

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.
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This paper, by employing a ruthless simplification of an inherently complex vibrational problem, provided a way of using the easily measured infrared spectra of metal carbonyl molecules, in the region of CO stretching, to reach conclusions about structure and bonding in such substances. [The *SC*¹ indicates that this paper has been cited over 625 times since 1962.]

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"So much progress has been made in the field of metal carbonyl chemistry since 1962 that it is not easy to cast one's mind back to the state of affairs at that time and shortly before. As in all other fields of chemistry, infrared (ir) spectroscopy was the major structural tool; X-ray crystallography was not yet commonly used and ¹³C nmr had not become practical for metal carbonyls. Chemists working with metal carbonyl derivatives depended heavily on ir spectra to follow reactions, identify products, and, to a lesser extent, to infer structures, based on the number of CO bands observed. They also recognized that because of a relationship between the CO frequencies and the extent of metal to CO π -electron donation it was possible to draw at least qualitative inferences about the bonding in substituted metal carbonyl compounds from their ir spectra. Unambiguous and semiquantitative relationships were not available because other factors besides bond force constants influenced the stretching frequencies.

"I was one of the few if not, perhaps, the only person who knew the carbonyl chemis-

try intimately enough to be aware of exactly what the key questions were and what sort of data were available, while at the same time being conversant with the theory of molecular vibrations.¹ I had been playing with ideas for a useful simplification of the molecular force field in such molecules for some time when Charles Kraihanzel (now professor of chemistry at Lehigh University) arrived for a postdoctoral year. It was necessary to design, synthesize, and measure a series of complexes in order to test these ideas, and over the academic year 1961-1962 this was very ably done by Kraihanzel. We ended up with a coherent, eminently practical, and empirically substantiated treatment of the problem, which was submitted for publication in late April 1962.

"Our approach, commonly called the CKFF (Cotton-Kraihanzel force field), makes several sweeping, but, as it turns out, justified assumptions. For the most part, its success is due to the fact that 'CO vibrations' really do come very close to being purely CO vibrations, and small secondary effects of coupling to other oscillators do not vary enough to seriously undermine the method. Anharmonicity, which is totally omitted, is substantially invariant from case to case.

"Over the years the method has occasionally been criticized (unfairly, I think), but widely used. Some refinements (not all of which I think are justified) have been proposed.² The tedium of solving the secular equations has been relieved by computer programs.³ Recently, Timney made an elegant and streamlined extension⁴ and incisively dealt with matrix-isolated M(CO)_n fragments.

"This paper has become a Citation Classic because it met, and the basic concepts therein continue to meet, a real and widespread need on the part of inorganic chemists. It is interesting that a slightly later paper, extending the original work, is my second most-cited publication."⁵

1. Wilson E B, Jr., Decius J C & Cross P C. *Molecular vibrations; the theory of infrared and Raman vibrational spectra*. New York: McGraw-Hill, 1955. 388 p.
2. Graham W A G. An approach to the separation of inductive and mesomeric effects in complexes of the types LMn(CO)₅ and LMo(CO)₅. *Inorg. Chem.* **7**:315-21, 1968.
3. Darensbourg D J, Nelson H H & Murphy M A. Photochemical substitution reactions of group 6B metal tetracarbonyl norbornadiene complexes with ¹³CO. kinetics of subsequent thermal rearrangements in the stereospecifically labeled species, and relationship of these results to the photoinduced hydrogenation process. *J. Amer. Chem. Soc.* **99**:896-903, 1977.
4. Timney J A. Ligand effect constants: a new method for predicting the carbonyl stretching frequencies in transition metal compounds. *Inorg. Chem.* **18**:2502-6, 1979.
5. Cotton F A. Vibrational spectra and bonding in metal carbonyls. III. Free constants and assignments of CO stretching modes in various molecules: evaluation of CO bond orders. *Inorg. Chem.* **3**:702-11, 1964.
[The *SC*¹ indicates that this paper has been cited over 380 times since 1964.]