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Author: Richard M. Hedges

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THE ABSOLUTE INFRARED ABSORPTION BAND INTENSITIES OF THE METHYLENE GROUP VIBRATIONS OF SOME METHYLENE HALIDES

by

Richard M. Hedges

A Dissertation Submitted to the
Graduate Faculty in Partial Fulfillment of
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INTRODUCTION

Of the activity in infrared spectroscopy in recent years a relatively small (although increasing) fraction has been devoted to the investigation of the intensities of absorption bands. The reasons for this neglect are manifold, and include the involved nature of the experimental procedures required to obtain absolute infrared absorption intensities, the difficulty of performing normal coordinate analyses of polyatomic molecules, and even the occasional breakdown of the assumptions used in the theory whereby one derives the polar properties of chemical bonds from the absolute intensities. These various points will be discussed in detail in later sections.

In spite of these difficulties, there seems to be a great deal of information to be learned about the nature of chemical bonds from studies of absolute intensities of infrared absorption bands.

The research to be described in this thesis is an investigation of the absolute infrared absorption intensities of the vibrational bands principally ascribable to the stretching of the carbon-hydrogen bonds and the deformation (bending) of the hydrogen-carbon-hydrogen angle of some methyl halides. The particular series of compounds was chosen because a reasonably good potential function was available for them. This makes it possible to study the polar properties of the carbon-hydrogen bonds of these molecules and establish trends with variation of the halogens. The errors arising from the approximate nature of the theory appear in only a systematic way.

HISTORICAL BACKGROUND

Since work on intensities of infrared bands has been reviewed[1,2,3] several times in recent years, a complete review of the subject will not be attempted here. Rather, the recent work pertaining to carbon-hydrogen intensities and the polar properties of the carbon-hydrogen bond will be reviewed together with the work on the infrared spectra of the methylene halides.

The polar properties of carbon-hydrogen bonds have attracted a great deal of attention in the way of infrared intensity investigation. Probably much of this attention arises from interest in the sign of the C-H bond moment. The results of Coulson's[4] quantum mechanical calculations indicate that in methane the C-H polarity is $\overset{+}{C} - \overset{-}{H}$ with the bond moment equal to 0.4×10^{-10} e.s.u. Gent[5] in a review of the C-H polarity concluded that in acetylene the C-H polarity is $C^{-} - H^{+}$. This conclusion is compatible with chemical evidence for it is well known that acetylene is acidic and its hydrogens are quite labile.

The polarity of C-H bonds as a function of the state of hybridization of the carbon atom has been discussed by Walsh[6], who has shown that as the amount of p character decreases the carbon becomes more negative relative to the hydrogen. Thus, in methane, the state of hybridization is sp^3 and the polarity is $C^{+} - H^{-}$ and in acetylene with sp hybridization the polarity has reversed to $C^{-} - H^{+}$. Walsh also brought forth a corollary which stated that if a substituent on a carbon atom were replaced by a more electronegative substituent (X), more p character would be evoked in the carbon orbital participating in the C-X bond. These arguments were used in discussing bond strengths and polarities and molecular shapes.

The method of Wilson and Wells[7] for obtaining the intensities of infrared bands provided the impetus for the many intensity studies in recent years. This method, which is almost universally employed now, requires that sufficient non-absorbing foreign gas be added to the sample to broaden the rotational lines so as to eliminate violent fluctuations in intensity with frequency. The procedure requires the extrapolation of the apparent integrated absorption coefficient divided by the partial pressure to zero partial pressure of the absorbing gas. These two steps allow vibrational band intensities to be measured to a reasonable accuracy even with spectrographs of low resolving power. Ethylene[8], methane and ethane[9] were among the first compounds to be studied by the method of Wilson and Wells. For methane[9] $(\mu)_{CH}$ was found to be 0.31×10^{-18} e.s.u. and $\left(\frac{\partial\mu}{\partial r}\right)_{CH}$ was $\pm 0.55 \times 10^{-18}$ e.s.u. This value of $(\mu)_{CH}$ agrees reasonably well with the value calculated by Coulson[4] although it sheds no light on the sign of the dipole. In ethane $(\mu)_{CH}$ was estimated to be 0.3×10^{-18} e.s.u. from the parallel bending mode while both stretching modes yielded a value of $\pm 0.75 \times 10^{-10}$ e.s.u. for $\left(\frac{\partial\mu}{\partial r}\right)_{CH}$. In the case of ethylene it was also found that the value obtained for $(\mu)_{CH}$ was not a constant but was dependent on the mode of vibration, being 0.37×10^{-18} e.s.u. and 0.52×10^{-18} e.s.u. respectively, for the ν_5 and ν_7 inplane bending modes, and 0.77×10^{-18} e.s.u. for the ν_{11} out-of-plane bending mode, while $\left(\frac{\partial\mu}{\partial r}\right)_{CH}$ is 0.60×10^{-10} e.s.u. As a result of these measurements, the approximation of bond moment additivity, as it had been introduced by Rollefson and Havens[10], was seen to have some failings. Bell, Thompson and Vago[11] and later Cole and Thompson[12] studied the intensities of some bending modes of a number of substituted benzenes in solution. Their results suggested a mean value of 0.57×10^{-18} e.s.u. for $(\mu)_{CH}$ with the hydrogen atom being at the positive end of the C-H dipole. Francis[13] studied the intensities of several bands in twelve aliphatic hydrocarbons and found that $(\mu)_{CH}$ ranged from 0.2×10^{-18} e.s.u. to 0.4×10^{-18} e.s.u. and $\left(\frac{\partial\mu}{\partial r}\right)_{CH}$ to be about -0.75×10^{-10} e.s.u. (the hydrogen was assumed to be at the positive end of the C-H dipole).

There have been several studies made of the band intensities of different bands of acetylene. Calloman, McKean and Thompson[14] studied C-H stretching band intensity and deduced that $\left(\frac{\partial\mu}{\partial r}\right)_{CH}$ was 0.8×10^{-10} e.s.u.

Van Alten[15] studied the intensities of several bands in C_2H_2, C_2D_2 and C_2HD using a higher pressure of foreign gas than did Calloman, McKean and Thompson[14]. Wingfield and Straley[16] have studied the intensity of ν_5 bending vibration in C_2H_2 and C_2D_2 (also studied by Van Alten). The results of Van Alten and of Wingfield and Straley agree quite well, both yielding a value of $(\mu)_{CH}$ about 0.99×10^{-10} e.s.u. For $\left(\frac{\partial\mu}{\partial r}\right)_{CH}$, Van Alten obtained a value of 0.869×10^{-10} e.s.u.

The bond moments of HCN and DCN were obtained from intensities by Hyde and Hornig[17] who found a value of 1.13×10^{-18} e.s.u. for $(\mu)_{CH}$ and $\pm 1.05 \times 10^{-10}$ e.s.u. for $\left(\frac{\partial\mu}{\partial r}\right)_{CH}$. They also were able to show that if C is positive in the $C\equiv N$ dipole, then H is positive in the C-H dipole.

Barrow and McKean[18] studied infrared intensities in the methyl halides and found from the E modes that $\left(\frac{\partial\mu}{\partial r}\right)_{CH}$ ranges from $\pm$ 0.70 x 10^{-18} e.s.u. for methyl fluoride to $\pm$ 0.23 for methyl iodide. The values of $\left(\frac{\partial\mu}{\partial r}\right)_{CH}$ in the A_1 class, however, varied from 1.7 x 10^{-10} e.s.u. for methyl fluoride to about 0.9 x 10^{-10} e.s.u. for methyl iodide. The values of $(\mu)_{CH}$ were, in general, around 0.4 x 10^{-18} e.s.u.

The intensities of all but one of the bands of dimethyl acetylene have been examined by Mills and Thompson[19] who found the probable value of the C-H dipole in this compound to be about 0.4 x 10^{-18} e.s.u. and that of the C-C dipole to be about 1 x 10^{-18} e.s.u. They find that if the acetylenic carbon atoms have a residual negative charge (which is considered most probable), then the hydrogen atoms in the C-H bonds must carry a residual positive charge.

Recently, the work of Hisatsune and Eggers [20] on the intensities and bond moments of formaldehyde was published. The results chosen for the C-H properties were $(\mu)_{CH}$ equal to 0.50 x 10^{-18} e.s.u. ($C^- - H^+$) and $\left(\frac{\partial\mu}{\partial r}\right)_{CH}$ equal to 1.3 x 10^{-10} e.s.u., although, they did comment that the B_1 symmetry block gave an abnormally large $(\mu)_{CH}$ of about 1 x 10^{-18} e.s.u.

Flett[21] measured the intensities of the C-H stretching vibration bands of a number of toluene derivatives, which had substituents para to the methyl group, on the methyl group, or both. He was able to correlate the variation of the intensities of the aliphatic and aromatic C-H bands with the electron donor or acceptor character of the substituent. However, he did not attempt to obtain bond moments or bond moment derivatives.

There are still, perhaps, insufficient infrared intensity data available to properly evaluate its real position in molecular spectroscopy. However, it is apparent that, although bond moments and bond moment derivatives derived from intensity studies of different bands of a given molecule are not always consistent, the further study of vibrational band intensities will lead to a better insight of the electronic structure of molecules.

THEORY

Since the theory of infrared intensities and molecular normal coordinate analyses are well discussed elsewhere it would serve little purpose to repeat the development of the theory here. In particular, the excellent book by Wilson, Decius and Cross[22] provides quite complete derivations and discussions of these theories together with the references to the original literature of the developments. What will be attempted here is to provide a brief survey of the theory basic to the work to be described later.

Infrared Band Intensities

If one assumes the validity of the well known law for the absorption of monochromatic radiation, $I = I_o e^{-\alpha pl}$, where I_o is the intensity of the radiation incident upon a cell of length l containing an absorbing gas at partial pressure p, I is the intensity of the transmitted radiation and α is the molar absorption coefficient, then the absorption of a given absorption band may be described by the integrated absorption coefficient at unit pressure.

$$A = \int \alpha(\nu)\, d\nu = \frac{1}{pl}\int \ln \frac{I_o}{I}\, d\nu . \qquad (1)$$

The integration is carried out over the frequency range of the absorption band. With a spectrometer of infinite resolving power I_o/I would be measured directly, however, actual spectrometers do not measure I_o/I but rather measure the integral of intensities of frequencies over a range of frequencies.

$$T = \int I(\nu)\, g(\nu, \nu')\, d\nu . \tag{2}$$

T is the apparent intensity detected at an instrument setting ν' (the central frequency admitted by the finite slit) and $g(\nu, \nu')$ is the slit function, i.e. the fraction of the radiation of actual frequency ν admitted at the instrument setting ν'. The integration is carried out over the range of the finite slit width (all ν for which $g(\nu, \nu') \neq 0$) but since g soon vanishes outside a narrow range centered at ν', the integration can be carried to $\pm \infty$. Thus one may measure the apparent integrated absorption coefficient.

$$B = \int \alpha_{\text{apparent}}\, d\nu = \frac{1}{pl} \int \ln \frac{T_o}{T}\, d\nu' . \tag{3}$$

Wilson and Wells[7] have shown that if I_o does not vary rapidly over a slit width, and if either the resolving power is high compared to the variation in α or the resolving power does not change much over the band that

$$\lim_{pl \to 0} B = A. \tag{4}$$

By measuring B at different values of pl (by varying either p or l) and extrapolating B to zero pl, one can find A, the true integrated absorption intensity.

One can expand $\ln T_o/T$ for small absorption and keeping the first term of the expansion get

$$C = \frac{1}{pl} \int \frac{T_o - T}{T} \, d\nu \quad . \qquad (5)$$

This method was used by Bourgin[23]. This method is quite simple to use in that the "absorption areas" $\int \frac{T_o - T}{T} \, d\nu$ can frequently be measured directly on the recorder chart without replotting.

The true integrated absorption A may be obtained by extrapolation of C similar to the extrapolation of B. Although $\lim_{pl \to 0} C$ is equal to A and thus $\lim_{pl \to 0} B$, at all finite values of pl, C is less than B and the extrapolation curve of C has greater curvature than that of B, in practice, therefore, one may expect the extrapolation of B to yield a more accurate value for A than the extrapolation of C.

Because of the rotational fine structure of the vibrational band, exp ($-\alpha pl$) will ordinarily vary with extreme fluctuations on passing through the individual lines of the vibrational-rotational band. The addition of a sufficient pressure of non-absorbing foreign gas can broaden the lines of the rotational fine structure and eliminate the fluctuation in exp ($-\alpha pl$). Unless the spectrometer has high resolving power, it is still necessary to obtain A by extrapolating B. Although extreme fluctuation in exp ($-\alpha pl$) may be eliminated by pressure broadening of the rotational structure, there remains the variation of the absorption coefficient over slit width because of the band envelope.

In summary, the true integrated coefficient of a vibrational band by the Wilson and Wells method may be obtained if (1) the rotational fine structure is eliminated by pressure broadening, (2) the curves are extrapolated to zero pl product so that variations in absorption due to the envelope are eliminated, and (3) the apparent integrated absorption coefficient rather than the absorption is measured in order to make the extrapolation procedure valid at relatively high absorptions.

It is well known that an absorption intensity is related to the spectral transition probability[24] and thus to the matrix element of the dipole moment for the transition. In the case of the absorption band of the i'th fundamental vibration this relation[22] is

$$A_i = \int \alpha(\nu)\, d\nu = \frac{8\pi^2 N \nu_i}{3hc}\left\{\left|\mu_{ix}^{1,0}\right|^2 + \left|\mu_{iy}^{1,0}\right|^2 + \left|\mu_{iz}^{1,0}\right|^2\right\} \quad (6)$$

where A_i is the integrated intensity of the i'th band whose central frequency is ν_i, N is the number of molecules per unit concentration, h is Planck's constant, c is the velocity of light and $(\mu_{ix}^{1,0})$ is the x component of the dipole moment (or transition moment) for the transition between the ground and first excited states, similarly for $(\mu_{iy}^{1,0})$ and $(\mu_{iz}^{1,0})$.

If the dipole moment is now expanded in a power series in the normal coordinates, Q, the intensity can be related to the dipole moment change with vibration.[8]

$$A_i = \frac{N\pi}{3c}\left\{\left|\frac{\partial\mu_x}{\partial Q_i}\right|^2 + \left|\frac{\partial\mu_y}{\partial Q_i}\right|^2 + \left|\frac{\partial\mu_z}{\partial Q_i}\right|^2\right\} \quad (7)$$

Since the normal coordinates are related to the internal coordinates (usually combinations of bond coordinates, i.e. bond stretching and bond angle deformation) by linear transformation,

$$Q_i = \sum_j L_{ij} R_j \, , \quad (8)$$

the $\frac{\partial\mu}{\partial Q}$ are similarly related to $\frac{\partial\mu}{\partial R}$ —

$$\frac{\partial\mu_x}{\partial Q_i} = \sum_j L^{-1}_{ij} \frac{\partial\mu_x}{\partial R_j} . \qquad (9)$$

It is now possible to use the above results, together with the assumption of bond moment additivity, to calculate "effective charges" for bond stretchings $\frac{\partial\mu}{\partial r}$ and bond dipole moments. The $\frac{\partial\mu}{\partial R_K}$, where R_k is a bond angle deformation coordinate yield the dipole moments.

Normal Coordinate Analysis

A brief discussion of Wilson's F G Matrix method[22,25] for the mathematical analysis of molecular vibrations will be given here.

If for a molecule whose vibrations are simple harmonic motion, the coordinates of the atoms are expressed as generalized displacement coordinates, then the kinetic energy of the molecule (for nuclear displacements only) is

$$T = 1/2 \sum_i \sum_j a_{ij} \dot{q}_i \dot{q}_j \; ; \qquad (10)$$

where, within the framework of small vibration theory, the a_{ij}'s are constants. Similarly, the potential energy is

$$V = 1/2 \sum_i \sum_j b_{ij} q_i q_j \; ; \qquad (11)$$

where, b_{ij} is equal to $\left(\frac{\partial^2 V}{\partial q_i \, \partial q_j}\right)_0$ or the force constants for displacement. The Lagrangian equations of motion for the molecular vibrations are then

$$\sum_j a_{ij} \frac{d}{dt} \dot{q}_j + \sum_j b_{ij} q_j = 0 . \qquad (12)$$

For 3N degrees of freedom, there will be 3N such equations corresponding to i equal to 1, 2, 3, ... 3N. By means of an orthogonal transformation

$$q_i = \sum_k c_{ik} Q_k , \qquad (13)$$

one can obtain the normal coordinates Q_k, that allow one to express the kinetic and potential energy in pure quadratic form (i.e., free from cross products)

$$T = 1/2 \sum_k \dot{Q}_k^2 ; \qquad (14)$$

$$V = 1/2 \sum_k \lambda_k Q_k^2 . \qquad (15)$$

The λ_k are the 3N eigenvalues of the characteristic (or secular) equation

$$\left| \lambda a_{ij} - b_{ij} \right| = 0 ; \qquad (16)$$

and the c_{ik} is the matrix formed from the eigenvectors.

It can be seen from this characteristic equation that, in general, λ may occur with any element of the determinant. This can make the solution of such equations for some polyatomic molecules quite difficult, where the order of the characteristic equation is large. It is also frequently difficult to set up the a_{ij} in terms of internal coordinates so as not to include translations and rotations.

As a means of circumventing some of the difficulties of older methods of treating molecular vibrations, Wilson[25] devised the F G Matrix method. (An equivalent method was devised indepently and almost simultaneously by Eliashevich[26].)

In this method the elements of the G matrix are defined by the equation

$$G_{kl} = \sum_{i=1}^{3N} \frac{1}{m_i} B_{ki} B_{li} \quad (k,l = 1,2,\ldots(3N-6)) ; \qquad (17)$$

where N is the number of atoms and m_i is the mass of the ith atom. B_{ki} is an element of the transformation relating the Cartesian displacement coordinates x_i to the internal coordinates R_k.

$$R_k = \sum_i B_{ki} x_i . \qquad (18)$$

(In matrix notation this is $R = B_x$) The kinetic energy in terms of R_k is

$$2T = \sum_{k=1}^{3N-6} \sum_{l=1}^{3N-6} (G^{-1})_{kl} \dot{R}_k \dot{R}_l = \dot{R}' G^{-1} \dot{R} ; \qquad (19)$$

where G^{-1} is the inverse matrix of G, $\dot{R}$ is the column matrix whose elements are the $\dot{R}_k$ and $\dot{R}'$ is the transpose of $\dot{R}$. The potential energy is then expressed by

$$2V = \sum_{k=1}^{3N-6} \sum_{l=1}^{3N-6} F_{kl} R_k R_l = R' F R; \qquad (20)$$

in which F_{kl} is one of the force constants.

The secular equation is then

$$\left| F - G^{-1} \lambda \right| = 0 , \qquad (21)$$

which is comparable in form to that obtained earlier. However, if one multiplies through this secular equation by G, one obtains

$$\left| G F - G G^{-1} \lambda \right| = 0 , \qquad (22)$$

which is equivalent to

$$\left| G\ F - E\ \lambda \right| = 0 . \qquad (23)$$

Here E is the identity or unit matrix.

In this secular equation the λ occur only on the principal diagonal and with unit coefficients. This form is convenient for expansion as an algebraic equation in λ as well as for many numerical methods of solution of determinants. Perhaps one of the most objectionable qualities of this form is that it is not symmetrical about its principal diagonal.

In the case of a symmetrical molecule, one can construct internal symmetry coordinates, chosen so as to agree with the transformation properties of one of the symmetry species appropriate to the point group symmetry of the molecule. Since the symmetry species appropriate to the point group are orthogonal to one another, the use of symmetry coordinates factors the secular equation into block diagonal form, so that instead of having to solve a (3N-6) x (3N-6) determinant one may solve several of lesser order. The extent of reduction possible, of course, is dependent on the number of symmetry elements that the molecule possesses.

The a priori knowledge of how the symmetry of a molecule may affect the description of its spectra and eigenfunctions may be gained through the application of the techniques of group theory.[22,27,28]

The normal coordinates Q are related to R by the transformation

$$R = L\ Q ; \qquad (24)$$

in which L is chosen so that the energies in terms of Q are of the form

$$2V = Q' \; L' \; F \; L \; Q = Q' \Lambda \; Q , \qquad (25)$$

$$2T = \dot{Q}' \; L' \; G^{-1} \; L \; \dot{Q} = \dot{Q}' E \; \dot{Q} , \qquad (26)$$

in which Λ is a diagonal matrix of the λ's.

Thus

$$L' \; F \; L = \Lambda , \qquad (27)$$

$$L' \; G^{-1} \; L = E \qquad (28)$$

or

$$L \; L' = G , \qquad (29)$$

and

$$G \; F \; L = L \Lambda \qquad (30)$$

or

$$L^{-1} \; G \; F = \Lambda \, L^{-1} . \qquad (31)$$

Thus the elements in the rows of the secular equation supply the coefficients of the forward transformation (L) while the columns serve for the reverse transformation (L^{-1}). The solution of the secular equation yields eigenfunctions $\bar{L}$ which are related to the normal eigenfunctions L by a trivial constant. The expression

$$L' \; F \; L = \Lambda , \qquad (32)$$

provides a convenient normalizing condition.[29] The relationship between $\bar{L}$ and L is

$$\bar{L} = L \; D ; \qquad (33)$$

where D is a diagonal matrix of trivial constants. D may be found from the relation

$$\bar{L} F \bar{L} = D L' F L D = D \Lambda D \sim D r^2 \lambda r \delta rs . \qquad (34)$$

The relation

$$L L' = G \qquad (35)$$

serves as a convenient check.

EXPERIMENTAL METHOD

Materials

The compounds investigated were of the highest purity available. Since these compounds have simple infrared spectra which have been well analyzed and assigned,[30,31] it was possible to use the spectra as a check for impurities. Most of the compounds were used as received. CH_2Cl_2 was purchased from the Matheson Company. CH_2Br_2 and CH_2I_2 were purchased from Eastman Kodak Company. CH_2BrCl was given by Dow Chemical Company. CH_2F_2 and CH_2ClF were given by the Jackson Laboratory of the E. I du Pont de Nemours and Company.

It was necessary to purify the CH_2Br_2 by fractional distillation through a center rod column using about 40 theoretical plates in order to remove a trace (ca. 0.05%) of CH_2BrCl. Another sample of CH_2Br_2, which had been furnished by the Dow Chemical Company, contained in addition to the CH_2BrCl some $CHCl_2Br$ which apparently formed an azeotrope with the CH_2Br_2. Since the $CHCl_2Br$ could not be separated from the CH_2Br_2 by fractional distillation using 80 theoretical plates, the sample was not used.

Solution Measurements

The intensities of the two fundamental vibrations ν_1 and ν_6 (CH stretching vibrations) were measured in CCl_4 solution for CH_2Cl_2, CH_2BrCl, CH_2Br_2 and CH_2I_2. These intensities were measured on a Perkin-Elmer Model 13 infrared spectrophotometer equipped with a lithium fluoride prism and a slit servo mechanism that regulated the slit to provide constant I_o. Sodium chloride cells of 0.8 mm path length were used.

The intensities were determined using Ramsay's[32] extension of the method of absorption areas. Since the change in dispersion across the bands was small, it was possible to measure the absorption areas directly from the recorder chart. The area of each band was measured at least twice with a planimeter.

Several solutions of different concentration were measured for each molecule. The solutions were used immediately after preparation.

Vapor Phase Measurements

The intensities of the ν_1 , ν_6 and ν_3 bands of CH_2F_2, CH_2ClF, CH_2Cl_2, CH_2BrCl and CH_2Br_2 were measured in the vapor phase.

A Perkin-Elmer Model 112 infrared spectrophotometer (a single-beam instrument with a double-pass monochromator) was used for the vapor phase studies. A lithium fluoride prism was used to study the 3000 cm^{-1} region (ν_1 and ν_6) with a resolution of about 8 cm^{-1}. For the study of the 1400 to 1500 cm^{-1} region (ν_3) a CaF_2 prism was used with a resolution of 2 to 2.5 cm^{-1}.

The cell used for this work was a multiple reflection cell of the White type[33,34] designed by the author to match the aperature of the Perkin-Elmer Model 112 spectrometer. The 3 1/2 inch diameter mirrors in the brass cell have a 40 cm radius of curvature. The path lengths in the cell are multiples of 4 times the distance between the mirrors (4 x 40) or 160 cm. The path length of the cell is changed by rotation of one of the half mirrors about a vertical axis; the motion which rotates the mirror is transmitted into the cell by the action of a differential screw compressing a sylphon bellows to which a connecting rod is mounted. The external focussing optics used with the cell were essentially the same as those used by Pilston and White[35] for the Perkin-Elmer 10 meter cell.

A small glass vacuum manifold connected to the cell by heavy walled teflon tubing provided a filling system for the cell. Vapor pressure measurements were made with a large bore (9 mm I. D.) open end monometer and barometric readings by expansion from the manifold to the cell using the known ratio of these volumes to calculate the final pressure.

Samples of CH_2F_2 and CH_2ClF (both gases) were measured into the manifold directly from the cylinders containing them. Liquid samples were first allowed to degas by pumping on them, then the manifold was evacuated and the vapor pressure measured into the manifold.

After a sample had been measured into the cell, about one atmosphere of pressurizing gas was added. Nitrogen was used as the pressurizing gas for work in the 3000 cm^{-1} region and helium for work in the 1400 to 1500 cm^{-1} region. Helium was used here because interfering water vapor was detected in the cylinder of nitrogen at the time of these measurements.

For the measurements in the 1400 to 1500 cm^{-1} region, the optical path connecting the source housing, cell and monochromator was enclosed in a large plastic bag and the whole optical path (except that within the cell) was flushed dry with helium in order to lower the water vapor background as much as possible. It was not possible to eliminate the water vapor spectrum completely, but in most cases the interference was negligible.

The absorption bands of a sample were measured at several path lengths (usually four or five); the different path lengths were obtained by changing the path length within the multiple reflection cell. Background measurements were made with the cell evacuated and at the corresponding cell path lengths.

The bands were replotted on semi-logarithmic paper ($\ln \frac{I_o}{I}$ VS ν) and then the areas were measured at least twice with a planimeter. These areas ($\int \ln \frac{I_o}{I} d\nu$) were then plotted against the pl product and the true integrated absorption coefficients were obtained from the slope of these plots.

RESULTS

The measured integrated apparent band areas $\int \ln \frac{I_0}{I} d\nu$ for a given gas were plotted against the pl product. The true intensity A of a band was obtained from the limiting slope of this plot. In several cases where other bands slightly overlapped the band of interest, it was possible to separate them graphically. In the vapor phase, the ν_1 and ν_6 bands of all the compounds studied overlap one another to such an extent that graphical separation was not possible. However, since the peak intensities of these two bands were nearly equal in all cases, the individual band intensities of ν_1 and ν_6 have been taken as being equal to one half the true intensity sum obtained from the limiting slope of the intensity sum plots for ν_1 and ν_6 (figures 1 through 5).

With the exception of CH_2F_2 all the compounds studied exhibited quite simple structure for the ν_1 and ν_6 bands. Since CH_2F_2 is a much lighter molecule than the other molecules of the series, the P and R branches of the ν_6 perpendicular band are more pronounced. This fact is the main explanation of the different appearance of the 3000 cm^{-1} region of CH_2F_2. However, Stewart and Nielsen[36] have found from the high resolution spectra that a third band overlaps this region also. This third band is most likely the binary combination band of ν_3 and ν_8. It was not possible to make allowance for the intensity contribution of this third band, but since the ($\nu_3 + \nu_8$) band is very weak it is not believed to cause appreciable error.

The ν_3 bands of these compounds lie in the region 1370 to to 1520 cm^{-1}; this region is usually obscured by the absorption of atmospheric water vapor. Although the spectrometer was flushed with dry gas, this procedure did not completely eliminate the presence of water vapor lines from the background. Since the water vapor lines are quite sharp, it is conceivable that they might not be canceled out in the replotting of the absorption band of the sample gas and thus contribute to the experimental error. In particular, the ν_3 band region of CH_2BrCl and had rather strong water vapor lines present that probably caused considerable error in the measured band intensity. It may be seen in Table 1, where the band intensities are summarized that the CH_2BrCl ν_3 band intensity is somewhat out of line. Only in the region of the ν_3 band of CH_2Br_2 were the water vapor lines eliminated from the background.

Table 1. Absorption Band Intensities in Vapor Phase (cm^{-1} / atm.-cm)

	CH_2F_2	CH_2ClF	CH_2Cl_2	CH_2BrCl	CH_2Br_2
ν_1	104	39.6	20	5	2.17
ν_6	104	39.6	20	5	2.17
ν_3	2.11	5.95	5.52	0.391	0.839

The ν_3 band of CH_2F_2 has not been reported before as having been observed in the infrared. The Raman-effect data on CH_2F_2 show ν_3 to be at 1508 cm^{-1}. The ν_3 band of CH_2F_2 was observed in the infrared in this research at 1508 ± 5 cm^{-1}. Probably the interference of the water vapor spectrum has prevented the earlier detection of ν_3. The ν_3 band was slightly overlapped by the tail of the quite strong 1435 cm^{-1} ν_8 band of CH_2F_2. The band area of the CH_2F_2 ν_3 was separated graphically from the ν_8 tail. However, this procedure is subject to appreciable error.

In liquid phase the ν_1 and ν_6 bands of the methylene halides are separated considerably and were almost completely resolved. The intensities of the ν_1 and ν_6 bands of several methylene halides were measured in CCl_4 solution using Ramsay's method III.[32] It is to be noticed that the solution intensities are greatly different from the vapor phase intensities even if one considers only the intensity sums.

Table 2. Absorption Band Intensities in CCl_4 Solution (cm^{-1} / atm.-cm)

	CH_2Cl_2	CH_2BrCl	CH_2Br_2	CH_2I_2
ν_1	21.9	8.70	7.40	6.69
ν_6	10.1	19.4	28.5	40.1

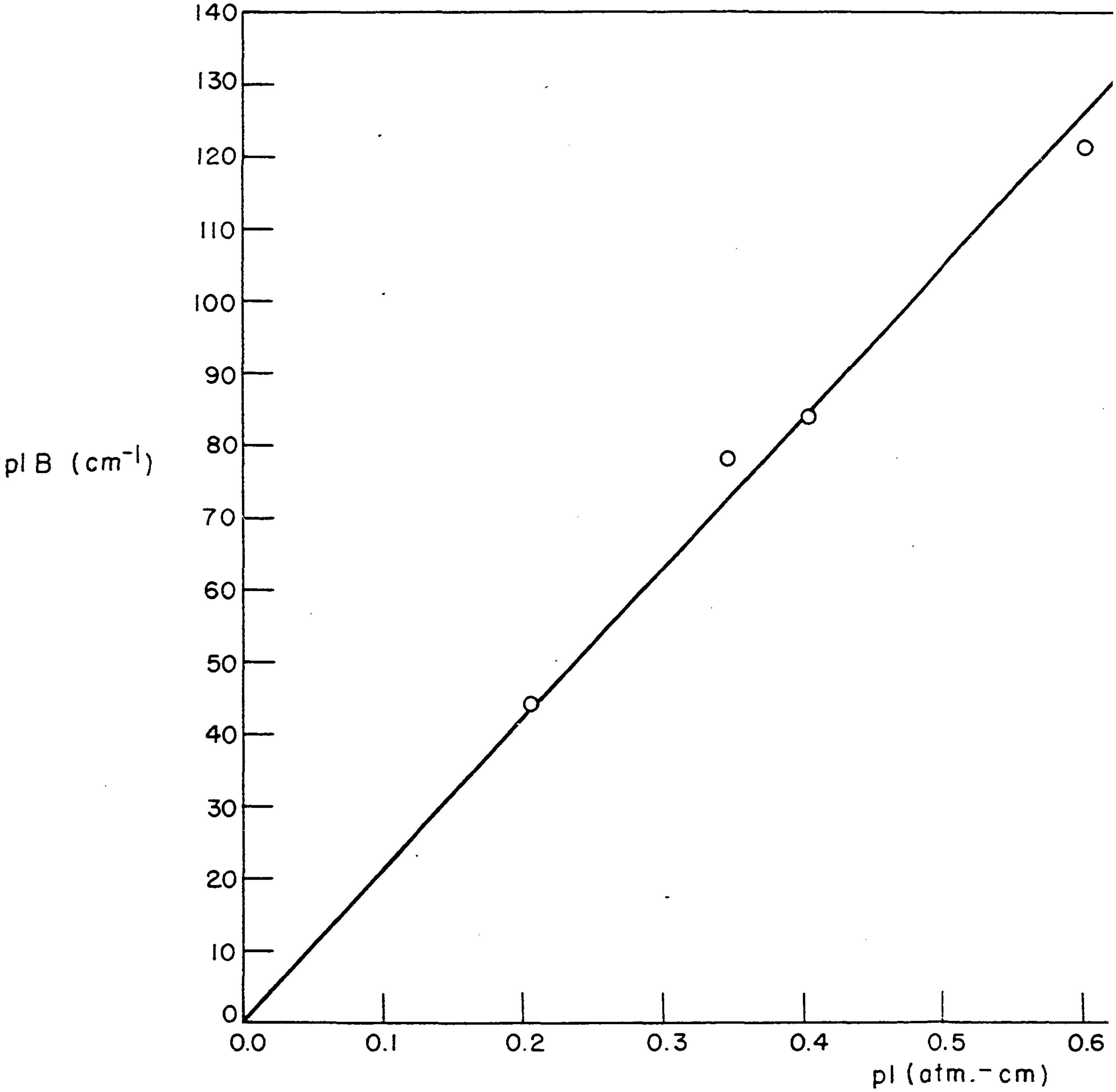
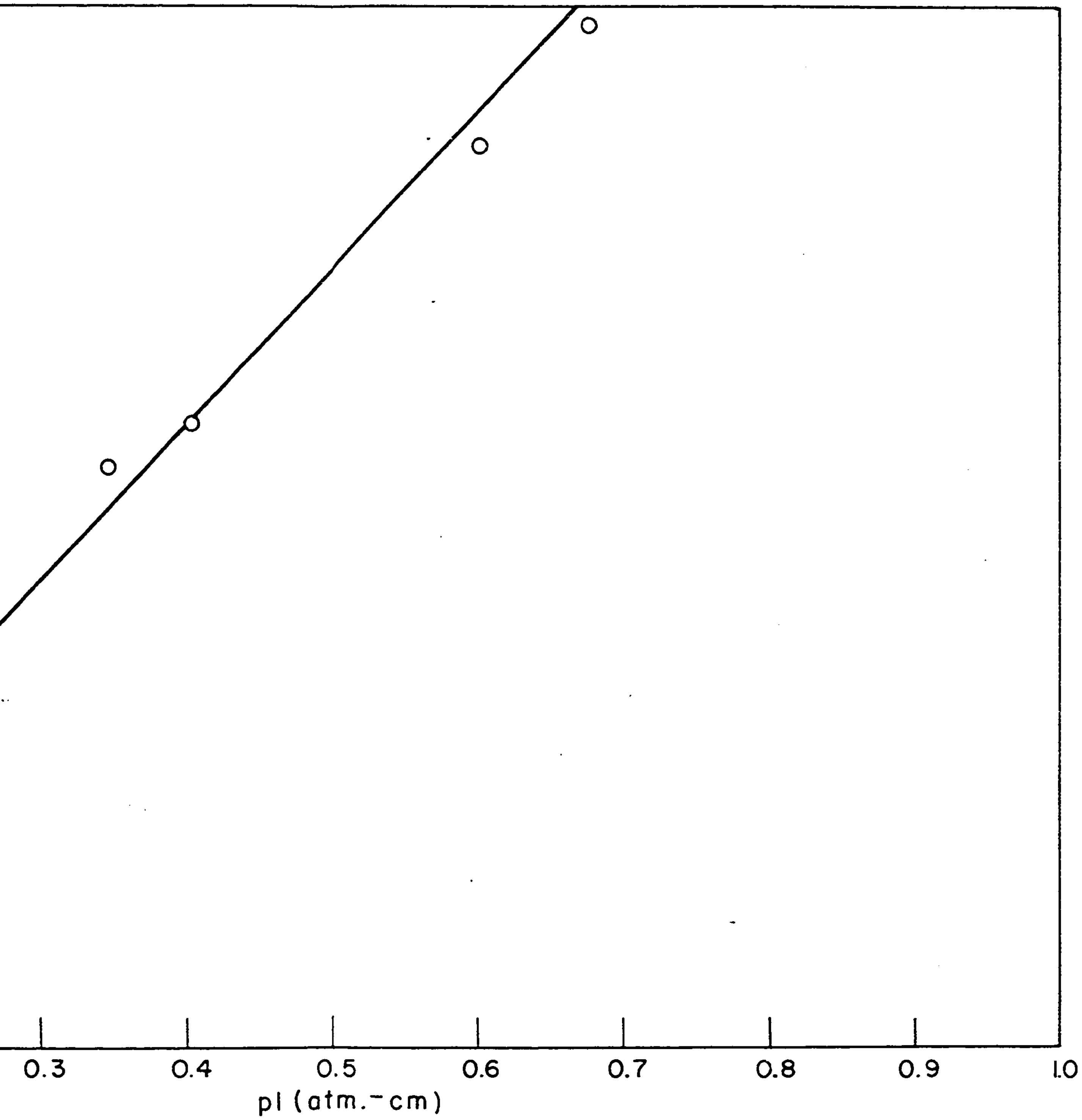


FIGURE I INTENSITY PLOT OF THE 3000 cm^{-1} BA



ITY PLOT OF THE 3000 cm^{-1} BANDS OF CH_2F_2 (ν_1 AND ν_6)

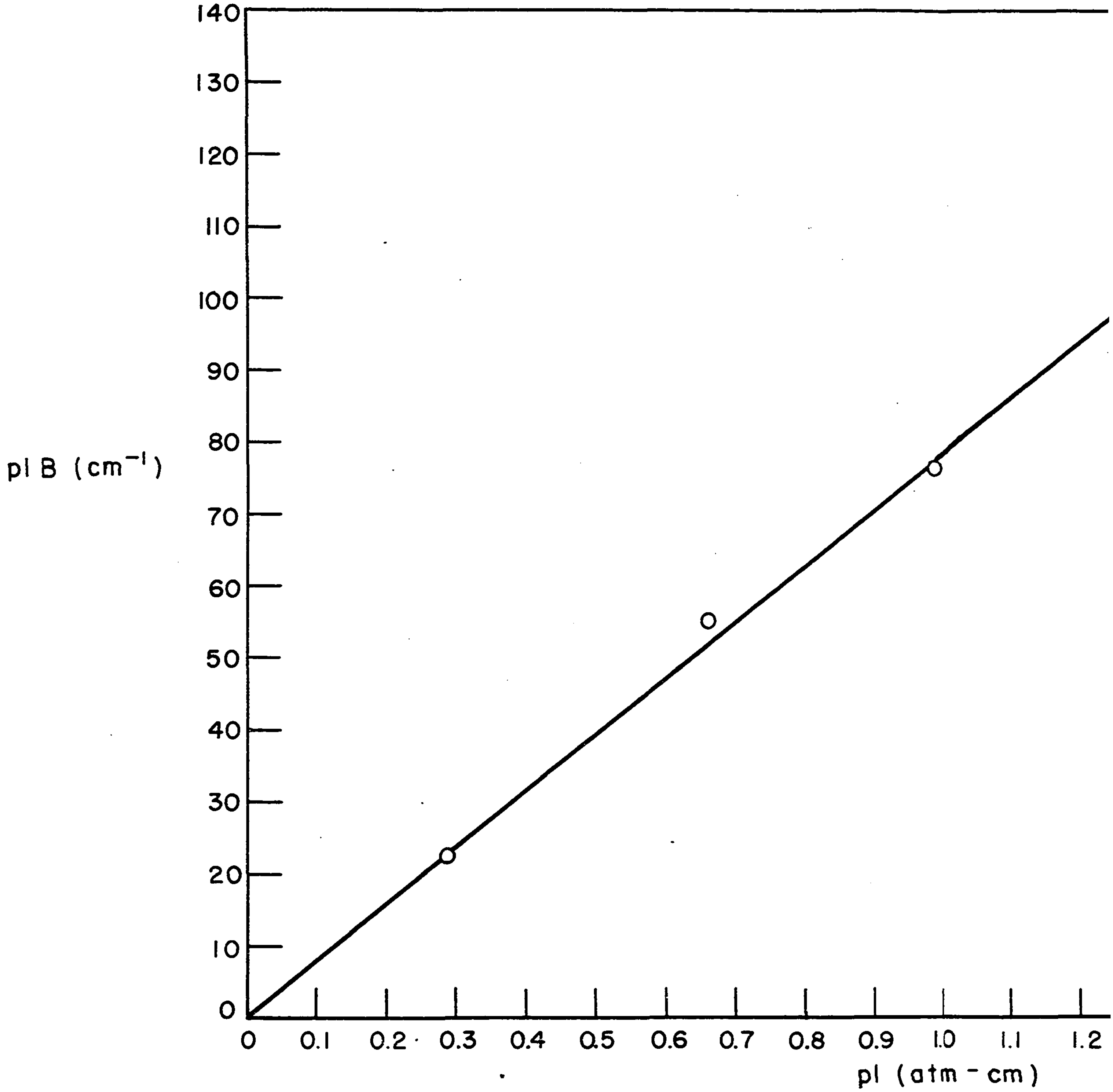
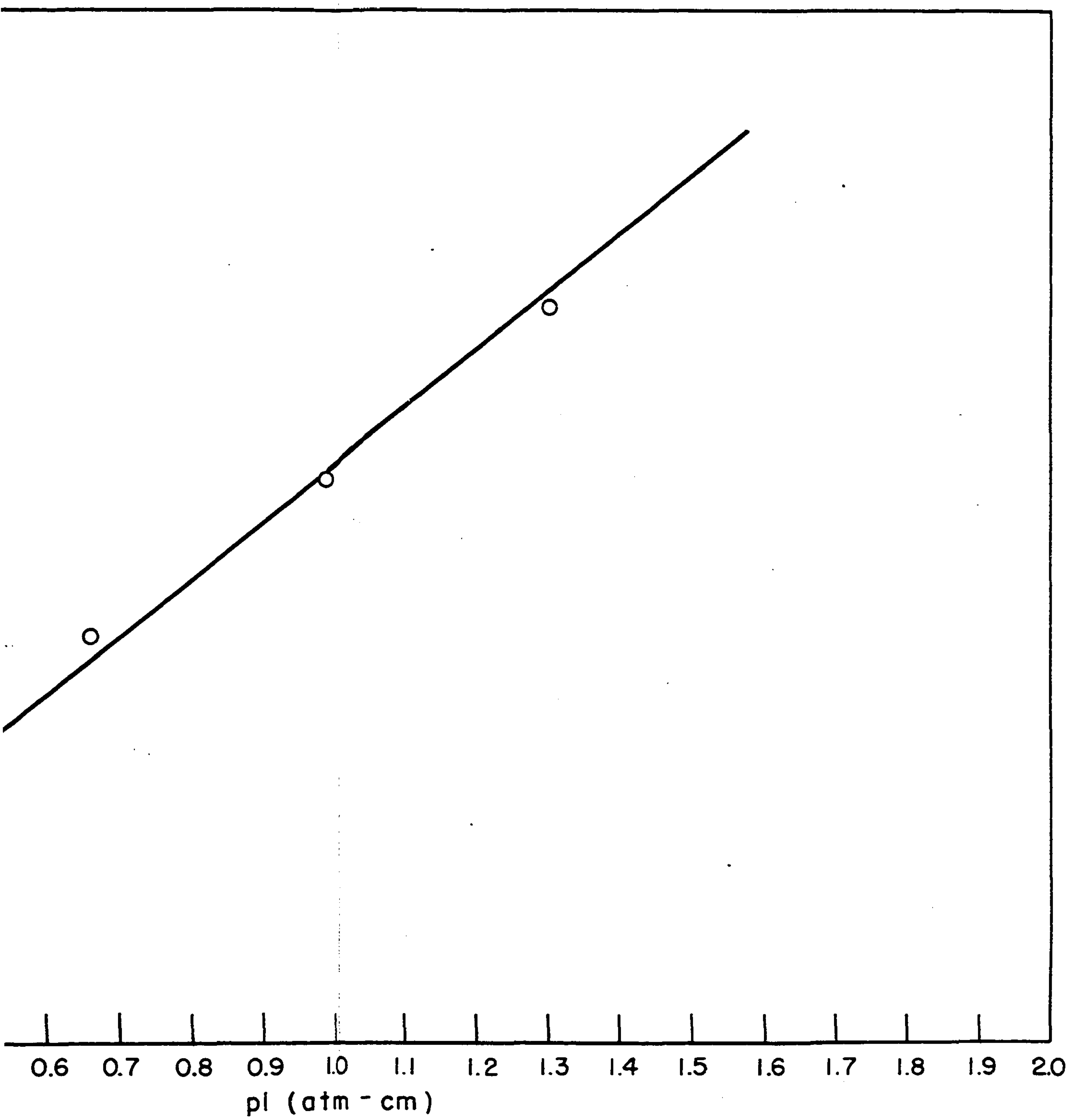


FIGURE 2 INTENSITY PLOT OF THE TWO 3000 cm^{-1}



ITY PLOT OF THE TWO 3000 cm^{-1} BANDS OF CH_2ClF (ν_1 AND ν_6)

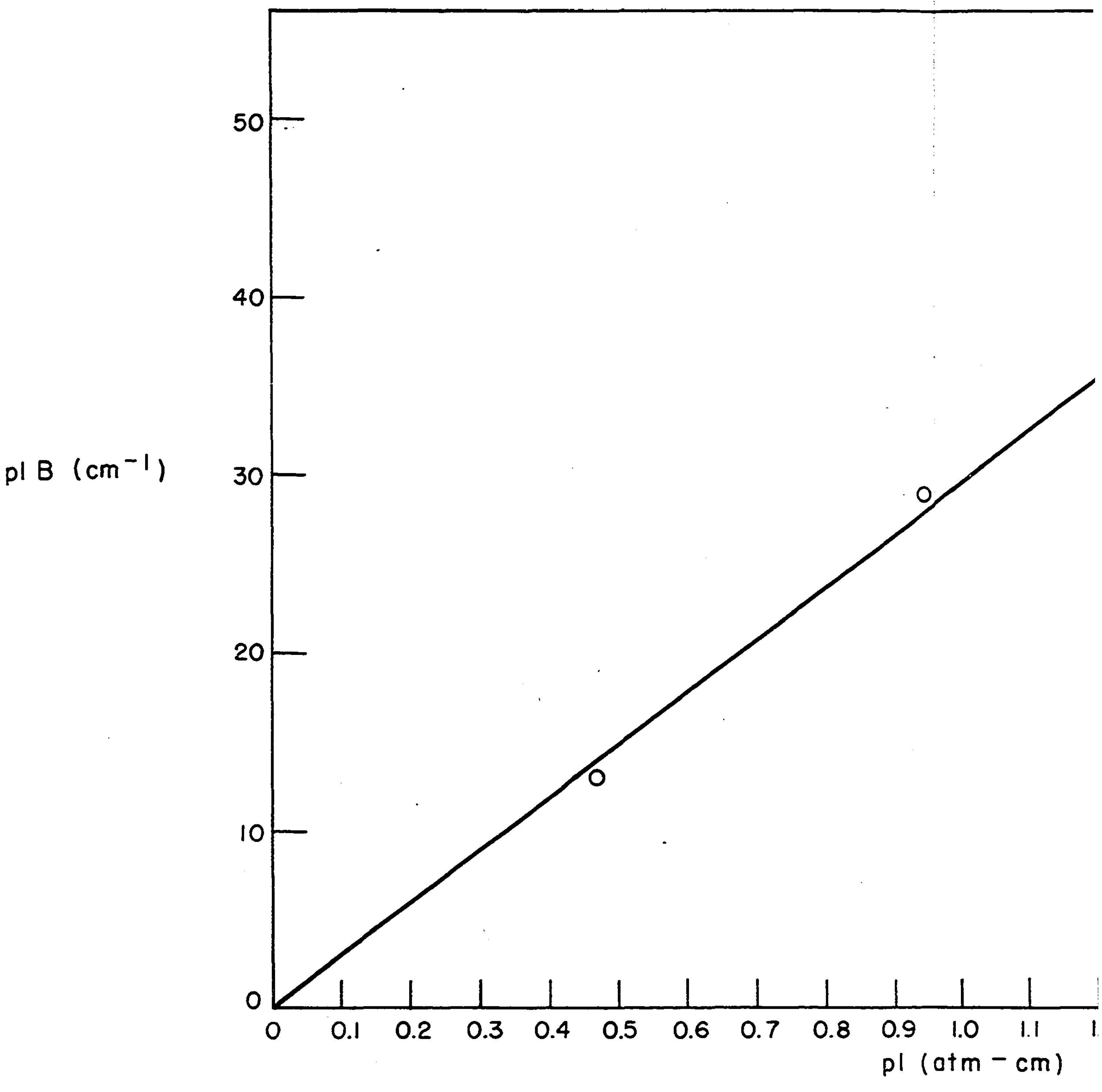
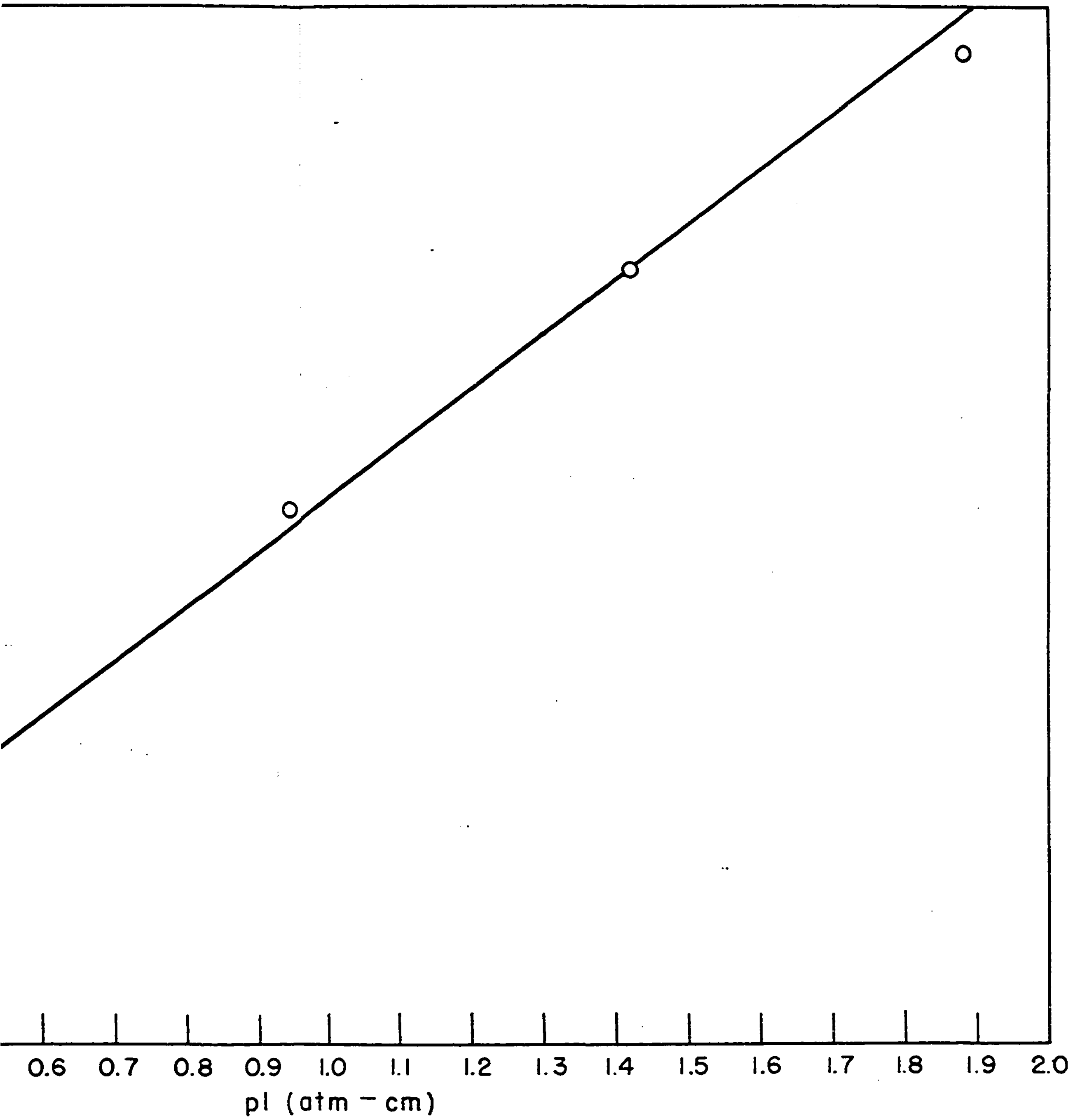


FIGURE 3 INTENSITY PLOT OF THE TWO 3000 cm



ITY PLOT OF THE TWO 3000 cm^{-1} BANDS OF CH_2Cl_2 (ν_1 AND ν_6)

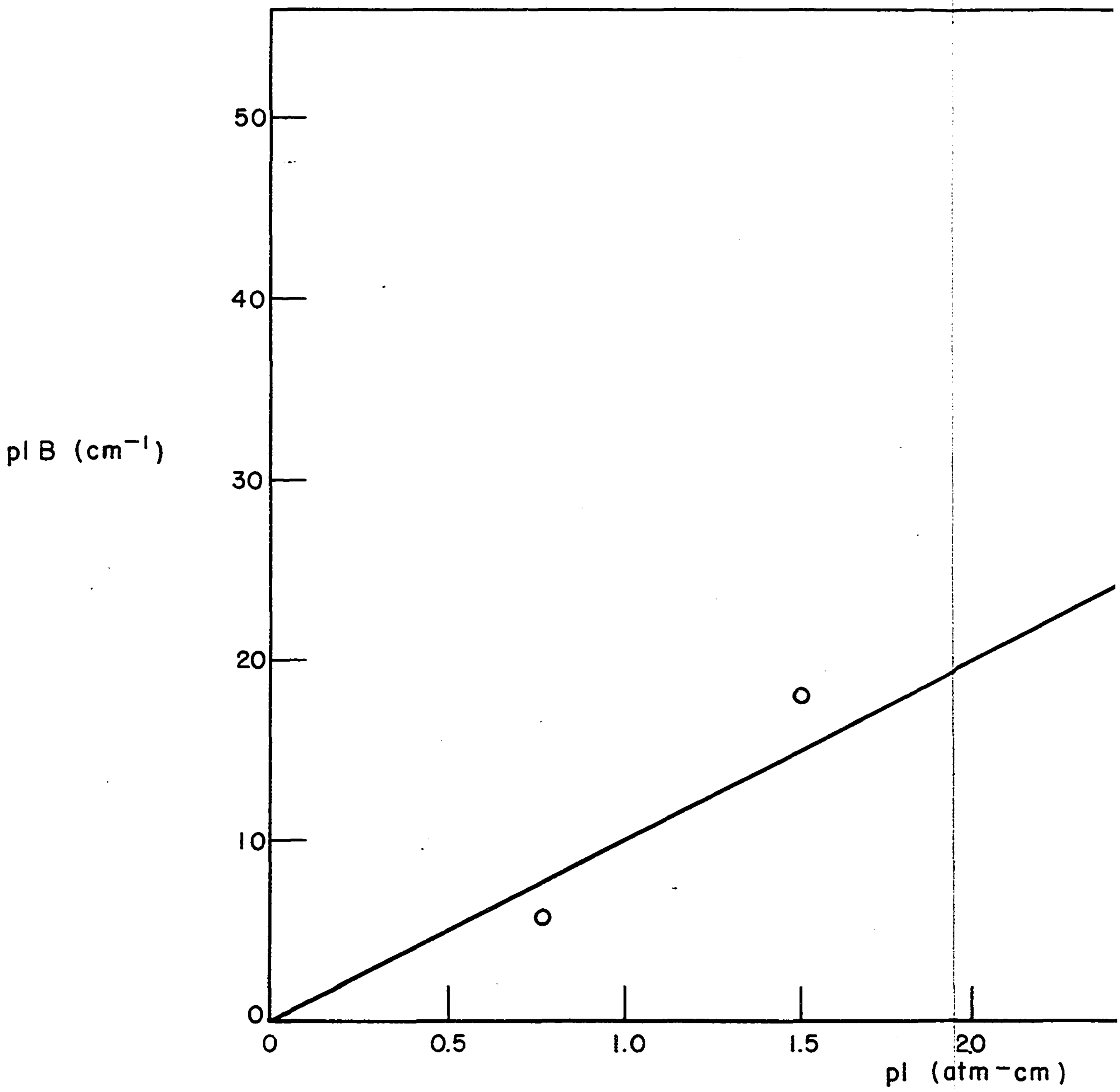
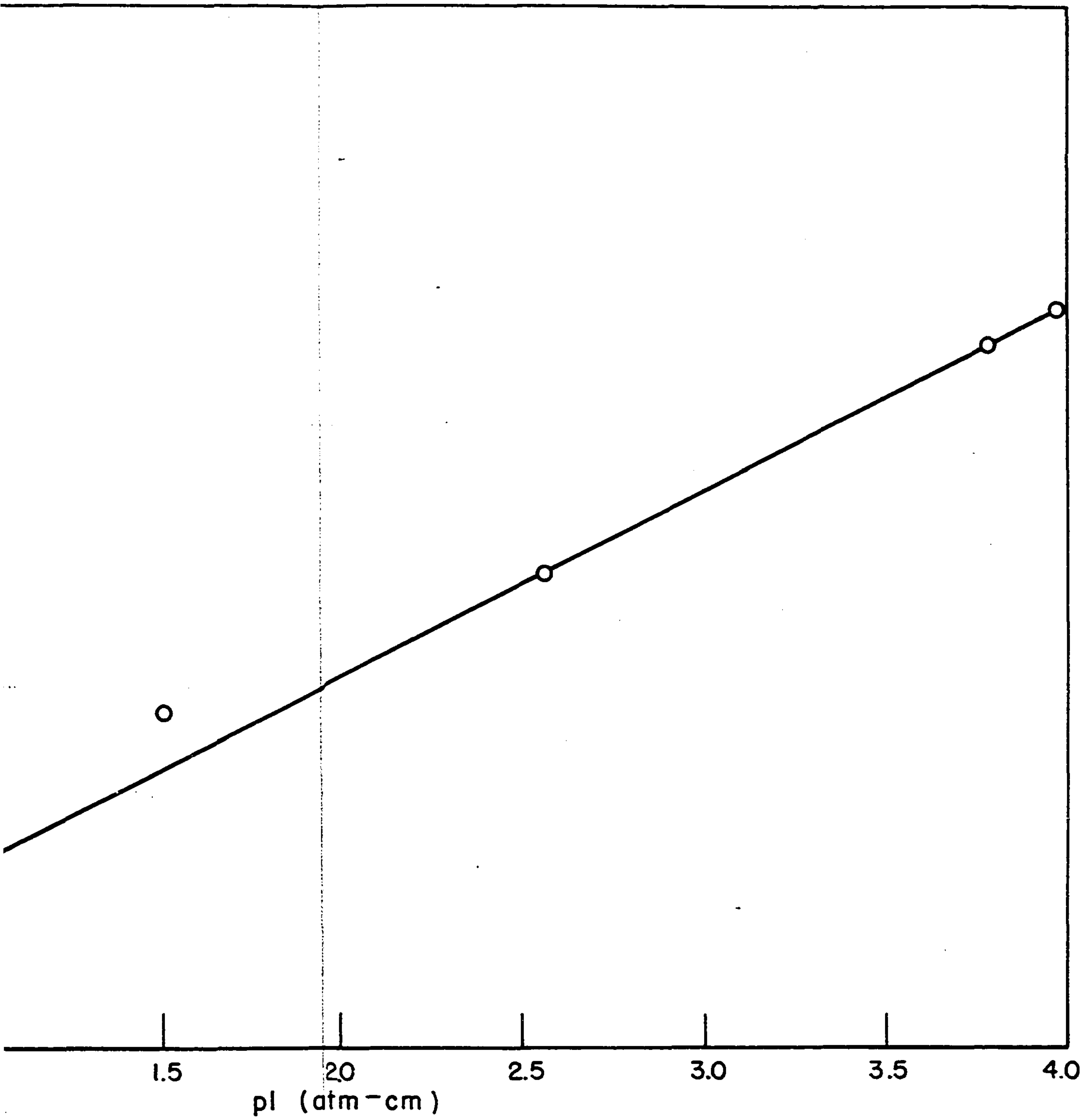


FIGURE 4 INTENSITY PLOT OF THE TWO 3000 cm



SITY PLOT OF THE TWO 3000 cm^{-1} BANDS OF CH_2BrCl (ν_1 AND ν_6)

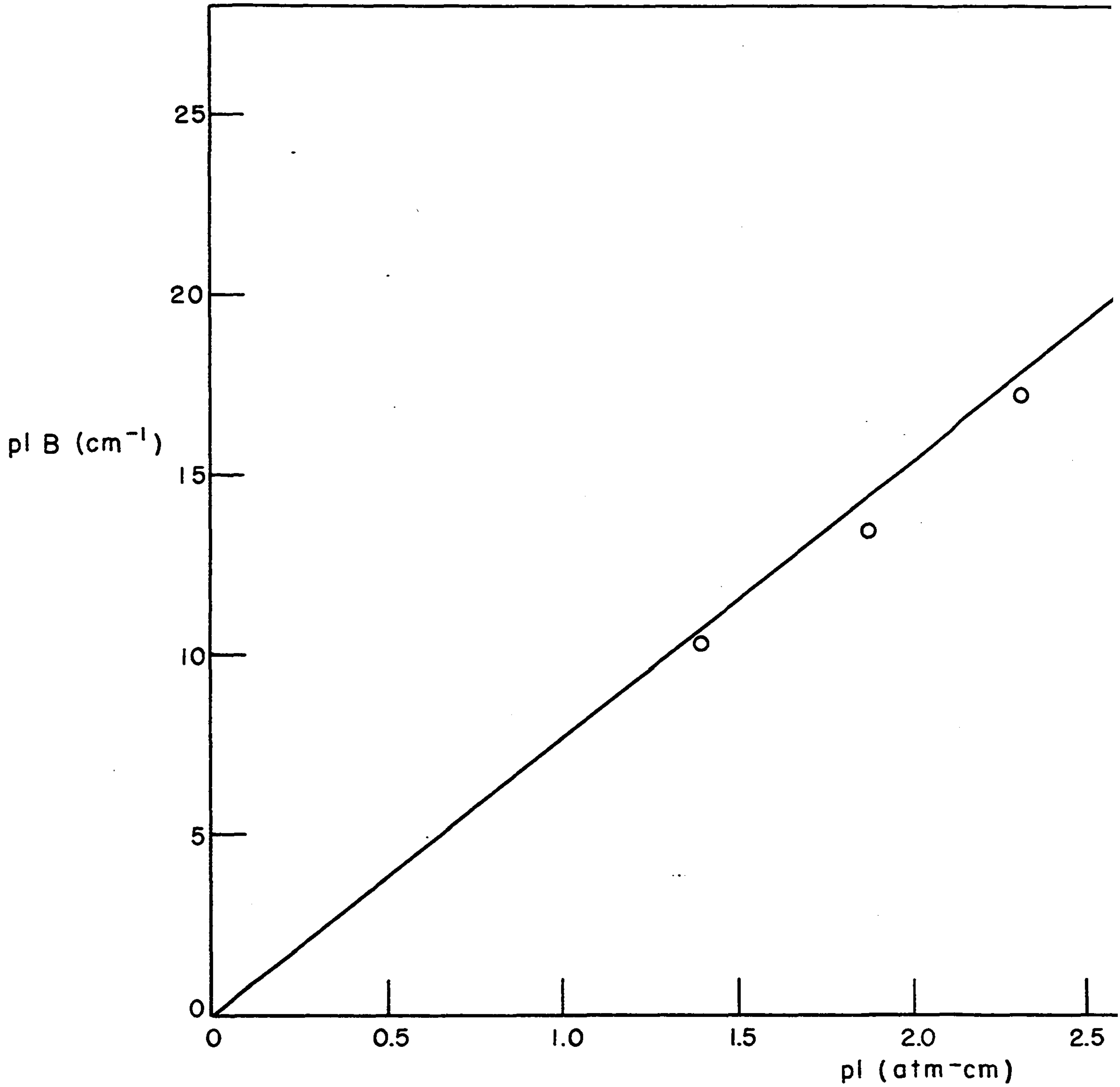
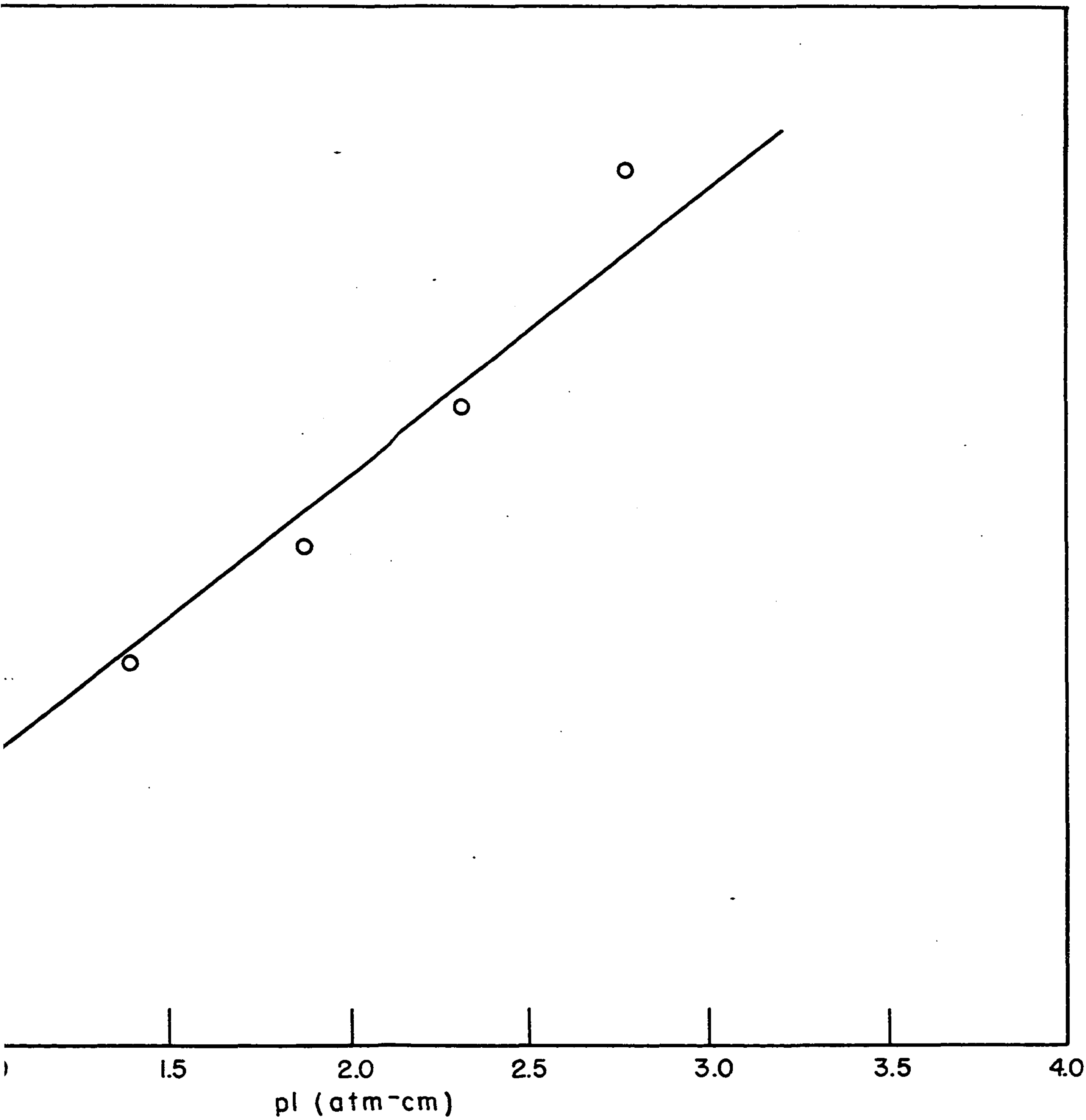


FIGURE 5 INTENSITY PLOT OF THE TWO 3000 cm^{-1} BAN



TY PLOT OF THE TWO 3000 cm^{-1} BANDS OF CH_2Br_2 (ν_1 AND ν_6)

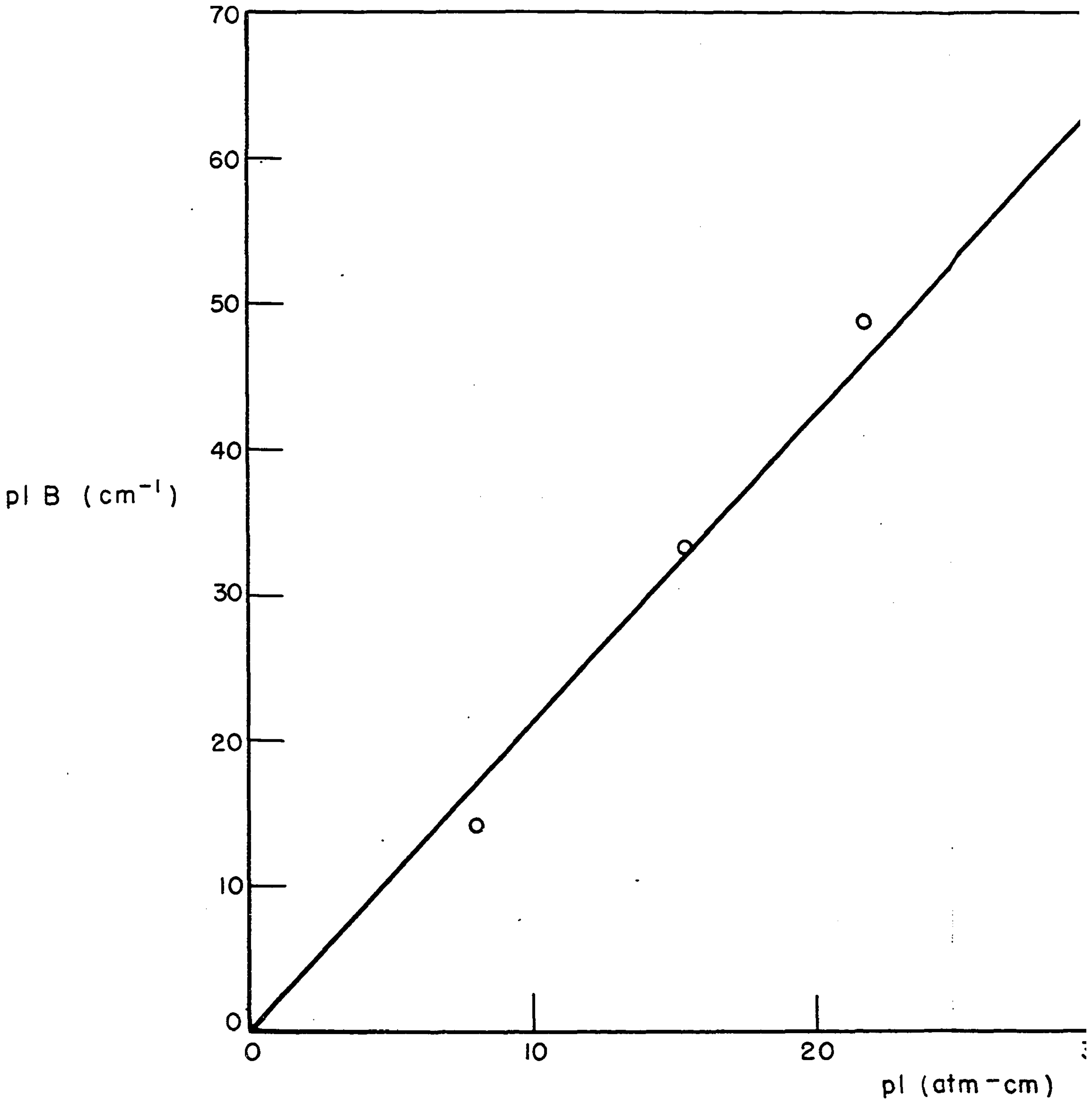
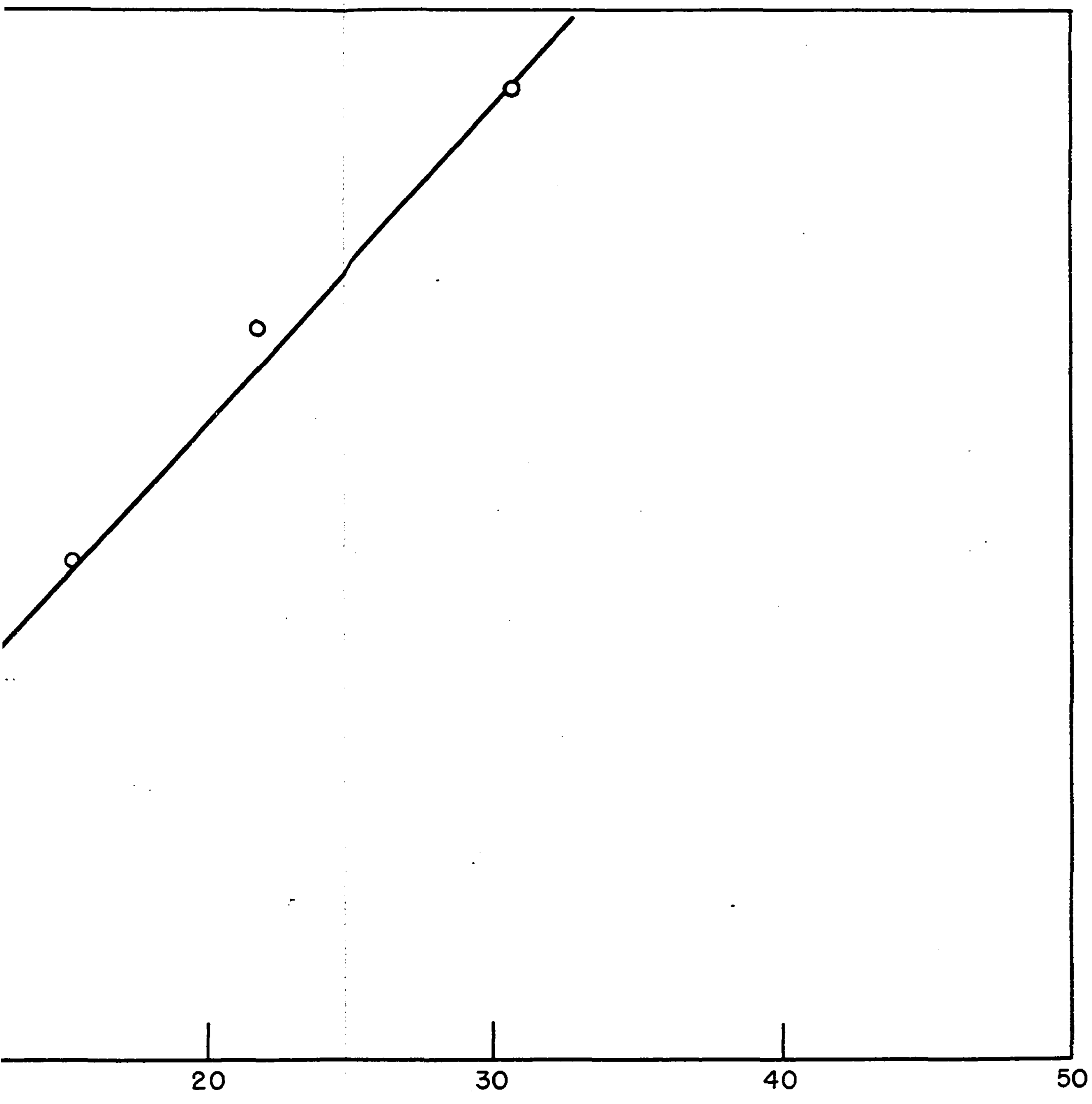


FIGURE 6 INTENSITY PLOT OF THE ν_3



RE 6 INTENSITY PLOT OF THE ν_3 BAND OF CH_2F_2

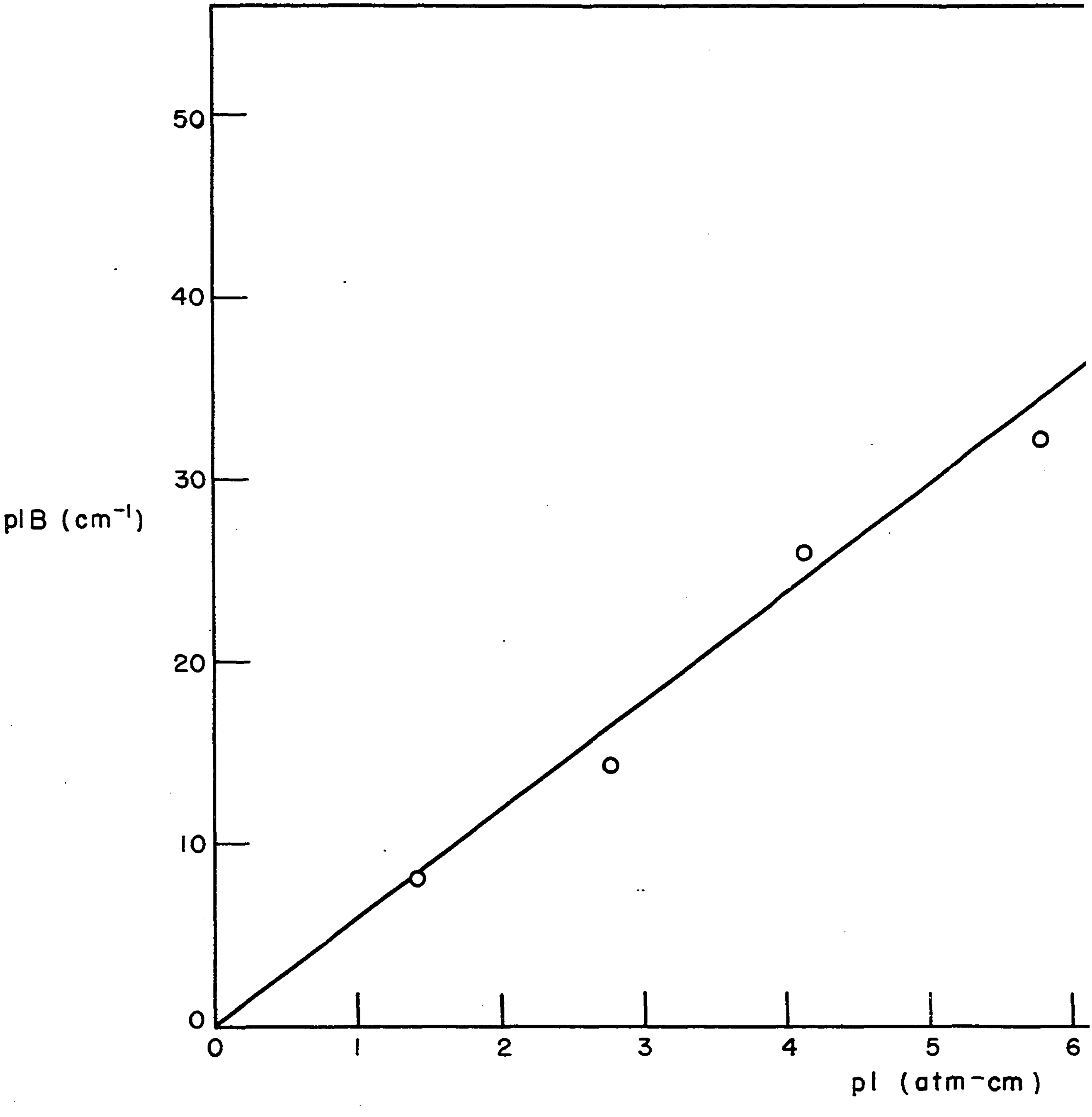
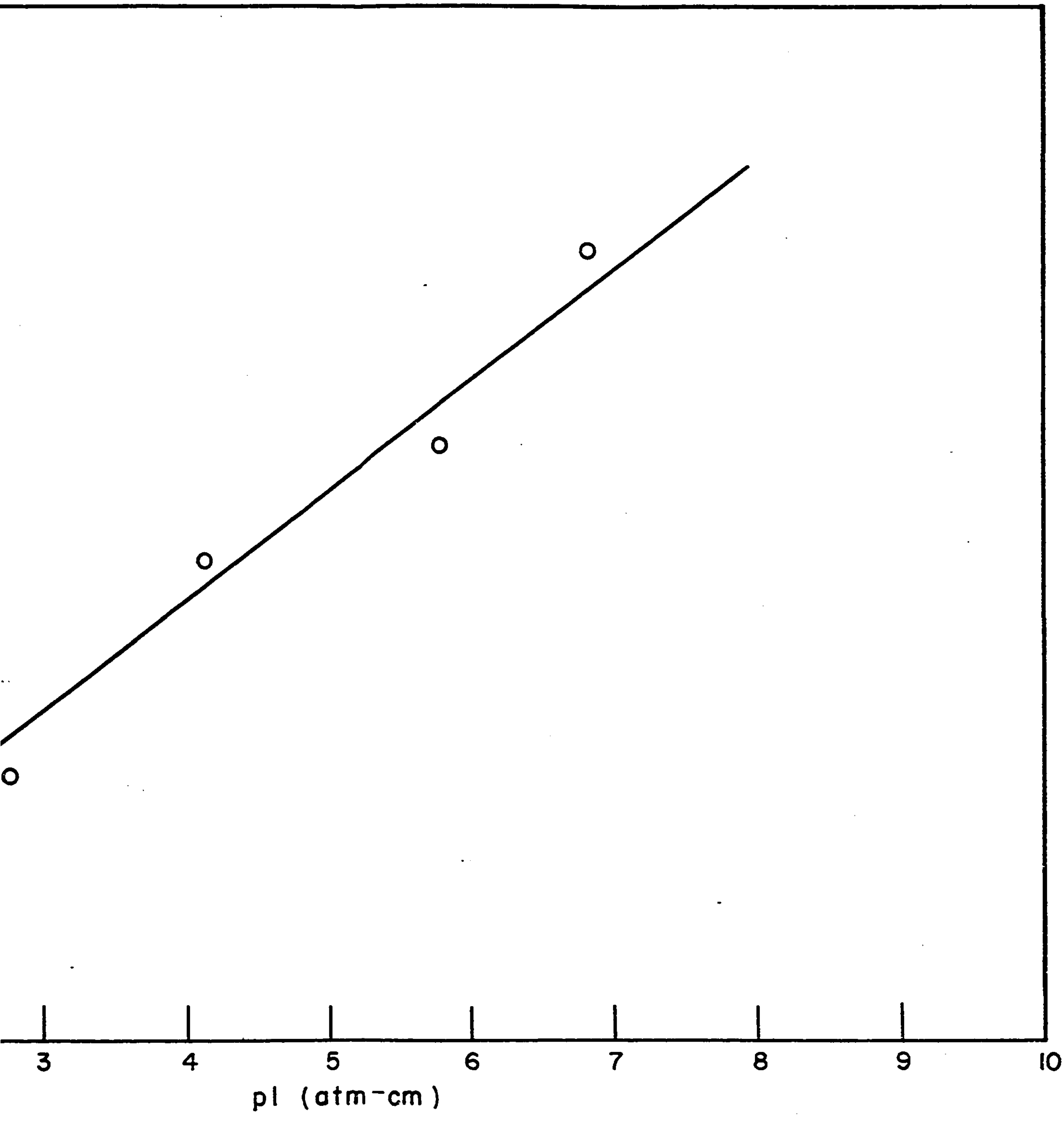


FIGURE 7 INTENSITY PLOT OF THE ν_3



E 7 INTENSITY PLOT OF THE ν_3 BAND OF CH_2ClF

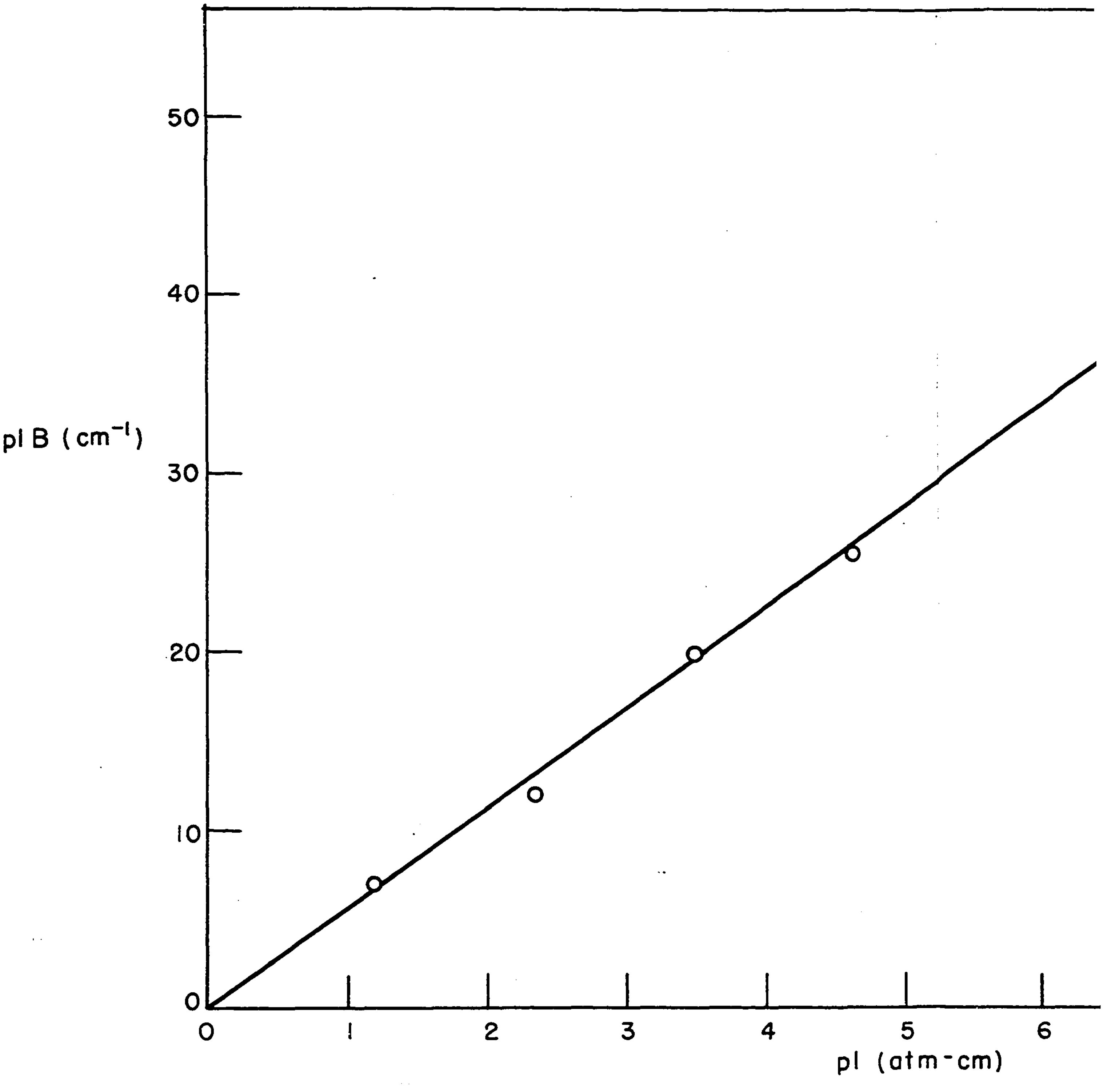
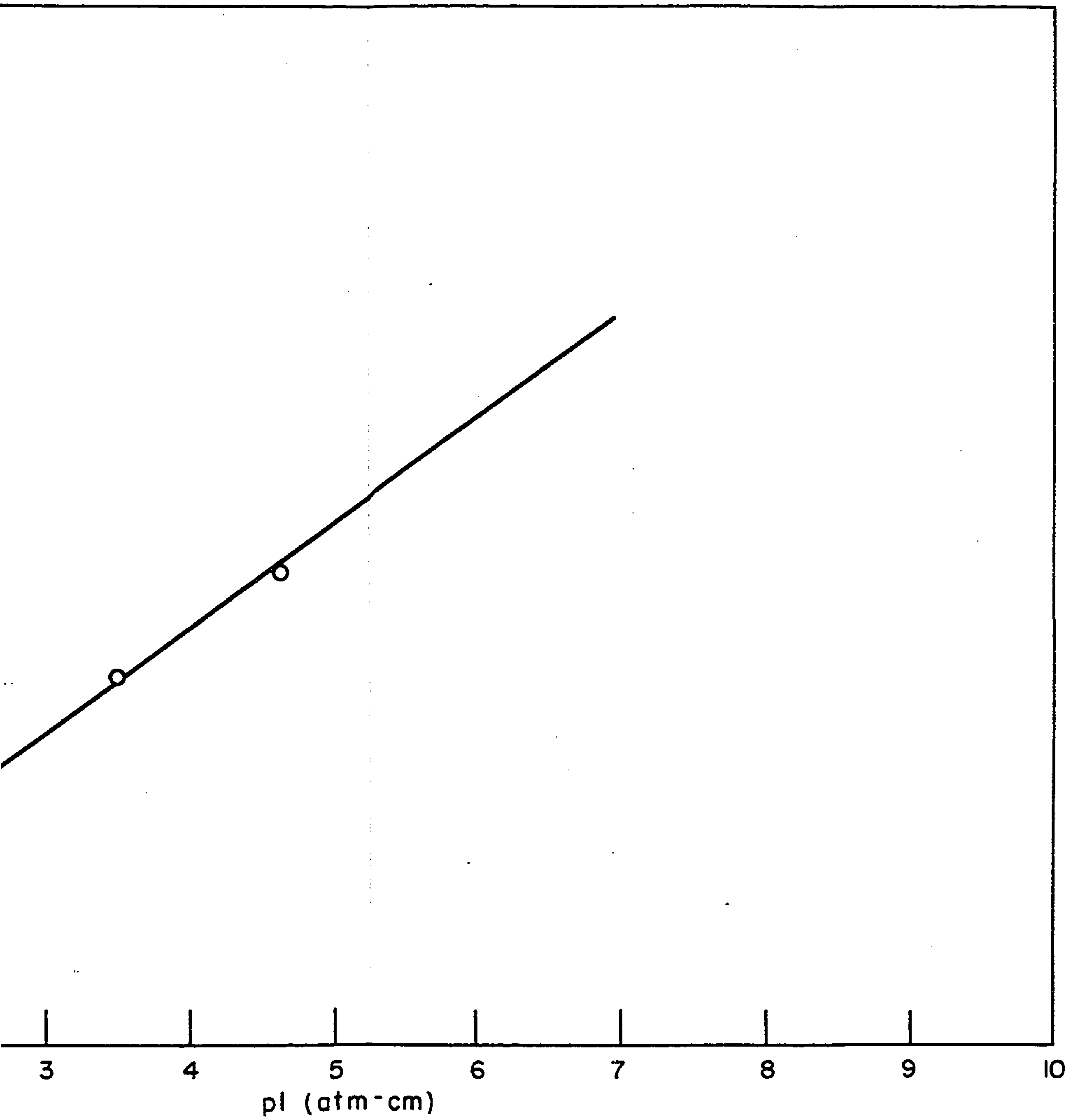


FIGURE 8 INTENSITY PLOT OF THE ν_3 BA



E 8 INTENSITY PLOT OF THE ν_3 BAND OF CH_2Cl_2

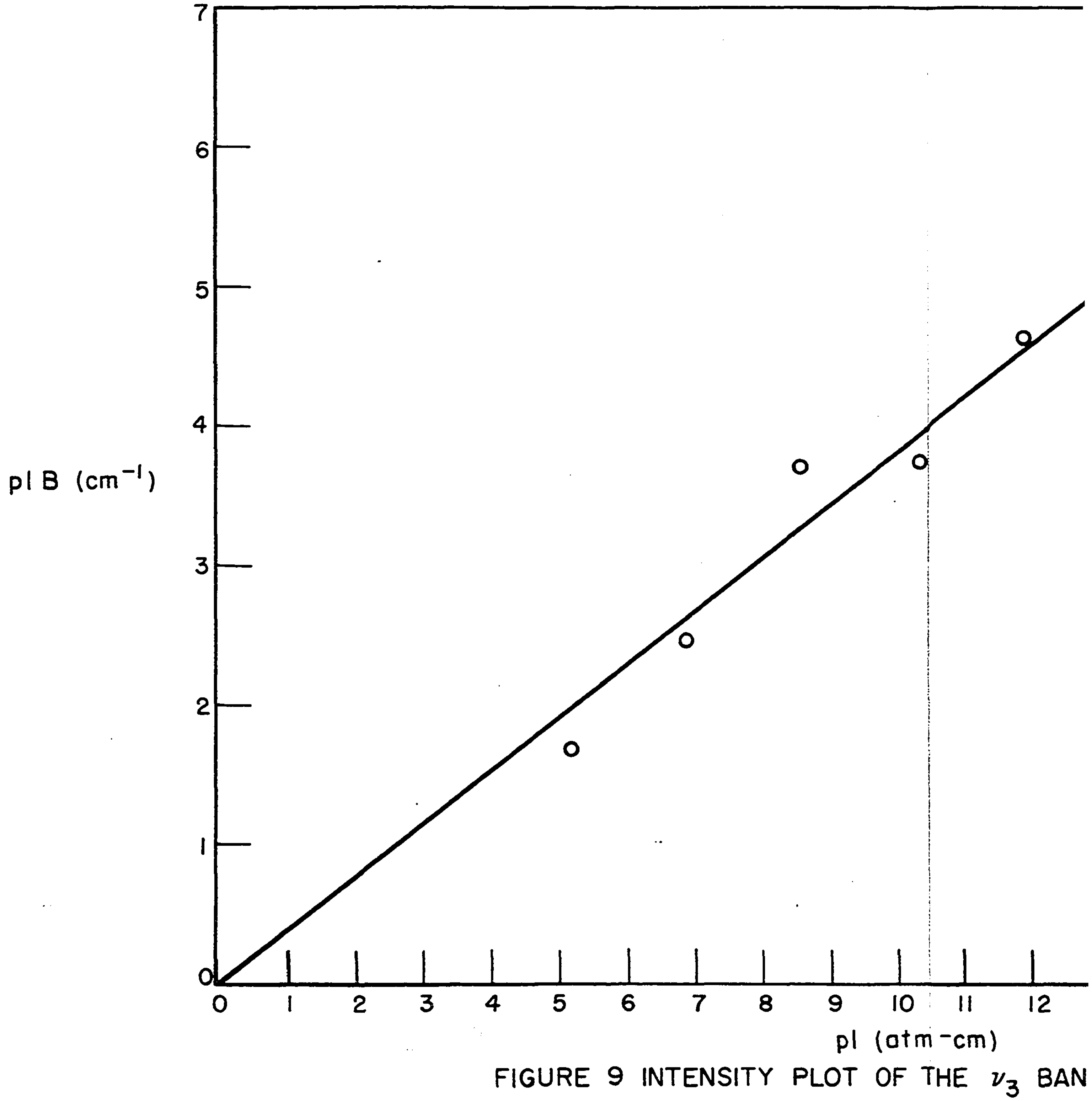
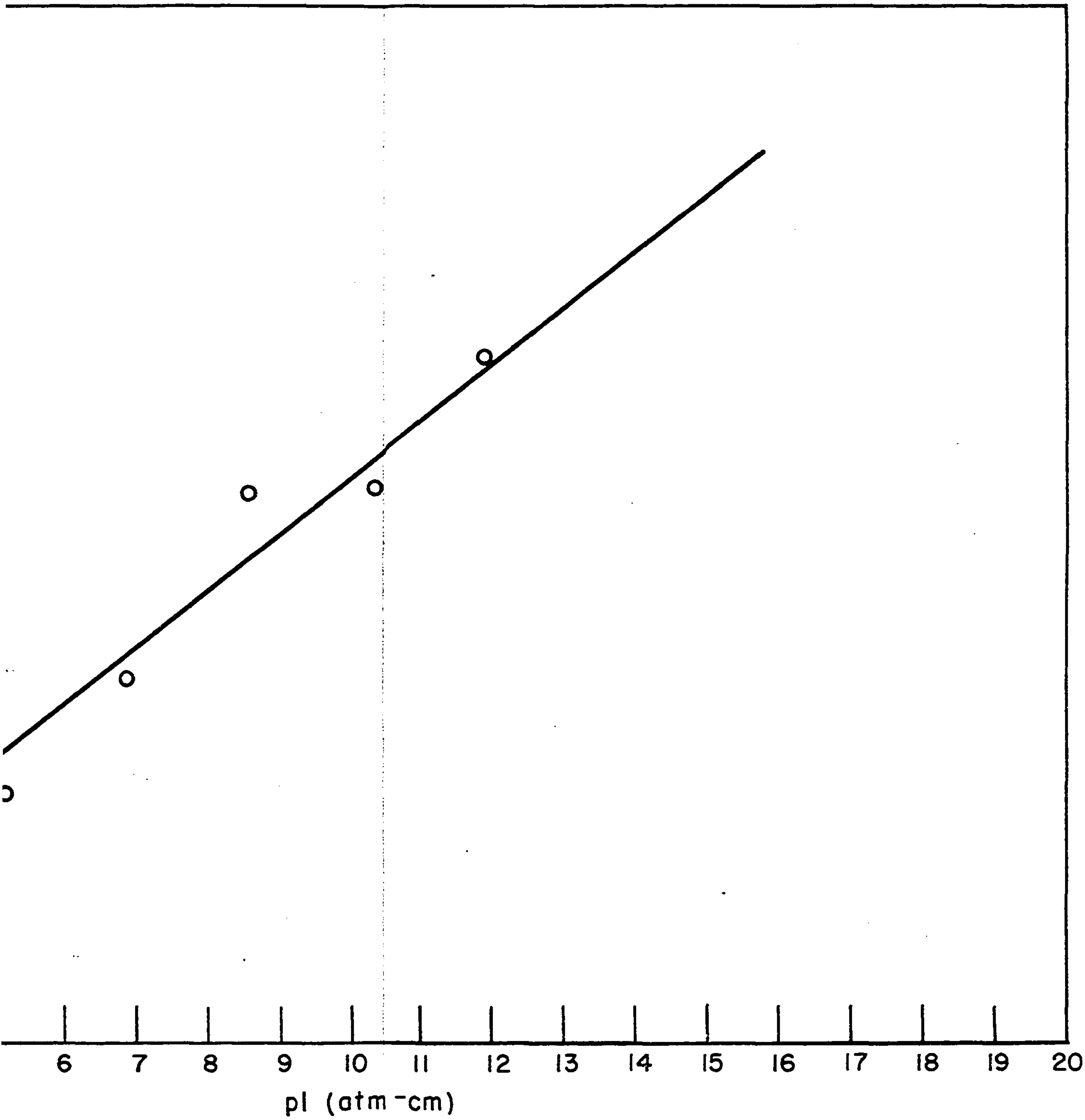


FIGURE 9 INTENSITY PLOT OF THE ν_3 BAN



RE 9 INTENSITY PLOT OF THE ν_3 BAND OF CH_2BrCl

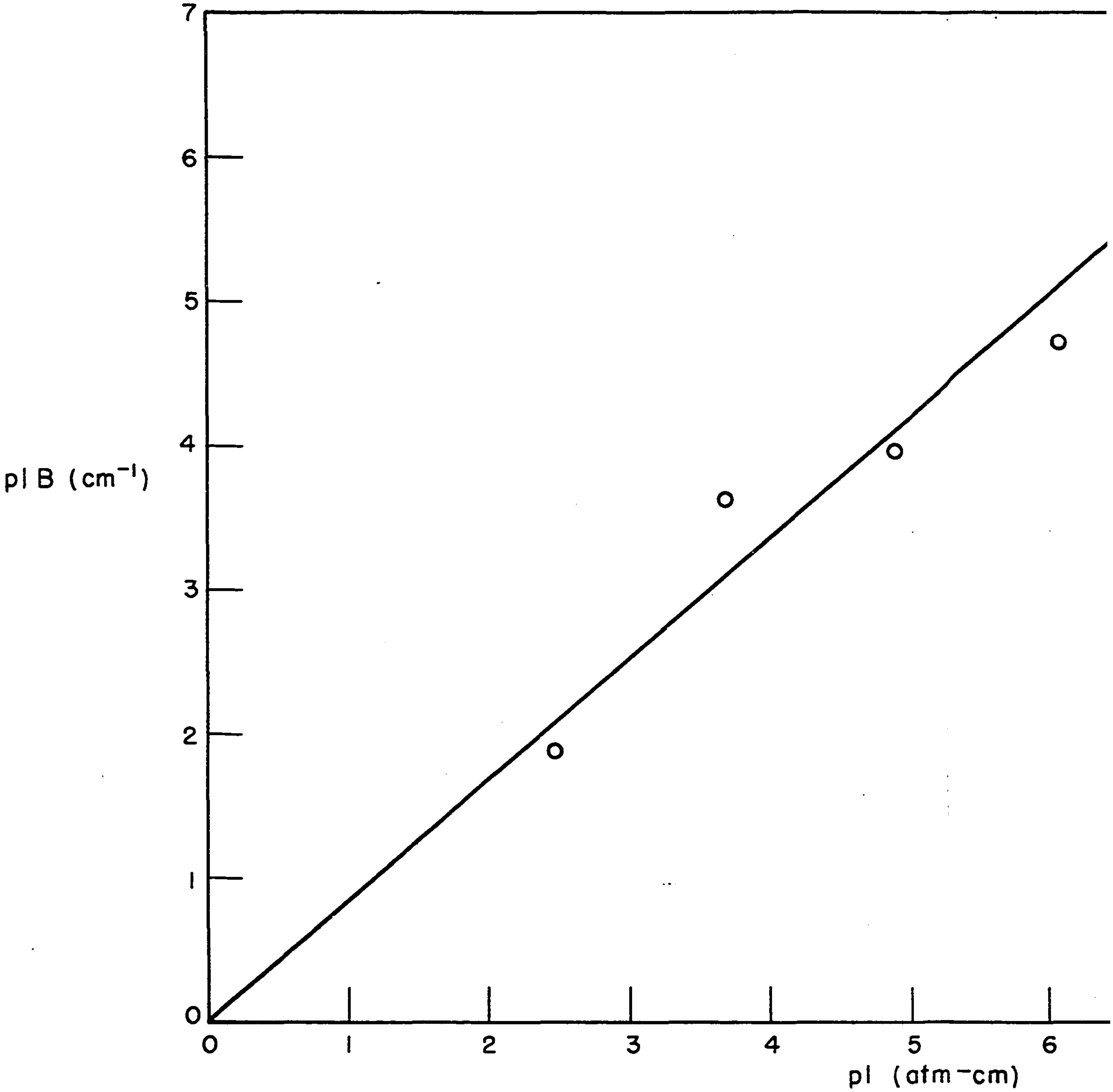
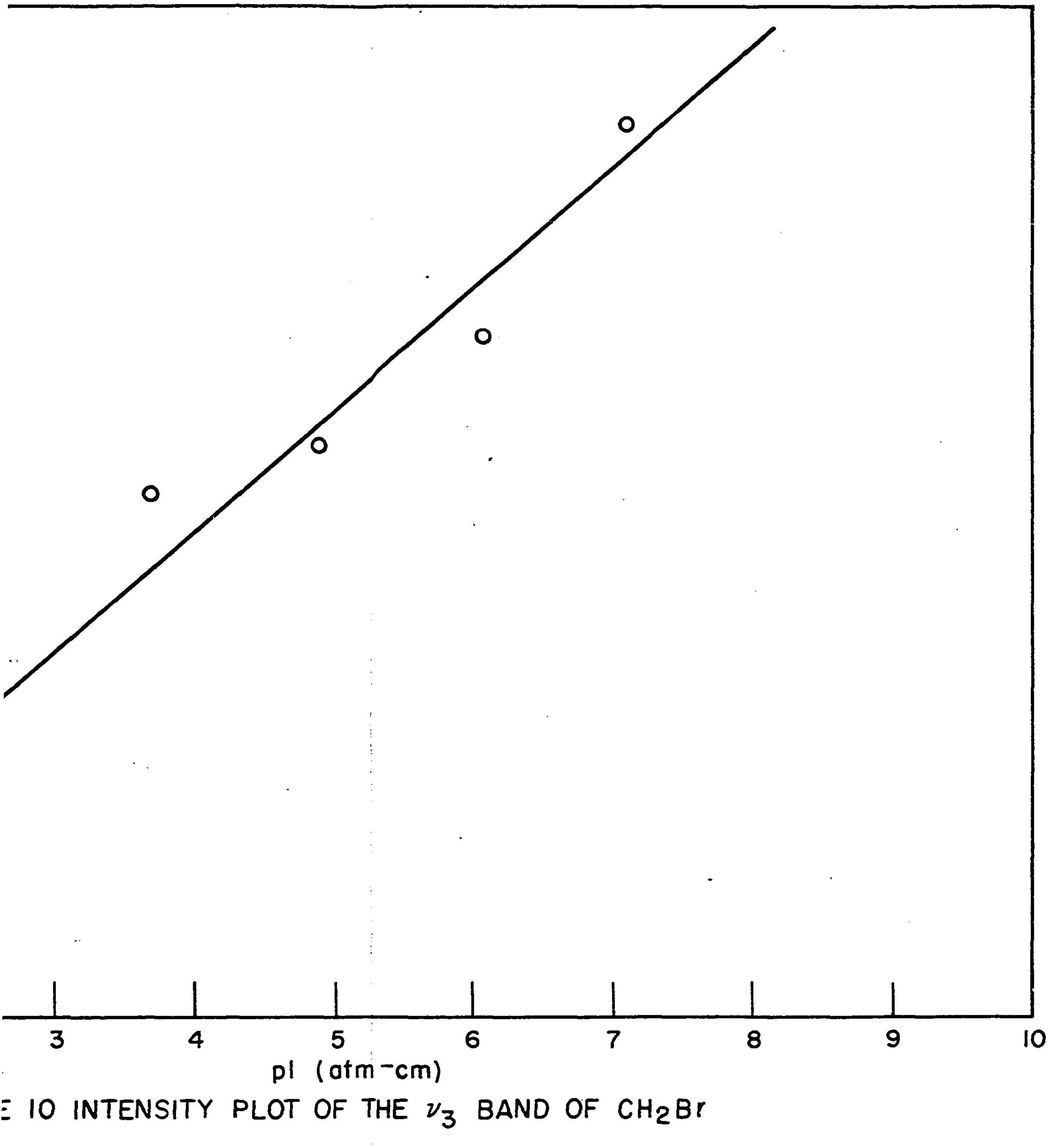


FIGURE 10 INTENSITY PLOT OF THE ν_3 BAN



E 10 INTENSITY PLOT OF THE ν_3 BAND OF CH_2Br

INTERPRETATION OF DATA

The intensity of a vibration band is related to the dipole moment change with vibration (7). If the intensity is measured in cm^{-1} / atm.-cm and $\frac{\partial \mu}{\partial Q}$ in e.s.u. then the relationship is

$$\frac{\partial \mu}{\partial Q_1} = \pm 5.653 \ (A_1)^{1/2} . \qquad (36)$$

Table 3 contains the values of $\frac{\partial \mu}{\partial Q}$ that were determined for the methylene halides studied based from the vapor phase intensities.

Table 3. $\left(\frac{\partial \mu}{\partial Q}\right)$'s Derived from Vapor Phase Intensities (e.s.u.)

	CH_2F_2	CH_2ClF	CH_2Cl_2	CH_2BrCl	CH_2Br_2
$\left(\frac{\partial \mu}{\partial Q_1}\right)$	58.8	35.6	25.3	12.7	8.32
$\left(\frac{\partial \mu}{\partial Q_\theta}\right)$	58.8	35.6	25.3	12.7	8.32
$\left(\frac{\partial \mu}{\partial Q_3}\right)$	8.20	13.8	13.3	3.54	5.18

In order to interpret the $\frac{\partial \mu}{\partial Q}$ in terms of bond moment parameters, the normal coordinate transformation matrices were needed. Normal coordinate calculations were made for CH_2F_2, CH_2Cl_2, CH_2Br_2, CH_2ClF and CH_2BrCl. The force constants necessary for these calculations were obtained from several sources. The force constants for CH_2Cl_2 and CH_2Br_2 were those determined by Decius[37] and the force constants for CH_2F_2 were those determined by Pace[38]. Pace's work was an extension of Decius' type of analysis to fluoromethanes but he found it was necessary to employ more interaction terms in his potential function. Plyler and Benedict[30] also extended Decius' type of analysis to fluoromethanes, and without introducing any more interaction terms. However, their calculated frequencies are in much poorer agreement with experiment than Pace's. The force constants used for CH_2BrCl and CH_2ClF were those of Decius[37] and Plyler and Benedict[30]. The additional constants required for the CH_2XY molecules were taken as the geometric mean of the corresponding constants involving a single constant after the method of Plyler and Benedict[30]. The normal coordinate calculations were carried out by the methods of Wilson[24].

The solution of the secular determinants arising in these calculations was accomplished by a iterative process[28,39] which yields the largest root (or eigenvalue) λ_r and at the same time the corresponding eigenvector $\bar{L}_r$. The eigenvector $\bar{L}_r$ is related to the normal coordinate L_r by a trivial constant.

To obtain the sub-dominant roots and their vectors, a matrix was reduced by the method described in Duncan, Frazer and Collar[39]. This requires the inverse function L_r^{-1} which may be obtained by use of the relation,

$$L_r' \; F = \lambda_r \; L_r^{-1} . \qquad (37)$$

Most of the calculations were carried out using a desk calculator, however, the A' vibrations of the CH_2XY molecules yield secular determinants of order 6 and their solution was too slow and tedious for that. These two sixth order secular determinants were solved using an

I. B. M. 602-A. The same type of iterative procedure was used but Aitken's[40] "deflation" procedure was used to reduce the matrices, since the other procedure tends to cause loss of significant figures if repeated many times.

The symmetry coordinates, G and F matrix elements, and force constants used in these calculations are presented in the appendix together with the L and L^{-1} transformation matrices.

The calculated frequencies are summarized in Table 4. The agreement of the calculated with observed frequencies is quite satisfactory for the most part. However, the agreement in the case of CH_2ClF is poorer than one would like and the calculated ν_4 of CH_2BrCl is distressingly high.

It is very likely that approximating the additional force constants required for the CH_2XY molecules as the geometric mean of the force corresponding to that of the molecules containing a single halogen, is a poor one. Since calculated frequencies are less sensitive to inexact eigenfunctions than are other parameters, it was not believed that the normal coordinates calculated for CH_2ClF and CH_2BrCl are sufficiently reliable for calculating bond moment parameters. Also the CH_2BrCl ν_3 intensity was obtained under working conditions which were very likely to cause error.

Table 4. Calculated and Observed Frequencies in cm^{-1}

Molecule	ν_i	Calc.	Obs.	Δ%
CH_2F_2	$\nu_1(A_1)$	3005	2949	1.9
	$\nu_3(A_1)$	1503	1508	-0.3
	$\nu_2(A_1)$	1127	1116	1.0
	$\nu_4(A_1)$	553	529	4.5
	$\nu_6(B_1)$	3084	3012	2.4
	$\nu_7(B_1)$	1218	1176	3.6
CH_2Cl_2	$\nu_1(A_1)$	2999	2985	0.5
	$\nu_3(A_1)$	1435	1424	0.8
	$\nu_2(A_1)$	715	706	1.3
	$\nu_4(A_1)$	297	286	3.8
	$\nu_6(B_1)$	3077	3048	1.0
	$\nu_7(B_1)$	899	898	0.1
CH_2Br_2	$\nu_1(A_1)$	2999	2988	0.4
	$\nu_3(A_1)$	1409	1385	1.7
	$\nu_2(A_1)$	576	579	-0.5
	$\nu_4(A_1)$	173	174	-0.6
	$\nu_6(B_1)$	3076	3065	0.3
	$\nu_7(B_1)$	810	813	-0.4

Table 4. (contd.)

Molecule	ν_i	Calc.	Obs.	Δ%
CH_2BrCl	$\nu_1(A')$	2999	2987	0.4
	$\nu_3(A')$	1421	1402	1.3
	$\nu_8(A')$	1245	1225	1.6
	$\nu_9(A')$	723	728	-0.7
	$\nu_2(A')$	599	606	-1.11
	$\nu_4(A')$	303	226	34.1
	$\nu_6(A'')$	3077	3060	0.6
	$\nu_5(A'')$	1140	1130	0.9
	$\nu_7(A'')$	847	852	0.6
CH_2ClF	$\nu_1(A')$	3005	2993	0.4
	$\nu_3(A')$	1543	1470	5.0
	$\nu_8(A')$	1425	1351	5.5
	$\nu_9(A')$	954	1068	-10.7
	$\nu_2(A')$	749	760	-1.4
	$\nu_4(A')$	388	385	0.8
	$\nu_6(A'')$	3080	3048	1.1
	$\nu_5(A'')$	1281	1234	3.6
	$\nu_7(A'')$	989	1004	-1.5

The relationships between the $\frac{\partial\mu}{\partial s}$ and bond moment parameters were obtained by considering the geometry of the molecule.

Table 5. Dipole Moment Change Transformation Coefficients for CH_2X_2 A_1 Vibrations

	$\left(\frac{\partial\mu}{\partial r}\right)_{CH}$	$\left(\frac{\partial\mu}{\partial r}\right)_{CX}$	μ_{CH}	μ_{CX}
$\frac{\partial\mu}{\partial s_1}$	$\sqrt{2/3}$			
$\frac{\partial\mu}{\partial s_2}$		$\sqrt{2/3}$		
$\frac{\partial\mu}{\partial s_3}$			$\sqrt{1/3}$	$-\sqrt{1/3}$
$\frac{\partial\mu}{\partial s_4}$			$-\sqrt{1/3}$	$\sqrt{1/3}$

When a symmetry species such as the B_1 of CH_2X_2 contains a rotation, one must be careful that the condition of no resultant angular momentum be imposed upon the vibration, when obtaining the transformations from $\frac{\partial\mu}{\partial s_k}$ to bond moment parameters. The transformations then will be several simultaneous equations.

Table 6. Coefficients of the Equations for CH_2X_2 B_1 Vibrations

$$\left(\frac{\partial\mu}{\partial s_k}\right) = a\left(\frac{\partial\mu}{\partial r}\right)_{CH} + b\mu_{CH} + c\mu_{CX}$$

Molecule	$\left(\frac{\partial\mu}{\partial s_k}\right)$	$\left(\frac{\partial\mu}{\partial r}\right)_{CH}$	μ_{CH}	μ_{CX}
CH_2F_2	S_6	1.15	-0.0738×10^8	-0.0738×10^8
	S_7		-0.607	0.210
CH_2Cl_2	S_6	1.15	-0.0675×10^8	-0.0675×10^8
	S_7		-0.669	0.148
CH_2Br_2	S_6	1.15	-0.0662×10^8	-0.0662×10^8
	S_7		-0.686	0.131

The coefficients from Table 5 and Table 6 together with appropriate L matrix transformations were used in deriving equations relating the $\frac{\partial\mu}{\partial Q_i}$ to the bond moments and bond moment derivatives. The coefficients of these equations are presented in Table 7.

Table 7. Coefficients of the Equations

$$\frac{\partial\mu}{\partial Q_i} = a\left(\frac{\partial\mu}{\partial r}\right)_{CH} + b\left(\frac{\partial\mu}{\partial r}\right)_{CX} + c\mu_{CH} + d\mu_{CX}$$

		a	b	c	d
CH_2F_2	1 (Q_1)	0.84×10^{12}	-0.05×10^{12}	0.11×10^{20}	-0.07×10^{20}
	3 (Q_4)	0.02×10^{20}	0.02×10^{20}	-1.21×10^{12}	0.04×10^{12}
	6 (Q_6)	1.20×10^{12}	0	0.04×10^{20}	-0.12×10^{20}
CH_2Cl_2	1 (Q_1)	0.84×10^{12}	-0.05×10^{12}	0.11×10^{20}	-0.05×10^{20}
	3 (Q_4)	0.02×10^{20}	0.06×10^{20}	-1.22×10^{12}	0.04×10^{12}
	6 (Q_6)	1.21×10^{12}	0	0.03×10^{20}	-0.09×10^{20}
CH_2Br_2	1 (Q_1)	0.84×10^{12}	-0.05×10^{12}	0.11×10^{20}	-0.04×10^{20}
	3 (Q_4)	0.02×10^{20}	0.05×10^{20}	-1.22×10^{12}	0.06×10^{12}
	6 (Q_6)	1.21×10^{12}	0	0.03×10^{20}	-0.09×10^{20}

If the assumption is made that the bond dipole moment does not change when the bond angles are deformed and also that the molecular dipole moment is the vector sum of the bond dipole moments, then it is possible to solve the equations of Table 7 and

$$\mu_T = \mu_{CH} + \mu_{CX} \qquad (38)$$

simultaneously for the bond moment parameters. The motion of halogen atoms is too slight in these vibrations to obtain $\left(\frac{\partial\mu}{\partial r}\right)_{CX}$ with significance. The results are summarized in Table 8 together with the values of the molecular dipole moments[41]. The values of $\left(\frac{\partial\mu}{\partial r}\right)_{CX}$ were calculated using the assumed values of μ_{CX} and μ_{CH}.

Table 8. Bond Polar Properties (in e.s.u.)

	CH_2F_2	CH_2Cl_2	CH_2Br_2
$\mu_{CX} \times 10^{-10}$	± 1.66 to 1.55	± 1.39 to 1.25	± 1.26 to 1.23
$\mu_{CH} \times 10^{-10}$	± 0.01 to 0.12	± 0.06 to 0.15	± 0.04 to 0.13
$\left(\frac{\partial\mu}{\partial r}\right)_{CH} \times 10^{-10}$	0.84 to 0.34	0.40 to 0.11	0.16 to 0.02
$\mu_T \times 10^{-10}$	1.93	1.62	1.5
$\mu_{CX} \times 10^{-10}$ (assumed)	1.5	1.3	1.2
$\mu_{CH} \times 10^{-10}$ (assumed)	-0.1	-0.1	-0.1

CONCLUSIONS

The infrared intensities and bond polar properties of the methylene halides show the pronounced effect of the different halogens on the effective charge $\left(\frac{\partial\mu}{\partial r}\right)$ of the C-H bonds. The effect on the μ_{CH} is apparently rather uniform. The μ_{CH} of the methylene halide molecules, however, is smaller than in most other carbon-hydrogen compounds.

The observation and intensity study of the CH_2F_2 ν_3 band confirms the assignment of this band, previously detected only in the Raman effect.

The great difference in the intensities of the ν_1 and ν_6 bands in solution compared to their intensities in vapor phase indicates strong solvent perturbations and suggest that one should be extremely cautious when attempting to interpret solution intensity data in terms of polar parameters of the isolated molecule.

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APPENDIX

The several matrices used in the normal coordinate calculations and the calculated normal coordinate transformation matrices are tabulated in this appendix. Included here are the general symmetry coordinates, G (kinetic energy) matrix and F (force constant) matrix elements for CH_2X_2 (A_1 and B_1 symmetries) and CH_2XY molecules.

Table 23 contains the values of the force constants that were used in the calculations.

The calculated normal coordinate transformation matrices for CH_2F_2, CH_2Cl_2 and CH_2Br_2 are contained in Table 24, and those for CH_2ClF and CH_2BrCl are contained in Table 25.

Table 9. CH_2X_2 Internal Coordinates

R_i	=	Δ(C-X_i)	α_1	=	Δ(X_1-C-H_1)
r_i	=	Δ(C-r_i)	α_2	=	Δ(X_1-C-H_2)
β	=	Δ(X-C-X)	α_3	=	Δ(X_2-C-H_2)
γ	=	Δ(H-C-H)	α_4	=	Δ(X_2-C-H_1)

Table 10. CH_2X_2 Symmetry Coordinates

A_1 Species

U	R_1	R_2	r_1	r_2	α_1	α_2	α_3	α_4	β_1	γ
S_1	0	0	$1/\sqrt{2}$	$1/\sqrt{2}$	0	0	0	0	0	0
S_2	$1/\sqrt{2}$	$1/\sqrt{2}$	0	0	0	0	0	0	0	0
S_3	0	0	0	0	0	0	0	0	$1/\sqrt{2}$	$-1/\sqrt{2}$
S_4	0	0	0	0	$-1/\sqrt{12}$	$-1/\sqrt{12}$	$-1/\sqrt{12}$	$-1/\sqrt{12}$	$2/\sqrt{12}$	$2/\sqrt{12}$
S_5	0	0	0	0	$1/\sqrt{6}$	$1/\sqrt{6}$	$1/\sqrt{6}$	$1/\sqrt{6}$	$1/\sqrt{6}$	$1/\sqrt{6}$

Table 11. CH_2X_2 Symmetry Coordinates

B_1 Species

U	R_1	R_2	r_1	r_2	α_1	α_2	α_3	α_4	β_1	γ
S_6	0	0	$1/\sqrt{2}$	$-1/\sqrt{2}$	0	0	0	0	0	0
S_7	0	0	0	0	1/2	-1/2	-1/2	1/2	0	0

Table 12. CH_2XY Internal Coordinates

$R_x = \Delta(\text{C-X})$ $\quad \alpha_{xi} = \Delta(\text{X-C-H}_i)$

$R_y = \Delta(\text{C-Y})$ $\quad \alpha_{ri} = \Delta(\text{Y-C-H}_i)$

$r_i = \Delta(\text{C-H}_i)$ $\quad \beta = \Delta(\text{X-C-Y})$

$\gamma = \Delta(\text{H-C-H})$

Table 13. CH_2XY Symmetry Coordinates
A' Species

U	R_x	R_y	r_1	r_2	α_{x1}	α_{x2}	α_{r1}	α_{r2}	β	γ
S_1	1	*								
S_2		1								
S_3			$1/\sqrt{2}$	$1/\sqrt{2}$						
S_4					$-1/\sqrt{6}$	$-1/\sqrt{6}$	$1/\sqrt{6}$	$1/\sqrt{6}$	$-1/\sqrt{6}$	$1/\sqrt{6}$
S_5							$1/\sqrt{6}$	$1/\sqrt{6}$		$-2/\sqrt{6}$
S_6					$1/\sqrt{6}$	$1/\sqrt{6}$			$-2/\sqrt{6}$	
S' [a]					$1/\sqrt{6}$	$1/\sqrt{6}$	$1/\sqrt{6}$	$1/\sqrt{6}$	$1/\sqrt{6}$	$1/\sqrt{6}$

* Blank spaces in U matrices are 0.

[a] $S' \equiv 0$. (redundant coordinate)

Table 14. CH_2XY Symmetry Coordinates
A" Species

U	R_x	R_y	r_1	r_2	α_{x1}	α_{x2}	α_{r1}	α_{r2}	β	γ
S_7	*						$1/\sqrt{2}$	$-1/\sqrt{2}$		
S_8			$1/\sqrt{2}$	$-1/\sqrt{2}$						
S_9					$1/\sqrt{2}$	$-1/\sqrt{2}$				

* Blank spaces in U matrices are 0.

Table 15. G Matrix Elements of CH_2X_2

A_1 Species

$$G_{11} = \frac{1}{m_H} + \frac{2}{3m_C}$$

$$G_{12} = \frac{-2}{3m_C}$$

$$G_{13} = \frac{-2\sqrt{2}}{3m_C}\left(\frac{1}{d} + \frac{1}{D}\right)$$

$$G_{14} = \frac{-2\sqrt{2}}{3m_C}\left(\frac{1}{d} - \frac{1}{D}\right)$$

$$G_{22} = \frac{1}{m_X} + \frac{2}{3m_C}$$

$$G_{23} = \frac{2\sqrt{2}}{3m_C}\left(\frac{1}{d} + \frac{1}{D}\right)$$

$$G_{24} = \frac{2\sqrt{2}}{3m_C}\left(\frac{1}{d} - \frac{1}{D}\right)$$

$$G_{33} = \frac{1}{d^2 m_H} + \frac{1}{D^2 m_X} + \frac{4}{3m_C}\left(\frac{1}{d} - \frac{1}{D}\right)^2$$

$$G_{34} = \frac{\sqrt{6}}{2}\left(\frac{1}{d^2 m_H} - \frac{1}{D^2 m_X}\right) - \frac{2\sqrt{6}}{3m_C}\left(\frac{1}{d^2} - \frac{1}{D^2}\right)$$

$$G_{35} = \frac{3}{2}\left(\frac{1}{d^2 m_H} + \frac{1}{D^2 m_X}\right) + \frac{2}{m_C}\left(\frac{1}{d} - \frac{1}{D}\right)^2$$

Table 16. G Matrix Elements of CH_2X_2

B_1 Species

$$G_{66} = \frac{1}{m_H} + \frac{4}{3m_c}$$

$$G_{67} = \frac{-2}{3m_c}\left(\frac{3}{D_X} + \frac{1}{d}\right)$$

$$G_{77} = \frac{1}{2m_H d^2} + \frac{3}{2m_X D_X^2} + \frac{1}{3m_c}\left(\frac{3}{D_X} + \frac{1}{d}\right)^2$$

Table 17. G Matrix Elements of CH_2XY $(m_x > m_y)$

A' Species

$$G_{11} = \frac{1}{m_x} + \frac{1}{m_c}$$

$$G_{12} = \frac{-1}{3m_c}$$

$$G_{13} = G_{23} = -\frac{2}{3m_c}$$

$$G_{14} = \frac{4\sqrt{3}}{9m_c}\left(\frac{1}{D_y} + \frac{2}{d}\right)$$

$$G_{15} = \frac{2\sqrt{3}}{9m_c}\left(\frac{1}{D_y} - \frac{1}{d}\right)$$

$$G_{16} = \frac{4\sqrt{3}}{9m_c}\left(\frac{1}{D_y} - \frac{1}{d}\right)$$

$$G_{22} = \frac{1}{m_y} + \frac{1}{m_c}$$

$$G_{24} = \frac{-4\sqrt{3}}{9}\ \frac{1}{dm_c}$$

$$G_{25} = \frac{-8\sqrt{3}}{9}\ \frac{1}{dm_c}$$

$$G_{26} = \frac{2\sqrt{3}}{9}\ \frac{1}{m_c}\left(\frac{1}{d} + \frac{3}{D_x}\right)$$

$$G_{33} = \frac{1}{m_H} + \frac{2}{3m_c}$$

$$G_{34} = -\frac{2\sqrt{6}}{9}\ \frac{1}{m_c}\left(\frac{1}{d} + \frac{1}{D_y}\right)$$

$$G_{35} = \frac{-\sqrt{6}}{9}\ \frac{1}{m_c}\left(\frac{1}{D_y} - \frac{5}{d}\right)$$

$$G_{36} = \frac{-\sqrt{6}}{9}\ \frac{1}{m_c}\left(\frac{2}{D_y} + \frac{3}{D_x} - \frac{1}{d}\right)$$

$$G_{44} = \frac{4}{3d^2m_H} + \frac{2}{3\ D_y\ m_y} + \frac{2}{9m_c}\left(\frac{11}{d^2} + \frac{3}{D_y^2} \quad \frac{10}{dD_y}\right)$$

Table 17. (contd.)

$$G_{45} = -\frac{1}{3d^2 m_H} + \frac{1}{3D_y^2 m_y} - \frac{1}{9m_c}\left(\frac{1}{d} - \frac{3}{D_y} + \frac{2}{dD_y}\right)$$

$$G_{46} = -\frac{2}{3d^2 m_H} + \frac{2}{3D_y^2 m_y} - \frac{1}{9m_c}\left(\frac{11}{d^2} - \frac{6}{D_y^2} - \frac{5}{dD_y}\right) - \frac{1}{9m_c}\left(\frac{3}{dD_x} - \frac{3}{D_y D_x}\right)$$

$$G_{55} = \frac{7}{3d^2 m_H} + \frac{1}{6D_y^2 m_y} + \frac{1}{18m_c}\left(\frac{59}{d^2} + \frac{3}{D_y^2} - \frac{14}{dD_y}\right)$$

$$G_{56} = \frac{1}{6d^2 m_H} + \frac{1}{3D_y^2 m_y} + \frac{1}{18m_c}\left(\frac{1}{d^2} + \frac{6}{D_y^2} - \frac{19}{dD_y}\right) + \frac{1}{18m_c}\left(\frac{3}{D_x D_y} - \frac{39}{dD_x}\right)$$

$$G_{66} = \frac{1}{3d^2 m_H} + \frac{2}{3D_y m_y} + \frac{3}{2D_x m_x} + \frac{1}{18m_c}\left(\frac{11}{d^2} + \frac{27}{D_x^2}\right) + \frac{1}{18m_c}\left(\frac{12}{D_y^2} + \frac{6}{dD_x} + \frac{12}{D_x D_y} - \frac{20}{dD_y}\right)$$

Table 18. G Matrix Elements of CH_2XY

A" Species

$$G_{77} = \frac{1}{d^2 m_H} + \frac{3}{2D_c^2 m_x} + \frac{1}{6m_c}\left(\frac{1}{d} + \frac{3}{D_c}\right)^2$$

$$G_{78} = \frac{-\sqrt{2}}{3m_c}\left(\frac{1}{d} + \frac{3}{D_c}\right)$$

$$G_{79} = -\frac{1}{2d^2 m} + \left(\frac{1}{d} + \frac{3}{D_y}\right)\left(\frac{1}{d} + \frac{3}{D_c}\right)\frac{1}{6m_c}$$

$$G_{88} = \frac{1}{m_H} + \frac{4}{3m_c}$$

$$G_{89} = \frac{-\sqrt{2}}{3m_c}\left(\frac{1}{d} + \frac{3}{D_y}\right)$$

$$G_{99} = \frac{1}{d^2 m} + \frac{3}{2D_y^2 m_y} + \frac{1}{6m_c}\left(\frac{1}{d} + \frac{3}{D_y}\right)^2$$

Table 19. F Matrix Elements of CH_2X_2

A_1 Species

$$F_{11} = f_r^1$$

$$F_{12} = F_{13} = F_{14} = 0$$

$$F_{22} = f_R^1 + f_R^2$$

$$F_{23} = f_{R\beta}^1 - f_{R\gamma}^1$$

$$F_{24} = \frac{-2}{\sqrt{6}} \left(f_{R\alpha}^1 + f_{R\alpha}^2 \right) + \frac{2}{\sqrt{6}} \left(f_{R\beta}^1 + f_{R\gamma}^1 \right)$$

$$F_{33} = f_\beta^1 + f_\gamma^1$$

$$F_{34} = \frac{-2}{\sqrt{6}} \left(f_{\beta\alpha}^1 - f_{\alpha\gamma}^1 \right) + \frac{1}{\sqrt{6}} \left(f_\beta^1 - f_\gamma^1 \right)$$

$$F_{44} = \frac{1}{3} \left(f_\alpha^1 + f_\alpha^2 + f_\alpha^3 + f_\alpha^4 \right) - \frac{4}{3} \left(f_{\beta\alpha}^1 + f_{\gamma\alpha}^1 \right) + \frac{1}{3} \left(f_\beta^1 + f_\gamma^1 \right)$$

Table 20. F Matrix Elements of CH_2X_2

B_1 Species

$$F_{66} = f_r^1$$

$$F_{67} = 0$$

$$F_{77} = \left(f_\alpha^1 + f_\alpha^2 \right) - \left(f_\alpha^3 + f_\alpha^4 \right)$$

Table 21. F Matrix Elements of CH_2XY

A' Species

$m_X > m_Y$

$$F_{11} = f^1_{R_x}$$

$$F_{12} = f^2_{R_{x\gamma}}$$

$$F_{13} = F_{23} = F_{24} = F_{35} = F_{36} = 0$$

$$F_{15} = \frac{\sqrt{6}}{3} \; f^2_{R_x\alpha_y}$$

$$F_{16} = \frac{\sqrt{6}}{3} \; f^1_{R_x\alpha_x}$$

$$F_{22} = f^1_{R_y}$$

$$F_{24} = \frac{1}{\sqrt{6}} \left(2f^1_{R_y\alpha_y} - f^1_{R_y\beta} - 2f^2_{R_y\alpha_x} \right)$$

$$F_{25} = \frac{\sqrt{6}}{3} \; f^1_{R_y\alpha_y}$$

$$F_{26} = \frac{\sqrt{6}}{3} \left(f^2_{R_y\alpha_x} - f^1_{R_y\beta} \right)$$

$$F_{33} = f^1_r$$

$$F_{44} = \frac{1}{6} \left(2f^1_{\alpha_y} + 2f^3_{\alpha_x} + f^1_{\gamma} - 4f^2_{\alpha_{x\gamma}} - 4f^4_{\alpha} + 2f^1_{\alpha_x} \right.$$
$$\left. + 2f^3_{\alpha_x} + f^1_{\beta} \right)$$

$$F_{45} = \frac{1}{3} \left(f^2_{\alpha_y} - f^2_{\alpha} - f^1_{\gamma} + f^3_{\alpha_y} - f^1_{\alpha_y} - f^4_{\alpha} + 2f^1_{\alpha_x\gamma} \right)$$

$$F_{46} = \frac{1}{3} \left(f^2_{\alpha} + f^4_{\alpha} - f^1_{\alpha_y} - f^3_{\alpha_x} + f^1_{\beta} \right)$$

Table 21. (contd.)

$$F_{55} = \frac{1}{3} (f_{\alpha}^{1} + 2f_{\gamma}^{1} + f_{\alpha}^{3})$$

$$F_{56} = \frac{1}{3} (f_{\alpha}^{2} + f_{\alpha}^{4})$$

$$F_{66} = \frac{1}{3} (f_{\alpha}^{1} + f_{\alpha}^{3} + 2f_{\beta}^{1})$$

Table 22. F Matrix Elements of CH_2XY

A" Species

$m_X > m_Y$

$$F_{77} = f_{\alpha}^{1} - f_{\alpha}^{4}$$

$$F_{78} = F_{89} = 0$$

$$F_{79} = f_{\alpha}^{2} - f_{\alpha}^{4}$$

$$F_{88} = f_{r}^{1}$$

$$F_{99} = f_{\alpha}^{1} - f_{\alpha}^{3}$$

Table 23. Force Constants

The following constants are assumed to be zero: f^1_{Rr}, $f^1_{R\gamma}$, f^2_r, $f^1_{r\alpha}$, $f^2_{r\alpha}$, $f^1_{r\beta}$, $f^1_{r\gamma}$, $f^2_{r\gamma}$, $f^1_{\alpha\beta}$, $f^2_{\alpha\beta}$, $f^2_{\beta\gamma}$, f^2_{γ}, and f^3_{γ}.

The numerical units are 10^5 dyne cm^{-1} for two stretching coordinates, 10^{-3} dyne for bending and stretching, and 10^{-11} dyne cm for two bending coordinates.

r_oC-F = 1.35 A, r_oC-Cl = 1.75 A, r_oC-Br = 1.88 A, all $\alpha_o = \beta_o = \gamma_o = 109^\circ\ 28'$.

Constant	Terms involved	X=F	X=Cl	X=Br	X=F (Pace)
f^1_R	$C{-}X_j : C{-}X_j$	6.26	3.383	2.840	6.246
f^2_R	$C{-}X_j : C{-}X_k$	0.96	0.332	0.186	0.967
f^1_r	$C{-}H_i : C{-}H_i$	5.04	5.04	5.04	5.04
$f^1_{R\alpha}$	$C{-}X_j : H{-}C{-}X_j$	0.40	0.340	0.305	0.659
$f^2_{R\alpha}$	$C{-}X_j : H{-}C{-}X_k$	-.21	-.164	-.152	0.000
$f^1_{R\beta}$	$C{-}X_j : X_j{-}C{-}X_k$	0.34	0.338	0.342	0.644
$f^2_{R\beta}$	$C{-}X_j : X_k{-}C{-}X_l$	-.34	-.249	-.190	0.00
f^1_{α}	$H_j{-}C{-}X_j : H_j{-}C{-}X_j$	0.875	0.687	0.589	0.952
f^2_{α}	$H_j{-}C{-}X_j : H_j{-}C{-}X_k$	0.050	0.009	-.005	0.179

Table 23. (contd.)

Constant	Terms involved	X=F	X=Cl	X=Br	X=F (Pace)
f_{α}^{3}	H_j-C-X_j : H_k-C-X_j	-.048	-.034	-.026	-.004
f_{α}^{4}	H_j-C-X_j : H_k-C-X_k	-.145	-.065	-.060	-.114
f_{β}^{1}	X_j-C-X_k : X_j-C-X_k	1.75	1.236	1.061	2.143
f_{β}^{2}	X_j-C-X_k : X_j-C-X_l	0.17	0.092	0.134	0.478
f_{β}^{3}	X_j-C-X_k : X_l-C-X_m	-.10	-.037	0.039	0.111
f_{γ}^{1}	H_j-C-H_k : H_j-C-H_k	0.530	0.530	0.530	0.530
$f_{R\gamma}^{2}$	C-X : H-C-H				-.145
$f_{\alpha\gamma}^{1}$	H-C-X : H-C-H				0.017
$f_{\beta\alpha}^{1}$	X_j-C-X_k : H-C-X_k				0.304

		X=Cl ; Y=F	X=Br ; Y=Cl
f_{R}^{2}	C-X : C-Y	0.565	0.2485
f_{β}^{1}	X-C-Y : X-C-Y	1.471	1.145
f_{α}^{2}	H_j-C-X : H_j-C-Y	0.21	0.002
$f_{R\ \alpha}^{2}$	C-X : H-C-Y	-.186	-.157 (=$f_{R\ \alpha}^{2}$)
$f_{R\ \beta}^{1}$	C-X : X-C-Y	0.339	0.340 (=$f_{R\ \beta}$)
f_{α}^{4}	H_j-C-X : H_l-C-Y	-.0861	-.062

Table 24. Normal Coordinate Transformations

L and L^{-1} (in units of $g^{-1/2}$)

CH_2X_2

CH_2F_2

$L\ (A_1)$	Q_1	Q_2	Q_3	Q_4
S_1	$1.023\ x10^{12}$	$0.03035\ x10^{12}$	$-0.002927\ x10^{20}$	$0.01986\ x10^{20}$
S_2	$-0.06399\ x10^{12}$	$0.3165\ x10^{12}$	$0.05702\ x10^{20}$	$0.02489\ x10^{20}$
S_3	$0.1566\ x10^{20}$	$-0.3213\ x10^{20}$	$0.1213\ x10^{12}$	$-1.010\ x10^{12}$
S_4	$-0.03337\ x10^{20}$	$-0.1009\ x10^{20}$	$0.3459\ x10^{12}$	$1.079\ x10^{12}$

$L^{-1}\ (A_1)$	S_1	S_2	S_3	S_4
Q_1	$0.9697\ x10^{-12}$	$-0.06272\ x10^{-12}$	$0.02720\ x10^{-20}$	$0.009039\ x10^{-20}$
Q_2	$0.20440\ x10^{-12}$	$2.729\ x10^{-12}$	$-0.2970\ x10^{-20}$	$-0.3451\ x10^{-20}$
Q_3	$-0.08186\ x10^{-20}$	$2.561\ x10^{-20}$	$1.962\ x10^{-12}$	$1.780\ x10^{-12}$
Q_4	$0.07521\ x10^{-20}$	$-0.5699\ x10^{-20}$	$-0.6560\ x10^{-12}$	$0.3243\ x10^{-12}$

$L\ (B_1)$	Q_6	Q_7
S_6	$1.046\ x10^{12}$	$0.03841\ x10^{12}$
S_7	$-0.1959\ x10^{20}$	$0.8325\ x10^{20}$

$L^{-1}\ (B_1)$	S_6	S_7
Q_6	$0.9480\ x10^{-12}$	$-0.04400\ x10^{-20}$
Q_7	$-0.2217\ x10^{-12}$	$1.191\ x10^{-20}$

Table 24. (contd.)

CH_2Cl_2

L (A_1)	Q_1	Q_2	Q_3	Q_4
S_1	1.023 x10^{12}	−0.01182 x10^{12}	−0.0002753 x10^{20}	0.02131 x10^{20}
S_2	−0.05879 x10^{12}	0.2724 x10^{12}	0.03898 x10^{20}	0.06778 x10^{20}
S_3	0.1371 x10^{20}	−0.1680 x10^{20}	0.1418 x10^{12}	−1.009 x10^{12}
S_4	−0.05314 x10^{20}	−0.1839 x10^{20}	0.1285 x10^{12}	1.107 x10^{12}

L^{-1} (A_1)	S_1	S_2	S_3	S_4
Q_1	0.9730 x10^{-12}	−0.03325 x10^{-12}	0.01620 x10^{-20}	−0.00191 x10^{-20}
Q_2	0.1976 x10^{-12}	3.088 x10^{-12}	−0.3625 x10^{-20}	−0.5214 x10^{-20}
Q_3	−0.02670 x10^{-20}	4.034 x10^{-20}	3.374 x10^{-12}	2.832 x10^{-12}
Q_4	0.08854 x10^{-20}	0.04714 x10^{-20}	−0.4526 x10^{-12}	0.4868 x10^{-12}

L (B_1)	Q_6	Q_7
S_6	1.050 x10^{12}	0.01770 x10^{12}
S_7	−0.1513 x10^{20}	0.7748 x10^{20}

L^{-1} (B_1)	S_6	S_7
Q_6	0.9491 x10^{-12}	0.02958 x10^{-20}
Q_7	−0.1368 x10^{-12}	1.295 x10^{-20}

Table 24. (contd.)

CH_2Br_2

L (A_1)	Q_1	Q_2	Q_3	Q_4
S_1	1.023 x10^{12}	0.008207 x10^{12}	-0.0002823 x10^{20}	0.02030 x10^{20}
S_2	-0.05752 x10^{12}	0.2444 x10^{12}	0.02420 x10^{20}	0.06673 x10^{20}
S_3	0.1323 x10^{20}	-0.1656 x10^{20}	0.08712 x10^{12}	-1.005 x10^{12}
S_4	-0.05656 x10^{20}	-0.1721 x10^{20}	0.08192 x10^{12}	1.107 x10^{12}

L^{-1} (A_1)	S_1	S_2	S_3	S_4
Q_1	0.9736 x10^{-12}	-0.02596 x10^{-12}	0.01384 x10^{-20}	-0.003697 x10^{-20}
Q_2	0.2119 x10^{-12}	3.363 x10^{-12}	-0.4378 x10^{-20}	-0.6045 x10^{-20}
Q_3	-0.08071 x10^{-20}	6.563 x10^{-20}	5.408 x10^{-12}	4.518 x10^{-12}
Q_4	0.08766 x10^{-20}	0.02489 x10^{-20}	-0.4599 x10^{-12}	0.4827 x10^{-12}

L (B_1)	Q_6	Q_7
S_6	1.050 x10^{12}	0.01369 x10^{12}
S_7	-0.1426 x10^{20}	0.7584 x10^{20}

L^{-1} (B_1)	S_6	S_7
Q_6	0.9499 x10^{-12}	-0.01715 x10^{-20}
Q_7	0.1787 x10^{-12}	1.315 x10^{-20}

Table 25. Normal Coordinate Transformations

L and L^{-1} (in units of $g^{-1/2}$)

CH_2XY

CH_2ClF

L (A')	Q_1	Q_2	Q_3
S_1	0.3197 x10^{12}	-0.02031 x10^{12}	-0.04296 x10^{12}
S_2	-0.1128 x10^{12}	0.3027 x10^{12}	-0.04820 x10^{12}
S_3	0.008181 x10^{12}	0.01338 x10^{12}	1.022 x10^{12}
S_4	0.2972 x10^{20}	-0.6000 x10^{20}	-0.1030 x10^{20}
S_5	0.09565 x10^{20}	0.08037 x10^{20}	0.1223 x10^{20}
S_6	0.08235 x10^{20}	0.4801 x10^{20}	-0.04762 x10^{20}

L (A')	Q_4	Q_5	Q_6
S_1	0.02178 x10^{20}	-0.05824 x10^{20}	-0.05704 x10^{20}
S_2	0.04142 x10^{20}	-0.1599 x10^{20}	-0.03518 x10^{20}
S_3	0.003739 x10^{20}	-0.04157 x10^{20}	0.001219 x10^{20}
S_4	0.5822 x10^{12}	-0.7682 x10^{12}	0.1135 x10^{12}
S_5	1.008 x10^{12}	1.099 x10^{12}	-0.001602 x10^{12}
S_6	-0.2588 x10^{12}	0.2045 x10^{12}	0.1933 x10^{12}

Table 25. (contd.)

CH_2ClF

L^{-1} (A')	S_1	S_2	S_3
Q_1	2.654 x10^{-12}	-0.5287 x10^{-12}	0.1247 x10^{-12}
Q_2	0.6459 x10^{-12}	2.051 x10^{-12}	0.1259 x10^{-12}
Q_3	-0.02808 x10^{-12}	-0.07332 x10^{-12}	0.9690 x10^{-12}
Q_4	-0.2489 x10^{-20}	1.112 x10^{-20}	0.01575 x10^{-20}
Q_5	-0.09831 x10^{-20}	-1.147 x10^{-20}	-0.1494 x10^{-20}
Q_6	-2.941 x10^{-20}	-2.029 x10^{-20}	0.06939 x10^{-20}

L^{-1} (A')	S_4	S_5	S_6
Q_1	0.1282 x10^{-20}	0.02865 x10^{-20}	0.6084 x10^{-20}
Q_2	-0.1254 x10^{-20}	0.1233 x10^{-20}	0.6364 x10^{-20}
Q_3	-0.02385 x10^{-20}	0.01055 x10^{-20}	-0.01359 x10^{-20}
Q_4	0.5253 x10^{-12}	0.6044 x10^{-12}	-0.1698 x10^{-12}
Q_5	-0.4768 x10^{-12}	0.3903 x10^{-12}	0.05112 x10^{-12}
Q_6	1.523 x10^{-12}	0.06030 x10^{-12}	3.043 x10^{-12}

Table 25. (contd.)

CH_2ClF

L (A'')	Q_7	Q_8	Q_9
S_7	0.7875×10^{20}	-0.1058×10^{12}	-0.5556×10^{20}
S_8	0.02096×10^{20}	1.050×10^{12}	0.01541×10^{20}
S_9	0.2749×10^{20}	-0.1368×10^{12}	0.9571×10^{20}

L^{-1} (A'')	S_7	S_8	S_9
Q_7	1.053×10^{-20}	0.1853×10^{-20}	0.6079×10^{-20}
Q_8	-0.01655×10^{-12}	0.9475×10^{-12}	-0.02485×10^{-12}
Q_9	-0.3048×10^{-20}	0.08229×10^{-20}	0.8666×10^{-20}

Table 25. (contd.)

CH_2BrCl

L (A')	Q_1	Q_2	Q_3
S_1	0.2366 x10^{12}	−0.1637 x10^{12}	−0.04047 x10^{12}
S_2	0.09534 x10^{12}	0.2836 x10^{12}	−0.04146 x10^{12}
S_3	0.01324 x10^{12}	0.003963x10^{12}	1.023 x10^{12}
S_4	0.2028 x10^{20}	−0.03931 x10^{20}	−0.07500 x10^{20}
S_5	0.06406 x10^{20}	−0.01627 x10^{20}	0.1174 x10^{20}
S_6	0.1749 x10^{20}	0.04836 x10^{20}	−0.03991 x10^{20}

L (A')	Q_4	Q_5	Q_6
S_1	0.07475 x10^{20}	−0.03857 x10^{20}	−0.05003 x10^{20}
S_2	−0.1055 x10^{20}	−0.06263 x10^{20}	−0.01354 x10^{20}
S_3	−0.001587 x10^{20}	−0.02115 x10^{20}	0.002937 x10^{20}
S_4	1.064 x10^{12}	−0.4387 x10^{12}	0.05273 x10^{12}
S_5	0.3491 x10^{12}	1.421 x10^{12}	−0.01237 x10^{12}
S_6	−0.5380 x10^{12}	0.1404 x10^{12}	0.1849 x10^{12}

Table 25. (contd.)

CH_2BrCl

L^{-1} (A')	S_1		S_2		S_3	
Q_1	2.737	$x10^{-12}$	1.565	$x10^{-12}$	0.3161	$x10^{-12}$
Q_2	-1.215	$x10^{-12}$	2.908	$x10^{-12}$	0.06495	$x10^{-12}$
Q_3	0.01897	$x10^{-12}$	-0.01932	$x10^{-12}$	0.9738	$x10^{-12}$
Q_4	-0.4297	$x10^{-20}$	-0.01298	$x10^{-20}$	-0.008758	$x10^{-20}$
Q_5	-0.07133	$x10^{-20}$	0.09364	$x10^{-20}$	-0.08957	$x10^{-20}$
Q_6	-3.263	$x10^{-20}$	-2.520	$x10^{-20}$	0.2739	$x10^{-20}$

L^{-1} (A')	S_4		S_5		S_6	
Q_1	0.2852	$x10^{-20}$	0.1970	$x10^{-20}$	0.7338	$x10^{-20}$
Q_2	0.2160	$x10^{-20}$	0.2832	$x10^{-20}$	-0.2307	$x10^{-20}$
Q_3	-0.006361	$x10^{-20}$	0.01075	$x10^{-20}$	-0.006677	$x10^{-20}$
Q_4	0.7216	$x10^{-12}$	0.2586	$x10^{-12}$	-0.3207	$x10^{-12}$
Q_5	-0.1575	$x10^{-12}$	0.6466	$x10^{-12}$	0.09420	$x10^{-12}$
Q_6	1.764	$x10^{-12}$	-0.09052	$x10^{-12}$	3.826	$x10^{-12}$

Table 25. (contd.)

CH_2BrCl

L (A")	Q_7	Q_8	Q_9
S_7	0.6502×10^{20}	0.01516×10^{12}	0.4195×10^{20}
S_8	-0.09999×10^{20}	1.050×10^{12}	-0.1083×10^{20}
S_9	-0.7002×10^{20}	0.004791×10^{12}	0.8674×10^{20}

L^{-1} (A")	S_7	S_8	S_9
Q_7	1.009×10^{-20}	0.1806×10^{-20}	0.8135×10^{-20}
Q_8	-0.01227×10^{-12}	0.9492×10^{-12}	-0.01515×10^{-12}
Q_9	0.4895×10^{-20}	0.03152×10^{-20}	0.7577×10^{-20}