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Normal Coordinate Analysis of Trigonal Bipyramidal XY_5 Type Molecules*

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Normal coordinate analysis has been carried out for trigonal bipyramidal XY_5 molecules such as PF_5, SbF_5, PCl_5 and $SbCl_5$. It has been found that the simple Urey-Bradley force field does not provide satisfactory results for the bending modes of these molecules. The results have been improved considerably by introducing an interaction constant between equatorial and axial angle coordinates. In carrying out normal coordinate analysis, the repulsive force constants were first estimated from a Lennard-Jones type potential. Then the stretching and bending force constants were adjusted to fit the observed frequencies. Finally, the new interaction constant was introduced to minimize the errors in the bending frequencies. The force constants thus obtained are consistent through the four molecules studied. Some conflicting band assignments made by previous investigators have been discussed on the basis of the present calculations.

The vibrational spectra of trigonal bipyramidal XY_5 type molecules have already been studied extensively. Although the band assignments for antimony pentachloride and phosphorous pentafluoride are consistent among several investigators, no difinite band assignments are yet available for antimony pentafluoride and phosphorus pentachloride. In the present investigation, we have carried out a systematic normal coordinate analysis of the four molecules mentioned above. The present work differs from the previous normal coordinate analyses in the following respects: (1) The most recent spectral data which were not available in previous investigations have been used. (2) A modified Urey-Bradley force field has been developed to express the potential energy. (3) All the force constants have been selected so that their values are consistent for the four molecules studied and are reasonable in view of their electronic structure.

Experimental

Most of the spectral data used for the normal coordinate analyses were taken from the literature. The Raman spectrum of phosphorus pentachloride was obtained, however, to confirm some of the calculated frequencies. A saturated benzene solution of phosphorus pentachloride (Baker Analyzed Reagent) was analyzed in a Hilger E-612 two-prism Raman spectrograph. Mercury light of wavelength 4358 Å was used for exciting the Raman transitions. A solution of Dupont rhodamine 5 GDN-Extra dye mixed with an ethanol solution of *p*-nitrotoluene was used to filter out the other mercury lines. Eastman 103a-J plates were employed to record the spectra. In addition to a number of Raman lines due to benzene, the following lines were observed for phosphorus pentachloride 585cm^{-1}(medium strong), 394 cm^{-1} (very strong), 282 cm^{-1} (strong), 273 cm^{-1} (strong), 264 cm^{-1} (medium strong). The transitions below 200 cm^{-1} could not be observed because of strong background scattering. Figure 1 shows the microdensitometer reading plotted against the frequency in the range between 430 and 200 cm^{-1}.

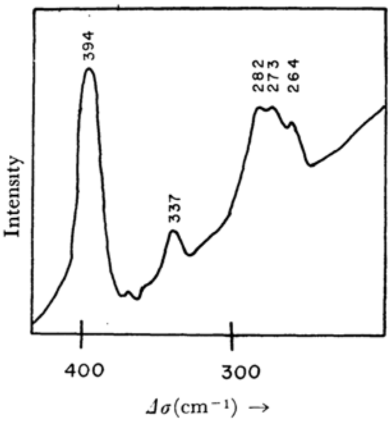

Fig. 1. Microdensitometer tracing vs. frequency for PCl_5.

Procedure of Calculation

The trigonal bipyramidal XY_5-type molecule shown in Fig. 2 belongs to the point group D_{3h}, and its twelve normal modes of vibration are grouped into the four species A_1', A_2'', E', and E''. The appropriate symmetry coordinates used are given in Table I, and the elements of the $\boldsymbol{G}$ and $\boldsymbol{F}$ matrices are listed in Tables II and III. The $\boldsymbol{G}$ matrix elements were calculated using the bond distances reported in the literature.† The matrix secular

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† $SbCl_5$: $r=2.31$Å, $d=2.43$Å (Ref. 1a); PCl_5 : $r=2.04$Å, $d=2.19$Å (Ref. 1a); SbF_5: $r\approx d\approx 2.00$Å(Ref. 13); PF_5 : $r\approx d\approx 1.57$Å (Ref. 1b).

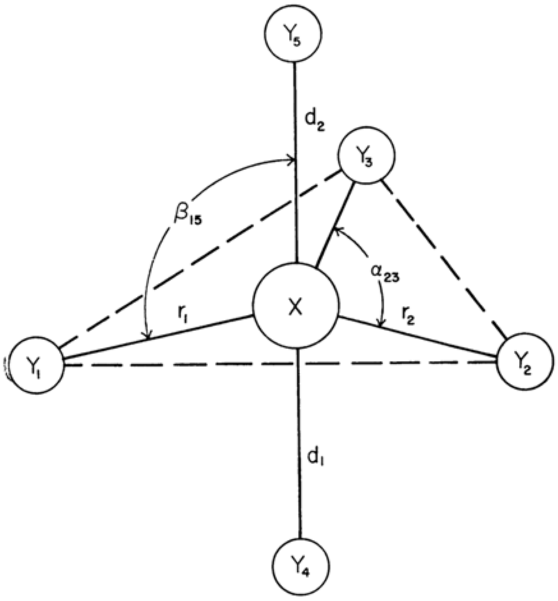

Fig. 2. Structure and internal coordinates of the trigonal bipyramidal XY_5 type molecule.

TABLE I. SYMMETRY COORDINATES FOR TRIGONAL BIPYRAMIDAL XY_5 TYPE MOLECULES

A_1'-species

$$S_1 = (1/\sqrt{3})(\Delta r_1+\Delta r_2+\Delta_3)$$
$$S_2 = (1/\sqrt{2})(\Delta d_1+\Delta d_2)$$
$$S_a = (1/\sqrt{3})(\Delta\alpha_{12}+\Delta\alpha_{23}+\Delta\alpha_{31}) \equiv 0$$
$$S_b = (1/\sqrt{6})(\Delta\beta_{14}+\Delta\beta_{24}+\Delta\beta_{34} +\Delta\beta_{15}+\Delta\beta_{25}+\Delta\beta_{35}) \equiv 0$$

A_2''-species

$$S_3 = (1/\sqrt{2})(\Delta d_1-\Delta d_2)$$
$$S_4 = (1/\sqrt{6})(\Delta\beta_{14}+\Delta\beta_{24}+\Delta\beta_{34}-\Delta\beta_{15}-\Delta\beta_{25}-\Delta\beta_{35})$$

E'-species

$$S_{5a} = (1/\sqrt{6})(2\Delta r_1-\Delta r_2-\Delta r_3)$$
$$S_{5b} = (1/\sqrt{2})(\Delta r_2-\Delta r_3)$$
$$S_{6a} = (1/\sqrt{6})(2\Delta\alpha_{23}-\Delta\alpha_{12}-\Delta\alpha_{31})$$
$$S_{6b} = (1/\sqrt{2})(\Delta\alpha_{31}-\Delta_{12})$$
$$S_{7a} = (1/\sqrt{12})(2\Delta\beta_{14}-\Delta\beta_{24}-\Delta\beta_{34} +2\Delta\beta_{15}-\Delta\beta_{25}-\Delta\beta_{35})$$
$$S_{7b} = (1/2)(\Delta\beta_{24}-\Delta\beta_{34}+\Delta\beta_{25}-\Delta\beta_{35})$$

E''-species

$$S_{8a}=(1/\sqrt{12})(2\Delta\beta_{14}-\Delta\beta_{24}-\Delta\beta_{34} -2\Delta\beta_{15}+\Delta\beta_{25}+\Delta\beta_{35})$$
$$S_{8b}=(1/2)(\Delta\beta_{24}-\Delta\beta_{34}-\Delta\beta_{25}+\Delta\beta_{35})$$

equations of the form $|GF-E\lambda|=0$ were solved for each species using an IBM 7094 electronic computer.

In order to express the potential energy, the simple Urey-Bradley force (SUBF) field[2] of the following type was first employed:

TABLE II. ***G***-MATRIX ELEMENTS*

A_1'-species

$$G_{11} = \mu_y,\ G_{12}=G_{21}=0,\ G_{22}=\mu_y$$

A_2''-species

$$G_{33} = 2\mu_x+\mu_y,\ G_{34} = G_{43} = -2\sqrt{3}\,\rho_r\mu_x,$$
$$G_{44} = 6\rho_r{}^2\mu_x+2\rho_r{}^2\mu_y$$

E'-species

$$G_{55} = \mu_y+(3/2)\mu_x,\ G_{56} = G_{65} = 3(\sqrt{3}/2)\rho_r\mu_x,$$
$$G_{57} = G_{75} = -(3/\sqrt{2})\mu_x\rho_d,$$
$$G_{66} = 3\rho_r{}^2\mu_y+(9/2)\rho_r{}^2\mu_x,$$
$$G_{67} = G_{76} = -3(\sqrt{3}/\sqrt{2})\mu_x\rho_r\rho_d,$$
$$G_{77} = 3\rho_d{}^2\mu_x+(3/2)\rho_d{}^2\mu_y$$

E''-species

$$G_{88} = 2\rho_r{}^2\mu_y+(3/2)\rho_d{}^2\mu_y$$

* μ_x and μ_y are the reciprocal masses of X and Y, while ρ_r and ρ_d are the reciprocals of the bond distances, r and d, respectively.

TABLE III. ***F***-MATRIX ELEMENTS

A_1'-species

$$F_{11} = K_r+4s^2{}_{rr}F_{rr}+2t^2{}_{rd}F'{}_{dr}+2s^2{}_{rd}F_{dr},$$
$$F_{12} = F_{21} = \sqrt{6}(-t_{dr}t_{rd}F'{}_{dr}+s_{dr}s_{rd}F_{dr}),$$
$$F_{22} = K_d+3t^2{}_{dr}F'{}_{dr}+3s^2{}_{dr}F_{dr}$$

A_2''-species

$$F_{33} = K_d+3t^2{}_{dr}F'{}_{dr}+3s^2{}_{dr}F_{dr},$$
$$F_{34} = F_{43} = \sqrt{3}\,r(t_{dr}s_{rd}F'{}_{dr}+t_{rd}s_{dr}F_{dr}),$$
$$F_{44} = rd(H_\beta-s_{rd}s_{dr}F'{}_{dr}+t_{rd}t_{dr}F_{dr})$$

E'-species

$$F_{55} = K_r+3t^2{}_{rr}F'{}_{rr}+s^2{}_{rr}F_{rr}+2t^2{}_{rd}F'{}_{dr}+2s^2{}_{rd}F_{dr},$$
$$F_{56} = F_{65} = -r(t_{rr}s_{rr}F'{}_{rr}+t_{rr}s_{rr}F_{rr}),$$
$$F_{57} = F_{75} = \sqrt{2}\,d(t_{rd}s_{dr}F'{}_{dr}+t_{dr}s_{rd}F_{dr}),$$
$$F_{66} = r^2(H_\alpha-s^2{}_{rr}F'{}_{rr}+t^2{}_{rr}F_{rr}),$$
$$F_{67} = F_{76} = -\sqrt{2}\,r^{3/2}d^{1/2}H_{\alpha\beta},$$
$$F_{77} = rd(H_\beta-s_{rd}s_{dr}F'{}_{dr}+t_{rd}t_{dr}F_{dr})$$

E''-species

$$F_{88} = rd(H_\beta-s_{rd}s_{dr}F'{}_{dr}+t_{rd}t_{dr}F_{dr})$$

* Here

$s_{dr}=t_{rd}=d/q_{dr},\ s_{rd}=t_{dr}=r/q_{dr},\ s_{rr}=\sqrt{3}/2,$

$t_{rr}=1/2,$

where

$q^2{}_{dr}=r^2+d^2.$

$$\begin{aligned} V=&\sum_i\,[K_r'r(\Delta r_i)+1/2K_r(\Delta r_i)^2]\\ &+\sum_i\,[K'{}_d d(\Delta d_i)+1/2K_d(\Delta d_i)^2]\\ &+\sum_{i<j}[H'{}_\alpha r_\alpha{}^2(\Delta\alpha_{ij})+1/2H_\alpha(r_\alpha\Delta\alpha_{ij})^2]\\ &+\sum_{i<j}[H'{}_\beta r_\beta{}^2(\Delta\beta_{ij})+1/2H_\beta(r_\beta\Delta\beta_{ij})^2]\\ &+\sum_{i<j}[F'{}_{rr}q_{rr}(\Delta q_{ij})+1/2F_{rr}(\Delta q_{ij})^2]\\ &+\sum_{k<j}[F'{}_{dr}q_{dr}(\Delta q_{jk})+1/2F_{dr}(\Delta q_{jk})^2] \end{aligned}$$

where Δr_i, Δd_i, $\Delta\alpha_{ij}$, $\Delta\beta_{ij}$, Δq_{ij}, and Δq_{jk} are, respectively, the change in the bond lengths r and d, the change in the bond angles α and β, and the change in the distances q_{rr} and q_{dr} between

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1) a) M. Rouaut, *Ann. Phys.*, **14**, 78 (1940); 1b) L. O. Brockway and J. Y. Beach, *J. Am. Chem. Soc.*, **60**, 1836 (1938).

2) T. Shimanouchi, *J. Chem. Phys.*, **17**, 245 (1949).

TABLE IV. UREY-BRADLEY FORCE CONSTANTS OF VARIOUS TRIGONAL BIPYRAMIDAL MOLECULES (md./Å)

	K_r	K_d	H_α	H_β	F_{rr}	F_{dr}	$H_{\alpha\beta}$
$SbCl_5$	2.20	1.83	0.06	0.085	0.08	0.13	0.043
PCl_5	2.10	1.00	0.07	0.15	0.10	0.55	0.07
SbF_5	5.30	4.60	0.095	0.12	0.07	0.10	0.07
PF_5	5.50	3.85	0.37	0.48	0.15	0.80	0.09

TABLE V. FUNDAMENTAL FREQUENCIES OF $SbCl_5$ (cm^{-1})*

		Siebert[4]	Wilmshurst[5]	Carlson[6]	Present work		
					Observed	Calculated	
						SUBF	MUBF
A_1'	σ_1	356(R)	356	356(R)	356	358	353
	σ_2	307(R)	307	307(R)	307	307	307
A_2''	σ_3	((390))	387(IR) 380(IR)	371(IR)	387 380	384	384
	σ_4	((131))	(156)	154(IR)	154	156	156
E'	σ_5	399(R)	398(IR)	395(IR, R)	398	399	402
	σ_6	182(R)	182	172(IR, R)	172	140	172
	σ_7	74(R)	74	72(R)	74	107	74
E''	σ_8	166(R)	166	165(R)	165	163	163

* In Tables V to VIII, the following abbreviations were used: frequencies followed by IR (gaseous or matrix-phase infrared spectra) or R (Raman spectra) were actually observed by the investigator reporting the data; frequencies taken from a previous investigator are denoted by numbers only; frequencies calculated from overtones or combination bands are in single parentheses ( ), and those obtained from normal coordinate analysis are in double parentheses (( )). The values calculated in the present investigation are compared in the tables with what we consider the best reported values.

TABLE VI. FUNDAMENTAL FREQUENCIES OF PCl_5 (cm^{-1})

		Siebert[4]	Wilmshurst and Bernstein[7]	Carlson[6]	Taylor and Woodward[9]	Present work		
						Observed	Calculated	
							SUBF	MUBF
A_1'	σ_1	392(R)	394(R)	393(R)	395	394(R)	394	394
	σ_2	271(R)	394(R)	?	370	264(R)	261	261
A_2''	σ_3	449(R)*	465(IR)	446(IR)	441	465	470	470
	σ_4	((124))	(176)	299(IR)	301	299	303	303
E'	σ_5	495(R)	592(IR, R)	580(IR, R)	581	592	562	588
	σ_6	190(R)	335(IR, R)	273(IR, R)	281	273(R)	247	278
	σ_7	100(R)	100	100(R)	100	100	132	100
E''	σ_8	190(R)	280(R)	289(R)	261	282(R)	277	277

* Although this mode is only infrared active, Siebert[4] claims that he observed it in the Raman spectrum, and he attributes the origin of this band to the distortion of the trigonal bipyramidal structure.

TABLE VII. FUNDAMENTAL FREQUENCIES OF SbF_5 (cm^{-1})

		Akers[12]		Gaunt and Ainscough[13]	Present work		
					Observed	Calculated	
						SUBF	MUBF
A_1'	σ_1	397(R)	718(R)	667(R)	718	709	709
	σ_2	265(R)	672(R)	264(R)	672	649	649
A_2''	σ_3	758(IR)	758(IR)	(294)	724	743	743
	σ_4	708(IR)	708(IR)	(212)	212	206	206
E'	σ_5	718(R) 724(IR)	397(R)	710(IR) 716(R)	758	772	774
	σ_6	672(R)	265(R)	498(IR)	265	199	258
	σ_7	224(R)	224(R)	ca. 90(R)	93	167	92
E''	σ_8	187(R)	187(R)	228(R)	224	234	234

Table VIII. Fundamental frequencies of PF_5 (cm^{-1})

		Gutowski and Liehr[16]	Pemsler and Planet[17]	Griffiths et al.[18]	Present work		
					Observed	Calculated SUBF	Calculated MUBF
A_1'	σ_1	—	—	817(R)	817	801	801
	σ_2	—	—	640(R)	640	628	628
A_2''	σ_3	948(IR)	948(IR)	945(IR)	945	958	958
	σ_4	576(IR)	576(IR)	576(IR)	576	542	542
E′	σ_5	1025(IR)	1029(IR) 1026(IR)	1026(IR, R)	1029 1026	1039	1055
	σ_6	534(IR)	534(IR)	533(IR, R)	534	495	535
	σ_7	—	—	301(IR)*	301	339	302
E″	σ_8	—	—	514(R)	514	536	536

* See Ref. 19.

nonbonded atoms. The symbols *K*, *H*, and *F* represent stretching, bending, and repulsive force constants, respectively. The primed letters donote first derivatives; r, d, r_α, r_β, q_{rr}, and q_{dr} are the values of the distances at equilibrium; they are inserted to make the dimensions of the force constants the same. The quantities *K′* and *H′* vanish in the final result, since they can be expressed in terms of *F′* using the equilibrium condition. *F′* was taken as $-0.1F$ by assuming that the repulsive energy between the nonbonded atoms is proportional to r^{-9}.

In adjusting the force constants, we first estimated the reasonable values for the repulsive force constants from a Lennard-Jones type potential. Figures III and IV illustrate the repulsive force constants which are derived from the 6-12 Lennard-Jones potentials for Ne⋯Ne and Ar⋯Ar repulsions, respectively. Then, we have adjusted these values to obtain the best fit to the observed frequencies. The final repulsive force constants thus obtained are plotted in the same figures together with those used by Shimanouchi and his coworkers[3] for other molecules. It is seen that our values are quite close to those predicted from the Lennard-Jones potentials. Table IV lists the final sets of force constants thus obtained. Tables V to VIII compare the observed frequencies with those calculated for each molecule. It is seen immediately that the two bending modes (σ_6 and σ_7) belonging to the E′ species show marked deviation from the observed frequencies. Evidently, the SUBF field is not satisfactory for trigonal bipyramidal XY_5 type molecules.

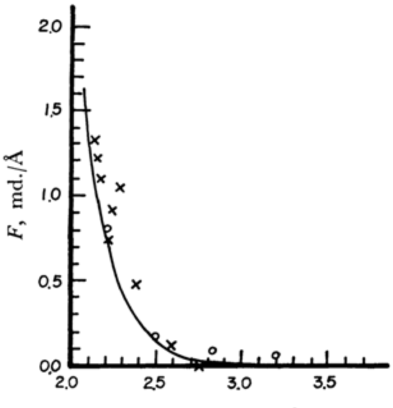

Fig. 3. Repulsive force constants derived from 6-12 Lennard-Jones potential for Ne⋯Ne repulsion and F⋯F repulsive force constants (×, Shimanouchi et al.; ○, present work)

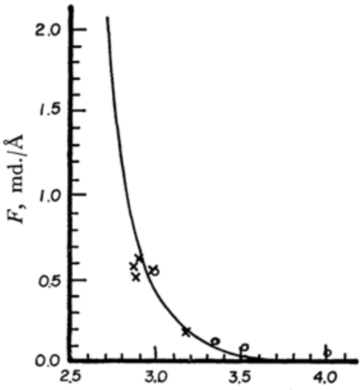

Fig. 4, Repulsive force constants derived from 6-12 Lennard-Jones potential for Ar⋯Ar repulsion and Cl⋯Cl repulsive force constants (×, Shimanouchi et al.; ○, present work)

In order to improve these results, we have introduced an additional force constant to the SUBF field. After several trials, we have found that the addition of a term, $\sum_{k\neq i<j}[H_{\alpha\beta}(r_\alpha\Delta\alpha_{ij})(r_\beta\Delta\beta_{ik})]$ to the potential energy improves the results considerably. Here, $H_{\alpha\beta}$ denotes an angle-angle interaction constant between α and β which lie in planes perpendicular to each other and share

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[3] J. Hiraishi, I. Nakagawa and T. Shimanouchi, *Spectrochim. Acta*, **20**, 819 (1964).

a common bond. The last columns in Tables V to VIII indicate the calculated frequencies obtained by using this modified Urey-Bradley force (MUBF) field. It is seen that the agreement between calculated and observed frequencies becomes quite satisfactory; the average deviation for 32 frequencies is 1.1%, and the maximum deviation is 34 cm^{-1}.

Results and Discussion

Antimony Pentachloride.—Table V compares the calculated frequencies with those observed by Siebert (Raman),[4] Wilmshurst (gaseous-phase IR),[5] and Carlson (Raman and matrix-phase IR).[6] All the band assignments made by these investigators are consistent with each other, and the calculated frequencies are in perfect agreement with those observed.

Phosphorus Pentachloride.—As is seen in Table VI, the previous band assignments differ seriously among the investigators. Siebert[4] assigned a Raman line at 271 cm^{-1} to σ_2, whereas Carlson assigned it to σ_6 (E′ species) because an infrared band was observed at 273 cm^{-1}. Wilmshurst and Bernstein[7] assigned a Raman line at 394 cm^{-1} to both σ_2 and σ_1 on the assumption of accidental degeneracy. However, this assignment seems highly unlikely because, with this assumption, the stretching force constants for both the axial and the equatorial bonds would have to be of the same magnitude. On the contrary, an electron diffraction[1] and a tracer study[8] show that the axial and the equatorial bonds are not equivalent. Although Taylor and Woodward[9] assigned a Raman line at 370 cm^{-1} to σ_2, it is rather weak as is seen in Fig. 2. The corresponding line for antimony pentachloride is relatively strong. We, therefore, assigned it to a combination band ($\sigma_6+\sigma_7$ or $\sigma_2+\sigma_7$).

According to our normal coordinate analysis, σ_2 should be around 260 cm^{-1}. As is shown in Fig. 2, we have observed three Raman lines in the region 290—260 cm^{-1} using the photographic method. Therefore, the line at 264 cm^{-1} which is closest to our calculated frequency, is assigned to the σ_2 mode. It should be mentioned that Wilmshurst and Bernstein[7] also observed a Raman line at 264 cm^{-1} which they attributed to a combination band. However, one of the fundamentals (176 cm^{-1}), which was assumed to be a component of this combination band, was not observed by Carlson[6] in his infrared spectrum. Therefore, the Raman line at 264 cm^{-1} cannot be a combination band.

The calculated frequency for σ_4 (303 cm^{-1}) is in good agreement with that observed by Carlson (299 cm^{-1})[6] in the infrared spectrum. The frequencies predicted by Wilmshurst and Bernstein (176 cm^{-1})[7] and by Siebert (124 cm^{-1})[4] are too low for this mode. Furthermore, Carlson did not observe any infrared band arount 176 or 124 cm^{-1}. The calculated frequency for σ_5 (588 cm^{-1}) is in good agreement with that observed by Wilmshurst and Bernstein (592 cm^{-1}), and is fairly close to that observed by Carlson (580 cm^{-1}). Although Siebert assigned it to a Raman line at 495 cm^{-1}, it was found that this line is due to phosphorus oxychloride contaminated in a solution of phosphorus pentachloride.

The calculated frequency for σ_6 (278 cm^{-1}) is in good agreement with that observed by Carlson (273 cm^{-1})[6] and by the present investigators (273 cm^{-1}). Carlson observed this mode both in the infrared and Raman spectra. Therefore, it must belong to the E′ or A′′ species. Although Taylor and Woodward[9] assigned σ_6 to a Raman line at 281 cm^{-1}, no infrared band was observed at this frequency. On the other hand, Wilmshurst and Bernstein[7] assigned it at 335 cm^{-1}. However, Taylor and Woodward did not observe any Raman line near 335 cm^{-1}.

The calculated frequency for σ_8 (277 cm^{-1}) is close to the Raman line observed at 282 cm^{-1} in the present work. This line was also observed by Wilmshurst and Bernstein and by Calrson, and was assigned by both to the σ_8 mode.

Recently, Radhakrishnan[10] and Krynauw et al.[11] have carried out normal coordinate analysis of phosphorus pentachloride using the band assignments made by Wilsmshurst and Bernstein[7] and by Carlson[6], respectively. Our results are different from those of previous workers since our band assignments and force field are different from theirs.

Antimony Pentafluoride. — The infrared and Raman spectra of antimony pentafluoride were observed by Akers[12] and by Gaunt and Ainscough,[13] but their band assignments are in complete disagreement, as is seen in Table VII. Furthermore, Akers presented two different sets of band assignments both of which differ from that of Gaunt and Ainscough. Nagarajan,[14] and Haarhoff and Pistorius[15] have carried out normal coordinate analysis using the band assignments by

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4) H. Siebert, *Z. anorg. u. allgem. Chem.*, **265**, 303 (1951).

5) J. K. Wilmshurst, *J. Mol. Spectry*, **5**, 343 (1960).

6) G. L. Carlson, *Spectrochim. Acta*, **19**, 1291 (1963).

7) J. K. Wilmshurst and H. J. Bernstein, *J. Chem. Phys.*, **27**, 661 (1957).

8) J. Downs and R. E. Johnson, ibid., **22**, 143 (1954).

9) M. J. Taylor and L. A. Woodward, *J. Chem. Soc.*, **1963**, 4670.

10) M. Radhakrishnan, *Indian J. Pure Appl. Phys.*, **1**, 437 (1963).

11) G. N. Krynauw, C. W. F. T. Pistorius and M. C. Pistorius, *Z. Physik. Chem.*, **43**, 213 (1964).

12) L. K. Akers, Univ. Microfilms (Ann Arbor, Michigan), Pub. No. 12965 (1955).

13) J. Gaunt and J. B. Ainscough, *Spectrochim. Acta*, **10**, 57 (1957).

14) G. Nagarajan, *Bull. soc. chim. Belg.*, **72**, 563 (1963).

15) P. C. Haarhoff and C. W. F. T. Pistorius, *Z. Naturforsch.*, **14A**, 972 (1959).

Gaunt and Ainscough, and have obtained a large negative interaction force constant between two axial bond stretching coordinates in the general valence force field. They suggested that this might be due to incorrect assignments for σ_2 and σ_3 made by Gaunt and Ainscough.

In order to solve these conflicting band assignments, it is useful to consider the frequency order observed in antimony pentachloride and phosphorus pentachloride. From Table V and VI, it is seen that the stretching frequencies (σ_1, σ_2, σ_3, and σ_5) are much higher than the bending frequencies (σ_4, σ_6, σ_7, and σ_8), and the order of the stretching frequencies is always σ_5(asym. in-plane) $>$ σ_3(asym. out-of-plane) $>$ σ_1(sym. in-plane) $>$ σ_2(sym. out-of-plane) the six fundamental observed by Akers[12] and the two fundamentals observed by Gaunt and Ainscough[13] were rearranged with this trend in mind. The four bending frequencies were also rearranged so as to obtain the frequency order $\sigma_6 > \sigma_8 > \sigma_4 > \sigma_7$, which was found to hold for antimony pentachloride. As is seen in Table VII, the agreement between the calculated and observed frequencies is quite satisfactory. It should be mentioned that the set of the fundamentals selected by the present investigators can account for all the other observed frequencies on the assumption that they are overtones and combination bands.

Phosphorus Pentafluoride.—Table VIII compares the calculated frequencies with those observed by Gutowski and Liehr (infrared),[16] by Pemsler and Planet (infrared),[17] and by Griffith et al. (infrared and Raman).[18,19] All the band assignments made by these investigators are consistent with one another and agree quite well with the calculated frequencies.

Trends in Force Constants.—The force constants listed in Table IV have several interesting implications. First of all, the stretching force constants involving the fluorine atoms are much larger than those involving the chlorine atoms. This is consistent with the fact that the heat of formation of phosphorus pentafluoride (−290 kcal./mol.) is much larger than that of phosphorus pentachloride (−95.35 kcal./mol.). Secondly, the stretching force constants for the equatorial bonds (K_r) are larger than those for the axial bonds (K_d) in all the four molecules studied. This trend is consistent with the results of X-ray[20] and electron diffraction[1] studies which indicate that the equatorial bonds are shorter than the axial bonds.

Table IV also indicates that the bending force constants of the fluorides are always larger than those of the corresponding chlorides, and that the bending force constants of the phosphorus compounds are always larger than those of the corresponding antimony compounds. All these changes which occur upon the replacement of either the central or the halogen atom can be explained satisfactorily in terms of the electron pair repulsion theory developed by Gillespie.[21] His theory also predicts that the bending force constants for the axial bond angle (H_β) should be larger than that for the equatorial bond angle (H_α). As is seen in Table IV, this was found to be the case.

As stated previously, the repulsive force constants follow the trends predicted from the 6—12 Lennard-Jones potential. Therefore, their values increase progressively as the bond distances decrease. Thus, we have the following orders:

$$F_{rr}(\mathrm{SbF_5}) < F_{dr}(\mathrm{SbF_5}) < F_{rr}(\mathrm{PF_5}) < F_{dr}(\mathrm{PF_5})$$

$$F_{rr}(\mathrm{SbCl_5}) < F_{rr}(\mathrm{PCl_5}) < F_{dr}(\mathrm{SbCl_5}) < F_{dr}(\mathrm{PCl_5})$$

It has already been shown that the introduction of an angle-angle interaction constant, $H_{\alpha\beta}$, improves the calculated frequencies for the σ_6 and σ_7 modes considerably. It is interesting to note that these two vibrations are responsible for "pseudorotation" which was proposed by Berry[22] for trigonal bipyramidal XY_5 type molecules. Since the angles α and β must be interchanged during pseudorotation, it is reasonable to introduce such an interaction term in the potential energy.

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