Vapour-phase Intensity Studies of the Raman-active Bands of Group 6 Hexafluorides

By **R. J. H. Clark** * and **N. R. D'Urso**, Christopher Ingold Laboratories, University College London, 20 Gordon Street, London WC1H 0AJ

The vapour-phase Raman spectra of sulphur(VI), selenium(VI), and tellurium(VI) fluorides have been recorded with 488.0- and/or 514.5-nm excitation at *ca.* 0.5 atm and *ca.* 295 K. The intensities of the $\nu_1(a_{1g})$, $\nu_2(e_g)$, and $\nu_5(t_{2g})$ bands have been determined relative to that of the $\nu_1(a_1)$ band of methane as external standard, and this has permitted the calculation of Raman scattering activities and differential cross sections for each band. Molecular-($\bar{\alpha}_j'$), bond-($\bar{\alpha}'_{\mathrm{MX}}$), and bond-component ($\alpha'_{\parallel}$, $\alpha'_{\perp}$) polarisability derivatives, as well as bond anisotropies (γ_{MX}), have been deduced in all cases. The $\bar{\alpha}'_{\mathrm{MF}}$ values are in the order $\bar{\alpha}'_{\mathrm{SeF}}$ (1.73) > $\bar{\alpha}'_{\mathrm{TeF}}$ (1.65) > $\bar{\alpha}'_{\mathrm{SF}}$ (1.35 Å^2), which agrees with the predictions of a delta-function potential model of chemical bonding and hence with fractional Pauling covalent bond characters of SF (0.61) $\geqslant$ SeF (0.60) $\gg$ TeF (0.47). A Pauling electronegativity for tellurium of 2.25 is deduced on the basis of the model.

RECENT gas-phase intensity studies on the Raman-active bands of spherical-top molecules have been directed to the calculation of molecular ($\bar{\alpha}'_j$) and bond ($\bar{\alpha}'_{\mathrm{MX}}$) polarisability derivatives, bond-anisotropy derivatives (γ'_{MX}), bond anisotropies (γ_{MX}) and related quantities,[1,2] and to the effects of the internal field on Raman differential-scattering cross sections ($d\sigma/d\Omega$).[1,3] In this context, our attention was brought to the hexafluorides SF_6, SeF_6, and TeF_6 for which intensity measurements had been carried out some years ago with mercury-arc excitation, but only on the totally symmetric fundamental in each case.[4] A complete study on these molecules, *i.e.* on all the three Raman-active fundamentals, and the calculation of all the appropriate electro-optical parameters therefore seemed appropriate, particularly as such experimental studies can now be carried out with the benefits of powerful argon-ion laser excitation. The resulting values for the various parameters, in particular $\bar{\alpha}'_{\mathrm{MX}}$ values, compare favourably with values calculated for this parameter on the basis of a delta-function model for chemical bonding, in which allowance is made for the charge density removed from the bonding region because of the polar nature of the MX bonds.[5]

EXPERIMENTAL

The hexafluorides were obtained from Cambrian Chemicals Co. (SF_6), ROC/RIC (SeF_6), and Ozark Mahoning Co. (TeF_6) and used without further purification.

The Raman spectra were recorded by use of a Spex 1401 spectrometer in conjunction with Coherent Radiation models 52 and 12 argon-ion lasers. The scattered radiation was collected at 90° and focused by a *f*/0.95 lens on to the entrance slit of the 0.75-m Czerny Turner monochromator after having been passed through a polarisation scrambler. The gratings (Bausch and Lomb, 1 200 lines per millimetre) were blazed at 500 nm. The method of detection was photon counting by a cooled RCA C31034 (grade I) phototube and linear display. The 488.0- and 514.5-nm exciting lines were used with powers in the range 1—8 W, the laser beam traversing the cell once only.

The intensity measurements were carried out with an extra-cavity cell arrangement.[1,2] This involved the measurement of the intensity of a standard (the a_1 band of methane) at a known temperature (*ca.* 295 K) and pressure (*ca.* 0.5 atm).[†] The cell was then emptied and refilled with the sample at a known temperature and pressure and, after temperature equilibration, the intensities of the sample bands were then measured. This procedure was then repeated 6—22 times by use of a bracketing technique. The advantages of the extra-cavity arrangement are (*a*) freedom from any internal-field effect [3] and (*b*) the avoidance of possible overlapping of sample and reference bands. The disadvantage of the arrangement lies in the possibility of minor disarrangement of the cell during the exchange of gases.

Band areas were determined by the cut-and-weigh procedure and are considered accurate to ±10%. All the quoted band intensities have been corrected for the spectral response of the instrument.[6]

In the case of tellurium(VI) fluoride, the intense $\nu_1(a_{1g})$ band overlaps slightly the much weaker $\nu_2(e_g)$ band, and hence the intensity of the latter was deduced from the relation $I_{\mathrm{total}}(e_g) = (7/3)I_{\perp}(e_g)$ (allowance being made for the loss of intensity due to the insertion of the analyser); this relation follows from the fact that the $\nu_1(a_{1g})$ and $\nu_2(e_g)$ bands have depolarisation ratios of zero and 0.75 respectively.

RESULTS AND DISCUSSION

Treatment of Data.—The intensities of the bands arising from the three Raman-active fundamentals $\nu_1(a_{1g})$, $\nu_2(e_g)$, and $\nu_5(t_{2g})$ of the hexafluorides are given in Table 1 relative to that arising from the $\nu_1(a_1)$ fundamental of methane as external standard. The scattering activity of the standard has been taken, as previously,[1,2] to be $1\,226 \times 10^{-9}$ cm^4 g^{-1} mol^{-1} (203.5 N $\times 10^{-32}$ cm^4 g^{-1}) which is equivalent to a Raman differential-scattering cross section of 3.035×10^{-30} cm^2 mol^{-1} sr^{-1} for 514.5-nm excitation and 3.889×10^{-30} cm^2 mol^{-1} sr^{-1} for 488.0-nm excitation, to an $\bar{\alpha}'_1$ value of 2.13 Å^2 N$^{\frac{1}{2}}$ g$^{-\frac{1}{2}}$ and thus to an $\bar{\alpha}'_{\mathrm{CH}}$ value of 1.07 Å^2.

[†] Throughout this paper: 1 atm = 101 325 Pa.

[1] R. J. H. Clark and P. D. Mitchell, *J.C.S. Faraday II*, 1975, 515.

[2] R. S. Armstrong and R. J. H. Clark, *J.C.S. Faraday II*, 1976, 11.

[3] J. R. Nestor and E. R. Lippincott, *J. Raman Spectroscopy*, 1973, **1**, 305.

[4] D. A. Long and E. L. Thomas, *Trans. Faraday Soc.*, 1963, 1026.

[5] T. V. Long and R. A. Plane, *J. Chem. Phys.*, 1965, **43**, 457.

[6] Y. M. Bosworth and R. J. H. Clark, *J.C.S. Dalton*, 1974, 1749.

The relative molar intensities (accurate to ± 14%) have been converted into polarisability derivatives by use of relation (1).[6] $\bar{\alpha}'_j$ and γ'_j are, respectively, the

$$\frac{I_jM_1}{I_1M_j} = f\frac{g_j}{g_1}\left(\frac{45\bar{\alpha}'^2_j + 7\gamma'^2_j}{45\bar{\alpha}'^2_1 + 7\gamma'^2_1}\right)$$

$$\text{where } f = \frac{f_j}{f_1} = \left(\frac{\nu_0 - \nu_j}{\nu_0 - \nu_1}\right)^4 \frac{\nu_1}{\nu_j}\left[\frac{1 - \exp(-\nu_1/\boldsymbol{k}T)}{1 - \exp(-\nu_j/\boldsymbol{k}T)}\right],$$

$$f_j = \frac{1}{\nu_j}\left[\frac{(\nu_0 - \nu_j)^4}{1 - \exp(-\nu_j/\boldsymbol{k}T)}\right] \qquad (1)$$

mean molecular polarisability derivative and the anisotropy derivative with respect to the normal coordinate Q_j, degeneracy g_j, ν_0 is the exciting frequency, and ν_j is the frequency shift of the normal mode j. The Raman differential-scattering cross section for the jth fundamental, $d\sigma_j/d\Omega$, relates the incident irradiance (power per unit area) to the integrated radiant intensity (power per unit solid angle per mol) and is given by expression (2) [2,7] where $(SA)_j$, the scattering activity, is

$$d\sigma_j/d\Omega = 0.969\,44 \times 10^{-37} f_j\,(SA)_j \qquad (2)$$

defined as in (3). Alternatively, Raman differential-scattering cross sections may be obtained directly from

$$(SA)_j = g_j(45\bar{\alpha}'^2_j + 7\gamma'^2_j) \qquad (3)$$

the band intensities measured relative to the standard by the relation $d\sigma_j/d\Omega = (I_jM_1/I_1M_j)(d\sigma_1/d\Omega)$. Bond-polarisability derivatives were calculated from the appropriate mean molecular-polarisability derivative *via* relation (4) [6] where m_X is the mass of the X atom in a

$$\bar{\alpha}'_1 = \left(\frac{n}{m_X}\right)^{\frac{1}{2}}\bar{\alpha}'_{MX} \qquad (4)$$

molecule of general formula MX_n. Thus, since $\gamma' = 0$ and $g_j = 1$ for totally symmetric modes of spherical-top molecules we obtain (5) with $\bar{\alpha}'_{CH}$ taken, as indicated

$$\bar{\alpha}'_{MF} = \bar{\alpha}'_1(MF_6) \times \left(\frac{19.00}{6}\cdot\frac{4}{1.008}\right)^{\frac{1}{2}}\bar{\alpha}'_{CH} \qquad (5)$$

above, to be 1.07 Å². The resulting $\bar{\alpha}'_{MF}$ values (Table 2) are *ca.* 13% higher than those originally reported by Long and Thomas,[4] 3% of this being accounted for by the revised value for $\bar{\alpha}'_{CH}$; this level of agreement is very satisfactory in view of the technically difficult nature of the measurements involved.

TABLE 1

Relative molar intensities and Raman differential-scattering cross-sections of Raman-active bands of the hexafluorides studied

Molecule	Mode	λ_0/nm	$\tilde{\nu}$/cm^{-1} [a]	$10^{14}f_j$	$(1/f)$ (I_jM_1/I_1M_j) [b]	10^7SA	$10^{30}(d\sigma/d\Omega)$ [c]
SF_6	$\nu_1(a_{1g})$	514.5	773.6	1.603	0.13_0	1.59_4	2.48
	$\nu_2(e_g)$	514.5	642.1	2.029	0.039_4	0.48_3	0.95_0
	$\nu_5(t_{2g})$	514.5	522.9	2.651	0.019_7	0.24_2	0.62_1
	$\nu_1(a_{1g})$	488.0	773.6	1.998	0.12_4	1.52_0	2.94
	$\nu_2(e_g)$	488.0	642.1	2.526	0.038_6	0.47_3	1.15_9
	$\nu_5(t_{2g})$	488.0	522.9	3.295	0.019_9	0.24_4	0.77_9
SeF_6	$\nu_1(a_{1g})$	514.5	708.0	1.792	0.20_7	2.54	4.41
	$\nu_2(e_g)$	514.5	658.3	1.966	0.062_2	0.76_3	1.45_3
	$\nu_5(t_{2g})$	514.5	402.5	3.788	0.033_0	0.40_5	1.48_6
	$\nu_1(a_{1g})$	488.0	708.0	2.232	0.21_2	2.60	5.62
	$\nu_2(e_g)$	488.0	658.3	2.447	0.057_4	0.70_4	1.66_9
	$\nu_5(t_{2g})$	488.0	402.5	4.703	0.031_2	0.38_2	1.74_4
TeF_6	$\nu_1(a_{1g})$	514.5	697.6	1.826	0.19_0	2.33	4.12
	$\nu_2(e_g)$	514.5	671.5	1.916	0.046_2	0.56_6	1.05_1
	$\nu_5(t_{2g})$	514.5	312.3	5.470	0.025_9	0.31_8	1.68_4

[a] Ref. 1. [b] Corrected for the spectral response of the instrument. See text for definition of f. [c] The differential-scattering cross sections are quoted for 295 K. At this temperature, the band at 2 916.7 cm^{-1}, $\nu_1(a_1)$ of the standard methane, has $d\sigma/d\Omega = 3.889 \times 10^{-30}$ for 488.0-nm excitation and 3.035×10^{-30} cm² mol^{-1} sr^{-1} for 514.5-nm excitation.

TABLE 2

Molecular-polarisability derivatives [a] and related quantities for the hexafluorides

Molecule	$\bar{\alpha}'_1(MF_6)$	$\bar{\alpha}'_{MF}$	γ'_2	γ'_5	γ'_{MF}	γ_{MF}	r_{MF}	$\alpha'_{\parallel}$	$\alpha'_{\perp}$
SF_6	0.758	1.35_0	0.75_4	0.43_9	1.90	0.86_4	1.564 [b]	2.62	0.72
SeF_6	0.975	1.73_5	0.93_4	0.55_9	2.35	1.19	1.688 [b]	3.30	0.95
TeF_6	0.929	1.65_4	0.82_1	0.50_2	2.07	1.15	1.824 [c]	3.03	0.97

[a] All the molecular-polarisability and anisotropy derivatives are given in Å² N$^{\frac{1}{2}}$ g$^{-\frac{1}{2}}$, bond-polarisability derivatives in Å², γ_{MF} values in Å³, and MF bond lengths (r_{MF}) in Å. The standard is taken to be $\bar{\alpha}'_{CH}$ = 1.07 Å². All the polarisability derivatives and γ_{MF} values are considered accurate to ±7%. $\alpha'_{\parallel}$ and $\alpha'_{\perp}$ are considered accurate to ±0.2 and ±0.1 Å² respectively. [b] V. C. Ewing and L. E. Sutton, *Trans. Faraday Soc.*, 1963, **59**, 1241. [c] H. M. Seip and R. Stølevik, *Acta Chem. Scand.*, 1966, **20**, 1535.

For the $\nu_2(e_g)$ fundamental of an MF_6 molecule, $\bar{\alpha}'_2 = 0$ and therefore we obtain (6) with $g_1 = 1$, $g_2 = 2$,

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[7] W. F. Murphy, W. Holzer and H. J. Bernstein, *Appl. Spectroscopy*, 1969, **23**, 211. $I_j/M_j = (d\sigma_j/d\Omega)I_0$ where I_0 is the incident irradiance (power per unit area).

and $\bar{\alpha}'_1(CH_4) = 2.13$ Å^2 N$^{\frac{1}{2}}$ g$^{-\frac{1}{2}}$ as indicated above. Likewise, for the $\nu_5(t_{2g})$ fundamental of an MF_6 molecule,

$$\gamma'_2 = \left(\frac{g_1}{g_2} \cdot \frac{45}{7} \cdot \frac{1}{f} \cdot \frac{I_2 M_1}{I_1 M_2}\right)^{\frac{1}{2}} \bar{\alpha}'_1(CH_4) \qquad (6)$$

$\bar{\alpha}'_5 = 0$ and therefore we obtain (7) with $g_1 = 1$, $g_2 = 3$,

$$\gamma'_5 = \left(\frac{g_1}{g_5} \cdot \frac{45}{7} \cdot \frac{1}{f} \cdot \frac{I_5 M_1}{I_1 M_5}\right)^{\frac{1}{2}} \bar{\alpha}_1'(CH_4) \qquad (7)$$

and $\bar{\alpha}'_1(CH_4)$ as indicated above. The γ'_2 and γ'_5 values for SF_6, SeF_6, and TeF_6 are included in Table 2.

On the basis of the Wolkenstein theory of bond polarisabilities [8-11] it is possible to determine the parallel ($\alpha'_{\parallel}$) and perpendicular ($\alpha'_{\perp}$) components of the bond-polarisability derivative by use of the relations (8)—(10).[6] The resulting values for $\alpha'_{\parallel}$ and $\alpha'_{\perp}$ are given in

$$\bar{\alpha}'_{MX} = \tfrac{1}{3}(\alpha'_{\parallel} + 2\alpha'_{\perp}) \qquad (8)$$

$$\gamma'_{MX} = \alpha'_{\parallel} - \alpha'_{\perp} \qquad (9)$$

$$\gamma'_2 = (3/m_X)^{\frac{1}{2}} \gamma'_{MX} \qquad (10)$$

Table 2. In addition it is possible to calculate the anisotropy of the MX bond polarisability ($\gamma_{MX} = \alpha_{\parallel} - \alpha_{\perp}$) from relation (11) [6] where r_{MX} is the MX bond length

$$\gamma'_5 = (2/r_{MX})(3/m_X)^{\frac{1}{2}} \gamma_{MX} \qquad (11)$$

in Å and the other symbols have their previously given meanings. The resulting values for γ_{MX} (in Å^3) are also included in Table 2.

The dependence of Raman band intensities on the squares of the polarisability derivatives means that the signs of the latter are not determined. Hence two sets of results for $\alpha'_{\parallel}$ and $\alpha'_{\perp}$ are obtained in each case. The reason for the choice given has been discussed previously.[6]

Polarisability Derivatives.—It has long been considered that in a covalent bond there is greater electron density in the bonding region than in an ionic bond. Since polarisability is a measure of how readily the electronic distribution can be distorted under an applied electromagnetic field, the change in the molecular polarisability on changing the distance between two nuclei should be an effective measure of the covalency of a chemical bond. A delta-function potential model for chemical bonding has been derived [5] which leads to expression (12) for the bond-polarisability derivative with respect to change of bond length. Here χ and $Z_{eff.}$

$$\bar{\alpha}'_{MX} = \frac{2\chi^{\frac{1}{2}} p r^3}{3 Z_{eff.} a_0} \left(\frac{n}{2}\right) \qquad (12)$$

are the geometric means of the electronegativities and effective nuclear charges, respectively, of M and X, Z_{eff} in each case being taken to be the atomic number of the atom minus the number of inner-shell electrons, a_0 is the Bohr radius (in Å), p is the fractional Pauling covalent character $\{ = \exp[-(\frac{1}{4})(\chi_M - \chi_X)^2]\}$, $\frac{n}{2}$ is the bond order, and r is the MX equilibrium internuclear distance (in Å). Bearing in mind the semi-empirical nature of the theory and the uncertainties associated with some of the parameters in this equation (particularly that associated with $Z_{eff.}$), it is surprising how well $\bar{\alpha}'_{MX}$ values calculated on the basis of this equation have compared with experimental values for α'_{MX} in the case of tetrahalides,[1,2] trihalides,[12] octahedral ions,[6] and related species.[13] A comparison between calculated and experimental values for α'_{MF} is accordingly presented here for the first time in Table 3, the calculated values being based on the best available estimates of Pauling electronegativities of the relevant elements (that for tellurium being poorly defined) [14,15] and the assumption of an MF bond order of unity. The resulting $\bar{\alpha}'_{MF}$(calc.) values are all *ca.* 60% of the $\bar{\alpha}'_{MF}$(expt.) values. As indicated above, close numerical agreement between $\bar{\alpha}'_{MF}$(calc.) and $\bar{\alpha}'_{MF}$(expt.) values could not be expected, but it is very gratifying that the order of the experimental values, $\bar{\alpha}'_{SeF} > \bar{\alpha}'_{TeF} > \bar{\alpha}'_{SF}$, is predicted exactly by the theory. Indeed it is tempting to reverse the calculation and, by assuming the essential correctness of the Long and Plane theory,[5] to derive a Pauling electronegativity for tellurium of 2.25.

TABLE 3

Comparison of calculated and experimental values of MF bond-polarisability derivatives

Molecule	χ_M [a]	χ_F [a]	p [b]	$\bar{\alpha}'_{MF}$/Å^2 calc.	$\bar{\alpha}'_{MF}$/Å^2 expt.	$\bar{\alpha}'_{MF}$(calc.)/$\bar{\alpha}'_{MF}$(expt.)
SF_6	2.58	3.98	0.61_3	0.82	1.35	0.60
SeF_6	2.55	3.98	0.60_0	1.00	1.73	0.58
TeF_6	2.25	3.98	0.47_3	0.97	1.65	0.59

[a] Pauling electronegativities χ_M and χ_F. [b] Pauling covalent bond character $p = \exp[-(\frac{1}{4})(\chi_M - \chi_F)^2]$.

The order of the $\bar{\alpha}'_{MF}$ values, which may at first sight appear unexpected, is attributable partly to the r^3 term, *i.e.* to the overall size and therefore polarisability of the scattering molecule (leading to an expected order of S < Se < Te), and partly to the electronegativity of the Group (6) atom, in particular in so far as it determines p, the Pauling covalent bond character of the MF bonds (leading to an expected order of S $\geqslant$ Se $\geqslant$ Te). The resulting order is thus a compromise between these two effects.

In common with earlier conclusions [2,16] on bond-

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polarisability derivatives, it is clear that $\alpha'_{\parallel}$ is much larger than $\alpha'_{\perp}$ and is thus the quantity which principally determines Raman band intensities.

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