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Low-Frequency Modes of Molecular Crystals. XX† Acetaldehyde and Acetaldehyde-d_4

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Abstract—The far infrared (550–33 cm^{-1}) and Raman (300–10 cm^{-1}) spectra of solid CH_3CHO and CD_3CDO have been recorded. The torsion appears in the solid phase spectra of both techniques at approximately 205 cm^{-1} (V_3 = 2.10 kcal). Compared to the infrared data, the Raman data were found to be far superior, and eighteen of the twenty-one predicted intermolecular fundamentals were resolved in the Raman spectrum of solid acetaldehyde. Out of the nine predicted translations, seven could be confidently assigned and at least nine of the twelve predicted librations were observed.

1. Introduction

Previously, a number of molecules with a single methyl rotor were examined to determine the effect of phase changes on the barrier to internal rotation.[1] Included in this study were a number of ethane derivatives i.e., ethyl and acetyl halides. It was found that the barrier height increased on going from the gas phase to the solid phase by approximately 20%. The barrier heights were approximately the same (4.5 kcal/mole) for the three ethyl halides (Cl, Br, I), and the two acetyl halides, CH_3CClO and CH_3CBrO, revealed considerably lower barriers (1.9 kcal/mole) than their ethyl halide counterparts in the solid. To continue the study on the effects of phase changes upon torsional barriers and the determination of the lattice modes of molecular crystals, we have initiated a study of the

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far infrared and Raman spectra of solid CH_3CHO and its deuterated analogue.

Vibrational assignments for the intramolecular fundamentals, except for the torsion have been published by a number of authors.[2-10] In the most recent and also the most complete study, Hollenstein and Günthard[10] assigned the torsional mode from combination bands in the mid-infrared spectra of both the solid and gas. Their assignment for the gas was in agreement with that previously proposed by Winther and Hummel.[11] Direct observation of the torsional mode in the far infrared spectrum of the gas has also been reported[12-14] with the data of Souter and Wood being consistent with the barrier obtained from microwave studies[10,14-16] In an earlier study Möller[12] had reported a torsional frequency of 175 cm^{-1} which is at variance with the most recent work, so we have reinvestigated the far infrared spectrum of the gas in order to try to determine the origin of this discrepancy.

2. Experimental

Acetaldehyde samples were obtained from Eastman Kodak and K and K Laboratories and kept free from air between usage in evacuated vessels. Deuterated acetaldehyde, CD_3CDO, was purchased from Merck, Sharp and Dohme, with a stated purity of 99.5% and it was used without further purification.

Infrared spectra were recorded between 700 and 33 cm^{-1} on a Beckman Model IR-11. Water vapor was removed from the instrument housing by purging with dry air. The instrument was calibrated against the spectrum of atmospheric water by using the assignments of Hall and Dowling.[17] Spectra of polycrystalline samples were obtained by depositing, in vacuum, thin films onto a silicon plate cooled by boiling nitrogen. Spectra of the vapors were obtained from samples contained in a Beckman 10-meter variable path-length gas cell equipped with polyethylene windows. In addition, the far infrared spectrum of acetaldehyde in the gas phase was also recorded on a Jarrell–Ash 78–900 double-beam evacuated grating spectrometer equipped with a liquid-helium cooled gallium-doped germanium detector through the courtesy of Professor Lord.

Raman spectra were recorded with a Cary Model 82 spectrophoto-

meter[18] equipped with an argon-ion laser using the 5145 Å green line for excitation. The instrument was calibrated with neon emission lines. A jacketed cold cell, in which a capillary could be inserted was used to obtain the Raman spectra of the solids. Variable temperatures ranging from – 195 °C to ambient, could be obtained by allowing cold nitrogen to flow through the cell around the capillary. Temperatures were measured with a thermocouple inserted in the refrigerant stream.

3. Results and Discussion

The far infrared spectra of CH_3CHO and CD_3CDO are shown in Figs. 1 and 2, respectively. For the " light " molecule, there are five rather broad bands observed, whereas only four are observed for the deuterium compound. The frequencies of the observed bands are listed in Table 1 and the apparent shift factors appear confusing at first, particularly, for the two broad bands between 100 and 135 cm^{-1}. The determination of the band center for these two broad bands was quite difficult because of the breadth of the bands. Also, it is quite clear that these bands originate from intermolecular motions so the frequencies are dependent on the sample temperature and the crystallinity of the samples. To minimize these effects, the samples were always annealed until no further changes were noted in the frequencies or band contours. All samples were annealed to about

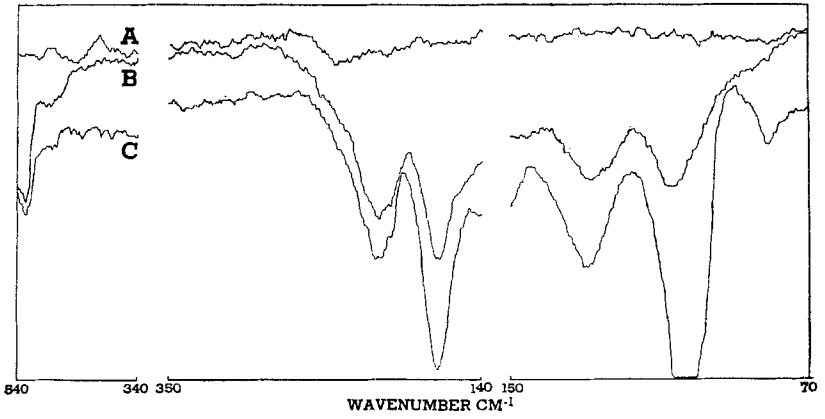

Figure 1. Far infrared spectrum of solid CH_3CHO.

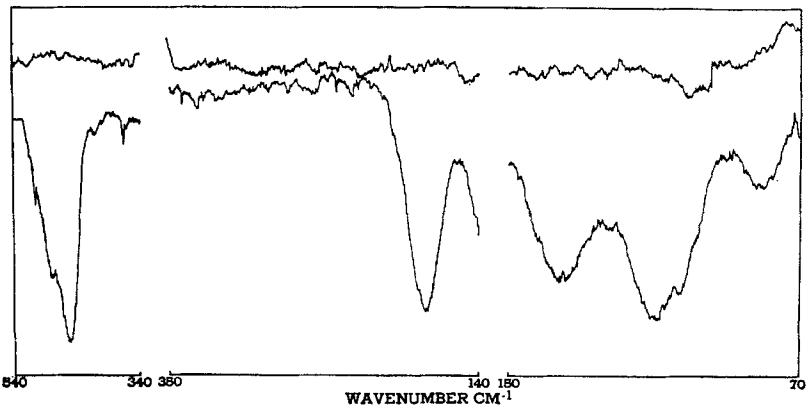

Figure 2. Far infrared spectrum of solid CD_3CDO.

$-140\,^{\circ}C$; the spectra were then obtained with the sample temperature maintained as close to $-190\,^{\circ}C$ as possible. Nevertheless, differences of 3 or 4 cm^{-1} in band centers were observed for successive recordings of the same sample.

Inspection of the Raman data shown in Figs. 3 and 4 reveals a much better definition of the "individual" lattice modes. For example, the broad band at 128 cm^{-1} in the infrared spectrum of the "light" compound is clearly resolved into four definite lines in the Raman effect. Thus, consistent shift factors were obtained from the Raman data for the lattice modes of the two isotopic species. The base line was quite flat to 15 cm^{-1} and a lattice mode was clearly

TABLE 1 Low Frequency (cm^{-1}) Infrared Modes of Acetaldehyde

CH_3CHO (gas)	CH_3CHO (solid)	CD_3CDO (gas)	CD_3CDO (solid)	Assignment
507	520	446	454	CCO bend
143[a]	207			Torsion
	169		170	Lattice
	128		134	Lattice
	103		110	Lattice
			103 shoulder	
	81		81	Lattice

[a] Several weak, closely spaced bands were observed on the high frequency side of this main Q branch along with two additional Q branches on the low frequency side of the main line (see text).

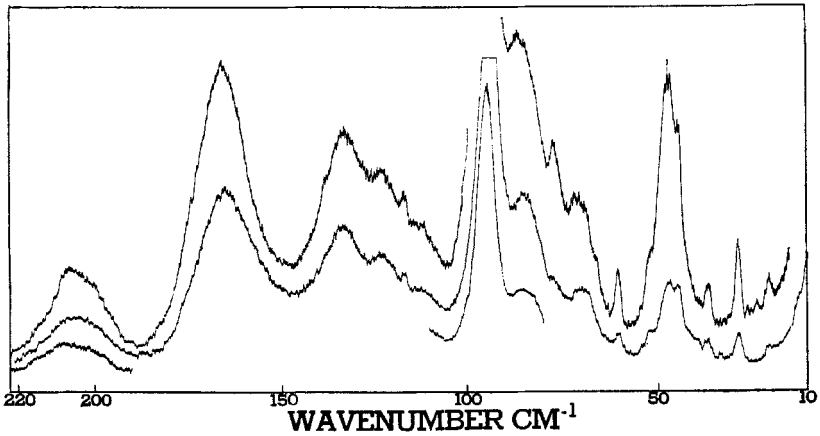

Figure 3. Raman spectrum of solid CH_3CHO.

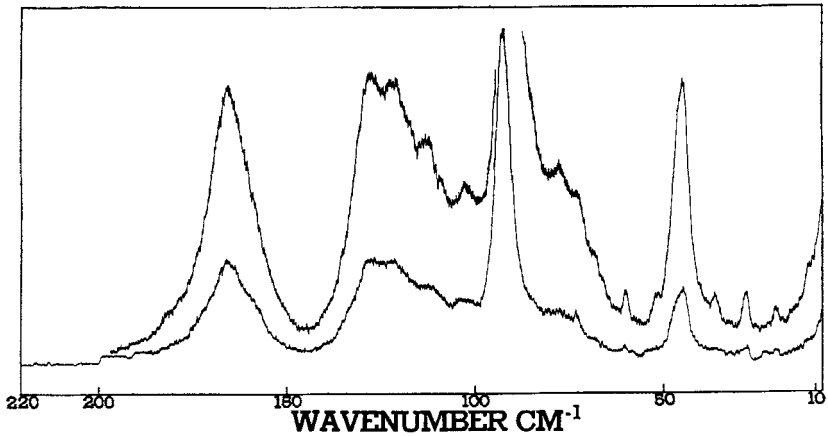

Figure 4. Raman spectrum of solid CD_3CDO.

detected at 20 cm^{-1} in both Raman spectra. Most of the low frequency lines were quite sharp and their centers could be accurately measured; however, the observed shift factors with deuteration are quite small.

Methyl Torsion

An inspection of both the infrared and Raman spectra of the " light " molecule above 200 cm^{-1} compared to the corresponding

spectra in the same region of the deuterated molecule shows the complete disappearance of the band(s) in this region. It either shifts to the low frequency side of the 170 cm^{-1} line or the high frequency side of the 127 cm^{-1} line. Since the latter shift factor is larger than the theoretical one calculated for the torsional motion or any of the librational motions, it seems reasonable to assign the 159 cm^{-1} shoulder in the spectrum of the deuterated molecule as arising from the same motion that leads to the 201 cm^{-1} line in the " light " molecule. Thus, the 207 cm^{-1} line and 201 cm^{-1} shoulder in the Raman spectrum are assigned the methyl torsional modes. The two bands are attributed to correlation field splitting in the crystal (see next section), which results from four molecules in the unit cell. This assignment agrees well with the 204 cm^{-1} prediction made by Hollenstein and Günthard[10] for the torsional mode in the solid state from the assignment of combination bands.

As pointed out in the introduction, Möeller[12] assigned the torsion to a strong band at 175 cm^{-1} in the infrared spectra of the gas phase. We have also been able to observe this band as well as a strong band at 270 cm^{-1} but only after the sample has been exposed for a period of time to the air. Freshly purified material did not show these two bands. Fateley and Miller[13] also had noted the absence of the 175 cm^{-1} band in their study of the infrared spectrum of the gas; however, they did report six weak absorption bands around 270 cm^{-1} in addition to the torsional mode which they assigned as being centered at 150 cm^{-1}. This assignment has also been used in the normal coordinate calculations of acetaldehyde.[10,19] Souter and Wood[14] recently reported the far infrared results on gaseous CH_3CHO and CD_3CHO and they assigned the torsional mode for the " light " molecule at 143 cm^{-1} and attributed the peak at 150 cm^{-1} in the spectrum taken by Fateley and Miller to imperfect drying of the sample. Our gas phase results for the " light " compound are consistent with those published by Souter and Wood. In Fig. 5 is shown the far infrared spectrum in the torsional region with a spectra slit width of 0.5 cm^{-1}. On the high frequency side of the main Q branch of this type C band is the rotational fine structure with an average spacing of about 3 cm^{-1}. In addition to the Q branch at 143 cm^{-1} there are two more well defined Q branches at 122 and 115 cm^{-1} which can be readily assigned to the first excited states of the torsional

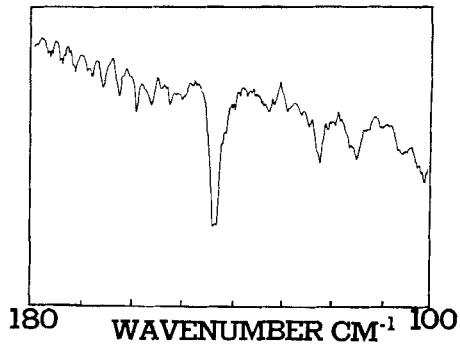

Figure 5. Far infrared spectrum with a spectral slit width of 0.5 cm^{-1} for CH_3CHO in the gaseous state. Pressure 500 mm with a path length of 30 cm.

mode. The fine structure on the low frequency side of the main Q branch is obscured by these excited state bands; however, there is no question that the band is centered at 143 cm^{-1}. Thus, the methyl torsional mode shifts from 143 to 204 cm^{-1} (average of 207 and 201 cm^{-1} lines) with solidification. This is one of the largest shifts observed for a methyl torsional mode in going from the gas to the solid state.

In order to obtain the barriers to internal rotation from the observed torsional frequencies in the gas and solid phases the F value (reduced moment parameter) must be determined from the structural parameters of the molecule. The values reported from Wilson's microwave analysis were used for the gas phase.[15] For the crystalline state we used the bond distances reported by A. J. Richard[20]; however, since the geometry of the methyl group is not known with any certainty in the solid, a tetrahedral orientation of the C—H bonds and a C—H bond distance of 1.08 Å was assumed. The difference between the F values obtained from two phases (see Table 2) appears to be insignificant.

Condensation of acetaldehyde results in an approximate one kcal/mole increase in the torsional barrier. The increase is considerably larger than those observed for the acetyl halides which are enumerated in Table 3. The large difference probably results from the intermolecular potentials for acetaldehyde more nearly approximating the intramolecular potential for the methyl torsion than it does for the acetyl halides. The barriers for the methyl rotations in

TABLE 2 Barriers to Internal Rotation of Acetaldehyde

State	CH_3CHO Gas	CH_3CHO Solid	CD_3CDO Gas	CD_3CDO Solid
F value (cm^{-1})	7.62	7.60	4.53	4.45
Torsional frequency (cm^{-1})	1.43	204	116	162
Barrier (kcal/mole)	1.11	2.10	1.13	2.02

TABLE 3 Three-fold Barriers to Internal Rotation

Compound	Barrier Height (V_3) kcal/mole	Method	State	Reference
CH_3CHO	1.11	IR	gas	14
	2.10	IR	solid	this work
CD_3CDO	1.13	IR	gas	21
	2.06	IR	solid	this work
CH_3CFO	1.04	MW	gas	22
CH_3CClO	1.3	MW	gas	23
	1.85	IR	solid	24
CH_3CBrO	1.3	MW	gas	25
	1.97	IR	solid	24
CH_3ClO	1.3	MW	gas	26

the ethyl halides usually increase by 0.5 to 0.8 kcal/mole but the percentage change is less compared to the acetyl halides, since the barriers for ethyl halides in the gas phase are three or four times as large as those for the acetyl halides.

INTERMOLECULAR FUNDAMENTALS

A. J. Richard has found the crystalline structure of CH_3CHO to be $C_{2v}^9(P_{na}2_1)$ with the molecules occupying C_1 sites and four molecules per unit cell.[20] From the group theoretical considerations of Halford[27] and Hornig[28] one can predict the following representations for the lattice modes of CH_3CHO:

$$\Gamma = A_1(6) + A_2(6) + B_1(6) + B_2(6).$$

The acoustical translations fall into the species:

$$\Gamma(AT) = A_1 + B_1 + B_2.$$

Thus, 21 spectroscopically active lattice modes are expected. The representations for the optical translations and librations are then:

$$\Gamma(OT) = 2A_1, (IR, R) + 3A_2(R) + 2B_1(IR, R) + 2B_2(IR, R)$$
$$\Gamma(OL) = 3A_1, (IR, R) + 3A_2(R) + 3B_1(IR, R) + 3B_2(IR, R).$$

Table 4 gives the factor group analysis of acetaldehyde.

TABLE 4 Factor Group Analysis of Crystalline CH_3CHO

Molecule	Site	Factor
C_s	C_1	$C_{2v}^9 = P_{na}2_1$
R_z, X, Y a'	a	a_1 Z
		a_2 R_z
		b_1 X, R_y
Z, R_x, R_y a''		b_2 Y, R_x

Theoretically, the intermolecular fundamentals may be distinguished by analyzing the observed frequency shift of a motion upon deuteration of the molecule. The shift factor for a translation upon deuteration of acetaldehyde should be proportional to the square root of the mass of CD_3CDO to that of CH_3CHO, or 1.04. Similarly, those shift factors associated with the librations depend upon the moments of inertia around the three principal axes of a molecule and its isomer. The principal moments of inertia for acetaldehyde were determined using the structure for the solid. Therefore, the theoretical shift factor for a libration which occurs about the "a" principal axis of acetaldehyde is 1.24, while it is calculated to be 1.11 and 1.10 for a libration about the "b" and "c" axes, respectively. The shift factors obtained experimentally are usually much smaller than the predicted values due to the large amount of anharmonicity associated with the intermolecular fundamentals. Also, since the cell does not contain a symmetry center, the librations and translations can be mixed.

From the Raman spectra of CH_3CHO and CD_3CDO_3 (see Figs. 3 and 4), eighteen of the twenty-one predicted intermolecular fundamentals are readily observed. Because of the great similarity between the two spectra, all corresponding bands were easily identified. In fact, the effect of deuteration on the spectrum of acetaldehyde appears to be the shifting of the whole center portion of the spectrum a bit closer to the exciting line. Within this center region only one

band apparently does not shift. From the band contours of the 117 cm^{-1} and 113 cm^{-1} bands in acetaldehyde, it is believed that the 117 cm^{-1} band shifted to the sharp 103 cm^{-1} band in deuterated acetaldehyde, whereas the broader 113 cm^{-1} band does not shift upon deuteration of the molecule. In Table 5 are listed the observed Raman frequencies and the corresponding shift factors obtained for the solid acetaldehyde isomers.

TABLE 5 Low Frequency Raman Modes of Acetaldehyde

CH_3CHO (solid)	CD_3CDO (solid)	Shift factor
207	165.5	1.24
201	159.5	1.25
166	166.5	1
137	131	1.04
133	127.5	1.04
123	121.5	1.01
117	103	1.09
113	112.5	1
95	92	1.03
86.5	77.5	1.11
77.5	73	1.05
71	68.5	1.03
66	66	1
60	60	1
52	52	1
47	45	1.04
44.5	45	1
36	36	1
28	28	1
20	20	1

Those bands observed with a shift factor of one may be assigned to the translational motions of the lattice. Nine optical translations are predicted in the Raman effect and there are nine band assignments reported with a shift factor of one. However, translations are usually weak and the assignment of the strong bands 166 cm^{-1} and 45 cm^{-1} to translations must be considered tentative.

Librations about the " *b* " or " *c* " principal axes of acetaldehyde in the lattice are clearly not distinguishable from the shift factor data; however, those librations about the " *a* " principal moment

should exhibit the largest shift factor for an intermolecular fundamental. The bands associated with the 1.11 and 1.09 shift factors may then be assigned to this libration. As a result of these assignments, seven of the nine translations may be confidently reported. Also at least nine of the twelve librations are reported where two of the bands observed may be assigned to a libration about the " a " axis of the molecule in the crystal.

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REFERENCES

1. Durig, J. R., Player, C. M. and Bragin, J., *J. Chem. Phys.* **54,** 460 (1970).
2. Gerding, H. and Lecomte, J., *Rec. trav. chim.* **58,** 614 (1939).
3. Gerding, H., Nijveld, W. J. and Rijnders, G. W. A., *Rec. trav. chim.* **60,** 25 (1941).
4. Thompson, H. W. and Harris, G. P., *Trans. Faraday Soc.* **38,** 37 (1942).
5. Morris, J. C., *J. Chem. Phys.* **11,** 230 (1943).
6. Seewan-Albert, H. and Kahovec, L., *Acta. Phys. Austriaca* **1,** 342 (1948).
7. Pitzer, K. S. and Weltner, W. J., *J. Am. Chem. Soc.* **71,** 2842 (1949).
8. Hadni, M. A., *Compt. rend.* **238,** 2150 (1954).
9. Evans, J. C. and Bernstein, H. J., *Can. J. Chem.* **34,** 1083 (1956).
10. Hollenstein, H. and Günthard, H. H., *Spectrochim. Acta* **27A,** 2027 (1971).
11. Winther, F. and Hummel, D. O., *Spectrochim. Acta* **25A,** 417 (1969).
12. Möeller, M. K., *Spectroscopie Moleculaire*, 3977 (1960).
13. Fateley, W. F. and Miller, F., *Spectrochim. Acta* **17,** 857 (1961).
14. Souter, C. E. and Wood, J. L., *J. Chem. Phys.* **52,** 674 (1970).
15. Kilb, R. W., Lin, C. C. and Wilson, E. B., Jr., *J. Chem. Phys.* **26,** 1695 (1956).
16. Herschbach, D. R., *J. Chem. Phys.* **31,** 91 (1959).
17. Hall, R. T. and Dowling, J. M., *J. Chem. Phys.* **47,** 2454 (1967); **52,** 1161 (1970).
18. This instrument was purchased with funds from the National Science Foundation through grant No. GP-28068.
19. Cossee, P. and Schactschneider, J. H., *J. Chem. Phys.* **44,** 97 (1965).
20. Richard, A. J., *Acta Cryst.* **1,** 645 (1954).
21. Fateley, W. G., *J. Chem. Phys.* **44,** 97 (1966).
22. Pierce, L. and Krisher, L. C., *J. Chem. Phys.* **31,** 875 (1959).
23. Sinnott, K. M., *J. Chem. Phys.* **34,** 851 (1961).

24. Durig, J. R., Player, C. M., Jr. and Bragin, J., *J. Chem. Phys.* **54**, 460 (1971).
25. Krisher, L. C., *J. Chem. Phys.* **33**, 1237 (1960).
26. Moloney, M. J. and Krisher, L. C., *J. Chem. Phys.* **45**, 3277 (1966).
27. Halford, R. S., *J. Chem. Phys.* **14**, 8 (1946).
28. Hornig, D. F., *J. Chem. Phys.* **16**, 1063 (1948).