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Metal Isotope and Temperature Effects on the Raman Spectra of Diironenneacarbonyl, $Fe_2(CO)_9$, and Triirondodecacarbonyl, $Fe_3(CO)_{12}$. Identification of Fe–Fe Stretching Frequencies

C. B. COOPER III, S. ONAKA and D. F. SHRIVER
Department of Chemistry, Northwestern University, Evanston, Illinois 60201
and L. DANIELS, R. L. HANCE, B. HUTCHINSON and R. SHIPLEY
Department of Chemistry, Abilene Christian University, Abilene, Texas 79601, U.S.A.

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Diironenneacarbonyl is unique among the metal carbonyls in having three CO ligands bridging the metal–metal bond [1, 2]. The effect of these bridging ligands on the Fe–Fe stretching frequency is of considerable interest for empirical frequency–structure correlations [3]. This vibrational mode however has eluded observation [4]. The present identification of the metal–metal stretch was made possible by a combination of low temperature Raman spectroscopy and metal isotope effects. In this first report on the use of metal isotopes in metal–metal bonded systems, the isotopic data is essential to distinguish between two possibilities for the Fe–Fe stretch.

Polycrystalline samples of natural abundant and ^{54}Fe substituted $Fe_2(CO)_9$ and $Fe_3(CO)_{12}$ were sealed in 5 mm Pyrex tubes and cooled to *ca.* 10 °K. A backscattering geometry was utilized to illuminate the samples with 15 mW of line-focused 514.5 nm Ar^+ ion radiation. Laser and Ne atomic spectra were used for calibration. A band observed around 260 cm^{-1} for $Fe_2(CO)_9$, which exhibits a significant isotope effect, is identified as the metal–metal mode. The magnitude of this isotopic shift, $\nu(^{54}Fe)-\nu(^{NA}Fe) = 1.3 \pm 0.3$ cm^{-1}, is close to that calculated using a pseudo diatomic approximation for two $Fe(CO)_3$ moieties (1.9 cm^{-1}). Another band at 315.5 cm^{-1} also was considered as a possible M–M stretch, but this assignment was rejected because this Raman line displays no isotopic shift within experimental error (± 0.3 cm^{-1}). Only one other feature at 451.0 cm^{-1}, which is tentatively assigned as an M–C–O stretch, displays a significant isotope shift. Increased laser power leads to a decrease in intensity of the 260 cm^{-1} band with a concomitant increase in a feature at 240 cm^{-1}. This latter band may originate from a photolysis product, such as $Fe_2(CO)_8$, which has been observed in infrared matrix isolation experiments [5], or from $Fe_3(CO)_{12}$.

The metal–metal stretching frequency for $Fe_2(CO)_9$ (260 cm^{-1}) is the highest such frequency yet observed for a dinuclear carbonyl species having a formal metal–metal bond order of one. In contrast, first row dinuclear carbonyls exhibit metal–metal stretching frequencies between 224–256 cm^{-1} when two bridging carbonyls are present and around 150 cm^{-1} in the absence of bridging ligands. The high iron–iron stretching frequency of $Fe_2(CO)_9$ can be attributed to the large restoring force that the bridging carbonyl ligands impart to the $(\mu_2\text{-}(CO)_3)Fe_2$ system. In carbonyl bridged systems the restoring force for the metal–metal stretch originates from direct metal–metal bond stretching, metal–carbon bond stretching and M–C–M angle deformation. Vibrational data do not allow unambiguous assessments of the individual contributions to the metal–metal stretching frequency because a redundancy exists between the internal Fe–Fe and $Fe(\mu_2\text{-}(CO)_3)Fe$ coordinates.

We have also obtained data on $Fe_3(CO)_{12}$, another molecule for which there is no reliable identification of the Fe–Fe stretching frequency [4]. The Raman spectrum at 10 °K exhibits a feature at 176 cm^{-1} which displays a *ca.* 2 cm^{-1} isotope shift indicating that it is associated with the Fe–Fe stretch. A broad feature at 240 cm^{-1} is not sufficiently well defined to obtain an isotopic shift, but it is likely that this band also involves metal–metal stretching.

The Fe–Fe stretching frequencies for both $Fe_2(CO)_9$ and $Fe_3(CO)_{12}$ which are not observable at room temperature are dramatically enhanced at low temperature. It is clear that this low temperature enhancement and sharpening of low frequency Raman bands combined with metal isotope data may be useful for the identification of metal–metal stretching modes in other polynuclear complexes.

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