

Cotton F A. Vibrational spectra and bonding in metal carbonyls. III. Force constants and assignments of CO stretching modes in various molecules; evaluation of CO bond orders. *Inorg. Chem.* 3:702-11, 1964.

[Department of Chemistry, Massachusetts Institute of Technology, Cambridge, MA]

Data for a large number of substituted group VI carbonyls and for some manganese carbonyl halides and their derivatives are treated. A relationship between CO bond orders and CO force constants is delineated and used to deduce, from differences in the calculated CO stretching constants, the changes in CO bond orders. It is also shown that absolute values of the bond orders may be estimated. [The SC¹® indicates that this paper has been cited in over 445 publications.]

F.A. Cotton

Department of Chemistry and Laboratory
for Molecular Structure and Bonding
Texas A&M University
College Station, TX 77843-3255

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Even today, infrared spectroscopy is the most generally useful, and widely employed, physical method for characterizing metal carbonyl compounds, although carbon-13 nuclear magnetic resonance spectroscopy and X-ray crystallography have now also assumed very important roles. Back in the period 1960-1965 the situation was far more extreme; infrared spectra were essentially the *only* generally useful physical data obtainable for metal carbonyls. However, the raw data themselves did not convey all of the desired information potentially available. In 1962 a scheme for extracting quantitatively the information on relative bond strengths implicit in the raw frequencies was published, and its application to one set of representative compounds was demonstrated.¹ This paper subsequently became a *Citation Classic*.

The approach used, commonly known as the Cotton-Kraihanzel method (or force field, CKFF), provides a set of relatively simple, approximate equations by means of which the observed CO stretching frequencies for any six-coordinate, quasi-octahedral molecule can be used to obtain numerical values for the CO stretching force constants for the one or more types of CO groups present. The equations presented were essentially just "plug-ins," not re-

quiring the user to understand the underlying analysis. They provided the experimental chemist with a nearly painless way to employ the results from easily available spectral traces in comparing molecules of disparate composition (and hence qualitatively as well as quantitatively different spectra) with one another in respect to the donor and acceptor capacities of various ligands present along with the CO ligands.

When it became apparent that the method was being well received and used, I was encouraged to do more work with it (and on it) myself. In addition to a second paper with Charles S. Kraihanzel² in which another class of ligands, amines, was examined for group VI metals, I undertook a much broader examination of the use of the method in many other, more diverse, classes of compounds, and also examined some of its implications and approximations more thoroughly. In addition, the working equations for two more cases of importance that had not previously been given were presented. This latter study was published as the present *Citation Classic*.

The major points that were brought out in this paper were the following: (1) It was shown that the method can generally allow one to eliminate all incorrect assignments of the spectrum. (2) A correlation between CO force constants and CO bond orders was established. (3) The relative π -acceptor strengths of various ligands were established semiquantitatively and it was found, for example, that PF₃, long believed to be strong, is in fact the strongest one known, even stronger than CO itself when the two compete directly. (4) The relationship of the CKFF force constants to those that can be more rigorously calculated, with enormously greater effort, was discussed.

It was these extensions of the previous work, especially points (2) and (3), that undoubtedly led to this paper being so widely cited by workers in the field of metal carbonyl chemistry and coordination chemistry in general. It made it possible to get semiquantitative answers to very fundamental questions that constantly arose, and still arise,³ in dealing with mixed carbonyl molecules. The fact that the equations can now be solved on a computer further enhances their usefulness.

1. Cotton F A & Kraihanzel C S. Vibrational spectra and bonding in metal carbonyls. I. Infrared spectra of phosphine-substituted group VI carbonyls in the CO stretching region. *J. Amer. Chem. Soc.* 84:4432-8, 1962. (Cited 825 times.) [See also: Cotton F A. *Citation Classic*. (Thackray A, comp.) *Contemporary classics in physical, chemical, and earth sciences*. Philadelphia: ISI Press, 1986. p. 235.]
2. Kraihanzel C S & Cotton F A. Vibrational spectra and bonding in metal carbonyls. II. Infrared spectra of amine-substituted group VI carbonyls in the CO stretching region. *Inorg. Chem.* 2:533-40, 1963. (Cited 225 times.)
3. Bucknor S, Cotton F A, Falvello L R, Reid A H & Schmulbach C D. Reactions of small molecules with Re₂Cl₂(PEt₃)₂. 1. Structural and spectroscopic studies of several products resulting from reaction with carbon monoxide. *Inorg. Chem.* 25:1021-7, 1986.