Far-Infrared Spectroscopy of Quadruply Bonded M₂X₄L₄ Complexes

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Far-infrared spectra are reported for mulls of the compounds $Mo_2X_4L_4$ (X = Cl, Br, I; L = PMe₃, PEt₃, P(*n*-Pr)₃, P(*n*-Bu)₃, AsMe₃) and $W_2Cl_4(PMe_3)_4$ and for a single crystal of $Mo_2Cl_4(PMe_3)_4$. Assignments have been made, using predictions of absorption intensities from a vector addition model and of freqencies by correlations to related molecules, of the ν_6 [b₂, ν(MX)], ν_8 [b₂, δ(MMX)], ν_{10} [e, ν(MX)], and ν_{11} [e, ν(MP)] modes. The spectra of $Mo_2Cl_4(PR_3)_4$ complexes are complicated by the presence of internal ligand deformation modes in the same frequency region as ν_{10}.

Introduction

Complexes of the type $M_2X_4L_4$ (M = Mo, W; X = halide or pseudohalide; L = uncharged σ-donor)[4] constitute the most extensive class of quadruply metal–metal-bonded dimers, with nearly 100 compounds being reported since the preparation of $Mo_2Cl_4(PEt_3)_4$ in 1972.[5] The wide variety of derivatives available allows examination of the relative contributions of metal and ligand to the electronic structures and physical properties of quadruply bonded dimers.[6] In the course of earlier studies of these issues, we discovered that the ¹(δ → δ*) electronic absorption and ¹(δ* → δ) fluorescence bands of the complexes $Mo_2X_4(PMe_3)_4$ (X = Cl, Br, I), $Mo_2Cl_4(AsMe_3)_4$, and $W_2Cl_4(PMe_3)_4$ display an extraordinary amount of vibronic structure at low temperature, containing progressions in as many as eight vibrational modes.[6b,k,l] Since the interpretation of this vibronic structure and subsequent determination of the molecular and electronic structure of the ¹(δδ*) excited state depend upon a detailed understanding of the nature and frequencies of the normal modes of vibration of these species, we have obtained far-infrared spectra of these and other derivatives of the $M_2X_4L_4$ type to complement and expand our previously reported[6f] assignments of their resonance Raman spectra.

Experimental Section

The complexes $Mo_2X_4(PR_3)_4$ (X = Cl, R = Me,[7] Et,[8] *n*-Pr,[8] *n*-Bu;[8] X = Br, R = Me;[6f] X = I, R = Me[6f]), $Mo_2Cl_4(AsMe_3)_4$,[6f] $Mo_2Cl_4(PMe_2-Ph)_4$,[8] $Mo_2Cl_4(PMePh_2)_4$,[8] and $W_2Cl_4(PMe_3)_4$[9] were prepared and purified by standard procedures. $Mo_2Br_4(PEt_3)_4$ and $Mo_2I_4(PEt_3)_4$ were synthesized according to the procedure developed for their trimethylphosphine analogues.[6f]

Far-infrared spectra were recorded of petroleum-jelly mulls held between polyethylene plates. The mulls were prepared from freshly recrystallized samples in a helium-filled glovebox and were placed in the infrared cells under an inert atmosphere. Samples were stable under measurement conditions. Spectra were recorded with a nitrogen-purged Digilab FTS-40 FT-IR spectrometer. Background spectra (petroleum-jelly blanks) were subtracted from the spectra of the mull samples. The experimentally observed precision of the peak positions of the intense absorptions is ±1 cm⁻¹.

Far-infrared spectra of single crystals of $Mo_2Cl_4(PMe_3)_4$ were measured for large thin plates grown by slow evaporation from dichloromethane solution. The well-developed crystal face was (101).[6h] The crystals were attached to polyethylene sheets with petroleum jelly and masked with copper foil into which apertures slightly smaller than the crystals had been cut.

Results and Discussion

General Considerations. The frequencies of far-infrared (far-IR, ν < 500 cm⁻¹) bands have been reported for many quadruply bonded complexes of the $Mo_2X_4L_4$ type;[8,10] however, far-IR data are not available for the series $M_2X_4(PMe_3)_4$ (M = Mo, X = Cl, Br, I; M = W, X = Cl). A tabulation of far-IR frequencies[10a] led to the identification of a pair of bands in several $Mo_2Cl_4L_4$

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Table I. Far-Infrared Data for Selected Mo₂X₄L₄ Complexes[a]

Mo₂Cl₄L₄							
L = PMe₃[b]	L = PEt₃[c]	L = P(n-Pr)₃[c]	L = P(n-Bu)₃[d]	L = AsEt₃[e]	L = SMe₂[d]	L = SEt₂[d]	L = NMe₂H[f]
346	333 s	328 s	*326 m*	*325 vs*	350 m	*335 s*	*335*
324 m	309 w	279 m	*278 m*	*275 m*	294m	*286 m*	*322*
279 m	285 m				280 sh		

Mo₂Br₄L₄					
L = PEt₃[c]	L = P(n-Pr)₃[c]	L = P(n-Bu)₃[d]	L = AsEt₃[e]	L = SMe₂[d]	L = NMe₂H[f]
			340 m		
270 w, br	266 w	*260 m*	270 s	265 s	*286 s*
			215 m		*264 s*

[a] Frequences are in cm⁻¹. Entries in italics are those that have been previously assigned to ν(MoX). [b] Reference 10i. [c] Reference 8. [d] Reference 10a. [e] Reference 10g. [f] Reference 10c.

derivatives and a single band in corresponding bromo complexes as ν(MoX); these assignments, which have been adopted by subsequent workers, are summarized in Table I. There appear to be no assignments of infrared-active ν(MoI) modes for Mo₂I₄L₄ complexes or of any vibrational modes other than the Raman-active ν(WW)[9b] for W₂Cl₄(PR₃)₄ compounds.

Before presenting our far-infrared data, we will first discuss the nature of the modes we expect to observe. Crystallographic studies on several M₂X₄(PR₃)₄ complexes indicate that they adopt the D_{2d} structure sketched as follows:[6f,7,10i,11]
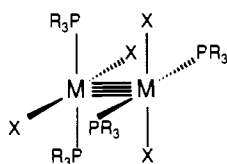
In the case of trimethylphosphine-containing complexes, the crystallographic site symmetry is lower than D_{2d}, but no significant distortion (including of the orientation of the phosphine methyl groups) from the idealized symmetry is seen. Considering only the M₂X₄P₄ skeleton and ignoring (for the moment) internal modes associated with the phosphine ligands, 18 normal modes are predicted (5a₁ + a₂ + 2b₁ + 4b₂ + 6e), one of which (a₂) is both Raman and infrared silent. The remaining 17 are all, in principle, Raman active, while only 10 (4b₂ + 6e) are infrared active. This information, along with the mode numbering scheme we have adopted, is summarized in Table II, and the displacements of the symmetry coordinates are illustrated in Figure 1. Note that we have varied from symmetry block ordering of the modes so that torsion is the highest-numbered mode.

Coordinates of the same symmetry can, of course, mix with one another. Such mixing is expected to be significant for the various skeletal deformation coordinates, since the eclipsed D_{2d} structure should induce correlation of metal–halide and metal–phosphine bending motions. Mixings among the metal–ligand stretching coordinates are expected to be less, unless the frequencies of the zero-order (unmixed) modes are similar; this should also be true for the mixing of skeletal coordinates with internal vibrational coordinates of the ligands. Because of the complexity of the problem, we conclude that performing normal mode calculations on these systems would not be productive; despite the large amount of experimental data that are available (vide infra), the problem is hopelessly underdetermined. Our analysis will, of necessity, be a qualitative one.

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Table II. Symmetry Coordinates for the D_{2d} M₂X₄L₄ Structural Skeleton

description	no.	species	activity[a]
ν(MM)	ν₁	a₁	R
ν(MX)	ν₂	a₁	R
ν(ML)	ν₃	a₁	R
δ(MMX)	ν₄	a₁	R
δ(MML)	ν₅	a₁	R
ν(MX)	ν₆	b₂	R, IR
ν(ML)	ν₇	b₂	R, IR
δ(MMX)	ν₈	b₂	R, IR
δ(MML)	ν₉	b₂	R, IR
ν(MX)	ν₁₀	e	R, IR
ν(ML)	ν₁₁	e	R, IR
δ(MMX)	ν₁₂	e	R, IR
δ(MML)	ν₁₃	e	R, IR
δ(XMX)	ν₁₄	e	R, IR
δ(LML)	ν₁₅	e	R, IR
δ(XML)	ν₁₆	b₁	R
δ(XML)	ν₁₇	a₂	
τ(MM)	ν₁₈	b₁	R

[a] R = Raman; IR = infrared.

Some semiquantitative considerations are still relevant, however. It can be seen from the forms of the zero-order ν₆ [b₂, ν(MX)], ν₇ [b₂, ν(ML)], ν₁₂ [e, δ(MMX)], and ν₁₃ [e, δ(MML)] normal modes that, while all are formally IR active, they would have zero dipole moments, and hence no infrared intensity, if the M–M–X or M–M–L angles were equal to 90°. From X-ray crystallographic data,[6f,7] the M–M–X and M–M–L angles are 112–115 and 102–103°, respectively. These modes are therefore expected to have non-zero intensity, but to be weak relative to the ν₁₀ [e, ν(MX)], ν₁₁ [e, ν(ML)], ν₈ [b₂, δ(MMX)], and ν₉ [b₂, δ(MML)] modes.

We can predict the infrared intensity ratios of the stretching modes by using a simple vector addition model, which yields $I(e)/I(b_2) = I(\nu_{10})/I(\nu_6)$ (or $I(\nu_{11})/I(\nu_7)$) $= (\tan^2 \theta)/2$, where θ is the M–M–X or M–M–L angle. We thus predict $I(\nu_{10})/I(\nu_6) = 2$–3.5 and $I(\nu_{11})/I(\nu_7) \cong 10$. For ν(MX) the b₂ mode will be weaker than the e mode, while for ν(MP) the b₂ mode is predicted to be vanishingly weak relative to the e mode. Analogous application of this model to the bending modes yields $I(b_2)/I(e) = 2 \tan^2 \theta$, predicting that e-symmetry ν₁₂ and ν₁₃ will be extremely weak relative to b₂-symmetry ν₈ and ν₉.

Ligand Modes. All of the skeletal modes discussed above can be expected to have frequencies less than 450 cm⁻¹, and we will restrict our present study to that spectral region. Most of the phosphine or arsine internal modes will have frequencies considerably high than this[12] and thus will be energy-factored from the skeletal modes and need not be considered. There are a few candidates for low-frequency ligand modes, however.

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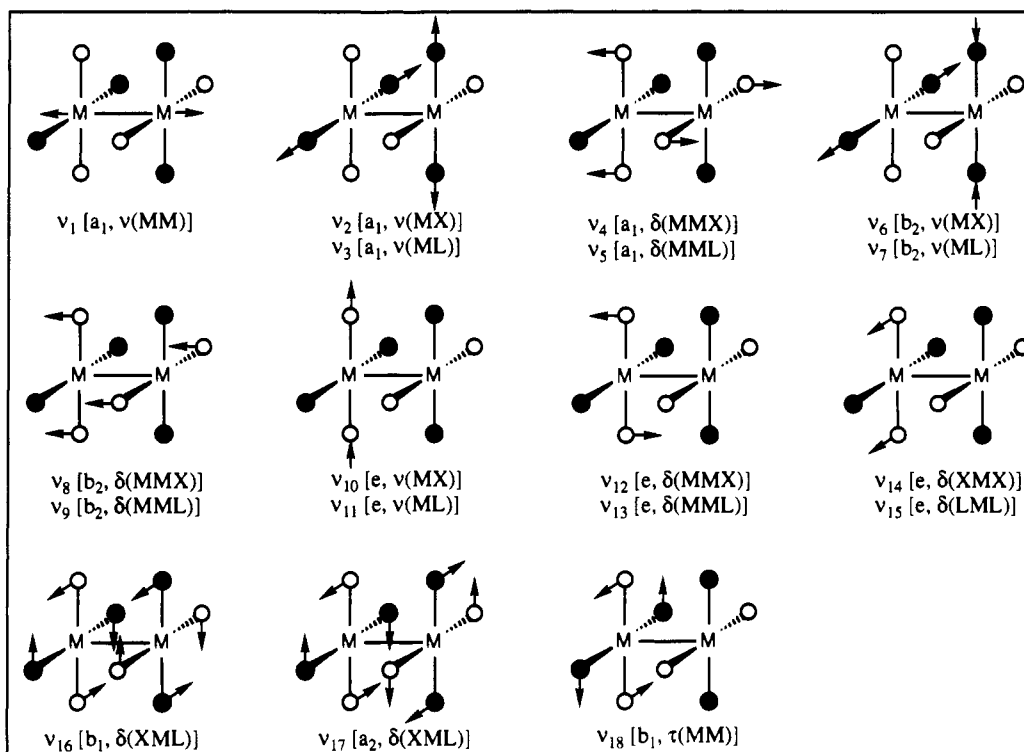
Figure 1. Symmetry coordinates of the $M_2X_4L_4$ structural skeleton. For any degenerate (e) pair or for cases where there are equivalent M_2X_4 and M_2L_4 modes, only one coordinate is shown.

Table III. Raman Fundamental Modes for Selected $M_2X_4L_4$ Complexes[a]

mode	$Mo_2Cl_4(PMe_3)_4$[b]	$Mo_2Cl_4(AsMe_3)_4$[b,c]	$Mo_2Br_4(PMe_3)_4$[b]	$Mo_2I_4(PMe_3)_4$[b]	$W_2Cl_4(PMe_3)_4$[d]
ν_1 [a_1, $\nu(MM)$]	355 vs	356 vs	352 vs	343 vs	261 s
ν_2 [a_1, $\nu(MX)$]	274 m	278 m	159 m	105 w	300 m
ν_3 [a_1, $\nu(ML)$]	235 w	217 vw (?)	235 w	248 m	226 w

[a] Freqencies are in cm^{-1}. $T = 20$ K unless otherwise noted. [b] Reference 6f. [c] $T = 300$ K. [d] Solid state; $\lambda_{ex} = 530.9$ nm. Additional Raman bands: 312 w, 288 w, 270 sh, 161 m, 122 m.

One low-frequency ligand mode is methyl torsion, which is observed[12] at ca. 200 cm^{-1} for PMe_3 and $AsMe_3$ at $T = 14$ K. At room temperature these bands are extremely weak and broad,[12] which is typical for methyl torsions,[13] and we presume that the methyl torsion modes of the complexes of this study will be similarly weak at room temperature.

Ligand deformation modes, on the other hand, may provide fairly strong infrared absorptions, as demonstrated by the spectra of the uncomplexed ligands. For example, the $\delta(CPC)$ modes of PMe_3 ($T = 14$ K) are located at 315 cm^{-1} (symmetric mode) and at 288 and 269 cm^{-1} (asymmetric mode, split in the crystal),[12a] and the analogous modes for $AsMe_3$ are at 265 cm^{-1} and at 249 and 222 cm^{-1} (split in the crystal);[12b] the lower frequencies for the arsine arise from the mass effect. For more complex R groups, additional PR_3 deformation modes may occur in the far-infrared region. For example, n-Pr and n-Bu groups display[14] $\delta(CCC)$ modes near 350 cm^{-1}. We also expect $\delta(CCP)$ modes to lie in the same general region. The spectral complexity that can result is typified by the vibrational spectrum of PEt_3;[12c] fortunately, most of the numerous lines that are observed are quite weak.

Raman Spectra. Raman spectra for several of these complexes have previously been presented and discussed in detail.[6f] The assigned fundamental vibrations, which are limited to the three totally symmetric stretching modes, are summarized in Table III. The assignment of $\nu(MoP)$ for these compounds was tentative

since, for halo complexes, this mode receives little resonance enhancement upon $^1(\delta \rightarrow \delta^*)$ excitation. We have, however, subsequently obtained resonance Raman data for another Mo_2X_4-$(PMe_3)_4$ compound that supports the assignment: the spectrum of $Mo_2(CCSiMe_3)_4(PMe_3)_4$ displays[15] three strong, totally symmetric fundamentals at 362 (ν_1, $\nu(MoMo)$), 397 (ν_2, $\nu(MoC)$), and 254 cm^{-1} (ν_3, $\nu(MoP)$), together with overtones and combinations of them. This value for $\nu(MoP)$ compares favorably with $\nu(NiP) = 273$ cm^{-1} for *trans*-$Ni(PEt_3)_2Cl_2$,[16a] which was established by metal-isotope substitution. We emphasize this point because there are many erroneous assignments in the literature of $\nu(MP)$ to higher frequency vibrations.[16] In most cases, a ligand deformation mode has been mistakenly so assigned.

It should be noted that most of the weak, unassigned Raman features tabulated in our earlier report[6f] correspond to strong infrared absorptions (vide infra), as is expected from the mutual infrared and Raman allowedness of b_2- and e-symmetry modes. Specifically, only two lines, in addition to the a_1 modes in Table III, are observed in the Raman spectrum of $Mo_2Cl_4(PMe_3)_4$ (153, 108 cm^{-1})[6f] that do not closely match IR bands. We tentatively assign these as ν_4 [a_1, $\delta(MoMoCl)$] and ν_5 [a_1, $\delta(MoMoP)$], respectively, as is consistent with the rough frequency rule that, for a bent triatomic A–B–C unit, $\delta(ABC) \simeq 1/4[\nu(AB) + \nu(BC)]$. In support of this assignment, combination tones of each of these with ν_1 are observed. A similar analysis of the Raman

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spectra of Mo$_2$Br$_4$(PMe$_3$)$_4$ and Mo$_2$I$_4$(PMe$_3$)$_4$ was not possible due to the extreme weakness of all bands but ν_1.

We also include Raman data for W$_2$Cl$_4$(PMe$_3$)$_4$ in Table III, the assignments for which deserve some discussion. As in our earlier Raman study,[6f] we can use the experimental bond distances[7] of W$_2$Cl$_4$(PMe$_3$)$_4$ and Mo$_2$Cl$_4$(PMe$_3$)$_4$ to infer whether or not the Raman-active normal modes are nearly pure symmetry coordinates (ν_1, ν_2, and ν_3; see Figure 1) or are mixed. This is done using empirical force constant/bond distance relationships devised previously.[17] Satisfactory agreement between calculated and observed frequencies is found for ν_1, ν_2, and ν_3 of Mo$_2$-Cl$_4$(PMe$_3$)$_4$ and for ν_1 and ν_2 of W$_2$Cl$_4$(PMe$_3$)$_4$. The value calculated for ν_3(WP), however, is 265 cm^{-1}, compared to the observed frequency of 226 cm^{-1}. This is very likely due to coupling of the a$_1$ W–W and W–P stretches of W$_2$Cl$_4$(PMe$_3$)$_4$; ν(WW) is found at 261 cm^{-1} and mixes with ν(WP) to depress the frequency of the latter. For Mo$_2$Cl$_4$(PMe$_3$)$_4$, ν_1 is observed at 355 cm^{-1}, compared to ν_2 = 274 and ν_3 = 235 cm^{-1}; thus, the a$_1$ modes in this system are energy-factored (ν(MM) is considerably higher in energy than either metal–ligand stretch) and the symmetry coordinates are adequate representations of the normal modes.

Finally, several weak Raman lines are also observed for W$_2$-Cl$_4$(PMe$_3$)$_4$ (Table III). All but one of them correspond to intense infrared absorptions (vide infra) and therefore to modes of e or b$_2$ symmetry. The exception is the 161-cm^{-1} feature, which therefore presumably has a$_1$ or b$_1$ symmetry; we tentatively assign it to ν_4 [a$_1$, δ(WWCl)].

Far-Infrared Spectra. The far-infrared spectra of the Mo$_2$X$_4$-(PMe$_3$)$_4$ compounds proved to be unexpectedly difficult to interpret. We therefore studied related derivatives in which the neutral ligand or metal was systematically varied. We will divide our discussion between the chloro complexes, for which considerably more data were accumulated, and the bromo and iodo derivatives.

(a) Chloro Complexes. The infrared spectra of Mo$_2$Cl$_4$(PMe$_3$)$_4$ and Mo$_2$Cl$_4$(AsMe$_3$)$_4$ are illustrated in Figures 2A and 3; a summary of frequencies and their assignments, along with those for other M$_2$Cl$_4$L$_4$ derivatives, is set out in Table IV. The intensities of the higher frequency peaks in the spectra of Mo$_2$-Cl$_4$(PMe$_3$)$_4$ and Mo$_2$Cl$_4$(AsMe$_3$)$_4$ are far larger than those of the other features, to an extent greater than is apparent from the figures; mull spectra do not obey Beer's law because of dispersion and scattering effects, resulting in saturation of intense features relative to weak ones. The spectrum of Mo$_2$Cl$_4$(PMe$_3$)$_4$ was of a thicker and more concentrated mull, chosen so as to better display the weaker low-frequency features; saturation has greatly decreased the relative intensities of the lines at 349, 327, and 283 cm^{-1}. Effects of this sort should be kept in mind when the spectra presented in this paper are considered.

Since the reported spectrum of AsMe$_3$ indicates that intense modes for this ligand should not occur in the 250–340-cm^{-1} range,[12b] assignment of the 337- and 288-cm^{-1} bands of Mo$_2$-Cl$_4$(AsMe$_3$)$_4$ to ν(MoCl) modes is logical. This assignment is consistent with previous assignments for related compounds (Table I); we particularly draw attention to the nearly identical far-infrared spectrum of Mo$_2$Cl$_4$(SEt$_2$)$_4$[10a] and also to the close relationship to the far-infrared spectra of Mo$_2$Cl$_8$$^{4-}$ salts.[18,19] The group-theoretical prediction for the latter (D_{4h} symmetry) is that there are two IR-active ν(MoCl) modes (e$_u$ and a$_{2u}$) that are strictly analogous to the IR-active e and b$_2$ ν(MoCl) symmetry modes of D_{2d} Mo$_2$Cl$_4$L$_4$ compounds; they are observed at 307 and 275 cm^{-1}.[19]

Figure 2. Far-infrared absorption spectra of Mo$_2$X$_4$(PMe$_3$)$_4$ as petroleum-jelly mulls: (A) X = Cl; (B) X = Br; (C) X = I.

Figure 3. Far-infrared absorption spectrum of Mo$_2$Cl$_4$(AsMe$_3$)$_4$ as a petroleum-jelly mull.

We assign the 337-cm^{-1} line to ν_{10}[e, ν(MoCl)] and that at 288 cm^{-1} to ν_6 [b$_2$, ν(MoCl)], because of the higher intensity of the former. An additional reason for assigning the 288-cm^{-1} band to ν_6 is that, according to the forms of the normal modes (Figure 1), the ν_6 and a$_1$-symmetry ν_2 (ν_2 = 278 cm^{-1})[6f] ν(MoCl) modes should have similar frequencies if the coupling between the two MoCl$_2$L$_2$ fragments is small. This approximation, which has proven valid for other binuclear systems,[14b,17a] is likewise consistent with correlations among the infrared and Raman spectra of the Mo$_2$Cl$_8$$^{4-}$ [18,19] and the Re$_2$X$_8$$^{2-}$ [18,20] ions.

In light of these observations, it was puzzling to us that Mo$_2$-Cl$_4$(PMe$_3$)$_4$ displays two intense lines, at 347 and 327 cm^{-1}, near where ν_{10} [e, ν(MoCl)] was expected. The obvious explanation that the degenerate e mode might be split in the crystal (as allowed by the crystallographic C_2 site symmetry[7]) would not appear to be justified in view of the extremely small crystallographic deviations of the molecule from D_{2d} symmetry. Several measurements on related compounds were therefore performed with

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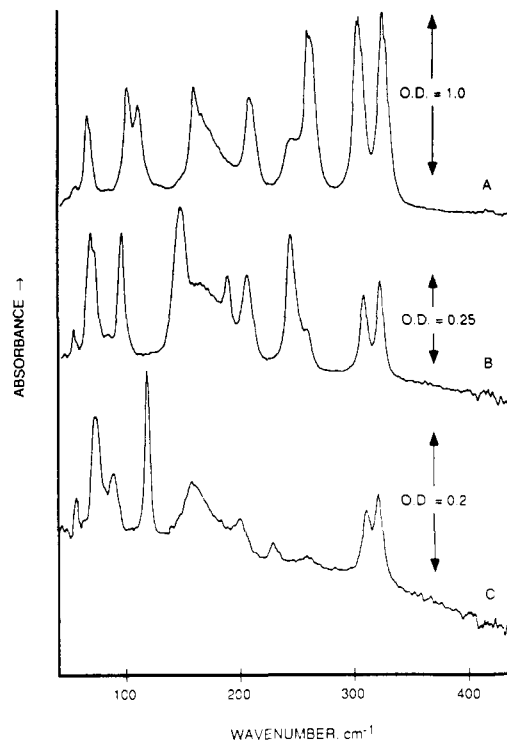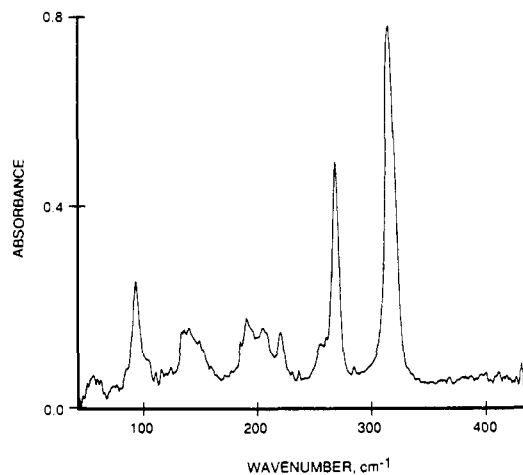(19) Clark, R. J. H.; Franks, M. L. *J. Am. Chem. Soc.* **1975**, *97*, 2691–2697.

(20) Clark, R. J. H.; Stead, M. J. *Inorg. Chem.* **1983**, *22*, 1214–1220.

Table IV. Far-Infrared Data for M₂Cl₄L₄ Complexes[a]

mode	M = Mo L = PMe₃	M = Mo L = PEt₃	M = Mo L = P(n-Pr)₃	M = Mo L = P(n-Bu)₃	M = Mo L = AsMe₃	M = W L = PMe₃
δ(CCC), δ(CCP)		380 w	392 w, 363 w	390 w, 354 w		
ν₁₀ [e, ν(MCl)]	345 s, 327 s[b]	330 s	325 s	328 s	337 s	338 s, 311[b]
ν₆ [b₂, ν(MCl)]	283 s	282 s	276 s	280 s	288 s	289 s
δ(CEC) (E = P, As)	267 w				278 w, 238 m, 222 m, 209 m[c]	268 w
ν₁₁ [e, ν(MP)]	230 m	234 m	229 m	225 m		~200 sh (?)
methyl torsion (?)	195 w, sh	206 w, sh	209 w, sh			
ν₈ [b₂, δ(MMX)]	181 m	157 m	140 m	137 m	159 m	183
not assigned	131 m	127 w			111 m	149 w
	121 m				72 w	133 m
	86 m					122 m
						85 m
						75 w

[a] Frequencies are in cm⁻¹. [b] ν₁₀ and a δ(CPC) mode are mixed to yield two intense lines. [c] One of these features may be ν₁₁ ν(MoAs).

Figure 4. Far-infrared absorption spectra of Mo₂X₄(PEt₃)₄ as petroleum-jelly mulls: (A) X = Cl; (B) X = Br; (C) X = I.

Figure 5. Unpolarized far-infrared absorption spectrum of the (101) face of a single crystal of Mo₂Cl₄(PMe₃)₄.

the aim of resolving this ambiguity. The far-infrared spectrum of Mo₂Cl₄(PEt₃)₄ is illustrated in Figure 4A, and spectra of P(n-Pr)₃ and P(n-Bu)₃ analogues are included in Table IV. The two most intense lines in all of these spectra, near 330 and 280 cm⁻¹, can be assigned to the ν₁₀ (e) and ν₆ (b₂) ν(MoCl) modes, respectively. The relative intensities and frequencies of the assigned ν(MoCl) modes are consistent in all cases with the consideration set out above. As the size of the phosphine R group increases, additional ligand deformation modes are expected (and observed) in the same general spectral region as the ν(MoCl) modes. In general, the ligand deformation modes observed between 350 and 450 cm⁻¹ behave as unmixed local oscillators and are much weaker than the ν(MoCl) modes.[21] Of importance to the assignment of the spectrum of Mo₂Cl₄(PMe₃)₄ is the fact that the crystal structure of Mo₂Cl₄(PEt₃)₄ is highly disordered,[10i,11s] so that a higher effective symmetry than for the PMe₃ homologue would not be expected. These results thus do not support the hypothesis of a split ν₁₀ [e, ν(MoCl)] mode for Mo₂Cl₄(PMe₃)₄.

The far-infrared spectrum of W₂Cl₄(PMe₃)₄ (Table IV) displays an even stronger similarity to that of Mo₂Cl₄(PMe₃)₄. Given this, the 289-cm⁻¹ line is assigned to ν₆ [b₂, ν(WCl)], while

the 338- and 311-cm⁻¹ lines are assumed to be analogous to the 347- and 327-cm⁻¹ lines of the molybdenum compound. Differences in the relative intensities of these three lines are evident, however, with the highest-frequency line being the weakest one for the tungsten compound.

To probe this problem in further detail, we examined far-infrared spectra of single crystals of Mo₂Cl₄(PMe₃)₄ (Figure 5). The (101) crystal face of the monoclinic lattice that was examined presents the Mo₂ axis exactly perpendicular to the examining light beam.[6h,7] Thus, for unpolarized exciting light,[22] the intensity ratio of transitions that are dipole-allowed with polarization perpendicular (⊥, e) and parallel (∥, b₂) to Mo₂ should be modified relative to isotropic (i.e., mull) values according to

$$(I_\perp/I_\parallel)_{\text{isotropic}} = 2(I_\perp/I_\parallel)_{(101) \text{ crystal face}}$$

That is, ∥z-polarized transitions (b₂) should appear twice as intense relative to ⊥z-polarized transitions (e) in the unpolarized spectrum of the (101) crystal face, as compared to their relative intensities in the mull spectra. From this we infer that the bands at 283 and 181 cm⁻¹ are of b₂ symmetry; all other intense lines appear to be x,y-polarized and hence to be of e symmetry. For the 283-cm⁻¹ band, this finding is consistent with our assignment of it as ν₆ [b₂, ν(MoCl)]. We additionally assign the 181-cm⁻¹ line to ν₈ [b₂, δ(MoMoCl)]. An alternative assignment of this band to ν₇ [b₂, ν(MoP)] is excluded both because the agreement of the frequency with that of ν₃ [a₁, ν(MoP)] is poor (Table III)

(21) The far-infrared spectra of Mo₂Cl₄(PMe₂Ph)₄ and Mo₂Cl₄(PMePh₂)₄ were also recorded. These spectra are more complicated than those of the trialkylphosphine complexes because there are a number of metal-sensitive phenyl modes in the far-infrared region (Whiffen, D. H. *J. Chem. Soc.* **1956**, 1350–1356). While detailed assignments are precluded by this complication, there are, nonetheless, candidates for ν₁₀ and ν₆ in each spectrum. For the PMe₂Ph complex, they are found respectively at 319 (and/or 332) and 280 cm⁻¹, while for the PMePh₂ complex they are at 337 and 295 cm⁻¹. In addition, bands attributable to ν₁₁ [e, ν(MoP)] are observed at 229 and 220 cm⁻¹ for the PMe₂Ph and PMePh₂ complexes, respectively.

(22) We initially intended to obtain polarized single-crystal far-infrared spectra. Unfortunately, standard gold-grid polarizers cut down transmitted light (already quite low for the single-crystal samples) so drastically that our FT spectrometer was unable to maintain a stable lock over the long accumulation times that were required.

Table V. Far-Infrared Data for $Mo_2X_4L_4$ Complexes[a]

	$Mo_2Br_4L_4$		$Mo_2I_4L_4$	
mode	L = PMe₃	L = PEt₃	L = PMe₃	L = PEt₃
δ(CPC), δ(CCC), δ(CCP)		415 w		413 m
	344 m	360 m	342 m	358 m
	329 m	338 s	332 m	338 s
		318 vw, sh		317 w, sh
	278 w	285 w	279 w	280 w
		264 w		248 w	255 vw
ν_{10} [e, ν(MoX)]	264 s	240 m	177 m	180 w
ν_{11} [e, ν(MoP)]	225 m	b	219 m	226 s
ν_6 [b₂, ν(MoX)]	208 m	181 m	137 s	132 m
ν_8 [b₂, (MoMoX)]	166 s	147 m	91 s	76 w (?)
not assigned	186 w, sh	200 vw	107 m	107 m
	114 s			
	86 s	86 w		74 w

[a] Frequencies are in cm⁻¹. [b] Possibly obscured by the 240-cm⁻¹ band.

and because ν_7 is expected to be very weak (vide supra). The analogous absorption in the spectrum of $Mo_2Cl_4(AsMe_3)_4$ occurs at 159 cm⁻¹.

Having excluded the more obvious possibilities with these additional data, we now propose an explanation for the ν(MCl) regions of the spectra of $Mo_2Cl_4(PMe_3)_4$ and $W_2Cl_4(PMe_3)_4$. As noted earlier, PMe_3 has a symmetric δ(CPC) mode at 315 cm⁻¹.[12] For the crystallographic orientation found for $Mo_2Cl_4(PMe_3)_4$ and $W_2Cl_4(PMe_3)_4$,[7] this vibration yields modes of a₁, b₂, and e symmetries. We suggest that a near degeneracy of the δₛᵧₘ-(CPC) and ν(MCl) coordinates of e symmetry has resulted in strong mixing between them that is unique for these two compounds.[23] As will be shown later, δ(CPC) modes are indeed observed in this spectral region for the bromo and iodo analogues of $Mo_2Cl_4(PMe_3)_4$, but they are considerably weaker than the absorptions of the chloro complex; intensity-stealing from ν_{10} [e, ν(MoCl)] is likely to be involved in the spectrum of Mo_2Cl_4-$(PMe_3)_4$. We suggest that the absence of comparable effects in the spectra of the longer-alkyl-chain phosphine complexes is a consequence of decreased mixing of ν(MoCl) with internal phosphine modes, arising from energy-factoring of the ν(MoCl) and δ(CPC) modes, thus removing their degeneracy, and/or that the orientation of the alkyl chains breaks the symmetry under which this mixing is allowed.

Turning to the assignment of the remaining skeletal modes, we note that two absorptions (ca. 230 and 150 cm⁻¹) in addition to ν(MoCl) are conserved in the spectra of the *n*-alkylphosphine complexes (Figure 3). We assign these features to ν_{11} [e, ν-(MoP)] and ν_8 [b₂, δ(MoMoCl)], respectively (Table IV). The variation of frequency of ν_8 with phosphine alkyl group may result from sensitivity of the δ(MoMoCl) potential surface to steric bulk and/or mass (kinematic coupling) of the phosphine ligand and indicates that the mode is far from pure δ(MoMoCl).

Several low-frequency lines are not assigned (Table IV). For $Mo_2Cl_4(PMe_3)_4$, the single-crystal data suggest that these unassigned lines are all of e symmetry. There are four remaining unassigned skeletal vibrational modes of e symmetry: ν_{12}, ν_{13}, ν_{14}, and ν_{15}. We do not have any good rationale for detailed assignments of these modes, however; an additional problem is that lattice modes may also appear in the <200-cm⁻¹ region.

(b) Bromo and Iodo Complexes. The far-infrared spectra of $Mo_2X_4(PR_3)_4$ (X = Br, I) are displayed in Figure 2B,C for R = Me and in Figure 4B,C for R = Et; frequencies and assignments are summarized in Table V. One obvious aspect of these spectra

Table VI. Metal–Ligand Stretching Frequencies for $Re_2X_8^{2-}$ [a]

	ν(ReX)[b]		
X	a₁g	eᵤ	a₂ᵤ
Cl	361	332	347
Br	211	232	220
I	152	178	162

[a] References 18, 20, and 26. [b] Frequencies are in cm⁻¹.

Table VII. Estimated Metal–Ligand Stretching Frequencies for $Mo_2X_4L_4$ Compounds

	ν(MoX)[a]		
X	a₁ ν_2	e ν_{10}	b₂ ν_6
Cl	278	337	288
Br	162	235	183
I	117	181	134

[a] Frequencies are in cm⁻¹. Values for X = Cl are those experimentally determined for $Mo_2Cl_4(AsMe_3)_4$, while those for X = Br and I are calculated, on the basis of the values of Table VI.

is that whereas the ν(MoCl) bands were by far the strongest lines in the spectra of the chloro homologues, the ν(MoBr) and ν(MoI) modes are sufficiently weak that many other modes have comparable intensities. In our experience,[14b,24] this is a fairly common phenomenon, and it is probably related to lower bond dipole moments for the lower-electonegativity polarizable halides.

Another aspect of these spectra that is quite clear is that bands attributable to ligand deformations occur in the 300–400-cm⁻¹ region. Thus, the doublets in the spectra of the $Mo_2X_4(PMe_3)_4$ (X = Br, I) complexes near 340 cm⁻¹ are assigned to symmetric δ(CPC) modes; lines in the same region for the triethylphosphine derivatives are (less specifically) also assigned to phosphine deformation modes. Our claim in the preceding section that such modes should occur in this spectral region for the chloro complexes is thus supported.

As an aid to assigning the lower frequency bands, we have obtained estimates for the frequencies of ν(MoX). It has been observed[25] that ν(MX) for structurally related molecules often scales systematically along the series Cl, Br, I. For the compounds of this study, the only suitable reference compounds that have well-established ν(MX) frequencies are the D_{4h}-symmetry $Re_2X_8^{2-}$ (X = Cl, Br, I) ions,[18,20,26] whose a₁g, eᵤ, and a₂ᵤ ν(ReX) frequencies are summarized in Table VI. These three modes correlate to the a₁, e, and b₂ modes, respectively, of $Mo_2X_4L_4$; in Table VII we present calculated ν(MoX) (X = Br, I) frequencies that have been scaled to the frequencies for $Mo_2Cl_4(AsMe_3)_4$ according to the $Re_2X_8^{2-}$ values.

It can be seen that the calculated ν(MoX) (X = Br, I) values are close to that of ν(MoP) assigned earlier. In such a situation, it may be difficult to distinguish the two types of vibrational modes; mixing between them may also be significant. It is encouraging, however, that the predicted ν_2 (a₁) frequencies (Table VII) are in reasonable agreement with the experimental values (Table III).

In Table V we suggest assignments of the IR-active ν(MoX) modes in accord with Table VII. The 264- and 208-cm⁻¹ peaks

(23) The $M_2X_4(PMe_3)_4$ compounds exhibit additional weak absorptions near 270 cm⁻¹; these may reasonably be assigned to the asymmetric (CPC) modes. Assignments of δ(CAsC) modes for $Mo_2Cl_4(AsMe_3)_4$ are not as straightforward, since many weak lines are observed below 300 cm⁻¹; we suggest assignment of the features at 273 cm⁻¹ and at 238, 222, and 209 cm⁻¹ to the symmetric and asymmetric deformations, respectively. Metal–chloride deformation modes and metal–arsine stretching modes may also contribute to the latter cluster of lines.

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(25) Clark, R. J. H.; Williams, C. S. *Inorg. Chem.* **1965**, *4*, 350–357.

(26) The two IR-active ν(ReX) modes of $Re_2X_8^{2-}$ were not individually assigned in ref 20. We have given assignments consistent with those of ref 18 (where assignments were made on the basis of normal mode calculations) and with other considerations outlined elsewhere in this paper. It should be noted that a more recent force field calculation on $Re_2Cl_8^{2-}$ (Larson, E. M.; Brown, T. M.; Von Dreele, R. B. *Acta Crystallogr.* **1986**, *B42*, 533–538) reverses our assignments of the a₂ᵤ and eᵤ ν(ReCl) modes; while we do not believe that their assignments are as internally consistent as those given in Table VI, particularly since the calculation does not correctly predict the experimentally established[20] ν(ReRe) frequency, the scaling factors are, in fact, little affected by this reversal because of the closeness in frequency of these two modes.

in the spectrum of $Mo_2Br_4(PMe_3)_4$ are respectively assigned as ν_{10} [e, $\nu(MoBr)$] and ν_6 [b_2 $\nu(MoBr)$], in good agreement with the literature values[10g] of 270 and 215 cm^{-1} for $Mo_2Br_4(AsEt_3)_4$ (Table I). In addition, the fairly intense line at 225 cm^{-1} is assigned to ν_{11} [e, $\nu(MoP)$], which is consistent with our assignments of this mode for chloro complexes, while the line at 166 cm^{-1} is attributable to ν_8 [b_2, $\delta(MoMoBr)$]. It should be noted that the intensity of this latter band is anomalously high, and it is thus possible that ν_6, ν_8, and, perhaps, ν_7 are mixed for this compound.

Assignments are not as clear for $Mo_2Br_4(PEt_3)_4$, and substantial shifts of the lines from their positions for $Mo_2Br_4(PMe_3)_4$ seem to be required. We assign the 181- and 143-cm^{-1} lines to ν_6 [b_2, $\nu(MoBr)$] and ν_8 [b_2, $\delta(MoMoBr)$] and suggest that ν_{10} [e, $\nu(MoBr)$] and ν_{11} [e, $\nu(MoP)$] may be nearly superimposed, and perhaps strongly mixed (vide infra), to form the 240-cm^{-1} feature.

For $Mo_2I_4(PMe_3)_4$, the calculated $\nu(MoI)$ values in Table VII suggest assignment of the sharp line at 137 cm^{-1} to ν_6 [b_2, $\nu(MoI)$]. We then assign the 219- and 177-cm^{-1} bands to ν_{11} [e, $\nu(MoP)$] and ν_{10} [e, $\nu(MoI)$], respectively. While the peak intensity of the 177-cm^{-1} feature is less than that of the 137-cm^{-1} feature, integration indicates that the former band is in fact more than twice as intense as the latter, in agreement with the prediction of our vector addition model (vide supra). The breadth of the 177-cm^{-1} band may arise from a solid-state splitting, since the iodo complex is not isomorphous with its chloro and bromo homologues.[6f] We also suggest assignment of the 91-cm^{-1} feature to ν_8 [b_2, $\delta(MoMoI)$].

Turning finally to $Mo_2I_4(PEt_3)_4$, however, an apparent contradiction appears. While features at 226, 180, and 132 cm^{-1} all agree well in frequency with bands assigned as ν_{11} [e, $\nu(MoP)$], ν_{10} [e, $\nu(MoI)$], and ν_6 [b_2, $\nu(MoI)$] for $Mo_2I_4(PMe_3)_4$, the intensity of the 180-cm^{-1} line seems far too low to be consistent with that predicted for ν_{10}, with the 226-cm^{-1} band instead having an appropriate intensity relative to ν_6 at 132 cm^{-1}. The only explanation that we can advance at this time is that the e-symmetry ν_{10} and ν_{11} modes are mixed because of their frequency proximity, with ν_{11} stealing most the intensity of ν_{10}. According to this explanation, mixing must be less for $Mo_2I_4(PMe_3)_4$.

Concluding Remarks. As we have seen, the assignment of the skeletal vibrational modes of these molecules is far from straightforward, both because internal deformation modes of the ligands are found in the same spectral region as the skeletal modes and because considerable mixing among modes of the same symmetry occurs in some cases. Despite the evident fact that mixing effects prevent simple assignments of observed vibrational peaks to individual symmetry coordinates in some cases, the symmetry coordinates nonetheless provide a useful conceptual framework within which to view the vibrational assignments. This is clearly indicated by the self-consistent frequency shifts among compounds possessing analogous $M_2X_4L_4$ skeletons. It should be noted that mixing effects have mainly complicated the assignment of the e-symmetry modes; we consider our assignments for b_2-symmetry modes to be firm.