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Raman Spectra of $M_2(OR)_6$ and M_2R_6 (M = Mo, W) Compounds: Assignment of the $M\equiv M$ Stretching Frequency in M_2X_6 Dimers

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Raman spectroscopy has been widely utilized to investigate the metal−metal stretching vibrations $\nu_{M\equiv M}$ in tetragonally substituted, metal−metal quadruply bonded M_2X_8 transition metal dimers.[1−3] Assignments of $\nu_{M\equiv M}$ are generally straightforward for such compounds based on a combination of resonance Raman techniques, ligand substitution, and comparisons among homologous series of compounds.

By contrast, the identification of $\nu_{M\equiv M}$ for the class of trigonally substituted, triply bonded compounds M_2X_6 (M = Mo, W), has been problematic. The only Raman study of $X_3M\equiv MX_3$ dimers in the literature involved the hexaamides $M_2[N(CH_3)_2]_6$ (M = Mo, W) and the corresponding perdeuterated analogues $M_2[N(CD_3)_2]_6$.[4,5] In that work, Chisholm, Cotton, and co-workers concluded that extensive coupling of low-frequency ligand vibrational modes with $\nu_{M\equiv M}$ made assignment of the latter impossible.

In this communication, we report the results of Raman studies of a series of hexaalkyl compounds $M_2(CH_2R)_6$ [M = Mo, W; R = $C(CH_3)_3$, $Si(CH_3)_3$] and hexaalkoxide compounds $M_2(OR)_6$ [M = Mo, W; R = $C(CH_3)_3$, $C(CD_3)_3$, $C(CH_3)_2CF_3$, 1-adamantyl). The vibrational coupling of $\nu_{M\equiv M}$ with low-frequency ligand modes is weaker than in the hexaamide dimers, because these compounds display bands which can be confidently assigned to $\nu_{M\equiv M}$.

The M_2X_6 complexes were prepared by standard methods,[6−10] and their Raman spectra were obtained using low-power red (632.8 nm) continuous-wave excitation. The spectra of the homologous pair of $M_2[CH_2Si(CH_3)_3]_6$ (M = Mo, W) compounds appear in Figure 1; they are strikingly similar save for one band which shifts dramatically between the Mo and the W dimers. This situation contrasts with that observed in the $M_2[N(CH_3)_2]_6$ Raman experiments, where all of the low-frequency bands shifted when the metal was changed. The metal-sensitive band is located at 369 cm^{-1} for $Mo_2[CH_2Si(CH_3)_3]_6$ and at 299 cm^{-1} for the W analogue. The ratio of these frequencies ($\nu_{Mo\equiv Mo}/\nu_{W\equiv W}$ = 1.23) compares well to the ratio of 1.38 expected for the hypothetical bare metal diatomics (Mo_2 and W_2) with equal force constants. We therefore assign these features as the metal−metal stretching frequencies $\nu_{M\equiv M}$.

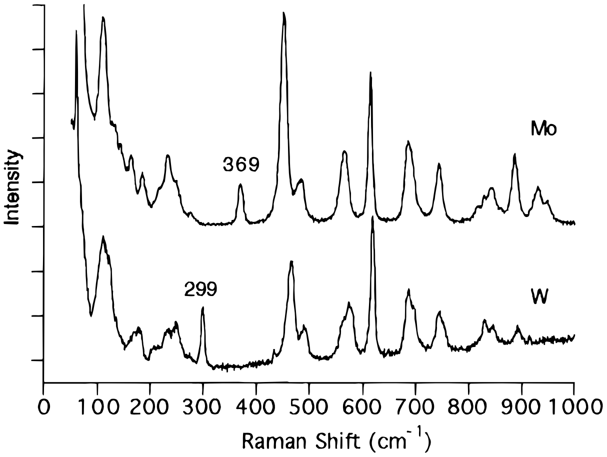

Figure 1. Raman spectra of $Mo_2(CH_2SiMe_3)_6$ and $W_2(CH_2SiMe_3)_6$ at 298 K. Laser: λ_{exc} = 632.8 nm, power at sample ≈ 7 mW. Monochromator: spectral slit width = 4 cm^{-1}, step increments = 1 cm^{-1}; photon counting for 1 s intervals; 4 and 10 co-added scans for Mo and W compounds, respectively.

Table 1. $\nu_{M\equiv M}$ (cm^{-1}) for M_2X_6 Compounds

X	M = Mo	M = W	$\nu_{Mo\equiv Mo}/\nu_{W\equiv W}$[a]
$OC(CH_3)_3$	386	303	1.27
$OC(CD_3)_3$	363	285	1.27
$OC(CH_3)_2CF_3$	360	280	1.29
O-1-adamantyl	369	274	1.35
$CH_2C(CH_3)_3$	361	292	1.24
$CH_2Si(CH_3)_3$	369	299	1.24

[a] For diatomic Mo_2 and W_2 with the same force constant, $\nu_{Mo\equiv Mo}/\nu_{W\equiv W}$ = 1.38.

The Raman spectra of several other pairs of molybdenum and tungsten alkoxide and alkyl compounds show behavior similar to that of the trimethylsilylmethyl dimers (Table 1), namely very similar low-frequency spectra for each pair except for one dramatically shifted band. The assigned metal−metal frequencies for the Mo_2 compounds cluster in a narrow range around 368 ± 10 cm^{-1}, while the assigned $\nu_{W\equiv W}$ frequencies cluster around 289 ± 10 cm^{-1}. One would not expect this sort of consistency in $\nu_{M\equiv M}$ or in the ratio of the dimolybdenum to ditungsten frequencies over the range of compounds studied if ligand vibrational modes were mixing substantially with the metal−metal stretching coordinate. Only the hexa-*tert*-butoxide dimers $M_2[OC(CH_3)_3]_6$ exhibit bands significantly outside the ranges, which may arise from slight mixing of a low-frequency ligand mode (corresponding to the 349 cm^{-1} band in *tert*-butyl alcohol) with $\nu_{M\equiv M}$. The shifts in $\nu_{M\equiv M}$ in the spectra of the perdeuterated analogues $M_2[OC(CD_3)_3]_6$ as compared to the parent *tert*-butoxides (23 and 18 cm^{-1} for the Mo_2 and W_2 species, respectively; Table 1) bear out this hypothesis in that they are too large to explain by any application of a simple harmonic oscillator model.[11] The other ligands do not have normal modes (as judged by the Raman spectra of the free alcohols or alkanes) close enough in frequency to mix significantly with $\nu_{M\equiv M}$. For example, the hexakis(1-adamantoxy)

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compounds display bands clearly attributable to $\nu_{M\equiv M}$, reflecting the absence of Raman bands between 100 and 400 cm^{-1} in 1-adamantanol.

The assigned $\nu_{M\equiv M}$ frequencies in this study compare well with the limited data found in the literature. In the bridged, tetragonally-substituted, triply-bonded $[Mo_2(HPO_4)_4]^{2-}$ ion,[12] $\nu_{Mo\equiv Mo}$ appears at 360 cm^{-1}, in agreement with our observed $\nu_{Mo\equiv Mo}$ values. Additionally, an empirical bond distance/force constant correlation for fifth period diatomics[13] predicts $\nu_{Mo\equiv Mo} = 363$ cm^{-1} (in the diatomic approximation) with a force constant $k = 3.72$ mdyn/Å for $Mo_2[CH_2Si(CH_3)_3]_6$, from the crystallographically determined Mo≡Mo distance of 2.167 Å;[14] this predicted frequency agrees quite well with the observed value of 369 cm^{-1}. The analogous correlation for sixth period diatomics predicts $\nu_{W\equiv W} = 270$ cm^{-1}, $k = 3.93$ mdyn/Å for $W_2[CH_2Si(CH_3)_3]_6$ (W≡W bond distance of 2.254 Å),[15] still in reasonable agreement with the observed 299 cm^{-1} given the assumptions in the correlation. These force constants are larger than those reported for the quadruply bonded Mo_2X_8 (ca. 3.3–3.5 mdyn/Å) and W_2X_8 (ca. 3.6 mdyn/Å) compounds.[3] Furthermore, the bands we have assigned as $\nu_{M\equiv M}$ for the hexaalkyls are absent in the IR spectra,[6,7] consistent with the expected mutual exclusion of IR and Raman bands for an A_1 metal–metal stretching mode in a molecule with a center of inversion (the approximate crystallographic symmetry of the M_2C_6 core in the dimers is D_3).[6,14,15]

One further observation strengthens our $\nu_{M\equiv M}$ assignments. When our Raman spectrum of $W_2[OC(CH_3)_3]_6$ ($\lambda_{exc} = 632.8$ nm) is compared with a spectrum of the same compound recorded using 1064 nm excitation on a Fourier transform Raman spectrometer,[16] the band at 303 cm^{-1} (which we have assigned as $\nu_{W\equiv W}$) shows five times greater intensity for 632.8 nm excitation as for 1064 nm excitation, when scaled to the intensity of a pure ligand mode at 793 cm^{-1} and corrected for the ν^4 dependence of the scattered intensity. No other band exhibits an intensity ratio (I_{632}/I_{1064}) greater than 2, and all bands which can be directly correlated with bands in the Raman spectrum of *tert*-butyl alcohol display ratios of 1.0 ± 0.1. We attribute the significant intensity increase of the 303 cm^{-1} band in the 632.8 nm spectrum relative to the 1064 nm spectrum to preresonance Raman intensity enhancement involving the metal–metal-centered electronic transition at 378 nm in $W_2[OC(CH_3)_3]_6$.[10,17] The observed intensity increase is within 10% of the value calculated from a theoretical expression[18] for the excitation frequency dependence of preresonance Raman intensities in the case of a single electronic transition (the Albrecht *A* term).

Not every sample for which we have recorded Raman spectra exhibits a clearly assignable metal–metal stretching band. For example, the spectra of the hexakis(cyclohexoxides) $M_2[O\text{-}c\text{-}C_6H_{11}]_6$ resemble those of the hexakis(dimethylamides) in that most of the low-frequency bands shift when the metal is changed. We are undertaking crystallographic and spectroscopic studies to determine which parameters correlate with our ability to assign $\nu_{M\equiv M}$ in the Raman spectra. Preliminary data suggest, unsurprisingly, that compounds in which the M≡M–X angle approaches 90° (at which angle the ligand-based and metal–metal modes are essentially orthogonal) function better in this regard. However, this cannot be the only important factor, as some compounds with M≡M–X angles greater than those in the $M_2(NMe_2)_6$ dimers exhibit assignable spectra, while others with angles near 90° do not. The presence or absence of low-frequency ligand vibrational modes also appears a contributing issue, but again not a determining one; cyclohexanol exhibits no bands in the regions where we observe $\nu_{M\equiv M}$, yet the spectra of the dimetal hexakis(cyclohexoxides) are unusable.[19] These studies will be reported in due course.

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(11) Two limiting ways to predict the shift of $\nu_{M\equiv M}$ upon deuteration are to treat the vibrational motion as that of a pure metal diatomic (for which the frequency shift is zero), and as that of two $M[OC(CH_3)_3]_3$ units. For the latter, the calculated "diatomic" harmonic oscillator frequency shifts are 16 cm^{-1} for the Mo_2 compound and 10 cm^{-1} for the W_2 compound, based solely on the mass change resulting from deuteration of the *tert*-butoxide ligands.

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(19) A reviewer commented that the physical separation of CH_3 groups from the dimetal core might be a crucial determinant. This intriguing hypothesis unfortunately cannot be tested easily; triply bonded $M_2(CH_3)_6$ and $M_2(OCH_3)_6$ compounds are unknown and unlikely to be preparable. However, the fact that the hexakis(cyclohexoxides), which represent species with physically separated CH_2R groups, do not give assignable spectra, while the hexaneopentyl and hexakis(trimethylsilylmethyl) dimers (representing adjacent CH_2R groups) do, suggests that this view is incorrect.