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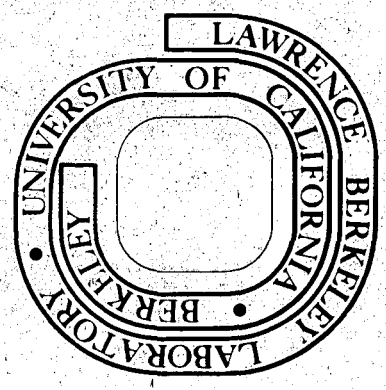
POTENTIAL FUNCTION FOR THE ν_7 VIBRATION OF
PHOSPHORUS PENTAFLUORIDE

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Kenneth S. Pitzer, and Ira W. Levin

April 1975

Prepared for the U. S. Energy Research and
Development Administration under Contract W-7405-ENG-48

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POTENTIAL FUNCTION FOR THE ν_7
VIBRATION OF PHOSPHORUS PENTAFLUORIDE

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ABSTRACT

The gas phase Raman spectrum of the ν_7 fundamental of PF_5 has been observed under spectral resolutions approaching 1 cm^{-1} . With the use of a two dimensional harmonic oscillation basis set and a potential function of the form $V(\rho, \phi) = \frac{1}{2} a \rho^2 - b \cos(3\phi) \rho^3 + c \rho^4$, the observed spectrum was interpreted to yield a barrier to axial-equatorial fluorine atom interchange of 1371 cm^{-1} (3.92 KCal/mole).

INTRODUCTION

The ν_7 vibrational transition of the trigonal bipyramidal molecule PF_5 has been the subject of numerous investigations. In earlier work,¹ ν_7 could not be unambiguously assigned to either the E' equatorial bend or the E' axial bend, or some appropriate linear combination of these modes. More recent studies,²⁻⁶ however, clearly establish that ν_7 is predominantly the E' equatorial bending distortion. Both the low frequency of the ν_7 vibration and its role in the axial-equatorial fluorine interchange process,^{1^a,7-9} prompted an investigation¹⁰ in which gas phase Raman spectra of ν_7 were measured in an effort to observe "hot" bands. In the Raman spectrum, Witt et. al.¹⁰ observed the fundamental at 174 cm^{-1} and an additional transition at 177 cm^{-1} . They correctly reasoned that a one-dimensional anharmonic potential was not consistent with the observed spectrum because a progression of other transitions would certainly be observed to either the high or the low energy side of the fundamental depending on the order (cubic and/or quartic) and the sign of the anharmonic term(s). They suggested other possibilities for the additional transition, but none were pursued in detail.

One important aspect of the ν_7 vibration which has not been properly considered in previous work is that ν_7 is a doubly degenerate vibration; hence, it must be described by a two-dimensional potential. To the usual isotropic harmonic oscillator approximation, which gives a potential of $D_{\infty h}$ symmetry, one gets evenly spaced vibrational levels

with a degeneracy of $(n+1)$. This is an accidental degeneracy because the maximum allowed true degeneracy under $D_{\infty h}$ is two. If anharmonic terms are added to the harmonic potential this accidental degeneracy would be lifted; thus all levels with $n \geq 2$ would be split into two or more sublevels. We can go one step further and lower the symmetry of the potential to D_{3h} , which is the actual symmetry of the force field for a $MF_5(D_{3h})$ molecule. This anisotropy is especially important for PF_5 because motions along the E' bending coordinates leading to axial-equatorial interchange are expected to be energetically favored over other directions in E' bending space. Under D_{3h} symmetry, which also has a maximum allowed true degeneracy of two, some of the doubly degenerate levels under $D_{\infty h}$ will be further split into two components. In general, it is the lifting of the excess degeneracy of the isotropic harmonic oscillator which gives rise to the extra transition observed by Witt et. al. In order to support this interpretation we have re-measured the Raman spectra of the ν_7 vibration under higher instrumental resolution than previous investigations and have found additional transitions which are correctly predicted by this approach (i.e., a D_{3h} potential).

EXPERIMENTAL

Raman spectra of gaseous PF_5 were observed at room temperature for sample pressures varying from 500-700 torr. Figure 1 displays a survey spectrum for ν_7 obtained with a multipass gas cell and a Jarrell Ash Model 400 Raman spectrophotometer equipped with an argon ion laser operating at 600 mw at 488.0 nm.¹¹ Survey traces were scanned with spectral slits of 2.0 cm^{-1} . Spectra requiring larger chart dispersions and narrower slit widths (about 1 cm^{-1}) for determining accurate frequency measurements were recorded with a Spex Raman spectrophotometer. Exciting radiation of about 1 w in either the 488.0 or 514.5 nm lines of an argon ion laser was used with the Spex spectrophotometer. For the higher resolution studies the sample was contained in a cylindrical glass cell equipped with a Teflon stopcock. Both back and forward scattered Raman radiation from two passes of the laser beam were collected with suitable spherical mirrors and an f/1 lens. Dispersed radiation was detected with a surface cooled ITT FW 130-S20 surface photomultiplier.

Commercial samples of PF_5 were purified to remove N_2 and CO prior to scanning a spectrum. Other impurities, such as SiF_4 and POF_3 , were present in small quantities; however, transitions from these species do not occur in the 180 cm^{-1} region of interest. Multiple spectral scans were recorded under various instrumental conditions for a number of sample pressures to verify the existence of weak features. Long

integration times of 10-50 seconds, coupled with slow scan speeds of $0.5 \text{ cm}^{-1}/\text{min}$, were used to record the spectra from which the reported frequencies were determined. The large chart sizes of these scans precludes direct journal reproduction; consequently, only a survey scan is presented.

Spectra observed with the Spex monochromator at 1 cm^{-1} resolution differ, however, from the survey scan in Fig. 1 in several respects. The broad peak at 165 cm^{-1} is split into two features at 164 and 167 cm^{-1} . The 175 cm^{-1} feature displays a shoulder at 173 cm^{-1} . A shoulder also appears on the high frequency side of the 178 cm^{-1} Q branch about 180 cm^{-1} . Finally, in addition to the 191 cm^{-1} feature, a weaker transition is discerned at 194 cm^{-1} .

DISCUSSION

The v_7 energy levels for PF_5 were computed with a potential of the form

$$V(\rho, \phi) = \frac{1}{2} a\rho^2 - b\cos(3\phi)\rho^3 + c\rho^4$$

where a , b , and c are potential constants and ρ and ϕ are polar displacement coordinates which are related to the conventional symmetry coordinates (S_{7x}, S_{7y}) ¹² by the usual transformations. The advantage of displaying the potential in polar displacement coordinates is to make it obvious that the potential has D_{3h} symmetry. The derivation of this potential, to be discussed in a future paper, is analogous to a recent formulation of the one-dimensional potential describing the inversion of $\text{MX}_3(\text{C}_{3v})$ molecules.¹³ Essentially, a pseudo-Jahn-Teller effect has been used to couple the D_{3h} ground electronic state to higher states via the axial-equatorial interchange symmetry coordinates (S_6, S_7) .¹²

A model¹⁴ has been developed which shows that the above potential not only represents the potential for small displacements in the equatorial bend coordinates but also approximates the axial-equatorial fluorine interchange potential. Near the equilibrium structure the axial-equatorial interchange path occurs mainly along the equatorial bend coordinates.

Approximate estimates of the constants a, b and c can be obtained by use of this model at large displacements. The results are

$$\begin{aligned} \underline{a} &= K_0 \\ \underline{b} &= \frac{K_0}{2S_0} \\ \underline{c} &= \frac{K_0}{8S_0^2} \end{aligned} \quad (2)$$

where K_0 is the curvature of the potential at the D_{3h} equilibrium geometry and S_0 is the location of the C_{4v} maximum along the interchange path of lowest energy (for the $\phi = 0^\circ, 120^\circ, 240^\circ$ directions) which connects equivalent D_{3h} configurations. These relations were derived by requiring the first derivative of the above potential to be zero at the two neighboring D_{3h} configurations (i.e., at $\rho = 0, 2S_0$) and at the C_{4v} transition intermediate ($\rho = S_0$). In addition the second derivative of the potential was set equal to the curvature K_0 at the equilibrium geometry.

The curvature K_0 is estimated as the force constant in the expression $K_0 = (5.9 \times 10^{-7})(\nu_7^2)M_7$, where ν_7 is 175 cm^{-1} and M_7 is the reduced mass associated with the S_{7x} coordinate. M_7 was calculated by the high-low frequency separation¹⁵ for the E' symmetry species in which S_7 is taken as the low frequency vibration. Thus $K_0 \approx .089 \text{ mdyn/\AA}$. Geometrically, the C_{4v} configuration is not unique; hence, only a reasonable estimate of $S_0 = .8 S_{7x}(D_{3h}) = 1.57 \text{ \AA}$ can be made. $S_{7x}(D_{3h})$ represents the change in the S_{7x} coordinate in moving between neighboring D_{3h} con-

figurations. From these values of K_0 and S_0 we estimate $a = .089$ mdyn/Å, $b = .028$ mdyn/Å² and $c = .0045$ mdyn/Å³. If one substitutes the above relations into the potential and evaluates the potential at the C_{4v} geometry ($\rho = S_0$), an estimate of the axial-equatorial interchange barrier can be made. We find $E(C_{4v}) = \frac{K_0 S_0^2}{8} = 1371 \text{ cm}^{-1}$ (392 Kcal/mole). A more detailed discussion of axial-equatorial interchange barriers for the entire MF_5 series (PF_5 , AsF_5 , VF_5 , TaF_5 , NbF_5) will follow in a future paper.

We now return to the refinement of the constants a , b and c using the Raman data. The constants a , b and c were chosen to reproduce the $0 \rightarrow 1$ ($A_1' \rightarrow E'$) vibrational transition at 175 cm^{-1} , the $1 \rightarrow 2$ ($E' \rightarrow E'$) transition at 178 cm^{-1} , and the $1 \rightarrow 2$ ($E' \rightarrow A_1'$) transition at 164 cm^{-1} . The fit to the remaining levels, obtained with these constraints, is summarized in Table 1. The values of the potential constants were determined to be $a = .09080$ mdyn/Å, $b = .03$ mdyn/Å², and $c = .007$ mdyn/Å³. The energy level calculation was done using a two-dimensional harmonic oscillator basis set and the coordinate transformation methods of Gwinn et. al.¹⁶ A maximum N value of $N = 15$ was used where $N = n_x + n_y$ is the total vibrational quantum number of the basis state. The value of $N = 15$ yielded a total of 136 basis functions. The reduced mass was calculated to be $M_7 = 4.901$ amu using Wilson's high-low frequency approximation.¹⁵

Table 1 demonstrates two essential properties of the above potential. First it shows that one can simultaneously fit the $0 \rightarrow 1$, and the two

1→2 transitions. Secondly, it shows the remarkably good agreement obtained for all six 2 → 3 transitions while only trying to fit the 0 → 1 and 1→2 transitions. It should be mentioned that we refined the potential parameters a, b, c by hand only to the point where it was quite clear that our D_{3h} potential is an adequate representation of the actual potential.

The sensitivity of the computed 1 → 2 transitions for various values of a, b and c is displayed in Figure 2. These curves were generated for various values of b and c while the harmonic constant a was always adjusted to place the 0 → 1 transition at the observed value of 175 cm^{-1} . There are two interesting features to these curves: (1) the $E' \rightarrow A_1'$ transition drops off sharply with increasing b, and (2) the $E' \rightarrow E'$ transition is relatively insensitive to changes in b. In fact, the 3 cm^{-1} difference between the 0 → 1 and 1 → 2 ($E' \rightarrow E'$) transitions is largely due to the quartic constant c. These observations can be qualitatively accounted for by examining the second order perturbations of the cubic term evaluated in the isotropic two dimensional harmonic oscillator basis.

It is well-known that the wave functions of an isotropic two dimensional oscillator can be written¹⁷ in polar coordinates as

$$\psi = l_{nk}(\rho) e^{im\phi} \quad |m| = 0, 1, 2, \dots$$

$$n = |m| + 2k \quad k = 0, 1, 2, \dots$$

The resulting states and their symmetry under the D_{3h} point group are found in Table 2. The $\cos(3\phi)$ dependence of the cubic term will

mix states with $\Delta m = \pm 3$. For the A_1' state of the $n = 2$ level we see that it is connected by the cubic term only to states higher in energy, such as the two A_1' states of the $n = 3$ level. To second order this can only serve to lower the $1 \rightarrow 2$ ($E' \rightarrow A_1'$) transition with increasing b relative to 175 cm^{-1} . On the other hand the E' state of the $n = 2$ level is connected to the E' state directly beneath and the E' state directly above, which tends to cancel the second order effect of the cubic term and leaves the $1 \rightarrow 2$ ($E' \rightarrow E'$) transition relatively insensitive to b .

In addition to the frequencies assigned in Table 1, a feature at 173 cm^{-1} and, possibly, a feature at 152 cm^{-1} remain unassigned. The observed spectrum is further complicated by the vibration-rotation interaction expected for the degenerate E' vibrational mode. Levin³ and Lockett et. al¹⁸ have shown that ζ_7 should be about -0.15 . Through a consideration of the Coriolis ζ sum rule and the Coriolis ζ interaction constants observed for ν_5 and ν_6 , Witt et al¹⁰ computed the contours expected for a vibration-rotation contour for $-0.40 \leq \zeta_7 \leq 0.30$. The $\Delta\nu_{\text{OP,RS}}$ varies from 20.0 to 23.5 cm^{-1} for this variation in ζ . We assign the features at 167 and 187 cm^{-1} as the OP and RS maxima associated with the 175 cm^{-1} ($0 \rightarrow 1$) transition. This corresponds to a $\Delta\nu_{\text{OP,RS}}$ of 20 cm^{-1} with an estimated uncertainty of about 2 cm^{-1} ; that is, the $\Delta\nu_{\text{OP,RS}}$ splitting is consistent with a value for ζ between 0.0 and -0.4 . Using the form of the potential in eq. (1), the calcula-

tion could be used to determine the nine Q branches for the 3 → 4 hot band transitions. On the basis of populations determined from vibrational partition functions, these transitions are expected to be significantly weaker than the 0→1, 1→2 and 2→3 transitions. The weakness of the 3→4 transitions coupled with their number, prevents assignment of these features from traces recorded under the present instrumental conditions.

As one might expect the other $MF_5(D_{3h})$ molecules such as AsF_5 , TaF_5 and NbF_5 should show a ν_7 spectra very similar to that of PF_5 . We are currently studying AsF_5 and find this to be the case.

ACKNOWLEDGMENTS

We wish to thank both Dr. James Willis for his aid in obtaining survey Raman spectra for PF_5 and Professor H. L. Strauss for helpful discussions. L.S.B., J.J.K. and K.S.P. express their appreciation to the U. S. Atomic Energy Commission for their support.

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11. Certain commercial instruments are identified to specify completely the experimental procedure. In no case does such identification imply a recommendation or endorsement by the institutions involved in this research.
12. The relevant symmetry coordinates for the E' species bending modes are defined as follows:

$$S_{6x} = 1/\sqrt{12} r_a \Delta (2\beta_{14} - \beta_{24} - \beta_{34} + 2\beta_{15} - \beta_{25} - \beta_{35})$$

$$S_{6y} = 1/2 r_a \Delta (\beta_{24} - \beta_{34} + \beta_{25} - \beta_{35})$$

$$S_{7x} = 1/\sqrt{6} r_e \Delta (2\alpha_{23} - \alpha_{12} - \alpha_{13})$$

$$S_{7y} = 1/\sqrt{2} r_e \Delta (\alpha_{13} - \alpha_{12}) ,$$

where α represents the equilibrium PF_3 equatorial angles and β represents the equilibrium axial angles, r_a and r_e are defined as the equilibrium axial and equatorial bond distances, respectively.

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Table 1

Observed, computed frequencies (cm^{-1}) and assignments for Q branches in ν_7 region

Transition ^a	Species	ν_{calc}	ν_{obs}
0 → 1	$A_1' \rightarrow E'$	175.0	175
1 → 2	$E' \rightarrow E'$	177.9	178
	$E' \rightarrow A_1'$	164.6	164
2 → 3	$E' \rightarrow E'$	154.7	159 (w)
	$A_1' \rightarrow E'$	168.0 ^b	...
	$E' \rightarrow A_1'$	178.4 ^b	
	$E' \rightarrow A_1'$	182.0	180 Sh
	$A_1' \rightarrow A_1'$	191.7	191 Sh
	$A_1' \rightarrow A_1'$	195.3	194

^bThe positions of the 168.0 and 178.4 cm^{-1} features are perhaps obscured by the "OP" maximum and the 178 cm^{-1} Q branch, respectively.

^aUnder D_{3h} symmetry for an E' vibration, such as ν_7 , all rotation-vibration transitions are allowed in the Raman spectrum, while in the infrared spectrum, only $\Delta m = \pm 1$ are allowed.

Table 2

States and symmetries under D_{3h} for an isotropic
two dimensional harmonic oscillator

level (n)	degeneracy	m	k	symmetry
0	1	0	0	A_1'
1	2	1	0	E'
2	3	0	1	A_1'
		2	0	E'
3	4	1	1	E'
		3	0	$2A_1'$
4	5	0	2	A_1'
		2	1	E'
		4	0	E'
5	6	1	2	E'
		3	1	$2A_1'$
		5	0	E'

FIGURE CAPTIONS

Fig. 1. Survey gas-phase Raman spectrum for the ν_7 vibration of PF_5 .

Fig. 2. Calculated $1 \rightarrow 2$ (ν_7) transitions for PF_5 .

O represents the $E' \rightarrow A_1'$ transition.

Δ represents the $E' \rightarrow E'$ transition.

For curves A, B and C, $c = 0.0, 0.005$ and $0.010 \text{ m dyn/\AA}^3$ respectively.

PF₅
ν₇

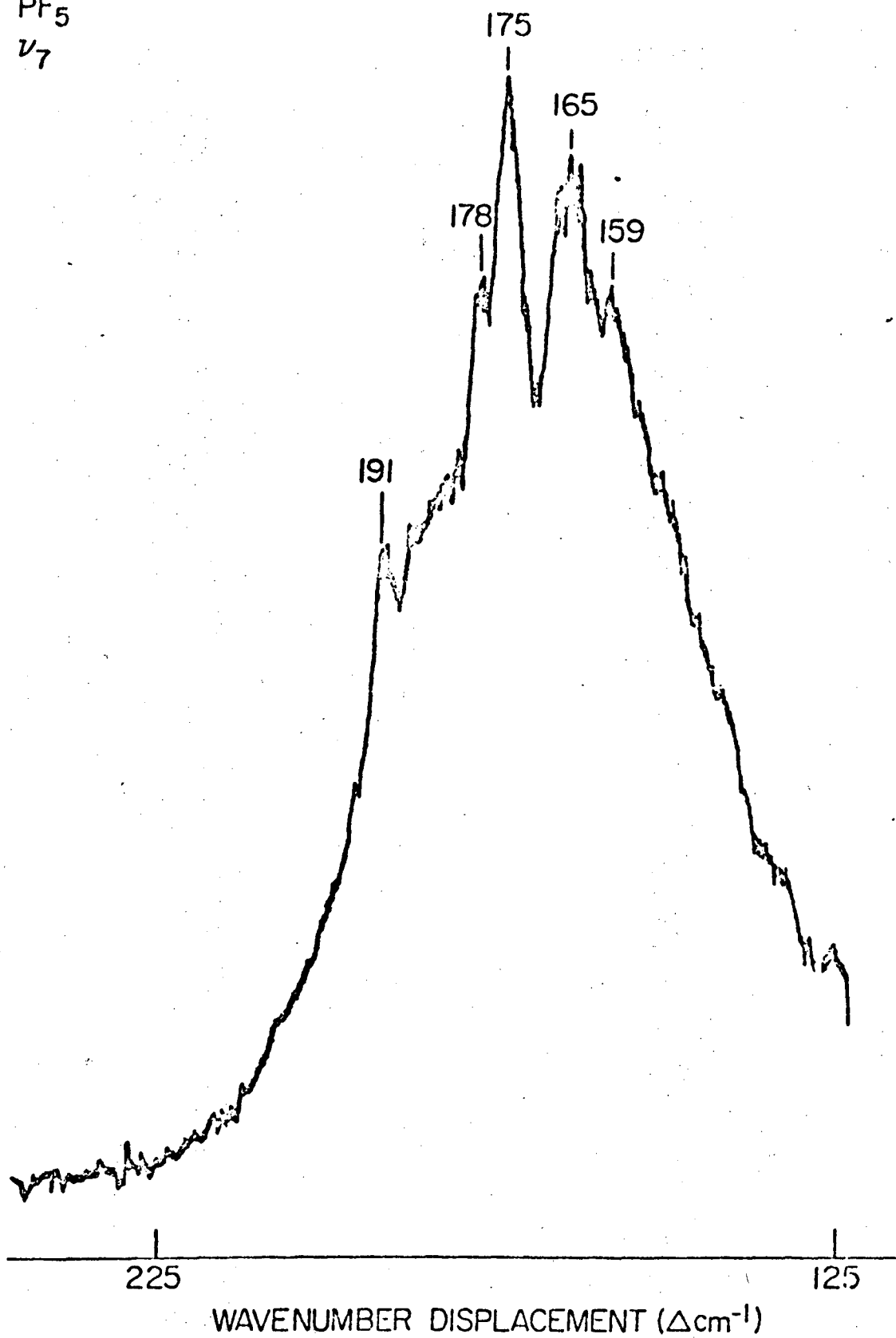


Fig. 1.

CALCULATED 1-2 (ν_7) TRANSITIONS FOR PF₅

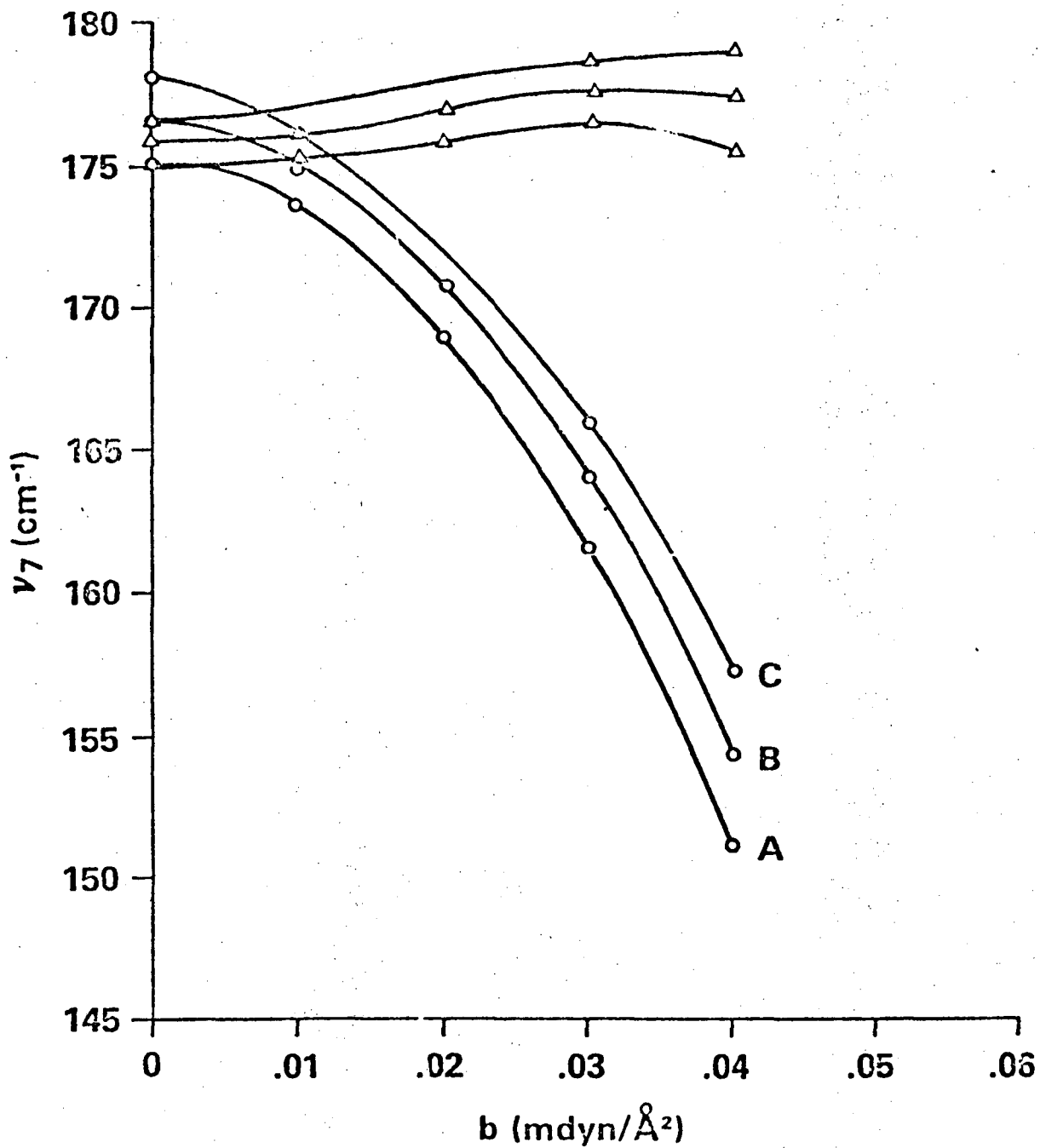


Fig. 2.

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