

TABLE VII. Vapor and crystal frequencies in  $\text{cm}^{-1}$  of  $\text{CH}_3\text{OH}$  and  $\text{CH}_3\text{OD}$ .

	vapor	$\text{CH}_3\text{OH}$ crystal	shift	vapor	$\text{CH}_3\text{OD}$ crystal	shift
<i>a'</i> fundamentals:						
OH stretching	3687	{3261 <sup>a</sup> 3173 <sup>a</sup> }	-470 <sup>b</sup>	2720	{2420 <sup>a</sup> 2366 <sup>a</sup> }	-327 <sup>b</sup>
$\text{CH}_3$ asym. stretching	2973	2955	-18	2965	2962	-3
$\text{CH}_3$ sym. stretching	2845	2829	-16	2840	2838	-2
$\text{CH}_3$ asym. bending	1477	1468	-9	1500	1476	-24
$\text{CH}_3$ sym. bending	1455	1445	-10	1458	1465	+7
OH bending	1346	{1514 <sup>a</sup> 1492 <sup>a</sup> }	+146 <sup>b</sup>	867	{998 <sup>a</sup> 949 <sup>a</sup> }	+107 <sup>b</sup>
CO stretching	1034	1029	-5	1041	1027	-14
$\text{CH}_3$ rocking	1116	1142	+26	1160	1163	+3
<i>a''</i> fundamentals:						
$\text{CH}_3$ stretching	2973	2955	-18	2965	2962	-3
$\text{CH}_3$ bending	1415	1426	+11	1427	1443	+16
$\text{CH}_3$ rocking	1233	1256	+23	1228	1240	+12
crystal fundamentals:						
OH bending		{824 <sup>a</sup> 698 <sup>a</sup> }			{593 <sup>a</sup> 502 <sup>a</sup> }	
translation frequency (?)		520 <sup>a</sup>				
translation frequency		372 <sup>a</sup>			359 <sup>a</sup>	

<sup>a</sup> Frequencies extrapolated to 0°K.

<sup>b</sup> Shifts calculated using averages of the two components in the crystal.

### 3.2 Liquid Spectra

The frequencies of the liquid bands are listed in Tables I-IV. Assignments were made mainly by comparison with vapor spectra.

The infrared spectra of all four liquids are as expected, and there is little difference between the infrared and Raman liquid frequencies. The infrared bands are mostly fairly broad, and those due to OH stretching and bending motions are, as is common with hydrogen-bonded substances, very broad. The usual shifts from the vapor frequencies occur, i.e.,  $\text{CH}_3$  stretching and bending and CO stretching modes are little affected, and the OH stretching frequency decreases and the OH bending frequency increases. A very broad band, which is not present in the vapor, occurs in the range 450 to 850  $\text{cm}^{-1}$  in  $\text{CH}_3\text{OH}$  and  $\text{CD}_3\text{OH}$  and in the range 350 to 630  $\text{cm}^{-1}$  in  $\text{CH}_3\text{OD}$  and  $\text{CD}_3\text{OD}$ , which is clearly due to the out-of-plane bending mode of the hydrogen-bonded OH, and was already so assigned in liquid  $\text{CH}_3\text{OH}$  and  $\text{CH}_3\text{OD}$  by Stuart and Sutherland.<sup>6,32</sup>

### 3.3 Solid Spectra

Solid films condensed at liquid-nitrogen temperature were visibly transparent and their spectra consisted of broad bands resembling those of liquids. Only relatively small shifts from the liquid frequencies occurred, the largest shifts being observed for the OH and OD out-of-plane bending modes. One new band of moderate intensity appeared near 300  $\text{cm}^{-1}$ . The solids were presumably glasses.

<sup>32</sup> A. V. Stuart and G. B. B. M. Sutherland, *J. Chem. Phys.* **20**, 1977 (1952).

Upon warming, the films became snowy-white at about  $-140^\circ\text{C}$ , their spectra became sharper, all fundamental bands that involve mainly motions of the O-hydrogen atom split into two components of comparable intensity, some weak bands in the region 2100 to 2600  $\text{cm}^{-1}$  sharpened and resolved into several components, a few other bands appeared to split into two closely separated components of unequal intensity, and the band near 300  $\text{cm}^{-1}$  sharpened. The transformation was irreversible, and evidently the films had crystallized.

Further sharpening of the spectrum and some additional splitting into two components of unequal intensity occurred when the crystalline films were cooled to  $-180^\circ\text{C}$ . Some bands were sensitive to temperature, those involving OH motion generally broadening and shifting towards the vapor frequencies as the temperature increased. These changes were completely reversible.

In both  $\text{CH}_3\text{OH}$  and  $\text{CH}_3\text{OD}$  there is a first-order solid-solid phase transition, at  $-113.5^\circ\text{C}$  in  $\text{CH}_3\text{OH}$  and at  $-109.9^\circ\text{C}$  in  $\text{CH}_3\text{OD}$ <sup>33,34</sup> and this presumably also occurs in  $\text{CD}_3\text{OH}$  and  $\text{CD}_3\text{OD}$ , perhaps at somewhat higher temperatures. An attempt was made to observe a change of spectrum when the phase changed. Films of all four methanols were held near  $-120^\circ\text{C}$  and  $-108^\circ\text{C}$  for two hours. By comparison with observations on bulk specimens<sup>35,36</sup> this should be long enough for the phase change to be complete. There was no essential

<sup>33</sup> D. W. Davidson, *Can. J. Chem.* **34**, 1243 (1956).

<sup>34</sup> D. W. Davidson, *Can. J. Chem.* **35**, 458 (1957).

<sup>35</sup> L. A. K. Staveley and A. K. Gupta, *Trans. Faraday Soc.* **45**, 50 (1949).

<sup>36</sup> L. A. K. Staveley and M. A. P. Hogg, *J. Chem. Soc.* 1013 (1954).



difference between the spectra, the small changes in frequency and breadth of bands being consistent with the temperature variation of the bands in the low-temperature phase.

The assignment of the bands was made mainly by comparison with the vapor spectra, and is given in Tables I-IV. However, the coupling that occurs in the vapor is modified in the solid, and the identification of some of the bands is uncertain. Bands due to dilute  $\text{CH}_3\text{OH}$  in  $\text{CH}_3\text{OD}$  and to dilute  $\text{CD}_3\text{OH}$  in  $\text{CD}_3\text{OD}$  occur. These are listed in Tables II and IV and discussed in Sec. 4.4. In  $\text{CH}_3\text{OH}$  and  $\text{CD}_3\text{OH}$  there is a band near  $500\text{ cm}^{-1}$ , and in all four there is a band near  $320\text{ cm}^{-1}$ . They are discussed in Sec. 4.3. For a later paper we shall need the frequencies of  $\text{CH}_3\text{OH}$  and  $\text{CH}_3\text{OD}$  at  $0^\circ\text{K}$ . Those that shift with temperature have been extrapolated linearly to  $0^\circ\text{K}$  using the data of Tables I-IV and some data at intermediate temperatures which we have not reported. The results are in Table VII.

The sum of the frequency shifts from vapor to crystal for  $\text{CH}_3\text{OH}$  is 1.49 times that for  $\text{CH}_3\text{OD}$ , and that for  $\text{CD}_3\text{OH}$  is 1.44 times that for  $\text{CD}_3\text{OD}$ . The factor expected if the force constants for the four methanols are the same in the vapor and are the same in the solid is 1.41, in rough agreement with the experiment.

The two  $\text{CH}_3$  internally asymmetrical stretching modes of species  $a'$  and  $a''$  are not resolved in the vapor. In the crystalline solid the bands are much narrower and several peaks occur. The two modes appear to be separated in all four methanols by about 20 to  $30\text{ cm}^{-1}$ . This is readily accounted for by the occurrence of Fermi resonance between one of the internally asymmetrical  $\text{CH}_3$  stretching modes and the first overtone of one of the  $\text{CH}_3$  bending modes, resulting in a shift of both the overtone and the stretching mode.

Bands occur in the spectrum of  $\text{CH}_3\text{OH}$  and  $\text{CD}_3\text{OH}$  at  $1370$  and  $1354\text{ cm}^{-1}$  at  $-180^\circ\text{C}$ . The intensity of these bands decreases very markedly as the temperature is increased and small shifts of frequency downwards occur. The downward shifts are consistent with the bands' being first overtones of the OH out-of-plane bending mode at  $685\text{ cm}^{-1}$  in both  $\text{CH}_3\text{OH}$  and  $\text{CD}_3\text{OH}$ , and the intensity is possibly due to Fermi resonance with the OH in-plane bending mode that is symmetrical relative to the chain. The resonance decreases as the frequency of the out-of-plane bending mode shifts downward with rising temperature.

#### 4. DISCUSSION OF SPECTRA OF CRYSTALLINE SOLIDS

##### 4.1 $\beta$ -Phase

The high temperature ( $\beta$ ) phase of methanol belongs to the centro-symmetrical space group  $D_{2h}^{17}-Cmcm$ .<sup>37</sup> The molecules are arranged in hydrogen-bonded zig-zag chains and two chains, each containing two molecules,

<sup>37</sup> K. J. Tauer and W. N. Lipscomb, *Acta Cryst.* **5**, 606 (1952).

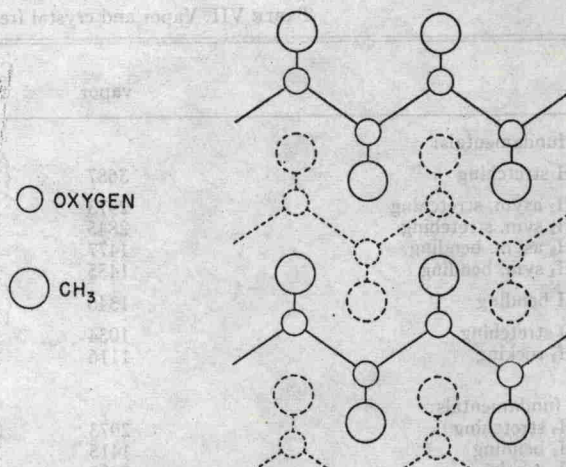


FIG. 7. Diagrammatic sketch of the crystal of methanol. Atoms represented by solid lines are in the plane of the paper, and those represented by broken lines are below the plane of the paper.

pass through the unit cell. The structure is shown diagrammatically in Fig. 7. The full symmetry of the x-ray diffraction pattern implies that the methyl group (treated as one atom) and the oxygen and hydrogen atoms of one chain lie in one plane, and that the hydrogen atoms are midway between the oxygens. The rather large thermal amplitude of approximately  $0.32\text{ \AA}$  rms perpendicular to the chain<sup>37</sup> and the high dielectric constant of the  $\beta$ -phase<sup>34,38,39</sup> were interpreted<sup>27</sup> to indicate that the apparent x-ray symmetry might be the mean of two forms in which the methyl groups are off the plane of the oxygen atoms in the same chain.

The only infrared-active fundamental modes of a crystal are those which are totally symmetrical with respect to translation, i.e., those in which all unit cells vibrate in phase.<sup>40,41</sup> If the crystal is anharmonic then combinations of forbidden fundamentals with lattice modes may be active, and their intensity will probably be quite strongly temperature-dependent. In none of the bands that we observed does the intensity increase markedly as the temperature increases from  $-180^\circ\text{C}$  to  $-108^\circ\text{C}$ , and so we will assume that only allowed fundamentals are seen.

There are four molecules in the unit cell, and consequently each internal mode of the isolated methanol molecule gives four modes in the crystal that may be active, and so some splitting of the frequencies of the isolated molecule is expected.

Experimentally, each of the three bands that are due to the motions of the O-hydrogen atoms have two components of comparable intensity, usually about 50 to  $100\text{ cm}^{-1}$  apart. The other bands are either not split

<sup>38</sup> C. P. Smyth and C. S. Hitchcock, *J. Am. Chem. Soc.* **56**, 1084 (1934).

<sup>39</sup> C. P. Smyth and S. A. McNeight, *J. Am. Chem. Soc.* **58**, 1597 (1936).

<sup>40</sup> S. Bhagavantam and T. Venkatarayudu, *Group Theory and its Applications to Physical Problems* (Andhra University, Waltair, India, 1951).

<sup>41</sup> D. F. Hornig, *J. Chem. Phys.* **16**, 1063 (1948).