N, O, O, Cl or N, O, O, Br. The absence of any significant dependence of the spectra of complexes **1** and **2** upon R indicates that the stereochemistries are also not very dependent on R. These results are best explained if the copper atoms are essentially planar, in agreement with the conclusions from the magnetic data.

Formation of the Complexes.—As expected from the ease of formation of complexes analogous to **2** without ring substituents,[1,5,7] the copper halid eadducts of the copper(II) complexes of 5-chloro- and 5-bromosalicylaldimines were formed readily by similar methods. The binuclear complexes derived from 5,6-benzosalicylaldimine were much more difficult to prepare, and in some cases the reaction mixtures had to stand for up to 2 weeks before sufficient yields of the complexes were obtained, and in other cases, *viz.*, when R = *n*-propyl, *n*-butyl, *n*-octyl, and cyclopentyl, only the starting materials were recovered. Of the *n*-alkyls, only the methyl complexes could be prepared in sufficient quantities for magnetic and spectral measurements. Binculear complexes derived from copper(II) 5-nitrosalicylaldimines and 3,5-dichlorosalicylaldimines also failed to form, probably because of the low solubility of the starting materials.

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Pentacoordinated Molecules. XIV.[1] Molecular Vibrations and Stereochemical Nonrigidity of the Trigonal-Bipyramidal Model MX_3Y_2

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Based on complete infrared and Raman vibrational spectra, a normal mode analysis of the series of trigonal-bipyramidal molecules PF_5, AsF_5, VF_5, PCl_3F_2, PCl_5, $SbCl_5$, $Sb(CH_3)_5$, and $NbCl_5$ has led to a description of the ground-state motions. Barrier energies for intramolecular exchange are compared for a square-pyramidal and tetragonal-pyramidal intermediate. The conclusion shows that either process gives a similar ordering and magnitude of barrier energies for these molecules. Examination of appropriate combinations of bending coordinates modified in most cases by ligand reorganization leads to a classification of model processes for intramolecular exchange mechanisms in terms of relative strengths of equatorial and axial bonds. Application is seen in transition metal chemistry. Further, transferability of data allows estimation of an exchange barrier for the hypothetical PH_5 molecule. The latter is considered the only case where a tunneling mechanism for exchange might be significant.

Introduction

Vibrational data have now appeared on a sufficient number of trigonal-bipyramidal molecules of D_{3h} symmetry to warrant a systematic normal mode analysis. Such an analysis while defining an appropriate force field allows an estimate of the "rigidity" of this class of molecules with respect to stereochemical change.

A particularly interesting change to a tetragonal-pyramidal structure has been discussed[2] in connection with a plausible mechanism[3] by which some trigonal bipyramids undergo intramolecular exchange as observed by nmr measurements.[4,5] What is needed is some insight into other possible intramolecular processes and an examination of their relative importance. By analyzing internal motions of a series of related molecules showing variations in both ligands and central atoms, useful statements regarding competitive mechanisms should result.

For the molecules to be considered, infrared and Raman spectra have been recorded and fundamental frequency assignments have been made in each case. Most of the vibrational data are recently available and have been the subject of some force constant analyses.[6-13]

It is the purpose of this paper to attempt to identify the various types of stereochemical changes involved in intramolecular rearrangements of trigonal-bipyramidal molecules that may be induced by internal vibrational modes. Based on vibrational data and bonding

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TABLE I

FUNDAMENTAL FREQUENCIES FOR TRIGONAL-BIPYRAMIDAL MOLECULES OF D_{3h} SYMMETRY (cm^{-1})

Description[a]	PF_5[13-15]	AsF_5[13]	VF_5[12]	PCl_3F_2[15]	PCl_5[16]	$SbCl_5$[16b]	$Sb(CH_3)_5$[17,c]	$NbCl_5$[18]	PH_5[d]
A_1' Species									
MX_3 sym str	817	733	719	387	395	356	493		2200
MX_2' sym str	640	642	608	633	370	307	414		1800
A_2'' Species									
MX_2' antisym str	945	787.4	784	867	441	371	456	396	2400
MX_3 out-of-plane bend	576	400.4	331	328	301	154	213	126	1400
E' Species									
MX_3 antisym str	1026	811.4	810	625	581	395	516	444	2550
MX_3 in-plane bend	533	372	282	404	281	172	195	159	1300
MX_2' bend	179	123	(150)[b]	122	100	72	108	99	450
E'' Species									
MX_3X_2' rock	514	388	350	357	261	165	239		1200

[a] The primes in the mode description refer to axial atoms. [b] An assumed frequency. See ref 19. [c] Only the vibrations associated with the trigonal-bipyramidal framework are listed since the simplification is made that the CH_3 group acts as a unit. [d] Synthesized frequencies for the hypothetical PH_5 molecule.[19]

considerations, it should then prove possible to infer reasonably the lowest energy intermediate involved in such processes for other trigonal bipyramids whose vibrational spectrum has been adequately characterized.

Vibrational Frequencies

Values of the fundamental frequencies for the molecules to be considered are listed in Table I.[13-19] PF_5, PCl_3F_2, PCl_5, and $SbCl_5$ have been discussed before[2] in connection with the estimation of barrier energies for intramolecular exchange proceeding *via* a tetragonal-pyramidal intermediate. Comparison will be made here with barrier energies calculated for a process proceeding through a square-pyramidal intermediate for these as well as the other molecules listed in Table I.

An assumed value[2] previously was used for the axial bending frequency for PF_5. Levin[14b] has since reported a band at 179 cm^{-1} observed in the laser Raman spectrum of the solid at liquid nitrogen temperatures and assigned it as the missing fundamental.

Procedure

The basis for the discussion involves the consideration of bending coordinates or combinations thereof. These are chosen as

$$S_4 = (-\Delta\beta_1 - \Delta\beta_2 - \Delta\beta_3 + \Delta\beta_1' + \Delta\beta_2' + \Delta\beta_3')/\sqrt{6}$$

of A_2'' species

$$S_{6a} = (-2\Delta\alpha_{23} + \Delta\alpha_{12} + \Delta\alpha_{13})/\sqrt{6}$$

$$S_{6b} = (-\Delta\alpha_{12} + \Delta\alpha_{13})/\sqrt{2}$$

$$S_{7a} = (2\Delta\beta_1 - \Delta\beta_2 - \Delta\beta_3 + 2\Delta\beta_1' - \Delta\beta_2' - \Delta\beta_3')/\sqrt{12}$$

$$S_{7b} = (-\Delta\beta_2 + \Delta\beta_3 - \Delta\beta_2' + \Delta\beta_3')/2$$

of E' species and

$$S_{8a} = (2\Delta\beta_1 - \Delta\beta_2 - \Delta\beta_3 - 2\Delta\beta_1' + \Delta\beta_2' + \Delta\beta_3')/\sqrt{12}$$

$$S_{8b} = (-\Delta\beta_2 + \Delta\beta_3 + \Delta\beta_2' - \Delta\beta_3')/2$$

of E'' species for trigonal bipyramids of D_{3h} symmetry. The internal coordinates are shown in Figure 1.

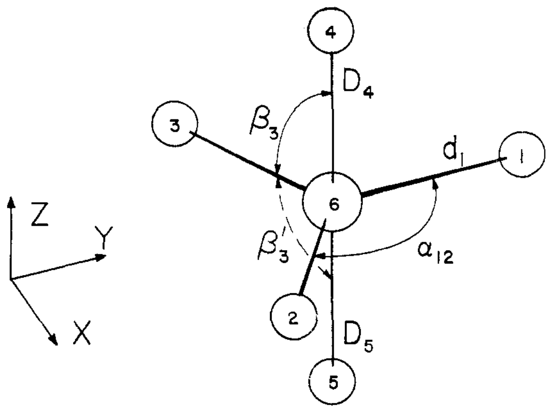

Figure 1.—Coordinates for a trigonal-bipyramidal molecule.

A computer program previously developed for normal-coordinate analyses of trigonal-bipyramidal molecules of various symmetries[2,20] by the *GF* matrix method was used to define a potential field and obtain a description of the normal modes. The normal mode displacements were normalized to the ground-state vibrational energies.

Table II lists the values of the symmetry force constants. The forms of the normal modes for the bending vibrations are shown in Figures 2–5 for potential field *A* of Table II. They serve to illustrate the changes in relative amplitudes of the various atoms brought about by mass changes and force constant variations from molecule to molecule.

Table III lists values of the amplitudes of participating symmetry coordinates contributing to the makeup of the normal modes for e′ species of field *A*. These values are the elements L_{ik} of the L matrix in $S = LQ$

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TABLE II

SYMMETRY FORCE CONSTANTS (MDYN/Å)

	PF_5 (ν_7 179 cm^{-1})	AsF_5	VF_5	PCl_3F_2	PCl_5	$SbCl_5$	$Sb(CH_3)_5$	$NbCl_5$	PH_5
					A_1'				
F_{11}	7.470	6.013	5.785	3.128	3.258	2.647	2.152		2.874
F_{22}	4.583	4.613	4.137	4.484	2.859	1.968	1.518		1.924
F_{12}	0.0	0.0	0.0	0.0	0.0	0.0	0.0		0.0
					A_2''				
F_{33}	4.193	4.304	3.858	3.448	1.804	1.733	1.557		3.227
F_{44}	1.113	0.6376	0.3842	0.6321	0.4338	0.1623	0.1726		0.5064
F_{34}	−0.5	0.0	−0.1	−0.1	−0.5	0.0	−0.2		−0.2
					E′ (Field *A*)				
F_{55}	5.501	5.321	4.839	2.326	2.494	2.201	2.024	2.776	3.689
F_{66}	0.7821	0.4040	0.2103	0.9781	0.3490	0.1599	0.09901	0.1241	0.3215
F_{77}	0.1766	0.08848	0.1306	0.06911	0.1038	0.05773	0.05917	0.1117	0.08127
F_{56}	−0.1	−0.1	−0.2	−0.5	−0.2	0.0	−0.1	−0.2	−0.1
					E″				
F_{88}	0.8404	0.4814	0.3917	0.5142	0.4014	0.1617	0.1445		0.2412
					E′ (Field *B*)				
F_{55}	5.449	5.443	4.809		2.099	2.189	2.011	2.848	3.677
F_{66}	0.09867	0.06257	0.07704		0.06820	0.03016	0.07581	0.08975	0.03841
F_{77}	1.523	0.7554	0.3861		0.8352	0.3075	0.1804	0.2053	0.6766
F_{56}	−0.2	−0.3	−0.2		−0.2	0.0	−0.3	−0.3	0.0

TABLE III

NORMALIZED *L* MATRIX ELEMENTS FOR E′ SPECIES OF POTENTIAL FIELD *A*

	PF_5 (ν_7, 179 cm^{-1})		
S_5	0.3113	0.06412	−0.005020
S_6	0.3555	−0.4199	−0.02139
S_7	0.2403	−0.09086	0.3227
	AsF_5		
S_5	0.2693	0.01061	−0.001859
S_6	0.1461	−0.4432	−0.01410
S_7	0.1106	−0.08423	0.3157
	VF_5		
S_5	0.2864	0.005423	−0.005459
S_6	0.1681	0.4624	−0.06431
S_7	0.1485	0.1448	0.3079
	PCl_3F_2		
S_5	0.2314	0.1516	0.009942
S_6	0.4568	−0.1450	0.01422
S_7	0.3217	0.04673	−0.3503
	PCl_5		
S_5	0.2738	−0.04007	0.007158
S_6	0.3529	0.3234	0.02754
S_7	0.2605	0.08942	−0.2318
	$SbCl_5$		
S_5	0.2006	−0.01624	0.001889
S_6	0.1322	0.3221	0.01843
S_7	0.09312	0.06710	−0.2276
	$Sb(CH_3)_5$		
S_5	0.2800	0.02001	0.003719
S_6	0.04119	0.4832	0.03676
S_7	0.06077	0.08295	−0.3374
	$NbCl_5$		
S_5	0.2099	0.01431	−0.009086
S_6	0.1064	0.3373	−0.08936
S_7	0.1084	0.1384	0.2090
	PH_5		
S_5	−1.019	−0.04791	0.002020
S_6	0.0007997	−1.767	0.01287
S_7	−0.06380	−0.07364	−1.211

where *Q* is the normal mode matrix. Bond distances used in the computations are taken from the literature.[12,13,18,21–25]

Potential Field

Since the quantity of vibrational data is insufficient to characterize a complete force constant set, simplification is achieved by examining the effect of varying the interaction force constants (over the range −0.8 to +0.7 mdyn/Å) on values of the principal symmetry force constants.

For a_2'' species only one interaction constant is involved; whereas, three are present in the *F* matrix for e′ species. Variation of either stretch–bend, F_{56} or F_{57}, produced about the same variation in the diagonal elements. The bend–bend interaction, F_{67}, should be of lesser significance and was not considered. The variations in the principal force constants were not too great (∼±10% for a variation in interaction constants of ±0.4 mdyn/Å). Similar variations were reported by Hoskins and Lord[13] for AsF_5.

If convergence was not a problem, a zero value was assigned to the interaction constant. Otherwise a

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(21) M. Rouault, *Ann. Phys.* (Paris), **14**, 78 (1940).

(22) K. W. Hansen and L. S. Bartell, *Inorg. Chem.*, **4**, 1775 (1965).

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slightly negative value is listed in Table II since regions of nonconvergence were invariably found for positive values of interaction constants. In the case of the e′ species two acceptable force fields result.

Some assignments of vibrational data of trigonal-bipyramidal molecules, accompanied by force constant analyses, have led to the designation of the lowest frequency fundamental as primarily an axial bending motion[12,13,20] (field *A* in Table II) while others[9,26,27] have designated the lowest frequency fundamental as the equatorial in-plane bending motion (field *B* in Table II). These two assignments are a consequence of the underdetermined character of the potential field. This problem has been commented on by Van Der Voorn, *et al.*,[8] in comparing force constants for PF_5, PCl_3F_2, and PCl_5. Previous considerations[27] were complicated by the use of 301 cm^{-1} assigned[28] as the ν_7 fundamental frequency in PF_5.

The assignment of the lowest frequency fundamental as an axial rather than an equatorial bending motion is favored by the lower stretching force constants and longer bond distances (where observable)[21–24,29] for axial bonds compared to equatorial bonds for these molecules. Both considerations imply weaker axial than equatorial bonds. The symmetry force constants for both assignments are included in Table II.

If one compares frequencies for axial bending modes and equatorial in-plane bending modes for the series PF_5 (D_{3h}), CH_3PF_4 (C_{2v}), $(CH_3)_2PF_3$ (C_{2v}), and $(CH_3)_3PF_2$ (D_{3h}), only modest changes in the former frequency are expected, since all members have fluorine atoms in the axial position, while considerably greater changes in the latter frequency should result as the ratios of fluorine atoms to methyl groups decrease in the equatorial positions. The two sets of frequencies for the compounds as listed are 179, 179, 184, and 190 cm^{-1} for the axial modes and 533, 467, 459, and 417 cm^{-1} for the equatorial modes.[30] It is seen that the frequencies assigned in the manner cited are much more compatible with expectations than if the reverse were the case.

On the other hand, Coriolis ζ constants calculated from band-shape analysis[13] of AsF_5 and PF_5 are in better agreement[19] with the assignment of the lowest frequency fundamental as an equatorial bending motion.[31]

Barrier Heights

Previously, barrier heights were calculated[2] for intramolecular exchange of some trigonal-bipyramidal molecules (including PF_5, PCl_5, $SbCl_5$, and PCl_3F_2 under consideration here) proceeding *via* a tetragonal-pyramidal intermediate. Considering the likelihood of the alternate potential field commented on in the last section, a calculation should be carried out in this case as well. As before,[2] the harmonic potential function is approximated as $V = {}^1/_2F_{66}S_6{}^2 + {}^1/_2F_{77}S_7{}^2$, where the symmetry force constants now take on values for the force field *B* of Table II.

Minimization of the potential with respect to the S_{6a} and S_{7a} symmetry coordinates results in the barrier heights in Table IV (field *B*) for the molecules listed in Table I. The results have been modified to include anharmonicity corrections.[2]

TABLE IV
CALCULATED ENERGY BARRIERS FOR INTRAMOLECULAR EXCHANGE

	Field *A*		Field *B*	
	Δ*E* (tetrag py), kcal/mol	β_1, deg	Δ*E* (sq py), kcal/mol	β_1, deg
PF_5 (122 cm^{-1})	7.5	118.3	7.7	91.4
PF_5 (179 cm^{-1})	14.4	116.6	15.3	93.2
AsF_5	9.4	116.8	11.8	94.1
VF_5	12.3	112.4	13.3	98.2
PCl_3F_2	8.5	119.1	...	...
PCl_5	12.9	115.5	14.9	93.8
$SbCl_5$	8.9	114.9	8.9	94.6
$Sb(CH_3)_5$	8.1	112.6	12.7	103.2
$NbCl_5$	12.9	110.2	14.9	103.5
PH_5	6.9	116.1	6.3	92.7

Table IV (field *A*) lists the barrier energies calculated in a similar fashion for field *A* of Table II. The latter barriers are a few tenths of a kcal/mol lower than those reported earlier. The present procedure of minimizing a combination of symmetry coordinates provides a more favorable exchange coordinate than use of a single normal coordinate.[2]

The geometries of the two intermediates are given in terms of β_1 (see Figure 1). The barrier heights correspond to a tetragonal pyramid for potential field *A* while the barrier heights for potential field *B* correspond, as expected, to a slightly distorted square pyramid. Regardless of which potential function proves to be correct, it is seen (Table IV) that the magnitude and ordering of barrier energies are approximately the same in the two cases. For field *A* the order is

$$PCl_5 \sim NbCl_5 > VF_5 > AsF_5 > SbCl_5 > PCl_3F_2 > Sb(CH_3)_5 > PF_5\ (\nu_7\ 122\ cm^{-1}) > PH_5$$

while for field *B* it is

$$PCl_5 \sim NbCl_5 > VF_5 > Sb(CH_3)_5 > AsF_5 > SbCl_5 > PF_5\ (\nu_7\ 122\ cm^{-1}) > PH_5$$

Using the newly assigned bending frequency of 179 cm^{-1} for PF_5, a relatively high barrier is obtained. The barrier is higher than that for PCl_5 which is thought[32] not to be undergoing intramolecular exchange at room temperature. In contrast, PF_5 shows ^{19}F nmr equiva-

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

[27] A recent discussion is given by S. J. Cyvin and J. Brunvoll, *J. Mol. Struct.*, **3**, 151 (1969), and references cited therein.

[28] J. E. Griffiths, *J. Chem. Phys.*, **42**, 2632 (1965).

[29] S. M. Ohlberg, *J. Am. Chem. Soc.*, **81**, 811 (1959).

[30] A. J. Downs and R. Schmutzler, *Spectrochim. Acta*, **21**, 1927 (1965); **23A**, 681 (1967).

[31] A check of computer programs is possible in the case of PF_5 and AsF_5. Hoskins and Lord[13] computed symmetry force constants using a computer program of J. H. Schachtschneider and R. G. Snyder, *Spectrochim. Acta*, **19**, 117 (1963). Using Hoskin and Lord's frequencies and force field, we calculate force constant values agreeing with their set to within 0.01 mdyn/Å in each case.

[32] E. L. Muetterties, W. Mahler, and R. Schmutzler, *Inorg. Chem.*, **2**, 613 (1963).

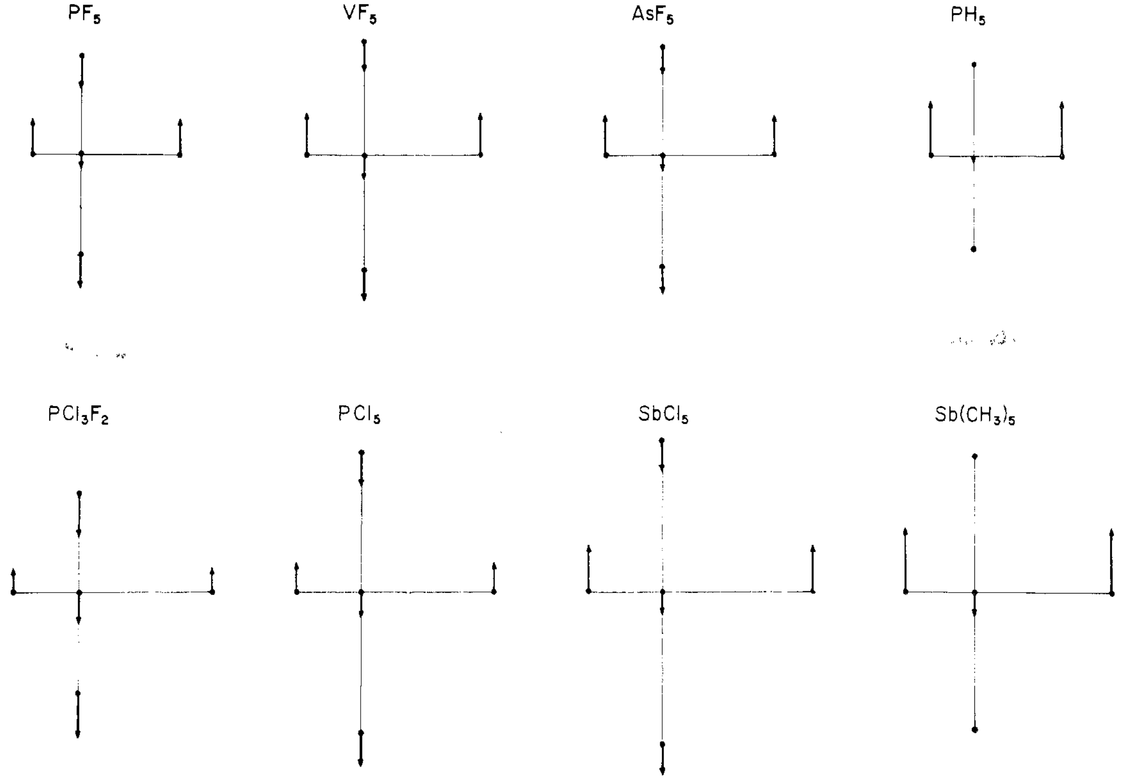

Figure 2.—Normal mode amplitudes for the out-of-plane equatorial bend (a_2'' species). The view shows atoms 1, 4, 5, and 6 (see Figure 1) in the plane of the drawing with atoms 2 and 3 (on the left of each figure) superimposed one behind the other. See text for a description of the scale.

TABLE V

INTRAMOLECULAR EXCHANGE COORDINATES FOR D_{3h} TRIGONAL-BIPYRAMIDAL MOLECULES

Route	Bond strengths[a]	Sym coord	Intermediate	Unique atom[b]	Ligand rearrangement	Figure
1	Strong eq–weak ax.	$S_{6a} + S_{7a}$	Tetrag py	1	No	4a
2	Strong eq–weak ax.[c]	$S_{6b} + S_{7b}$	Tetrag py	2, 3	Yes	4b
3	Weak eq–strong ax.	$S_{6a} + S_{7a}$	Nearly sq py	1	No	3a
4	Weak eq–strong ax.[c]	$S_{6b} + S_{7b}$	Nearly sq py	2, 3	Yes	3b
5	Weak eq–weak ax.	$S_{8a} + S_{6b}$	Pentag planar		Yes	5
6	Weak eq–weak ax.	S_{8b}	Pentag planar		Yes	5
7	Weak eq–weak ax.		Ionization ($MX_4^+X^-$)[d]			

[a] No exchange assumed for strong eq–strong ax. case [b] The unique atoms refer to nonequivalent atoms in the intermediate. Refer to Figure 1 for numbering. [c] Routes 2 and 4 give slightly higher but comparable orderings of exchange barriers compared to routes 1 and 3, respectively (see Table IV). However, ligand rearrangement energy must also be considered in the former routes. [d] Not an intramolecular route.

lence at the lowest temperatures studied[33,34] (~−190°). Assuming the exchange mechanism is realistic, the implication is that the frequency assignment may not be proper especially since it was observed[14b] in the solid in a region complicated by contaminating HF lattice vibrations. Consequently, barrier energies are also listed for ν_7 122 cm^{-1}, a value closer to that observed[15,20] for this frequency in related molecules.

Of the molecules listed in Table IV, in no case has it been rigorously proven that intramolecular exchange is occurring although, it is a highly likely process for PF_5, AsF_5, and $Sb(CH_3)_5$. Evidence for exchange does not exist for the other molecules listed in Table I.

An experiment which would definitely establish the plausibility of a pseudorotation process would be the observation of spectroscopic splitting, analogous to that observed for the ammonia molecule. In the latter molecule the ν_2 bend at 950 cm^{-1} shows a band splitting of about 36.5 cm^{-1} corresponding to the sum of the inversion splittings (tunneling frequencies) of the ground and first excited vibrational states for ν_2.[35]

Considering the magnitude of the barriers in Table IV, exchange frequencies for tunneling are calculated to be too small for spectroscopic observation in all cases except that for the hypothetical PH_5 molecule containing the much lighter proton ligands. About a 1-cm^{-1} splitting for the ν_7 vibration is calculated for

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(33) H. S. Gutowsky, D. W. McCall, and C. P. Slichter, *J. Chem. Phys.*, **21**, 279 (1953).

(34) E. L. Muetterties and W. D. Phillips, *J. Am. Chem. Soc.*, **81**, 1084 (1959).

(35) G. Herzberg, "Molecular Spectra and Molecular Structure. II. Infrared and Raman Spectra of Polyatomic Molecules," D. Van Nostrand Co., Inc., New York, N. Y., 1945, p 223.

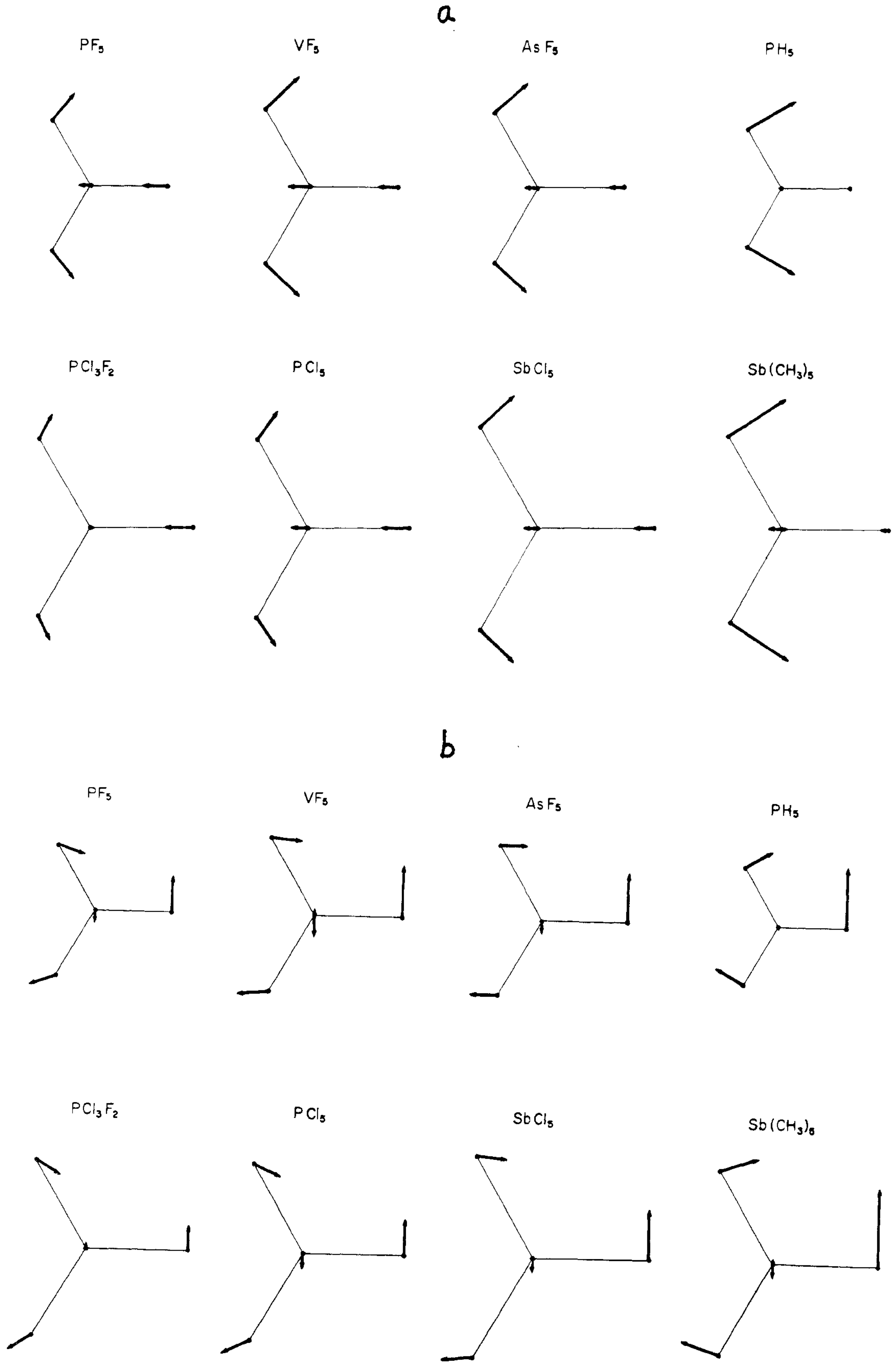


Figure 3.—Normal mode amplitudes for the in-plane equatorial bend (field A) made up of (a) the a subset symmetry coordinates and (b) the b subset symmetry coordinates of e′ species. View is down the C_3 axis. The smaller arrow of the two from the central atom in VF_5 and $Sb(CH_3)_5$ represents axial atom displacements.

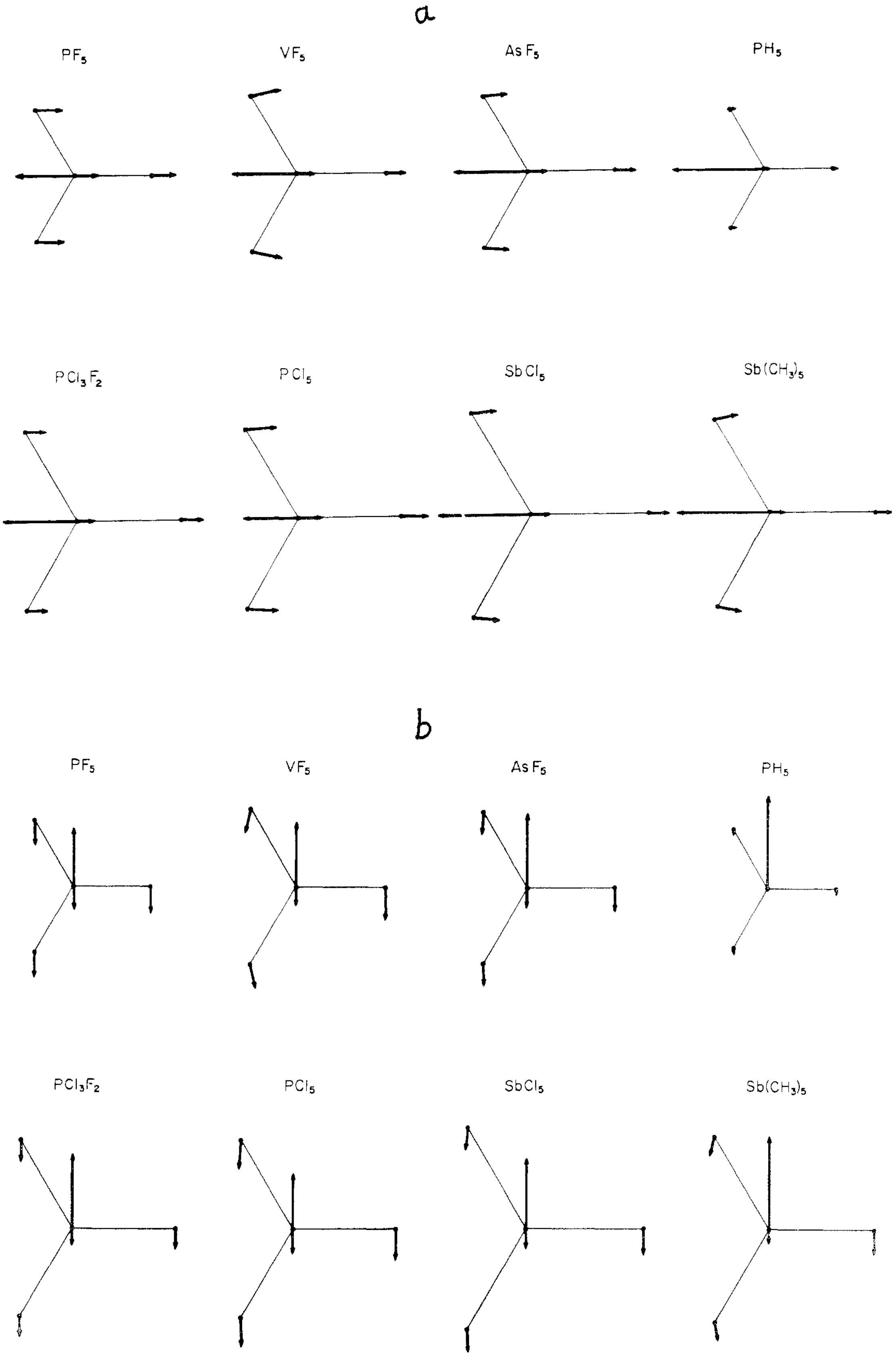


Figure 4.—Normal mode amplitudes for the axial bend (field *A*) made up of (a) the a subset symmetry coordinates and (b) the b subset symmetry coordinates of e′ species. View is down the C_3 axis. The axial atom displacements are shown by the longer arrows in (a) and (b) emanating from the central atom.

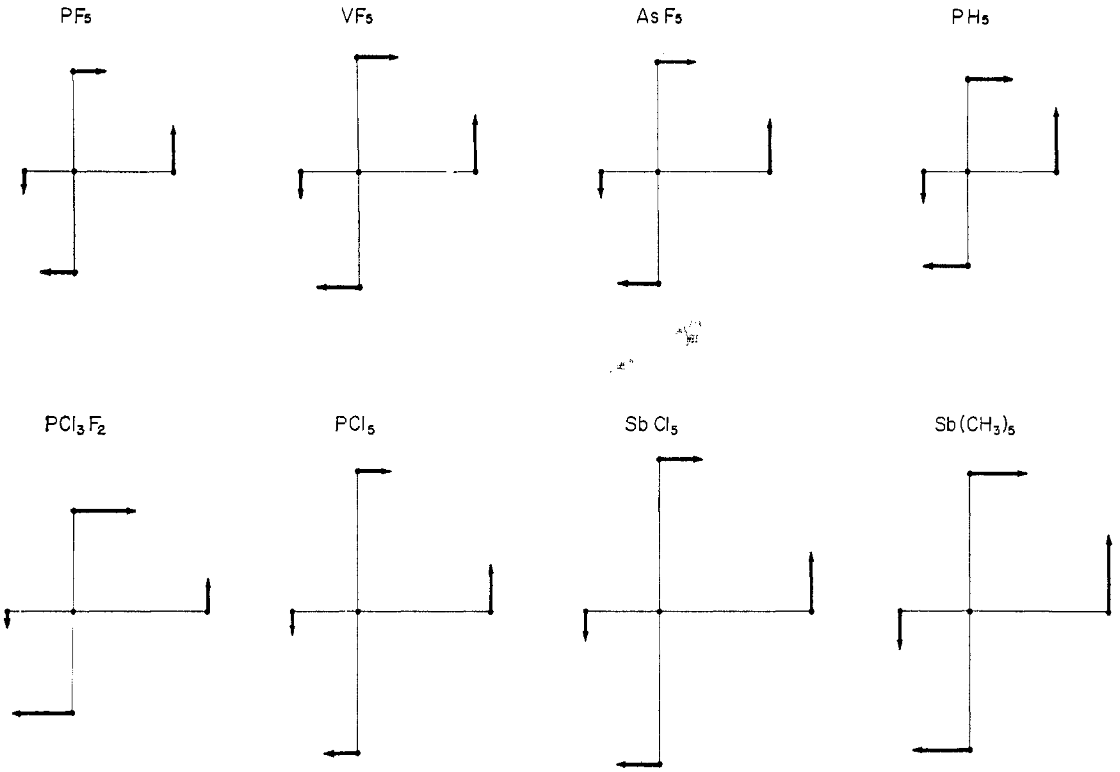


Figure 5.—Normal mode amplitudes for the rocking vibration of e″ species. Degenerate component view as in Figure 2. The other degenerate component of e″ species is viewed orthogonal to this component along the C_2 axis containing atoms 1 and 6.

the latter molecule. A similar splitting is expected for PH_4F which should be dipolar and give rise to corresponding microwave lines.

Exchange Coordinates

In considering possible routes to intramolecular exchange induced by internal vibrational motions, essentially three observable situations might arise for trigonal-bipyramidal molecules of D_{3h} symmetry. These may be classified with regard to relative strengths of equatorial and axial bonds.

The processes deemed most important are described in Table V, listing the major contributing symmetry coordinates and configuration of the intermediate in the exchange. Appropriate figures are referred to for a clearer idea of the formation of the intermediates. Figures 2–5 represent the classical amplitudes computed for the ground vibrational states and are shown on a scale 20 times that used for the bond distances for all molecules except the hypothetical PH_5. For the latter molecule, a scale factor of 10 was necessary to obtain a comparable drawing.

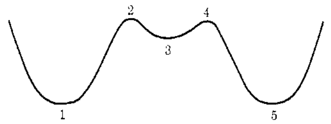
For the molecules under discussion, the vibrational potential function A uniformly indicates weak axial bonds relative to equatorial bonds based on comparisons of bond stretching force constants (Table II) and bond distances.[21–24,29] This leads to the lowest energy intermediate in agreement with the barrier heights in Table IV as a tetragonal pyramid. The relative amplitudes for this process result largely from the type shown in Figure 4a with a small contribution from that in Figure 3a (route 1, Table V).

The alternate potential B implies relatively weak equatorial compared to axial bonds based on the large-amplitude in-plane bending motion. Exchange by this route leads to a nearly square-pyramidal intermediate. The large degree of in-plane bending motion (Figure 3a) is combined with lesser amounts of axial bend (Figure 4a) and is arrived at no matter which phase of the motion is considered (route 3, Table V). In each case, the unique position would be occupied by an equatorial atom; hence exchange could take place intramolecularly.

Exchange intermediates formed by considering large-amplitude motions from either of the bending symmetry coordinates S_{6b} or S_{7b}, or some combination thereof, are less likely for D_{3h} trigonal-bipyramidal molecules because some ligand rearrangement is involved in reaching the symmetrical intermediates. Ligand rearrangement is necessary to allow equivalence of equatorial and axial atoms in the exchange process. However in a less symmetrical trigonal bipyramid, for example, the hypothetical PH_4I molecule, assuming the heavy iodine atom is in an equatorial position (C_{2v} symmetry) and does not move appreciably during the exchange, a square pyramid could result with little involvement of ligand reorganizational energy. For the latter process the principal motion is considered to be due to the type defined by the S_{6b} symmetry coordinate (Figure 3b) for the case of weak equatorial–strong axial bonds (route 4, Table V).

In category three of Table V for trigonal bipyramids with both weak equatorial and axial bonds, a most reasonable exchange coordinate leads to a planar pentagonal arrangement of ligands for cases where large amplitude rocking vibrations ν_8 represent the exchange coordinates (routes 5 and 6, Table V). In these instances either the S_{8a} or S_{8b} symmetry coordinates (Figure 5) would be principally responsible for bringing the axial atoms into a planar position with the equatorial ligands. Accompanied by some ligand repulsion a D_{5h} intermediate results.

The potential diagram would contain a saddle point (3) associated with the planar pentagon while the difference in energy between the hump heights (2 and 4) and the saddle point would represent ligand rearrangement energy. The exchange barrier between equivalent trigonal bipyramids (1 and 5) is shown as the energy difference between either 1 and 2 or 4 and 5 in the above figure. Of course, in all of the above processes, certain mixing of stretching coordinates may serve to reduce the barrier energy.



Possible candidates for routes 3 or 4 of Table V are $CuCl_5^{3-}$ in $[Cr(NH_3)_6][CuCl_5]$ or $Ni(CN)_5^{3-}$ in $[Cr(NH_2CH_2CH_2NH_2)_3][Ni(CN)_5]\cdot 1.5H_2O$. X-Ray investigations,[36,37] recently available, show trigonal-bipyramidal structures with shorter axial distances in each case. In addition to a distorted trigonal-bipyramid environment in the latter compound, $Ni(CN)_5^{3-}$ also exists in a square-pyramidal environment, each structure hydrogen bonded to water.[37] However, no evidence appears to exist showing exchange phenomena for these substances.

It does not seem worthwhile to consider more extensive processes. At present, little experimental evidence exists for some of the ones already mentioned. If the need arises, more complex calculations may be profitable, taking into account anharmonicity assuming suitable spectroscopic information becomes available.

What has been discussed here are possible routes for intramolecular exchange as a result of considerable amplitude in bending vibrations.[38] As pointed out,[2] pseudorotation may occur or energy barriers may be reduced at least in collisional processes especially important in condensed-state media.

Acknowledgment.—Support of this research by the National Science Foundation is gratefully acknowledged as is use of the CDC 3600 computer.

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[36] K. N. Raymond, D. W. Meek, and J. A. Ibers, *Inorg. Chem.*, **7**, 1111 (1968).

[37] K. N. Raymond, P. W. R. Corfield, and J. A. Ibers, *ibid.*, **7**, 1362 (1968).

[38] Recent papers [P. C. Lauterbur and F. Ramirez, *J. Am. Chem. Soc.*, **90**, 6722 (1968); E. L. Muetterties, *ibid.*, **90**, 5097 (1968); **91**, 1639 (1969)] discuss topological aids to visualizing stereoisomerization *via* pseudorotation routes for trigonal-bipyramidal molecules.

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Synthesis and Properties of Certain Uranyl Aminopolycarboxylates

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The uranyl chelates of iminodiacetic acid with a ratio (metal:ligand) of 1:2, of nitrilotriacetic acid with ratios of 1:1 and 3:2, of ethylenediaminetetraacetic acid with ratios of 1:1 and 2:1, and of *trans*-cyclohexanediaminetetraacetic acid with ratios of 1:1 and 2:1 have been prepared and characterized by elemental analyses, infrared spectroscopy, and thermal analyses. Their probable structures are discussed.

Introduction

Although the coordination chemistry of oxycations of hexavalent uranium has been studied rather extensively, researches on uranyl chelates of analytically important aminopolycarboxylic acids such as ethylenediaminetetraacetic acid (H_4EDTA) and its analogs have been restricted principally to solutions. Brintzinger and Hesse[2] isolated the 1:1 uranyl–nitrilotriacetic acid (H_3NTA) and the 1:1 uranyl–EDTA chelates. The 2:1 uranyl–EDTA chelate has been prepared recently by Bhat and Krishnamurthy.[3] However, the physical properties of these solids have not been reported.

Differential thermal analysis (dta) and thermogravimetric analysis (tga) of some of the aminopolycarboxylic acids and many metal–EDTA chelates have been reported[4] in recent years. Charles[5] studied recently a series of alkali metal salts of Nd–EDTA chelates by tga, dta, and thermomanometric analysis. Bhat and Iyer[6] used the tga technique for many metal–EDTA chelates and concluded that although no generalizations could be made about the stability, decomposition involves either a two-step process or a one-step process.

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[1] This report is based on portions of a thesis to be submitted by M. Krishnamurthy to the Graduate School of Howard University in partial fulfillment of the requirements for the Ph.D. degree.

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