

FIG. 8. Symmetry of one chain in the methanol crystal.

or are split by only 10 to 20 cm^{-1} , and the higher-frequency component is usually far less intense than the lower. It seems very likely that the splitting of the O-hydrogen bands is due to coupling of the motions of molecules in the same unit cell. The splitting of the other bands is referred to below.

We consider first the spectrum of the whole unit cell.

Space-Group Analysis

For analyzing the crystal spectrum, the analysis based on the factor group of the space group^{40,42} is appropriate. The factor group of the space group D_{2h}^{17} is isomorphous with the point group D_{2h} . We call the a , b , and c axes of the unit cell the x , y , and z directions, so that the x axis is perpendicular to the plane of the chains, the z axis is parallel to the chain axis, and the y axis is the remaining axis. Under the symmetry D_{2h} both the OH stretching and OH in-plane bending modes split into four components in the crystal, two, of species b_{1u} and b_{2u} , being infrared-active, and two, of species b_{1g} and b_{2g} , being Raman-active. The OH out-of-plane bending vibration gives four components in the crystal, one of which, of species b_{3u} , is infrared-active, two, of species a_g and b_{1g} , are Raman-active, and one, a_u , is forbidden in both Raman and infrared spectra. We find experimentally that the OH stretching and in-plane bending modes give two infrared-active modes, as expected, but the OH out-of-plane bending mode also gives two components, which disagrees with the above predictions. The possibility that the splitting occurs because of Fermi resonance with an overtone is very unlikely because similar bands occur in all four methanols. It follows, therefore, that the symmetry of the unit cell is lower than the apparent x-ray symmetry.

There are two possible causes of the high apparent x-ray symmetry. Either the hydrogen atoms are not observed, or the chains are of lower symmetry, but they are irregularly oriented in such a way as to give this apparent x-ray symmetry. It seems likely, therefore, that either the O-hydrogen atoms are not at the midpoint of the line joining the oxygen atoms, or the methyl groups are not coplanar with the oxygen atoms, or both these dissymmetries occur. Whichever occur, each chain has two possible orientations, and it is likely

that these orientations are irregularly distributed, so giving the apparent x-ray symmetry. If this occurs, then there are no rigorous selection rules. However, as only a limited number of bands occurs, approximate selection rules must hold, and these are almost certainly those appropriate for an isolated chain. The isolated-chain approximation has frequently been used for discussing the spectrum of polymer molecules,⁴³⁻⁴⁶ in which, however, the covalent bonding along the chains is much stronger than the hydrogen-bonding in the methanol chains. Accordingly, we now discuss the spectrum expected for an isolated chain.

Line-Group Analysis

A possible structure of the isolated chain that is consistent with the observed x-ray symmetry and with the arguments of the foregoing paragraphs is a chain in which the carbon, oxygen, and hydrogen atoms are coplanar and the hydrogen atom is not midway between the two oxygen atoms. The spectrum of the chain is best considered in terms of the one-dimensional space group (or line group)⁴⁴ that describes the symmetry of the chain. The symmetry elements of the chain (Fig. 8) are an infinite number of translations along the z axis, one C_2 screw axis along the z axis, one reflection plane yz , and one glide plane xz . The only modes that are potentially active in infrared or Raman spectra are those that are in phase in all unit segments of the chain,^{43,44} and consequently the factor group of the line group is appropriate for analyzing the spectrum. It is isomorphous with the point group C_{2v} . Under this symmetry both the OH stretching and OH in-plane bending modes give two components, of species a_1 and b_2 , both of which are infrared-active, as observed. The two components of the OH out-of-plane bending mode are of species a_2 and b_1 , of which only the b_1 mode is infrared-active. Since two infrared modes are observed, then the planar chain with the hydrogen not midway between the two oxygen atoms is not consistent with the infrared spectrum. It follows that further relaxation of the symmetry is necessary, and hence that either the carbon or the hydrogen or both are out of the plane of the oxygen atoms.

We now inquire whether the spectrum is consistent with the methyl group's being out of the plane of the oxygen atoms and the hydrogen atom's being midway between the oxygen atoms. The assumed structure of the chain is that of the low-temperature form (see below) in which the methyl groups on one side of the chain are above the plane of the oxygen atoms and those in the other side are below the plane. There are two possible chains consistent with this structure according

⁴³ C. Y. Liang, S. Krimm, and G. B. B. M. Sutherland, *J. Chem. Phys.* **25**, 543 (1956).

⁴⁴ M. C. Tobin, *J. Chem. Phys.* **23**, 891 (1955).

⁴⁵ R. E. Moynihan, *J. Am. Chem. Soc.* **81**, 1045 (1958).

⁴⁶ A. Novak and E. Whalley, *Trans. Faraday Soc.* **55**, 1484 (1959).

⁴² H. Winston and R. S. Halford, *J. Chem. Phys.* **17**, 607 (1949).

as the methyl groups on a particular side of the chain are above or below the plane of the chain. They are assumed to be irregularly distributed so as to give the x-ray symmetry. We assume, as we assumed above, that, although rigorous selection rules do not hold, the observed spectrum is closely related to the spectrum of an isolated chain. The corresponding point group is C_{2h} . The hydrogen atom is at the center of symmetry, and so all motions of the hydrogen atom destroy the center of symmetry. Their species are therefore either a_u or b_u and they are allowed in the infrared spectrum.

The infrared spectrum thus strongly confirms Tauer and Lipscomb's somewhat tentative suggestion that the chains in methanol are puckered. It does not prove that the O-hydrogen atom is not midway between the oxygen atoms, though this seems likely by analogy with other compounds.

We now discuss briefly the splitting of the vibrations that do not involve mainly O-hydrogen atoms. If the symmetry of the chain is C_{2h} , then in the isolated-chain approximation only one active vibration occurs for each of these vibrations in the vapor. If the symmetry C_{2h} is destroyed by moving the O-hydrogen atom, it is likely that the intensity of bands that were forbidden and that now become active will be rather low. This agrees with experiment. Another explanation of the experimental results is that the low-intensity component is due to a combination of the main vibration with a low-frequency lattice vibration. It is not possible at present to decide between these two explanations and so the chain symmetry C_{2h} cannot be rigorously eliminated.

4.2 α -Phase

According to Tauer and Lipscomb the low-temperature (α) phase has probably the space symmetry $C_{2h}^2 - P2_1/m$.³⁷ The molecules are arranged in hydrogen-bonded zig-zag chains, the methyl groups on one side being above the plane of the oxygen atoms and the methyl groups on the other side being below. Weak superlattice reflections suggested that the unit cell may be twice that proposed and that perhaps the methyl groups are alternately staggered relative to their neighbors in the chain. Such small changes in symmetry should make no detectable difference in the infrared spectrum and are neglected in this discussion.

No significant change in spectrum is observed in passing from the β to the α phase. The heat of transition is only 170 cal mole⁻¹³⁶ so only very small shifts of frequency are expected. The number of fundamental bands does not alter, and hence the selection rules are not significantly altered, as expected for the structure of the α -phase proposed by Tauer and Lipscomb. If we neglect a possible superlattice, there are only two molecules in the unit cell. If the hydrogen atoms are midway between the oxygen atoms then the point group isomorphic with the factor group is C_{2h} , and as discussed above each of the three O-hydrogen motions should give two

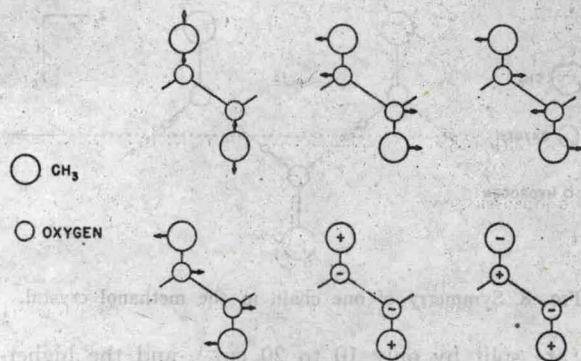


FIG. 9. Expected infrared-active fundamentals of a methanol chain that involve motion of the whole molecules.

infrared-active components. Any reduction in symmetry will not affect the number of infrared-active bands due to the motions of the O-hydrogen atom.

4.3 Lattice Modes

A weak, moderately broad band occurs in the spectrum of CH₃OH at -180°C at 520 cm^{-1} and in CD₃OH at $\sim 510\text{ cm}^{-1}$. The OD out-of-plane bending bands obscure any band of similar frequency that may occur in CH₃OD and CD₃OD. A moderate, sharp band occurs in the spectra of all the methanols at the following frequencies at -180°C : CH₃OH, 357 cm^{-1} ; CH₃OD, 344 cm^{-1} ; CD₃OH, 339 cm^{-1} ; CD₃OD, 331.5 cm^{-1} . The frequency of all these bands decreases on warming, and the bands are not observed in the liquids. In the spectra of the vitreous films the band near 500 cm^{-1} is not observed, and the bands near 340 cm^{-1} are considerably broader and at a lower frequency than in the crystalline films. The isotope shifts for both bands are small, and so they cannot be connected with the CH₃ internal rotation. Neither is it possible to explain them as difference bands involving the internal fundamentals. They must, therefore, be due to external modes of the molecules. The 500-cm^{-1} band is quite weak and it might be an overtone.

Since there are two molecules in the unit cell in the α phase, neglecting the possible superlattice, there are six nonzero fundamentals in which the whole molecules move that are potentially active in the infrared. These are roughly represented in Fig. 9. Modes 1 and 2 are closely related to translational modes of the isolated molecules. The four other modes that are derived from the translations of isolated molecules are three translations of the chain and one rotation about the chain axis, which are of zero frequency in the isolated chain. If the symmetry of the chain is C_{2h} , and the O-hydrogen atoms are midway between the oxygen atoms then vibrations 1, 2, 3, and 6 of Fig. 9 preserve the center of symmetry and should be infrared-inactive. Vibrations 4 and 5, which destroy the center of symmetry should be infrared-active. The first overtones of all these vibrations are fully symmetrical and should be infrared-in-