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Vibrational Study of the Effects of High External Pressures on the Structure and Phase Behavior of Pentacarbonyl(methyl)manganese(I) and Pentacarbonyl(methyl)rhenium(I)

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Micro-Raman spectra of crystalline $CH_3M(CO)_5$ (M = Mn, Re) have been recorded in the CO stretching and low-energy regions at ambient temperature and selected pressures up to 40 kbar with the aid of a diamond-anvil cell. The IR spectrum of the manganese compound was similarly investigated in the CH stretching region at various pressures up to 18 kbar. The vibrational data indicate that both complexes undergo a phase transition (most probably second order): $CH_3Mn(CO)_5$, at ~9 kbar; $CH_3Re(CO)_5$, at ~22 kbar. The plots of pressure vs wavenumber for the CO stretching modes reveals that the π-back-bonding interactions between the metals M and the CO groups (especially the axial ones trans to CH_3) in the low-pressure phase of $CH_3Mn(CO)_5$ and in both phases of $CH_3Re(CO)_5$ are appreciably strengthened by increases in the applied external pressure. The vibrational modes in the low-pressure phases exhibit similar pressure dependences, in agreement with the isomorphous structures of the two compounds. There are significant differences, however, in the pressure dependences of the vibrational modes of the high-pressure phases. The extent of the π-back-bonding is apparently steadily decreasing for $CH_3Mn(CO)_5$, while it is increasingly favored for $CH_3Re(CO)_5$.

Introduction

Vibrational spectroscopy has played an crucial role over the past 40 years in the characterization of new organometallic compounds. These vibrational studies are especially important because they provide useful information about the molecular and crystal structures of the solid complexes, as well as about the nature of the chemical bonding involved. Moreover, by carefully monitoring the changes that take place in the vibrational spectra when the temperature or pressure is varied, it is possible to detect phase transitions. Part of our recent vibrational work has been concerned with the use of micro-Raman spectroscopy to detect pressure-induced phase transitions in high-symmetry inorganic compounds such as $Cs_2[B_{12}H_{12}]$,[1] o-$C_2B_{10}H_{12}$,[2] and $K_2[SnBr_6]$.[3] These particular high-pressure investigations were prompted by our success in coupling a diamond-anvil cell to a micro-Raman spectrometer.[1] During the past year, we have turned our attention to studying the effects of high pressure on the IR and micro-Raman spectra of organometallic species, especially transition-metal carbonyl complexes. This is a relatively unexplored area, except for the work of Adams and his co-workers.[4-7]

The molecular structures and bonding of $CH_3Mn(CO)_5$ and $CH_3Re(CO)_5$ have received considerable attention over the years, chiefly because these complexes have a simple σ bond between a transition metal and an organic alkyl group. Furthermore, they are ideal prototypes for studying homogeneous, organometallic-catalyzed reactions such as the hydroformylation of alkenes.[8] The structure of the manganese compound has been investigated by a wide variety of techniques, including vibrational[9-13] and NMR spectroscopy[14,15] and X-ray,[9] electron,[16,17] and incoherent inelastic neutron diffraction.[9] The room-temperature X-ray diffraction data indicate that $CH_3Mn(CO)_5$ crystallizes in the orthorhombic space group *Pcmn* (isomorphous with *Pnma*, D_{2h}[16]) with four molecules per unit cell located at C_s sites. The complex is nearly statistically disordered over the six octahedral coordination sites. However, low-temperature IR and Raman data for both $CH_3Mn(CO)_5$ and $CH_3Re(CO)_5$ show no evidence of order–disorder phase transitions, even at temperatures as low as 10 K,[9,18] suggesting that the structures are still orientationally disordered under these conditions. Several theoretical models have been proposed to account for the bonding in the $CH_3M(CO)_5$ molecules,[10,11,14,15] with most attention being paid toward the interactions between the CH_3 groups and the transition metals M and the influence of these interactions on those between the metals M and the five CO groups. In this paper, we report the results of an investigation of the effects of high external pressures on the room-temperature micro-Raman spectra of $CH_3Mn(CO)_5$ and $CH_3Re(CO)_5$. Some high-pressure IR data for the CH stretching region of the manganese compound are also presented.

Experimental Section

Crystalline $CH_3Mn(CO)_5$ was prepared by first treating $Mn_2(CO)_{10}$ with methanolic NaOH followed by CH_3I[19] and then subsequent purification by vacuum sublimation (25 °C, 0.1 Torr). The purity of the final product was established by the absence of any impurity peaks, especially those due to $Mn_2(CO)_{10}$ and $Mn(CO)_5(COCH_3)$, in the IR, Raman, and ^{13}C NMR spectra. The analogous $CH_3Re(CO)_5$ complex was prepared by reacting $Na[Re(CO)_5]$ with CH_3I in THF solution.[20] The precursor rhenium salt was synthesized by treating $Re_2(CO)_{10}$ with 1% NaHg amalgam in THF solution. The purity of the $CH_3Re(CO)_5$ crystals was again verified spectroscopically (IR, Raman, ^{13}C NMR).

The Raman and ruby fluorescence (vide infra) specta were recorded on an Instruments S.A. U-1000 Ramanor spectrometer equipped with a Nachet optical microscope and interfaced to an IBM PS/2 Model 60 microcomputer. The excitation source was the 514.532-nm line of a Spectra-Physics Model 164 5-W argon ion laser. The laser power was about 30 mW at the samples. The sample being examined and a tiny ruby chip (used as the internal pressure calibrant[21]) were placed in the 400-μm hole of a stainless-steel gasket (400 μm thick) mounted between the faces of the two opposing Type IIA diamonds of a diamond-anvil cell (DAC; Diacell Products, Leicester, U.K.). The DAC was then mounted onto an X-Y stage, and a 4× microscope objective was used to focus the laser beam onto the sample and to collect the backscattered radiation. Infrared spectra (4-cm^{-1} resolution) were acquired on a Nicolet Model 6000 FT-IR spectrometer. The DAC for the pressure IR work was purchased from High Pressure Diamond Optics Inc., Tucson, AZ. This cell was mounted on a SpectraTech optical bench with f4 condensing

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Table I. Pressure Dependences of Observed Raman and IR Bands of $CH_3Mn(CO)_5$

low-pressure phase			high-pressure phase			
ν, cm^{-1}	$d\nu/dP$, cm^{-1}/kbar	$d \ln \nu/dP$, $kbar^{-1} \times 10^{-2}$	ν, cm^{-1}	$d\nu/dP$, cm^{-1}/kbar	$d \ln \nu/dP$, $kbar^{-1} \times 10^{-2}$	assgnt[a]
2992	2.09	0.070	3016	0.46	0.015	ν_{18}, e, $\nu(CH)_{asym}$
2918	1.92	0.066	2943	0.95	0.034	ν_1, a_1, $\nu(CH)_{sym}$
2816	0.77	0.027	2824	0.44	0.015	$2\nu_{20}$, $\delta(CH_3)_{asym}$
2110	0.46	0.022				ν_2, a_1, $\nu(CO^{eq})$
2036	0.00	0.00	2037	0.40	0.020	ν_{12}, b_1, $\nu(CO^{eq})$
1975	−0.82	−0.041	1967	0.30	0.015	ν_3, a_1, $\nu(CO^{ax})$
			443	0.43	0.097	ν_{25}, e, $\delta(MnCO^{eq})$
419	1.09	0.26	430	0.51	0.12	ν_7, a_1, $\nu(MnCH_3)$
408	0.87	0.21	418	0.75	0.17	ν_8, a_1, $\nu(MnCO^{eq})$

[a] From refs 9 and 10.

Table II. Pressure Dependences of Observed Raman Bands of $CH_3Re(CO)_5$

low-pressure phase			high-pressure phase			
ν, cm^{-1}	$d\nu/dP$, cm^{-1}/kbar	$d \ln \nu/dP$, $kbar^{-1} \times 10^{-2}$	ν, cm^{-1}	$d\nu/dP$, cm^{-1}/kbar	$d \ln \nu/dP$, $kbar^{-1} \times 10^{-2}$	assgnt[a]
2126	0.44	0.021	2135	0.31	0.015	ν_2, a_1, $\nu(CO^{eq})$
2050	0.69	0.033	2063	0.22	0.011	} ν_{12}, b_1, $\nu(CO^{eq})$
2042	0.24	0.012	2047	0.19	0.0094	
1955	−0.15	−0.0070	1949	−0.33	−0.016	ν_3, a_1, $\nu(CO^{ax})$
472	0.99	0.21	490	0.67	0.14	ν_6, a_1, $\nu(ReCO^{aq})$
452	0.85	0.19	467	0.44	0.094	ν_7, a_1, $\nu(ReCH_3)$

[a] From refs 10 and 18.

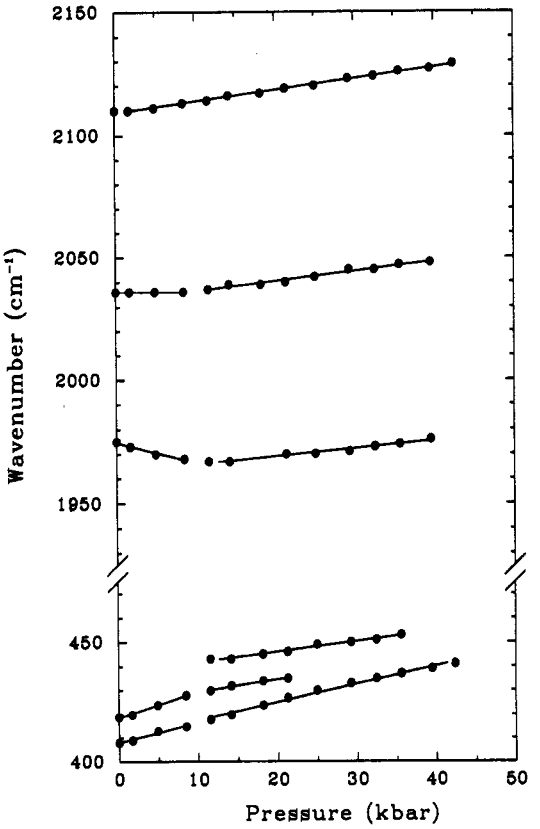

Figure 1. Pressure dependences of observed Raman bands of $CH_3Mn(CO)_5$.

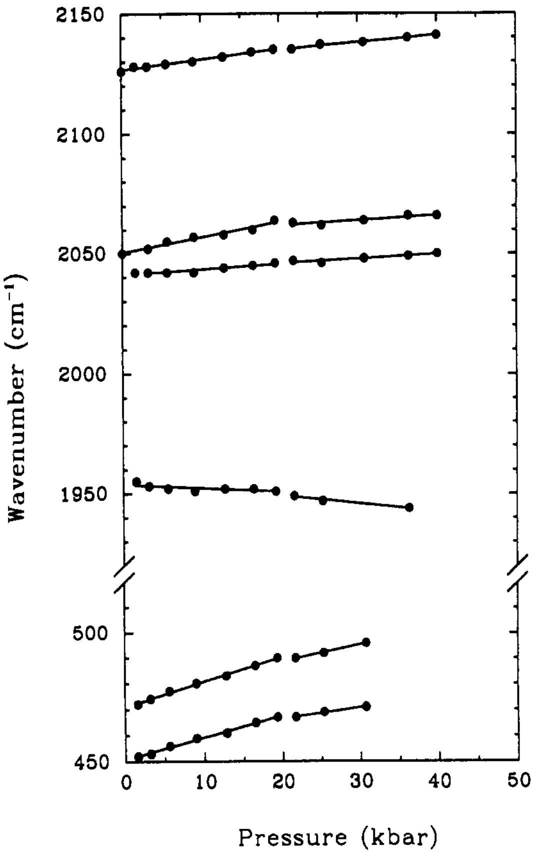

Figure 2. Pressure dependences of observed Raman bands of $CH_3Re(CO)_5$.

optics in the sample chamber of the spectrometer. A mixture of 0.14% w/w $NaNO_3$ in NaBr was used as the pressure calibrant.[22] The sample and the calibrant were placed in the 300-μm hole of a 100 μm thick stainless-steel gasket.

Results and Discussion

The wavenumber shifts observed with changes in pressure for the strong peaks in the carbonyl stretching [$\nu(CO)$], metal–carbon stretching [$\nu(M-C)$], and metal–carbonyl bending [$\delta(MCO)$] regions of the micro-Raman spectra of $CH_3Mn(CO)_5$ and $CH_3Re(CO)_5$ are presented in Figures 1 and 2, respectively. The discontinuities occurring in the pressure/wavenumber plots for most of the bands indicate the presence of phase transitions at ~9 kbar for $CH_3Mn(CO)_5$ and at ~22 kbar for $CH_3Re(CO)_5$. It should be emphasized that no phase transitions had been detected for either compound in the low-temperature vibrational measurements however.[9,18] The discontinuities in Figures 1 and 2 are not abrupt, and so it is most likely that the pressure-induced

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phase transitions are second-order, i.e., similar to those reported for the isomorphous $Mn(CO)_5Br$[5] and $Re(CO)_5Br$[4] complexes. The values calculated for the pressure sensitivities, $d\nu/dP$, and the relative pressure sensitivities, $d \ln \nu/dP$, in the different phases are given in Table I and II.

Micro-Raman Spectra. (a) CO Stretching Region. The a_1 equatorial CO stretching mode (ν_2) of $CH_3Mn(CO)_5$ shifts steadily from its original position (2110 cm^{-1}) to higher wavenumbers as the applied pressure is increased, and the subsequent pressure vs wavenumber plot shows no change in slope at the phase transition. Prior to the transition, the b_1 equatorial CO stretching mode (ν_{12}) is almost independent of pressure and remains at ~2036 cm^{-1}. Immediately following the phase transition, this mode begins to shift to higher energies. On the basis of a factor group analysis reported earlier for the isomorphous $Mn(CO)_5Br$ complex,[23] the b_1 CO stretching mode (ν_{12}) should appear as a doublet ($a_g + b_{2g}$) in the Raman spectrum of the crystalline solid. This correlation splitting is detectable at ambient pressure as a shoulder at 2053 cm^{-1} on the side of the main 2036-cm^{-1} band; this shoulder shifts toward higher energies with increasing pressure at almost same rate as does the 2036-cm^{-1} band, but is not fully resolved. The a_1 axial CO stretching mode (ν_3) appears as a broad band centered at 1975 cm^{-1} at ambient pressure. The broadness of this band is a good indication that the crystal is disordered.[9] The band displays a large negative pressure sensitivity prior to the phase transition, while, immediately after it, the band begins to shift to higher energies.

In the low-pressure phase of $CH_3Re(CO)_5$, the ν_2, ν_{12}, and ν_3 CO stretching modes exhibit pressure dependences similar to those of $CH_3Mn(CO)_5$, as would be expected since the two compounds are isomorphous at ambient pressure. The b_1 mode (ν_{12}) is clearly split into a double under pressure in the rhenium case. The higher energy component of the doublet has the larger pressure sensitivity, especially in the low-pressure range. This result indicates that pressure not only causes both components to shift to higher wavenumbers but augments the factor group splitting as well. The two components of ν_{12} have significantly larger pressure sensitivities than do those associated with the ν_{12} mode of $CH_3Mn(CO)_5$. In the high-pressure phase of $CH_3Re(CO)_5$, unlike that of $CH_3Mn(CO)_5$, the ν_3 CO stretching mode continues to be displaced to lower wavenumbers with increasing pressure.

The pressure dependences of the vibrational modes of a crystalline solid depend chiefly on the interplay of three factors: (1) the nature of the chemical bonding involved in the vibrational modes, (2) the anharmonicities of the modes, and (3) the relative orientations of the molecules in the unit cell of the crystal. For the $CH_3M(CO)_5$ derivatives, the application of external pressure to the crystal lattices leads to a compression of the unit cells, which in turn results in an increase in the energies of all the vibrational modes. This accounts for the observed shifts of the various modes toward higher wavenumbers, since the interatomic and intermolecular interactions increase as the separations become smaller. Moreover, because pressure is expected to lead to decreases in the differences between the various force constants associated with a molecular crystal,[24] the M–C(O) bonds should be strengthened since their force constants are smaller than those for the CO bonds.[10] As pointed out earlier by Adams and Ekejiuba,[5] the strengthening of the M–C(O) bonds in such systems must be due to increases in the extent of π-back-bonding from the metal M to the π^* orbitals on the CO ligands. This pressure effect weakens the CO bonds and results in shifts of the $\nu(CO)$ modes to lower wavenumbers as the applied pressure is increased. Therefore, the experimentally observed pressure dependences of the $\nu(CO)$ modes are considered to be the net result of these two opposing effects.

In the low-pressure phase of $CH_3Mn(CO)_5$, the pressure dependences of the ν_2, ν_{12}, and ν_3 modes exhibit trends similar to those for the corresponding modes of $CH_3Re(CO)_5$. The π-back-bonding in the $M{-}CO^{ax}$ bonds is strengthened much more with increasing pressure than is that for the $M{-}CO^{eq}$ bonds. The same effect has been reported previously for the $Mn(CO)_5Br$.[5] At higher pressures, the pressure dependences of the axial CO stretching modes (ν_3) of the two compounds are significantly different. In the low-pressure phase of $CH_3Mn(CO)_5$, ν_3 has a negative pressure sensitivity, while, after the phase transition, this pressure dependence is dramatically reversed. The same mode in $CH_3Re(CO)_5$ continues to be shifted to lower energies with increasing pressure, and the pressure sensitivity is even more negative. The values of the pressure dependences of ν_3 for the low-pressure phases of $CH_3Mn(CO)_5$ and $CH_3Re(CO)_5$ are −0.82 and −0.15 cm^{-1} $kbar^{-1}$, respectively. These data indicate that the π-back-bonding between the central metal and axial CO group in $CH_3Mn(CO)_5$ is strengthened appreciably more upon the application of pressure than is that in $CH_3Re(CO)_5$. This observation can be best explained in terms of the methyl trans effect.

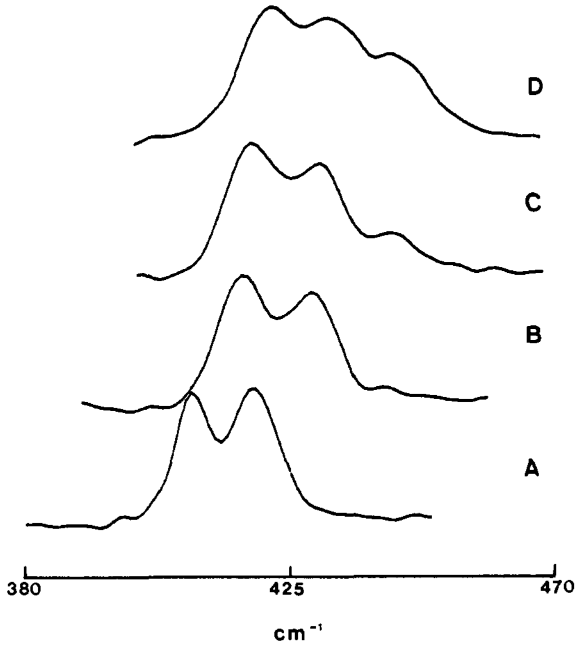

Figure 3. Raman spectra (380–470 cm^{-1}) of $CH_3Mn(CO)_5$ at (A) 1.7 kbar, (B) 11.4 kbar, (C) 14.2 kbar, and (D) 18.2 kbar.

According to McQuillan and co-workers,[10] the trans effect of the methyl group in $CH_3M(CO)_5$ (M = Mn, Re) is the result of two opposing tendencies: the π effect and σ effect. The former strengthens the $M{-}CO^{ax}$ bond by increasing the population of axial carbonyl π^* orbital through interaction with the metal d_{xz} and d_{yz} orbitals. The latter weakens the $M{-}CO^{ax}$ bond because the presence of the inductive methyl group leads to an increase in the electron density at the metal atom through the σ bond. Our data show that pressure strongly enhances the π effect rather than the σ effect. McQuillan and co-workers[10] have further pointed out that the π effect in $CH_3Mn(CO)_5$ is greater than is the σ effect, but in $CH_3Re(CO)_5$, the two effects are almost identical.[10] This may explain why the ν_3 mode of $CH_3Mn(CO)_5$ has a larger negative pressure sensitivity than does that of $CH_3Re(CO)_5$. From a comparison of the values of the negative pressure sensitivities for the axial CO group, $Mn(CO)_5Br$ would be expected to exhibit the highest negative pressure sensitivity, since the π effect is known to predominate in this compound and is greater than that for either $CH_3Mn(CO)_5$ or $CH_3Re(CO)_5$ at ambient pressure.[10] In fact, $Mn(CO)_5Br$ exhibits the smallest negative value, −0.067 cm^{-1} $kbar^{-1}$.[5] It is possible that the lattice contraction resulting from the applied pressure may reduce the internal motion of the methyl group, and so perhaps a slowly rotating CH_3 group may have a larger π effect than does a rapidly rotating CH_3 group. After the phase transition, the ν_3 mode of $CH_3Mn(CO)_5$ begins to shift toward higher energy, as does the same mode for $Mn(CO)_5Br$, but the $\nu(CO^{ax})$ mode in $CH_3Re(CO)_5$ keeps moving toward lower energy. These results provide good evidence that the two compounds have different bonding interactions in their high-pressure

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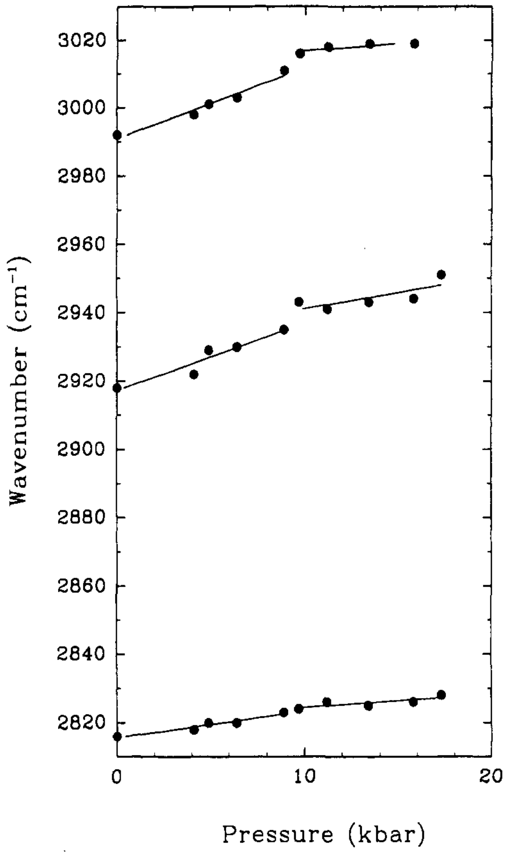

Figure 4. Pressure dependence of observed IR bands (C–H stretching region) of $CH_3Mn(CO)_5$.

phases. The pressure-enhanced π-back-bonding of the axial CO group depends strongly on the nature of the trans atom and the geometry of molecule. For example, when the geometry of $Re_2(CO)_{10}$ is changed from staggered to eclipsed under the influence of high pressure,[6] the π-back-bonding from Re to the axial CO is sharply increased, but no such effect is observed for either $Mn_2(CO)_{10}$ or $MnRe(CO)_{10}$.[6,7] In the high-pressure phase of $CH_3Mn(CO)_5$, it does seem that application of pressure either changes the relative orientation of the molecules in the unit cell or it distorts the molecular geometry such that the extent of π-back-bonding is decreased.

(b) Low-Energy Vibrations. In the low-pressure phase of $CH_3Mn(CO)_5$, only two relatively strong peaks, ν_7 (a_1 Mn–CH_3 stretching) and ν_8 (a_1 Mn–CO^{eq} stretching), can be readily monitored with changes in pressure. Both peaks shift towards higher wavenumbers significantly faster with increasing pressure than do the related CO stretching modes. The ν_7 mode is appreciably sensitive. There is an additional feature that provides further evidence of a phase transition. At 11.4 kbar (just slightly above the phase transition), a new band suddenly appears at approximately 443 cm^{-1}, which gains intensity dramatically as the pressure is increased (Figure 3). On extrapolation to zero pressure, this band is predicted to be at 436 cm^{-1} and would correspond to δ_{25}, the e (metal–equatorial CO) bending mode, which is very weak in the normal Raman spectrum and proved to be undetectable by using the DAC at ambient pressure.

The most intense peaks in the low-energy region for $CH_3Re(CO)_5$ are ν_6 (a_1 Re–CO^{ax} stretching) and ν_7 (a_1 Re–CH_3 stretching). Their pressure dependences show obvious discontinuities at the transition pressure. The $d\nu/dP$ value for ν_7, 0.85 cm^{-1} kbar^{-1}, is smaller than that for $CH_3Mn(CO)_5$, 1.09 cm^{-1} kbar^{-1}, because the Re–CH_3 bond is appreciably stronger than is the Mn–CH_3 bond. The Re–CO^{ax} vibration is much more sensitive to the phase transition than is the Re–CO^{eq} mode.

FT-IR Spectra. High-pressure IR measurements were undertaken only for the manganese complex and then only in the CH stretching region. Attempts to obtain complementary Raman data in this region failed due to the strong fluorescence background present. Three CH stretching peaks were detected at ambient pressure at 2992 [ν_{18}, e $\nu(CH)_{asym}$], 2918 [ν_1, a_1 $\nu(CH)_{sym}$], and 2816 cm^{-1} [$2\nu_{20}$, $2\delta(CH_3)_{asym}$], the last two peaks are believed to be in Fermi resonance with each other. All three peaks shift to higher wavenumbers with increasing pressure (Figure 4), and there are discontinuities in the pressure vs wavenumber plots for all three bands at 8.9 kbar, providing additional support to the Raman work for a pressure-induced phase transition in $CH_3Mn(CO)_5$ at about this pressure. The two higher energy bands have very large sensitivities in the low-pressure phase, indicating that increasing pressure leads to a significant shortening of the C–H distances.

Mode Gruneisen Values. Isothermal compressibilities (κ) are not known for the $CH_3M(CO)_5$ compounds, but assuming $\kappa = 1 \times 10^{-2}$ kbar^{-1}, a typical value for many molecular crystals, the mode Gruneisen values (γ_i) can be calculated from eq 1 and are

$$\gamma_i = (1/\kappa)(d \ln \nu_i/dP)_T \qquad (1)$$

numerically equal to the values of $(d \ln \nu/dP) \times 10^{-2}$ shown in Tables I and II. The γ_i values obtained are comparable to those determined for the internal modes of similar organometallic compounds.[5,7]

Because of the orientational effects of the CH_3 groups, no lattice modes were detected for either compound, even at very low temperatures.[18] In our high-pressure micro-Raman measurements, the fluorescence background due to the diamonds proved to be too intense to permit examination of the lattice-mode region.

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