibrations described in Appendix I refer to combinations of the same methyl vibrations in agreement with vibrational symmetry classes a' and a". For example, a nondegenerate vibration such as $\nu_s CH_3$, from each methyl group can be combined in-phase to form a normal vibration of symmetry type a' or out-of-phase to form a normal vibration of type a". Analogous in-phase and out-of-phase vibrations occur in the C_{β}' isomer. However, they cannot be differentiated by a plane of symmetry.

Vibrational assignments are presented for the fundamental and combination modes in Tables 15 and 16. Of the 33 normal vibrations only five, the CH stretch, two CSC deformation vibrations and two methyl torsional vibrations, have not been assigned. The first is covered by the stronger methyl stretching vibrations while the others are certainly below 300 cm^{-1}. No attempt has been made to assign relative degeneracies for multiple bands of a given vibration, Some indication of these degeneracies may be gained from the

Table 15. Assignments for the fundamental modes of isopropyl thiocyanate

Vibration	Frequency (cm^{-1})[a]
$\nu_{as}CH_3$	2979, 2932
ν_sCH_3	2871
$\nu(CN)$	2153
$\delta_{as}CH_3$	1462, 1446
δ_sCH_3	1388, 1372
$\delta(CH)$	1318, 1247
γCH_3	1157, 1057, 934 and 920[b]
$\nu(CC)$	1119, 884
$\nu(S-C)$	688
$\nu(C_\alpha -S)$	585
$\delta(SCN)$	455, 407
$\delta(CCC)$	403[b]
$\delta(CCS)$	329, 308

[a] All frequencies are from the liquid state unless otherwise indicated.

[b] Solid state frequency.

splitting found in the spectrum of the solid state.

The symmetric CC stretching modes are assigned in opposition to Sheppard's (76) analysis for isopropyl halides.

Table 16. Assignments for the combination bands of isopropyl thiocyanate

Frequency (cm^{-1})[a]	Assignment (cm^{-1})
2998[b]	2946 + 52 = 2998[b]
2917[b]	2866 + 52 = 2918[b]
2846	2153 + 688 = 2841
2768	1388 + 1388 = 2776
2733	2153 + 586 = 2739
2553	2153 + 407 = 2560
2506	1388 + 1119 = 2507
2250	1318 + 934 = 2252
1267[b]	687 + 585 = 1272[b]
1258	934 + 329 = 1263
1171[b]	1124 + 52 = 1176
815	407 + 407 = 814
468	416 + 52 = 468

[a] All frequencies are from the liquid state unless otherwise indicated.

[b] Solid state frequency.

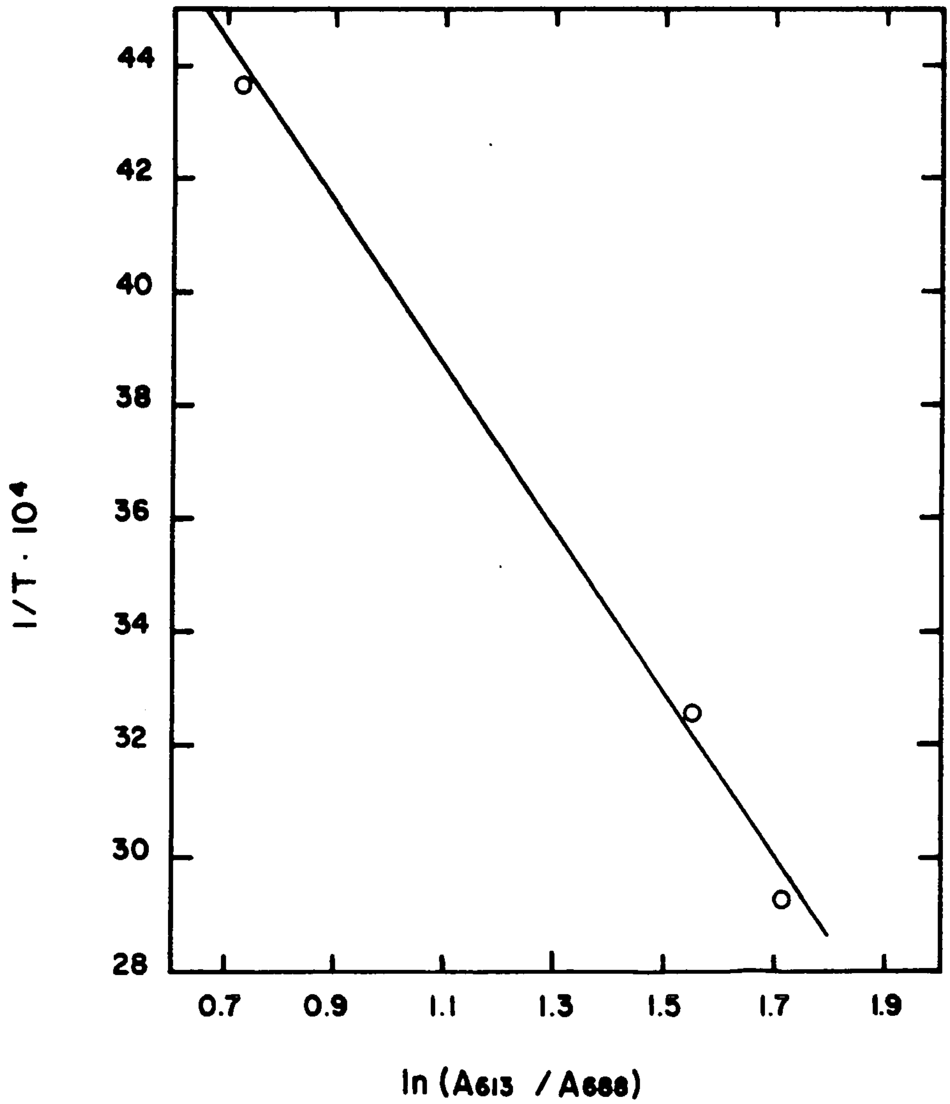
In reviewing these assignments and some Sheppard made for tert-butyl halides (75) an anomalous correlation appeared between the behavior of the CC stretching vibrations in alkyl halides and simple branched hydrocarbons. As discussed in Appendix D, a reversal of Sheppard's assignments for the lowest frequency CC stretch and methyl rock in both the isopropyl and tert-butyl halides yields a greatly improved correlation. Several authors (33, 57) have implied the same reversal in their assignments. However, they did so without acknowledgment of the difference in assignments.

Following the same procedure as was employed for ethyl thiocyanate, a ΔH^o of 1.36 kcal. per mole was found between the two isomeric species of isopropyl thiocyanate. Measured integrated intensity ratios for the absorption bands originating in the S-C stretch of each isomer are presented in Table 17. A graphical plot of $\ln(A_{613}/A_{688})$ versus the inverse of the temperature, (1/T), is shown in Figure 18. $\Delta H^o/R$ was calculated directly from the slope of the curve in Figure 18.

Table 17. Integrated intensities for the S-C stretches in liquid phase isopropyl thiocyanate

Temperature	A_{613}/A_{688}	Number of Observations
228.7°K	2.057± .061	4
307.1°K	4.690± .057	3
341.6°K	5.487± .248	4

Figure 18. Temperature dependence of the integrated intensity ratio A_{613}/A_{688}



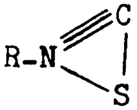
44
42
40
38
36
34
32
30
28
1/T · 10⁴
0.7
0.9
1.1
1.3
1.5
1.7
1.9
ln (A613 / A688)

ALKYL ISOTHIOCYANATES

Historical Background

Spectral information on the alkyl thiocyanates is frequently coincident in the literature with similar data for the alkyl isothiocyanates. Therefore many of the citations used in the previous discussion will also occur in this discussion. Coblentz (14) simultaneously reported the infrared spectra of methyl and ethyl isothiocyanate. He was not able to resolve the doublet about 2150 cm^{-1} for either compound. Gordy and Williams (26) repeated the investigation without improving the experimental results.

Dadieu and Kohlrausch (17, 18) were the first to observe the 2150 cm^{-1} doublet in the Raman spectra of both methyl and ethyl isothiocyanate. Reasoning that these frequencies occur in a spectral region characteristic of triple bonds Dadieu (17) postulated that



represented the molecular formula for an alkyl isothiocyanate. The 2150 cm^{-1} doublet would then involve two ring vibrations. Furthermore, he believed that this formula would explain why the alkyl isothiocyanates showed so little tendency to polymerize. This molecular formula had been considered previously by Perschke (68). However, by means of a parachor calculation, Perschke had discarded it as being much less probable than the formula R-N=C=S which contains a linear isothiocyanate functional group.

An alternate explanation of the doublet was proposed by Badger (5). According to this proposal one of the very strong bands about 2150 cm^{-1} is a fundamental transition of the isothiocyanate group, N=C=S. Similar adjacent double bond groups, occurring for example, in carbon dioxide and allyl derivatives, exhibit normal vibrations in the 2400 to 2000 cm^{-1} region. Badger further suggested that the intensity of the other absorption band resulted from a Fermi resonance interaction between the first excited state of the expected isothiocyanate fundamental and the second excited state of another normal mode about 1080 cm^{-1}. Hibben (32) was quick to point out that similar molecular systems have a closely related distribution of normal vibrations without showing an analogous doubling.

The Raman spectra of methyl and ethyl isothiocyanate were measured by Goubeau and Gott (27). They performed a simplified force constant calculation for methyl isothiocyanate assuming that the molecule was linear and the methyl group could be reduced to a point mass. As a result of their calculation they assigned one of the bands about 2150 cm^{-1} and one at 1087 cm^{-1} to the internal stretching vibrations of the isothiocyanate group. Furthermore, they assigned $\nu(C_{\alpha}-N)$ to the rather low frequency of 645 cm^{-1}.

Vogel-Högler (88) reported polarization data for most of the principal Raman lines.

The notation system used to distinguish the internal vibration of the isothiocyanate group was proposed by Thomas (86). His force constant calculations (85) for isothiocyanic acid indicated that the stretching vibrations were more aptly described as symmetric and asymmetric NCS stretches, ν_{as}(NCS) and ν_{s}(NCS).

In a cursory investigation of the intense absorption bands about 2150 cm^{-1}, Caldow and Thompson (12) found it impossible to interpret the observed band splitting. Lieber, Rao and Ramachandran (52) presented incomplete spectral data for several alkyl and aryl isothiocyanates. Corresponding to their inexplicably low frequency for ν (CN) in the alkyl thiocyanates, they report low frequencies for the doublet about 2150 cm^{-1}. They did suggest that the resonance form

$$R - \overset{+}{N} \equiv C - \underset{\cdot\cdot}{\overset{\cdot\cdot}{S}}:^{-}$$

contributes more to the molecular structure of alkyl isothiocyanates than does any other form. Sometime earlier Hunter and Partington (36) had discounted this resonance structure since it implied a dipole moment three times higher than that observed experimentally.

Svatek, Zahradnik and Kjaer (83) published an interesting paper dealing extensively with several alkyl isothiocyanates. Studying the 2150 cm^{-1} doublet in both carbon tetrachloride and chloroform solutions, they observed significant intensity shifts which they ascribed to solvent-solute interactions. In addition they characterized a strong absorption band in the 1350 to 1300 cm^{-1} region as originating in a CH deformation vibration of the alpha carbon but being greatly enhanced because of the proximity of the isothiocyanate group.

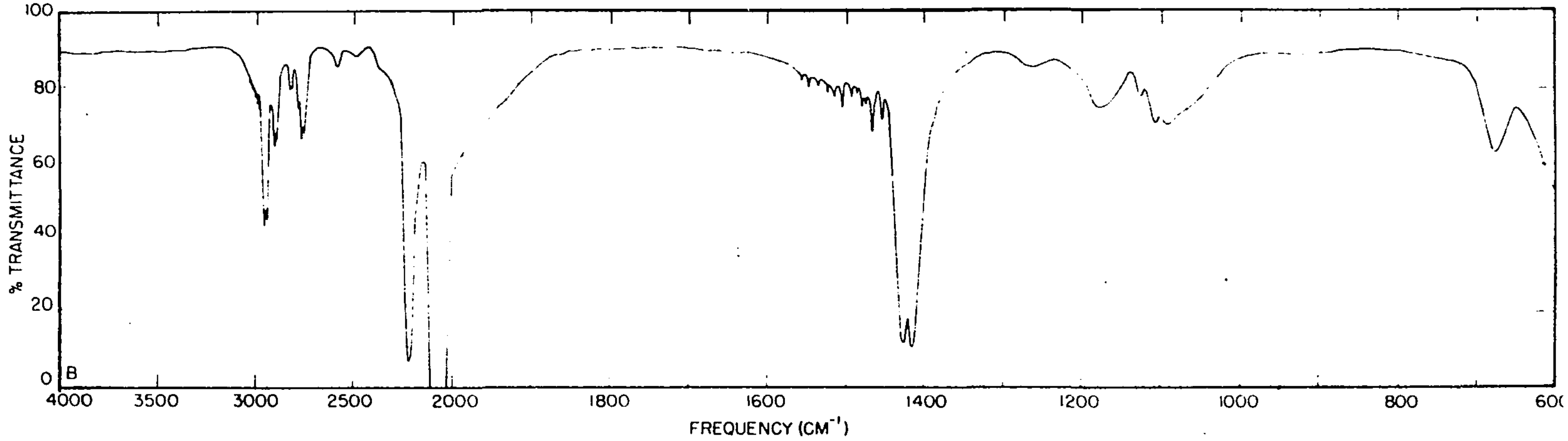
There is almost a complete lack of unanimity in the assignments for the isothiocyanate group vibrations in the three vibrational analyses (15, 28, 58) that have appeared for methyl isothiocyanate. Some of the difficulties encountered in these assignments illustrate the pitfalls which await investigators who choose the most simple derivatives of a series of compounds as being also the most representative. The key to interpreting the vibrational spectra of alkyl isothiocyanates lies in the correct assignment for three vibrations, $\nu_{as}(NCS)$, $\nu_{s}(NCS)$ and $\nu\,(C_{\alpha}-N)$. These vibrations shall then be discussed first.

The observed infrared absorption frequencies for methyl, ethyl, n-propyl, isopropyl, n-butyl and tert-butyl isothiocyanate are presented in Appendix F, Tables 47 through 52. Spectra of these compounds appear in Figures 19 through 25. Raman frequencies are given in Table 61.

Figure 19. Infrared spectra of methyl isothiocyanate

(A) liquid state

(B) vapor state


100
80
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20
0
% TRANSMITTANCE
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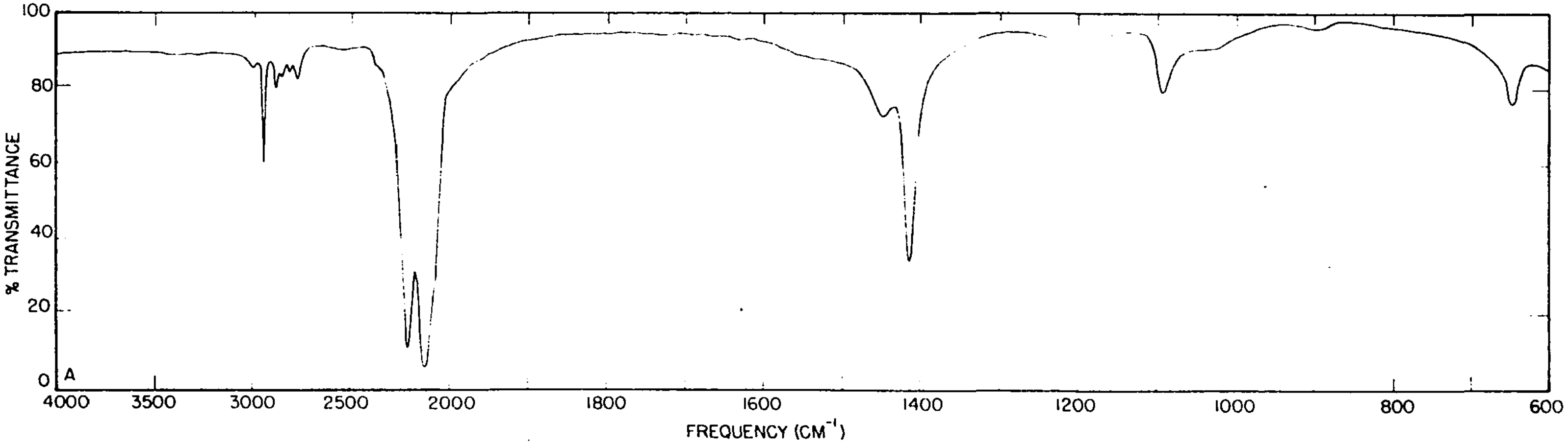
1600
1400
1200
1000
800
60
FREQUENCY (CM^{-1})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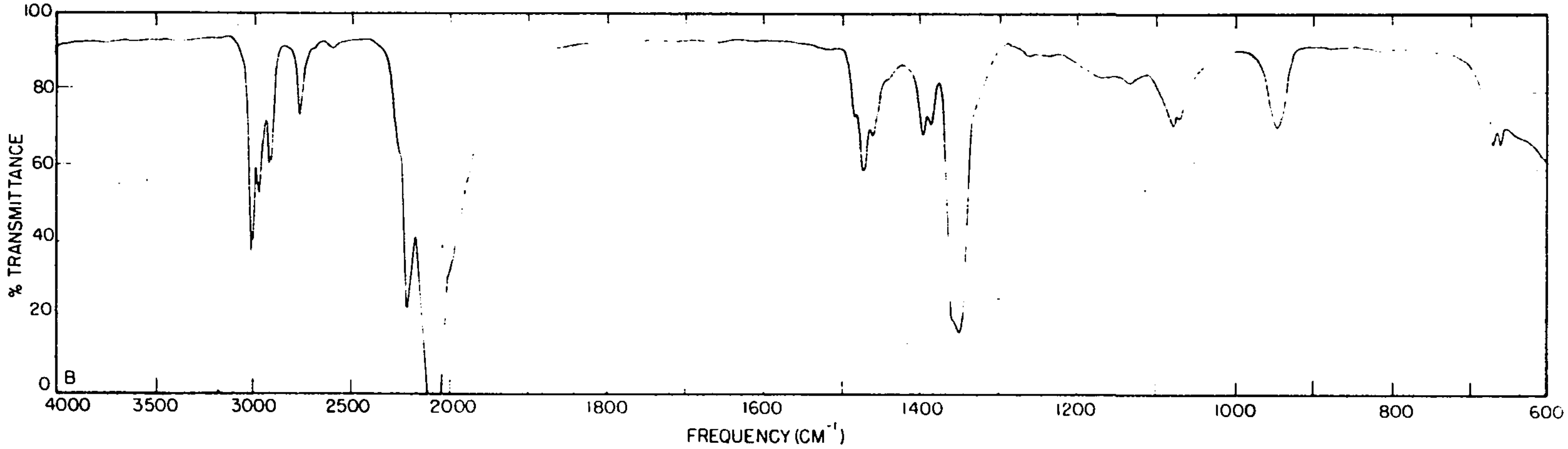
FREQUENCY (CM^{-1})

Figure 20. Infrared spectra of ethyl isothiocyanate

(A) liquid state

(B) vapor state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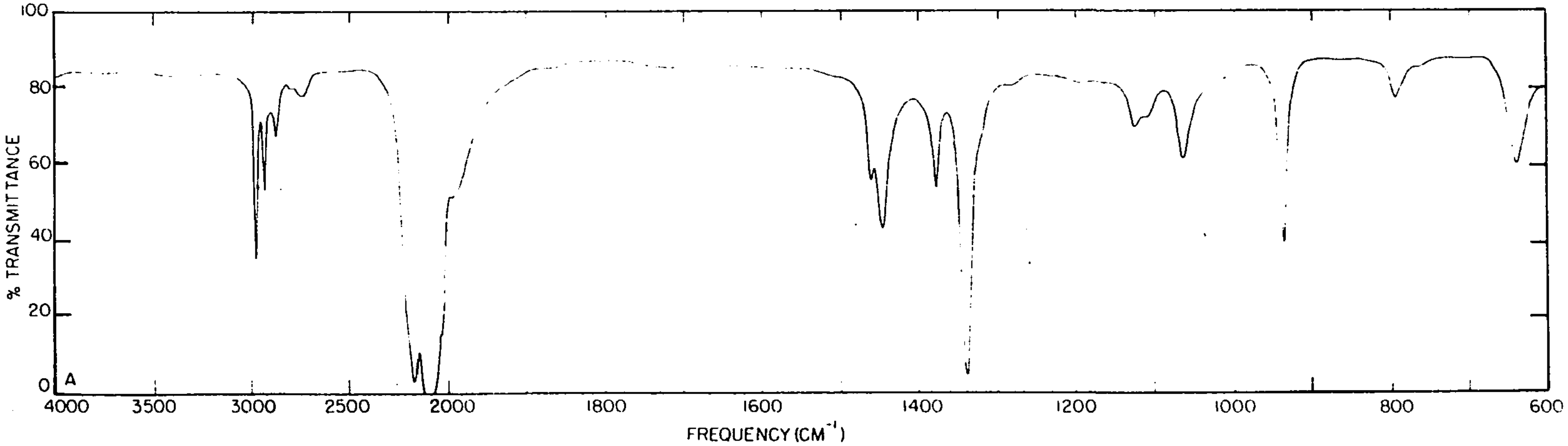
FREQUENCY (CM⁻¹)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% TRANSMITTANCE
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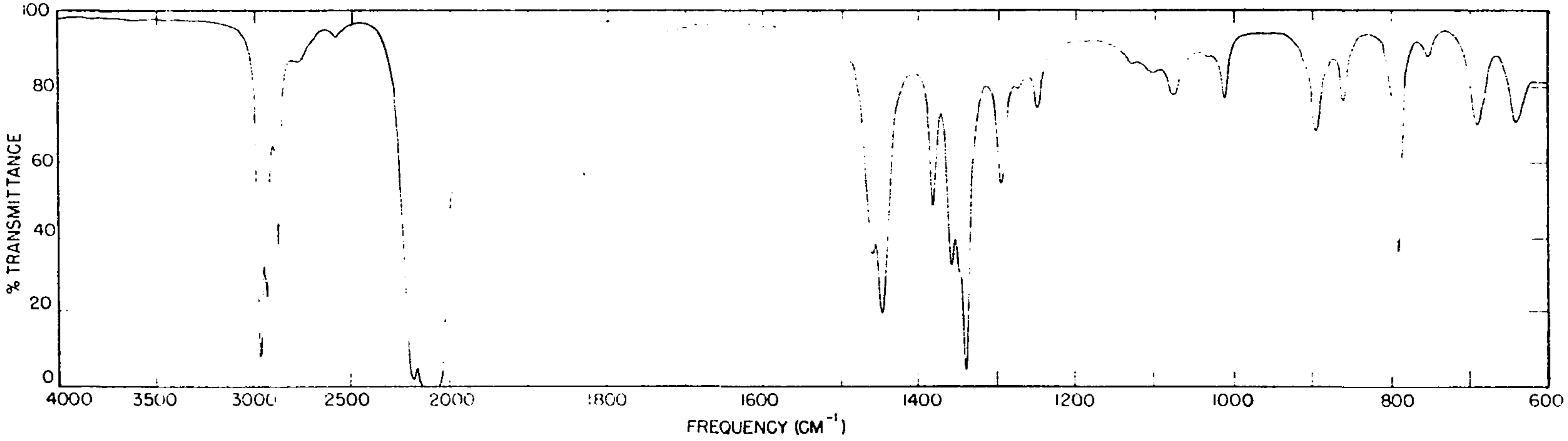
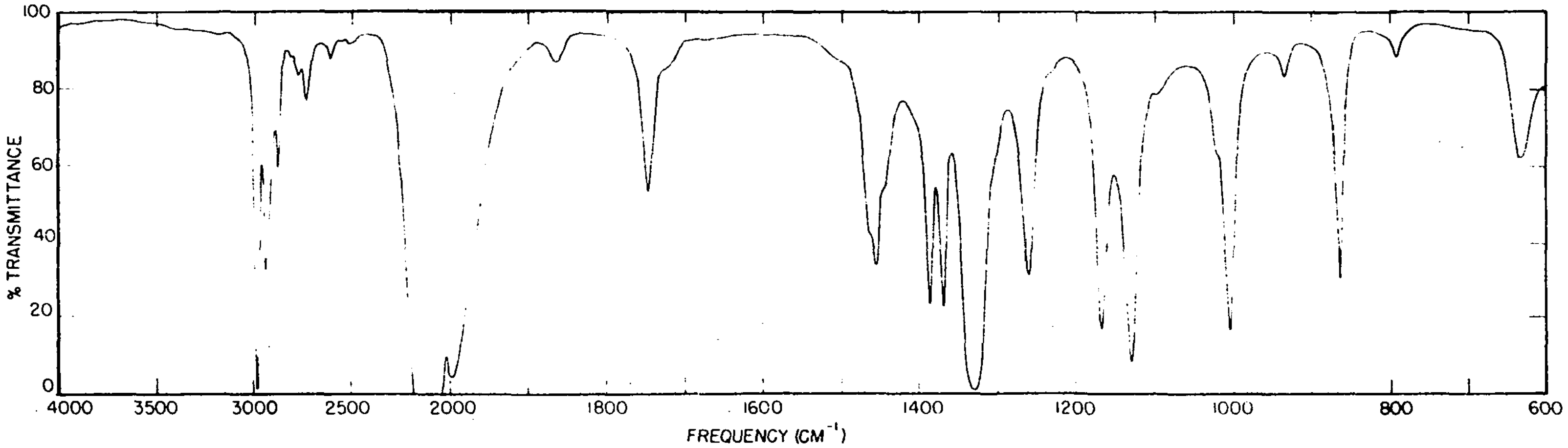
FREQUENCY (CM⁻¹)

Figure 21. Infrared spectrum of n-propyl isothiocyanate



100
80
60
40
20
0
% TRANSMITTANCE
4000
3500
3000
2500
2000
1800
1600
1400
1200
1000
800
600
FREQUENCY (CM^{-1})

Figure 22. Infrared spectrum of isopropyl isothiocyanate


100
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% TRANSMITTANCE
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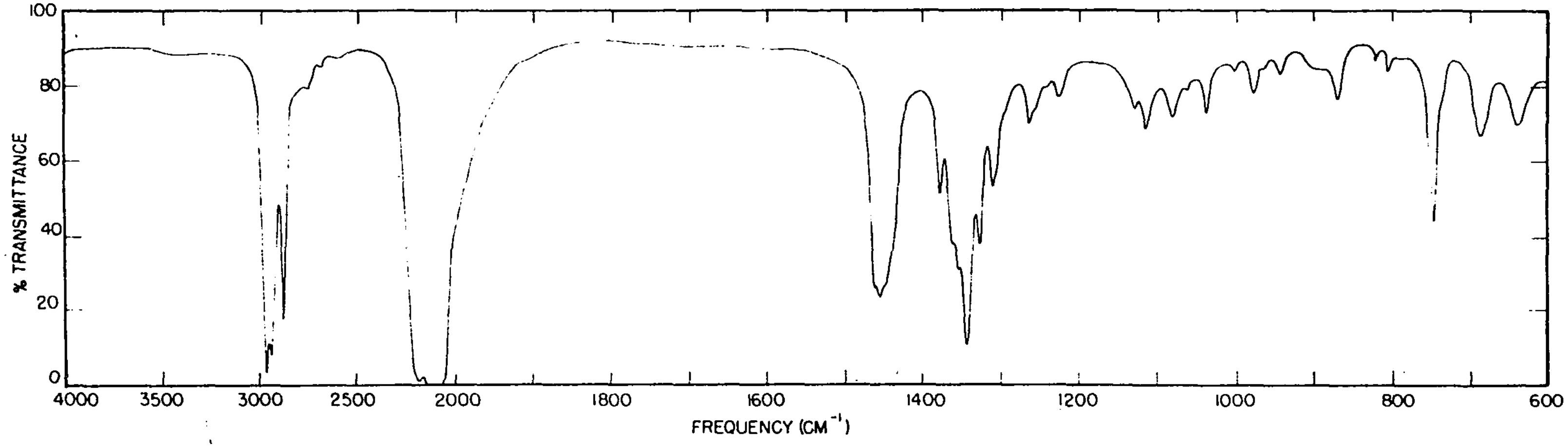
600
FREQUENCY (CM⁻¹)

Figure 23. Infrared spectrum of n-butyl isothiocyanate


% TRANSMITTANCE
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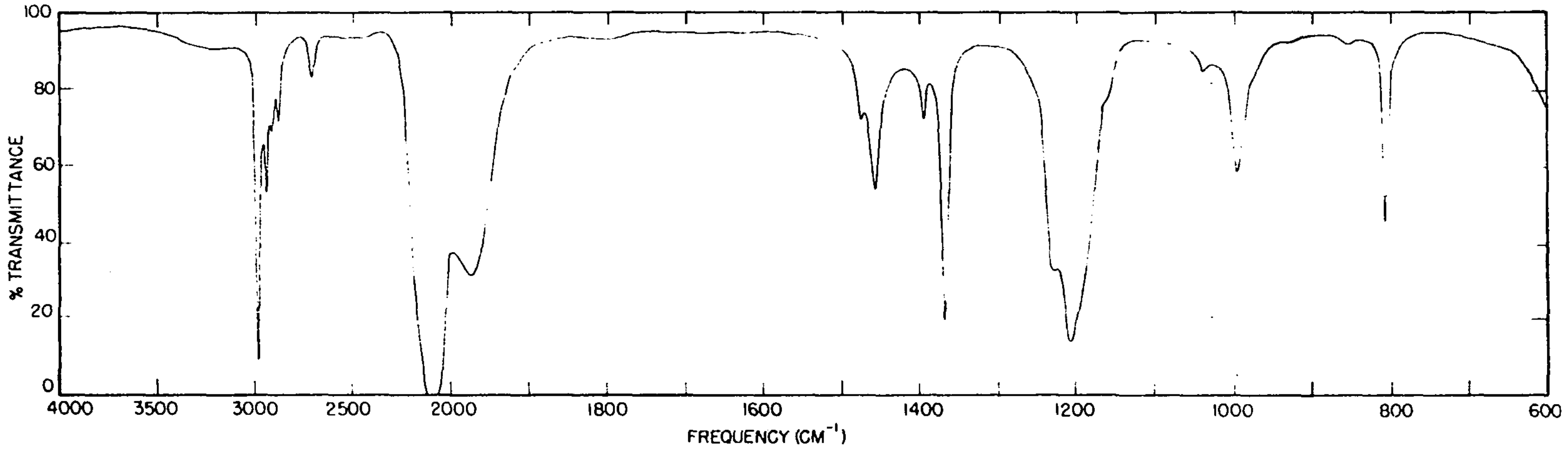
FREQUENCY (CM^{-1})

Figure 24. Infrared spectrum of tert-butyl isothiocyanate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% TRANSMITTANCE
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3000
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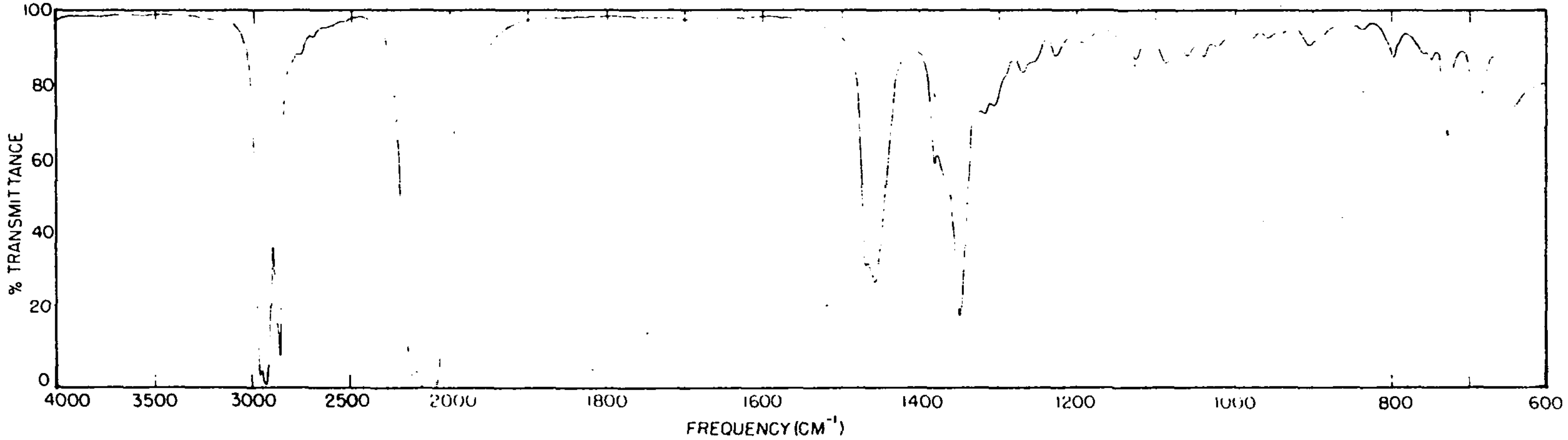
1600
1400
1200
1000
800
600
FREQUENCY (CM^{-1})

Figure 25. Infrared spectrum of n-heptyl isothiocyanate


100
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% TRANSMITTANCE
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1600
1400
1200
1000
800
600
FREQUENCY (CM^{-1})

Isothiocyanate Group Vibrations

Any discussion of the isothiocyanate group vibrations must necessarily begin with the 2150 cm^{-1} doublet. These very intense bands completely dominate the vibrational spectrum of the alkyl isothiocyanates. While distinct correlations do appear in this region among the spectra of methyl, ethyl, isopropyl and tert-butyl isothiocyanate, subtle differences arise making a unified discussion for all four compounds difficult. The problems are compounded by an increase in complexity in the spectra obtained from solid state samples at liquid nitrogen temperature as compared to spectra from liquid samples at room temperature. Arbitrarily the discussion will begin with consideration of the 2150 cm^{-1} doublet in the spectrum of methyl isothiocyanate in the liquid state and solutions.

Although there is general acceptance (15, 28, 58) in the recent literature of Badger's (5) proposed explanation on the origin of the 2150 cm^{-1} doublet, no corroborative evidence either for or against this hypothesis has been offered. Strong evidence in support of this proposal does exist in the "puzzling" (58) intensity and frequency shifts in the 2150 cm^{-1} doublet associated with changes in physical state or solvent. The magnitude of the intensity changes found for methyl isothiocyanate may be seen in Figure 26. Quantitative data for both the frequency shifts

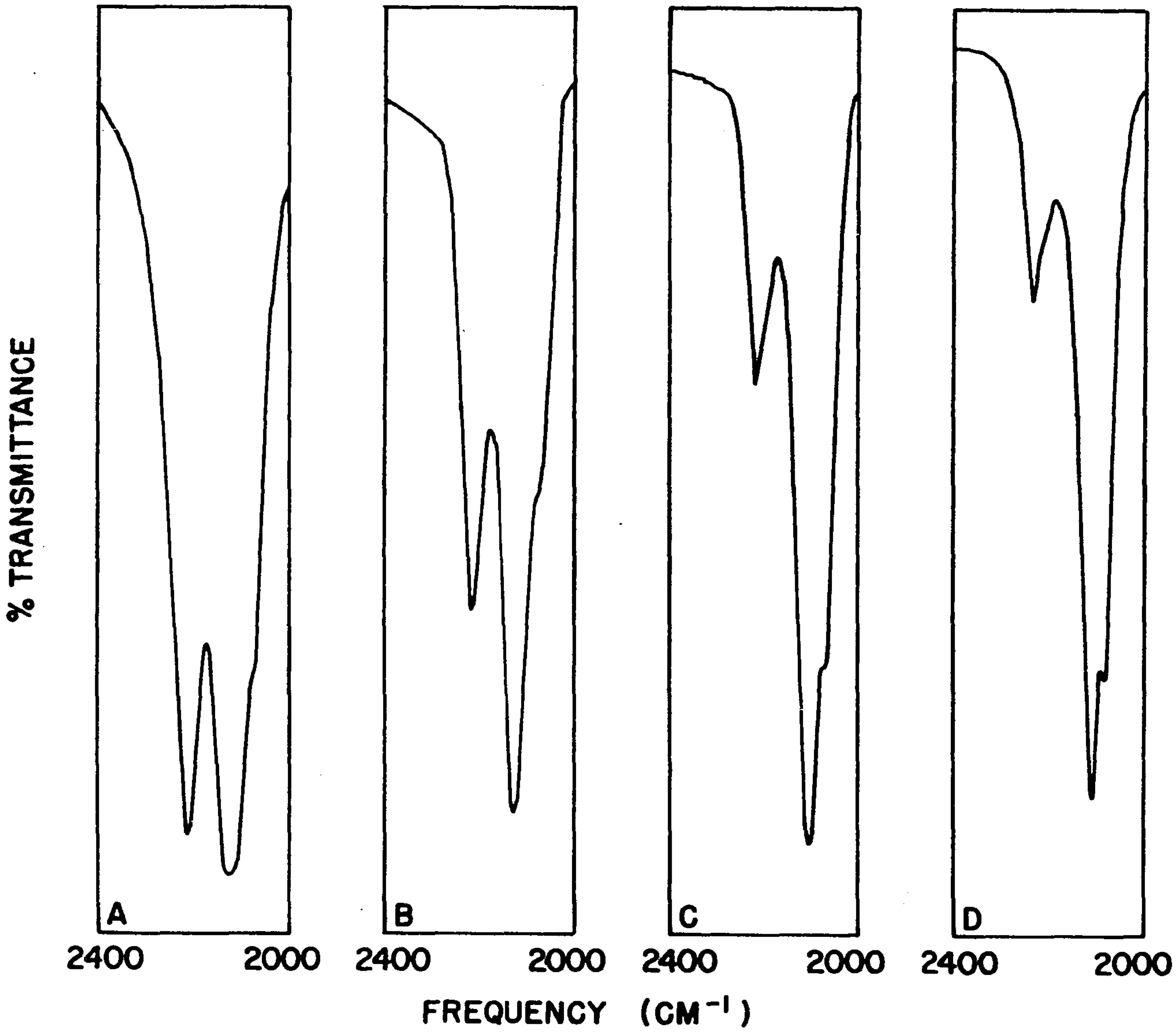
Figure 26. The 2150 cm^{-1} doublet of methyl isothiocyanate in

(A) the liquid state,

(B) chloroform,

(C) carbon tetrachloride, and

(D) cyclohexane solutions


% TRANSMITTANCE
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2000
2400
2000
2400
2000
2400
2000
FREQUENCY (CM^{-1})

and intensity changes are presented in Table 18. There is a pronounced relationship between the ratio of the integrated intensities, A_{2100}/A_{2200}, and the difference between the frequency calculated for the overtone of the 1088 cm^{-1} (liquid state) fundamental and the observed frequencies for the doublet. The observed relationship is in accord with a Fermi interaction and assignment of the higher frequency member of the doublet to the transition more closely related to the original overtone.

Table 18. Absorption data for the 2150 cm^{-1} doublet in methyl isothiocyanate

Phase or	Frequency (cm^{-1})			Calculated		Intensity
Solvent	Observed		Calculated[a]	Displacement		A_{2200}/A_{2100}
liquid	2206	2124	2176	30	52	1.90
$CHCl_3$	2213	2124	2190	23	66	2.19
CCl_4	2225	2108	2202	23	94	4.12
CS_2	2221	2104	2200	21	96	5.03
C_6H_{12}	2223	2103	2204	19	101	5.65

[a] Calculated frequency is twice the observed value for the fundamental about 1090 cm^{-1}. For complete data on solution spectra see Table 53.

These conclusions follow directly from consideration of Fermi resonance. As discussed previously, Fermi resonance is an interaction between energy levels and results in a mixing of the eigenfunctions for the original energy levels. Consequently transitions from the ground state to either of the final resonance levels will have a transition moment exhibiting characteristics of transitions to both of the original energy levels. For example, in the present case the unperturbed energy levels are the first excited state, $v = 1$, of the asymmetric NCS stretching vibration and the second excited state, $v = 2$, of a fundamental 1088 cm^{-1} above the ground state. It is quite reasonable to expect that almost all of the absorption intensity about 2150 cm^{-1} originates in the transition to the first excited level of the asymmetric NCS stretch. Only rarely are overtone transitions, $\Delta v = 0 \longrightarrow 2$, of even moderate intensity. As a result of Fermi resonance an enhanced intensity should occur for the transition more closely related to the overtone. This results from a contribution to the transition moment of the overtone through resonance, by the transition moment of the unperturbed fundamental ν_{as}(NCS).

The magnitude of this enhancement, or intensity transfer, is dependent upon the strength of the resonance interaction. An indication of the latter quantity may be gained from the coefficients c and d which relate the original eigenfunctions to the eigenfunctions for the final resonance states. As shown in Appendix B the coefficients are

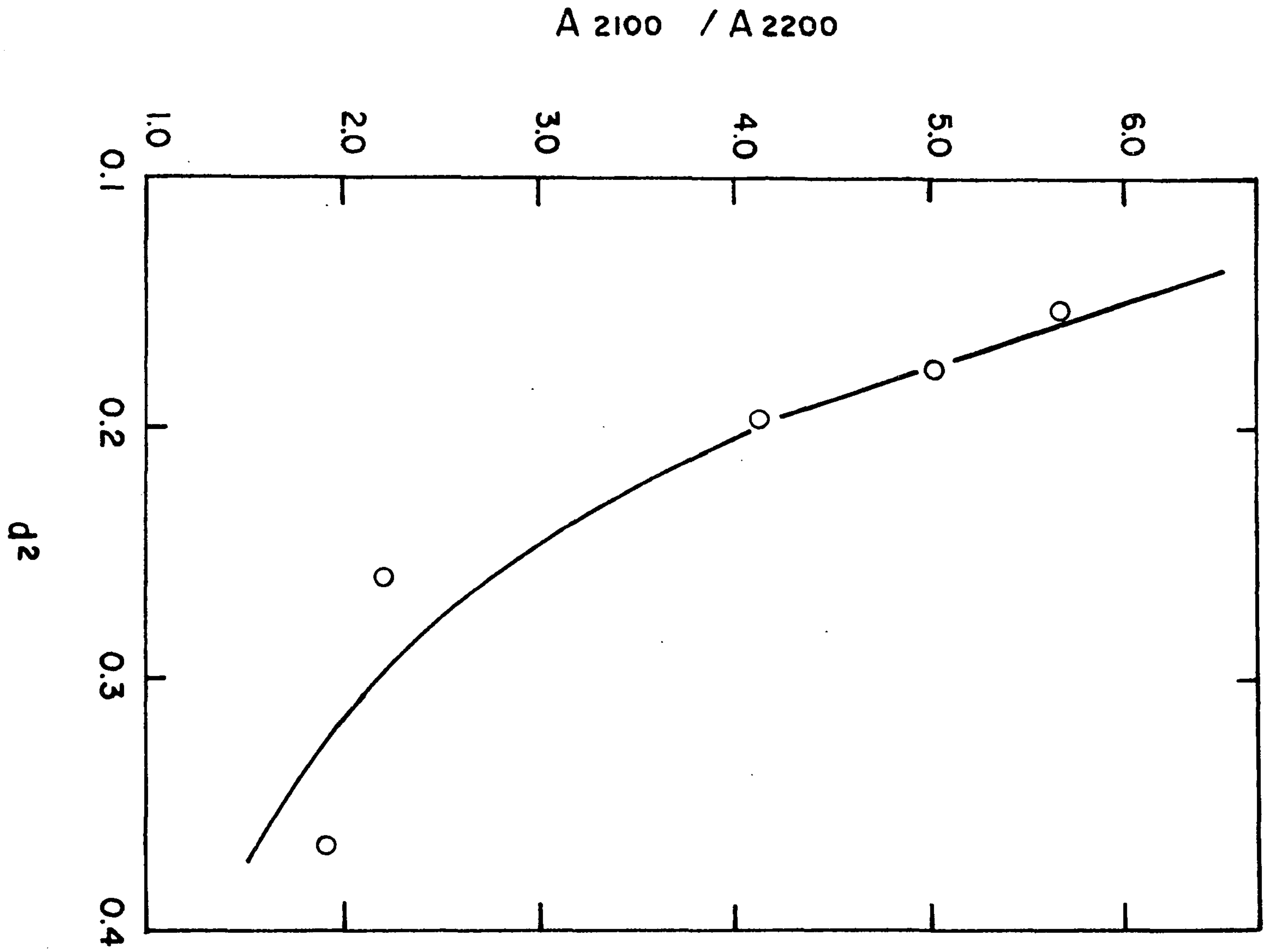
$$c = \frac{(E_a - E_b + \delta)^{\frac{1}{2}}}{(2)^{\frac{1}{2}}(E_a - E_b)^{\frac{1}{2}}} \qquad d = \frac{(E_a - E_b - \delta)^{\frac{1}{2}}}{(2)^{\frac{1}{2}}(E_a - E_b)^{\frac{1}{2}}}$$

where E_a and E_b are the observed energies and δ is the difference in the unperturbed energies, E_n^o and E_i^o. It is assumed, without loss in generality, that E_a and E_n^o are greater than E_b and E_i^o. In the problem under study E_n^o and E_i^o correspond to the second excited state of the 1088 cm^{-1} fundamental and the first excited state ν_{as}(NCS), respectively. The coefficients c and d can be related to the absorption data for methyl isothiocyanate presented in Table 18. It is necessary to make an assumption with respect to E_n^o. The most reasonable value for E_n^o is twice the calculated energy for the 1088 cm^{-1} fundamental. Although not strictly valid, since it does not take into account anharmonicity factors, this assumption is a fairly good approximation. The relationship

$$\nu_a + \nu_b = \nu_n^o + \nu_i^o$$

is then used to calculate the unperturbed frequency ν_i^o. In substantiation of Badger's proposal a correlation, shown in Figure 27, does exist between the integrated intensity ratio and d^2. The relative decrease in intensity for the higher frequency band of the doublet corresponding to a decrease in the resonance interaction validates its

Figure 27. Correlation between the resonance coefficient d^2 and the integrated intensity ratio A_{2100}/A_{2200}


A 2100 / A 2200
1.0
2.0
3.0
4.0
5.0
6.0
0.1
0.2
0.3
0.4
d2

assignment to the transition more closely related to the overtone mode.

While still limiting the discussion to the liquid state, vibrational assignments for the 2150 cm^{-1} region can now be made for ethyl, isopropyl and tert-butyl isothiocyanate. Methyl isothiocyanate exhibits a doublet with approximately equal intensities for both absorption bands. Conversely in the spectra of the other isothiocyanates one absorption band is dominant. In each compound the stronger band is assigned to the vibrational transition more closely related to ν_{as}(NCS). There is a complete parallelism between the assignments in methyl and ethyl isothiocyanate. As compared to methyl isothiocyanate a small decrease in frequency, from 1088 to 1063 cm^{-1}, is found in ethyl isothiocyanate for the fundamental associated with the overtone part of the Fermi doublet. Consequently the overtone also appears slightly lower in frequency, at 2183 cm^{-1}. A reversal of intensity in the Fermi doublet is observed in the spectrum of tert-butyl isothiocyanate. This reflects a still further decrease to 994 cm^{-1} for the fundamental responsible for the overtone at 1976 cm^{-1}. The more intense higher frequency shoulder on the principle maximum, a triplet instead of the usual doublet is found in the spectrum of isopropyl isothiocyanate. Corresponding to tert-butyl isothiocyanate, the low frequency shoulder at 1999 cm^{-1} is assigned as the overtone of the fundamental at 1004 cm^{-1}. Tentatively the high frequency shoulder is assigned as a combination transition. Enhancement of the overtone transitions in ethyl, isopropyl and tert-butyl isothiocyanate is indicative that Fermi resonance is also present in these compounds. Hence, these assignments are not meant to imply either unperturbed vibrational transitions or energy levels. Conversely a correlation is implied between the molecules and also between the observed transitions and the unperturbed transitions to which they are more closely related.

Throughout the previous discussion no attempt has been made to assign the 1088 cm^{-1} fundamental of methyl isothiocyanate or its analogues at 1063, 1004 and 994 cm^{-1} in the spectra of ethyl, isopropyl and tert-butyl isothiocyanate. Two alternate assignments, ν_s(NCS) and $\nu(C_\alpha$-N) are possible for the 1088 cm^{-1} absorption band. As can be seen in Table 19 both proposed assignments have received support. Any discussion of an assignment for ν_s(NCS) must be coupled with a discussion about $\nu(C_\alpha$-N). Assignment of ν_s(NCS) to either the 1088 or 644 cm^{-1} absorption bands has as an immediate result the alternate designation for $\nu(C_\alpha$-N).

Goubeau and Gott (27) made their assignments as a result of a force constant calculation for methyl isothiocyanate. Since these calculations are based upon assumptions that are not valid, the assignments cannot be considered to be more than tentative.

Table 19. Assignments proposed for ν_s(NCS) and ν(C_α-N) in methyl isothiocyanate

Authors	Frequency (cm^{-1})[a] ν_s(NCS)	 ν(C_α-N)
Goubeau & Gott (27)	1087	645
Costoulas & Werner (15)	656	1097
Miller & White (58)	1088	893[b]
Ham & Willis (28)	640	1090

[a] Frequencies included in the table are those published by the author to whom they are ascribed.

[b] Assigned the 644 cm^{-1} band to the in-plane NCS deformation vibration.

To find support for their assignments, Ham and Willis (28) performed a first order perturbation calculation. A secular equation, of the same form as found in Fermi resonance calculations, was set up for the isolated isothiocyanate group. In terms of frequencies (cm^{-1}) the secular equation is

$$\begin{vmatrix} \nu_n - \nu & \phi \\ \phi & \nu_i - \nu \end{vmatrix} = 0$$

where ν_n and ν_i are the frequencies for the individual bonds in the isothiocyanate group before interacting. Phi, ϕ, is the interaction element. These authors state that a consistent assignment scheme will have a single valued solution for $\emptyset$. There are several ways to express the solutions, ν_a and ν_b, of the secular determinant. One of the simplest and most useful expressions is

$$\nu_a + \nu_b = \nu_n + \nu_i.$$

While the interaction element does not appear directly in this equation, a single valued solution for $\emptyset$ will occur only if the equality of sums is maintained. Frequencies for ν_{NC} (ν_n) and ν_{CS} (ν_i) were calculated by Ham and Willis from a semi-empirical bond distance-stretching frequency relationship (4) and from the average of the asymmetric and symmetric stretches in carbon disulfide. Table 20 presents a comparison of the sums $\nu_a + \nu_b$ and $\nu_n + \nu_i$ for several molecules. Only two, methyl isothiocyanate and thiocyanic acid, are taken from Ham and Willis. There is excellent agreement between the two sums in carbon oxysulfide, isocyanic acid and isothiocyanic acid. Interestingly Ham and Willis offered methyl isocyanate as proof that their approach had some merit. The data used by these authors gives a sum of 3644 cm^{-1} and is in fair agreement with the "theoretical" value of 3593 cm^{-1}. Unfortunately in their calculations they employed the data of Eyster and Gillette (22) for methyl isocyanate. As shall be discussed later, these data are inaccurate above 1000 cm^{-1}. A much

Table 20. Comparison of frequency summations for first order perturbation calculations

Molecule	ν_n	ν_i	Sum	ν_a	ν_b	Sum
	Frequency (cm^{-1})					
OCS	1843[a]	1090[b]	2933	2064	859	2923
HNCO	1843[a]	1750[c]	3593	2274	1327	3601
HNCS	1750[c]	1090[b]	2840	1963	860	2823
CH_3NCO	1843[a]	1750[c]	3593	2288	1440	3728
CH_3NCS	1750[c]	1090[b]	2840	2154[d] 2154	644 1088	2798 3242

[a] Estimated from the asymmetric and symmetric stretches of carbon dioxide.

[b] Estimated from the asymmetric and symmetric stretches of carbon disulfide.

[c] Estimate from reference 28.

[d] Estimated from observed frequencies for Fermi doublet.

poorer agreement is found for the redetermined frequencies in methyl isocyanate. Implicit in the calculations of Ham and Willis is the assumption that the isothiocyanate group, or the isocyanate group, can be mathematically isolated. A similar assumption was made by Thomas (85) in normal coordinate calculations for both isocyanic and isothiocyanic acid. In both molecules the NH frequency is found about 3500 cm^{-1} (31, 71) and is isolated from the rest of the normal vibrations. Thus the agreement between the two sums for these two molecules and carbon oxysulfide is not surprising. The validity of mathematically isolating the isothiocyanate group in the methyl derivative is not as apparent. Unambiguously, the C_α-N stretch in methyl isocyanate can be assigned to an absorption band at 852 cm^{-1}. Either of the two assignments, 1088 or 644 cm^{-1}, in methyl isothiocyanate involves a very significant shift in frequency. Therefore, it is not likely that such an elementary treatment for the isothiocyanate group should be valid in methyl isothiocyanate. Another result of these calculations seems to be anomalous. Ham and Willis calculated an interaction element of 670 cm^{-1} for methyl isothiocyanate. This is unexpectedly large as compared with 506 and 433 cm^{-1} found for carbon dioxide and carbon disulfide. The interaction element is a measure of the extent of the interaction between the original energy levels and is inversely proportional to their initial separation. There is no reason to expect that methyl isothiocyanate, where the original energy levels are 660 cm^{-1} apart, should have a larger interaction element than carbon dioxide, where the unperturbed levels are degenerate.

Although Costoulas and Werner (15) proposed the same assignments as Ham and Willis (28) for ν_s(NCS) and $\nu(C_\alpha$-N), they offered different substantiating arguments. Costoulas and Werner justified their assignment of $\nu(C_\alpha$-N) to the absorption band at 1088 cm^{-1} by drawing an analogy with methylamine where this vibrational transition occurs at 1045 cm^{-1}. Methylamine is an extremely poor choice for such a comparison since there is little in common between the amine and isothiocyanate functional groups other than that they both contain a nitrogen atom. Furthermore, methylamine does not offer any basis for assigning the 910 and 852 cm^{-1} frequencies found for $\nu(C_\alpha$-N) in methyl azide (55) and methyl isocyanate (22), respectively. The absorption band, at 1090 cm^{-1}, in the vapor state spectrum of methyl isothiocyanate exhibits a hybrid type band structure. Costoulas and Werner correlated this band structure with an observation that the transition moment for $\nu(C_\alpha$-N) is not parallel to the figure axis. However, the alternate assignment, ν_s(NCS) also has a transition moment that is not parallel to the figure axis. In addition ν_{as}(NCS) exhibits a hybrid band structure. This may possibly be a consequence of Fermi resonance involving ν_{as}(NCS). In a third attempt to validate their assignments Costoulas and Werner compared the following data:

	ν(C=S)	ν(C=O)
CH_3NCX	?	1440
Cl_2CX	1121	1828

where X is either an oxygen or sulfur atom. From these frequencies and their associated force constants, Costoulas and Werner were lead to predict a 738 cm^{-1} frequency for ν (C=S). They reasoned that a decrease in frequency to 644 cm^{-1} could be explained by the coupling interaction of adjacent double bonds and a contribution by the resonance form $R\text{-}\overset{+}{N}\equiv C\text{-}S^{-}$. This analysis deserves immediate comment. A direct ratio calculation of the frequencies for phosgene, thiophosgene and methyl isocyanate yields a 880 cm^{-1} frequency for ν(C=S) in methyl isothiocyanate. Force constants have not been published for either methyl isocyanate or methyl isothiocyanate. Hence, it is difficult to substantiate their frequency of 738 cm^{-1} for the unperturbed vibration (C=S). Coupling of adjacent double bonds is found in methyl isocyanate and in line with the previous discussion it is difficult to justify a greater interaction in methyl isothiocyanate than in methyl isocyanate. As pointed out by Ham and Willis the resonance form $R\text{-}\overset{+}{N}\equiv C\text{-}S^{-}$ is not substantiated by bond distances (6) or dipole measurements (36).

Miller and White (58) did not attempt to justify their assignments for ν_s(NCS) and $\nu(C_\alpha\text{-}N)$. However, they did state that both vibrations taking part in the Fermi interaction must originate in the isothiocyanate functional group. Consequently they assigned the 1088 cm^{-1} fundamental to ν_s(NCS). Miller and White did not completely discount the alternate assignment of $\nu(C_\alpha\text{-}N)$ to this absorption band.

The calculations and other evidence used to substantiate the assignments shown in Table 19 do not tolerate close inspection. The spectrum of methyl isothiocyanate by itself is insufficient to resolve the enigma posed by ν_s(NCS) and ν (C_α -N). Specific assignments for the complex spectra found in the carbon-sulfur spectral region of the alkyl thiocyanates were made possible only by using as an interpretive tool the spectral characteristics observed for ν (C_α -X). Likewise, the problems encountered in the assignment of ν (C_α -N) can be resolved by application of the finding for ν (C_α -X). Associated with the 1088 cm^{-1} absorption band in methyl isothiocyanate are the absorption bands at 1063, 1004 and 994 cm^{-1} in the spectra of ethyl, isopropyl and tert-butyl isothiocyanate, respectively. Similarly, counterparts to the 644 cm^{-1} absorption band are found at 638, 634 and 615 cm^{-1}. Therefore both series of absorption bands roughly fulfill Sheppard's observation that ν(C_α -X) decreases consistently upon substitution of the alpha carbon with successive methyl groups. For neither series of bands is the observed frequency decrease nearly as regular as that found in alkyl halides or thiocyanates. Rotational isomerism about the C_α -C_β bond cannot occur in methyl, ethyl, isopropyl or tert-butyl isothiocyanate. However, n-alkyl derivatives do have rotationally isomeric configurations resulting from restricted rotation about the C_α -C_β bond. Hence, as compared to ethyl isothiocyanate a "splitting" should be found for $\nu(C_{\alpha}\text{-N})$ in n-alkyl isothiocyanates. The "splitting" results from the addition to the liquid state spectrum, again as compared to ethyl isothiocyanate, of a new absorption band 30 to 60 cm^{-1} higher in frequency than the value found for $\nu(C_{\alpha}\text{-N})$ in ethyl isothiocyanate. Indeed, the expectations are completely fulfilled by the 644 cm^{-1} series. In the three n-alkyl isothiocyanates studied, n-propyl, n-butyl and n-heptyl, two absorption bands are observed. They are found at 688 ± 2 and 640 ± 1 cm^{-1}. Furthermore, the lower frequency band disappears in the spectrum obtained from a solid state sample of n-propyl isothiocyanate at liquid nitrogen temperature. The analogy with $\nu(C_{\alpha}\text{-X})$ is complete. Similar simplication of the vibrational spectrum about 1050 cm^{-1} is not observed for solid n-propyl isothiocyanate. Therefore the 644 cm^{-1} band in the spectrum of methyl isothiocyanate and its counterparts in the other alkyl isothiocyanates are assigned to $\nu(C_{\alpha}\text{-N})$. As a direct consequence $\nu_s(NCS)$ is assigned to the series of bands originating with the 1088 cm^{-1} fundamental in methyl isothiocyanate.

The assignments by Miller and White of $\nu(C_{\alpha}\text{-N})$ to the absorption band at 893 cm^{-1} has not been discussed. Their assignment results from a forced assignment of the in-plane deformation, $\delta_{\parallel}(NCS)$, to the 644 cm^{-1} absorption band. This in turn resulted from a lack of an alternate assignment for the CNC angle deformation vibration.

Observation of a weak infrared absorption at 338 cm^{-1} resolved this difficulty. In addition, corresponding assignments are not available for $\nu(C_\alpha\text{-N})$ at 893 cm^{-1} in ethyl or isopropyl isothiocyanate.

Although the assignments in Tables 22, 25, 27 and 29 are a direct result of the preceeding observations, a more subtle interpretation should not be completely discounted. From the data presented by Ham and Willis (28), the frequencies for phosgene and thiophosgene employed by Costoulas (15) and the calculations of Thomas (85), a frequency from 900 to 850 cm^{-1} might well be expected for ν_s(NCS). Likewise, a 875 to 800 cm^{-1} frequency might be expected for $\nu(C_\alpha\text{-N})$ on the basis of the 910 and 852 cm^{-1} frequencies observed for the same vibrations in methyl azide (55) and methyl isocyanate (22). Both vibrations in all isothiocyanates must be of the same symmetry class. Hence, it is not unreasonable to expect that these two vibrations should enter into a resonance interaction. As a result both normal modes would be shifted significantly in frequency. The resulting vibrational transitions would then be hybrids of the unperturbed transitions. However, the rotational splitting still should be observed for the transition more closely related to $\nu(C_\alpha\text{-N})$. Interestingly the intensities of ν_s(NCS) and $\nu(C_\alpha\text{-N})$ are inversely coupled. A sharp increase in intensity is found for ν_s(NCS) in going from methyl to tert-butyl isothiocyanate. Simultaneously a decrease in intensity is found for $\nu(C_\alpha\text{-N})$. This may possibly reflect a decrease in coupling corresponding to an increase in the separation between the original energy levels. The separation increase would result from the normal frequency decrease for $\nu(C_\alpha\text{-N})$ in going from methyl to tert-butyl isothiocyanate. A normal coordinate analysis for methyl isothiocyanate possibly might resolve this question.

The only internal vibrations of the isothiocyanate group that have not been assigned are the in-plane and out-of-plane deformation vibrations, δ(NCS) and δ(NCS). In the spectrum of isothiocyanic acid the deformation vibrations are observed at 600 cm^{-1} and 469 cm^{-1} (71). Correspondingly they are assigned to the absorption bands at 569 and 440 cm^{-1} in the spectrum of methyl isothiocyanate.
A summary of the observed frequency ranges for vibrations internal to the isothiocyanate group is presented in Table 21.

Table 21. Frequency ranges for the characteristic vibrations of the isothiocyanate group

Vibration	Frequency (cm^{-1})	Intensity
ν_{as}(NCS)	2130 to 2090	very strong
ν_s(NCS)	1090 to 990	weak to moderate
$\delta_\perp$(NCS)	570 to 520	moderate
$\delta_{\parallel}$(NCS)	440 to 425	moderate

Restricted Rotation about the C_α -N Bond

Almost all of the preceeding discussion has been concerned with the interpretation of spectra from liquid state samples at room temperature. Spectra recorded for methyl, ethyl, isopropyl and tert-butyl isothiocyanate at liquid nitrogen temperature are in general quite similar to those recorded at room temperature. A marked exception is found in the 2300 to 2000 cm^{-1} region where shifts in intensity and frequency along with an increase in complexity are observed. The differences in this region between spectra from liquid and solid state samples are illustrated in Figures 28 and 29. Unless otherwise indicated, all frequencies in the following discussion are from solid state samples at liquid nitrogen temperature.

Methyl isothiocyanate exhibits a reversal in intensity for the Fermi doublet. The higher frequency member of the doublet is considerably enhanced in intensity and is the stronger part of the doublet. Both principle maxima are slightly elevated in frequency (2225 and 2141 cm^{-1} for the solid state versus 2206 and 2124 cm^{-1} for the liquid state) as compared to the liquid state. In contrast to the data in Table 18, the calculated frequency for the overtone part of the Fermi doublet, 2166 cm^{-1}, is closer to the low frequency member of the doublet. Hence, the change of state, liquid to solid, is associated with a sufficient increase

Figure 28. Infrared spectra in the 2150 cm^{-1} region for ethyl isothiocyanate in the

(A) solid state and

(B) liquid state

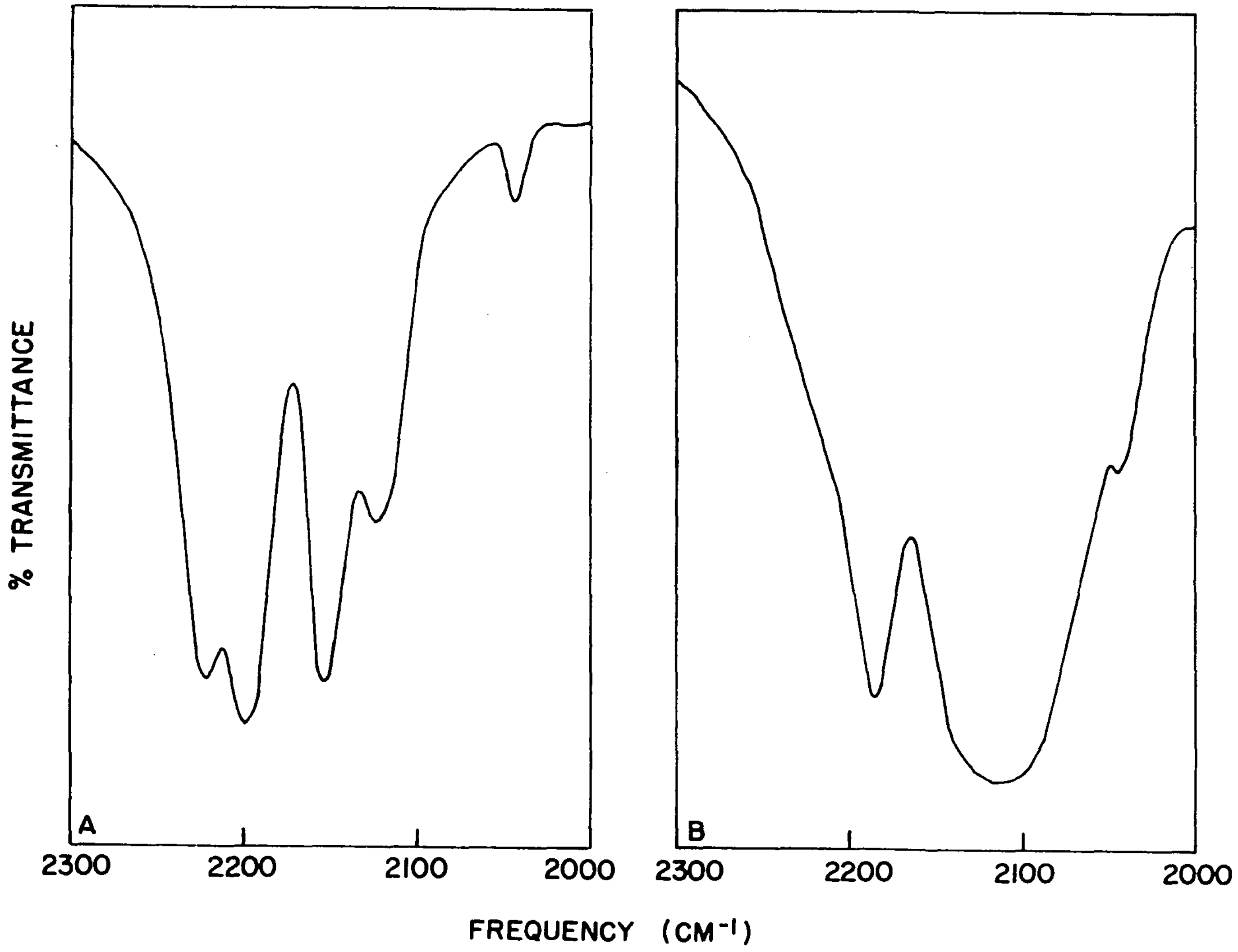
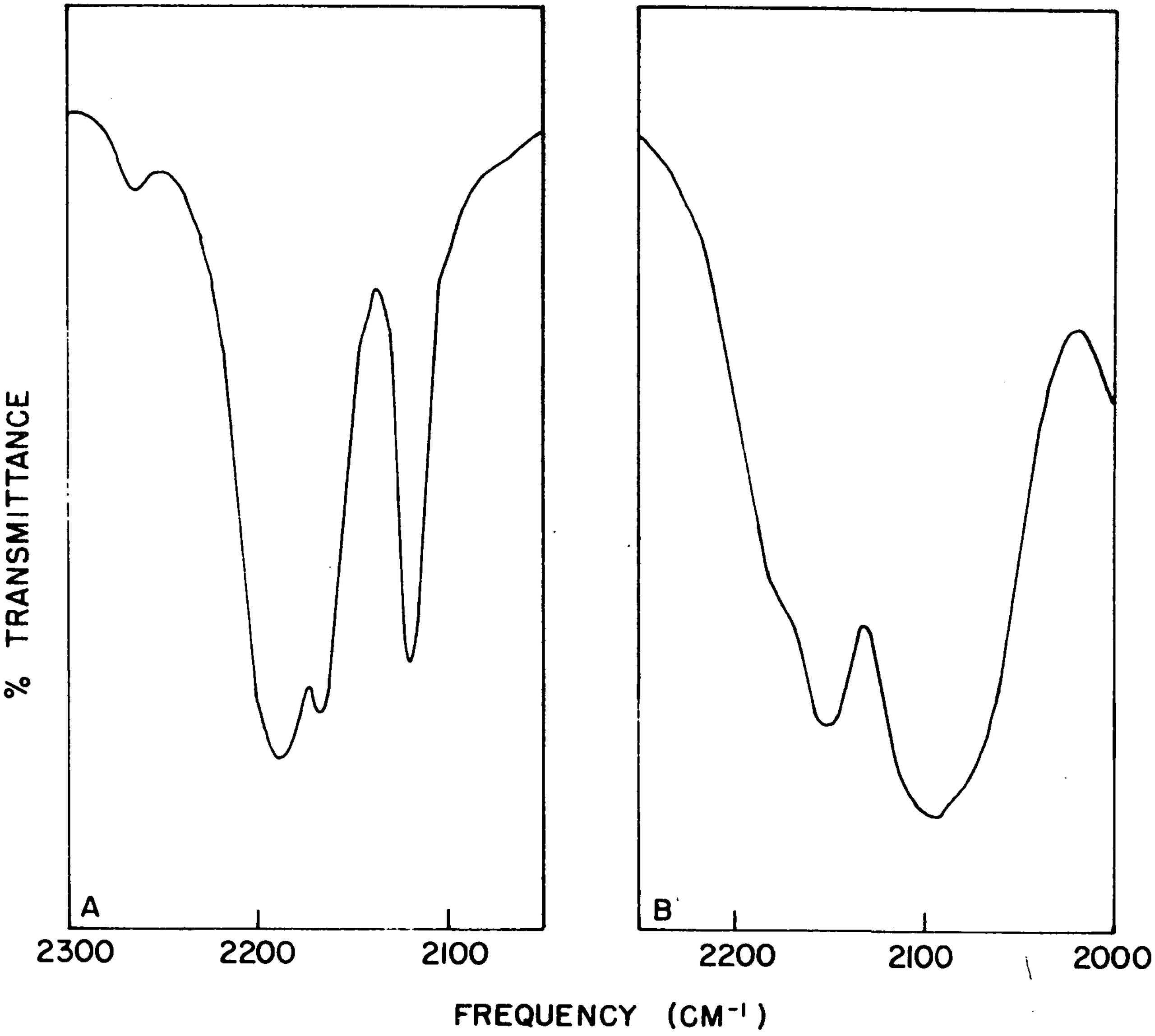

% TRANSMITTANCE
A
B
2300
2200
2100
2000
2300
2200
2100
2000
FREQUENCY (CM-1)

Figure 29. Infrared spectra in the 2150 cm^{-1} region for isopropyl isothiocyanate in the

(A) solid state and

(B) liquid state


% TRANSMITTANCE
A
B
2300
2200
2100
2200
2100
2000
FREQUENCY (CM⁻¹)

in frequency, approximately 50 cm^{-1}, to elevate ν_{as}(NCS) to a higher frequency than the unperturbed overtone. Similarly, for tert-butyl isothiocyanate a 57 cm^{-1} increase is found for ν_{as}(NCS) with the same change of phase. The increase in frequency is more readily discerned in tert-butyl isothiocyanate since ν_{as}(NCS) is already, in the liquid state, higher in frequency than the overtone.

Ethyl and isopropyl isothiocyanate also seem to exhibit a sharp rise in frequency for ν_{as}(NCS) in the liquid to solid phase transition. However, a considerable increase in spectral complexity is superimposed upon this frequency shift and the resulting spectra are not as readily interpreted. The increase in complexity, shown in Figures 28 and 29, originates from restricted rotation about the C_{α}-N bond. Fateley and Miller (24) observed an infrared transition at 128 cm^{-1} in the spectrum of solid state methyl isothiocyanate. Assuming that this absorption band is invariant between solid and vapor states, they were able to relate the observed frequency with an internal symmetric threefold barrier against free rotation about the C_{α}-N bond. Two possibilities were available for the assignment of this absorption band. Assignment as the fundamental transition of the methyl torsional vibration implies a barrier height of 700 cal. per mole. Alternately, assignment as the torsional overtone, 0 to 2(A), implies a barrier of 380 cal. per mole. The latter assignment is preferred since it is in better agreement with a tentative microwave (24) result of 275± 150 cal. per mole. This barrier is considerably below kT of room temperature. Consequently, free rotation is found for the methyl group with respect to a coordinate axis fixed in the isothiocyanate group.

Potential barriers against rotation about the C_α-N bond in ethyl and isopropyl isothiocyanate will be of the same magnitude as observed in methyl isothiocyanate. Hence, at room temperature free rotation of the isothiocyanate group results in a single molecular species for both ethyl and isopropyl isothiocyanate. This is in sharp contrast to the corresponding thiocyanates where two discrete isomers of each compound are spectroscopically detectable. Interestingly, an extraordinarily large half-peak height band width, approximately 110 cm^{-1}, was measured for ν_{as}(NCS) in both ethyl and isopropyl isothiocyanate in the liquid state. Reflection of free rotation about the C_α-N bond in ν_{as}(NCS) is not surprising. Ham and Willis (28) have shown qualitatively that the largest contribution to ν_{as}(NCS) comes from the unperturbed ν(N=C). In the thiocyanates it was the corresponding vibration, ν(S-C) which exhibited the "splitting" due to rotational isomerism about the C_α-S bond. At liquid nitrogen temperature the internal barrier exceeds kT. Consequently, free rotation about the C_α-N bond axis is inhibited and discrete rotational isomers appear. The configurations for the rotational isomers of ethyl and isopropyl isothiocyanate are analogous to the forms shown in Figure 16. In addition the nomenclature used to denote the isomeric forms of the alkyl thiocyanates is applicable to the alkyl isothiocyanates.

Four absorption bands are observed, at 2226, 2199, 2154 and 2123 cm^{-1}, in the spectrum of ethyl isothiocyanate in the solid state. Two, the highest and lowest frequency members of the quartet, are assigned as overtones of fundamentals appearing at 1108 and 1063 cm^{-1}. The remaining two bands are assigned to $\nu_{as}(NCS)$ in the separate isomers. Exact assignments can be inferred from the spectra of methyl and tert-butyl isothiocyanate. Methyl isothiocyanate has only one configuration, H_α, and $\nu_{as}(NCS)$ is found at 2225 cm^{-1}. Using the relationship

$$\nu_a + \nu_b = \nu_n + \nu_i$$

found previously for Fermi resonance, the calculated frequency for the unperturbed $\nu_{as}(NCS)$ is 2000 cm^{-1}. Likewise, tert-butyl isothiocyanate has only one configuration, C''_β, and $\nu_{as}(NCS)$ is found at 2147 cm^{-1}. Therefore the absorption bands at 2199 and 2154 cm^{-1} in the spectrum of ethyl isothiocyanate are assigned to $\nu_{as}(NCS)$ in the H'_α and C_β configurations, respectively.

An irregularity is observed in the solid state spectrum of isopropyl isothiocyanate. The absorption band at 2189 cm^{-1}

is assigned, in agreement with the preceeding assignments for methyl and ethyl isothiocyanate, to ν_{as}(NCS) in the H_{α}'' isomeric configuration. On the basis of 2154 and 2147 cm^{-1} frequencies for ν_{as}(NCS) in ethyl and tert-butyl isothiocyanate for the C_{β} configurations, a 2150 cm^{-1} frequency is expected for the C_{β}' isomer of isopropyl isothiocyanate. Unexpectedly, an absorption band does not occur at 2150 ± 5 cm^{-1} in the spectrum of isopropyl isothiocyanate. However, two absorption bands do appear at 2167 and 2120 cm^{-1}. The two absorption bands probably result from a Fermi resonance interaction between the first excited state of ν_{as}(NCS) in the C_{β}' isomer and a combination level. A transition corresponding to the combination mode also appears in the spectrum from the liquid state. A requirement for Fermi resonance is that the symmetry classes for the interacting energy levels must be the same. This requirement is easily met in the C_{β}' isomer were the molecular symmetry is C_1 and there is only one vibrational symmetry class. In the other isomer, H_{α}'', symmetry prohibits the same combination from interacting with the first excited state of ν_{as}(NCS). The symmetry class of the combination is A" as opposed to ν_{as}(NCS) which is of symmetry type a'. The calculated frequency for the unperturbed ν_{as}(NCS) in the C_{β}' isomer is 2151 cm^{-1}. This is in good agreement with the 2154 and 2147 cm^{-1} frequencies found for the C_{β} and C_{β}'' configurations in ethyl and tert-butyl isothiocyanate.

Specific assignments for the vibrational spectra of methyl, ethyl, isopropyl and tert-butyl isothiocyanate can now be discussed.

Methyl Isothiocyanate

Methyl isothiocyanate has C_s molecular symmetry with the H-C_α-N=C=S skeleton lying on a plane of symmetry. A seven atom molecule like methyl isothiocyanate has 15 vibrational degrees of freedom. Calculations for the number of normal modes of vibration in each symmetry species indicates that ten belong to symmetry type a' and five to type a". Interestingly, Costoulas and Werner (15) stated that there are 11 vibrations of type a' and only four of type a". Inexplicably, Costoulas and Werner are in error.

Assignments for the fundamental vibrations appear in Table 22. Stretching and deformation vibrations of the methyl group can be readily assigned. The methyl stretching vibrations, $\nu_{as}CH_3$ and ν_sCH_3 are found at 2991 and 2933 cm^{-1} in the spectrum of the liquid state. Likewise, the deformation vibrations, $\delta_{as}CH_3$ and δ_sCH_3 are assigned to absorption bands at 1444 and 1411 cm^{-1}. In the vapor state spectrum all four fundamentals, $\nu_{as}CH_3$, ν_sCH_3 $\delta_{as}CH_3$ and δ_sCH_3 exhibit the highly characteristic band shapes of a symmetric top. This is especially apparent for $\nu_{as}CH_3$ and $\delta_{as}CH_3$ where the vibration-rotation fine structure is

Table 22. Assignments for the fundamental modes of methyl isothiocyanate

Vibration	Frequency (cm^{-1})^{a}	Degeneracy
$\nu_{as}CH_3$	2991	2
$\nu_{s}CH_3$	2933	1
$\nu_{as}(NCS)$	2124^{b}	1
$\delta_{as}CH_3$	1444	2
$\delta_{s}CH_3$	1411	1
$\gamma_{\parallel}CH_3$	1120	1
$\nu_{s}(NCS)$	1088	1
$\gamma_{\perp}CH_3$	1008	1
$\nu\ (C_{\alpha}-N)$	644	1
$\delta_{\perp}(NCS)$	569	1
$\delta_{\parallel}(NCS)$	440	1
$\delta\ (CNC)$	338	1
$\Gamma\ CH_3$	100^{c}	1

[a] All frequencies are from the liquid state unless otherwise indicated.

[b] Low frequency part of Fermi doublet. Contains a greater contribution from the unperturbed fundamental.

[c] Calculated from the observed absorption band at 128 cm^{-1} by the method utilized in (24).

composed of a series of equidistant lines superimposed upon a broad diffuse base. The observed band structure is that of a perpendicular band of a symmetric top molecule. Even the predicted intensity pattern (29), strong-weak-weak-strong is observed for both of these absorption bands. For degenerate vibrations in a symmetric top the separation between the adjacent lines is given by

$$\Delta \nu = 2\ (A - B)$$

where A and B are the rotational constants corresponding to the moments of inertia I_a and I_b. While methyl isothiocyanate is not a true symmetric top, the third moment of inertia I_c is approximately equal to I_b and both are much greater than I_a. Hence, using Mecke's (29) approximation for a slightly asymmetric top, the separation between the adjacent lines is

$$\Delta \nu = 2 \left\{ A - \tfrac{1}{2}(B + C) \right\}$$

Using the rotational constants for methyl isothiocyanate, as determined by Beard and Dailey (6),

$$A = 2.61\ \text{cm}^{-1} \qquad B = 0.08498\ \text{cm}^{-1} \qquad C = 0.08358\ \text{cm}^{-1}$$

the calculated separation is 5.06 cm^{-1}. For $\nu_{as}CH_3$ and $\delta_{as}CH_3$ the observed separations are 9.0 and 12.71 cm^{-1}. Costoulas and Werner (15), who also correlated the vapor state spectrum with that of a symmetric top, stated that the difference between the observed and calculated separations was indicative of a strong Coriolis coupling. Inclusion of the Coriolis factor, ξ, into the equation for the splitting yields

$$\Delta \nu = 2 \left\{ A(1 - \xi) - \tfrac{1}{2} (B + C) \right\} .$$

Values of -0.75 and -1.46, respectfully, are calculated for ξ from the spacings in $\nu_{as}CH_3$ and $\delta_{as}CH_3$. These results, especially the latter value, are incompatible with theory since the Coriolis factor is limited to values between +1 and -1. Consequently, a more subtle interpretation is required for the vapor state spectrum of methyl isothiocyanate.

Methyl thiocyanate is also a slightly asymmetric top. However, as has been discussed previously, the vapor state spectrum of this molecule is that of an asymmetric top. The principal difference between these two molecules is the magnitude of the internal barrier against rotation about the C_α -X bond. In methyl thiocyanate the internal barrier is 1.09 kcal. per mole. Hence, free rotation does not exist at room temperature and the molecule must be considered as a rigid frame. Contrastingly, in methyl isothiocyanate the barrier about the C_α -N bond is 0.38 kcal. per mole. Since at room temperature kT is equal to 0.6 kcal. per mole, the methyl group can rotate freely with respect to the rigid frame of the isothiocyanate group. The vibration-rotation band system exhibited by $\nu_{as}CH_3$ and $\delta_{as}CH_3$ reflects the free rotation of the methyl group, <u>not</u> the rotation of the entire molecule. To a first approximation, the observed spacings are then given by

$$\Delta \nu = 2 \left\{ M(1 - \xi) \right\}$$

where M is the rotational constant of the methyl group about its own symmetry axis. Even in a first approximation, Coriolis coupling must be included for the degenerate vibrations $\nu_{as}CH_3$ and $\delta_{as}CH_3$. Assuming the CH bond distance to be 1.10 Å and the HCH angle to be 109.5°, the calculated value for M is 5.18 cm^{-1}. Using this value of M, the Coriolis constants for $\nu_{as}CH_3$ and $\delta_{as}CH_3$ are 0.13 and -0.23. The calculated values are comparable in both sign and magnitude with similar coupling constants shown in Table 5 for the methyl halides. The preceeding calculation is approximate since M is critically determined by a specific choice for the CH bond distance. However, this calculation does lend support to the interpretation of the vibration-rotation band system found for $\nu_{as}CH_3$ and $\delta_{as}CH_3$ in terms of the free internal rotation of the methyl group.

In contrast to the methyl stretching and deformation vibrations, the in-plane and out-of-plane methyl rocking modes, $\gamma_{\parallel}CH_3$ and $\gamma_{\perp}CH_3$, have been assigned in several contradictory ways. There is general agreement (15, 28, 58) in assignment of the absorption band at 1175 cm^{-1} in the vapor state spectrum to one of the methyl rocking modes. Costoulas and Werner (15) have assigned this band to

$\gamma_{\perp} CH_3$ and the $\gamma_{\parallel} CH_3$ to a strong polarized Raman line at 894 cm^{-1}. Usually $\gamma_{\parallel} CH_3$ appears at a higher frequency than $\gamma_{\perp} CH_3$ and almost always above 1040 cm^{-1} (8). Miller and White (58) indicated an obvious reluctance in their separate assignment of absorption bands at 1189 (their frequency from a liquid state spectrum) and 1175 cm^{-1} (vapor state) to the two methyl rocking vibrations. I was unable to detect an absorption band about 1190 cm^{-1} in the liquid state spectrum of methyl isothiocyanate. Furthermore, neither Costoulas and Werner (15) nor Ham and Willis (28) reported an absorption band at or very near to this frequency. Ham and Willis (28) indecisively proposed assignment of one CH_3 rock to either an absorption band at 1270 or 895 cm^{-1}. They did not attempt to distinguish between $\gamma_{\parallel} CH_3$ and $\gamma_{\perp} CH_3$. The first assignment is unrealistically high and the second coincides with the assignment of Costoulas and Werner.

Two molecules, methyl azide and methyl isocyanate, are structurally quite similar to methyl isothiocyanate. In the former, Mantica and Zerbi (55) have assigned the methyl rocking vibrations to absorption bands at 1140 and 1035 cm^{-1}. Assignments for the same vibrations in methyl isocyanate (see the discussion for this molecule in the section on alkyl isocyanates) are to absorption bands at 1132 and 1023 cm^{-1}. Hence, the weak absorption bands at 1120 and 1008 cm^{-1} are assigned, respectively, to $\gamma_{\parallel} CH_3$

and $\gamma_{\perp}\mathrm{CH}_3$. In the solid state spectrum the coincident absorption bands at 1118 and 1021 cm^{-1} gain considerably in intensity. The band maxima in the vapor state spectrum at 1126 and 1107, which appear as a shoulder to ν_s(NCS), probably originate from $\gamma_{\parallel}\mathrm{CH}_3$. However, it should be noted that a reasonable combination or overtone assignment for the 1175 cm^{-1} band in the vapor state has not been forthcoming. A comparison of the vapor and liquid state spectra of methyl isocyanate show only a small shift, from 1141 to 1132 cm^{-1}, for $\gamma_{\perp}\mathrm{CH}_3$.

Through an analogy with methylamine, Costoulas and Werner assigned the methyl torsional vibration to a frequency of 270 cm^{-1}. A more recent investigation (24) has resulted in the detection of a vibrational transition at 128 cm^{-1}. Several assignments are possible for this transition. However, the assignment which gives the best agreement with an internal barrier of 275 ± 150 cal. per mole (microwave value) is the first overtone transition, 0 to 2(A), for the methyl torsional mode. Using this assignment Fateley and Miller calculated a barrier of 380 cal. per mole.

Vibrational assignments for the overtone and combination transitions in methyl isothiocyanate are presented in Table 23.

The thermodynamic functions of methyl isothiocyanate have been calculated and appear in Table 24. A similar table has been prepared by Costoulas and Werner (15).

Table 23. Assignments for the combination bands of methyl isothiocyanate

Frequency (cm^{-1})[a]	Assignment (cm^{-1})
3079	2206 + 885 = 3091
3004	2124 + 885 = 3009
2864	1444 + 1411 = 2855
2843	2206 + 644 = 2850
2796	1411 + 1411 = 2822
2766	2124 + 644 = 2768
2553	1444 + 1120 = 2564
2519[c]	1408 + 1118 = 2526[c]
2206[b]	1088 + 1088 = 2176[b]
2037[c]	1408 + 628 = 2036[c]
1255[c]	628 + 628 = 1256[c]
1221	644 + 569 = 1213
885	440 + 440 = 880

[a] All frequencies are from the liquid state unless otherwise indicated.

[b] High frequency part of Fermi doublet. Contains greater contribution from unperturbed overtone.

[c] Solid state frequency.

Table 24. Thermodynamic properties of methyl isothiocyanate[a]

Temperature °K	$-(F^o-H_o^o)/T$		S^o		C	
	Tr+R	Vib	Tr+R	Vib	Tr+R	Vib
273.16	54.12	2.69	62.07	5.75	7.95	6.63
298.16	54.82	2.96	62.77	6.32	7.95	7.33
300	54.87	2.98	62.82	6.36	7.95	7.38
400	57.16	4.15	65.11	8.91	7.95	10.09
600	59.37	6.57	68.33	13.91	7.95	14.54

[a] Values listed in table are in units of calories per degree per mole.

Structural constants for methyl isothiocyanate were taken from Beard and Dailey (6). Reasonable agreement is found between the values in Table 24 and those published by Costoulas and Werner (15) for the translational and rotational contribution to the thermodynamic properties. Considerable disparity is found for the vibrational contribution. The principal origin of this disparity lies in the assignment of the methyl torsional vibration and the method of calculating the contribution from this degree of freedom. The assignment by Costoulas and Werner for the methyl torsional vibration has already been discussed. Costoulas and Werner calculated the contribution to the thermodynamic functions by this degree of freedom in the same manner as they did for the other 14 vibration degrees of freedom. This does not take into account the effects of free or restricted internal rotation. Pitzer (70) has prepared tables which take into account these factors. The values listed in Table 24 were calculated employing Pitzer's tables (70) for the methyl torsional mode and Torkington's tables (87) for the other vibrational modes.

Ethyl Isothiocyanate

Ten-atom molecular systems, such as ethyl isothiocyanate, have 24 vibrational degrees of freedom. The type of normal modes expected for this compound are indicated in Appendix I, Table 65. Assignments are given in Table 25 for 22 of the 24 fundamentals. Not assigned are the methyl torsional vibration and the CNC angle deformation, δ (CNC). The former vibration most certainly occurs below 300 cm^{-1} and the angle deformation should be extremely weak as it was in methyl isothiocyanate.

Most of the vibrations internal to the ethyl group are readily assigned. In comparison to ethyl thiocyanate, the deformation vibrations occur somewhat higher in frequency and weaker in intensity in the spectrum of ethyl isothiocyanate. An exception is the CH_2 wag at 1342 cm^{-1}. Svatek, Zahradnik and Kjaer (83) have observed a strong band about this frequency in seven n-alkyl isothiocyanates. Coupled with the extremely intense ν_{as}(NCS), this absorption band

Table 25. Assignments for the fundamental modes of ethyl isothiocyanate

Vibration	Frequency (cm^{-1})[a]	Degeneracy
$\nu_{as}CH_3$	2988	2
$\nu_{as}CH_2$	2942	1
ν_sCH_3, ν_sCH_2	2883	2
$\nu_{as}(NCS)$	2114[b]	1
CH_2 bend	1463	1
$\delta_{as}CH_3$	1449	2
δ_sCH_3	1379	1
CH_2 wag	1342	1
CH_2 twist	1282	1
$\gamma_{\parallel} CH_3$	1127	1
$\gamma_{\perp} CH_3$	1111	1
$\nu_s(NCS)$	1065	1
ν (CC)	938	1
CH_2 rock	796	1
ν (C_α-N)	638	1
$\delta_\perp$ (NCS)	536	1
$\delta_\perp$ (CCN)	448[c]	1
$\delta_\parallel$ (NCS)	435[c]	1
$\delta_\parallel$ (CCN)	382	1

---

[a] All frequencies are from the liquid state unless otherwise indicated.

[b] Low frequency part of Fermi doublet. Contains a greater contribution from the unperturbed fundamental.

[c] Solid state frequency.

should serve as a useful diagnostic tool in conformational analysis for complex isothiocyanates containing a CH_2NCS unit.

On the basis of Raman polarization data (88) the in-plane CCN deformation is assigned to the absorption band at 382 cm^{-1}. The region between 380 and 450 cm^{-1} contains three skeletal vibrations, $\delta_{\parallel}$(CCN), $\delta_{\perp}$(CCN) and $\delta_{\parallel}$(NCS), and it is unrealistic to expect that the normal vibrations do not reflect a mixing of these vibrational modes.

Table 26 contains proposed assignments for the overtone and combination modes of ethyl isothiocyanate. Five combinations found in methyl isothiocyanate reoccur in Table 26.

Isopropyl Isothiocyanate

An insight into the normal vibrations of isopropyl isothiocyanate can be gained from Appendix I, Table 66 and the discussion on the spectrum of isopropyl thiocyanate. Assignments are presented in Table 27 for 28 of the 33 normal vibrations. No attempt has been made to assign specific degeneracies for individual absorption bands of a multiply degenerate vibration. Similar to the analysis for the vibrational spectrum of ethyl isothiocyanate, the methyl torsional and CNC deformation vibrations are not assigned. Neither is the CH stretching vibration which is most probably covered by the stronger methyl and methylene stretching vibrations.

Table 26. Assignments for the combination bands of ethyl isothiocyanate

Frequency (cm^{-1})^{a}	Assignment (cm^{-1})
2918^{b}	1465 + 1465 = 2930^{b}
2832^{b}	1451 + 1380 = 2831^{b}
2814	2183 + 638 = 2821
2753	2114 + 638 = 2752
2222^{b}	1108 + 1108 = 2216^{b}
2183^{c}	1065 + 1065 = 2130
2043	1111 + 938 = 2049
1993	1065 + 938 = 2003
1325^{b}	939 + 382 = 1321^{b}
869	435 + 435 = 870

[a] All frequencies are from the liquid state unless otherwise indicated.

[b] Solid state frequency.

[c] High frequency part of Fermi doublet. Contains greater contribution from unperturbed overtone.

A majority of the assignments for vibrations internal to the isopropyl group are in agreement with those proposed by Sheppard (76) and need no further comment. The strong band at 1332 cm^{-1} is assigned to a CH deformation vibration. Svatek, Zahradnik and Kjaer (83) have observed that this absorption band is characteristic of a CHNCS atomic grouping.

Table 27. Assignments for the fundamental modes of isopropyl isothiocyanate

Vibration	Frequency (cm^{-1})[a]
$\nu_{as}CH_3$	2985, 2938
$\nu_{s}CH_3$	2877
$\nu_{as}(NCS)$	2093[b]
$\delta_{as}CH_3$	1465, 1457
$\delta_{s}CH_3$	1387, 1370
δ (CH)	1332, 1260
γ CH_3	1170, 1021, 934
ν (CC)	1130, 863
$\nu_{s}(NCS)$	1004
ν (C_α -N)	634
δ (NCS)	536, 437
δ (CCN)	459, 335
δ (CCC)	393

[a] All frequencies are from the liquid state unless otherwise indicated.

[b] Low frequency part of Fermi doublet. Contains greater contribution from the fundamental.

This is an extremely intense absorption band and should be useful in detecting secondary isothiocyanates.

Assignments for combination bands of isopropyl isothiocyanate appear in Table 28.

Table 28. Assignments for the combination bands of isopropyl isothiocyanate

Frequency (cm^{-1})[a]	Assignments (cm^{-1})
2817	1457 + 1370 = 2827
2734	2093 + 634 = 2727
2265[c]	1132 + 1132 = 2264[c]
2149[b]	1130 + 1004 = 2134
1999	1004 + 1004 = 2008
1867	934 + 934 = 1868

[a] All frequencies are from the liquid state unless otherwise indicated.

[b] Higher frequency part of a Fermi doublet. Contains greater contribution from the unperturbed fundamental.

[c] Solid state frequency.

Tert-butyl Isothiocyanate

The normal modes of vibration for a tert-butyl functional group result from a coupling of the group vibrations from the three equivalent methyl groups. Tert-butyl isothiocyanate has C_s molecular symmetry with one methyl group centered on the symmetry plane and the remaining two methyl groups occupying equivalent sites on opposite sides of the symmetry plane. Hence, the normal vibrations result from a coupling between the group vibrations of the individual methyl groups and can be distinguished by the symmetry plane. For example, a nondegenerate vibration (with respect to an individual methyl group) such as $\nu_s CH_3$ from one of the methyl units can couple with the same vibration in the other two methyl units in three distinct ways. They can couple completely in phase and form a vibrational mode which maintains the symmetry plane, i.e., a vibration of symmetry type a'. There are two ways in which the vibrations can be coupled such that two methyl groups move in phase and one out of phase. If the out of phase methyl group is the one lying on the symmetry plane then the symmetry plane is still maintained and the vibration will again be of type a'. However, if the out of phase methyl group is the one of the two lying off the symmetry plane the symmetry plane is not maintained during the vibration and the normal mode will be of type a". The normal modes of vibration for tert-butyl derivatives in Appendix I can be visualized in this manner.

Of the 42 normal vibrations of tert-butyl isothiocyanate 37 have been assigned. As with the vibrational analysis of ethyl and isopropyl isothiocyanate the unassigned vibrations are the methyl torsional and CNC angle deformation vibrations. The assignments shown in Table 29

Table 29. Assignments for the fundamental modes of tert-butyl isothiocyanate

Vibration	Frequency (cm^{-1})[a]
$\nu_{as}CH_3$	2987, 2941, 2913
$\nu_{s}CH_3$	2877
$\nu_{as}(NCS)$	2090
$\delta_{as}CH_3$	1477, 1460
$\delta_{s}CH_3$	1397, 1370
ν (CC)	1229, 805
γ CH_3	1209, 1036, 927
$\nu_{s}(NCS)$	994
ν (C_α-N)	615
δ (NCS)	525, 429
δ (CCC) and δ (CCN)	489, 336

[a] All frequencies are from the liquid state unless otherwise indicated.

are compatible with those of Sheppard (75) for tert-butyl halides. Exceptions discussed separately are the CC

Table 30. Assignments for the combination bands of tert-butyl isothiocyanate

Frequency (cm^{-1})[a]	Assignments (cm^{-1})
2190[b]	1200 + 987 = 2187[b]
1976	994 + 994 = 1988

[a] All frequencies are from the liquid state unless otherwise indicated.

[b] Solid state frequency.

stretching and methyl rocking vibrations. Since there is little new information in this analysis further discussion would be superfluous.

ALKYL ISOCYANATES

Historical Background

Even in comparison with the alkyl isothiocyanates and thiocyanates there is a paucity of information in the literature on the vibrational spectra of alkyl isocyanates. For example, there is only one paper on the Raman spectra of the alkyl isocyanates as compared to four and five, respectively, for the alkyl isothiocyanates and thiocyanates. Likewise, there is only one vibrational analysis published for methyl isocyanate as compared to four for the respective thio derivatives.

Kopper and Pongratz (49) published the Raman spectra of the three simplest alkyl isocyanates. They ascribed the strong Raman lines at 1409, 1435 and 1421 cm^{-1} in the spectra of methyl, ethyl and isopropyl isocyanate, respectively, to a vibration internal to the isocyanate group. A vibrational analysis for methyl isocyanate has been published by Eyster and Gillette (22). Their investigation was concerned solely with the vapor state spectrum. Unfortunately, Eyster and Gillette chose potassium bromide optics to cover the entire infrared spectral region. Although their low frequency data are of unusually high quality for the date (1940) in which the work was performed, frequencies above 1000 cm^{-1} are in considerable error. For example, they report the very strong $\nu_{as}(NCO)$ as having a frequency of

2232 cm^{-1}. The redetermined frequency is 2282 cm^{-1}. Likewise, absorption bands reported at 1412 and 1377 cm^{-1} were found to have frequencies of 1433 and 1417 cm^{-1} when remeasured. Some errors in interpretation result from these frequency discrepancies.

A comprehensive investigation of ν_{as}(NCO) was published by Hoyer (35). He was unable to derive a meaningful correlation for ν_{as}(NCO) in the more than 40 isocyanates that he studied. Two recent papers have appeared on auxilliary facets of the vibrational spectra of the alkyl isocyanates. Fateley and Miller (24) have reported an infrared transition at 143 cm^{-1} for methyl isocyanate in the solid state at liquid nitrogen temperature. The near infrared spectra, 1.2 to 2.7 microns, has been reported by David (19).

In conformity with the discussions on the vibrational spectra of the alkyl isothiocyanates the normal modes of vibration completely internal to the isocyanate functional group will be discussed first. Observed infrared spectral data for the alkyl isocyanates appears in Appendix G, Tables 54 to 59. Spectra of these compounds appear in Figures 30 through 34. Raman data for methyl, ethyl and isopropyl isocyanate are presented in Appendix H, Table 62.

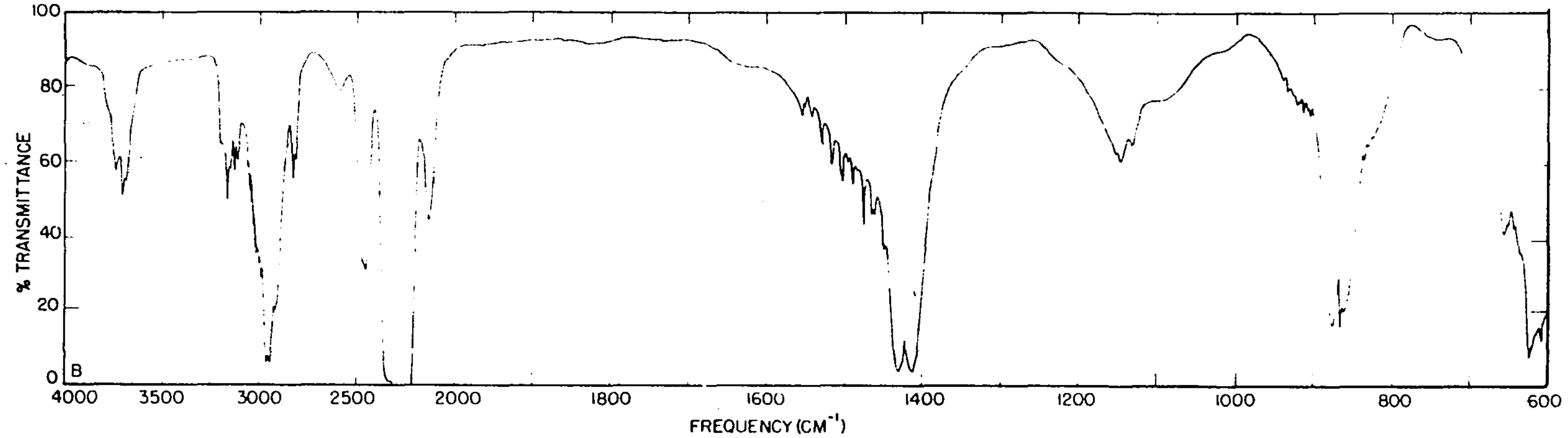
Isocyanate Group Vibrations

Thomas (86) has proposed that the stretching vibrations internal to the isocyanate group are more accurately described in terms of completely coupled vibrations ν_{as}(NCO)

Figure 30. Infrared spectra of methyl isocyanate

(A) liquid state

(B) vapor state


B
% TRANSMITTANCE
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3500
3000
2500
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1400
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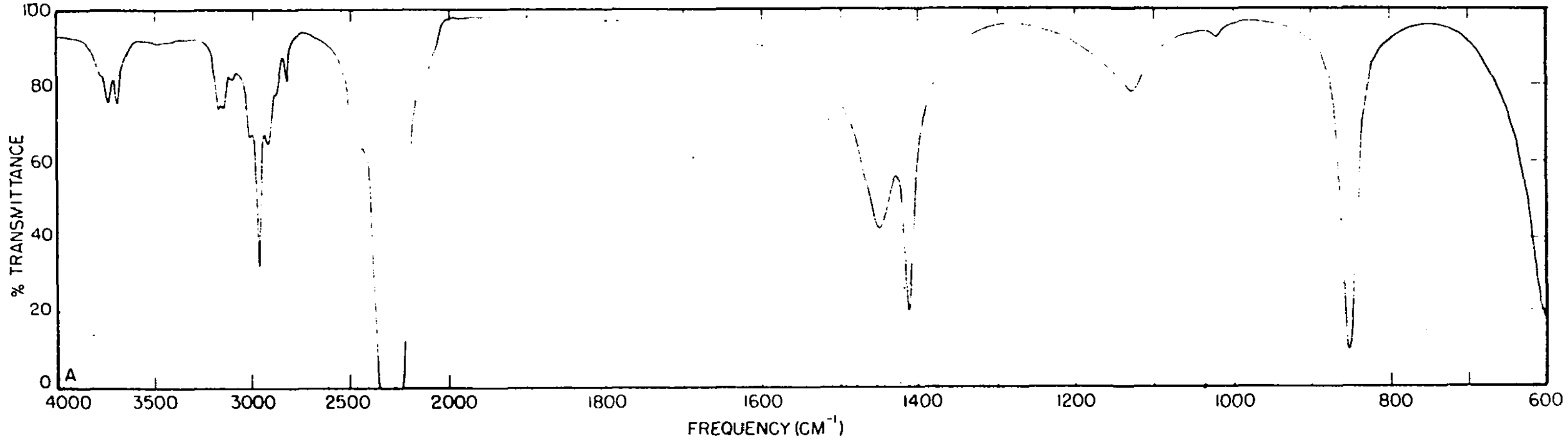
800
600
FREQUENCY (CM⁻¹)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1800
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1400
1200
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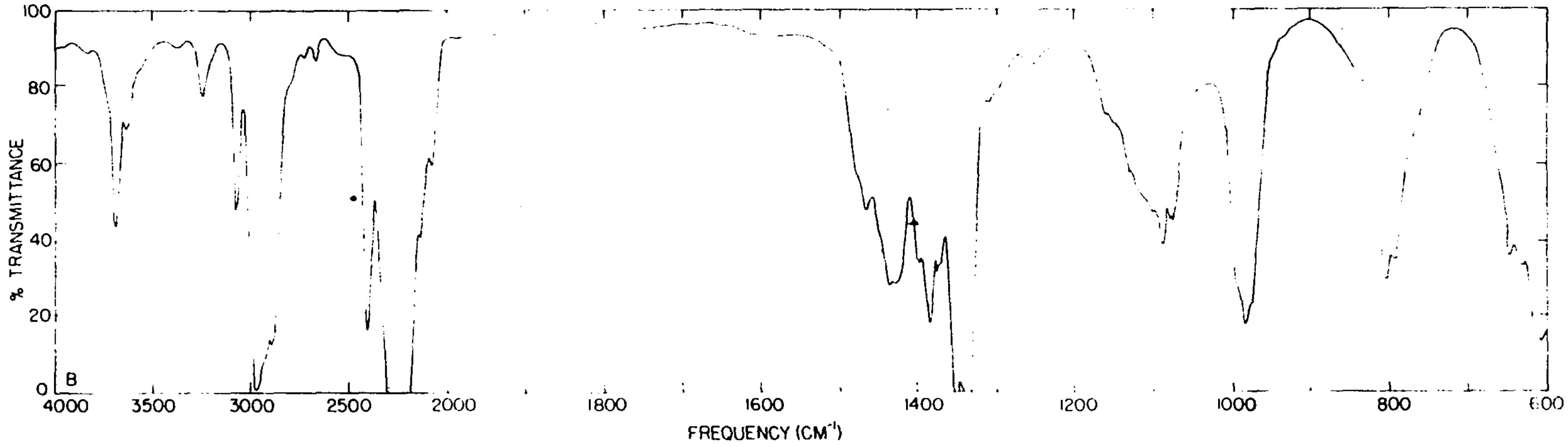
600
FREQUENCY (CM⁻¹)

Figure 31. Infrared spectra of ethyl isocyanate

(A) liquid state

(B) vapor state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1200
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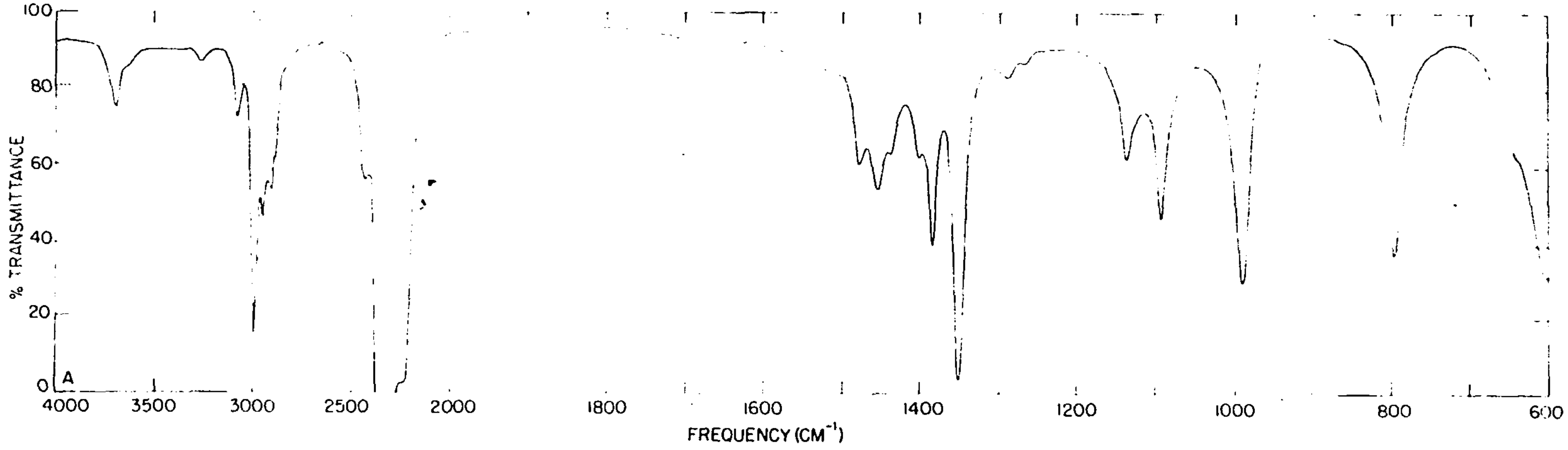
600
FREQUENCY (CM⁻¹)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1200
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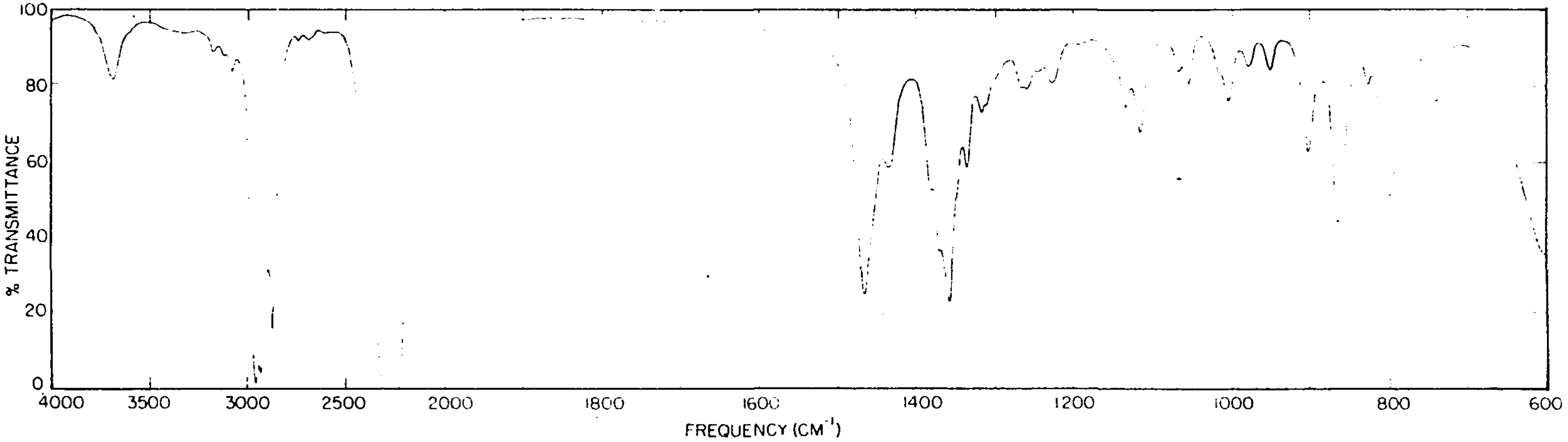
800
600
FREQUENCY (CM⁻¹)

Figure 32. Infrared spectrum of n-propyl isocyanate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60
40
20
0
4000
3500
3000
2500
2000
1800
1600
1400
1200
1000
800
600
FREQUENCY (CM^{-1})

Figure 33. Infrared spectrum of isopropyl isocyanate

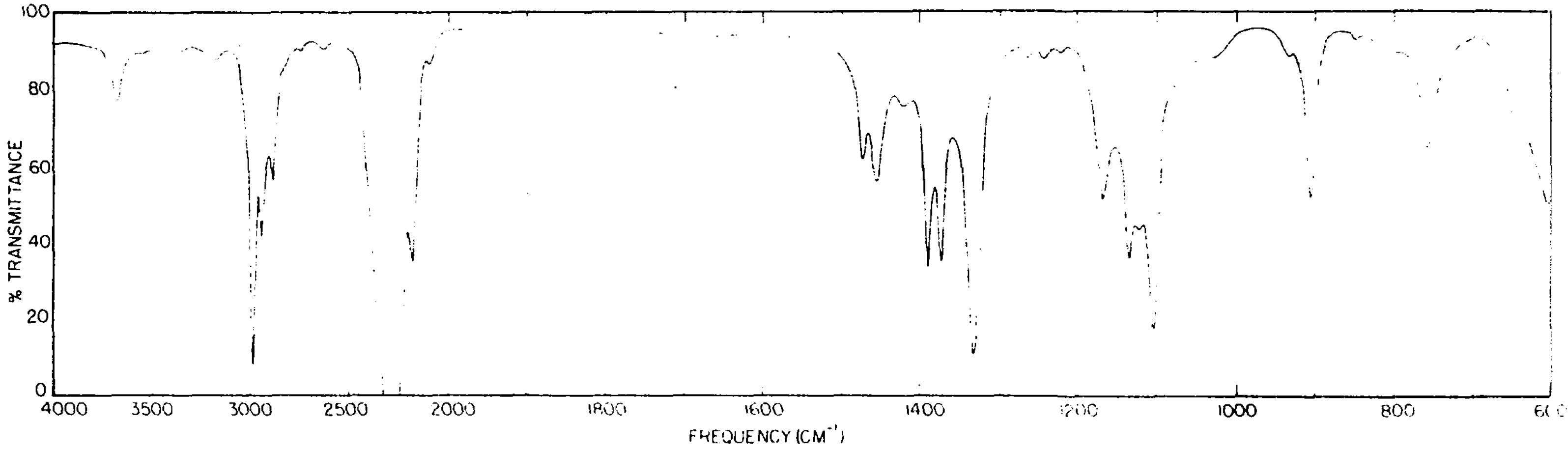
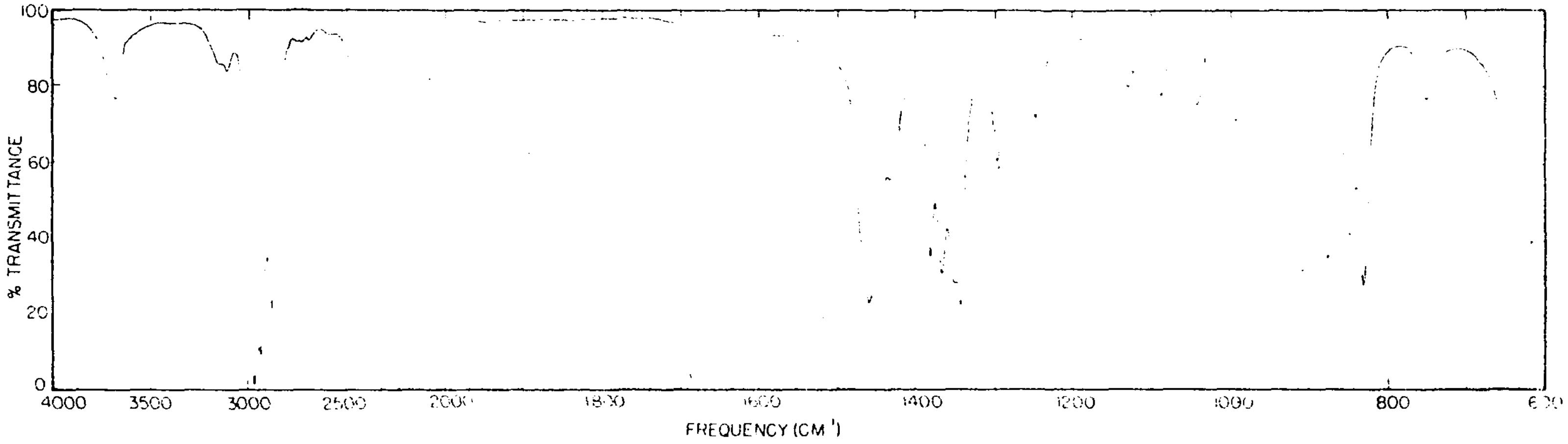

100
80
60
40
20
0
% TRANSMITTANCE
4000
3500
3000
2500
2000
1800
1600
1400
1200
1000
800
600
FREQUENCY (CM⁻¹)

Figure 34. Infrared spectrum of n-butyl isocyanate



100
80
60
40
20
0
% TRANSMITTANCE
4000
3500
3000
2500
2000
1800
1600
1400
1200
1000
800
600
FREQUENCY (CM⁻¹)

and ν_s(NCO) rather than as ν(N=C) and ν(C=O). This proposal undoubtedly originated from his normal coordinate analysis of ioscyanic acid (85). Thomas calculated that the restoring force constants are

$f_{NC} = 15.0\text{x}10^5$ dynes/cm and $f_{CO} = 14.3\text{x}10^5$ dynes/cm.

The near equality of force constants implies a near equality of the unperturbed energy levels since the masses of the atoms are quite similar. Perhaps the strongest evidence for the proposed coupling lies in the infrared and Raman activity of the internal isocyanate stretching vibrations. Individually, the unperturbed vibrations ν(N=C) and ν(C=O) should exhibit strong transitions in both the infrared and Raman effect. The assignments by previous investigators of ν_{as}(NCO) to a very strong infrared absorption band about 2275 cm^{-1} (20, 22, 35) and ν_s(NCO) to a strong Raman line about 1430 cm^{-1} (32, 49) have been well established and need provoke little further discussion. This does not imply that the assignment by Eyster and Gillette (22) of ν_s(NCS) to the infrared absorption band at 1412 cm^{-1} (their data) is accepted. Most assuredly this is not the case. However, this shall be discussed in the section on methyl isocyanate. It is important to observe that ν_{as}(NCO) has not been found in the Raman effect (49). Very weak absorption bands have been found coincident to the strong Raman lines at

1434 and 1421 cm^{-1} in the spectra of ethyl and isopropyl isocyanate. This spectral activity implies a close analogy between the isocyanate functional group and carbon dioxide. The $C_{\infty v}$ molecular symmetry of carbon dioxide results in the following activity for the two internal stretching vibrations:

ν_{as}(OCO)	infrared active, Raman inactive
ν_s (OCO)	infrared inactive, Raman active.

The selection rules governing the isocyanate group are those resulting from the high degree of pseudosymmetry found within this group.

David (19) has assigned the first overtone of ν_{as}(NCO) to an absorption band about 2.642 microns (3785 cm^{-1}) found in 23 alkyl and aryl isocyanates. As stated above ν_{as}(NCO) is found at 2275 cm^{-1}. Hence, the first overtone should appear about 4550 cm^{-1}, or 2.20 microns. Rarely do anharmonicity corrections result in differences between observed and calculated frequencies for overtone and combination bands greater than 15 cm^{-1}. Occasionally, when Fermi interactions are present, discrepancies of 40 to 50 cm^{-1} are found. However, anharmonicity differences of 750 cm^{-1} implied by David's assignment seems implausible. The bands observed by David at 2.66 and 2.638 microns appear to correspond to the combination band, ν_{as}(NCO) + ν_s(NCO), found in this investigation at 3698 and 3674 cm^{-1} for ethyl and isopropyl isocyanate. There is some discrepancy in the frequencies calculated from David's reported wavelengths and those observed in this investigation. David does acknowledge that his data about 2.6 microns could be inaccurate.

The analogy between the isocyanate functional group and carbon dioxide leads to an interesting prediction with respect to the first overtone ν_{as}(NCO). Specifically, the first overtone of ν_{as}(NCO) should not be infrared active. The first overtone will be of the same symmetry class as ν_s(NCO), or by analogy, ν_s(OCO), and thus should appear in the Raman spectrum but not the infrared. This expectation is fulfilled since a reasonable assignment for the first overtone of ν_{as}(NCO) about 4550 cm^{-1} does not appear in the data published by David.

Deformation vibrations for the isocyanate group are found about 600 cm^{-1}(31). Only one absorption band is observed in spectra of methyl and ethyl isocyanate in the liquid state. While spectra from the vapor state of these compounds may possibly be interpreted in terms of two fundamentals (22), it is not completely self evident. Only in spectra from solid state samples are two descrete absorption bands observed. By analogy with isocyanic acid (31) the in-plane deformation vibration is assigned to the lower frequency absorption band.

A summary is given in Table 31 for the frequency ranges observed for the internal vibrations of the isocyanate group.

Table 31. Frequency ranges for the characteristic vibrations for the isocyanate group

Vibration	Frequency (cm^{-1})	Intensity
ν_{as}(NCO)	2300 to 2250	very strong
ν_{s}(NCO)	1450 to 1400	very weak
$\delta_{\perp}$(NCO)	650 to 600	poorly defined
$\delta_{\parallel}$(NCO)	600 to 590	strong

Restricted Rotation about the C_{α}-N Bond

Comparison of spectra from solid and liquid states for several alkyl isothiocyanates permitted a relative estimate of the internal barrier versus kT. Most of the information was derived from a study of ν_{as}(NCS). A similar study for the alkyl isocyanates was not possible since in the solid state spectra the absorption band assigned to ν_{as}(NCO) decreases sharply in intensity and usually exhibits a poorly defined band envelope.

The spectra of methyl, ethyl and isopropyl isocyanate will be considered next.

Methyl Isocyanate

The number and type of normal vibrations in methyl isocyanate are exactly the same as found in methyl isothiocyanate. Assignments are presented in Table 32 for all 15 fundamental vibrations of methyl isocyanate. Stretching and deformation vibrations of the methyl group are readily assigned to absorption bands at 3000, 2960, 1453 and 1416 cm^{-1}. In each case the frequencies found for methyl isocyanate are slightly higher than the corresponding values found for methyl isothiocyanate. Almost an exact duplicity exists between the vapor state spectra of methyl isocyanate and methyl isothiocyanate with respect to the methyl group vibrations.

Eyster and Gillette (22) have assigned $\nu_s(\mathrm{NCO})$ and $\delta_s\mathrm{CH}_3$ in the vapor state spectrum to absorption bands at 1412 and 1377 cm^{-1}. It should be noted that the remeasured frequencies are 1433 and 1417 cm^{-1}. Comparison of the vapor state spectrum for methyl isocyanate and methyl isothiocyanate, Figures 19 and 30, immediately shows that their assignments are incorrect. Both bands originate in $\delta_s\mathrm{CH}_3$ and are the P and R branches of the absorption band. There is also an almost exact parallelism in the liquid state spectra from the two methyl derivatives. In both the liquid and vapor state spectra of methyl isocyanate there does not appear to be a discrete absorption band assignable to

Table 32. Assignments for the fundamental modes of methyl isocyanate

Vibration	Frequency (cm^{-1})[a]	Degeneracy
$\nu_{as}CH_3$	3000	2
$\nu_{s}CH_3$	2960	1
$\nu_{as}(NCO)$	2288	1
$\delta_{as}CH_3$	1453	2
$\nu_{s}(NCO)$	1437[b]	1
$\delta_{s}CH_3$	1416	1
$\gamma_{\parallel}CH_3$	1132	1
$\gamma_{\perp}CH_3$	1023	1
$\nu\ (C_{\alpha}-N)$	852	1
$\delta_{\perp}(NCO)$	613[b]	1
$\delta_{\parallel}(NCO)$	596	1
$\delta\ (CNC)$	353[c]	1
$\Gamma\ CH_3$	96[d]	1

[a] All frequencies are from the liquid state unless otherwise indicated.

[b] Solid state frequency.

[c] Frequency from (15).

[d] Calculated value from observed frequency at 143 cm^{-1} by method outlined in (24).

ν_s(NCO). The 1409 cm^{-1} Raman line found by Kopper and Pongratz (49) is coincident with $\delta_s CH_3$. Consequently, it appears that ν_s(NCO) must be in the broad band envelope of $\delta_{as}CH_3$ at 1453 cm^{-1}. An absorption band does appear at 1437 cm^{-1} in the solid state spectrum and it has been tentatively assigned to ν_s(NCO).

Vibration-rotation fine structure for $\nu_{as}CH_3$ and $\delta_{as}CH_3$ in the vapor state spectra of methyl isocyanate is that of a perpendicular band in a symmetric top. The band structure consists of a series of equidistant band maxima from the Q branch superimposed upon a diffuse background of the P and R branches. The observed separation between the individual maxima in $\nu_{as}CH_3$ and $\delta_{as}CH_3$ are 12.95 and 9.18 cm^{-1}. Application of the formula

$$\Delta\nu = 2\left\{A(1-\xi) - \tfrac{1}{2}(B + C)\right\}$$

to the observed separations yields the highly improbable values -2.93 and -1.75 for the Coriolis constants in the normal vibrations $\nu_{as}CH_3$ and $\delta_{as}CH_3$. Rotational constants employed in this calculation are

$$A = 1.686\ \text{cm}^{-1} \qquad B = 0.1607\ \text{cm}^{-1} \qquad C = 0.1509\ \text{cm}^{-1}$$

and are in turn calculated from the electron diffraction analysis published by Eyster, Gillette and Brockway (23). Failure of this equation to reasonably interpret the observed separations again implies that the vibration-rotation fine structure results from the free rotation of the methyl group rather than rotation of the entire molecule.

Assignment of $\nu(C_\alpha - N)$ to an absorption band at 852 cm^{-1} conforms with the assignment proposed by Eyster and Gillette. This normal mode exhibits a considerable shift in frequency, 18 cm^{-1}, in conjunction with the vapor to liquid state phase transition.

Fateley and Miller (24) have observed a transition at 143 cm^{-1} in the far infrared spectrum of methyl isocyanate. Several transitions, all involving the methyl torsional vibration, represent possible assignments for this absorption band. The assignments and associated barriers are given below (24):

Assignment	Barrier (kcal. per mole)
$0 \rightarrow 1$	1200
$0 \rightarrow 2$ (A)	560
$0 \rightarrow 2$ (B)	400

Vibration-rotation fine structure for $\nu_{as}CH_3$ and $\delta_{as}CH_3$ implies a barrier the order of magnitude of kT room temperature (0.60 kcal. per mole) or less. Consequently the first assignment, 0 to 1, seems to be ruled out. Comparison of the structural data for methyl isocyanate (23) and methyl isothiocyanate (6) shows that the CNC angle is smaller in the isocyanate, i.e., 125° versus 142°. Consequently, the isocyanate group should be, as compared to the isothiocyanate

Table 33. Assignments for the combination bands of methyl isocyanate

Frequency (cm^{-1})[a]	Assignment (cm^{-1})
3726	2288 + 1453 = 3724
3680	2288 + 1416 = 3704
3160	2318 + 852 = 3170
3135	2288 + 852 = 3140
3089	2254 + 852 = 3106
2912	1453 + 1453 = 2906
2871[b]	1437 + 1437 = 2874[b]
2870	2282 + 596 = 2878
2813	1416 + 1416 = 2832
2570	1453 + 1132 = 2585
2460	1453 + 1023 = 2476
2318	1440[c]+ 852 = 2292
2254	1416 + 852 = 2268
2131	3000 - 852 = 2148

[a] All frequencies are from the liquid state unless otherwise indicated.

[b] Solid state frequency.

[c] Estimated frequency.

group, in closer proximity to a CH bond in the high potential energy eclipsed configuration of the methyl derivative. A direct implication of this closer proximity is a higher internal barrier about the Cα-N bond. Either of the two remaining assignments fulfills this speculation. By analogy with methyl isothiocyanate, where the $0 \rightarrow 2(A)$ assignment is employed for a similar absorption band, the second assignment indicated above seems preferable.

The thermodynamic functions of methyl isocyanate have been calculated and appear in Table 34.

Table 34. Thermodynamic properties of methyl isocyanate[a]

Temperature °K	$-(F^o-H_o^o)/T$		S^o		C	
	Tr+R	Vib	Tr+R	Vib	Tr+R	Vib
273.16	52.59	2.44	60.54	5.07	7.95	5.52
298.16	53.29	2.66	61.24	5.55	7.95	6.19
300	53.34	2.68	61.29	5.59	7.95	6.22
400	55.63	3.70	63.58	7.70	7.95	8.94
600	58.85	5.92	66.60	12.36	7.95	13.60

[a] Values listed in table are in units of calories per degree of mole.

Ethyl Isocyanate

Of the 24 normal modes of vibration expected for ethyl isocyanate, 22 are assigned in Table 35. Only the methyl

Table 35. Assignments for the fundamental modes of ethyl isocyanate

Vibration	Frequency (cm^{-1})[a]	Degeneracy
$\nu_{as}CH_3$	2988	2
$\nu_{as}CH_3$	2943	1
$\nu_{s}CH_3$, $\nu_{s}CH_2$	2883	2
$\nu_{as}(NCO)$	2280	1
CH_2 bend	1472	1
$\delta_{as}CH_3$	1451	2
$\nu_{s}(NCO)$	1432	1
$\delta_{s}CH_3$	1381	1
CH_2 wag	1348	1
CH_2 twist	1286	1
$\gamma_{\parallel}CH_3$ rock	1134	1
$\gamma_{\perp}CH_3$ rock	1092	1
$\nu(CC)$	988	1
$\nu(C_{\alpha}-N)$	794[b]	1
CH_2 rock	794[b]	1
$\delta_{\perp}(NCO)$	608[c]	1
$\delta_{\parallel}(NCO)$	595	1
$\delta_{\perp}(CCN)$	417	1
$\delta_{\parallel}(CCN)$	397	1

[a] All frequencies are from the liquid state unless otherwise indicated.

[b] Degeneracy split in both solid and vapor states.

[c] Solid state frequency.

torsional and CNC deformation vibrations remain unassigned. A close parallelism is found for the frequencies in the vibrations internal in the ethyl group between ethyl isocyanate and ethyl isothiocyanate. A major exception is the CC stretching vibration where a 50 cm^{-1} difference is found between the two molecules. This possibly reflects the even larger difference between the two molecules with respect to $\nu(C_\alpha$-N).

An unexpected accidental degeneracy is found for ν (C_α-N) and the CH_2 rock in ethyl isocyanate. In methyl and isopropyl isocyanate $\nu(C_\alpha$-N) can be assigned without reservation to absorption bands at 852 and 753 cm^{-1}, respectively. The sharp decrease in frequency for $\nu(C_\alpha$-N) is in agreement with the findings of Sheppard (see Table 1). Consequently, a frequency of approximately 800 cm^{-1} is expected for $\nu(C_\alpha$-N) in ethyl isocyanate. Comparison with ethyl isothiocyanate implies a similar frequency for the CH_2 rock. The vibrations have mutually perpendicular transition moments and thus if accidently degenerate should not couple and repell each other. Only one absorption band is found at 794 cm^{-1} in the liquid state spectrum. In contrast two maxima are seen in both the solid and vapor state spectra.

The CCN deformation vibrations are readily assigned to absorption bands at 417 and 397 cm^{-1}. There is considerable difference in frequency between these deformation vibrations and those of the isocyanate group. As a result the absorption bands associated with the CCN deformation vibrations are well defined and symmetrical. This is in sharp contrast to the spectrum of ethyl isothiocyanate where the absorption bands of the deformation vibrations are markedly asymmetric.

Vibrational assignments for the combination bands of ethyl isocyanate are presented in Table 36.

Table 36. Assignments for the combination bands of ethyl isocyanate

Frequency (cm^{-1})[a]	Assignment (cm^{-1})
3698	2280 + 1432 = 3712
3633	2218 + 1432 = 3650
3263	2280 + 988 = 3268
3075	2280 + 794 = 3074
2901	1451 + 1451 = 2902
2419	1432 + 988 = 2420
2218	1432 + 794 = 2226
2140	1348 + 794 = 2143
2090	1472 + 630[b] = 2102
1399	988 + 417 = 1405

---

[a] All frequencies are from the liquid state unless otherwise indicated.

[b] Estimated frequency.

Table 36. (Continued)

Frequency (cm^{-1})	Assignment (cm^{-1})
1375^c	982 + 398 = 1380^c
1262	630^b + 630^b = 1260

[c] Solid state frequency.

Isopropyl Isocyanate

Vibrational assignments for isopropyl isocyanate appear in Tables 37 and 38. As expected, vibrations originating with in the isopropyl group have very similar frequencies in isopropyl isocyanate and isopropyl isothiocyanate. Five of the 33 fundamentals are not assigned. They are exactly the same normal modes (the CH stretch, methyl torsional and CNC deformation vibrations) that were left unassigned in the spectrum of isopropyl isothiocyanate.

Svatek, Zahradnik and Kjaer (83) have stated that CH_2NCS and CHNCS units could be detected by strong bands about 1345 and 1330 cm^{-1}. Inspection of the infrared spectra of ethyl and isopropyl isocyanate indicates that these observations can be generalized further. Ethyl and isopropyl isocyanate have strong absorption bands at 1348 and 1331 cm^{-1}, respectively. These bands have the same

Table 37. Assignments for the fundamental modes of isopropyl isocyanate

Vibration	Frequency (cm^{-1})
$\nu_{as}CH_3$	2984, 2939
$\nu_s CH_3$	2883
$\nu_{as}(NCO)$	2270
$\delta_{as}CH_3$	1472, 1455
$\nu_s(NCO)$	1421
$\delta_s CH_3$	1389, 1372
$\delta(CH)$	1331, 1264
γCH_3	1167, 1098, 946[b] and 928
$\nu(CC)$	1133, 904
$\nu(C_\alpha -N)$	753
$\delta(NCO)$	629, 595
$\delta(CCN)$	460, 352
$\delta(CCC)$	410

[a] All frequencies are from the liquid state unless otherwise indicated.

[b] Frequency from (49).

assignments, CH_2 wag and CH deformation, in the respective isocyanates and isothiocyanates. Hence, the absorption bands about 1345 and 1330 cm^{-1} should be useful in the detection and recognition of CH_2-N= and CH-N= functional groups.

Table 38. Assignments for the combination bands of isopropyl isocyanate

Frequency (cm^{-1})[a]	Assignment (cm^{-1})
3674	2270 + 1421 = 3691
2393	1264 + 1133 = 2397
2172	1421 + 753 = 2174
1242	629 + 629 = 1258
1221	629 + 595 = 1224

[a] All frequencies are from the liquid state.

Tert-butyl Isocyanate

While the spectrum of this compound has not been recorded in this investigation, a fairly complete list of absorption frequencies has been published by Califano, Scarpati and Speroni (13). The only exception that can be taken to their assignments is that for $\nu(C_\alpha\text{-N})$. They assign this vibration to an absorption band at 847 cm^{-1}. This absorption band is more reasonably assigned to the totally symmetric CC stretching vibration. Two reasons can be found for the reassignment. Firstly, in methyl, ethyl and isopropyl isocyanate the frequencies found for $\nu(C_\alpha\text{-N})$ form the series 852, 796 and 753 cm^{-1}. This clearly implies a frequency about 700 cm^{-1} for $\nu(C_\alpha\text{-N})$ in tert-butyl isocyanate. Secondly, the totally symmetric CC stretch should appear about 850 cm^{-1}. This is clearly shown in the following data for the symmetric CC stretch in ethyl and isopropyl esters of both isocyanic and isothiocyanic acids.

	isocyanate	isothiocyanate
ethyl	988	938
isopropyl	904	863
tert-butyl	?	805

While the published spectrum of tert-butyl isocyanate does go as low as 675 cm^{-1} an alternate choice for $\nu(C_\alpha -N)$ is not seen.

SUGGESTIONS FOR FUTURE WORK

Perhaps the major difficulty in this investigation was the lack of accurate structural data for the three methyl derivatives. Additional microwave studies do not appear to be the solution since a rigorous interpretation of the observed transitions is fraught with difficulty. An electron diffraction study is more probably the correct approach.

Some interpretive problems, especially the assignments for ν_s(NCS) and $\nu(C_\alpha - N)$, may possibly be resolved by a normal coordinate analysis of the three methyl derivatives studied in this investigation. This may be illusive since some arbitrary choices may have to be made with respect to some of the force constants.

The major question not answered in this investigation concerns the internal barrier about the C_α-N bond in methyl isocyanate. Solution of this question awaits better structural data for the molecule and more infrared data below 250 cm^{-1} for the vapor state.

However, most of the interesting research problems in molecules containing the isocyanate, isothiocyanate and thiocyanate functional groups are found in aromatic compounds. Some recent vibrational analyses for phenyl isocyanate pose quite interesting interpretive problems. In the aryl derivatives several of the same phenomena occur, e.g., Fermi resonance and free rotation, that were found in the alkyl compounds. While vibrational analyses have appeared for the isocyanate and isothiocyanate none has been yet published for phenyl thiocyanate. It should be interesting to apply some of the observations found for the isocyanate, isothiocyanate and thiocyanate group vibrations in alkyl derivatives to the spectra of aromatic molecules containing the same functional groups.

SUMMARY

The complex spectra exhibited by the alkyl thiocyanates in the 725 to 550 cm^{-1} spectral region has been studied in some detail. Increases in spectral complexity for the (C_α-X) stretching vibrations due to restricted rotation about the C_α-C_β bond and the resulting rotational isomerism has been investigated previously. However, the observed complexity cannot be entirely explained on this basis alone. Only with the inclusion of restricted rotation about the C_α-S bond and the associated rotational isomerism is it possible to propose a unified explanation to account for all of the absorption bands observed in the 725 to 550 cm^{-1} region. Spectroscopically discrete, although chemically inseparable, isomers of ethyl thiocyanate and isopropyl thiocyanate were detected. In the former compound the H_α' and C_β isomers were distinguished by absorption bands at 686 and 654 cm^{-1}. Both absorption bands are assigned to the same fundamental, ν(S-C), but originate in the separate isomers. Likewise, the isomeric forms, H_α'' and C_β', of isopropyl thiocyanate are characterized by absorption bands at 688 and 613 cm^{-1}. In addition to the interpretation of the carbon-sulfur stretching vibrations, vibrational analyses are presented for methyl, ethyl and isopropyl thiocyanate.

Restricted rotation about the C_α-X bond and the associated rotational isomerism has been also observed for the

alkyl isothiocyanates. However, the magnitude of the barrier against free rotation about the C_α-N bond in alkyl isothiocyanates is considerably smaller than the barrier for C_α-S bond in the alkyl thiocyanates. The respective barriers, in the methyl derivatives, are 0.38 and 1.09 kcal. per mole. Hence, in methyl isothiocyanate at room temperature the methyl group rotates freely with respect to the isothiocyanate reference frame. The free rotation of the methyl group in methyl isothiocyanate is reflected in the vibration-rotation fine structure observed for $\nu_{as}CH_3$ and $\delta_{as}CH_3$ in the vapor state spectrum. Interpretation of the observed spacings between the individual components of the Q branch in terms of the entire molecule rotating results in implausible Coriolis coupling constants. Another consequence of free rotation about the C_α-N bond is the lack, at room temperature, of discrete rotational isomers in ethyl and isopropyl isothiocyanate. Marked increases in complexity are observed for ν_{as}(NCS) in the spectra of ethyl isothiocyanate and isopropyl isothiocyanate at liquid nitrogen temperature. The observed increase in spectral complexity for ν_{as}(NCS) is interpreted in terms of isomers completely analogous to those found for ethyl and isopropyl thiocyanate. Comparison of spectra from solid state and liquid state samples of several alkyl isothiocyanates has resolved the interpretive difficulties which beset previous investigators in assigning ν_s(NCS) and $\nu(C_\alpha$-N). The C_α-N stretching vibration was assigned to absorption bands about 640 cm^{-1} on the basis of a "splitting" observed in this region in n-propyl isothiocyanate as compared to ethyl isothiocyanate. Only one of the two absorption bands found, at 690 and 642 cm^{-1}, in the liquid state spectrum of n-propyl isothiocyanate remain in the spectrum of a solid state sample at liquid nitrogen temperature. A result of this analysis is the assignment of ν_s(NCS) to absorption bands in the 1100 to 980 cm^{-1} region. Vibrational assignments are presented for methyl, ethyl, isopropyl and tert-butyl isothiocyanate.

Less conclusive results have been obtained from the study of the alkyl isocyanates. This resulted primarily from the poorly defined spectra recorded for alkyl isocyanates at liquid nitrogen temperature. Free rotation of the methyl group at room temperature in methyl isocyanate was implied from vibration-rotation fine structure observed for $\nu_{as}CH_3$ and $\delta_{as}CH_3$ in the vapor state spectrum. Vibrational analyses are presented for methyl, ethyl and isopropyl isocyanate.

For all three classes of compounds studied frequency ranges are stated for the vibrations completely internal to the specific functional group.

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Finally to wife to whom I dedicate this work,

Men do not think
Of sons and daughters, when they fall in love

E. B. Browning

APPENDIX A: SECULAR DETERMINANT FOR MOLECULAR VIBRATIONS

The vibratory motion of atomic nuclei in a complex molecule is described by the Lagrangian equations of motion

$$\frac{d}{dt}(\partial L/\partial \dot{q}_i) - (\partial L/\partial q_i) = 0 \qquad i = 1,2,3\ldots$$

where q_i are the generalized displacement coordinates and L is the Lagrangian function. In the problem under consideration the system is defined by its kinetic energy, T, and potential energy, V. Furthermore, the displacement coordinates satisfy the system independently of time so that T does not involve time directly. The kinetic energy is expressed as

$$2T = \sum_{ij} a_{ij}\, \dot{q}_i\, \dot{q}_j$$

where the coefficients a_{ij} are dependent upon the choice of coordinates. A Taylor's series expansion about the equilibrium position will yield for the potential energy

$$V = V_o + \sum_i (\partial V/\partial q_i)_o\, q_i + \tfrac{1}{2} \sum_{ij} (\partial^2 V/\partial q_i\, \partial q_j)_o\, q_i\, q_j$$
$$+ \frac{1}{3!} \sum_{ijk} (\partial^3 V/\partial q_i\, \partial q_j\, \partial q_k)_o\, q_i\, q_j\, q_k \cdots$$

with the subscript zero referring to evaluation of the derivatives at the equilibrium position of the atomic masses. V_o is the potential energy of the system at the equilibrium position and can be defined by convention to be equal to zero. Since the system under consideration is conservative with respect to energy the force acting on the nuclei in the equilibrium position are also equal to zero. Third and higher order terms involve anharmonicity corrections and in a first approximation will be assumed equal to zero. The expansion then is reduced to

$$2V = \sum_{ij} b_{ij} q_i q_j$$

where

$$b_{ij} = (\partial^2 V/\partial q_i \, \partial q_j)_o.$$

An internal assumption of simple harmonic motion would have led directly to this form for the potential energy.

Since the kinetic energy is not a direct function of the displacement coordinates the Lagrangian equations may be rewritten as

$$\frac{d}{dt}(\partial T/\partial \dot{q}_i) - (\partial V/\partial q_i) = 0 \qquad i = 1,2,3 \ldots 3n\text{-}6$$

Substitution of the relationships for the kinetic and potential energy into this equation will then yield

$$\sum_j (a_{ij} \ddot{q}_j + b_{ij} q_j) = 0 \qquad i = 1,2,3 \ldots 3n\text{-}6$$

Each term in the summation may be dealt with individually since $\ddot{q}_j$ and q_j are parallel vectors. The solutions for the individual terms can be readily recognized as being of the form

$$q_j = q_j^o \ \cos(2\pi\nu t)$$

where ν is the frequency of the simple harmonic motion that the nuclei undergo during a vibration. Substitution of the individual term solutions into the equations of motion results in a set of 3n-6 simultaneous, homogeneous linear equations

$$\sum_j (b_{ij} - \lambda a_{ij})\, q_j^o - 0 \qquad i = 1,2,3 \ldots 3n-6$$

where $\lambda = 4\pi^2 \nu^2$. For the equations of motion to coexist the determinant of the coefficients must have solutions such that

$$\left| b_{ij} - \lambda a_{ij} \right| = 0.$$

The resulting frequencies, ν , are the vibrational frequencies associated with the normal modes of the molecule.

APPENDIX B: MATHEMATICAL FORMULATION OF FERMI RESONANCE

If the unperturbed energies, E_n^o and E_i^o, of two vibrational levels having the same symmetry are almost equal in magnitude a resonance interaction can occur between the energy levels. As a result of this interaction, denoted Fermi resonance if the interaction is between vibrational levels, the energy levels are "pushed" apart. Perturbation theory can be employed to calculate the differences between the original and final energy levels.

The generalized eigenfunction for the resulting energy levels will be of the normalized form

$$\phi = a\,\phi_n^o + b\,\phi_i^o$$

where ϕ_n^o and ϕ_i^o are the zeroth order orthonormal eigenfunctions associated with the unperturbed energy levels E_n^o and E_i^o. The energy, E, associated with ϕ is given by

$$E = \int \phi H \phi \, d\tau \Big/ \int \phi \phi \, d\tau$$

where H is the Hamiltonian. Substitution for ϕ in terms of the original eigenfunctions then yields the equation

$$E = (a^2E_n^o + 2abW_{ni} + b^2E_i^o) \,/\, (a^2 + 2abS + b^2)$$

where $W_{ni} = W_{in}$ since H is Hermitian, S = 0 since the original eigenfunctions are orthogonal and

$$W_{ni} = \int \phi_n^o \, H \phi_i^o \, d\tau , \qquad S = \int \phi_n^o \, \phi_i^o \, d\tau$$

$$\text{and } E^o = \int \phi^o \, H \, \phi^o \, d\tau .$$

Through a variation of E with respect to the coefficients a and b the secular determinate

$$\begin{vmatrix} E_n^o - E & W_{ni} \\ W_{ni} & E_i^o - E \end{vmatrix} = 0$$

is obtained. Until this point E has been taken as a general parameter. There are two solutions, E_a and E_b, of the secular determinate and they will be of the form

$$E_a = E_{ni} + \tfrac{1}{2}(4W_{ni}^2 + \delta^2)^{\frac{1}{2}}$$

$$E_b = E_{ni} - \tfrac{1}{2}(4W_{ni}^2 + \delta^2)^{\frac{1}{2}}$$

where

$$E_{ni} = (E_n^o + E_i^o)/2 \quad \text{and} \quad \delta = (E_n^o - E_i^o).$$

The solutions may also be expressed by means of sum and difference equations.

$$E_a + E_b = E_n^o + E_i^o$$

$$E_a - E_b = (4W_{ni}^2 + \delta^2)^{\frac{1}{2}}$$

The coefficients a and b can be determined by substitution of E_a and E_b into the secular equations. When this is done the resulting eigenfunction are

$$\phi_a = c\,\phi_n^o - d\,\phi_i^o \qquad \phi_b = c\,\phi_i^o + d\,\phi_n^o$$

with the coefficients c and d being given by

$$c = (E_a - E_b + \delta)^{\frac{1}{2}} / \, 2^{\frac{1}{2}}(E_a - E_b)^{\frac{1}{2}}$$

and

$$d = (E_a - E_b - \delta)^{\frac{1}{2}} / \, 2^{\frac{1}{2}}(E_a - E_b)^{\frac{1}{2}}.$$

The coefficient d is an excellent measure of the extent of the resonance interaction. If there is no interaction δ will be equal to $(E_a - E_b)$ and consequently d will be equal to zero. As d approaches zero the wavefunctions ϕ_a and ϕ_b will tend toward the unperturbed eigenfunctions, ϕ_n^o and ϕ_i^o.

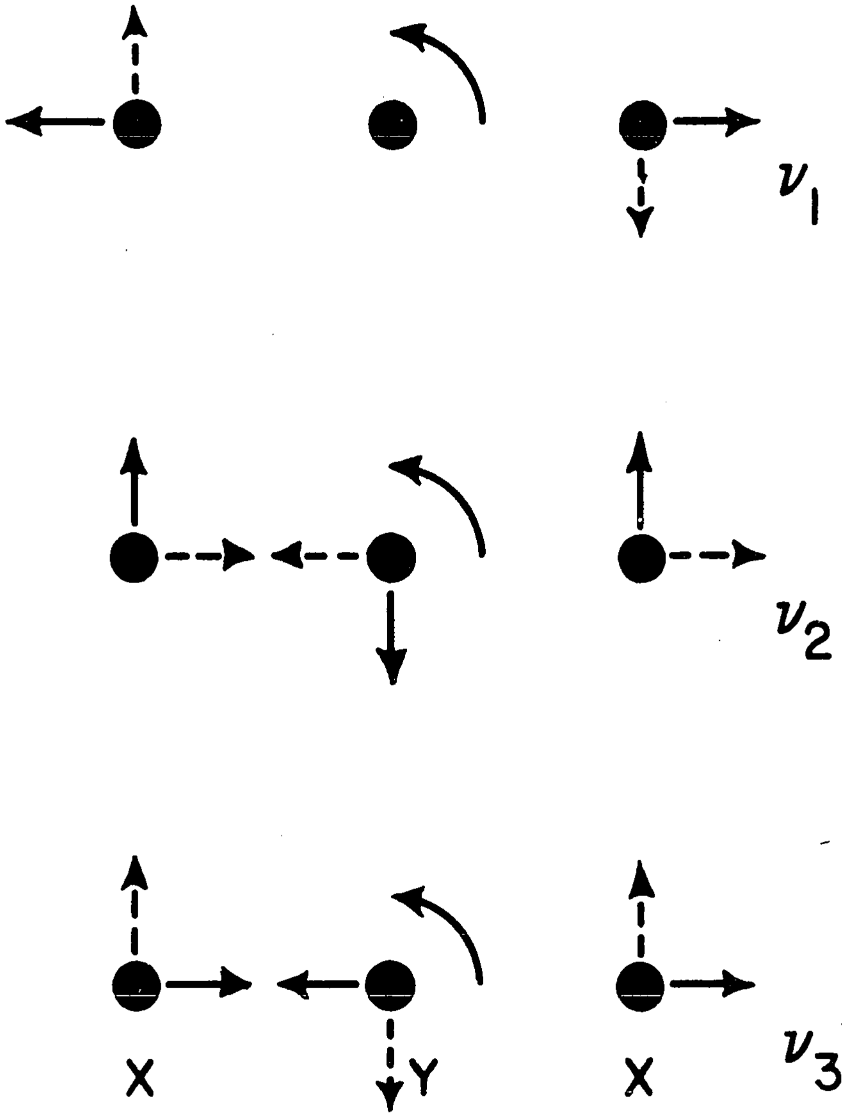
APPENDIX C: CORIOLIS COUPLING OF MOLECULAR VIBRATIONS

If the motion of a particle is referred to a uniformly rotating coordinate system, apart from the acceleration produced by the acting forces, two additional accelerations appear. They are the centrifugal and Coriolis accelerations. Unlike the centrifugal acceleration, the Coriolis acceleration will occur only if the particle is in linear motion. The Coriolis acceleration may be thought of as the resultant of an apparent force, called the Coriolis force. This force is directed at right angles to both the direction of motion and the axis of rotation in such a way that a right handed screw progressing in the direction of the Coriolis force will carry the linear velocity vector into the angular momentum vector over the smaller of the two angles between them.

The effect of Coriolis forces in a rotating vibrating molecule can be most readily visualized in a linear symmetric triatomic molecule X-Y-X. Figure 35 shows the three normal vibrations for such a molecule. The direction of rotation for the entire molecule is indicated by the counterclockwise arrow. The solid lines represent the displacement coordinates for each normal vibration and the broken line arrows show the Coriolis forces. No attempt has been made to draw the forces and displacement coordinates to scale. As seen from this figure excitation of ν_2 produces a Coriolis force

Figure 35. Coriolis coupling in the normal modes of vibration for a symmetrical linear triatomic molecule X-Y-X

The direction of rotation for the entire molecule is indicated by the counter-clockwise arrows. Normal modes of vibration are indicated by solid arrows and the Coriolis forces are indicated by dashed arrows.


ν1
ν2
X
Y
X
ν3

which tend to excited ν_3. Conversely, excitation of ν_3 tends to excited ν_2. If the frequencies ν_2 and ν_3 are fairly close the two vibrations will couple. Simultaneous with this coupling will be a mixing of the unperturbed energy levels and their corresponding eigenfunctions.

For the example cited above the unperturbed frequencies are usually not very close together. Thus the Coriolis coupling is only a relatively small perturbation. However, for degenerate vibrations of more complicated systems the effect of Coriolis coupling is considerable, a case in point being the degenerate vibrations of the methyl halides.

APPENDIX D: CC STRETCHING AND METHYL ROCKING ASSIGNMENTS IN ISOPROPYL AND TERT-BUTYL HALIDES

In a series of papers (73, 75, 76) Sheppard has analyzed the vibrational spectra of simple alkyl halides. During the course of this investigation certain anomalies appeared in the assignments of the CC stretching and methyl rocking vibrations in isopropyl and tert-butyl halides. The spectral data and assignments proposed by Sheppard (75, 76) for the 1250 to 800 cm^{-1} region are summarized in Tables 39 and 40.

Table 39. Spectral data and vibrational assignments for the isopropyl halides

Frequency (cm^{-1})[a,b]			Assignments[c]	
Chloride	Bromide	Iodide		
1128.5dp	1126 dp	1125	ν(CC)	a"
1060.5p	1038 p	1018.5p	ν(CC)	a'
1160.5	1155.5p	1146.5p	γCH_3	a'
949	946	941	γCH_3	a"
934.5	931	926.5	γCH_3	a"
882.5p	878 p	873 dp	γCH_3	a'

[a] Values presented in the table represent an average of the infrared and Raman frequencies listed in reference 76.

[b] Raman polarization is indicated by p and dp.

[c] Vibrational symmetry classes are based upon C_s molecular symmetry.

Table 40. Spectral data and vibrational assignments for the tert-butyl halides

Frequency (cm^{-1})[a,b]			Assignments[c]	
Chloride	Bromide	Iodide		
1237 dp	1236 dp	1226.5	ν(CC)	e
1156 p	1143.5p	1135	ν(CC)	a_1
1028.5dp	1034 p	1025	γCH_3	e
917.5dp	932 dp	927.5	γCH_3	e
811 p	803.5p?	802.5	γCH_3	a_1

[a] Values presented in the table represent an average of the infrared and Raman frequencies listed in reference 75.

[b] Raman polarization is indicated by p and dp.

[c] Vibrational symmetry classes are based upon C_{3v} molecular symmetry.

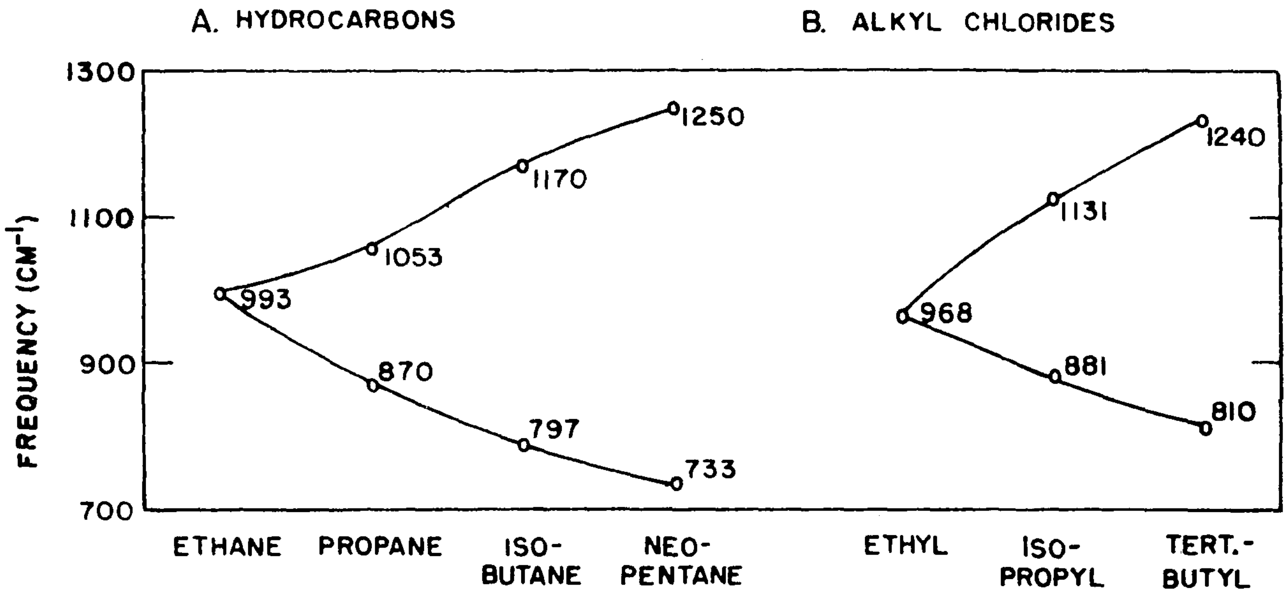
The a_1 CC stretching vibration in tert-butyl halides was assigned on the basis of calculations by Wagner (89) indicating that the triply degenerate CC vibration in neopentane, at 1250 cm^{-1} (80), splits in the less symmetrical tert-butyl derivatives into a doubly degenerate vibration at approximately the same frequency and a symmetrical vibration at a lower frequency. Sheppard referred to a vibrational analysis (81) of neopentane and its alkyl derivatives in which the triply degenerate CC vibration splits into a "similar" pattern. An analogous result for isopropyl derivatives was obtained from Wagner's (89) analysis of isobutane. As a consequence of the CC assignments, the remaining bands in the 1250 to 800 cm^{-1} region for both types of compounds were assigned to methyl rocking vibrations.

Perhaps the most serious difficulty with this analysis is the assignment of the 806 cm^{-1} band to the a_1 methyl rocking vibration in tert-butyl halides. This frequency is unusually low as compared with other assignments for totally symmetric methyl rocking vibrations and it is difficult to find any reason for this anomaly. A comparison of frequencies for the lowest symmetrical rocking vibration shows a decrease of 70 cm^{-1} from isopropyl to tert-butyl derivatives. Since the only modification has been the replacement of a hydrogen atom with a methyl group, it seems reasonable to assume the major cause of this low frequency lies in an interaction or coupling centered on the methyl group. However a comparison of the methyl rocking frequencies in propane, isobutane and neopentane indicates that analogous substitution produces insignificant shifts (77). Further investigation of the Raman spectrum of isobutane (3) shows the absence of bands between 953 and 797 cm^{-1}, the latter band being unambiguously assigned to the nondegenerate totally symmetric CC stretching vibration. Likewise, the Raman spectrum of neopentane (80) exhibits a void between 921 and 733 cm^{-1}, where again the latter band is unambigously assigned to the totally symmetric CC stretching vibration.

It therefore appears more reasonable to assign the 806 cm^{-1} band to a symmetric CC stretching vibration, which has been characterized in this region, rather than to a methyl rocking vibration. If this is done the 878 cm^{-1} band in isopropyl derivatives must also be reassigned to a symmetric CC stretching vibration. As a result of this change the symmetric methyl rocking vibrations are assigned to the 1062 and 1153 cm^{-1} series. Figure 36 shows the correlation between the CC frequencies in hydrocarbons and the revised assignments in alkyl chlorides.

This analysis does not preclude an interaction between methyl rocking and skeletal stretching vibrations of the same symmetry class. Infrared spectra of deuterated propane (77) and neopentane (80) show clearly that an interaction does exist and therefore that group vibration assignments are useful only as a first approximation. However, clearly the 968, 881 and 810 cm^{-1} bands in alkyl chlorides correspond to the same basic type of vibrations that produces the 993, 870, 797 and 733 cm^{-1} bands in the hydrocarbon series. Further the infrared spectrum of deuterated neopentane shows clearly that, as a first approximation, the 733 cm^{-1} can be assigned to a skeletal stretching vibration.

Figure 36. Correlation of CC stretching frequencies


A. HYDROCARBONS
B. ALKYL CHLORIDES
FREQUENCY (CM^{-1})
1300
1100
900
700
993
1053
1170
1250
870
797
733
968
1131
1240
881
810
ETHANE
PROPANE
ISO-BUTANE
NEO-PENTANE
ETHYL
ISO-PROPYL
TERT.-BUTYL

APPENDIX E: OBSERVED INFRARED ABSORPTION FREQUENCIES FOR THE ALKYL THIOCYANATES

The following notation was used to describe the relative intensities of the absorption bands.

vs	very strong absorption
s	strong absorption
m	moderate absorption
w	weak absorption
vw	very weak absorption
sh	appears as a shoulder to a stronger absorption

Table 41. Observed infrared absorption frequencies (cm^{-1}) for the vapor, liquid and solid states of methyl thiocyanate

Vapor state	Liquid state	Solid state
	3999 (w)	
	3923 (w)	
		3044 (w)
3032 (m)	3027 (m)	3026 (s) 3004 (w)
2962 2952 (s) 2944	2943 (m)	
	2853 (w)	2858 (m)
	2833 (w)	2836 (w)
	2615 (vw)	
	2558 (vw)	
	2411 (vw)	
	2308 (vw)	
2182 2174 (s) 2165	2158 (s)	2160 (s)
	2109 (w)	2130 (w) 2110 (w)
1435 (s)	1431 (s)	1447 (s) 1420 (m)
1338 1328 (m) 1320	1320 (s)	1307 (s)
996 981 (m)	989 (s)	999 (s) 995 (vw)
968 (m)	973 (m)	969 (s)

Table 41. (Continued)

Vapor state	Liquid state	Solid state
		927 (w)
	813 (m)	822 (m)
	699 (w)	699 (m) 693 (vw)
	675 (w)	679 (m)
	645 (w)	659 (w)
	460 (w)	466 (m)
	407 (m)	408 (s)
	190[a]	
		131[b]

[a] Frequency from (58).

[b] Frequency from (24).

Table 42. Observed infrared absorption frequencies (cm^{-1}) for the liquid and solid states of ethyl thiocyanate

Liquid state	Solid state
2976 (s)	2995 (m)* 2973 (s)
	2947 (w)
2935 (s)	2934 (m)
2900 (sh)	2896 (w)
2875 (m)	2873 (w)
2835 (w)	2842 (w)*
2699 (w)	
2614 (vw)	
2553 (vw)	
2486 (vw)	
2438 (vw)	
2349 (vw)	
	2199 (w)
2155 (s)	2155 (s)
2103 (w)	2127 2106 (w)
1451 (s)	1459 (m)* 1448 (s)
1428 (s)	1431 (m)*
1381 (s)	1379 (s)*
	1305 (vw)
1273 (s)	1273 (s)*

Table 42. (Continued)

Liquid state	Solid state
1250 (sh)	1245 (s)*
1062 (s)	1063 (s)*
	1055 (w)
	1047 (vw)
969 (s)	968 (s)
	960 (sh)
810 (vw)	
774 (s)	776 (s)*
686 (w)	685 (m)
654 (w)	
624 (m)	630 (s)*
468 (vw)	
453 (vw)	
407 (m)	418 (s)
330 (w)	
311 (w)	

*Average of two frequencies usually split by 3 to 5 cm^{-1}.

Table 43. Observed infrared absorption frequencies (cm^{-1}) for the liquid state of n-propyl thiocyanate

Liquid state
2973 (s)
2940 (s)
2880 (s)
2804 (vw)
2744 (vw)
2668 (vw)
2624 (vw)
2552 (vw)
2487 (vw)
2430 (vw)
2409 (vw)
2156 (s)
2107 (vw)
1460 (s)
1445 (sh)
1423 (s)
1382 (s)
1343 (m)
1296 (s)
1243 (s)
1212 (sh)
1096 (m)

Table 43. (Continued)

Liquid state
1090 (m)
1071 (m)
1056 (m)
1037 (m)
991 (vw)
900 (m)
892 (m)
840 (m)
809 (vw)
782 (s)
738 (m)
706 (m)
674 (w)
647 (w)
619 (w)
459 (vw)
405 (m)

Table 44. Observed infrared absorption frequencies (cm^{-1}) for the liquid and solid states of isopropyl thiocyanate

Liquid state	Solid state
	2998 (w)
2979 (s)	2978 2970 (m)
2932 (s)	2946 2932 (m)
	2917 (w)
2871 (m)	2866 (w)
2846 (w)	2842 (w)
2768 (vw)	
2733 (vw)	
2553 (vw)	
2506 (vw)	
2250 (vw)	
2154 (s)	2154 (s)
2104 (vw)	2103 (vw)
1462 (s)	1471 1469 (s)
1446 (s)	1451 1445 (s)
	1439 (sh)
1388 (s)	1386 (s)
1372 (s)	1371 (s)
1318 (w)	1310 (w)

Table 44. (Continued)

Liquid state	Solid state
	1267 (sh)
1258 (sh)	1258 (s)
1247 (s)	1247 (s)
	1171 (m)
1157 (s)	1157 (vw)
	1128 (vw)
1119 (m)	1124 (m)
1057 (s)	1057 (s)
	952 (vw)
934 (m)	938 (w)
	920 (m)
884 (m)	884 (s)
879 (sh)	
815 (w)	828 (vw)
688 (m)	687 (m)
613 (m)	
586 (m)	585 (m)
527 (vw)	518 (w)
	468 (vw)
455 (w)	454 (vw)
407 (m)	416 (m)
	403 (vw)
329 (w)	
308 (w)	

Table 45. Observed infrared absorption frequencies (cm^{-1}) for the liquid state of n-butyl thiocyanate

Liquid state
2964 (s)
2937 (s)
2874 (s)
2737 (vw)
2654 (vw)
2552 (vw)
2155 (s)
1465 (s)
1458 (s)
1438 (m)
1424 (m)
1382 (m)
1367 (w)
1354 (w)
1339 (w)
1306 (w)
1291 (m)
1267 (m)
1231 (m)
1190 (w)
1101 (w)
1079 (w)

Table 45. (Continued)

Liquid state
1058 (w)
1009 (w)
996 (w)
968 (w)
919 (w)
873 (w)
794 (w)
781 (w)
744 (m)
730 (w)
704 (w)
678 (w)
653 (vw)
622 (m)
493 (vw)
473 (vw)
444 (vw)
405 (m)
324 (vw)

Table 46. Observed infrared absorption frequencies (cm^{-1}) for the liquid state of sec-butyl thiocyanate

Liquid state
2975 (s)
2935 (s)
2877 (s)
2745 (vw)
2683 (vw)
2552 (vw)
2400 (vw)
2156 (s)
2105 (vw)
2041 (vw)
1454 (s)
1383 (s)
1349 (w)
1338 (w)
1293 (s)
1282 (m)
1227 (s)
1151 (m)
1118 (w)
1101 (vw)
1074 (m)
1060 (m)
1014 (w)

Table 46. (Continued)

Liquid state
997 (m)
981 (w)
959 (m)
913 (w)
844 (w)
820 (w)
813 (w)
791 (s)
687 (w)
663 (w)
606 (w)
576 (w)
513 (w)
408 (m)

APPENDIX F: OBSERVED INFRARED ABSORPTION FREQUENCIES FOR THE ALKYL ISOTHIOCYANATES

The following notation was used to describe the relative intensities of the absorption bands.

vs	very strong absorption
s	strong absorption
m	moderate absorption
w	weak absorption
vw	very weak absorption
sh	appears as a shoulder to a stronger absorption

Table 47. Observed infrared absorption frequencies (cm^{-1}) for the vapor, liquid and solid states of methyl isothiocyanate

Vapor state	Liquid state	Solid state
	3079 (w)	3080 (vw)
	3004 (w)	
3033 3024 3015 3006 2997 2988 2978	2991 (w)	2988 (w)
2961 2950 (m)	2933 (m)	2931 (m)
2908 2897 (vw)	2864 (w)	2858 (m)
2828 2817 (w)	2843 (w)	2848 (m)
2791 (w)	2796 (w)	2791 (w)
2772 2760 (w)	2766 (w)	2759 (w)
2590 (vw)	2553 (w)	2551 (w)
		2519 (w)
2228 (m)	2206 (vs)	2225 (vs)
2111 2096 (vs)	2124 (vs)	2141 (vs)
2083 (sh)		2037 (w)
1507 1495 1482 1469 1456	1444 (m)	1440 (s)

Table 47. (Continued)

Vapor state	Liquid state	Solid state
1430 1419 (s)	1411 (s)	1408 (s)
		1255 (w)
		1218 (vw)
	1221 (w)	1178 (vw)
1176 (w)		
1126 1107 (w)	1120 (w)	1118 (m)
1090 (m)	1088 (w)	1083 (s)
	1008 (w)	1021 (w)
	885 (w)	872 (m)
676 (m)	644 (m)	628 (s)
535 (m)	569 (w)	568 (m)
418 405 (w)	440 (w)	434 (s)
353[a]	338 (vw)	
		128[b]

---

[a] Frequency from (15).

[b] Frequency from (24).

Table 48. Observed infrared absorption frequencies (cm^{-1}) for the vapor, liquid and solid states of ethyl isothiocyanate

Vapor state	Liquid state	Solid state
2999 2992 (m)	2988 (m)	2990 (s)
2968 2960 (m)	2942 (m)	2940 (m)
2906 2900 (m)		2918 (vw)
	2883 (m)	2880 (w)
		2832 (w)
	2814 (w)	2814 (w)
2752 (w)	2753 (w)	
2203 (s) 2076 (vs)	2183 (vs) 2114 (vs)	2222 (vs) 2199 (vs) 2154 (vs) 2123 (vs)
	2043 (sh)	2041 (m)
	1993 (w)	1995 (w)
1470 (m)	1463 (m)	1465 (s)
1459 (m)	1449 (m)	1448 (s)
1394 1385 (m)	1379 (m)	1380 (s)
1349 (s)	1342 (s)	1343 (s)
		1325 (sh)
	1282 (w)	1284 (w)
	1127 (w)	1131 (m)
	1111 (w)	1108 (m)

Table 48. (Continued)

Vapor state	Liquid state	Solid state
1074 1065 (m)	1065 (w)	1063 (s)
941 (m)	938 (m)	939 (s)
		869 (w)
	796 (w)	794 (m)
668 (w)	638 (m)	623 (s)
534 (m)	536 (m)	542 (w)
	453 (w)	448 (m)
		435 (m)
	382 (w)	382 (m)

Table 49. Observed infrared absorption frequencies (cm^{-1}) for the liquid state of n-propyl isothiocyanate

Liquid state
2969 (s)
2938 (s)
2877 (s)
2393 (w)
2186 (sh)
2132 (sh)
2098 (vs)
2075 (sh)
1462 (s)
1450 (s)
1384 (s)
1360 (s)
1350 (sh)
1342 (s)
1297 (m)
1250 (w)
1126 (vw)
1100 (vw)
1076 (w)
1031 (w)
1011 (w)
895 (m)

Table 49. (Continued)

Liquid state
859 (m)
790 (m)
753 (w)
690 (m)
642 (m)
529 (m)
459 (m)
373 (w)
311 (w)
291 (w)

Table 50. Observed infrared absorption frequencies (cm^{-1}) for the liquid and solid states of isopropyl isothiocyanate

Liquid state	Solid state
2985 (m)	2990 (m)
2938 (w)	2940 (w)
2877 (m)	2878 (w)
2817 (w)	
2734 (w)	
	2265 (w)
2149 (vs) 2093 (vs)	2189 (vs) 2167 (vs) 2120 (vs)
1999 (sh)	
1867 (w)	
1465 (m)	
1457 (m)	
1387 (m)	1384 (m)
1370 (m)	1367 (m)
1332 (s)	1334 (s)
1260[a]	
1170 (m)	1170 (m)
1130 (m)	1132 (s)
1021 (sh)	1020 (w)
1004 (m)	1000 (m)

---

[a] Absorption band partially covered by an impurity.

Table 50. (Continued)

Liquid state	Solid state
934 (w)	932 (w)
863 (m)	865 (m)
634 (m)	615 (m)
536 (m)	542 (w)
	468 (w)
459 (w)	453 (w)
437 (w)	430 (w)
393 (w)	393 (w)
335 (w)	336 (w)

Table 51. Observed infrared absorption frequencies (cm^{-1}) for the liquid state of n-butyl isothiocyanate

Liquid state
2961 (s)
2938 (s)
2871 (s)
2739 (w)
2662 (vw)
2585 (vw)
2175 (vs-sh)
2134 (vs-sh)
2104 (vs)
1465 (sh)
1458 (s)
1451 (sh)
1438 (m)
1381 (m)
1365 (sh)
1357 (sh)
1348 (s)
1330 (m)
1313 (m)
1266 (w)
1228 (w)
1131 (w)

Table 51. (Continued)

Liquid state
1116 (w)
1082 (w)
1062 (vw)
1039 (w)
1002 (vw)
978 (w)
944 (vw)
870 (w)
821 (vw)
806 (vw)
748 (m)
686 (m)
639 (m)
531 (m)
502 (m)
452 (m)
419 (w)
328 (w)

Table 52. Observed infrared absorption frequencies (cm^{-1}) for the liquid and solid states of tert-butyl isothiocyanate

Liquid state	Solid state
2987 (s)	2988 (m)
2941 (m)	2940 (w)
2913 (sh)	
2877 (w)	2876 (w)
	2710 (w)
	2190 (s)
2090 (vs)	2147 (vs)
1976 (s)	
1477 (w)	1478 (m)
1460 (m)	1458 (m)
1397 (w)	1385 (s)
1370 (s)	1367 1363 (s)
1229 (s)	1247 (s) 1225 (w)
1209 (s)	1200 (s)
1036 (w)	1039 (w)
994 (m)	987 (m)
927 (w)	929 (w)
805 (m)	803 (m)
615 (w)	588 (m)
525 (m)	530 (m)
489 (m)	483 (s)
429 (w)	423 (w)
336 (w)	

Table 53. Observed infrared absorption frequencies (cm^{-1}) for methyl isothiocyanate in various solvents

CH_3Cl[a]	CCl_4[b]	CS_2[c]	C_6H_{12}[d]	$(CH_3)_2CO$[e]
	2993	2986		
2945	2941	2932		
2879	2881	2874		
2839				
2811	2809	2808		
2774	2775	2774		
2213	2225	2221	2223	2206
2124	2108	2104	2103	2124
2074	2075	2070	2078	
1455				
1416	1416	1413		
1095	1101	1100	1102	
		660	665	656

[a] 0.211 moles methyl isothiocyanate per liter solution.

[b] 0.200 moles methyl isothiocyanate per liter solution.

[c] 0.274 moles methyl isothiocyanate per liter solution.

[d] 0.302 moles methyl isothiocyanate per liter solution.

[e] 0.286 moles methyl isothiocyanate per liter solution.

APPENDIX G: OBSERVED INFRARED ABSORPTION FREQUENCIES FOR THE ALKYL ISOCYANATES

The following notation was used to describe the relative intensities of the absorption bands.

vs	very strong absorption
s	strong absorption
m	moderate absorption
w	weak absorption
vw	very weak absorption
sh	appears as a shoulder to a stronger absorption

Table 54. Observed infrared absorption frequencies (cm^{-1}) for the vapor, liquid and solid states of methyl isocyanate

Vapor state	Liquid state	Solid state
3746 (w)	3726 (w)	3717 (w)
3711 3696 (w)	3680 (w)	3645 (w)
3207 3197 (w)		
3172 (w)	3160 (w)	
3157 (w)	3135 (w)	3113 (w)
3127 (w)	3089 (vw)	3067 (w)
3082 3073 3064 3057 3047 3038 3029 3021 3012 3002	3000 (m)	3025 (w)
2972 2956 (s)	2960 (s)	2970 (m)
2927 (sh)	2912 (m)	2917 (m)
		2871 (w)
	2870 (sh)	2845 (w)
2832 2818 (w)	2813 (w)	
2590 (vw)	2570 (vw)	
2469 (m)	2460 (sh)	
		2313 (s)

Table 54. (Continued)

Vapor state	Liquid state	Solid state
2308 (vw)	2318 (vs)	2290 (s)
2282 (vs)	2288 (vs)	2269 (s)
2265 (vs)	2254 (vs)	2237 (s)
2128 (w)	2131 (sh)	
1555 1542 1529 1517 1504 1491 1477 1467 1464 1452	1453 (s)	1455 (m)
		1437 (m)
1433 1417 (s)	1416 (s)	1385 (s)
1149 1133 (w)	1132 (w)	1136 (m)
1017 (vw)	1023 (vw)	
878 863 (s)	852 (s)	852 (s)
654 646 (m)		613 (m)
636 629 626 623 616 610 607 604 602 600	596 (s)	577 (m)

Table 54. (Continued)

Vapor state	Liquid state	Solid state
595		
582		
576		
		143[a]

[a] Frequency from (24).

Table 55. Observed infrared absorption frequencies (cm^{-1}) for the vapor, liquid and solid states of ethyl isocyanate

Vapor state	Liquid state	Solid state
3711 (m)	3698 (w)	
3657 (w)	3633 (w)	
3269 (w)	3263 (w)	
3101 (w)	3075 (w)	
2990 (s)	2988 (s)	2993 2979 (m)
		2963 (w)
2946 (s)	2943 (s)	2931 (m)
2910 (s)	2901 (sh)	2893 (w)
	2873 (s)	
2430 (s)	2419 (sh)	
2287 (vs)	2280 (vs)	2292 (vs)
2236 (vw)	2218 (vw)	2216 (sh)
2174 (sh)	2140 (sh)	2134 (w)
2110 (w)	2090 (sh)	
1472 (m)	1472 (m)	1476 (s)
1453 (m)	1451 (m)	1469 (m) 1456 (s)
1436 (m)	1432 (m)	1432 (w)
1408 (m)	1399 (m)	1404 (vw)
1399 (s)	1381 (m)	1385 (s)
1384 1379 (m)		1375 (s)

Table 55. (Continued)

Vapor state	Liquid state	Solid state
1353 (vs)	1348 (s)	1348 (s)
	1286 (w)	1281 (m)
	1262 (w)	
	1134 (m)	1137 (s)
1098 (w)	1092 (m)	1086 (s)
993 (s)	988 (s)	982 (s)
814 803 (s)	794 (s)	800 (w) 791 (s)
656 641 (sh)	630 (sh)	608 (s)
623 613 (s)	595 (s)	573 (s)
	417 (sh)	427 (m)
	397 (m)	398 (m)

Table 56. Observed infrared absorption frequencies (cm^{-1}) for the liquid state of n-propyl isocyanate

Liquid state
3688 (w)
3112 (vw)
2970 (s)
2939 (s)
2883 (s)
2750 (vw)
2724 (vw)
2673 (vw)
2373 (vw)
2280 (vs)
2180 (sh)
2100 (w)
1462 (s)
1434 (sh)
1381 (s)
1369 (s)
1353 (s)
1345 (s)
1300 (m)
1278 (w)
1251 (w)
1131 (w)

Table 56. (Continued)

Liquid state
1112 (w)
1091 (w)
1046 (w)
910 (s)
879 (s)
850 (s)
833 (m)
752 (m)

Table 57. Observed infrared absorption frequencies (cm^{-1}) for the liquid and solid states of isopropyl isocyanate

Liquid state	Solid state
3674 (s)	
2984 (s)	2988 (s)
2939 (m)	2934 (m)
2883 (m)	2870 (w)
2393 (sh)	
2270 (vs)	2300 (s)
2172 (s)	2171 (w)
1472 (m)	1463 (m)
1455 (m)	1455 1446 (m)
1421 (vw)	
1389 (m)	1387 (s)
1372 (m)	1372 (s)
1331 (s)	1346 1339 (s)
	1327 (m)
1264 (vw)	
1242 (vw)	
1221 (vw)	
1167 (m)	1168 (s)
1133 (m)	1134 (m)
1122 (sh)	1119 (w)

Table 57. (Continued)

Liquid state	Solid state
1102 (s)	1107 (s)
928 (vw)	931 (vw)
904 (m)	898 (m)
753 (m)	746 (s)
629 (sh)	621 (s)
595 (s)	579 (s)
460 (w)	480 (vw)
410 (m)	393 (w)
352 (m)	

Table 58. Observed infrared absorption frequencies (cm^{-1}) for the liquid state of n-butyl isocyanate

Liquid state
2688 (w)
3174 (vw)
3120 (vw)
3082 (vw)
2963 (s)
2938 (s)
2877 (s)
2738 (vw)
2683 (vw)
2279 (vw)
2083 (w)
1464 (s)
1433 (m)
1381 (m)
1370 (m)
1358 (s)
1334 (m)
1316 (w)
1309 (w)
1265 (w)
1257 (w)
1244 (w)

Table 58. (Continued)

Liquid state
1227 (w)
1133 (w)
1114 (m)
1065 (w)
1052 (w)
1013 (w)
1002 (w)
975 (w)
948 (w)
899 (m)
863 (m)
825 (w)
796 (m)
737 (w)

Table 59. Observed infrared absorption frequencies (cm^{-1}) for the liquid state of tert-butyl isocyanate

Liquid state[a]
2978 (m)
2934 (w)
2909 (w)
2876 (w)
2256 (vs)
1482 (vw)
1459 (w)
1392 (m)
1366 (m)
1237 (s)
1186 (m)
1037 (w)
847 (m)

[a] Data from (13).

APPENDIX H: OBSERVED RAMAN FREQUENCIES FOR THE ALKYL ISOCYANATES, ISOTHIOCYANATES AND THIOCYANATES

The following notation was used to describe the Raman spectra.

1. The numbers in brackets denote the relative intensity of the Raman line.

2. Measured polarization ratios are presented after the intensity. In some cases only p and dp, polarized and depolarized, are indicated.

3. The symbol b in conjunction with the intensity indicates a relatively broad Raman line.

Table 60. Observed Raman frequencies (cm^{-1}) for the alkyl thiocyanates

CH_3SCN^a	$CH_3CH_2SCN^a$
3020 (4b) dp	2973 (8)
2940 (11) 0.04	2933 (12) p
2835 (0)	2873 (5)
2155 (15) 0.20	2790 ($\frac{1}{2}$)
2109 ($\frac{1}{2}$)	2155 (15) 0.25
1428 (2b) 0.83 1318 (1) 0.40	1450 (5) 1428 (5) } 0.89
1252 (00)	1380 ($\frac{1}{2}$)
982 ($\frac{1}{2}$)	1269 (2)
698 (6b) 674 (10b) } 0.21	1245 (1) 1101 (1)
456 (2) 0.77 397 ($\frac{1}{2}$)	1063 (5) 1047 (1) } 0.39
190 (12b) 0.77	969 (5) 0.83
	682 (4) dp?
	649 (3) 624 (12) } 0.23
	454 (1) dp
	388 (0)
	326 (6)
	307 ($\frac{1}{2}$) p?
	161 (8) 0.90

[a] Data from (88).

Table 61. Observed Raman frequencies (cm^{-1}) for the alkyl isothiocyanates

CH_3NCS[a]	CH_3CH_2NCS[a]	$(CH_3)_2CHCH_2NCS$[b]
2985 (5b)	2985 (9)	2966 (4)
2934 (14) 0.30	2954 (8) p	2933 (4)
2803 (3)	2942 (12)	2902 (4)
2201 (5b) 0.74	2912 (6)	2862 (4)
2116 (6b) 0.74	2875 (6) dp?	2170 (3b)
1445 (2) dp?	2742 (2)	2100 (3b)
1412 (14) 0.60	2216 (2b) 0.57	1449 (4b)
1094 (10) 0.20	2181 (5)	1390 (2)
894 (4b) 0.32	2114 (6b) 0.59	1348 (4)
652 (12b) 0.23	1463 (5)	1300 (2)
450 (2) p?	1446 (5b)	1250 (½)
	1378 (2) 0.76	1130 (¼)
	1341 (6) 0.70	1082 (3b)
	1322 (00)	1045 (1)
	1280 (3) 0.86	951 (2b)
	1182 (0)	888 (½)
	1106 (3) p	816 (3)
	1064 (10) 0.16	690 (3b)
	937 (6) 0.58	419 (1b)
	902 (1) dp?	
	795 (4) 1.00	
	655 (10sb) 0.23	
	644 (6b)	
	383 (9) p	

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[a] Data from (88).

[b] Data from (17).

Table 62. Observed Raman frequencies (cm^{-1}) for the alkyl isocyanates.

CH_3NCO[a]	CH_3CH_2NCO[a]	$(CH_3)_2CHNCO$[a]
2994 (0)	2981 (3)	2984 (5b)
2951 (5)	2946 (4)	2922 (6b)
1453 (5b)	2877 (2b)	2872 (4)
1409 (5)	1456 (3)	1455 (4b)
852 (6)	1434 (5)	1421 (4b)
353 (1b)	1346 (2)	1330 (4)
	1278 (2)	1165 (1)
	1085 (3)	1132 (1)
	987 (2)	1098 (1)
	791 (4)	946 (1)
	592 (1)	900 (2)
	397 (1)	753 (5)
		590 ($\frac{1}{2}$)
		458 ($\frac{1}{2}$)
		346 ($\frac{1}{4}$)

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[a] Data from (49).

APPENDIX I: NORMAL MODES OF VIBRATION FOR METHYL, ETHYL, ISOPROPYL AND TERT-BUTYL ESTERS OF ISOCYANIC, ISOTHIOCYANIC AND THIOCYANIC ACIDS

The following tables are based upon C_s molecular symmetry. Distribution of the normal modes into the vibrational symmetry calsses a' and a" are given in Table 63 and were calculated by group theory. In the following tables XYZ represents any of the three linear groups, NCO, NCS or SCN.

Table 63. Number of normal modes in the vibrational symmetry classes a' and a" for methyl, ethyl, isopropyl and tert-butyl esters of isocyanic, isothiocyanic and thiocyanic acids

Molecule	Number of Modes in Symmetry Class	
	a'	a"
CH_3XYZ	10	5
CH_3CH_2XYZ	15	9
$(CH_3)_2CHXYZ$	19	14
$(CH_3)_3CXYZ$	24	18

Table 64. The normal modes of vibration for methyl esters of isocyanic, isothiocyanic and thiocyanic acids

Description	Symmetry Class	Notation
CH_3 asym. stretch	a"	$\nu_{as}CH_3$
CH_3 asym. stretch	a'	$\nu_{as}CH_3$
CH_3 sym. stretch	a'	$\nu_{s}CH_3$
YZ stretch[a]	a'	ν (YZ)
CH_3 asym. deform.	a"	$\delta_{as}CH_3$
CH_3 asym. deform.	a'	$\delta_{as}CH_3$
CH_3 sym. deform.	a'	$\delta_{s}CH_3$
In-plane CH_3 rock	a'	$\gamma_{\parallel}CH_3$
Out-of-plane CH_3 rock	a"	$\gamma_{\perp}CH_3$
XY stretch[a]	a'	ν (XY)
C_α-X stretch	a'	$\nu (C_\alpha -X)$
XYZ in-plane deformation	a'	$\delta_{\parallel}(XYZ)$
XYZ out-of-plane deform.	a"	$\delta_{\perp}(XYZ)$
CXY angle deformation	a'	δ (CXY)
CH_3 torsional	a"	ΓCH_3

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[a] In the isocyanates and isothiocyanates instead of XY and YZ stretching vibrations the preferred notation involves symmetric and asymmetric XYZ stretches, $\nu_{as}(XYZ)$ and $\nu_{s}(XYZ)$.

Table 65. The normal modes of vibration for ethyl esters of isocyanic, isothiocyanic and thiocyanic acids

Description	Symmetry Class	Notation
CH_3 asym. stretch	a''	$\nu_{as}CH_3$
CH_3 asym. stretch	a'	$\nu_{as}CH_3$
CH_2 asym. stretch	a''	$\nu_{as}CH_2$
CH_3 sym. stretch	a'	$\nu_{s}CH_3$
CH_2 sym. stretch	a'	$\nu_{s}CH_2$
YZ stretch[a]	a'	ν (XZ)
CH_2 bend	a'	
CH_3 asym. deformation	a''	$\delta_{as}CH_3$
CH_3 asym. deformation	a'	$\delta_{as}CH_3$
CH_3 sym. deformation	a'	$\delta_{s}CH_3$
CH_2 wag	a'	
CH_2 twist	a''	
CH_3 in-plane rock	a'	$\gamma_{\parallel}CH_3$
CH_3 out-of-plane rock	a''	$\gamma_{\perp}CH_3$
CC stretch	a'	ν (CC)
CH_2 rock	a''	
XY stretch[a]	a'	ν (XY)
C_α -X stretch	a'	ν (C_α-X)

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[a] In the isocyanates and isothiocyanates instead of XY and YZ stretching vibrations the preferred notation involves symmetric and asymmetric XYZ stretches, ν_{as}(XYZ) and ν_{s}(XYZ).

Table 65. (Continued)

Description	Symmetry Class	Notation
XYZ in-plane deformation	a'	$\delta_{\parallel}(XYZ)$
XYZ out-of-plane deform.	a"	$\delta_{\perp}(XYZ)$
CCX in-plane deformation	a'	$\delta_{\parallel}(CCX)$
CCX out-of-plane deform.	a"	$\delta_{\perp}(CCX)$
CH_3 torsional	a"	ΓCH_3
CXY angle deformation	a'	$\delta(CXY)$

Table 66. Number and type of normal vibrations of isopropyl esters of isocyanic, isothiocyanic and thiocyanic acids

Description	Number of Modes in Symmetry Class		Notation
	a'	a"	
CH_3 asym. stretch	2	2	$\nu_{as}CH_3$
CH_3 sym. stretch	1	1	$\nu_{s}CH_3$
CH stretch	1	0	ν (CH)
CH_3 asym. deform.	2	2	$\delta_{as}CH_3$
CH_3 sym. deform.	1	1	$\delta_{s}CH_3$
CH deformation	1	1	δ (CH)
CH_3 rock	2	2	$\gamma\ CH_3$
CC stretch	1	1	ν (CC)
CH_3 torsional	1	1	$\Gamma\ CH_3$
Skeletal deform.	1	1	δ (CCX)
Skeletal deform.	1	0	δ (CCC)
XY stretch[a]	1	0	ν (XY)
YZ stretch[a]	1	0	ν (YZ)
XYZ deformation	1	1	δ (XYZ)
CXY deformation	1	1	δ (CXY)
C_α-X stretch	1	0	ν (C_α-X)

[a] In the isocyanates and isothiocyanates instead of XY and YZ stretching vibrations the preferred notation involves symmetric and asymmetric XYZ stretches, ν_{as}(XYZ) and ν_{s}(XYZ).

Table 67. Number and type of normal vibrations of tert-butyl esters of isocyanic, isothiocyanic and thiocyanic acids

Description	Number of Modes in Symmetry Class		Notation
	a'	a"	
CH_3 asym. stretch	3	3	$\nu_{as}CH_3$
CH_3 sym. stretch	2	1	$\nu_{s}CH_3$
CH_3 asym. deform.	3	3	$\delta_{as}CH_3$
CH_3 sym. deform.	2	1	$\delta_{s}CH_3$
CH_3 rock	3	3	γ CH_3
CC stretch	2	1	ν (CC)
CH_3 torsional	1	2	Γ CH_3
XY stretch[a]	1	0	ν (XY)
YZ stretch[a]	1	0	ν (YZ)
C_α -X stretch	1	0	ν (C_α-X)
XYZ deformation	1	1	δ (XYZ)
CCC deformation	2	1	δ (CCC)
CCX deformation	1	1	δ (CCX)
CXY deformation	1	1	δ (CXY)

[a] In the isocyanates and isothiocyanates instead of XY and YZ stretching vibrations the preferred notation involves symmetric and asymmetric XYZ stretches, ν_{as}(XYZ) and ν_s(XYZ).