

Raman Study of the Effect of High Pressure on the Order-Disorder Phase Transition in 2-Adamantanone

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(Received: February 19, 1986)

The pressure dependence of the Raman-active bands of the plastic crystal 2-adamantanone ($C_{10}H_{14}O$) has been investigated at room temperature for pressures up to 21 kbar, using a diamond anvil cell. A large hysteresis was observed, the transition pressures being 10.0 ± 0.2 and 6.9 ± 0.2 kbar for the compression and decompression cycles, respectively. The Raman spectrum of the high-pressure ordered phase exhibits band shifts and splittings similar to those observed for the ordered phase produced at low temperature (150 K), strongly suggesting that the same crystalline phase is being formed in each case. The Gruneisen parameters have been evaluated for the ordered ($0.031 < \gamma_i < 0.057$) and disordered ($0.011 < \gamma_i < 0.046$) phases and are slightly lower than those reported for adamantane ($C_{10}H_{16}$).

Introduction

2-Adamantanone ($C_{10}H_{14}O$) exhibits plastic-crystal properties similar to those of the parent cage molecule adamantane ($C_{10}H_{16}$)¹⁻⁶ with a reported phase transition at 178 K, compared with 208 K for adamantane itself. However, the transition behavior is not simple, because the temperature-induced phase transition involves a large thermal hysteresis and the transition temperatures depend upon the previous thermal history of the sample.⁵ At atmospheric pressure and room temperature, 2-adamantanone crystallizes in the $Fm3m$ (O_h^h) space group with four molecules per unit cell.^{1,2} The phase transition can also be induced by the application of high pressures,^{7,8} and Hara et al.³ have reported that the high-pressure, ordered crystal adopts a face-centered-cubic structure ($P4_21c, D_{2d}^4$), with two molecules per unit cell, very similar to that of adamantane⁸ and 2-methyladamantane.⁹ However, our variable-temperature FT-IR and Raman spectroscopic studies on 2-adamantanone have indicated that the low-temperature phase has at least four molecules per unit cell.⁶

The aims of the present work were to confirm, by Raman spectroscopy, that the pressure-induced, ordered phase in 2-adamantanone is the same as that obtained at low temperature and 1 atm and to compare the effects of pressure on the Raman spectra of the substituted derivative with similar studies on the parent adamantane.¹⁰

Experimental Section

2-Adamantanone (Aldrich Chemical Co.) was purified immediately prior to use by repeated sublimation at room temperature. The Raman spectra were recorded on a Spex Model 14018

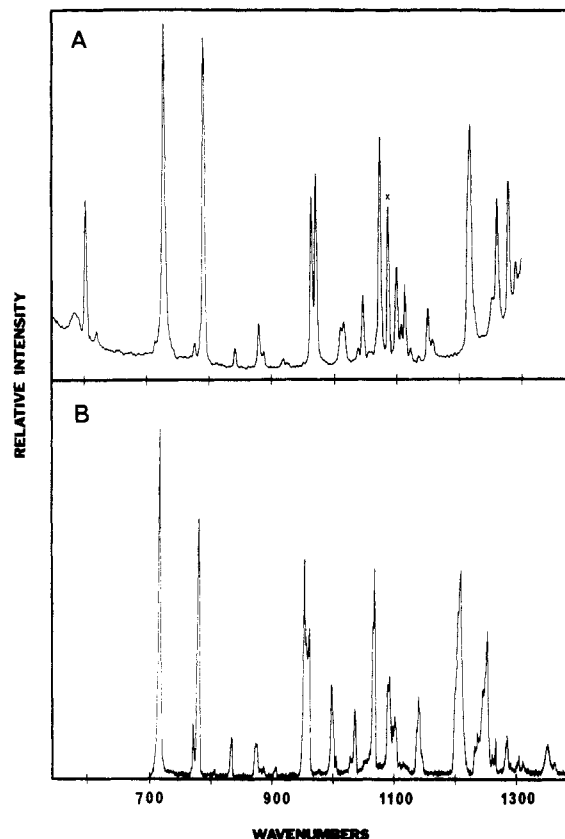


Figure 1. Comparison of the Raman spectra of 2-adamantanone: (A) at room temperature and 21 kbar, and (B) at 150 K and 1 atm. For trace A: laser excitation, 514.5 nm (200 mW at sample); 300- μ m slits; 2 s point⁻¹ spaced by 2 cm⁻¹; 2 scans. For trace B: laser excitation, 488.0 nm (120 mW at sample); 120- μ m slits; 10 s point⁻¹ spaced by 0.4 cm⁻¹; 1 scan. (x) Diamond peak.

spectrometer (1.0-m double monochromator/holographic gratings, 1800 lines/mm) with a cooled RCA C31034 photomultiplier. The excitation source was the 514.5-nm green line of a CRL Model 12 argon ion laser (ca. 200 mW at the sample). The data acquisition was performed by a Spex Model DM1 Datamate processor and the resulting spectral data were transferred to a Heurikon computer. Frequencies and bandwidths were calculated with software developed at NRC. The spectra were

- (1) Amoureux, J. P.; Bee, M. *J. Phys. C* **1980**, *13*, 3577.
- (2) Amoureux, J. P.; Bee, M. *Acta Crystallogr., Sect. B: Struct. Crystallogr. Cryst. Chem.* **1980**, *B36*, 2636.
- (3) Hara, K.; Osugi, J.; Taniguchi, Y.; Suzuki, K. *High Temp. High Pressures* **1980**, *12*, 221.
- (4) Amoureux, J. P.; Castelain, M.; Bee, M.; Arnaud, B.; Shouteenten, M. *J. Phys. C* **1982**, *15*, 1319.
- (5) Butler, I. S.; Cole, H. B. R.; Gilson, D. F. R.; Harvey, P. D.; McFarlane, J. D. *J. Chem. Soc., Faraday Trans.*, **1986**, *82*, 535.
- (6) Harvey, P. D.; Butler, I. S.; Gilson, D. F. R., unpublished results.
- (7) Hara, K.; Schuster, G. B.; Drickhamer, H. G. *Chem. Phys. Lett.* **1977**, *47*, 462.
- (8) Hara, K.; Katou, Y.; Osugi, J. *Bull. Chem. Soc. Jpn.* **1981**, *54*, 687.
- (9) Hara, K.; Katou, Y.; Osugi, J.; Taniguchi, Y.; Suguki, K. *Chem. Lett.* **1980**, 803.
- (10) Burns, G.; Dacol, F. H.; Weller, B. *Solid State Commun.* **1979**, *32*, 151.

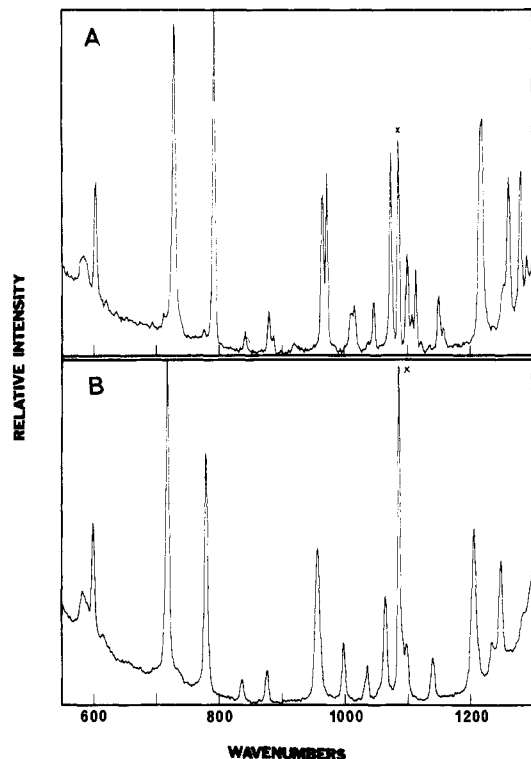


Figure 2. Room-temperature Raman spectra of solid adamantanone: (A) at 18 kbar and (B) at 1 atm. Conditions same as for Figure 1A. (X) Diamond peak.

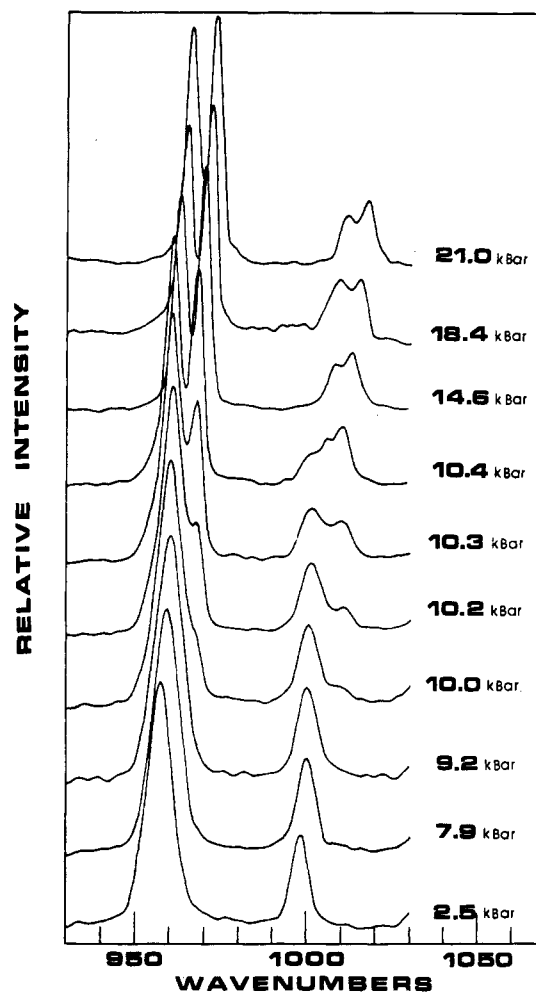


Figure 3. Room-temperature Raman spectra of the 930–1030-cm⁻¹ region as a function of increasing pressure. Same experimental conditions as Figure 1A.

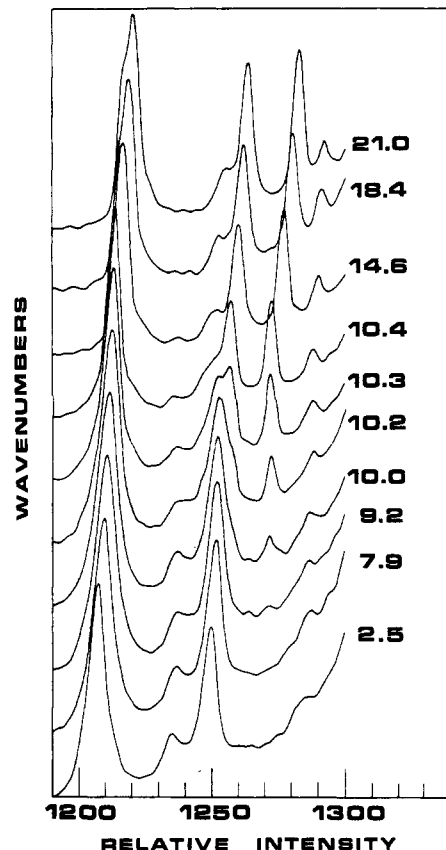


Figure 4. Room-temperature Raman spectra of 2-adamantanone as a function of increasing pressure for the region 1190–1300 cm⁻¹. Same experimental conditions as Figure 1A.

calibrated against emission lines of a standard neon lamp and the reported peak positions are considered accurate to ± 0.2 cm⁻¹. The diamond anvil cell was constructed of fully hardened maraging steel. A 0.23-mm-thick stainless steel gasket contained the sample and a small microcrystal of natural ruby as the pressure calibrant (pressure accuracy, ± 0.2 kbar). The temperature for all the experiments was 23 ± 1 °C and 20-min intervals were allowed for the pressure to stabilize between successive Raman measurements.

Results and Discussion

The Raman spectra of 2-adamantanone for the low-temperature phase (from ref 6) and the high-pressure phase are compared in Figure 1. Although there are some differences in the spectral resolution employed, the spectra do resemble each other quite well, and, in comparing the splittings wherever possible, it can be concluded that these two phases are indeed the same. The spectra of the low- and high-pressure phases are compared in Figure 2. As the pressure is increased, there are changes in the spectra of adamantanone throughout the 3500–500-cm⁻¹ region, but the C–H and C–O stretching regions are complicated by the broad overlapping bands. Changes in the Raman spectra in the 930–1070-cm⁻¹ region with increasing pressure are shown in Figure 3. This region covers the band at 955 cm⁻¹, attributed to a mixture of CH₂ rock + CC stretch + CCC bend, and the a₁ skeletal deformation at 997 cm⁻¹. At the transition pressure, the 955-cm⁻¹ band has shifted to 960 cm⁻¹ and a second band appears at 968 cm⁻¹. Both peaks move to higher energy with increasing pressure (see also Figure 5). The intensity of the skeletal mode decreases until the peak disappears at the transition, while new peaks grow and give a doublet in the high-pressure phase. Other significant changes occur in the 1190–1300-cm⁻¹ region, where the CH₂ wagging and twisting modes are found. With increasing pressure, a new band appears at about 1275 cm⁻¹, which continues to grow in intensity and to shift to slightly higher wavenumber (Figure 4). At the same time, the band near 1235 cm⁻¹ eventually disappears at the phase transition and a new band grows in at

TABLE I: Selected Raman Frequencies,^a Pressure Dependence, and Gruneisen Parameters (at Room Temperature) for Adamantanone

low-pressure phase ^b				high-pressure phase ^b				
ν , cm ⁻¹	$d\nu/dP$, cm ⁻¹ kbar ⁻¹	$d \ln \nu/dP$, kbar ⁻¹	γ	ν , cm ⁻¹	$d\nu/dP$, cm ⁻¹ kbar ⁻¹	$d \ln \nu/dP$, kbar ⁻¹	γ	assignt
716	0.63	8.92	0.046	724	0.60	7.95	0.053	cage breathing
776	0.60	6.67	0.040	786	0.68	8.55	0.057	CC str
834	0.44	5.40	0.028	838	0.45	5.38	0.036	CC str
874	0.42	5.11	0.026	876	0.43	4.88	0.033	CH ₂ rock
955	0.51	5.34	0.028	960	0.53	5.13	0.34	comb.
				968	0.52	5.88	0.039	
997	0.36	3.69	0.019	1010	0.66	6.47	0.043	skel. def
1034	0.54	5.69	0.029	1042	0.60	5.69	0.038	CH ₂ twist + CC str
1063	0.38	3.47	0.018	1070	0.50	4.72	0.031	CCH def
1139	0.43	3.89	0.020	1147	0.51	4.44	0.030	CH ₂ twist
1205	0.58	4.80	0.025	1213	0.68	5.57	0.037	CH ₂ twist
1235	0.29	2.20	0.011					CH ₂ wag
1248	0.43	3.41	0.018	1257	0.57	4.63	0.031	CH ₂ wag
				1273	0.97	7.39	0.049	CH ₂ wag

^a Assignments are based on those given in ref 14. ^b At 1 atm and at 10.4 kbar, respectively.

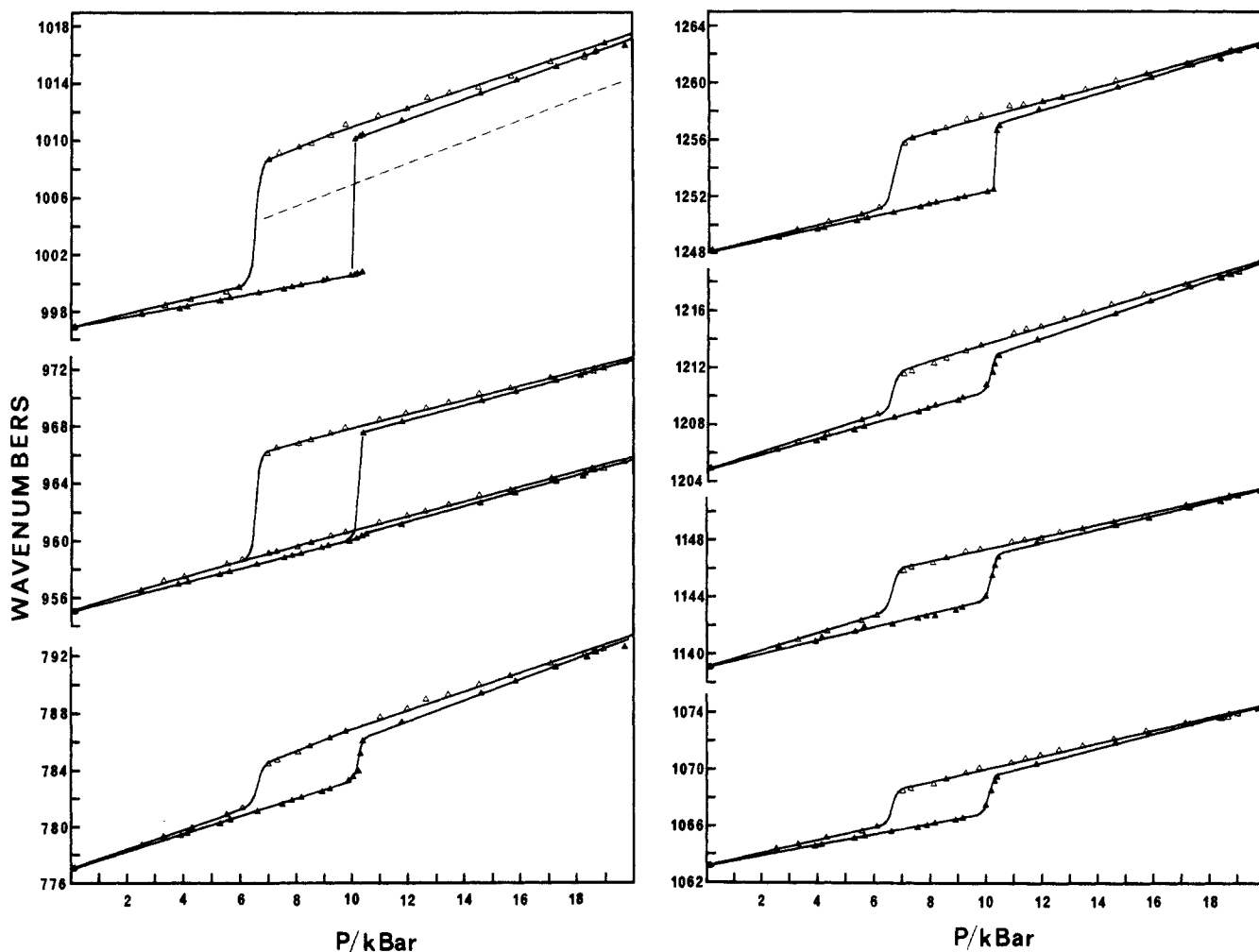


Figure 5. Frequency dependence as a function of pressure for both compression (▲) and decomposition (Δ). The dotted line shows the behavior of the shoulder at 1004 cm⁻¹ (see Figure 3).

about 1265 cm⁻¹. The intensities of the 1210- and 1290-cm⁻¹ peaks remain fairly constant throughout the pressure range investigated here, but there are some distinct changes in peak position. The frequencies, their pressure dependences, and Gruneisen parameters are listed in Table I.

The pressure dependences of the vibrational frequencies are shown in Figure 5. Certain vibrations of adamantanone are particularly sensitive (high $d\nu/dP$ values), notably the CH₂ wagging mode (active in the high-pressure phase only), the C-C stretching modes at 716 and 776 cm⁻¹, and the C-H deformation modes at 1034 and 1205 cm⁻¹. In adamantane itself, these same

vibrational modes are also the most pressure sensitive,¹⁰ and the pressure dependence of the vibrational frequency can be used to assign the (unshifted) vibrations of the substituted molecule. The pressure dependences of the vibrational frequencies for the high-pressure phase are somewhat greater than those for the phase below the transition pressure. This difference is most probably due to the increased crystal density [1.14 (1 atm), 1.5 g cm⁻³ (10 kbar)].⁸

Most of the spectral changes take place between 10.0 and 10.4 kbar on compression. On decompression, a large pressure hysteresis is observed (Figure 5), with the actual transition pressure

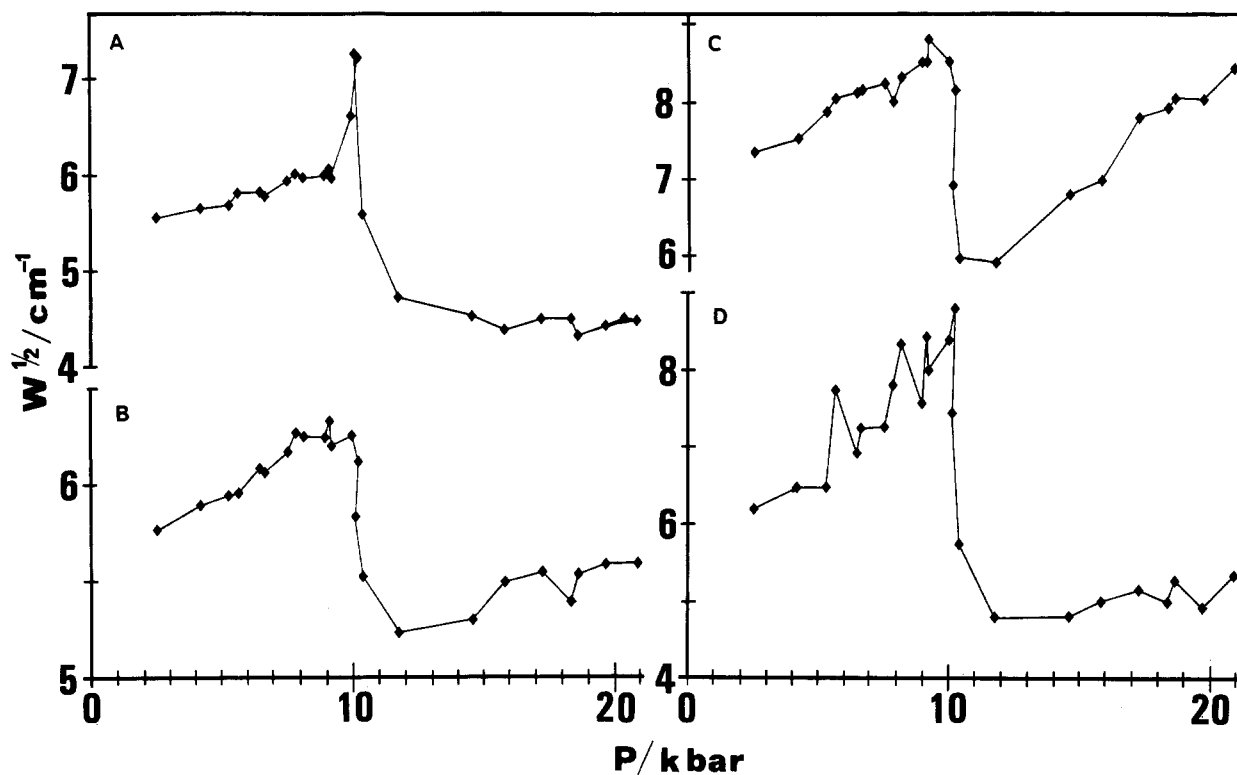


Figure 6. Bandwidths at half peak height as a function of pressure for selected bands: (a) 777 cm^{-1} , (b) 716 cm^{-1} , (c) 1207 cm^{-1} , (d) 875 cm^{-1} . Same experimental conditions as Figure 1A.

being 6.9 ± 0.2 kbar. These values are in only moderate agreement with the values found by Hara and co-workers⁸ of 8.65 and 4.71 kbar at a slightly lower temperature of 21 $^{\circ}\text{C}$.

Figure 6 illustrates the effect of increasing pressure on the band widths at half peak height of some selected bands. The bandwidths increase steadily up to the phase transition at 10 kbar; they then decrease sharply by about 1–4 cm^{-1} . Following this, the bandwidths begin to increase again. The factors that affect the widths of lines in the Raman spectra of plastic crystals have been discussed by Debeau and Depondt,¹¹ with particular reference to the vibrations observed at 758 and 1220 cm^{-1} in the plastic phase of adamantane. The symmetric mode, a_{1g} in the crystal, shows almost constant bandwidth with temperature since this vibration is not very sensitive to molecular deformations and the reorientations of neighboring molecules. The 1221- cm^{-1} e mode shows broadening with increasing temperature, due to coupling with rotations, either of the molecule itself or with its neighbors, since, in this case, the Raman tensor is not symmetric. In the pressure studies on adamantanone, we find that the cage breathing mode, now at 716 cm^{-1} , shows little variation in line width (0.7 cm^{-1} over a 10-kbar range) and an even smaller increase in the high-pressure phase. There is a small frequency shift at the transition of less than 2 cm^{-1} , but this peak shows one of the largest $d\nu/dP$ values. In comparison, the $\text{CH}_2 + \text{HCC}$ bending mode, shifted to 1205 cm^{-1} from 1220 cm^{-1} in adamantane, also has a high $d\nu/dP$ value and increases in frequency by 3 cm^{-1} at the transition but broadens by 1.5 cm^{-1} over the pressure range 2.5–10 kbar and by more than 2 cm^{-1} over 10 kbar in the high-pressure phase. One of the largest line broadening effects is shown by the weak mode at 875 cm^{-1} , assigned to the CH_2 rocking vibration of f_{1g} symmetry. These results seem to be in accordance with the proposals of Dubeau and Depondt¹¹ that reorientational effects are more easily observed when the molecular deformations are large.

Gruneisen Parameters. The mode Gruneisen parameter, γ_i , is defined as

$$\gamma_i = -d \ln \nu_i / d \ln V \quad (1)$$

where V is the unit cell volume. The volume dependence on the pressure for the low-temperature phase has been given by Hara and co-workers⁸ and can be derived for the high-pressure phase from Figure 2 of the same work. However, when $\ln V$ values, calculated at each pressure from these results, were used in eq 1, we did not obtain the expected straight line. For a constant temperature process, eq 1 can be rewritten as

$$\gamma_i = (1/K)(d \ln \nu_i / dP)_T \quad (2)$$

where K is the compressibility of the crystal and P is the external applied pressure. Plots of $\ln \nu$ vs. P gave straight lines and the Gruneisen parameters were calculated for both phases, using the compressibilities for the low- and high-pressure phases determined from the data cited in ref 8, of 0.0193 and 0.150 kbar^{-1} , respectively. For the low-pressure phase, the γ_i values fall in the range 0.011–0.046, while, for the high-pressure case, they are in the range 0.031–0.057. Although the Gruneisen parameters do tend to decrease with increasing wavenumber, there is no systematic change. In this respect adamantanone resembles adamantane¹⁰ and does not follow the trend reported for the internal modes in several other molecules.^{12,13}

Differential scanning calorimetric studies of adamantanone⁵ have shown that the phase transition temperatures and enthalpies depend upon the thermal history of the sample and that a second low-temperature phase results when the material is repeatedly cycled through the transitions. The present results refer to an uncycled sample.

Acknowledgment. This research was generously supported by NSERC (Canada), FCAC (Quebec), and McGill University (McConnell Foundation).

Registry No. $\text{C}_{10}\text{H}_{14}\text{O}$, 700-58-3.

(12) Zallen, R. *Phys. Rev. B: Solid State* **1974**, *B9*, 4485.

(13) Zallen, R.; Slade, M. L. *Phys. Rev. B: Condens. Matter* **1978**, *B18*, 5775.

(14) Bailey, R. T. *Spectrochim. Acta, Part A* **1971**, *27A*, 1447.

(11) Dubeau, M.; Depondt, Ph. *J. Chim. Phys. Phys.-Chim. Biol.* **1985**, *82*, 233.