On the Vibrational Assignment of IF_6^+

Sir:

In our paper on the IF_6^+ cation¹ we have assigned the A_{1g} stretching frequency of IF_6^+ to a band having a lower frequency than that assigned to the E_g stretching mode. This assignment was based mainly on intensity arguments. In the preceding note[2] Hardwick and Leroi propose a reversal of the original assignment and support this by Urey–Bradley force field (UBFF) calculations.

While Hardwick and Leroi's assignment certainly presents an interesting alternative, we disagree with their statement that their assignment is more reasonable than the original one. Our disagreement is based on the following arguments.

(I) The modified UBFF is as much an approximation as the force field used by us. There are many cases where approximative force fields failed to give meaningful results. With inclusion of a few more terms in the potential, reasonable values can surely be found that fit at once the vibrational frequencies and our ideas of chemical valence. Hence, we feel that the spectroscopic evidence is a stronger argument than the success or failure of an approximate force field.

(II) The intensity arguments used previously[1] by us are strongly supported by the data reported for a large number of isoelectronic, octahedral XF_6 molecules or ions. Table I lists the frequencies and relative intensities of the A_{1g} and E_g modes together with their frequency difference. Since the molecules and ions are arranged in Table I according to the position of their central atoms in the periodic system, it can be seen that $\Delta\nu$ is becoming increasingly smaller (and eventually may become even negative as for IF_6^+) with increasing oxidation number and increasing mass of the central atom. Furthermore, it is obvious that within this system there is no noticeable change of the intensity ratio between the A_{1g} and the E_g mode, whereas $\Delta\nu$ exhibits a very strong and systematic trend. Hence, it seems much more reasonable to reverse the sequence of the stretching modes rather than the intensity ratio.

(III) In our original paper[1] on IF_6^+ we have assigned the ν_4 mode of IF_6^+ to the band at 404 cm⁻¹ assuming coincidence with ν_4 of AsF_6^-. This assignment is not very satisfactory and had been made not out of conviction but by lack of any other alternative. There had been indication for the occurrence of a band at about 340 cm⁻¹ in the original spectra recorded on a Beckman IR-11 spectrophotometer. However, owing to experimental difficulties (window material, sampling technique, and grating change at 340 cm⁻¹) the presence of this band could not clearly be established. In the meanwhile, we have recorded the infrared spectrum of

TABLE I

FREQUENCIES AND RELATIVE INTENSITIES OF THE A_{1g} AND E_g MODES OF ISOELECTRONIC, OCTAHEDRAL XY_6 AND THEIR FREQUENCY DIFFERENCE

	SiF_6^{2-} [a]	PF_6^- [b]	SF_6 [c,d]	
A_{1g}	656 vs	735 vs	769 vs	
E_g	465 vw	563 w	640 w	
$\Delta\nu$	191	172	129	
	GeF_6^{2-} [e]	AsF_6^- [f-h]	SeF_6 [i]	
A_{1g}	627 s	679 ms	708 vs	
E_g	454 w	565 vw	662 w	
$\Delta\nu$	173	114	46	
	SnF_6^{2-} [j-l]	SbF_6^- [k,l]	TeF_6 [d]	IF_6^+ [h]
A_{1g}	593 s	675 s	701 s	708 vs
E_g	465 vw	583 vw	674 w	732 w
$\Delta\nu$	128	92	27	−24

[a] R. B. Badachhape, G. Hunter, L. D. McCory, and J. L. Margrave, *Inorg. Chem.*, **5,** 929 (1966). [b] K. Bühler and W. Bues, *Z. Anorg. Allgem. Chem.*, **308,** 62 (1961). [c] C. W. Gullikson, J. R. Nielsen, and A. T. Stair, *J. Mol. Spectry.*, **1,** 151 (1957). [d] J. Gaunt, *Trans. Faraday Soc.*, **49,** 1122 (1953). [e] J. E. Griffiths and D. E. Irish, *Inorg. Chem.*, **3,** 1134 (1964). [f] K. Bühler, Dissertation, Technical University, Stuttgart, Germany, 1959. [g] K. O. Christe and W. Sawodny, *Inorg. Chem.*, **6,** 313 (1967). [h] Reference 1. [i] J. Gaunt, *Trans. Faraday Soc.*, **49,** 1122 (1953). [j] P. A. W. Dean and D. F. Evans, *J. Chem. Soc., A*, 698 (1967). [k] K. O. Christe and W. Sawodny, to be submitted for publication. [l] G. M. Begun and A. C. Rutenberg, *Inorg. Chem.*, **6,** 2212 (1967).

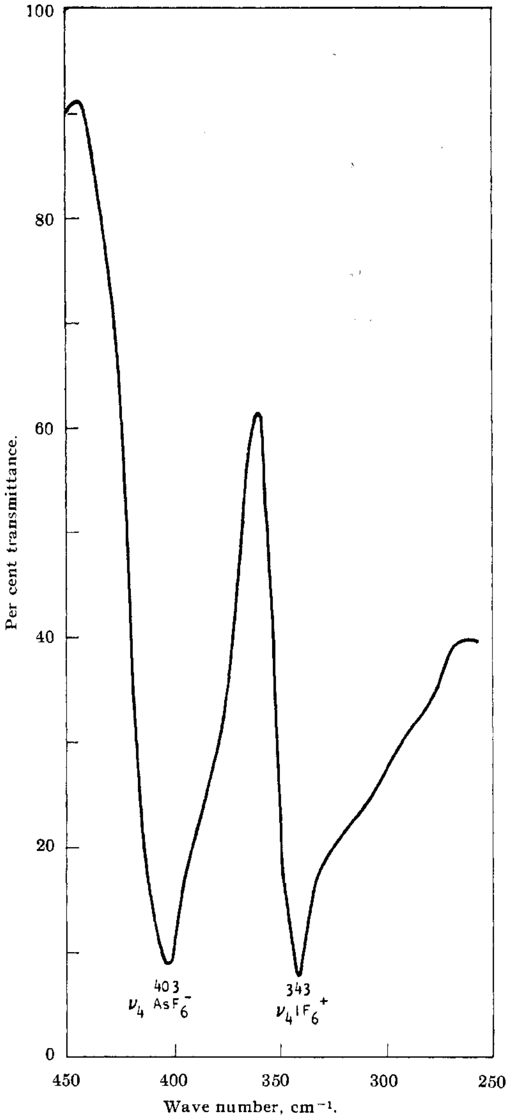

Figure 1.—Infrared spectrum of solid $IF_6^+AsF_6^-$.

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(1) K. O. Christe and W. Sawodny, *Inorg. Chem.*, **6**, 1783 (1967).
(2) J. L. Hardwick and G. E. Leroi, *ibid.*, **7**, 1683 (1968).

solid $IF_6^+AsF_6^-$ on a different instrument (Beckman IR-7 with CsI interchange). Figure 1 shows a typical spectrum of $IF_6^+AsF_6^-$ obtained under experimental conditions similar to those used with the Beckman IR-11 spectrophotometer.[1] This figure demonstrates that the band observed at about 340 cm^{-1} is real. Hence, this band is assigned to $\nu_4(F_{1u})$ of IF_6^+ resulting in a more satisfactory value for this mode. This new assignment causes the following changes in our original paper:[1] (i) Table II, infrared, 343 mw, δ_{asym}, $\nu_4(F_{1u})$ of IF_6^+; (ii) Table III, the symmetry force constants calculated for the F_{1u} block of IF_6^+ based on the new assignment are $F_{33} = 5.335$, $F_{34} = 0.023$, and $F_{44} = 0.459$ mdyn/A. The new value for F_{44} fits very well the series SbF_6^-, TeF_6, IF_6^+. The value of F_{34} decreased slightly, but the change is not significant as was stated in the original paper.[1] The value of F_{33} and, hence, the valence force constant remained unaltered owing to the very weak coupling between ν_3 and ν_4. Consequently, our conclusions concerning the bonding in IF_6^+ remain valid.

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Comment on the Choice of an Eight-Coordinate Polyhedron

Sir:

For each of the most commonly occurring coordination numbers (CN), four, five, six, and eight, there are two idealized coordination polyhedra (CP) of importance. These CP are the square and tetrahedron for CN four, the square pyramid and trigonal bipyramid for CN five, the octahedron and trigonal prism for CN six, and the square antiprism and triangular dodecahedron for CN eight. With increasing CN, it becomes increasingly difficult to distinguish the geometries of these polyhedron pairs. For CN eight the choice can be particularly subtle, especially when there is no distinctive crystallographically required symmetry for the metal atom complex. It is the intention of the present correspondence to point out the problems which arise and to provide useful criteria for deciding which idealized CP, if either, is more suitable for describing a particular eight-coordinate complex.

One possible way to distinguish the square antiprism from the triangular dodecahedron might be to examine a good three-dimensional model. Such an approach can lead to difficulties, however, not only because it lacks rigor, but because of the inherent similarity between the molecular frameworks of these two CP. A demonstration of this point is set forth in Figure 1, where stereoviews of the idealized CP and a structure which is halfway between the two are presented. From the drawings the reader can appreciate the necessity for the reference axes and the lines identifying the polyhedron edges. These can only be provided *after* the choice of CP has been made.

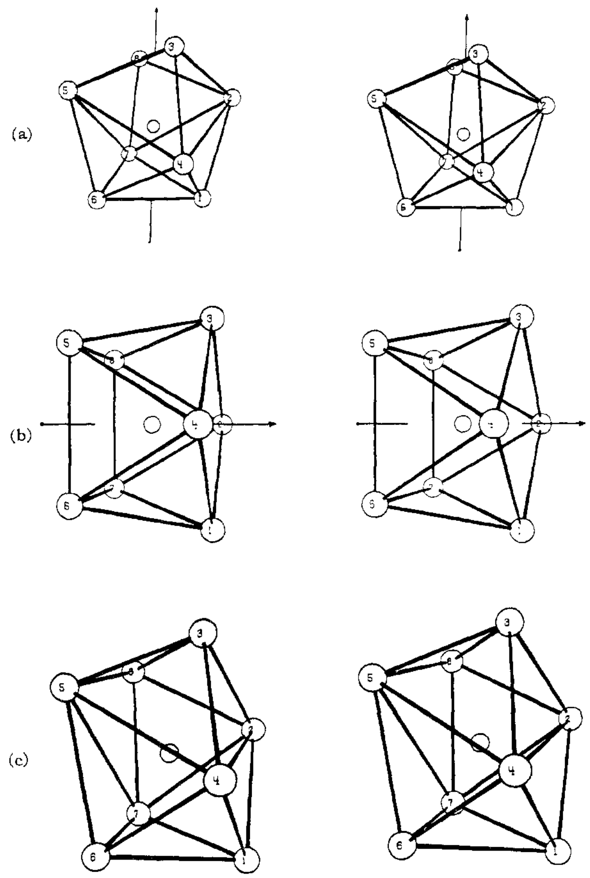

Figure 1.—(a) the idealized D_{2d} triangular dodecahedron; (b) the idealized D_{4d} square antiprism; (c) the idealized intermediate configuration. The views constitute stereoscopic pairs and can be viewed with a small hand stereoscope.

Previously,[1] attention has been focused on the polyhedron-shape parameters,[2-4] as defined originally by Hoard and Silverton[2] (see Figure 2). Although these parameters are without question the most useful set for describing the two CP, they are not necessarily the most convenient for distinguishing between CP. To illustrate, let us consider the angular-shape parameter, θ, which refers to the angle between a metal–ligand bond axis and the principal axis of the CP. There are some immediate difficulties since two such parameters (θ_a and θ_b) are generally defined for the dodecahedron as opposed to one for the antiprism[2] and since the principal axis, $\bar{8}$, of the square antiprism is orthogonal to the principal axis, $\bar{4}$, of the corresponding dodecahedron. By "corresponding dodecahedron," we mean the one

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(1) For references see S. J. Lippard, *Progr. Inorg. Chem.*, **8**, 109 (1967).
(2) J. L. Hoard and J. V. Silverton, *Inorg. Chem.*, **2**, 235 (1963).
(3) D. L. Kepert, *J. Chem. Soc.*, 4736 (1966).
(4) R. V. Parish, *Coord. Chem. Rev.*, **1**, 439 (1966).