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James E. Griffiths

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Molecular Structure of CF₃PCl₄: Infrared and Raman Spectra^{*}

JAMES E. GRIFFITHS

Bell Telephone Laboratories, Inc., Murray Hill, New Jersey (Received 14 July 1964)

The basic structure of the CF_4PCl_4 molecule has been established from a study of its vibrational spectrum. The CF_4 group occupies an axial position in the trigonal bipyramidal structure but no information is obtained concerning the height of the barrier to internal rotation.

All of the active fundamentals are assigned in the Raman spectrum $(\Delta \nu = 50-1500 \text{ cm}^{-1})$ and supplementary data were obtained from a pressure limited gas-phase study of the infrared spectrum (2000-280 cm⁻¹). Fundamental frequencies are: $a_1 = 1145$, 743, 493, 374, 324, 260; e = 1168, 587, 543, 304, 239, 193, and 94 cm⁻¹.

The compound is unstable thermally decomposing into CF₃Cl, CF₃PCl₂, PCl₃, and PCl₅.

INTRODUCTION

DURING the 15 years since the discovery of the fluorocarbon phosphorus compounds¹ a great deal of information about their chemistry has been collected.² Little definitive work using physical methods, however, has been done on their structures.^{3,4}

At the present time, there is little if any substantial evidence suggesting that the fluorocarbon phosphines and phosphoranes have anything except trigonal pyramidal and trigonal bipyramidal structures, respectively.^{2,5} Recent results of an ¹⁹F nuclear magnetic resonance study of CF₃PF₄, (CF₃)₂PF₃, and (CF₃)₃PF₂ and related molecules are consistent with trigonal bipyramidal structures but do not uniquely establish the basic framework in all cases.⁶ On the other hand, tetragonal pyramidal structures in some of the molecules studied were also considered, but evidence for such a framework does not appear to be as conclusive as in the case of a solid-state x-ray study of $P(C_6H_5)_5$ and Sb(C₆H₅)₅.⁷

The related trifluoromethylchlorophosphoranes, have not been studied in much detail either. Conductance measurements on $(CF_3)_2PCl_3$ and $(CF_3)_3PCl_2$ in acetonitrile suggest that observed differences in their behavior might be related to different structural features in these molecules.⁵ Definite evidence in support of the suggestion, however, is still lacking. The structure of the simplest compound in this class, CF_3PCl_4 , has not been investigated heretofore although detailed studies^{8,9} of its prototype, PCl₄F support a trigonal bipyramidal structure with an axial F atom.

It is of interest therefore to try to establish the internal structures of the fluorocarbonhalophosphoranes and the relative positions of the fluorocarbon groups therein. The first of these, CF_3PCl_4 , is treated in this paper using Raman and infrared vibrational spectroscopic methods.

EXPERIMENTAL

All volatile compounds were manipulated in a glass vacuum system in which stopcocks and ground-glass joints were lubricated with a chlorofluorocarbon grease.¹⁰ Trifluoromethyldichlorophosphine was obtained from the room-temperature interaction of CF₃PI₂¹ with excess mercuric chloride in vacuo. Subsequent fractional vaporization and condensation yielded a tensimetrically pure sample of CF_3PCl_2 (vp at 17.3°, 330.4 mm; literature value.11 329.1 mm). Purified chlorine gas (24.19 mM) was condensed in small portions on 24.2 mM of CF₃PCl₂, and the mixture was warmed slowly from -196° C to room temperature. The product was purified by passing it through a series of U-tube traps cooled to -45.3° , -64° , -95° , and -196° C; the desired fraction was retained at -64° C forming a white crystalline solid at that temperature (mp of CF₃PCl₄, -52° C¹²). Only traces of a slightly volatile white solid, presumably PCl5, remained behind when the more volatile CF_3PCl_4 from the -64° trap was condensed in an evacuated Raman sample tube. The latter was made from 7-mm-o.d. glass tubing and the contents were sealed under vacuum.

Raman frequency displacements from the 4358-Å Hg line were recorded photoelectrically using a Cary

^{*} Presented in part at the Symposium on Molecular Structure and Spectroscopy, Ohio State University, June 1964, Paper K11, and before the Inorganic Chemistry Division of the American Chemical Society, Chicago, Illinois, September 1964.

Chemical Society, Chicago, Illinois, September 1964. ¹ F. W. Bennett, G. R. A. Brandt, H. J. Emeléus, and R. N. Haszeldine, Nature 166, 225 (1950). ² H. C. Clark, Advan. Fluorine Chem. 3, 19 (1963), and refer-

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³ H. J. M. Bowen, Trans. Faraday Soc. 50, 463 (1954).

⁴ J. Donohue, Acta Cryst. **15**, 708 (1962) and references cited therein.

⁵ H. J. Emeléus and G. S. Harris, J. Chem. Soc. **1959**, 1494. ⁶ E. L. Muetterties, W. Mahler, and R. Schmutzler, Inorg.

Chem. 2, 613 (1963). ⁷ P. J. Wheatley, Proc. Chem. Soc. 1962, 251; J. Chem. Soc. 1964, 2206.

⁸ R. R. Holmes, R. P. Carter, Jr., and G. E. Peterson (unpublished results).

⁹ J. E. Griffiths, R. P. Carter, Jr., and R. R. Holmes, J. Chem. Phys. 41, 863 (1964). ¹⁰ Halocarbon Products Corporation, 82 Burlews Court,

Halocarbon Froducts Corporation, 82 Burlews Court, Hackensack, New Jersey. ¹¹ L. K. Petersen and A. B. Burg, J. Am. Chem. Soc. **86**, 2587

^{(1964).} ¹² W. Mahler and A. B. Burg, J. Am. Chem. Soc. 80, 6161 (1958).

Model 81 spectrophotometer and depolarization factors were obtained employing cylindrical polaroid sheets. The temperature within the lamp housing of the instrument was reduced to about 40°C by inserting a watercooled jacket between the lamp and the sample. Despite this precaution, the sample partially decomposed during 6 h of irradiation forming CF₃Cl, CF_3PCl_2 , PCl_3 , and PCl_5 in much the same way as CF₃PBr₄ has previously been shown to break down.¹³ No Raman lines due to CF₃Cl or CF₃PCl₂ were observed, however, since they tended to confine themselves in the vapor state in the empty parts of the sample tube outside of the lamp housing. The strongest Raman lines of PCl₅ and PCl₃ were observed, and their presence was confirmed after completion of the Raman measurements by an examination of the infrared spectrum of the sample. Trifluoromethyl chloride¹⁴ and CF₃PCl_{2¹⁵} were also identified as major products of the thermal decomposition of CF₃PCl₄ in the same way and by separating them in a pure form.

Infrared spectra were recorded using a Perkin-Elmer Model 421 spectrophotometer in the range 2000–280 cm^{-1} employing a double-grating interchange. Samples were confined in a 10-cm glass cell fitted with CsI windows. The measurements, however, were limited by the small pressure range available with CF₃PCl₄. The upper limit was about 9 mm because the vapor pressure of the sample at 20°C is only about 10 mm.¹² Fortunately, the fundamentals which are most difficult to study in the Raman effect because of a lack of intensity give rise to very strong infrared absorption bands.

RESULTS

The Raman spectrum is shown in Fig. 1 and the infrared spectrum in regions of interest appears in Fig. 2. The results are collected in Table I. The Raman spectrum of liquid PCl₃ is reproduced in Fig. 4.

SELECTION RULES

As a first approximation CF3PCl4 may be considered to be a derivative of PCl₅. Since PCl₅ has a trigonal bipyramidal structure,^{16,17} the CF₃ group in CF_3PCl_4 may be in an axial [Fig. 3(a)] or in an equatorial [Fig. 3(b)] position. A less likely model involves a tetragonal pyramid with the CF₃ group at the apex and the four chlorine atoms forming the corners of the base [Fig. 3(c)]. The case where the

 CF_3 group is at a corner of the basal plane of a tetragonal pyramid [Fig. 3(d)] is considered to be so unlikely that it is not discussed further. It is shown, however, that one of the other models fits the data so much better that the neglect of the least likely model is justified.

The models may be further defined in terms of the height of the barrier to internal rotation of the CF₃ group against the residual framework of the molecule. The two extreme cases for each structural model involve a high and a low (or zero) barrier. For the high-barrier cases, the usual group-theory analyses predict C_{3v} , C_s , and C_s as the effective point groups for the CF₃ group in the axial and equatorial positions in the trigonal bipyramidal models and in the axial position of the tetragonal pyramidal model, respectively. For the low-barrier cases the effective point groups may be higher and by assuming that the CF₃ group is the attached top and the rest of the molecule is the framework, the secular equations can be factored on the basis of higher symmetries.¹⁸ The results of these operations are summarized in Table II, and selection rules for each of the six models appear as well.

ASSIGNMENTS AND DISCUSSION

The data of Table I can most conveniently be analyzed in terms of the model belonging to the C_{3v} point group, i.e., a CF₃ group in an axial position of a trigonal bipyramidal structure. For this structure the Raman and infrared spectra should consist of thirteen active fundamentals, six of which are expected to be polarized. It is the depolarization data which is capable of offering the most convincing evidence for the structure. Table II shows, for example, that the total number of polarized lines in the Raman effect is rather sensitive to the basic structure and to the height of the internal torsional barrier. It is only in the case of the trigonal bipyramidal structure with an axial CF3 group where the number of polarized lines gives no information about the height of the torsional barrier.

Before proceeding to the analysis of the Raman spectrum, it is essential to recognize the effects caused by the presence of PCl₃ and PCl₅ which occur as impurities because of the thermal instability of CF₃PCl₄. The decomposition of this molecule, which parallels that of CF₃PBr₄, occurs in two ways¹³:

$$x CF_3 PCl_4 \rightarrow x CF_3 Cl + x PCl_3$$
, (1)

$$yCF_{3}PCl_{4}+yPCl_{3}\rightarrow yCF_{3}PCl_{2}+yPCl_{5}.$$
 (2)

The net result is given by (1)+(2):

 $(x+y)CF_3PCl_4 \rightarrow xCF_3Cl+yCF_3PCl_2+yPCl_5$

+(x-y)PCl₃. (3)

¹³ A. B. Burg and J. E. Griffiths, J. Am. Chem. Soc. 82, 3514

^{(1960).} ¹⁴ E. K. Plyler and W. S. Benedict, J. Res. Natl. Bur. Std., 47, 202 (1951). ¹⁵ J. E. Griffiths, unpublished observations on the infrared and

Raman spectra of pure CF₃PCl₂ were available for comparison. ¹⁶ G. L. Carlson Spectrochim. Acta 19, 1291 (1963) and refer-

ences cited therein. ¹⁷ M. J. Taylor and L. A. Woodward, J. Chem. Soc. 1963, 4670.

¹⁸ B. L. Crawford and E. B. Wilson, Jr., J. Chem. Phys. 9, 323 (1941). For an application of these principles see, D. F. Eggers, Jr., H. E. Wright, and D. W. Robinson, *ibid.* 35, 1045 (1961)



FIG. 1. Raman spectrum of liquid CF₄PCl₄(AMPL.=amplification, SBSS=single beam, single slit, SBDS=single beam, double slit).

When x > y, as appears to be the case here, PCl₃ causes the greatest effect in the Raman spectrum. Of the four Raman lines of PCl₃, only the pair at 515 and 485 cm⁻¹ appear obvious in the spectrum of CF₃PCl₄. A broad, weak, polarized line is observed at 509 cm⁻¹ and corresponds to $\nu_1(a_1)$ and to a lesser extent $\nu_3(e)$ of the PCl₃ impurity. The relative intensity of this line increases with time. The remaining lines of PCl₂ at 260 and 189 cm⁻¹ are not readily distinguishable because they are covered by the more intense lines at 260 and 193 dm⁻¹ arising from CF₃PCl₄. That these two lines are not due to PCl₃ alone was established by a comparison of the intensities of the lines in the sample and the lines determined for pure PCl₃ (cf. Fig. 4).

The strongest line in the spectrum of PCl₅ was observed as an extremely weak polarized Raman line at 395 dm⁻¹ in the spectrum of CF₃PCl₄. None of the

Infrared (gas)		R	aman (liquid))	
 cm ¹	Ι	Δν	Polarization	I	Assignments
•••	•••	94	0.86	52	$\nu_{14}(e)$
•••	•••	193	0.86	14	$\nu_{13}(e)$
•••	•••	239	0.86	14	$\nu_{12}(e)$
•••	•••	260	0.8	21	$\nu_6(a_1)$
•••		304	0.87	8	$v_{11}(e)$
		324	0.8	4	$\nu_{5}(a_{1})$
• • •		374	0.33	100	$\nu_4(a_1)$
•••	•••	395	0.68	<1	PCl ₅ impurity
427	w				CF ₂ PCl ₂ impurity
		493	0.40	12	$v_{2}(a_{1})$
507	vs	510	0.35	- 9	PCl ₂ impurity
543	m	540	0.86	4	$r_{n}(e)$
587	vs	584	0.87	2	$v_0(\ell)$
616	w		•••		$y_4 + y_{12} = 613(E)$
•••		728		16	$y_2 + y_{12} = 732(E)$
		743	0.33	$\hat{7}$	$v_{0}(n_{1})$
		779	(n)	3	$y_1(x_1)$ $y_1(x_1) = 779(A_1 + A_2 + E)$
		,	(1)	0	$y_{10} + y_{12} = 777(A_1 + A_2 + E),$
1145	178	1144	(n)	16	$y_{1} + y_{13} - y_{1} + (211 + 212 + 22)$
1168	10	1168	(P)	2.0	$r_1(\omega_1)$
1100	v 3	1232		1 2	$v_8(0)$ $v_8+v_9=1236(4.)$
		12.52		1.2	F2 F3 - 1200(21[)

TABLE I. Vibrational spectrum of CF₃PCl₄.*

^a s=strong, m=medium, w=weak, v=very, p=polarized. Raman line intensities are measured relative to the strongest being equal to 100. The so-called "lamp ghosts" near $\Delta \nu$ =143 and 167 cm⁻¹, which are shown in Fig. 1, are not listed in this table.



FIG. 2. Infrared spectrum of gaseous CF₃PCl₄.

TABLE II. Structure and symmetry possibilities for CF3PCl4.

STRUCTURAL	TRIGONAL BIPYRAMID				TETRAGONAL PYRAMID	
CF3 POSITION	AXIAL		EQUATORIAL		AXIAL	AXIAL
EFFECTIVE POINT GROUP	C _{3V}	C3V	C ₃	C _{2V}	Cs	C4V
BARRIER HEIGHT	нісн	LOW	HIGH	LOW	HIGH	LOW
TOTAL FUNDAMENTALS	14	14	21	17	21	15
RAMAN ACTIVE	13	13	21	17	21	14
INFRARED ACTIVE	13	13	21	15	21	11
COINCIDENCES	13	13	21	15	21	11
IR-R INACTIVE	1	1	0	0	0	1
RAMAN POLARIZED	6	6	13	7	13	5

remaining lines could be attributed to CF_3Cl or CF_3PCl_2 , the spectra of which were available for comparison.^{14,15} Since these are the most volatile components of the mixture, they tended to exist in the vapor phase in the empty parts of the Raman sample cell.

Of the remaining Raman lines, three at 728, 778, and 1232 cm⁻¹ arise from combination tones and these will be discussed later.



FIG. 3. Possible structures for CF_3PCl_4 .



FIG. 4. Raman spectrum of liquid PCl₃.

With the above features of the spectrum established there remain thirteen lines and six of these are polarized as expected for the C_{3v} model. The vibrations of the atoms in CF₃PCl₄ can be considered to a reasonable approximation to consist of those in an isolated CF₃ group, in an isolated PCl₄ group, and those which are not localized within either group.

In the first there are two C-F stretching modes $(a_1 \text{ and } e)$ and two CF₃ deformation modes $(a_1 \text{ and } e)$, and the frequencies of these may be expected near 1100-1200 cm⁻¹, 745 and 550 cm⁻¹ by comparison with the spectra of a wide range of compounds containing a single CF₃ group.¹⁹ The only molecule containing a PCl₄ group which has been studied in detail is PCl₄F.⁹ By comparison, one expects the antisymmetric and symmetric PCl₃ stretching and deformation modes to occur near 590, 400, 310, and 260 cm⁻¹, respectively. The axial P-Cl stretching mode is expected at a slightly lower frequency than the symmetric PCl₃ stretching mode. A value near 340 cm⁻¹ seemed reasonable.

The frequency of the C-P stretching mode is especially dependent upon the corresponding bond distance, and because these distances are long in fluorocarbon phosphorus compounds,³ a frequency in the 450–550 cm⁻¹ range was expected. Since the CF₃ and PCl₄ rocking modes were expected to be strongly coupled to other modes, the frequencies of these could not be predicted. The C-P-Cl (axial) bending mode, however, was expected near 100 cm⁻¹. It has previously been noted that similar modes in PF₅, PCl₂F₃, PCl₃F₂, PCl₄F, and PCl₅ occur near 100 cm⁻¹ and do not appear to shift appreciably as the masses of the atoms are changed.⁹

The two lines at 1144 and 1168 cm⁻¹ are assigned to the symmetric and antisymmetric C-F stretching modes $\nu_1(a_1)$ and $\nu_8(e)$, respectively, on the basis of comparisons with other assignments made for molecules containing a CF₃ group¹⁹ and on the strength of polarization information. The low intensity and proximity of these lines made the polarization measurements much less reliable than one would like. The infrared data (Fig. 2, Table I) do not clarify this point either because the moments of inertia parallel and perpendicular to the symmetry axis are both large and are not expected to be greatly different. Thus, the P-R separation in the band contour of the parallel band was not resolved. The ambiguity, however, is not too important because at these high frequencies a reversal of the assignments would have little effect on the calculated thermodynamic quantities. The CF₃ deformation modes $\nu_2(a_1)$ and $\nu_{10}(e)$ occur at 743 and 540 cm⁻¹, respectively. The first is polarized and the second is depolarized as required.

The antisymmetric stretching vibration of the PCl₃ moiety, $\nu_9(e)$, is assigned to the weak depolarized Raman line at 584 cm⁻¹ by comparison with a similar assignment for a line at 592 cm⁻¹ in the Raman spectrum of PCl₄F. In the gas-phase infrared spectrum, this fundamental is observed as a very strong band at 588 cm⁻¹. The symmetric PCl₃ and P-Cl (axial) stretching modes $\nu_4(a_1)$ and $\nu_5(a_1)$ are assigned to the two polarized lines at 374 and 324 cm⁻¹, respectively. It is significant to note that the 374-cm⁻¹ line is the most intense in the Raman effect, but it could not be detected in the infrared at the limited pressure of gas available. The corresponding mode in PCl₄F, however, was detected without difficulty in both spectra. If the equatorial chlorine atoms are not coplanar with phosphorus, the symmetric stretching mode should have appreciable intensity in the infrared. As the chlorine atoms approach coplanarity with the central atom the intensity of the infrared band should decrease reflecting a decrease in $(\partial M_z/\partial \xi_4)^2$. Since it was not observed, it is suggested that in CF₃PCl₄ the C-P-Cl₃ angle must be close to 90°, but in PCl₄F the F-P-Cl₃ angle must be somewhat greater. The latter conclusion is based upon a straightforward calculation of the repulsive forces exerted upon the PCl₃ units in CF₃PCl₄ and PCl₄F by the F atoms in the CF₃ group and the axial chlorine atom in the former and by the axial F and Cl atoms in the latter. The bond lengths which were assumed for this purpose were C-F=1.34, C-P=1.94, \angle FCF= 108.5°, \hat{P} -Cl=2.05 in CF₃PCl₄ and P-F=1.57 and P-Cl=2.05 in PCl_4F . These values were those found for $(CF_3)_3P^3$ and for PF_5^{20} and are close to the x-ray values obtained for (CF₃P)₄ and (CF₃P)_{5.4}

The out-of-plane and in-plane PCl₃ deformation modes $\nu_6(a_1)$ and $\nu_{11}(e)$ can be assigned with little if any ambiguity to the polarized line at 260 cm⁻¹ and the depolarized line at 304 cm⁻¹, respectively. The first agrees with the similar assignment for the 260-cm⁻¹ line in PCl₄F, and the second occurs at a slightly lower frequency than the comparable mode in PCl₄F (339 cm⁻¹).

²⁰ L. O. Brockway and J. Y. Beach, J. Am. Chem. Soc. **60**, 1836 (1938).

¹⁹ S. N. Nabi and N. Sheppard, J. Chem. Soc. 1959, 3439.

Four lines remain to be assigned to the four modes which cannot be localized in either group. The highestfrequency polarized line at 493 cm⁻¹ must correspond to the C-P stretching mode $v_3(a_1)$, for the remaining lines are all depolarized and, therefore, correlate with the degenerate modes. The lowest-frequency Raman line at 94 cm⁻¹ is assigned to the C-P-Cl (axial) bending mode by analogy with the assignments made for similar lines in the spectra of PF5, PCl₂F3, PCl₃F2, PCl₄F, and PCl₅.⁹ The two rocking modes are assigned to the depolarized lines at 193 and 239 cm⁻¹. Extensive coupling with other modes is apt to make specific assignments rather speculative. The lower frequency line, however, can best be described as a CF₃ rocking mode because of a similar Raman line already observed in the spectra of CF₃CN (192 cm⁻¹).²¹ The other line by elimination is described as arising from a PCl₄ rocking mode.

Three other weak lines at 728, 779, and 1232 cm^{-1} were also observed, and they are assigned satisfactorily as binary combination tones in Table I.

Although the spectra are in complete agreement with the C_{3v} structure, it is unfortunate that no information could be found for the value of the barrier to internal rotation of the CF₃ group. An examination of a molecular model of CF3PCl4 using atoms with normal covalent radii indicates considerable resistance to internal rotation of the CF₃ group. In this case, however, the frequency of the C-P stretching mode is comparable with that of other fluorocarbon phosphines. It is concluded that the C-P bond is longer in CF₃PCl₄ than in ordinary organophosphorus compounds. This should result in a lower barrier to internal rotation than one would expect on the basis of the molecular model. The symmetric PCl₃ and P-Cl stretching modes also occur at lower frequencies than the comparable modes in PCl₄F and might indicate that the P-Cl bonds are longer in CF₃PCl₄. This feature, however, would also arise if there were a coupling of ν_3 , ν_4 , and ν_5 . It may be possible to extract a quantitative estimate of the barrier height from a study of the pure rotational spectrum of CF₃PCl₄.

Before accepting the vibrational analysis already outlined, it is necessary to re-examine the data in terms of the other structural models. The high-barrier models for the other trigonal bipyramidal structure (equatorial CF_3) and for the tetragonal pyramidal structure can be immediately eliminated because of the large number of lines (21) required for them. It would be unreasonable to expect that eight lines escaped detection. Furthermore, there is no question that the impurity lines attributed to PCl₃ and PCl₅ are actually due to CF_3PCl_4 . The impurities were isolated after the Raman experiments and independently identified.

The low-barrier case for the tetragonal pyramidal

TABLE III. Fundamental frequencies of CF₃PCl_{4.^a}

No.	Species	Activity	Description	cm ⁻¹
1 2 3 4	<i>a</i> 1	R(pol); ir	Sym. CF ₃ stretch Sym. CF ₃ deform. C-P stretch Sym. PCL stretch	1145 743 493 274
56			Axial P-Cl stretch Out of plane PCl ₃ deform.	324 260
7	a_2	inactive	torsion	•••
8 9 10 11 12 13 14	е	<i>R</i> (dp); ir	Antisym. CF_3 stretch Antisym. PCl_3 stretch Antisym. CF_3 deform. Antisym. PCl_3 deform. Rocking (- PCl_4) Rocking (- CF_3) C-P-Cl axial bend	1168 587 543 304 239 193 94

^a Gas phase values are used when available.

model is possible if one line lacked sufficient intensity for detection. The five polarized line requirement eliminates this model. It is much easier to mistake a weakly polarized line for a depolarized one than the reverse. The depolarization data for the C-F stretching modes are admittedly poor, but in this frequency range $(1100-1200 \text{ cm}^{-1})$ the tetragonal pyramidal model also requires one polarized and one depolarized line. Therefore, the error, if one exists, must occur for the lower frequency lines; it is in this region, however, where the data are most reliable.

The low-barrier case for the equatorial CF₃ group in a trigonal bipyramidal framework can also be eliminated. If this structure were correct, four additional lines would have to be present and one of these would be polarized. Although unlikely, such a situation is certainly possible, either through a lack of intensity or because of accidental degeneracies. On the other hand, the spectrum of such a structure would be expected to have certain features which are in conflict with experimental data. First, there would be four stretching modes involving the axial and equatorial chlorine atoms. The equatorial Cl-P-Cl unit should yield symmetric and antisymmetric PCl₂ stretching frequencies near 400 cm⁻¹, and these may be nearly overlapped. The 374-cm⁻¹ (polarized) line could represent these modes. The antisymmetric stretching mode involving the axial Cl-P-Cl unit would have to be assigned to the 584-cm⁻¹ line (depolarized) and the corresponding symmetric mode to the 324-cm⁻¹ line (polarized). Since the axial Cl-P-Cl angle is probably 180° or nearly so, the 584-cm⁻¹ line is probably too high (cf. $v_5 = 440 \text{ cm}^{-1}$ for PCl₅),^{16,17} and there are no other suitable lines at lower frequencies. Moreover, at least one of the modes in this model assigned to the 374-cm⁻¹ line should lead to strong absorption in the infrared. Since none was observed, even taking into account small frequency shifts which often accompany changes

²¹ W. F. Edgell and R. M. Potter, J. Chem. Phys. 24, 80 (1956).

in state, it seems more reasonable to eliminate the C_{2v} model from consideration.

The analysis of the vibrational spectra in terms of a C_{3v} model seems quite satisfactory, and in the absence of any evidence to the contrary, it is considered to be correct. The fundamental frequencies are collected in Table III. Thermodynamic functions are not evaluated at this time because of a lack of accurate bond distances and further information on the barrier height.

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Study of the Born–Oppenheimer Approximation with Application to H_2

GEORGE A. FISK* AND BERNARD KIRTMAN

Department of Chemistry, University of California, Berkeley, California

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A method for evaluating energy corrections due to breakdown of the Born-Oppenheimer (BO) approximation in ordinary diatomic molecules has been developed. It is shown that the effective potential for nuclear motion depends upon both the vibrational momentum and the internuclear distance. Energy levels for H₂ have been calculated by numerical solution of the Schrödinger equation for motion in this effective potential. The v=0 level is shifted ~ 0.2 cm⁻¹ by non-BO terms as compared to the total anharmonicity correction of about 30 cm⁻¹. This shift is an order of magnitude too small to explain the difference between the best theoretical and experimental values of D_0^{0} .

INTRODUCTION

O^{NE} of the most fundamental approximations of molecular quantum mechanics is the Born-Oppenheimer¹ separation of nuclear and electronic wavefunctions. Although this factoring of the total wavefunction is in general an excellent approximation, recent experimental results² have been accurate enough to warrant a quantitative investigation of the errors involved in the Born-Oppenheimer treatment. This paper presents a method for evaluating energy shifts due to nuclear-electronic coupling and applies this method to H_2 .

The complete nonrelativistic Hamiltonian for a diatomic molecule is presented and its matrix elements are evaluated in a Born-Oppenheimer basis. The Van Vleck transformation is then applied to reduce this matrix to approximate block diagonal form. This yields a total effective potential for nuclear vibration which contains two types of terms resulting from nuclear-electronic coupling. The first type (adiabatic) is simply a function of internuclear distance which must be added to the electronic energy to define the vibrational potential. The second type (nonadiabatic) contains the operator d/dR. After certain simplifications the effect of coupling on the energy levels of H_2 is calculated by solving the appropriate Schrödinger

equation numerically. It is shown that energy effects arising from the nonadiabatic coupling terms are not large enough to explain discrepancies between experimental energies and present most accurate theoretical energies. The coupling corrections are compared to vibrational energy effects arising from anharmonic contributions to the electronic energy. The generalization of the method to other diatomic molecules is mentioned.

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The complete nonrelativistic Hamiltonian for a diatomic molecule with N electrons and total mass M[and with center of mass (CM) motion explicitly separated from internal motion] is

$$H = (2M)^{-1} P_{CM}^{2} + (2m_{e})^{-1} \sum_{i=1}^{N} p_{i}^{2} + (2M_{N})^{-1} \sum_{i,k=1}^{N} \mathbf{p}_{i} \cdot \mathbf{p}_{k}$$
$$+ V(\mathbf{r}_{1}, \cdots \mathbf{r}_{N}, R) + (2\mu_{N})^{-1} P_{R}^{2}$$
$$+ (2\mu_{N}R^{2})^{-1} \{ P_{\phi}^{2} / \sin^{2}\theta + (1/\sin\theta) P_{\theta} \sin\theta P_{\theta} \} + (2\mu_{N}R^{2})^{-1}$$
$$\times \{ (l_{x} - l_{z} \cot\theta)^{2} + l_{y}^{2} + 2(l_{x} - l_{z} \cot\theta) P_{\phi} / \sin\theta - (l_{y} / \sin\theta)$$
$$\times (\sin\theta P_{\theta} + P_{\theta} \sin\theta) \}, \quad (1)$$

where m_e and M_N are, respectively, the mass of an electron and the total mass of the nuclei, while μ_N is the reduced nuclear mass $M_1M_2/(M_1+M_2)$. \mathbf{p}_i and \mathbf{p}_k are electronic momenta, V is the electrostatic potential

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¹ M. Born and R. Oppenheimer, Ann. Physik **84**, 457 (1927). ² G. Herzberg and L. L. Howe, Can. J. Phys. **37**, 636 (1959).