CO Force Constants and CO–CO Interaction Constants of Metal Carbonyls: a Reply to L. H. Jones

Sir:

I want to discuss and contest some of the statements made by Jones[1] in the preceding communication. He is certainly on the side of the angels in suggesting that a simplified force field may yield values for its few force constants which are somewhat different from those which would be obtained for these same force constants in a complete force field. I fail to see, however, that his computations prove anything of practical importance about the Cotton–Kraihanzel (C–K) force field. The statement he is at pains to refute, *viz.*, that the "highly simplified (Cotton–Kraihanzel) force field is not only practical but satisfactory in comparison to more elaborate schemes and that it comes fairly close to being literally correct in its assumptions..."[2] clearly contains three separate claims: (1) that the C–K method is practical; (2) that the C–K method is satisfactory; (3) that it comes *fairly close* to being literally correct in its assumptions. I fail to see that he successfully refutes any one of the three.

It is, of course, self-evident that the method is practical, in the sense of being clear and simple. Its practicality has not, in fact, been questioned.

There would also seem no doubt that the method is satisfactory for its intended purpose, which is to extract from the array of frequencies, which are determined by factors other than inherent C–O stretching constants, a reasonably accurate notion of the *relative* values of C–O stretching constants within one molecule and/or within a series of closely related molecules. I stress the word *relative*, for it has been made *very* clear indeed by me[3] that "the absolute values of the force constants obtained by the method used in this and the two preceding papers in the series are not significant, nor can these force constants be directly compared with those calculated by the same method for molecules with different structures." Any further demonstration that neglect of anharmonicity, solvent effects, incomplete force fields, etc., introduces error into the absolute values of the CO force constants is simply flogging an already well-lacerated dead horse.

Finally, there is the question of whether the assumptions in the C–K force field are in fact *fairly close* to being (not exactly!) literally true. It is to be recalled that there are *five* assumptions.[4] *Four* of these have not been challenged *at all* by Jones, and I know of no evidence that they are in any important sense incorrect! Indeed, there is abundant support for them.

Jones simply suggests that when a more complete force field and harmonic frequencies are used the assumption that $k_t = 2k_c$ is probably not in general valid and that fundamental significance should not be attached to this assumption. That may be, and very probably is, true. Nevertheless, this assumption has proven empirically useful in the many cases where anharmonicity corrections are not made and where it is only desired to obtain CO stretching constants despite the fact there are insufficient frequencies available to estimate k_c and k_t independently. It is a *fact* that for a very large number of molecules, when anharmonic frequencies and a CO-factored force field are used, $3 > k_t/k_c > 1$.

In conclusion, the main reason why the C–K method is serviceable is that the many force constants and frequencies which it neglects are substantially constant and transferable among related molecules—and indeed Jones' arguments themselves constantly resort to this assumption of transferability.

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[1] L. H. Jones, *Inorg. Chem.*, **7**, 1681 (1968).
[2] F. A. Cotton, A. Musco, and G. Yagupsky, *ibid.*, **6**, 1357 (1967).
[3] *Cf.* section VI of F. A. Cotton, *ibid.*, **3**, 702 (1964).
[4] F. A. Cotton and C. S. Kraihanzel, *J. Am. Chem. Soc.*, **84**, 4432 (1962).

Force Constants of Nonmetal Fluorides. The Vibrational Assignment of IF_6^+

Sir:

Recently, Christe and Sawodny[1] presented a complete discussion of the IF_6^+ ion, including a vibrational analysis of $IF_6^+AsF_6^-$ in which the A_{1g} stretching frequency (ν_1) of the octahedral IF_6^+ ion was assigned below the E_g stretching mode (ν_2). Based upon consideration of the force constants of a wide range of similar molecules, we feel that the opposite assignment is more reasonable.

The potential chosen for our calculations is the modified Urey–Bradley force field advanced by Shimanouchi,[2] which has proved successful in correlating the vibrational frequencies of a variety of octahedral[2,3] and tetrahedral[4] molecules. In addition, Abramowitz and Levin[5,6] have shown through complete vibrational analysis, in which Coriolis coupling data were included, that for the nonmetallic hexafluoride molecules SF_6, SeF_6, and TeF_6 this potential function is in fact a reasonable approximation to the true force field. We thus expect that the modified UBFF should be useful in determining the force constants of the isoelectronic IF_6^+ ion, where the additional information necessary to determine uniquely the constants in the complete generalized force field are not available. When Christe and Sawodny's assignments[1] are used to calculate these force constants, however, the fluorine–

[1] K. O. Christe and W. Sawodny, *Inorg. Chem.*, **6**, 1783 (1967).
[2] T. Shimanouchi, *J. Chem. Phys.*, **17**, 245, 734, 848 (1949); J. Hiraishi, I. Nakagawa, and T. Shimanouchi, *Spectrochim. Acta*, **20**, 819 (1964).
[3] S. N. Thakur and D. K. Rai, *J. Mol. Spectry.*, **19**, 341 (1966).
[4] A. Müller and B. Krebs, *ibid.*, **24**, 180 (1967).
[5] S. Abramowitz and I. W. Levin, *J. Chem. Phys.*, **44**, 3353 (1966).
[6] S. Abramowitz and I. W. Levin, *Inorg. Chem.*, **6**, 538 (1967).

fluorine repulsion constant (F) assumes a negative value. Since negative F values are meaningless theoretically and unprecedented experimentally,[2-4] we feel that the proposed assignment[1] should be inverted.

We have calculated[7] modified Urey–Bradley potential constants for IF_6^+ assuming $\nu_1 = 732$ cm^{-1} and $\nu_2 = 708$ cm^{-1}. The results are listed in Table I, where they are compared to the corresponding force constants calculated[7] for the entire series of known isoelectronic hexafluorides. It is clear that the force constants exhibit periodic trends, and it should be noted that these are the same trends observed for the tetrahedral halides of these elements by Müller and Krebs.[4] The new assignment for IF_6^+ correlates well with the analogous molecules, as well as providing a physically acceptable value of F.

TABLE I

MODIFIED UBFF CONSTANTS FOR IF_6^+ AND RELATED MOLECULES (MDYN/Å)[a]

	SiF_6^{2-} [b]	PF_5^- [c,d]	SF_6 [e,f]	
K	2.01	2.86	3.64	
H	0.07	0.25	0.42	
F	0.72	0.73	0.72	
k	0.02	0.37	0.36	
h	0.07	0.09	0.10	
	GeF_6^{2-} [d]	AsF_6^- [d,g]	SeF_6 [e,h]	
K	2.06	3.30	4.45	
H	0.00	0.18	0.34	
F	0.57	0.43	0.21	
k	0.03	0.21	0.31	
h	0.02	0.05	0.07	
	SnF_6^{2-} [d]	SbF_6^- [d,i]	TeF_6 [e,f]	IF_6^+ [j]
K	2.20	3.38	4.83	5.27
H	0.00	0.01	0.20	0.26
F	0.42	0.39	0.13	0.12
k	0.06	0.15	0.17	0.26
h	0.09	0.08	0.05	0.16

[a] K and H are the valence stretching and bending force constants, F is the nonbonded repulsion constant, and k and h are interaction constants proposed in ref 2. The remaining table footnotes list the references from which the frequencies used in these calculations were obtained. [b] R. B. Badachhape, G. Hunter, L. D. McCory, and J. L. Margrave, *Inorg. Chem.*, **5**, 929 (1966). [c] R. D. Peacock and A. W. Sharp, *J. Chem. Soc.*, 2762 (1959). [d] G. M. Begun and A. C. Rutenberg, *Inorg. Chem.*, **6**, 2212 (1967). [e] J. Gaunt, *Trans. Faraday Soc.*, **49**, 1122 (1953); **50**, 546 (1954); **51**, 893 (1955). [f] Reference 5. [g] Reference 1. [h] Reference 6. [i] Reference 9. [j] Our reassignment of frequencies from reference 1.

The abnormally high value obtained for h in IF_6^+ leads us to believe that ν_4 might also be incorrectly assigned. It would be fortuitous indeed if this mode has the same frequency in both IF_6^+ and AsF_6^- (as Christe and Sawodny assume[1]), since $G_{44} = 0.1687$ amu^{-1} for IF_6^+ and $G_{44} = 0.2120$ amu^{-1} for AsF_6^-. If the assignment of ν_4 is subsequently changed, then h is the only force constant in our calculation that will be affected.[8]

Christe and Sawodny[1] realized that the order of their assignment is unprecedented among octahedral molecules. In its support they listed the relative Raman intensities of the two bands in question, force constant calculations and comparison to other molecules, and a correlation of the diminution of the frequency difference $\nu_1 - \nu_2$ "with increase in the size of the central atom" [1] and with its oxidation number. This frequency difference (24 cm^{-1}) is indeed the smallest observed to date for any octahedral hexafluoride,[3,9] but since the size of the central atom in IF_6^+ will be *smaller* than that in TeF_6 (owing to the added positive charge), the additional contraction is not due to increasing size but must be due to other effects, such as charge. It should be noted that the revised assignment suggested here still fits the correlation between $\nu_1 - \nu_2$ and the position of the central atom in the periodic table suggested by Christe and Sawodny.[1,8] Furthermore, none of the force constant arguments previously advanced[1] would be qualitatively changed by inverting the frequency assignments of ν_1 and ν_2. It is somewhat disturbing that with our assignment the Raman intensities do not follow the empirical rule that A_{1g} bands are strongest. However, one must be careful in interpreting intensity ratios obtained from solids, where the molecules are subject to strong and often nonuniform external forces. Relative intensities contrary to expectation have in fact been observed for $SeCl_6^{2-}$, where the Raman scattering from ν_2 (E_g, 255 cm^{-1}) is stronger than that of ν_1 (A_{1g}, 299 cm^{-1}).[10,11]

We agree with the conclusion of Christe and Sawodny[1] that there is considerable difference between the stretching force constants for IF_6^+ and IF_5. Although the UBFF is not strictly applicable, owing to the presence of the lone pair, it is clear that the fluorine–fluorine repulsion constant in IF_5 must be positive, since the frequency of the A_1 in-plane stretching vibration (ν_2) is higher than that of the B_1 in-plane stretch (ν_4).[12] Calculations now in progress indicate that both the stretching force constant (K) and the repulsion constant (F) are directly transferable from IF_6^+ (using the revised assignment) to IOF_5. We hope to make available soon a more complete set of MUBFF constants for these and other sets of similar molecules.

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(7) The calculations were performed using an ALGOL version of the normal-coordinate analysis developed by J. H. Schachtschneider, Shell Development Co.; see Technical Report No. 57-65. We are grateful for the facilities and help of the staff at the Rich Computer Center, Georgia Institute of Technology, in relation to this work.

(8) This prediction has now been confirmed—see K. O. Christe and W. Sawodny, *Inorg. Chem.*, **7**, 1685 (1968).

(9) B. Weinstock and G. L. Goodman, *Advan. Chem. Phys.*, **9**, 169 (1965).

(10) I. R. Beattie and H. Chudzynska, *J. Chem. Soc.*, *A*, 984 (1967).

(11) T. Barrowcliffe, I. R. Beattie, P. Day, and K. Livingston, *ibid.*, 1810 (1967).

(12) G. N. Begun, W. H. Fletcher, and D. F. Smith, *J. Chem. Phys.*, **42**, 2236 (1965).

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