

Vibrational Spectroscopic Studies of μ -Hydrido-Bridged Metal Clusters. 3. $H_3Re_3(CO)_{12}$

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Assignments of the vibrational spectra of $H_3Re_3(CO)_{12}$ and its deuterium analogues are presented for the disordered solid phase and the matrix phase.

Even though the most common hydride ligands in metal cluster compounds are those bridging two metal atoms, a satisfactory explanation of their stretching frequencies, which span an unusually wide wavenumber range (1750–550 cm^{-1}), has appeared only recently.¹ The main reason for the inaccessibility of these vibrations is their inherent weakness and the large breadth in both the infrared and the Raman spectra. This difficulty has been overcome to a great extent by making measurements at low temperatures when these modes sharpen preferentially, thus assisting detection and assignment.^{2,3} However, the frequent observation of multiple components of the metal–hydrogen stretching modes in the infrared and Raman spectra, in many cases more than can be accounted for by the number of hydride ligands in the cluster molecule or by a factor group analysis, remains an unresolved problem.^{3,4} Kaesz and Saillant⁵ have postulated Fermi resonance as a cause of the broad features assignable to the hydridic modes in their room-temperature Raman spectra of some polymetallic hydrides. This hypothesis has been tested by Shriver et al.³ using a combination of low-temperature spectroscopy and ¹⁸O isotopic substitution experiments and has concluded against the above possibility as an explanation of the structure of the ca. 900- cm^{-1} band system of $HW_2(CO)_{10}^-$.

$H_3Re_3(CO)_{12}$ in the solution state has been shown to have a structure similar to that of $H_3Mn_3(CO)_{12}$.⁶ However, it displays twinning in the crystalline state and this has prevented a determination of its crystal structure.⁷ $H_3Re_3(CO)_{12}$ is a complex that shows a multiplicity of bands in the metal–hydrogen stretching region and also possesses the favorable property of sublimation in a vacuum without decomposition. Therefore, we have attempted a detailed analysis of its vibrational spectrum, including some matrix isolation work, in order to throw some light on the cause of the multiplicity of bands found assignable to hydrogenic modes.

Experimental Section

$H_3Re_3(CO)_{12}$ and its deuterium-substituted analogues were prepared by using literature methods.⁶ Infrared spectra, in the range 4000–200 cm^{-1} , were recorded on Perkin-Elmer 325, Perkin-Elmer 577, and Digilab FTS-14 spectrophotometers; a Beckman RIIC IR720M interferometer was used in the range 400–10 cm^{-1} . Raman spectra were recorded on a Spex Raman spectrophotometer Model 1401 equipped with a Spectra Physics Model 165 mixed-gas laser, the spectral resolution used being better than 3 cm^{-1} .

Matrix isolation work was carried out using argon as the matrix gas and an Air Products "Displex" closed-cycle refrigerator. Matrix window temperatures were of the order of 12 K, and deposition times ranged between 1/2 and 3 h. Long isolation times were necessary for the observation of the very weak hydrogenous bands in the spectra. The criterion for successful isolation at a single site was taken from the carbonyl stretching region where very sharp peaks showing a solution-like spectral pattern were observed (Figure 1).

Results and Discussion

To a first approximation it is convenient to divide the molecular vibrations into three main groups: the CO stretching modes, ν_{CO} ; the metal–metal stretches, ν_{MM} ; the metal–hydrogen vibrations, ν^{as}_{MH} , ν^s_{MH} and γ_{MHM} , where the first two modes of the latter set involve M–H bond stretching and the third mode is the hydrogen deformation out of the MHM plane (as and s denote asymmetric

and symmetric with respect to planes that approximately bisect the MHM angles).

The CO Stretching Vibrations, ν_{CO} . Assuming a molecular symmetry of D_{3h} for the solution state (vide infra), four infrared-active fundamentals ($a_2'' + 3e'$) are predicted and observed for this complex. These are 2096 (m), 2035 (s), 2012 (ms), and 1979 (m) cm^{-1} in dichloromethane solution (Figure 1). The assignments of these vibrations are given in Table I and were arrived at by analogy with the case of $H_3Mn_3(CO)_{12}$.⁸

The solid-state Raman spectrum of this complex, $H_3Re_3(CO)_{12}$ (Figure 1), eludes any meaningful assignment due to the much larger changes in the intensity pattern compared with the solution infrared spectrum than that observed in the case of the manganese analogue.⁸ The only comments that can be made at this stage are that the highest frequency mode is probably the totally symmetric breathing vibration and that there are two weak bands at ca. 2015 and 2005 cm^{-1} which are sensitive to deuterium substitution.

The Metal–Metal Stretching Vibrations, ν_{MM} . Figure 2 shows the Raman spectra of the isotopomers of the Re complex obtained at liquid-nitrogen temperatures. Onaka and Shriver⁹ have assigned the e' mode to a feature in the Raman spectrum at 143 cm^{-1} . Our low-temperature Raman spectrum has two features, one at 158 cm^{-1} and the other at 144 cm^{-1} , and either could be assigned to the e' mode when compared with the IINS results of White and Wright,¹⁰ who report peaks at 152 and 101 cm^{-1} that show IINS intensity. The differences in frequency between the IINS and either of the 158 or 144 cm^{-1} bands in the Raman spectrum would be reasonable as the former gives a weighted density of states spectrum covering the whole of k space while the latter technique probes only the $k \approx 0$ region. All these earlier assignments in the literature for the Re–Re vibrations were made by intuitive selection of peaks from those observed in the infrared or Raman spectra. We shall follow a different line of argument that depends on the fairly reliable assignment already made for the manganese complex.⁸ In considering the IINS data, the assignment criterion that only metal–metal bond stretches would involve hydrogen motion¹⁰ has been shown to be unreliable from the resonance Raman data on the $H_3Mn_3(CO)_{12}$ complex.⁸

All reliable assignments of the metal–metal vibrations in metal triangular clusters in the literature^{11,12} have the expected frequency ordering, $a_1' > e'$. Therefore, we would anticipate a similar pattern

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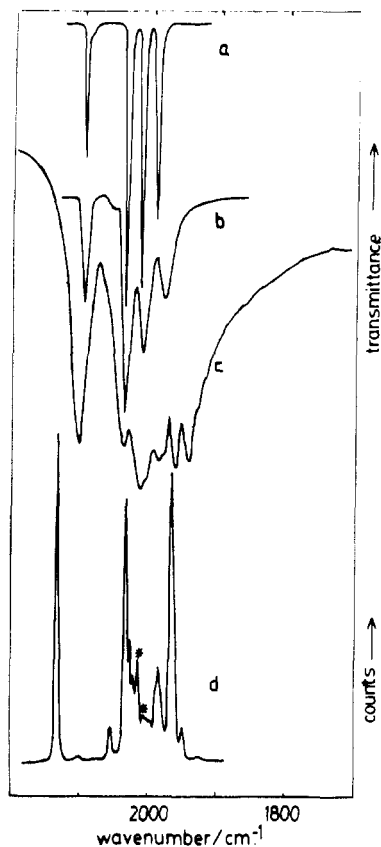


Figure 1. Vibrational spectra of $\text{H}_3\text{Re}_3(\text{CO})_{12}$ in the carbonyl stretching region: (a) infrared spectrum of the matrix phase in argon at ca. 10 K; (b) infrared spectrum in dichloromethane solution; (c) infrared spectrum of the solid state, a Nujol mull at ca. 100 K; (d) Raman spectrum of the solid state at ca. 100 K with the deuterium-sensitive features indicated with asterisks.

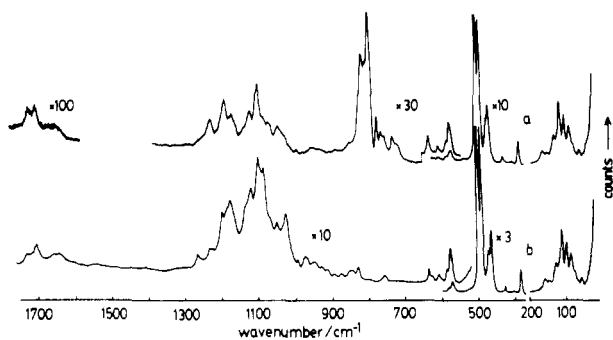


Figure 2. Raman spectra of the solid state (from ca. 20 to 1800 cm^{-1}) at ca. 100 K run by using the 488-nm exciting line from an argon ion laser of (a) $\text{D}_3\text{Re}_3(\text{CO})_{12}$ and (b) $\text{H}_3\text{Re}_3(\text{CO})_{12}$.

for the $\text{H}_3\text{Re}_3(\text{CO})_{12}$ complex. In the absence of direct experimental evidence, such as from the resonance Raman effect,⁸ we use the close structural similarity between the Mn and Re complexes as an assignment criterion.

In the Mn complex a lowering of F_r by ca. 9.5% was observed when going from $\text{Mn}_2(\text{CO})_{10}$ to $\text{H}_3\text{Mn}_3(\text{CO})_{12}$.⁸ An assumption of a similar decrease in F_r for the Re complex would give a value of ca. 74.2 N m^{-1} for the $\text{H}_3\text{Re}_3(\text{CO})_{12}$ complex compared to ca. 82 N m^{-1} for $\text{Re}_2(\text{CO})_{10}$.¹³ The interaction force constant, f_{rr} , in the case of $\text{H}_3\text{Mn}_3(\text{CO})_{12}$ was found to be ca. -10.3% of F_r . A similar relationship for $\text{H}_3\text{Re}_3(\text{CO})_{12}$ would give a value of -7.64 N m^{-1} for f_{rr} . These estimated values of F_r and f_{rr} are used in a simple calculation, similar to that performed⁸ for $\text{H}_3\text{Mn}_3(\text{CO})_{12}$. This gives calculated metal-metal vibrational frequencies of a_1' and e' in the case of the rhenium complex to be at ca. 127 and

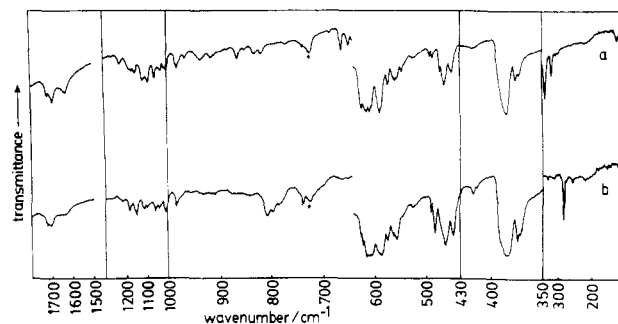


Figure 3. Infrared spectra of the solid state (Nujol mulls; from 100 to 1800 cm^{-1}) at ca. 100 K of (a) $\text{H}_3\text{Re}_3(\text{CO})_{12}$ and (b) $\text{D}_3\text{Re}_3(\text{CO})_{12}$.

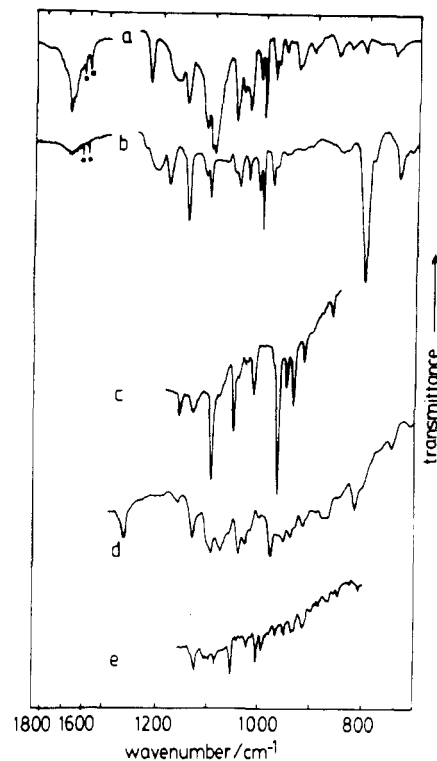


Figure 4. Infrared spectra of matrix-isolated samples at ca. 10 K in argon (from 700 to 1800 cm^{-1}) of (a) $\text{H}_3\text{Re}_3(\text{CO})_{12}$, (b) $\text{D}_3\text{Re}_3(\text{CO})_{12}$, (c) $\text{Re}_2(\text{CO})_{10}$, (d) $\text{Ru}_3(\text{CO})_{12}$, and (e) $\text{Os}_3(\text{CO})_{12}$. Bands marked with asterisks are due to matrix-isolated water.

ca. 106 cm^{-1} , respectively. An examination of the far-infrared and Raman spectra (Figures 2 and 3) provides a reasonable assignment. The a_1' mode is assigned to an observed frequency of ca. 128 cm^{-1} in the Raman and infrared spectra. The predicted frequency for the e' mode of ca. 106 cm^{-1} lies almost halfway between the two Raman bands at 112 and 100 cm^{-1} or the far-infrared bands at 116 and 103 cm^{-1} . Therefore, we assign these frequencies to the split e' mode. This splitting of ca. 12 cm^{-1} is quite reasonable when compared with those values reported in the literature for $\text{M}_3(\text{CO})_{12}$ ($\text{M} = \text{Ru}, \text{Os}$) complexes.¹⁴

The above assignment for the metal-metal stretching vibrations does however pose the same question on their inherent Raman intensities as in the case of the $\text{H}_3\text{Mn}_3(\text{CO})_{12}$ complex but to a lesser degree.⁸ Therefore, we extend the same arguments⁸ regarding the nature of the MHM bridges to explain the current observations.

The Metal-Hydrogen Vibrations. The frequency regions for asymmetric (ν^{as}) and symmetric (ν^{s}) hydrogen-metal stretching vibrations of μ -hydrides in a range of carbonyl compounds have previously been identified¹ at 1700 – 1300 cm^{-1} for ν^{as} and 1300 – 800 cm^{-1} for ν^{s} . The infrared and Raman spectra (Figures 2 and 3)

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Table I. Vibrational Spectral Frequencies and Assignments of H₃Re₃(CO)₁₂ and D_{3h}Re₃(CO)₁₂^a

			obsd freq. cm ⁻¹									
			H ₃ Re ₃ (CO) ₁₂			D _{3h} Re ₃ (CO) ₁₂						
matrix-isolated in Ar	IR		matrix-isolated in Ar	IR		Raman solid state	Raman solid state	IR		Raman solid state	assign	
	solid state	assign		solid state	assign			solid state	assign			solid state
2096 m	*2096 m		2132 vs		2100 vw	2132 vs		2100 vw		738 w	747 vvw	
2033 s	*2056 vw		2054 mw		2055 mw	2054 mw		2055 mw		724 w	721 vw	
	*2035 s		2034 s		2034 s	2034 s	a ₂ ' v _{CO}	683 vvw		715 vvw	709 vvw	
			2027 m		2025 m	2025 m		662 w				
2011 s	*2012 sm		2021 w		2018 vvw	2018 vvw		648 w	630 w		630 w	
			2015 m		2012 w	2012 w	e' v _{CO}	624 m sh	621 vw			
1989 m	*1979 m		2005 vvw		2005 vw	2005 vw	e' v _{CO}	623 vs	620 vw			
			1985 mw		1985 m b	1985 m b		614 s				
			1967 vs		1950 w	1950 w		608 s				
			1950 w		1725 vvw sh	1725 vvw		604 m sh	600 vw			
1692 w	1722 vw		1725 vvw sh		1706 w	1706 w		594 vvw sh	596 s			
	1697 w		1706 w		1635 vvw	1635 vvw		589 s				
	1635 w		1645 w b		1650 vvw b	1650 vvw b		572 w				
			1263 vvw		1260 vvw	1260 vvw		568 mw				
1220 w	1220 w		1231 vvw		1229 w	1229 w		558 w				
			1221 vvw		1229 w	1229 w		544 w sh				
			1197 w		1188 mw	1188 mw		545 vw				
			1183 vw sh		1175 w	1175 w		522 vw				
1171 vw	1175 vw sh		1173 w sh		1175 w	1175 w		490 w				
1149 w	1150 w		1151 w		1142 w	1142 w		484 w				
			1131 vw sh		1144 mw	1144 mw		484 w				
1111 w	1110 w		1096 mw		1110 vw	1110 vw		471 sm				
1100 w sh	1087 w		1096 mw		1105 vvw b	1098 mw		467 m sh				
1095 mw	1055 w		1081 w		1090 vw	1079 vvw sh		463 sm				
1054 w	1055 w		1063 vw sh		1050 vw	1063 vw		463 sm				
			1047 vw		1045 w	1040 w b		446 m				
1047 vw			1047 vw		1045 w	1040 w b		446 m				
1029 w	1025 vw		1021 w		1028 w	1023 vw sh		446 m				
1009 vw	1010 vw sh		1010 vw sh		1028 w	1023 vw sh		391 vs				
1001 mw	1000 w		1000 w		1008 vwsh	1000 w		390 vs				
980 w	980 vw		990 vvw		1000 w	990 vvw		376 m				
973 vw sh			990 vvw		980 w	990 vvw		376 m				
959 vvw	963 vw		965 vvw b		973 vw sh	974 vvw sh		373 w				
936 vw	933 vw		942 vvw b		950 vw b	950 vw b		373 w				
907 vvw	913 vw		923 vvw		925 vvw b	925 vvw b		370 w				
			910 vvw		906 vvw	906 vvw		338 w				
			890 vvw		890 vvw	890 vvw		320 vw b				
860 vw	862 w		870 vvw		866 vvw	866 vvw		289 m				
	849 vw		847 vvw		846 vw b	846 vw b		289 m				
833 vvw	829 vw		838 vvw		833 vvw sh	833 vvw sh		289 m				
806 vvw	816 vw		822 vw		802 sm	802 sm		263 w				
			753 vw		786 vvw sh	786 vvw sh		225 vw b				
					791 m	791 m		225 vw b				
					768 w	768 w		160 s				
					746 vvw	746 vvw		147 m				
								147 m				
								126 vw				
								128 s				
								116 vw				
								112 vs				
								103 w				
								87 s				
								76 m sh				
								57 s				

^a An asterisk indicates solution data in dichloromethane solution. vs = very strong; s = strong; sm = strong to medium; m = medium; mw = medium to weak; w = weak; vw = very weak; vvw = extremely weak; b = broad; sh = shoulder. The symmetry labels given for the assignments, except in the case of the hydride bridges, refer to D_{3h} molecular symmetry, which is more appropriate for solutions in dichloromethane and the matrix phase.

at ~ 298 and ~ 100 K of $\text{H}_3\text{Re}_3(\text{CO})_{12}$ shows bands in the above frequency regions assignable to the ν^{as} and ν^{s} modes.

The temperature- and deuterium-sensitive bands in the $\nu^{\text{as}}\text{ReHRe}$ region have very similar shapes in both the infrared and Raman spectra (Figures 2 and 3). The bands centered at ca. 1635 and ca. 1700 cm^{-1} are the probable candidates, whereas the weaker band at ca. 1725 cm^{-1} shows independent behavior. Next, it is relatively easy to pick the bands in the solid-state infrared spectrum (Figure 3) assignable to $\nu^{\text{s}}_{\text{ReDRc}}$ modes at 807, 796, and 784 cm^{-1} with a band at 738 cm^{-1} having gained some intensity by probably mixing with the above modes (*vide infra*). In the matrix-isolated infrared spectrum (Figure 4) there is only one peak at ca. 802 cm^{-1} assignable to the $\nu^{\text{s}}_{\text{ReDRc}}$ mode with another feature at ca. 737 cm^{-1} possibly gaining some intensity by mixing. In the solid-state Raman spectrum there are two fairly strong candidates for this vibration at 813 and 791 cm^{-1} together with several weak features at 768, 755, 721, and 709 cm^{-1} showing some deuterium sensitivity. The assignment of $\nu^{\text{as}}_{\text{ReDRc}}$ and $\nu^{\text{s}}_{\text{ReHRe}}$ are not so easy. A careful comparison of the $\text{H}_3\text{Re}_3(\text{CO})_{12}$ complex with the $\text{D}_3\text{Re}_3(\text{CO})_{12}$ complex in the infrared spectra indicates a large number of bands showing deuterium and temperature sensitivity. However, the $\nu^{\text{as}}_{\text{ReDRc}}$ mode in the Raman spectra could be assigned relatively easily to the bands at 1229 and 1188 cm^{-1} (the very weak band at 1169 cm^{-1} is present also in H_3Re_3 as a shoulder; Figure 2). These appear on deuteration when other bands due to $\nu^{\text{s}}_{\text{ReHRe}}$ disappear from this frequency region. This assignment gives a deuterium shift ratio of ca. 1.38, in excellent agreement with that found for the case of the Mn complex.⁸ In the infrared spectrum the two obvious candidates at 1175 and 1142 cm^{-1} give deuterium shift ratios of ca. 1.45 and ca. 1.43, which seem high. However, the band at 1142 cm^{-1} in the D_3Re_3 complex could be correlated to that at ca. 1150 cm^{-1} in the H_3Re_3 complex. This is clearly shown by the matrix isolation spectra (Figure 4); *vide infra*. The band at 1220 cm^{-1} in the spectrum of H_3Re_3 disappears on deuterium substitution. It is assigned to a Fermi resonance involving an overtone of γ_{ReHRe} at ca. 620 cm^{-1} as seen in the matrix spectra; *vide infra*. A similar band is found in the Raman spectrum at 1260 cm^{-1} . When this band disappears on deuteration in the infrared spectrum, a small band appears around 1215 cm^{-1} , which could be another candidate for the $\nu^{\text{as}}_{\text{ReDRc}}$ vibrational mode. These two assignments in the infrared spectrum, one at 1215 cm^{-1} and the other at 1175 cm^{-1} , give reasonable isotopic substitution ratios of ca. 1.4. The $\nu^{\text{s}}_{\text{ReHRe}}$ vibrations in the infrared spectrum are assignable to the bands at 1110 and 1087 cm^{-1} with probably another at 1055 cm^{-1} . These give deuterium isotopic shift ratios of 1.38, 1.37, and 1.35, respectively. The matrix isolation infrared spectra (Figure 4) in the $\nu^{\text{s}}_{\text{ReHRe}}$ region show quite a few bands with marked deuterium sensitivity. These are at 1220, 1171, 1149, 1111, 1100, 1095, 1054, 1041, and 1029 cm^{-1} with some weaker features at 936, 907, and 860 cm^{-1} . From the relatively clear assignment of the $\nu^{\text{s}}_{\text{ReDRc}}$ mode in the matrix spectrum at ca. 802 cm^{-1} and by assuming an isotopic shift ratio of ca. 1.35–1.4, we obtain a frequency range from ca. 1084 to ca. 1123 cm^{-1} for the $\nu^{\text{s}}_{\text{ReHRe}}$ mode.

Figure 4 also shows the same spectral region of the carbonyl clusters $\text{Re}_2(\text{CO})_{10}$, $\text{Os}_3(\text{CO})_{12}$ and $\text{Ru}_3(\text{CO})_{12}$, which are hydride-free, isolated in argon matrices at ca. 10 K. Clearly this spectral region is well populated with large numbers of overtone/composition bands of the ν_{MC} and ν_{MCO} fundamentals. It should be noted that these spectral features in all these spectra are extremely weak and become observable only after very long isolation times when thick enough matrices are obtained, still maintaining the dilution needed for proper isolation. Using the criterion that the bands left behind on deuterium isotopic substitution, with reduced intensity and/or slight frequency perturbations, would probably be the above-mentioned overtones or combinations gaining intensity in the hydride by Fermi resonance, we are left with bands at 1220, 1171, 1094, 1054, and 1041 cm^{-1} as candidates for the $\nu^{\text{s}}_{\text{ReHRe}}$ modes. The first two bands are too far removed from the $\nu^{\text{s}}_{\text{ReDRc}}$ band, thus giving unacceptably high deuterium substitution ratios to be $\nu^{\text{s}}_{\text{ReHRe}}$. However, the out-of-plane deformation of the hydride bridge, which is strongly mixed

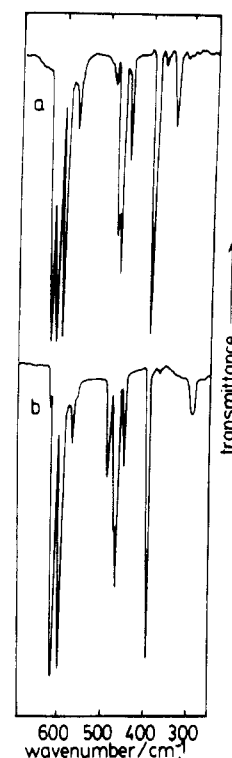


Figure 5. Infrared spectra of matrix-isolated samples at ca. 10 K in argon (from ca. 250 to 700 cm^{-1}) of (a) $\text{H}_3\text{Re}_3(\text{CO})_{12}$ and (b) $\text{D}_3\text{Re}_3(\text{CO})_{12}$.

with a δ_{MCO} mode, is assigned to ca. 611 and ca. 623 cm^{-1} ; *vide infra*. A frequency of 625 cm^{-1} had been assigned to this vibration in the literature.⁶ The overtones of these frequencies would account for these two highest frequency bands at 1220 and 1171 cm^{-1} . This leaves the bands at 1094, 1054, and 1041 cm^{-1} to be assigned mainly to $\nu^{\text{s}}_{\text{ReHRe}}$. Hydrogenous features in this region of the Raman spectrum are at 1263, 1197, 1173, 1096, 1081, 1047, and 1021 cm^{-1} . The first and the third of these are probably the overtones of the γ_{ReHRe} modes. Using a similar approach to that used for the assignment of the infrared spectrum, we assign the bands at 1096, 1047, and 1021 cm^{-1} to be mainly $\nu^{\text{s}}_{\text{ReHRe}}$ while the other bands probably gain intensity by Fermi resonance.

There are many weaker features showing deuterium sensitivity, for example, in the solid-state infrared spectrum at 963, 933, 913, 862, 849, 829, and 816 cm^{-1} . Their origin is not clear, because they disappear almost completely on deuteration. If these have gained intensity by Fermi resonance with the $\nu^{\text{s}}_{\text{ReHRe}}$ bands around 1080 cm^{-1} , then they should also show intensity in the deuterated compound by coupling with the $\nu^{\text{s}}_{\text{ReDRc}}$ mode around 800 cm^{-1} . One could easily find combinations of lower frequencies to fit the above weak features. For example, the deuterium-sensitive peak at 340 cm^{-1} (Figure 5) could be combined with the bands at 623, 593, 573, 522, 509, 489, and 476 cm^{-1} in the infrared or Raman spectra to give the above frequencies. There are two factors that could account for this disappearance of weak features on deuteration.

First, it is a well-known fact that the intensities of infrared vibrations involving deuterium have almost half the intensity associated with the same vibration involving hydrogen. Second, and perhaps more relevant in this case, there could be an additional disruption of the coupling mechanism that gives rise to these resonances. If one were to postulate mechanical coupling due to nonbonded interactions, steric in nature, the extent of such coupling would be greatly diminished when the amplitude of vibration of the hydride bridge is considerably reduced by the replacement of hydrogen by deuterium.

The bands in the ca. 500–650- cm^{-1} region, which are mainly due to δ_{MCO} , are best assigned by starting with the matrix spectrum. A band at 623 cm^{-1} disappears on deuterium substitution (Figure 5) and is to be assigned to γ_{MHM} , the out-to-plane deformation of the hydride bridge. This shows only very weak

Raman intensity even in the solid state, assignable probably to a very weak shoulder at ca. 621 cm^{-1} . This is as expected for a vibration where there is only a very small change in polarizability. This leaves two strong bands and one medium to weak band assignable to δ_{MCO} . The strongest peak out of these at ca. 611 cm^{-1} is most probably a_2'' , δ_{MCO} , of the equatorial ligands. A comparison of the intensities of these bands between the matrix infrared spectra of $\text{H}_3\text{Re}_3(\text{CO})_{12}$ and $\text{D}_3\text{Re}_3(\text{CO})_{12}$ clearly shows evidence for coupling between these two modes, γ_{MHM} at ca. 623 cm^{-1} and a_2'' , δ_{MCO} , at ca. 611 cm^{-1} , where the former has gained intensity from the latter. The remaining two bands at 596 and 568 cm^{-1} are assigned to the e' modes of δ_{MCO} character.

Using the D_{3h} model, one would expect four bands of symmetry $3e' + a_2''$ for the ν_{MC} modes to appear below ca. 500 cm^{-1} in the infrared spectrum. The matrix-isolated infrared spectrum of $\text{H}_3\text{Re}_3(\text{CO})_{12}$ shows (Figure 5) about this number of strong to medium bands insensitive to deuterium substitution at 371 (w), 391 (s), 446 (m), and 484 (w) cm^{-1} and a split pair at 471 (s) and 464 (s) cm^{-1} . In the D_3Re_3 spectrum a medium intense band appears at 485 cm^{-1} , which seems to overlap with the weak feature that was present at this frequency in the H_3Re_3 complex. This is probably a γ_{ReDRe} vibration, giving an isotopic shift ratio of ca. 1.29. However, there is another band in this region of the matrix spectrum that is sensitive to deuterium substitution. That is at 342 cm^{-1} in H_3Re_3 , moving down to 289 cm^{-1} in D_3Re_3 . This gives an isotopic shift ratio of ca. 1.17, which is quite low. In the solid-state infrared spectrum (Figure 3) there appear additional bands showing sensitivity, a medium-intense band moving from 320 cm^{-1} probably to 263 cm^{-1} , giving an isotopic shift ratio of ca. 1.22, and very weak features from 307 and 300 cm^{-1} to ca. 225 cm^{-1} , giving a ratio of ca. 1.35. At first sight these three frequencies at 623 , 341 , and 320 cm^{-1} appear to be candidates for the γ_{ReHRe} modes of three very different hydride bridges. There are three such modes in the Raman spectrum at 350 , 327 , and 313 cm^{-1} that are very weak and disappear on deuteration. However, large differences in the ReHRe angles are highly unlikely and are not evident from the rest of the spectra, as discussed below. Instead, we would argue that the deuterium-sensitive bands at 342 and 320 cm^{-1} in the solid state to be the $a_2'' + e''$ modes of the axial $\text{M}-\text{C}$ stretching vibrations, mixed with the out-of-plane deformation of the hydride bridges. A reduction in molecular symmetry from D_{3h} provides e'' with infrared intensity. In the argon matrix the molecular geometry would be closer to D_{3h} , thus reducing the e'' infrared intensity. This is also what would be expected for vibrationally distinct $\text{M}(\text{CO})_4$ centers in the vibrationally uncoupled case. There is support for this hypothesis in

the rest of the spectra where the number of bands observed in the matrix phase is closer to predictions using D_{3h} molecular symmetry. For example, in the $\nu^{\text{as}}_{\text{ReH}}$ region, two bands in the solid state give one band (one e' predicted under D_{3h}) in the matrix phase, in the $\nu^{\text{s}}_{\text{ReD}}$ region, three bands in the solid state again give one band (one e' predicted under D_{3h}) in the matrix. However, the $\nu^{\text{s}}_{\text{ReH}}$ and $\nu^{\text{as}}_{\text{ReD}}$ regions of the matrix spectra show appreciable splittings between the bands assigned. This could be understood if the molecular geometry in the matrix phase is not strictly D_{3h} , therefore giving slightly different MHM angles for the three bridges. This is evident from the breadth of the $\nu^{\text{as}}_{\text{ReH}}$ and $\nu^{\text{s}}_{\text{ReD}}$ modes already discussed. The presence of a large number of overtone/combination bands of the δ_{MCO} and ν_{MC} fundamentals in the frequency region below ca. 1300 cm^{-1} where $\nu^{\text{as}}_{\text{ReD}}$ and $\nu^{\text{s}}_{\text{ReH}}$ are found has already been well illustrated. The descent in symmetry from D_{3h} means that the three $-\text{HM}(\text{CO})_4$ units should be symmetrically different. This difference should appear as a frequency difference that might be too small to be observed easily in the case of the δ_{MCO} and ν_{MC} fundamentals. In the overtone/combination region a doubling of these frequency differences is to be expected. The metal hydride vibrations would, of course, couple to different extents to the symmetrically different metal centers in the molecule. Therefore, it is reasonable to expect the differences in the hydride bridges to be exaggerated in this region of the spectrum due to the different extents of coupling to these exaggeratedly different frequencies of the multiphonon vibrational modes.

Conclusion

Vibrational spectra of $\text{H}_3\text{Re}_3(\text{CO})_{12}$ in its disordered solid phase and the matrix phase are rationalized in terms of a molecular structure closer to D_{3h} symmetry in the matrix phase with respect to that in the solid phase. The multiplicity of bands in the ca. 1100-cm^{-1} region is explicable in terms of Fermi resonance with multiphonon bands due to ν_{MC} and δ_{MCO} vibrations.

From this fairly detailed study, one should conclude that the application of ν^{s} and $\nu^{\text{as}}_{\text{MH}}$ frequencies to estimate the MHM angles should be undertaken with caution where there is a multiplicity of possible candidates for these vibrations.

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