

AN ABSTRACT OF THE THESIS OF

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Title: THE INFRARED AND FAR-INFRARED SPECTRA OF SUBLIMED

FILMS OF FORMALDEHYDE

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The infrared spectra of liquid and solid films of formaldehyde were taken over the range of 35 to 4,000  $\text{cm}^{-1}$  using Beckman IR 7 and IR 11 spectrometers. A new overtone band and a new combination band were found as well as three fundamental peaks due to lattice vibrations and several peaks arising from combinations of internal and external modes of vibration. The peak at 180-195  $\text{cm}^{-1}$  is very strong and appears to be due to libration of the formaldehyde molecule about the principal axes perpendicular to the axis of the carbon-oxygen bond. The considerably weaker peaks appearing at 60 and 100  $\text{cm}^{-1}$  probably are due to rotation about the axis of the carbon-oxygen bond and to translation. The spectrum obtained in the near infrared region is essentially the same as the spectrum reported by Harvey and Ogilvie. The frequency shifts of the peaks for different states of condensation indicate that hydrogen bonding does not occur in the liquid or solid and that the intermolecular binding forces are due

largely to dipole-dipole interactions.

The Infrared  
and Far-Infrared Spectra of Sublimed Films of Formaldehyde

by

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THE INFRARED  
AND FAR-INFRARED SPECTRA OF SUBLIMED FILMS OF FORMALDEHYDE

CHAPTER I  
INTRODUCTION

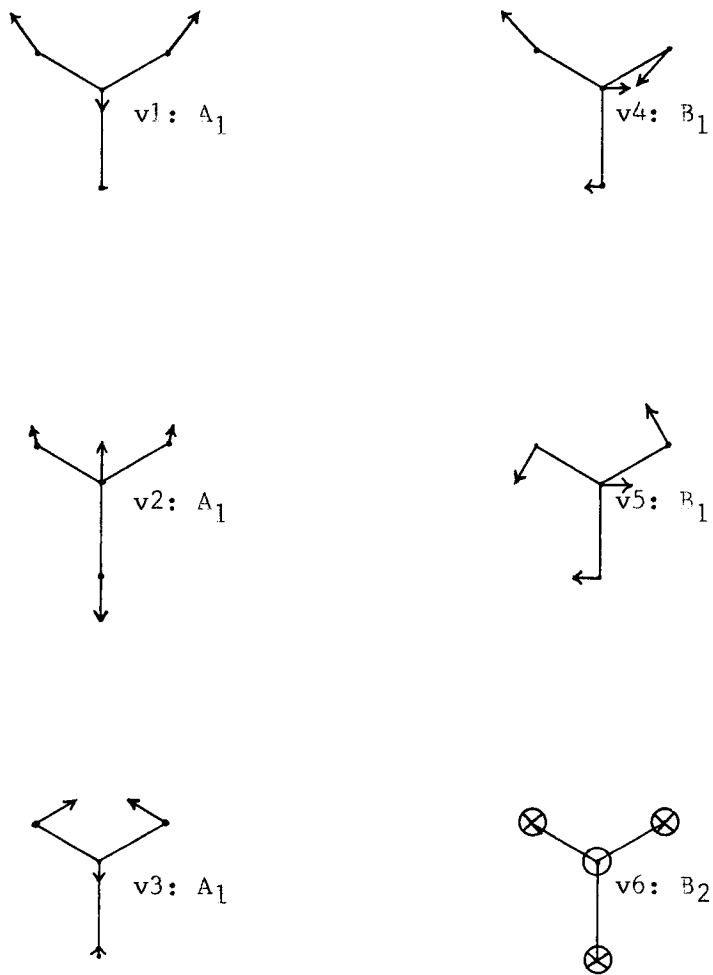
Atomic and molecular systems are generally believed to be adequately described by quantum mechanics. Using classical and quantum mechanics, one can find the motion of a particle if one knows the forces acting on the particle. Molecular forces are electromagnetic and described by a potential field. The behavior of a molecule or set of molecules then is determinable from a knowledge of the potential field associated with it. The information concerning the potential field of a molecular crystal which may be obtained from an infrared spectrum provides the motivation for this thesis.

The normally employed method of using vibrational spectra for obtaining information about the potential fields of molecules is the normal-coordinate method developed by Wilson (31), though less convenient integral techniques may also be used (7,9,20,33). The method essentially represents an attempt to describe the normal modes of vibration of a molecule. It makes use of the fact that the set of simultaneous differential equations describing the classical molecular motion in the harmonic approximation may be expressed

as an eigenvalue problem having the solution  $\det(GF - \lambda I) = 0$ , where the G and F matrices are defined by the equations  $2T = \dot{q}G\dot{q}$  and  $2V = qFq$ , in which T is the kinetic energy, V is the potential energy, and q is a mass-weighted cartesian coordinate. The determinant  $\det(GF - \lambda I)$  is called the secular determinant and the matrix  $D = GF$  is often called the dynamical matrix. Many calculations (3,5,6,13) using this method have been carried out for the formaldehyde molecule using infrared and microwave gas-phase data (1,8,11,12,16,17,23) as a basis, so that the normal motions of formaldehyde in the gaseous phase are well known. The six normal modes of vibration of formaldehyde are commonly labelled by a numerical subscript in order of decreasing symmetry and then frequency. Thus the  $\nu_1$ ,  $\nu_2$ , and  $\nu_3$  modes are symmetric with respect to the principal axis of the molecule and have frequencies  $\nu_1 > \nu_2 > \nu_3$ . The type of motion and the symmetry of the motion occurring for each of the six normal modes of formaldehyde are shown in Figure 1.

The normal-coordinate method is easily extended to an aggregate of molecules simply by treating the aggregate itself as a single entity or molecule. Using the adiabatic approximation, in which the electronic energy function is treated as a constant, allowing the molecular energy to be considered as a unique function of the nuclear coordinates, the interatomic wave equation of a molecule or molecular

Figure 1. Normal Coordinates of Formaldehyde Vibrations





aggregate may be approximately separated into three equations: one for translation of the system as a whole, one for rotation, and one for vibration, if the proper coordinates are used. The application of the vibrational equation to a molecular system is thoroughly discussed in the book by Wilson, Decius, and Cross (31). For a large molecular aggregate the translational and rotational equations may be disregarded if the aggregate is of macroscopic dimensions; that is, the interaction between vibration and other types of motion will be negligible, allowing the vibrational equation to be used without correction. The large number of parameters needed to solve the vibrational equation for a crystal, however, precludes any practical use for the exact equation. Simplifying assumptions must therefore be introduced to reduce the number of parameters and allow the determination of approximate solutions.

The most important general aid in the determination of crystal force fields is a knowledge of the crystal structure or symmetry, which can be obtained only by X-ray or neutron diffraction at the present time. If the crystal structure of formaldehyde were known, a detailed normal-coordinate analysis could be carried out using techniques which have been developed quite recently (2,4,22,24,25,27,30). Since the crystal structure of formaldehyde has not been determined, the normal-coordinate methods cannot be used here. There

is some hope, though, that the infrared data will give information on the crystal symmetry and on certain basic aspects of the crystal structure. If such information can be obtained, one can then use the information in a more sophisticated analysis and obtain, by this "pulling at the bootstraps", a crude understanding of the nature of the intermolecular and intramolecular forces in the crystal. Several assumptions must be made, though, before the infrared data can be interpreted without the aid of crystal-structure data. First, one must assume that the crystal vibrations have wave vectors which are equal to zero, which corresponds to having all of the unit cells of the crystal in phase with one another. The problem then is reduced to that of determining the vibrations of a single unit cell. Second, because the forces between molecules are much smaller than the forces between atoms of a single molecule in a molecular crystal, one may further simplify the problem by separating the crystal vibrations into internal and external, or lattice vibrations. In internal vibrations the atoms of a molecule move in such a way that the center of gravity of the molecule remains at rest and no rotation of the molecule occurs. In external vibrations each molecule as a whole undergoes rotational and translational motion. External modes are designated by the term symbols  $R_x$ ,  $R_y$ ,  $R_z$ ,  $T_x$ ,  $T_y$ , and  $T_z$ .

One may now approach the problem by introducing the lattice forces as a perturbation on the molecular forces in the unit cell. If one does not know the structure of the unit cell, as is the case here, one must then analyze the splittings which arise from the perturbations to determine which symmetries or structures are consistent with the observed pattern. Similarly, one may determine the symmetries or structures consistent with the pattern produced by the lattice modes and their combinations with the internal vibrations. Further details on the use of the "unit-cell" and "site-group" analyses may be found in the references in the bibliography (10,18,32). Information may also be gained from line-widths, changes in the intensity of peaks, and from other sources. A review (10) summarizing these empirical methods in the vibrational analysis of molecular crystals has been written by David A. Dows.

This study was initiated with the purpose in mind of determining as completely as possible the infrared spectrum of formaldehyde in its condensed phases and to determine from such data, using the methods described above, the behavior of the molecule in association with itself. The question of whether there is any hydrogen bonding or appreciable deformation of the molecule in the condensed phases is of special interest. It was also hoped that the data would be of use in the future determination of a general

force field for formaldehyde. Only two publications (15,26) have appeared to date on the spectral properties of condensed formaldehyde, both of which are investigations of the infrared spectrum of the molecule. In both publications the liquid phase was not investigated, and the spectral region studied was confined to the 650 to 4,500  $\text{cm}^{-1}$  region. In the publication of Harvey and Ogilvie (15) the spectrum of formaldehyde molecules trapped in an argon lattice was also studied. The high resolution and wide spectral region used in the present study should provide much new information, allowing a more detailed analysis of the nature of the forces involved in the self-association of formaldehyde molecules.

## CHAPTER II

## EXPERIMENTAL PROCEDURE AND RESULTS

Samples of formaldehyde were prepared by the author according to the method of Spence and Wilde (28). Commercial paraformaldehyde was placed in a petri dish and dried for at least two days in vacuum over anhydrous calcium sulfate. The dried polymer was then placed in bulb A of the distillation apparatus diagramed in Figure 2, where it was heated to 120 degrees centigrade with an oil bath while the traps B and C were being alternately heated by a gas flame and evacuated, thus freeing the walls of the traps of adsorbed oxygen. The stopcock F was closed, coolants were added to the traps, and the distillation allowed to proceed until several milliliters of monomeric formaldehyde had collected in the sample bulb C. Stopcock E was then closed and the formaldehyde stored in the sample bulb at liquid-nitrogen temperature for several weeks before a new sample was prepared.

Thin films of formaldehyde were prepared by subliming the formaldehyde directly from the sample bulb to the central window of an infrared cell of Wagner and Hornig (29) type. Adapters were added, so that the cell could simultaneously be connected to a vacuum pump and to the sample bulb. In a typical run the cell and all connecting chambers were evacuated and the centerpiece cooled by adding liquid nitrogen

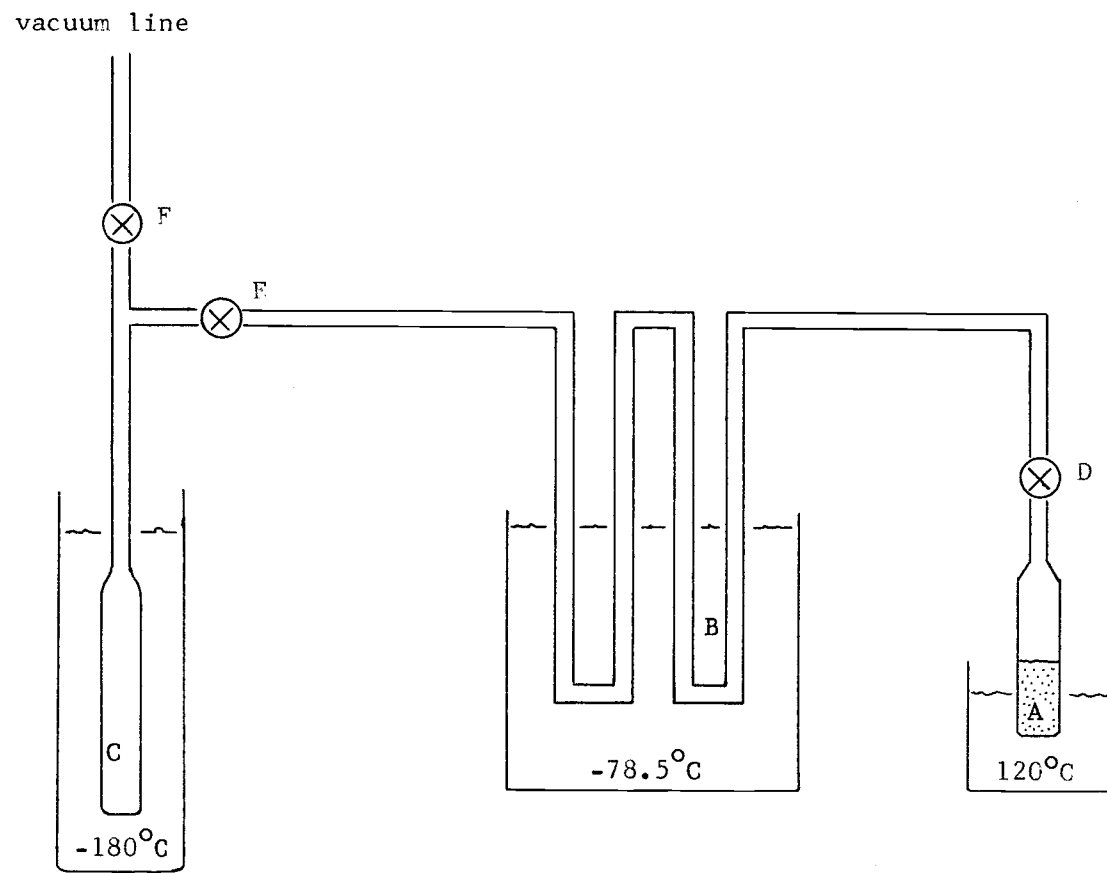


Figure 2. Distillation Apparatus

to the cold-finger. After allowing about thirty minutes for the centerpiece to cool to liquid-nitrogen temperature, the stopcock connecting the sample bulb to the cell was opened, and the sample bulb was allowed to warm up until the contents became liquid. The vapor pressure difference between the liquid formaldehyde and the formaldehyde in the cell was sufficient to cause rapid sublimation into the cell. When the film had reached the desired thickness, all connecting stopcocks were closed, and a spectrum of the sublimed film was taken. The film thicknesses were estimated as between 0.01 and 0.1 millimeter; the films used in the far infrared were of about twice the thickness of the films used in the near infrared.

The spectra were taken over the complete range of 35 to 4,000  $\text{cm}^{-1}$  with Beckman IR 7 and IR 11 infrared spectrometers which were purged of atmospheric moisture. Previous calibrations of the instruments indicate that all of the recorded frequencies are accurate to within one  $\text{cm}^{-1}$ . Sodium chloride and potassium bromide windows were used in taking the infrared spectra, and high-density polyethylene was used for the far-infrared region. An evacuated gas cell with polyethylene windows was placed in the reference beam in taking the far-infrared spectra. Spectra of liquid formaldehyde were taken only in the near infrared region, since warming of the solid films resulted in a resublimation off

of the central window when polyethylene was used as a substrate. The resublimation was caused by the heat liberated on condensation not being taken away quickly enough by the polyethylene, which has a low heat capacity and conductivity.

The spectra obtained are shown in the third figure; the far-infrared spectra are shown with the background noise omitted. The assignments and frequencies of all of the observed peaks are given in Table 1. Spectrum A is of a film which was obtained by solidification of a liquid film; the shape of the peak appearing at approximately  $1880\text{ cm}^{-1}$  was not reproducible. The absolute intensities of the peaks could not be compared with the results of Harvey and Ogilvie or Schneider and Bernstein because they did not report the thicknesses of the films they used.



mode	gas (16)	solid 77° (26)	solid 77° (15)	solid 4° (15)	liquid (this work)	solid 100° (this work)
v7: T						62w
v8: T						100m
v9: R <sub>x</sub> , R <sub>y</sub>						180-190vs
v6			1167.5vw	1172w		1166vw
v6	1163.5	1177w	1174 <sub>m</sub>	1174 <sub>m</sub>	1180m	1175w
v6			1177s	1176sh		1178m
v5				1241w		
v5			1239.5w	1244sh		1240w
v5			1246s	1246s		
v5	1247.4	1247m	1250vs	1250vs	1250m	1245-52s
v3			1490sh			
v3	1500.6	1491s	1495vs	1494vs	1500s	1495vs
v3			1506sh			
v2	1746.0	1712s	1711vs	1715vs	1730vs	1711vs
v2			1720sh			
v2 + v8						1825w
v2 + v9						1875m
v2 + v9						1920vw
2v5						2495w
v3 + v5		2729w	2727m	2727w		
v1	2766.4	2834s	2829vs	2829vs	2820s	
v4	2843.4	2890s	2885s	2885s	2885-90s	
2v3		2960m				
v2 + v5	3003.3	2997s	2991vs	2993m	3000m	
2v2		3414w	3402w	3404w	3428m	
?					3440w	
v1 + v2			4535vw			
v1 + v2			4539sh			
v2 + v4			4562w			

Table 1. Frequencies and Assignments for Formaldehyde Vibrations

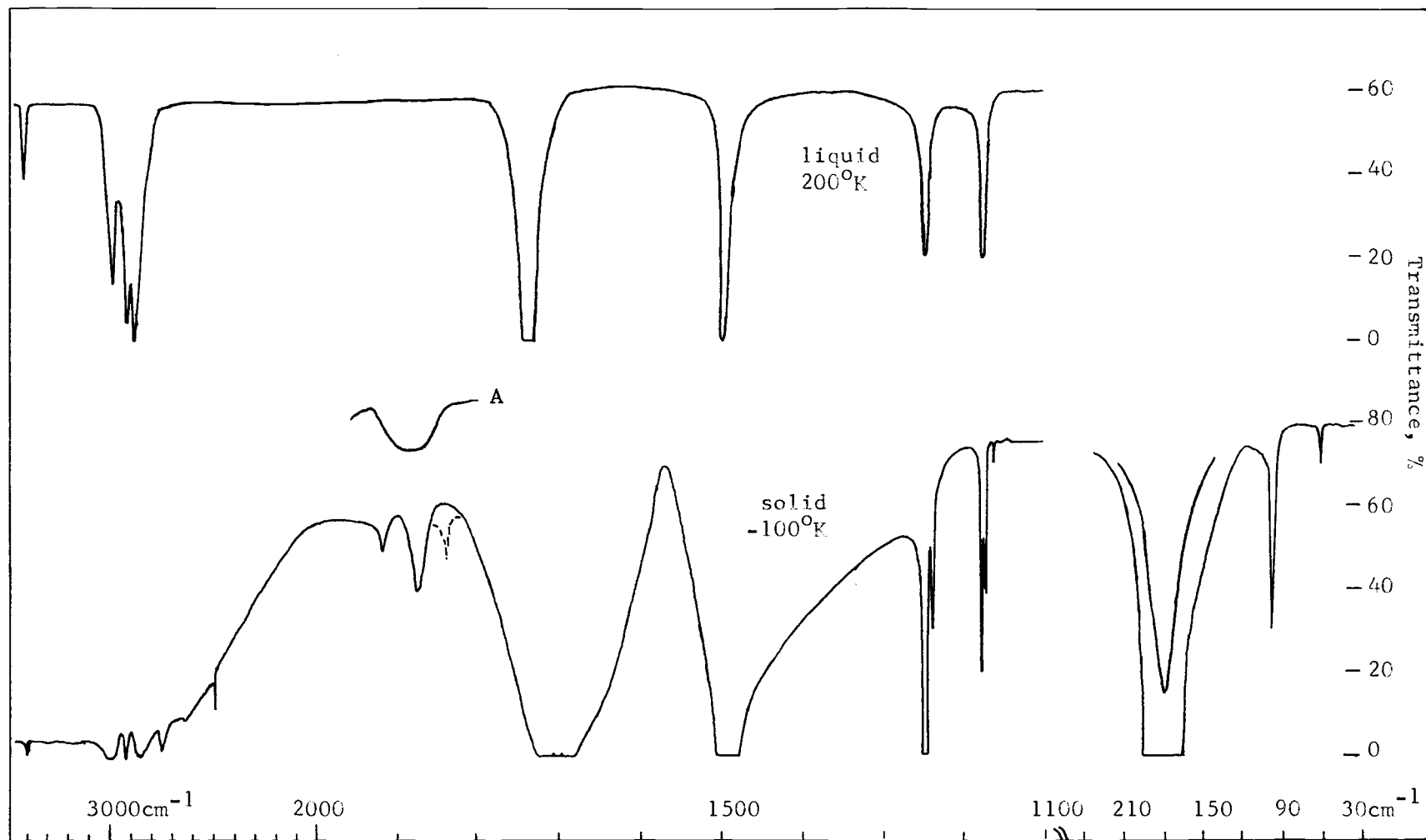


Figure 3. Infrared Spectrum of Condensed Formaldehyde

## CHAPTER III

## DISCUSSION AND CONCLUSIONS

For several reasons it is thought that the sublimed films used in this investigation were crystalline rather than amorphous. First, the fine structure of the  $\nu_5$  and  $\nu_6$  peaks was reproducible and distinct; in amorphous or semi-amorphous films peaks are generally broad and susceptible to change (21). Second, no changes in the spectra were observed upon warming the films; an amorphous film usually anneals into a crystalline form upon warming, resulting in an irreversible change in the spectrum. Harvey and Ogilvie also have observed no such changes for formaldehyde, but Schneider and Bernstein noted a change near the melting point for both formaldehyde and acetaldehyde and attributed the change to a phase transition. The existence of two crystalline phases, however, is doubtful in view of the spin-lattice relaxation time studies on acetaldehyde by Grude, et. al. (14). Third, the sublimation was rapid, a condition known to favor the formation of crystalline films (21).

Formaldehyde has been thoroughly studied in the gas phase, and from the gas-phase spectrum the assignments for the purely intramolecular vibrations of the solid and liquid phases are easily made. Two assignments,  $2\nu_5$  and  $\nu_2 + 185$ , are made of previously unobserved peaks. The lattice modes,

that is, the peaks in the far-infrared region, are labelled  $\nu_7$ ,  $\nu_8$  and  $\nu_9$  for convenience and are left as unassigned since the crystal structure of solid formaldehyde has not yet been determined.

Some insight into the nature of the lattice vibrations, though, may be obtained by using theoretical arguments and crude physical models. Librational modes, for example, would be expected to occur at higher frequencies than purely translational modes because of the smaller mass involved in a librational motion. Similarly, purely librational modes would be expected to have frequencies which would be roughly inversely proportional to the square roots of the moments of inertia of the principle axes about which the librations occur. Using the data on gaseous formaldehyde, one would then predict a frequency ratio of 1.00 to 1.07 to 2.83 for the librational modes of the solid. Thus the broad and intense peak at  $180\text{-}190\text{ cm}^{-1}$  could correspond to the two librations about the principle axes perpendicular to the axis of the double bond. Further, these two modes would be expected to be rather intense, a large change in dipole moment being associated with them, whereas the third librational mode would be expected to be unobserved (experimental results) or to appear very weakly at about  $450\text{ cm}^{-1}$ . The force constant for the third mode, however, would probably be considerably smaller than the force constants for the other two

librational modes, giving it a frequency lower than  $450 \text{ cm}^{-1}$ ; thus one of the two peaks at  $60$  and  $100 \text{ cm}^{-1}$  could be of librational character rather than translational, as predicted by the moment-of-inertia model.

One may calculate the expected intensities for the librational modes using the oriented-gas model if one neglects the molecular polarizability and assumes that the molecules are sufficiently restrained in the lattice that the librational motion is harmonic with respect to the angular displacement coordinate  $\theta_i$ . The predicted integrated absorption coefficients for these modes would then be given by

$$A_i = \frac{N \pi}{3,000 c^2} \left( \frac{\partial \mu_i}{\partial Q_i} \right)^2 \quad (1)$$

Upon substitution of the normal coordinate  $I_i^{1/2} \theta_i = Q_i$ , the equation reduces to

$$A_i = \frac{N \pi}{3,000 c^2} \frac{\mu_i^2}{I_i} \quad (2)$$

where  $N$  is Avogadro's number,  $c$  is the speed of light,  $\mu_i$  is the dipole moment along one of the principal axes, and  $I_i$  is one of the principal moments of inertia.  $A_i$  will be given in darks if cgs units are used for all of the other quantities. Using the gas-phase values reproduced by Herzberg (16, p. 612) for the molecular constants and the value of 2.33D (19) for the dipole moment, equation (2) predicts intensities of 1,780 and 1,560 darks for the two active librational

modes. From observation and taking into account the extra thickness of the films in the far-infrared region, one would estimate the peak at  $180\text{-}190\text{ cm}^{-1}$  to be about one half as intense as the peaks at  $1500$  and  $1700\text{ cm}^{-1}$ . Since the intense internal modes have intensities of about 7,000 darks in the gas phase (17), one would estimate the intensity of the  $180\text{-}190\text{ cm}^{-1}$  peak as about 3,500 darks, in good agreement with the oriented-gas model value of 3,340 darks.

The fine structure of the  $\nu_5$  and  $\nu_6$  bands may be attributed to several causes. The presence of about one percent of  $\text{C}^{13}$  in the samples may be expected to give rise to very weak satellite peaks below the main peaks. The spectral shifts for  $\nu_5$  and  $\nu_6$  have been calculated by Harvey and Ogilvie (15) to be 9 and  $12\text{ cm}^{-1}$ . Consequently, the peaks at  $1240$  and  $1166\text{ cm}^{-1}$ , which are shifted 9 and  $12\text{ cm}^{-1}$  from the main peaks, owe at least some, if not all, of their intensity to the presence of  $\text{C}^{13}$ . The further splitting of the  $\nu_6$  peak is most likely due to the presence of more than one molecule in each unit cell of the crystal.

The frequency shifts of  $\nu_1$  and  $\nu_2$  upon condensation indicate that in the condensed phases the formaldehyde molecules are bound to one another by oxygen-carbon rather than oxygen-hydrogen bonds and that this bonding is stronger in the solid than in the liquid. The ease with which liquid or solid formaldehyde polymerizes also attests to an association

via oxygen-carbon bonds for this molecule.

Finally, some information about the lattice vibrations may be obtained by comparing the data with the spectra of similar compounds. Thus deuterium, oxygen-eighteen, and carbon-fourteen isotopes may be used to determine the isotopic frequency shifts for formaldehyde. Often the nature of the vibrations can then be determined, since the isotopic shift is proportional to the degree of participation of the isotope in the vibration. No such studies have yet been undertaken for condensed formaldehyde. Often isoelectric or isostructural compounds can also be compared to advantage. A comparison of formaldehyde with ethylene, oxygen, phosgene and some compounds having the same crystal structure as formaldehyde would be useful, but easily interpreted far-infrared spectra of these compounds are not available.

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