Potential Field and Force Constants of Some Trigonal Bipyramidal Pentahalides†

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The valence-type force constants of PF_5, PCl_5, SbF_5, $SbCl_5$, $NbCl_5$ and $TaCl_5$ are evaluated by means of WILSON's $F-G$ matrix method, using existing infrared and RAMAN data. Anharmonicity is not taken into account.

Until two years ago, little progress had been made in interpreting the vibrational spectra of trigonal bipyramidal $X\,Y_5$ molecules. However, GAUNT and AINSCOUGH [1, 2] recently measured and interpreted the infrared and RAMAN spectra of $NbCl_5$ and SbF_5. They succeeded in making a complete assignment of the fundamental frequencies of both these molecules. It is now also possible to interpret the older RAMAN data for other pentahalides possessing this structure by analogy with GAUNT and AINSCOUGH's assignments.

The trigonal bipyramidal $X\,Y_5$ structure gives rise to two nondegenerate type A_1' vibrations (ν_1, ν_2), two nondegenerate type A_2'' vibrations (ν_3, ν_4), three doubly degenerate type E' vibrations (ν_5, ν_6, ν_7) and one doubly degenerate type E'' vibration (ν_8). ν_1, ν_2, ν_3 and ν_5 are stretching vibrations. All the other vibrations are angle deformations. The A_1' type vibrations are polarized in RAMAN scattering.

1. Coordinates

The normal coordinate treatment which follows is given in a somewhat cursory fashion, since much of the information can be found elsewhere [3].

Since there are twelve vibrational degrees of freedom, at least twelve internal coordinates are needed to describe the motion. We choose Δd_1, Δd_2, Δd_3, ΔD_4, ΔD_5, $d\Delta\alpha_{12}$, $d\Delta\alpha_{23}$, $d\Delta\alpha_{31}$, $d\Delta\beta_{51}$, $d\Delta\beta_{52}$, $d\Delta\beta_{53}$, $d\Delta\beta_{41}$, $d\Delta\beta_{42}$ and $d\Delta\beta_{43}$ (see Fig. 1). Δd_i is the change in length of an equatorial bond, ΔD_i is the change in length of an axial bond, $\Delta\alpha_{ij}$ is the change in the equatorial angle $Y_i X Y_j$, and $\Delta\beta_{ij}$ is the change in the "axial" angle $Y_i X Y_j$. The angles are multiplied by the bond length in order to maintain the same dimensions for the various force constants. It is assumed that the length d of an equatorial bond is the same as the length D of an axial bond. Strictly speaking, this assumption is unwarranted, but in practice this difference in length is seldom observable.

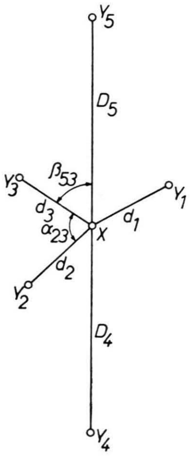

Fig. 1. The trigonal bipyramidal $X\,Y_5$ molecule (point group D_{3h}).

A suitable set of symmetry coordinates is the following:

Redundant coordinates:

$$R_a = d\,(\Delta\alpha_{12} + \Delta\alpha_{23} + \Delta\alpha_{31})/\sqrt{3} \equiv 0\,,$$

$$R_b = d\,(\Delta\beta_{41} + \Delta\beta_{42} + \Delta\beta_{43} + \Delta\beta_{51} + \Delta\beta_{52} + \Delta\beta_{53})/\sqrt{6} \equiv 0\,,$$

For the type A_1' vibrations,

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[1] J. GAUNT and J. B. AINSCOUGH, Spectrochim. Acta **10**, 52 [1957].

[2] J. GAUNT and J. B. AINSCOUGH, Spectrochim. Acta **10**, 57 [1957].

[3] J. S. ZIOMEK and C. B. MAST, J. Chem. Phys. **21**, 862 [1953].

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$$R_1 = (\Delta d_1 + \Delta d_2 + \Delta d_3)/\sqrt{3}\,,$$
$$R_2 = (\Delta D_4 + \Delta D_5)/\sqrt{2}\,.$$

For the type A_2'' vibrations,

$$R_3 = (\Delta D_4 - \Delta D_5)/\sqrt{2}\,,$$
$$R_4 = d(\Delta\beta_{41} + \Delta\beta_{42} + \Delta\beta_{43} - \Delta\beta_{51} - \Delta\beta_{52} - \Delta\beta_{53})/\sqrt{6}\,.$$

For the type E' vibrations,

$$R_{5a} = (2\,\Delta d_1 - \Delta d_2 - \Delta d_3)/\sqrt{6}\,,$$
$$R_{5b} = (\Delta d_2 - \Delta d_3)/\sqrt{2}\,,$$
$$R_{6a} = d(2\,\Delta\beta_{41} - \Delta\beta_{42} - \Delta\beta_{43} + 2\,\Delta\beta_{51} - \Delta\beta_{52} - \Delta\beta_{53})/\sqrt{12}\,,$$
$$R_{6b} = \tfrac{1}{2}\,d(\Delta\beta_{42} - \Delta\beta_{43} + \Delta\beta_{52} - \Delta\beta_{53})\,,$$
$$R_{7a} = d(2\,\Delta\alpha_{23} - \Delta\alpha_{12} - \Delta\alpha_{31})/\sqrt{6}\,,$$
$$R_{7b} = d(\Delta\alpha_{12} - \Delta\alpha_{31})/\sqrt{2}\,.$$

For the type E'' vibration,

$$R_{8a} = d(2\,\Delta\beta_{41} - \Delta\beta_{42} - \Delta\beta_{43} - 2\,\Delta\beta_{51} + \Delta\beta_{52} + \Delta\beta_{53})/\sqrt{12}\,,$$
$$R_{8b} = \tfrac{1}{2}\,d(\Delta\beta_{42} - \Delta\beta_{43} - \Delta\beta_{52} + \Delta\beta_{53})\,.$$

These symmetry coordinates are all normalized, mutually orthogonal, identically oriented, and transform according to the character table of the symmetry point group D_{3h}.

2. Potential Energy

The force constants used are f_β (representing the force associated with axial angle bending); $f_{\beta\beta}$ (interaction between axial bendings on the same side of the equatorial plane); $f'_{\beta\beta}$ (interaction between axial bendings on opposite sides of the plane when they have a bond in common) and $f''_{\beta\beta}$ (interaction between axial bendings on opposite sides of the plane when they do not have an equatorial bond in common). The definitions of the other force constants which are used are fairly obvious, and will not be given here.

The **F**-matrix elements are:
For the type A_1' vibrations,

$$F_{11} = f_d + 2\,f_{dd}\,, \qquad F_{12} = F_{21} = \sqrt{6}\,f_{\mathrm{d}D}\,,$$
$$F_{22} = f_D + f_{DD}\,.$$

For the type A_2'' vibrations,

$$F_{33} = f_D - f_{DD}\,,$$
$$F_{34} = F_{43} = \sqrt{12}\,(f_{D\beta} - f'_{D\beta})\,,$$
$$F_{44} = f_\beta + 2\,f_{\beta\beta} - f'_{\beta\beta} - 2\,f''_{\beta\beta}\,.$$

For the type E' vibrations,

$$F_{55} = f_d - f_{dd}\,,$$
$$F_{56} = F_{65} = 2\,(f_{\mathrm{d}\beta} - f'_{\mathrm{d}\beta})\,,$$
$$F_{57} = 7_{75} = f_{\mathrm{d}\alpha} - f'_{\mathrm{d}\alpha}\,,$$
$$F_{66} = f_\beta - f_{\beta\beta} + f'_{\beta\beta} - f''_{\beta\beta}\,,$$
$$F_{67} = F_{76} = -2\,(f_{\alpha\beta} - f'_{\alpha\beta})\,,$$
$$F_{77} = f_\alpha - f_{\alpha\alpha}\,.$$

For the type E'' vibration,

$$F_{88} = f_\beta - f_{\beta\beta} - f'_{\beta\beta} + f''_{\beta\beta}\,.$$

3. Kinetic Energy

The **G**-matrix elements are as follows:
For the type A_1' vibrations,

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

For the type A_2'' vibrations,

$$G_{33} = 2\,\mu_x\,, \quad G_{34} = G_{43} = 0\,, \quad G_{44} = 2\,\mu_y + 8\,\mu_x\,.$$

For the type E' vibrations,

$$G_{55} = \mu_y + 3\,\mu_x/2\,, \qquad G_{56} = G_{65} = -3\,\mu_x/\sqrt{2}\,,$$
$$G_{57} = G_{75} = 3\sqrt{3}\,\mu_x/2\,, \qquad G_{66} = 3\,\mu_y + 6\,\mu_x\,,$$
$$G_{67} = G_{76} = -3\sqrt{3}\,\mu_x/\sqrt{2}\,, \quad G_{77} = 3\,\mu_y + 9\,\mu_x/2\,.$$

For the type E'' vibration, $G_{88} = \tfrac{7}{2}\mu_y$.

μ_x and μ_y are the reciprocal masses of the X and Y atoms, respectively.

The secular equations for the various irreducible representations can now be constructed by applying the usual principles[4].

4. Vibrational Assignments and Force Constants

Gaunt and Ainscough[1, 2] observed the infrared and Raman spectra of SbF_5 and $NbCl_5$. They also assigned the fundamental frequencies for these two molecules, and their results are given in Table 1. In their Raman spectra they observed, among others, peaks at 228 and 95 cm^{-1} for SbF_5, and 153 and 106 cm^{-1} for $NbCl_5$. They assigned these peaks as follows:

SbF_5: $\nu_7(E') = 95\ cm^{-1}$, $\nu_8(E'') = 228\ cm^{-1}$;
$NbCl_5$: $\nu_7(E') = 153\ cm^{-1}$, $\nu_8(E'') = 106\ cm^{-1}$.

The above assignment for SbF_5 leads to values of F_{44}, F_{66} and F_{88} which are of the same order of

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[4] E. B. Wilson, jr., J. Chem. Phys. **7**, 1041 [1939]; **9**, 76 [1941].

magnitude, as would be expected. However, their assignment for $NbCl_5$ fails to accomplish this, and it appeared to be necessary to assign the $NbCl_5$ peaks in the following way:

$NbCl_5$: $\nu_7(E') = 106\ cm^{-1}$, $\nu_8(E'') = 153\ cm^{-1}$.

There is no particular reason why the earlier assignment should necessarily be correct.

The infrared spectrum of gaseous PF_5 has been investigated by PENNSLER and PLANET[5] and by GUTOWSKY and LIEHR[6]. They found only four fundamentals, the fifth infrared-active fundamental presumably occurring in the low-frequency region. The present assignment, shown in Table 1, was made on the basis of the band envelopes.

The RAMAN spectra of PCl_5, $SbCl_5$, $TaCl_5$ and $NbCl_5$ were observed by MOUREU and his associates[7–9]. They did not assign the observed peaks. The present assignments were made on the basis of the polarization of the RAMAN lines, and by analogy to GAUNT and AINSCOUGH's assignments[1, 2] for SbF_5 and $NbCl_5$. The results are listed in Table 1.

The force constants were evaluated in the usual way. In the cases of $NbCl_5$ and PCl_5 imaginary results were obtained for F_{55} and F_{66} if F_{56} is neglected. Since no isotopic data were available, the minimum values of F_{56} were found which yielded real values for F_{55} and F_{66}. F_{77} for $SbCl_5$ was calculated by splitting off ν_5 and ν_6 (which were not known) by means of WILSON's approximation[4].

Molecule	PF_5	PCl_5	SbF_5	$SbCl_5$	$NbCl_5$	$TaCl_5$
$\nu_1(A_1')$	—	409	667	356	412	460
$\nu_2(A_1')$	—	356	264 (?)	309	355	370
$\nu_3(A_2'')$	948	—	294	—	315	—
$\nu_4(A_2'')$	575.5	—	212	—	260	—
$\nu_5(E')$	1027.5	495	713	—	497	490
$\nu_6(E'$	534	449	491	400	396	410
$\nu_7(E')$	—	100	95	72	106	90
$\nu_8(E'')$	—	190	228	177	153	170

Table 1. Fundamental Frequencies in cm^{-1}.

Molecule	PF_5	PCl_5	SbF_5	$SbCl_5$	$NbCl_5$	$TaCl_5$
F_{11}	—	3.493	4.978	2.646	3.543	4.419
F_{22}	—	2.646	0.780	1.994	2.631	2.858
F_{33}	8.198	—	3.099	—	2.715	—
F_{44}	0.537	—	0.155	—	0.279	—
F_{55}	5.773	2.100	4.511	—	2.726	3.293
F_{56}	—	0.429	—	—	0.089	—
F_{66}	0.587	0.578	0.716	—	0.811	1.022
F_{77}	—	0.046	0.028	0.031	0.060	0.048
F_{88}	—	0.215	0.166	0.173	0.140	0.167

Table 2. *F*-matrix elements in units of 10^5 dynes cm^{-1}.

Molecule	PCl_5	SbF_5	$NbCl_5$	$TaCl_5$
f_d	2.564	4.667	2.998	3.668
f_{dd}	0.464	0.156	0.272	0.375
f_D (or $f_D + f_{DD}$)	2.646	2.323	2.673	2.858
f_{DD}	—	−0.776	−0.042	—
$f_\alpha - f_{\alpha\alpha}$	0.046	0.028	0.060	0.048
$f_{d\beta} - f'_{d\beta}$	0.214	—	0.044	—
$f_\beta - f_{\beta\beta}$	0.397	0.441	0.475	0.595
$f'_{\beta\beta} - f''_{\beta\beta}$	0.181	0.275	0.335	0.427
$f_{\beta\beta} - f''_{\beta\beta}$	—	−0.011	0.046	—

Table 3. Valence-type force constants in units of 10^5 dynes cm^{-1}.

The ***F***-matrices are listed in Table 2, and the valence-type force constants deduced from these, in Table 3. The valence-type constants are not listed for PF_5 and $SbCl_5$, since so few ***F***-matrices have here been evaluated that a separate listing is hardly warranted.

The magnitude of f_{DD} for SbF_5 is notable. The present authors feel that ν_2 or ν_3 may have been incorrectly assigned in this case. Further study is needed in the far infrared region of the spectrum of SbF_5.

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