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.

DEPARTMENT OF CHEMISTRY
MASSACHUSETTS INSTITUTE OF TECHNOLOGY
CAMBRIDGE, MASSACHUSETTS 02139
F. A. COTTON

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(2) F. A. Cotton, A. Musco, and G. Yagupsky, *ibid.*, **6**, 1357 (1967).
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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–

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