dimerized to an oxo-bridged Mo(V) species. Addition of 8-quinolinol (2:1 mole ratio) and water[14] to the preceding $Mo^{V}OCl_3$ and $Mo^{IV}Cl_4$ solutions resulted in absorption spectra with λ_{max} at 527, 376, and 310 nm for the $Mo^{V}OCl_3$ system and λ_{max} at 535, 375, and 310 nm for the $Mo^{IV}Cl_4$ system. These data are similar to those for monooxo-bridged dimeric Mo(V) complexes[7,8] and support the conclusion that the same dimeric molybdenum(V)–8-quinolinol salt or adduct is formed whether one starts with $Mo^{IV}Cl_4$ or $Mo^{V}OCl_3$ (see eq 4 and 6 for the flavin analogy of the probable formation process).

In summary, the dark purple color of the isolated compounds is characteristic of diamagnetic monooxo-bridged dimeric molybdenum(V) ($Mo^{V}{}_2O_3X_{4-8}$), as is the Mo=O infrared band at 983 cm^{-1} and the visible band at a λ_{max} 509–525 nm. The uv, infrared, and NMR data also are indicative of the HFl^+ species. The elemental analysis data in the Selbin paper support the conclusion that the isolated compounds have the general formula $(HFl^+)_2(Mo^{V}{}_2O_3Cl_6{}^{2-})$. Their data do not support the proposition that a coordination complex is formed between $Mo^{IV}OCl_3{}^-$ and HFl^+, nor do they support the conclusion that the isolated compounds contain Mo(IV).

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(13) The differences in λ_{max} between the $Mo^{IV}Cl_4$ solution and the $Mo^{V}OCl_3$ solution probably are due to the extra HCl that results from the hydrolysis of $Mo^{IV}Cl_4$ (reaction 1).
(14) Prior to the addition of water both solutions were dark green with absorption maxima at 625 and 400–450 nm, which is indicative of monomeric Mo(V) with the likely formula $Mo^{V}OCl_3$(8-quinolinol)$^-$.

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Raman Spectroscopic Identification of Metal–Metal Stretching Frequencies

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Sir:

Raman spectroscopy has proven to be very useful in the detection of metal–metal stretching frequencies for a variety of metal complexes.[1,2] Frequently, metal–metal stretching modes are found to exhibit high intensity; however their assignment on the basis of Raman intensity alone can be ambiguous. It is the purpose of this correspondence to illustrate some of the pitfalls in data collection and interpretation for metal–metal bonded systems and to correct some erroneous assignments.

The high intensity of ν_{M-M} arises in many cases from the fact that the sample is irradiated within or near an electronic transition involving the metal framework. This may lead to enhanced Raman scattering via resonance or preresonance mechanisms. An unwanted aspect of the electronic absorption is sample decomposition which occurs with many heat-sensitive colored materials. As first shown by Kiefer and Bernstein, this problem can be significantly alleviated by sample spinning[3] or by related methods of energy dispersion.[4] One of the simplest versions of this technique involves the rotation of a pressed solid sample. This type of apparatus is widely available from Raman instrument manufacturers and works well in many cases; however, the combined influence of the intense laser beam and exposure to the atmosphere can lead to unexpected results. For example, this spinner would seem adequate for $Fe_2(CO)_9$ which is reasonably stable in air and is photochemically fairly stable. Recently this technique was used on the determination of the Fe–Fe stretch of $Fe_2(CO)_9$ and $Fe_3(CO)_{12}$,[2] but as described below the reported spectra are those of decomposition products.

Raman spectra were obtained for polycrystalline samples under an inert atmosphere in disposable sealed 12-mm Pyrex tubes. Details of the sample spinner and back-scattering illumination are available in the literature.[5] For $Fe_2(CO)_9$, Raman bands of weak to medium intensity were observed at 78, 101, 122, 390, and ca. 453 cm^{-1}, but as shown in Figure 1, the spectrum is devoid of the reported intense 225-cm^{-1} Fe–Fe stretch. It is certain that the failure to observe this band does not arise from lack of sensitivity because other low-frequency modes as well as the CO stretching frequencies were observed. Samples of $Fe_2(CO)_9$ used in these experiments were identical with those employed in a detailed investigation of the CO stretch region and are of high purity as judged by carbon analyses and by the lack of infrared and Raman bands of probable impurities.[6] Thus, it is likely that the Raman spectrum reported earlier for $Fe_2(CO)_9$ arises instead from a decomposition product. Similarly, the reported metal–metal stretch for $Fe_3(CO)_{12}$ is reproduced only under conditions in which the sample is decomposed or laser damaged. Based on these results we suggest that Raman data on colored organometallics should be collected using inert-atmosphere conditions in conjunction with sample spinning, and spurious features should be sought by obtaining a spectrum for the laser-damaged material.

The erroneous assignments which are discussed above resulted in part from the high intensity of the observed bands and the currently accepted idea that M–M stretch modes may be assigned solely on the basis of high intensity. In this particular case the correlation of high intensity with M–M stretching modes was misleading, owing to the presence of decomposition products having intense low-frequency modes. Ambiguities also may arise in the assignment of M–M stretching modes when other intense vibrations appear in the low-frequency region. Metal carbonyls are especially troublesome since C–M–C deformation modes often appear in the same region of the spectrum as M–M stretches.

A comparison of spectra for $Re_2(CO)_8Br_2$, $Re_2(CO)_8Cl_2$, and $Re_2(CO)_{10}$ provides a striking example of this problem. As shown in Figure 2, the solid-state Raman spectra are quite similar for all three compounds. In the case of $Re_2(CO)_{10}$ the strong band around 125 cm^{-1} has been assigned to the Re–Re stretch,[7] and this assignment is supported by solution intensity analysis,[8a] which shows α(Re–Re) to be in the range expected for single metal–metal bonds. This assignment appears reasonable by all the currently available criteria for the detection of M–M stretching modes. As with much spectral work on complex molecules, there is the possibility of an alternate assignment,[8c,9] but most workers agree with the original assignment.[8]

It is, however, illogical to assign the ca. 125-cm^{-1} feature of $Re_2(CO)_8Br_2$ and $Re_2(CO_8)Cl_2$ as an M–M stretch, because these compounds do not contain metal–metal bonds. Both

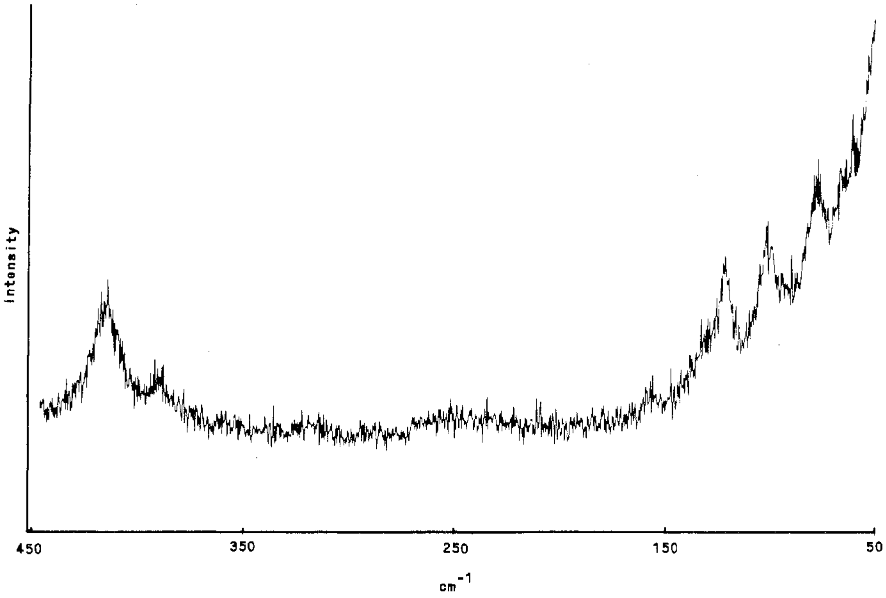

Figure 1. Raman spectrum of $Fe_2(CO)_9$ in 450–50-cm^{-1} range; monochromator band pass 2 cm^{-1}, and incident laser frequency 488 nm.

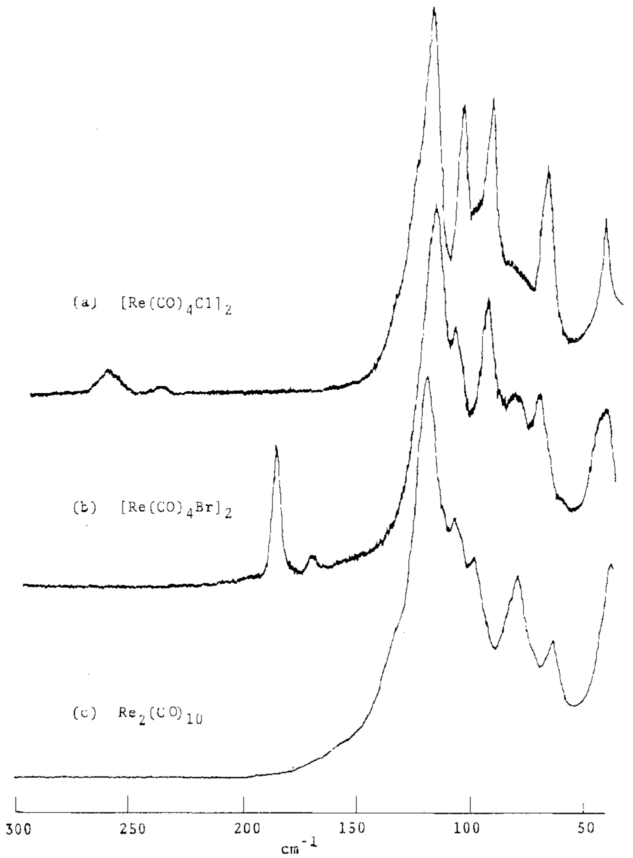

Figure 2. Raman spectra in the region 300–40 cm^{-1} for (a) $[Re(CO)_4Cl]_2$, (b) $[Re(CO)_4Br]_2$, and (c) $Re_2(CO)_{10}$. The monochromator band pass was 1 cm^{-1} and gain settings were 10^4 Hz for (a) and (b) and 3×10^4 Hz for (c). The incident laser frequency was 568.2 nm.

compounds are halide bridged, with the two bridging halides and four terminal carbonyls forming a nearly octahedral array around each rhenium nucleus. Following the conventional 18-electron rule, we expect no Re–Re bond. This has been verified for $Re_2(CO)_8Br_2$ by the observation of a Re–Re distance around 3.8 Å, which certainly qualifies as a nonbonded distance.[10] In the absence of crystallographic data, the Raman data might lead one to postulate an incorrect isomeric structure for $Re_2(CO)_8X_2$, involving a Re–Re bond. It is clear from this example that intensity data alone, and particularly intensity data on solids, may be misleading.

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