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A second-order phase transition in $\text{Mn}(\text{CO})_5\text{Br}$

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Although phase behavior in molecular crystals is widely studied using many techniques,¹ remarkably few of these reports deal with crystals composed of inorganic molecules. We have recently begun an in-

vestigation into the phase relations of metal carbonyl compounds under high pressures, partly in the hope that existence of a body of data of this kind will stimulate theoretical work on intermolecular potentials analogous

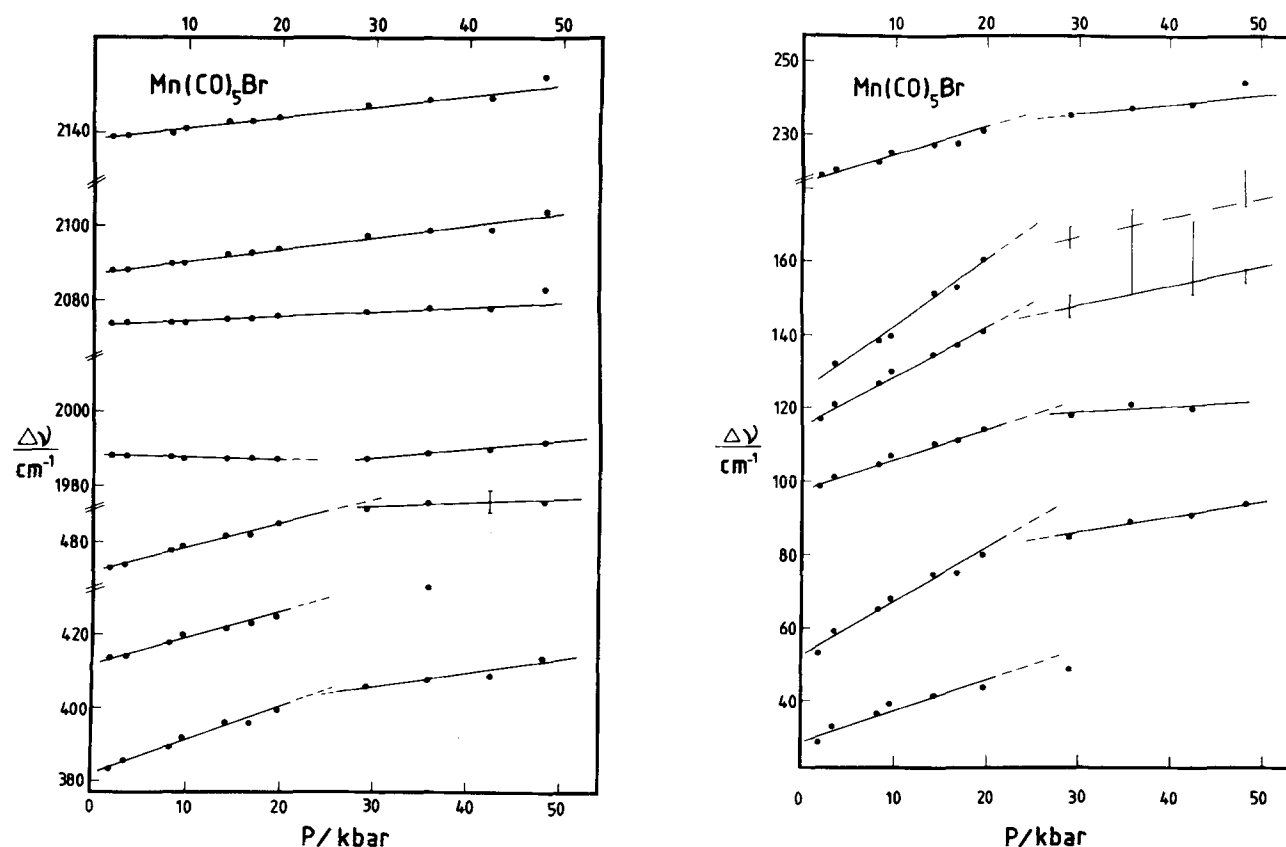


FIG. 1. Pressure dependencies of the Raman-active modes of $\text{Mn}(\text{CO})_5\text{Br}$.

to that currently developing for organic systems.²

We have obtained Raman spectra of $\text{Mn}(\text{CO})_5\text{Br}$ in a diamond anvil high pressure cell at hydrostatic pressures of up to 50 kbar ($1 \text{ kbar} = 10^8 \text{ Pa}$). The sample, which had been purified by resublimation, was contained within an inconel gasket of initial thickness 0.2 mm. A central hole, initially 0.4 mm diameter, contained the sample immersed within a pressure-transmitting fluid (4:1 methanol-ethanol), plus a grain of ruby (internal pressure calibrant^{3,4}). Raman spectra were obtained using 647 nm excitation. Results are shown in Fig. 1.

Existence of a phase change is shown by changes of slope in the $\tilde{\nu}_i/P$ plots: these concur in showing a transition pressure of $24 \pm 3 \text{ kbar}$. The lack of any discontinuity at this pressure, and the easy reversibility of the process, argue for a second-order transition. The transition could also be detected visually when a non-gasketed sample was compressed between the diamond anvils and examined under a microscope.

According to the Landau criterion, in a second-order phase transition the product phase space group must be a subgroup of that of the parent phase (D_{2h}^{16} , $z=2$).⁵ At the phase change in $\text{Mn}(\text{CO})_5\text{Br}$ no new bands appear and none are lost (except by coalescence due to differential pressure shifts). In particular, there are no major changes in the lattice mode region. These observations imply that the center-symmetric property of the parent cell is retained, and with it the IR Raman mutual exclusion rule, and that the number of molecules per primitive cell is unchanged. The new space group is therefore a *zellengleichen* subgroup of D_{2h}^{16} . Only three such possibilities exist⁶: C_{2h}^2 and C_{2h}^5 (two different axial transformations). The factor group of $\text{Mn}(\text{CO})_5\text{Br}$ II is uniquely identified thereby as C_{2h} . In the new space group the molecules are on general sites

(4e) in C_{2h}^5 or on two independent sets of C_s sites (2e) in C_{2h}^2 : both arrangements lead to identical lattice mode selection rules. More generally, since all g type symmetry species of D_{2h} correlate to g species of C_{2h} , and as all these g species are associated with Raman activity, it follows that there can be no change in the number of Raman bands at the phase change, whether of internal or external modes. Hence, the only spectroscopic evidence for a phase transition in this instance is a change of slope in the $\tilde{\nu}_i/P$ plots. No soft mode was found.

The only shift with pressure worthy of particular note is that of ν_2 , A_1 , the axial $\nu(\text{CO})$ mode. This exhibits a slight negative shift. Since metal-carbonyl bonds have lower force constants than the carbonyl group, it is to be expected that there will be an increase in the degree of synergic back-bonding from the metal, increasing the population of the π^* orbital on CO with a consequent drop in $\nu(\text{CO})$. However, compression of the lattice tends to raise the energies of all modes, carbonyl stretching modes included. Hence, what is observed is the difference of the two effects. Our results suggest that the increase in back bonding with pressure is proportionately greater for the axial than for the equatorial bonds.

The relative shifts shown in column 4 of Table I can be converted into mode Grüneisen parameters γ_i by dividing them by the isothermal compressibility χ_T . For molecular crystals χ_T has values near $10^{-2} \text{ kbar}^{-1}$: hence, if $\text{Mn}(\text{CO})_5\text{Br}$ has $\chi_T = 1 \times 10^{-2} \text{ kbar}^{-1}$, the values in column 4 are also the mode Grüneisens. We note that the two lattice modes have $\gamma_i \sim 2.8$. However Sherman has shown recently⁷ that molecular crystals in which the intermolecular forces can be represented by a Lennard-Jones 6-12 potential should have mode Grüneisen's close to 3.5. This implies that for

TABLE I. Pressure-sensitivities of the Raman-active vibrations of solid $\text{Mn}(\text{CO})_5\text{Br}$.

Mode	$\tilde{\nu}_i^0$	$\frac{\Delta\tilde{\nu}_i}{\Delta P}$ ($\text{cm}^{-1} \text{ kbar}^{-1}$)	$\frac{1}{\nu_i^0} \frac{\Delta\tilde{\nu}_i}{\Delta P}$ ($10^{-2} \text{ kbar}^{-1}$)	$\frac{\Delta\tilde{\nu}_i'}{\Delta P}$ ($\text{cm}^{-1} \text{ kbar}^{-1}$) ^a
A_1, ν_1 $\nu(\text{CO})$	2139	0.139	0.0065	
B_1, ν_9	2088	0.328	0.016	
E, ν_{15}	2074	0.171	0.008	
A_1, ν_2	1988.5	-0.067	-0.003	0.239
A_1, ν_4 $\nu(\text{Mn}-\text{C})$	473	0.645	0.14	0.109
E, ν_{18} $\delta(\text{MnCO})$	414	0.719	0.17	
A_1, ν_5 $\nu(\text{Mn}-\text{C})$	383.5	0.928	0.24	0.380
A_1, ν_6 $\nu(\text{Mn}-\text{Br})$	218.5	0.702	0.32	0.239
A_1, ν_7 $\delta(\text{CMnC})$	125	1.80	1.44	~ 0.54
E, ν_{20} $\delta(\text{CMnC})$	117	1.38	1.18	~ 0.52
E, ν_{22} $\delta(\text{CMnBr})$	98.5	0.825	0.84	0.159
Lattice modes	53	1.46	2.76	0.438
	29	0.819	2.82	

^aSlope of line after phase transition: no entry indicates that the slope is unchanged, or that the band was no longer observable.

$\text{Mn}(\text{CO})_5\text{Br}$ $\chi_T \cong 0.8 \times 10^{-2} \text{ kbar}^{-1}$, an entirely reasonable value.

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ERRATA

Erratum: A function useful for analyzing single-step one-dimensional Markov processes [*J. Chem. Phys.* **76**, 3762 (1982)]

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Equation (A5) of this paper was misprinted. It should read:

$$\pi_\delta(x) = \left[1 + \sum_{n=\gamma+1}^{x-1} \prod_{i=\gamma+1}^n \frac{a_-(i)}{a_+(i)} \right] / \left[1 + \sum_{n=\gamma+1}^{\delta-1} \prod_{i=\gamma+1}^n \frac{a_-(i)}{a_+(i)} \right], \quad \gamma + 1 \leq x \leq \delta - 1. \quad (\text{A5})$$

Erratum: The orange arc bands of CaO. Analysis of a $D, d^{1,3}\Delta - a^3\Pi$ system [*J. Chem. Phys.* **76**, 4689 (1982)]

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The T_e values listed in Table I are actually T_{e0} values. Deperturbed T_e values are obtained by adding the zero point energy of the $X^1\Sigma^+$ state, 365 cm^{-1} , to all four T_{e0} values: $T_e(a^3\Pi) = 8386(7) \text{ cm}^{-1}$, $T_e(A'^1\Pi) = 8693(6) \text{ cm}^{-1}$, $T_e(d^3\Delta) = 24817(7) \text{ cm}^{-1}$, $T_e(D^1\Delta) = 24752 \text{ cm}^{-1}$. The same error occurs in *Phys. Scr.* **25**, 312 (1982), Table VI. None of the conclusions, comparisons against *ab initio* predictions, or assignments of perturbations were based on incorrect T_e values. Figure 5 of the *Phys. Scr.* paper correctly summarizes the observed (i.e., perturbed) energy levels relative to $E=0$ at $^{40}\text{Ca}^{16}\text{O } X^1\Sigma^+ v=0, J=0$.