A STUDY OF THE INFRA-RED SPECTRA OF SOME REACTIVE SPECIES

by

John Franklin Ogilvie

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We accept this thesis as conforming to the required standard.

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Department of <u>Alms</u>

The University of British Columbia, Vancouver 8, Canada.

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ABSTRACT

Although there have been recorded many spectra of dispersions of reactive and unreactive molecules in inert matrices, there has been no real attempt to explain quantitatively the nature of the forces and interactions of these matrices that act on the molecular vibrations of the trapped species.

In the present study the infra-red spectra of formaldehyde and water in solid argon and nitrogen matrices and of solid formaldehyde are used as a basis for a discussion and analysis of the conditions that prevail in such matrices.

Isotope effects, molecular association, intermolecular coupling, rotation, the effect of trapping in different lattice positions, and matrix-gas frequency shifts are considered in the interpretation of the observed spectra.

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CHAPTER I. INTRODUCTION

I-1 The Problem

Two reactive species were investigated in the experimental part of this research. Because part of the inquiry as originally proposed was concerned with the formyl radical, formaldehyde, a by-product of some reactions which produce formyl, was studied. Preliminary spectra proved so interesting that it was realized there was much to explain of the nature of the conditions existing in a solid matrix.

Infra-red spectra of formaldehyde being such as to make a rotation hypothesis worth considering, the nuclear magnetic resonance spectrum of formaldehyde and the infra-red spectrum of water in a matrix were studied. An n. m. r. spectrum can often indicate, by the width of the observed absorption line, the presence of certain types of molecular motion (17). The water molecule has been the subject of several low temperature investigations, including some (1, 2, 3) in which molecular rotation in the lattice of an inert matrix was proposed to explain the observed spectra. Thus the obtaining of spectra of water by employing an experimental technic similar to that of the formaldehyde trials could provide information concerning the efficiency of isolation by the technic, and the plausibility of rotation as an explanation of the formaldehyde spectra.

Both the formaldehyde and water molecules are reactive, the former to polymerisation and the latter to a hydrogen-bonded condensed state association. Other common properties of these molecules include the same symmetry point group, C_{2v} , the same nuclear spin statistical weight factors, and well investigated

gas phase vibration-rotation spectra. These two molecules are therefore relatively closely related for the purposes of this investigation.

The method used to stabilise these reactive substances is the matrix isolation technic, which, in various modifications and applications to the spectroscopic study of reactive chemical species, has proved a useful experimental advance (21) - The method consists essentially of forming and freezing the species of interest (R) with a transparent, inert matrix (M) at a temperature sufficiently low (probably less than thirty to fifty per cent (4) of the melting point of the matrix material) that diffusion of the species R does not appreciably occur. Such substances as the rare gases, homopolar diatomic molecules (such as oxygen and nitrogen), and perhaps, for special purposes, infra-red absorbing molecules like carbon monoxide and carbon tetrachloride, are The suitable as matrices for infra-red spectroscopic studies. matrix ratio M/R can be sufficiently great, that the spectrum of R is not complicated by the effects of association of R. In the case that the latter condition applies, and due to the low temperatures involved, observed infra-red bands are considerably sharpened relative to band widths observed for pure solid and liquid substances at similar and higher temperatures. The conditions inherent in the matrix technic are similar therefore to those of an ideal gas, with the additional advantage that rotational effects, if any, will be small, due to the small number of rotational levels appreciably populated at the low temperature. Thus spectroscopic studies of reactive or strongly interacting species may be carried out without the complication

of overlapping rotational bands, as are prevalent in gas phase spectra.

I-2 Methods of investigation

The methods of investigation of this problem were the following:

- (a) the infra-red spectra of both water and formaldehyde were recorded in the gaseous and solid matrix states, and, for formaldehyde, in the solid state;
- (b) the proton magnetic resonance spectrum of formaldehyde was obtained to check the possibility of rotation;
- (c) a valence force potential function was assumed in order
 to calculate isotopic frequency shifts for the fundamental
 vibration modes of formaldehyde;
- (d) the influence of association of active species Wqs examined, and
- (e) the effects of some kind of molecular rotation and of various trapping sites were considered.

CHAPTER II. EXPERIMENTAL

II-1 Chemicals

The formaldehyde gas used in these experiments was prepared by heating paraformaldehyde (polyoxymethylene). The latter was in turn prepared in all cases by precipitating the polymer from Baker and Adamson reagent grade formalin solution, in some cases simply by allowing the formalin solution to evaporate, and in other cases by making the solution, filtered clear, slightly alkaline with sodium hydroxide, then collecting and washing the new precipitate that appeared after a day. All precipitates were then dried over anhydrous calcium chloride in a vacuum desiccator for a few days, then stored in another desiccator under atmospheric pressure until used. The melting points of a base-precipitated sample and an ordinary precipitate were respectively 170-171°C. and 175-176°C., compared with 180-181°C. and 143-145°C. for commercial technical and chemically pure paraformaldehyde samples. The infra-red spectra of the polymers in potassium bromide pellets were recorded on a Perkin-Elmer Infracord spectrophotometer. The base-precipitated samples gave spectra as illustrated in figure 1, very similar to that (in reference 7) of Y, a Eu-polyoxymethylene, especially in that the 3500 cm⁻¹ O-H stretching band was of much less intensity than the 2900 cm⁻¹ C-H stretching band. In the simply precipitated sample and the commercial chemically pure sample, the 3500 cm⁻¹ and 2900 cm⁻¹ bands were of similar intensity, whereas for the commercial technical sample the 3500 cm⁻¹ band was much more intense than the other. In the spectra of both commercial

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samples, there was a band at 1040 cm.⁻¹, lacked by both types of prepared sample. The 1040 cm⁻¹ band is attributed to the C-O stretching mode of the methoxyl group. The positions of hydroxyl and methoxyl groups in polymeric molecules of formaldehyde are the ends of the polymer chain. According to Walker (22) cyclic polymers do not depolymerize on vaporisation; since the gas and solid state spectra obtained in this work are (by comparison with 12 and 14) definitely due to monomeric formaldehyde, and since none of the four types of polymer tested are visibly soluble in acetone or water, (as are cyclic polymers) the polymers used in this research must be linear. The non-existence of a band at 1040 cm^{-1} and the small relative intensity of the 3500 cm^{-1} band therefore lead to the conclusion that the prepared polymers consist of a fairly large number of monomer units, probably greater than one The 3500 cm⁻¹ band may also be attributed to absorbed hundred. or adsorbed water. The presence of a band, very weak for all samples tested, at 1650 cm⁻¹, the H-O-H bending mode frequency, supports this suggestion; because, however, this band is extremely weak, the concentration of such water molecules must be very small.

From the preceding analysis, the base-precipitated polymer was deemed to be of sufficient purity for spectroscopic usage, and was accordingly employed for the low temperature spectra of formaldehyde. For the infra-red work, the polymer was outgassed by warming under vacuum, then heated to give the desired vapour pressure of formaldehyde. The latter gas was mixed, if required,

with a matrix gas.

The water used in the low temperature experiments was deionised water once distilled; the liquid was thoroughly outgassed before being mixed with the matrix gases. The argon was Matheson regular grade, 99.998% pure. The nitrogen was Matheson prepurified grade, greater than 99.996% pure. Mass spectra of samples of these gases, handled in the same manner as the infra-red samples, revealed that possible impurities were present in much smaller concentrations than the most dilute matrix sample prepared in this work.

II-2 Apparatus

The infra-red spectrophotometer used in the low temperature work was a Perkin-Elmer single-beam, double-pass instrument, model 112G, with a potassium bromide sixty-degree fore-prism and a seventy-five lines per millimeter grating blazed for twelve microns in the first order, and with thermocouple and lead sulphide detectors. The low temperature cell was of the Deurig-Mador type (5), having rotatable inner chamber, and equipped with caesium iodide windows. Attached to the metal of the base of the inner chamber of the dewar, below the deposition window, was a Au-Co:Ag-Au thermocouple. The dewar and auxiliary vacuum rack were specially constructed for the present work. The n. m. r. spectrometer used in part of this study was a Varian Associates V4200/4300B instrument operating at forty megacycles per second and 9395 gauss for proton resonance.

II-3 Procedure

The 112G spectrophotometer was calibrated by the use of

atmospheric water vibration-rotation bands, and some of the formaldehyde vibration-rotation bands (the formaldehyde gas being heated in a 9-cm. cell with sodium chloride windows).

For the nuclear magnetic resonance spectra, the gas from the alkali precipitate was further purified by being passed successively through three cold fingers immersed in ice baths at -5° C. and -12° C., and a dry ice--acetone bath below -55° C., be-fore condensing in an n. m. r. sample tube partially immersed in liquid nitrogen. This distillation was effected at a pressure below 1 mm. mercury. After the n. m. r. spectrum of the formal-dehyde thus prepared had been recorded, the sample was allowed to warm from 77° K. (heat being evolved) to room temperature, and another spectrum was recorded.

The samples for the infra-red experiments were prepared from the component gases (the latter themselves being prepared as noted in section II-1) by mixing in large bulbs. That the homogeneous mixing of gases is not a trivial consideration is illustrated by the spectra 1 and 2a in figure 3; the actual preparation of mixtures consisted of evaporating about 1 mm. mercury of the more dilute component into an evacuated 4-litre bulb followed by 20 or 30 cm. mercury of the other component. Spectra 1 and 2a were recorded following the deposition of the gas mixture four and twenty-four hours respectively after preparation. These spectra, in comparison with spectrum 5c (from a mixture prepared eighteen days before deposition, all mixtures being similarly prepared and deposited), indicate, by the intensity of the 2830 cm⁻¹ band (that band found in solid

formaldehyde) relative to the lower frequency adjacent bands of the isolated molecules, that mixed samples must be carefully prepared in order to ensure homogeneity.



After mixing, the samples were deposited on the internal window (maintained at or near 4°K. or 77°K. by means of liquid pest helium or nitrogen), the pressure of the gas flowing, the needle valve being measured by a thermocouple gauge. After a suitable deposition period, infra-red spectra of the deposited materials were recorded. In the cases of the matrix deposits at 4°K., additional spectra were recorded as the temperature increased after the exhausting of the liquid helium. The spectra derived from some trials follow, with a summary of conditions in table I.

| Spectrum No. Infra-red Spectra | Absorbing I Species | Matrix | Matrix Ratio M/R | Temp. OK. | Deposition Pressure (Microns) | Deposition Period (Minutes |
|--------------------------------------|-------------------------------------|--------------------|------------------------|-------------------------|-------------------------------------|----------------------------------|
| l | CH ₂ O | Ar | 300 | 4 | 350 | 60 |
| 2a b c | CH20 | Ar | 300 | 4 10 est. 20 est. | 300 | 60 |
| За Ъ с | CH ₂ O | none none Ar | 300 | 77 4 4 | 100 75 200 | 10 15 150 |
| 4a b c | CH20 | none none Ar | 300 | 77 4 4 | 100 75 200 | 10 15 150 |
| 5a b c | CH20 | none none Ar | 300 | 77 4 4 | 100 75 200 | 10 15 150 |
| 6ai aii b | H2O H2O H2O | Ar ? Ar | 300 ? 300 | 4 35 est. 4 | 300 300 | 120 120 |
| (7a b po | CH ₂ O lyoxymethylene | none none | | 77 295 | unknown unknown | |
| \Nuclear mag | netic resonance | e spectra | a | | | |

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Table I: Summary of experimental conditions for illustrated spectra.

(est. is an abbreviation for estimated)

Figure 3. The C-H stretching frequencies of formaldehyde 2900 cm-1 to 2775 cm-1

The formaldehyde is in each case partially isolated in an argon matrix, M/R = 300. Spectra 1 and 2a were deposited at 350 and 300 microns, 4 and 24 hours respectively after preparation. Spectra 2b and 2c show the effect of warmup on spectrum 2a.

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Figure 4. Infra-red absorption spectra of formaldehyde in condensed phases.

Spectrum 3a is of solid formaldehyde at 77° K.; 3b, at 4° K. Spectrum 3c is of formaldehyde in an argon matrix, M/R = 300, deposited at 200u for 150 minutes. The vibrations concerned are v6 about 1170cm⁻¹, v₅ around 1250 cm⁻¹ and a combination band v₁ + v₂ or v₂ + v₄. No absorption between 4450 and 4650cm⁻¹ was observed in the matrix trials when isolation was successful as indicated by other bands. The frequency scale of Figure 4 is discontinuous, the regions shown lying between 1185 and 1150 cm⁻¹, 1260 and 1230 cm⁻¹, and 4575 and 4500 cm⁻¹



Figure 5. Infra-red absorption spectra of formaldehyde in condensed phases.

Spectra 4a and 4b are of solid formaldehyde at 77°K. and 4°K. Spectrum 4c is of formaldehyde in an argon matrix, M/R = 300, deposited at 200u for 150 minutes. The vibrations concerned are the fundamentals v₃, v₂ and an overtone 2v₂. The frequency scale of figure 5 is discontinuous, the regions shown lying between 1515 and 1485 cm⁻¹, 1750 and 1700 cm⁻¹, and 3420 and 3**38**0 cm⁻¹



Figure 6. Infra-red absorption spectra of formaldehyde in condensed phases.

Spectra 5a and 5b are of solid formaldehyde at 77°K. and 4°K. Spectrum 5c is of formaldehyde in an argon matrix, M/R = 300, deposited at 200u for 150 minutes. The vibrations concerned are the combinations $v_2 + v_5$ and $v_3 + v_5$ with the fundamentals v_4 and v_1 between them. The frequency scale is continuous and runs from 3025 cm⁻¹ to 2700 cm⁻¹



Figure 7. Infra-red absorption spectra of water in an argon matrix.

Spectra 6a and 6b are of water in an argon matrix at 4° K., M/R = 300, deposited at 300u for 120 minutes. The solid lines of 6a and 6b represent the spectra observed at 4° K. in the O-H stretching and H-O-H bending regions, 3800 to 3350 cm⁻¹ and 1680 to 1565 cm⁻¹ respectively. The broken line of spectrum 6a is an absorption band traced during the same experiment as the other spectra of Figure 7., when the temperature had risen to about 40° K., and most of the argon had been pumped off.



Figure 8. Nuclear magnetic resonance absorption spectra of formaldehyde and polyoxymethylene.

Spectrum 7a represents the derivative curve of the absorption obtained when paraformaldehyde was heated and the gas passed into a n.m.r. sample tube at 77°K. Spectrum 7b resulted when the formaldehyde sample was allowed to warm to room temperature.

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CHAPTER III. RESULTS: TREATMENT AND DISCUSSION III-1 Experimental results

If one expected only a single sharp band for each normal mode of either molecule in the solid and matrix states, then the observed spectra would appear quite complex. Possible explanations for these complex spectra include the following: the isotope effect, molecular association, lattice mode coupling combinations, reaction with the matrix material, rotation either in a matrix or in a molecular crystal, and the trapping in different sites in a matrix. Each of these topics will be discussed in turn as it applies to each molecule.

The matrix spectra can be used to check solid phase assignments. The preceding statement implies a knowledge of gas phase assignments. Since these are well known for water and formaldehyde, the case of frequency shifts from the gas phase to the solid and matrix phases must also be considered.

Tables 3 and 4 give the infra-red absorption frequencies and intensities¹ for formaldehyde and water observed in this study, together with the calculated and observed frequencies of other work.

¹ The abbreviations for intensity in the following tables follow the frequencies which are in cm.¹ These abbreviations have the following meanings: v, very; w, weak; m, medium; s, strong, and sh, shoulder. Other abbreviations used in these tables are: Ass., assignment; H., Herzberg (see reference 23, page 300); N., Nielsen (see reference 14); S. B., Schneider and Bernstein (see reference 12); P., Pimentel (see reference 1); C. M., Catalano and Milligan (see reference 2); G., Glasel (see reference 3), and, w (prior to a frequency), the band appeared and disappeared during warmup. The letters with numerical subscripts

following the assignments in table 3 indicate the symmetry species of that mode, and are taken from reference 12. The symmetry of formaldehyde is discussed in appendix 1. The letters and numbers below the headings in table 3 indicate the experimental conditions. The headings on the last two columns signify the frequency shifts between matrix and gas, and between solid and matrix (argon matrix).

| Table 1. | The frequencies formalded on page 1 | uencies and hyde. For 17. | l intensi meanings | ties obser of abbre | rved in v viations, | various sp see the | footnot | f Ə | |
|------------------------------------------------------------------------------------------------------|-------------------------------------|---------------------------------|-----------------------|----------------------------|------------------------------------|------------------------------------------------------|-----------------------------------|-------------------|-----------|
| Ass. | Н. | N. | S.B. | T | nis | WOI | rk | ۵۷ _{m-9} | AV S-M |
| v _l (a _l) | 2780s | gas 2766.4 | 2834s | 2829 v s | 4 2829vs | Ar 2796vs 2800.5m 2809.5m w2817 w2823 | ^N 2 2799s 2808w | +30 | +33 |
| v ₂ (a ₁) | 1744vs | 1746.0 | 1712s | 1711sh 1720vs | 1715vs | 1732m 1738s 1742vs | 1736.5m 1739m | -4 | -27 |
| v 3 (a ₁) | 1503s | 1500.6 | 1491s | 1490sh 1495vs 1506sh | 1494vs | 1498m | 1495 (broad) | -3 | -4 |
| v4 (b1) | 2874 vs | 2843.4 | 2890s | 2885s | 2885s | 2862s 2871w 2880m | 2865m | +19 | +23 |
| v ₅ (b ₁) | 1280s | 1247.4 | 1247m | 1239.5w 1246s 1250vs | 1241w 1244sh 1246s 1250ys | 1245w 1247.5vw | 1 | -2 | +5 |
| v ₆ (b ₂) | 1167 s | 1163.5 | 1177m | 1167.5vw 1174m 1177s | 1172w 1174.5m 1176sh | 1164w 1167.5m 1124vw | · | +4 | -7 |
| $2_{v2}(A_{1})$ | | | 3414w | 3402w | 3404w | | | | |
| 2 _{v3} (A ₁) | 2973s | | 2960m | | | | | | |
| 2 _{v6} (A ₁)? | 2081w | | | | | | | | |
| v ₂ +v ₅ (B ₁) v ₃ +v ₅ (B ₁) |) | 3003.3 | 2997 2729w | 299 1vs 2727m | 2993m 2727w | 2996m 2718w 2721sh | 2720w | -7 | -3 -9 |
| V1+V2 V2+V4 | 4590w | | | 4535vw 4539sh 4562w | 4545 v ₩ 4562 v ₩ | | 4500 vw 4530 v w | | |

Table 3. The frequencies and intensities observed in the matrix spectra of water. The matrices are argon except in the case of Pimentel (P.) whose experiments employed nitrogen at 20°K. as a matrix.

| Ρ. | C. M. | G. | This work |
|------------------------------|------------------------------------------------------|--------------|--------------------------------------------------------------------------------|
| 1600 1615 1620 1633 | 1554 1572 1593 1608 1620 1638 1655 | | 1574 m 1593 vs 1602 m 1608 s 1610 s 1624 vs 1638 m 1663 w |
| 3355 | | | 3376 w |
| 3435 3510 | | 3508 | 3390 VW 3416 VW 3510 m |
| 3627 | | 3636 | 3574 vs 3633.5 w |
| 3691 | | 3689 | 3651 VW 3699 s |
| 3725 | 3730 ± 20 | 3724 3748 | 3725 m |
| | 3772 ± 20 | 3768 | Э777 m |

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III-2 The isotope effect

The isotope effect was investigated by applying a valenceforce potential function to the formaldehyde molecule. (The fraction of isotopic molecules in natural H_2^{100} is too small for infra-red detection, whereas for formaldehyde the carbon-13 isotopic species is abundant to the extent of one per cent of natural carbon; $C_2^{130} L_2^{16}$ is easily detected, by the Perkin-Elmer 112G spectrophotometer, in atmospheric carbon dioxide.)

The potential function assumed for formaldehyde was of the following form:

$$2V = k_1(\Delta r_1)^2 + k_2(\Delta r_2^2 + \Delta r_3^2) + k_3(r_2 \Delta \kappa 1)^2 + k_4(r_1r_2)(\omega r_2^2 + \Delta \kappa 3^2) + k_{12}(\Delta r_1)(\Delta r_2 + \Delta r_3) + k_4(r_1r_2)(\Delta 6)^2$$

where V is the potential energy,

- Δr_i is a small increment in the length of the i'th bond,
- $\Delta \kappa_1$ is a small increment in the i'th bond angle,
- △I is a small increment in the angle between the C-O bond and the plane containing the methylene group,
 - k_i is a the force constant representing the resistance to a change from the equilibrium nuclear positions,
- and k_{12} is an interaction constant connecting the C-H and C-O stretching modes.

Table 4 gives the force constants and the calculated frequencies for $C^{12}H_{2}^{1}O^{16}$, $C^{13}H_{2}^{1}O^{16}$, and $C^{12}H_{2}^{2}O^{16}$, together with the frequency shifts for the isotopic carbon molecules and the list of frequencies for d₂-formaldehyde from Herzberg (23), page 300. The v₆ force constant and frequencies were calculated from the equation II, 219 in Herzberg (23), page 180. The v₄ and v₅ force constants and frequencies were calculated by the Wilson

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FG matrix method (24), the secular equation being factored by means of internal symmetry co-ordinates (see appendix I).

Table 4. Calculated force constants and frequencies for isotopic formaldehyde molecules. (cf. reference 15).

| ۷i | k1 (md./A.) | $C^{12}H^{1}C^{0}C^{16}(cm.)$ | $C^{13}H^{1}C^{16}(cm.^{201})$ | ∠v _i (cm.l) | $C^{12}_{H^{2}O^{-1}}$ | H. (23) (cm ⁻¹) |
|----|----------------|-------------------------------|--------------------------------|---------------------------|------------------------|--------------------------------|
| ▼4 | $k_2 = 4.2757$ | 2843.4 | 2831.2 | -12.2 | 2121 | 2160 |
| ▼5 | $k_4 = 0.6536$ | 1247.5 | 1238.8 | - 8.7 | 974 | 990 |
| ▼6 | $k_5 = 0.9918$ | 1136.6 | 1151.8 | -11.8 | 930 | 938 |

Agreement between calculated and observed frequencies for d_2 formaldehyde is probably better than is apparent because the values stated by Herzberg are not zero lines, but refer simply to prominent features of the bands. That these features can be misleading is exemplified in a comparison of Herzberg's and Nielsen's sets of frequencies for $C^{12}H_2^1O^{16}$ in table 2.

Referring to table 2 and to spectrum 3a (in figure 4), one can see weak absorption bands at 1239.5 and 1167.5 cm⁻¹, shifts of -10.5 and -9.5 cm⁻¹ respectively from the most adjacent bands. Since the predicted shifts are -8.7 and -11.8 cm⁻¹, these weak bands may be assigned to $C^{13}H_2^1O^{16}$. Conversely, because there are bands of approximately the correct relative intensity and frequency shift in the solid state, the potential function utilized to predict the frequency shifts must fit the molecule well.

The frequencies calculated for formaldehyde- C^{13} , if they were observed in pure formaldehyde- C^{13} , would not necessarily be the frequencies observed in a mixed sample of isotopic species. The introduction of C^{13} atoms may perturb the selection rules which would otherwise permit absorption for

out-of-plane bending only in certain phase relations. Because the difference from the calculated shift for v_6 , the out-ofplane bending vibration, is small, the angle between the planes of neighbouring molecules is indicated to be close to a right angle, since the dipole interaction of neighbour molecules is a function of the cosine of the angle between these planes (20).

The agreement of calculated and observed frequencies for formaldehyde- C^{13} sprobably very good. No weak satellite bands have been definitely observed for the other fundamentals in the spectrum of solid formaldehyde. No satellite bands of the correct relative intensity have been seen in the matrix spectra, but the intensity of the most intense bands there has not been very great, chiefly due to the small amount of absorbing molecule deposited².

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III-3 Molecular association

Some of the observed bands in the matrix spectra may be due to association of formaldehyde or water molecules. Four experimental checks of this possibility are available: variation of matrix ratio, variation of deposition rate, warmup observations, and band width. By varying greatly the matrix ratio, one can, as Pimentel et al. (1) have done with water in nitrogen, assign certain bands to associated species and others to nonassociated species. This technic was not employed in this work. A relatively large deposition rate would be expected to warm the surface of the deposition window to such a temperature that diffusion in the matrix becomes appreciable. Deposition rates

^{2.} The amounts of formaldehyde and water actually deposited in matrices probably never exceeded forty micromoles.

were maintained as small as possible, and were otherwise not varied in these experiments.

The C-H and O-H stretching bands were continuously scanned during the warmup, i. e., as the sample was allowed to warm after the liquid helium in the dewar was exhausted. Diffusion becoming more rapid as the matrix slowly warms, bands attributable to associated species should increase in intensity at the expense of bands of monomeric species. The bands of associated species should lie in frequency between the corresponding bands of the well isolated case and the totally associated (molecular crystal) case. This effect was observed in both the cases of formaldehyde and water, and is illustrated in spectra 2a, 2b and 2c of figure 3. Here the three bands at 2796, 2800.5 and 2809.5 cm⁻¹ decrease in intensity while the bands at 2817 and 2823 cm⁻¹ increase. Just before the matrix material was pumped off, the latter bands were seen to decrease and to disappear, and a single band at 2829 cm⁻¹ rose and remained. The sequence was irreversible: the addition of more liquid helium to the dewar simply froze the deposit at whatever stage it had reached before recooling. Likewise for water, of the bands between 3480 and 3800 cm⁻¹, all decreased, apparently uniformly, with the exception of the 3510 cm⁻¹ band, which increased in intensity. A similar effect was noticed also, namely a slight, perhaps doubtful decrease of intensity of some intense bands on standing before warmup commenced. Morrow (25) and Glasel (3) have also observed this phenomenom, to a much greater extent in their work than in this. However, in these

experiments, no corresponding increases of other bands were observed, perhaps because there was some evaporation of the deposit when it was bathed in the radiation from the spectrometer source.

That absorption bands of substances dispersed in solid inert matrices were very sharp, compared even to the bands of the pure solid substance at the same temperature, was obvious early in this research. The fact that the absorption lines of the matrix-suspended material were usually of similar width to vibration-rotation lines of atmospheric gases, made difficult the finding of the former bands when they were in a region of the spectrum overlapped by atmospheric water vapour and carbon dioxide bands. Because one would expect that crystal field and weak intermolecular bonding effects would broaden absorption bands, relatively broad bands, such as that at 3510 cm⁻¹ for water in argon and that at 2817 cm⁻¹ for formaldehyde in both argon and nitrogen, may easily be identified with some associated species of these molecules. A comparison of spectra 1 and 2c in figure 3 indicates that non-mixing of the sample causes poor isolation since the effective matrix ratio Was much greater than it was planned to be.

Schneider and Bernstein have discussed (12) the molecular association and infra-red spectrum of solid formaldehyde; they speculate that the interaction between neighbours in planes perpendicular (also with the molecular C_2 axes **mutually**; perpendicular) to one another would explain the observed spectral shifts. They also suggest that two crystalline forms may exist.

In this work only one spectrum was ever observed and was obtained consistently in many trials. The bands of the formaldehyde deposited in a matrix and remaining after the matrix had evaporated were always of the same frequency as otherwise but were much broader than for pure formaldehyde freshly deposited. No change in frequency or width was observed when pure formaldehyde was allowed to stand for a day at 77°K. The spectra for the region 1100 to 1300 cm.⁻¹ obtained in this work differ from the spectra of the same region observed by Schneider and Bernstein; if the lower resolution of their instrument is considered, then the thin film of their work is probably closest to the conditions encountered in these experiments.

III-4 Lattice mode combinations

Combinations of internal vibrations with lattice vibrations may account for the structure observed in many of the fundamentals of formaldehyde and water in the molecular-crystal and inert matrix cases. In the Baman spectra of some crystals, lines very close (0 to 150 cm⁻¹) to the exciting line have been observed, and, according to Herzberg (23), are interpreted as due to vibrations of the lattice. These lattice modes may be torsional or translational lattice vibrations, of which the former are much more common (26). Because the frequencies of the v_5 and v_6 bands in solid formaldehyde are not very different from the gas phase zero line frequencies, and because the splitting of these bands in the solid phase is very small, the frequencies of lattice vibrations probably must also be small.

The lattice vibration frequencies observed for solid benzene (28) at 77° K. are 81, 101 and 124 cm⁻¹, of an order of magnitude larger than for formaldehyde. Another possible source (27) of splitting of nondegenerate vibrational modes is intermolecular coupling or correlation field splitting. The other principal source of vibrational splittings is of degenerate molecular modes, split by the decreasing symmetry of the local field of a molecule upon its condensation, but because there are no degenerate modes for C_{2v} molecules, this effect is not applicable to formaldehyde or to water. Ob-viously intermolecular coupling is negligible in the good isolation provided in an inert gas matrix, and probably the lattice vibrations can also be neglected in this case.

Reactions of the formaldehyde and water molecules with the matrix materials might be postulated as a cause of the multiple absorption bands observed in the regions of the fundamental frequencies. In this case one would expect that the solid phase frequencies should be shifted from the gas phase zero line. The frequencies of the O-H stretching modes in water are very sensitive to the environment of the molecule, such interactions normally leading to a decrease in frequency and a broadening of absorption bands. All the frequencies observed in the matrix phase spectra as sharp lines, are close to the corresponding fundamentals of the gas phase, indicating that interactions between the protons and matrix materials are small, and, for formaldehyde, differ little from the nitrogen matrix to the

argon matrix. During warmup in an water experiment, a broad band was observed around 3600 cm⁻¹ (broken line in figure 7. spectrum 6a) after most of the argon had been pumped off the deposition window. This band may be due to an argon hydrate. or, more probably, to some crystalline form of ice, or even. perhaps, to some hydrate of the very thin film of formaldehyde polymer remaining on the window from a previous formaldehyde experiment. Although in no previous study on ice has there been observed a band around 3600 cm.⁻¹, probably no other workers have attempted to form ice or, for that matter, argon hydrates, by similar procedures. At the low temperature (less than 70°K.) reaction of the water with the polyoxymethylene would not be expected. Moreover, to differentiate between an argon hydrate and an ice by means of the observed frequency is not possible, because both species are expected to shift the O-H stretching vibrations to lower frequencies, even lower than the observed shift, due to hydrogen bonding.

III-6 Rotation in solid formaldehyde

Since only a few rotational levels are appreciably populated at 77° K. or 4° K., rotation within the lattice of formaldehyde molecular crystals was considered in order to explain the structure of the vibration bands. There are many fewer levels populated at 4° K. than at 77° K., whereas there are more lines observed at the lower temperature due to the sharpening. Since nuclear resonance spectroscopy is capable of detecting some types of molecular motion, the n. m. r. spectrum of formaldehyde was studied.

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For formaldehyde at 77° K. the proton pair would be expected to give a 'doublet' signal such as I of figure 9, of which the recorded derivative of the absorption would be similar to II. The theoretical line shape for a proton pair in molecules of a polycrystalline material is given by III of figure 9. The splitting $\boldsymbol{\alpha}$, equal to $3\mu r^{-3}$ where μ is the proton magnetic moment and r the internuclear distance, corresponds roughly (but not exactly due to intermolecular broadening of the actual resonance line) to the distance between A and B in II. Rotation occurring about the axis perpendicular to the internuclear vector decreases the doublet splitting to $3/2\mu r^{-3}$.



I FIGURE 9. N.M.R. LINE SHAPES III For the dimensions of formaldehyde as given in appendix I, $3 \mu r^{-3} = 5.22$ gauss for the case of rotation, or $3/2 \mu r^{-3} = 2.61$ gauss if there is rotation.

That the quality of the trace was very poor was probably due to the small amount of formaldehyde, and consequently the low concentration of protons actually in the space of the spectrometer receiving coil. The experimental value of the doublet splitting is 8.5 ± 0.5 gauss (average of four trials: 8.3, 8.8, 7.8 and 9.1). (The experimental doublet splitting indicates a proton separation of 1.71 Å., compared to 1.89 Å. for the given geometry.) The possibility of rotation is therefore eliminated. For the formaldehyde polymer, a smaller receiving coil was used. Consequently a better trace was obtained. Since the spectrum (7b in figure 8) is quite different from the previous (7a), the sample at 77° K. was probably monomeric formaldehyde.

References 17 and 19 were consulted during the consideration of the proton magnetic resonance spectra of formaldehyde and polyoxymethylene.

The n. m. r. spectrum of the alkali-precipitated paraformaldehyde was also recorded; the spectrum is qualitatively similar to the broader band of figure 8, spectrum 7b. However in this case there is no central strong line, but the line width is very close, ll.5 gauss, to the previous line width which was 10.8 gauss for the broad line (compared to 2.9 gauss for the narrow central line).

III-7 Rotation of water and formaldehyde in matrix sites

To explain the multiplicity of sharp lines observed in the spectrum of water trapped in inert gas matrices, various workers (1, 2, 3) have suggested that the water molecule may be executing some kind of rotation within the lattice of the inert gas matrix. One of the reasons for such a proposal is the fact that the spectrum of water in nitrogen is very much simpler than that observed for rare gas matrices, the reasoning being that, because the sizes of the trapping sites in nitrogen are considerably smaller than for instance in argon, and because the non-spherical symmetry of nitrogen molecules would tend to prevent rotation, rotation can therefore occur in some rare gas

matrices, depending on the size of the atoms, but not in nitrogen. Shurvell (29) has observed that the spectrum in the D-O-D bending region of heavy water consists of two sharp lines in nitrogen, but of seven sharp bands in each of argon and krypton. The temperature dependence of intensity (2) of the water bands in argon also suggested that they may have arisen from vibrationrotation interaction.

A parallel set of observations has been made for formaldehyde in argon and nitrogen, in which only two lines were observed for v_1 and v_2 in nitrogen as contrasted with three each in argon (see table 2).

If water molecules were freely rotating in the rare gas matrices, what spectrum should one expect to observe? The number of possible absorption transitions is dependent on the number of populated levels. For the ammine radical (NH₂) at 4.2° K. in thermal equilibrium (30), 99.9 per cent of the molecules are in the 0[°]₀ rotational level, 0.09 per cent in 1[°]₋₁ and 0.002 per cent in 1[°]₀. Possibly a similar distribution exists for water at 4.2° K., since the rotational levels are of comparable spacing.

The selection rules that apply are $\Delta J = 0, \pm 1$; $J = 0 \iff J = 0$, and the parity of \mathcal{T} changes for v_3 , but remains fixed for v_1 and v_2 (16, 18). Therefore one would expect transitions from only the 0_0 level, three lines in all, one per normal mode, at 1635, 3693 and 3779 cm⁻¹

If there were a non-equilibrium population according to the prohibition of symmetric levels not combining with anti-

symmetric levels, but otherwise an equilibrium population of each of the ortho and para modifications, then the levels would be populated such that seventy-five per cent of the molecules were in the $O_0^{"}$ (para) state and twenty-five per cent in the $l_{-1}^{"}$ state. The calculated lines in this case are $J_{x'}$ $J_{x'}$ for v_3 : $l_{-1}^{"}$ $O_0^{"}$ 3779, $2J_2$ $l_{-1}^{"}$ 3801, $2J_2$ $l_{-1}^{"}$ 3863, $T_{x'}$ $J_{x'}$ and for v_1 , v_2 : $l_0^{"}$ $O_0^{"}$ 3693, l635, $l_{-1}^{"}+1$ $l_{-1}^{"}$ 3675, l618, $2J_1$ $l_{-1}^{"}$ 3711, l653.

Thus four bands are expected for v_3 and three each for v_1 and v_2 . In a comparison of the spacing between the calculated and observed bands, not one but two sets, each having different gas-matrix frequency shifts, are observed. These data are listed in table 5.

Table 5. Frequencies, frequency shifts and intensities for water at 4° K.

| Vl | gas 3675 s 3693 w 3711 m-s | 3699 | -12 | 3634 3651 | -41 -42 |
|----------------|------------------------------------------------|------------------------------|-------------------|----------------------|-------------------|
| v ₂ | 1617 s 1635 w 1653 m-s | 1608 1624 1638 | - 9 -11 -15 | 1574 1593 1610 | -43 -42 -43 |
| v 3 | 3732 m 3 779 w 3801 vs 3864 vw | 3708 3757 37 77 | -24 -22 -24 | | |

Of the observed lines not accounted for in the above table are 1602 and 3725 cm⁻¹ which have been observed for water in nitrogen (1) at 20^oK. as 1600 and 3725 cm⁻¹ The remainder but one of the bands, at 3510, 3416, 3396, 3376 and 1663 cm⁻¹, can be assigned, by their width and distance from the zero lines, to associated species. The very intense narrow line at 3574 cm⁻¹ is not explainable by the preceding analysis; shifts of more than 100 cm⁻¹ have to be rationalised in order to fit the observed sharp lines to the calculated gas phase frequencies for P_20 , but this presumably H_20 line lacks any adjacent sharp lines that can be used to form a set similar to others of table 5. The line acts normally on warmup, decreasing in phase with the other water lines, is not due to causes in the deposition window, and was produced equally strongly, relative to the other water lines, in both experimental trials of water in argon.

The intensity of a line can be calculated (16) and is proportional to the product of the line strength (or probability of rotational transition $J_{\tau'} - J_{\tau''}$) and the Boltzmann factor g exp (- E"/kT) (where g is the nuclear spin statistical weight factor, i(2i + 1) for para states (even values of r) and (i + 1)(2i + 1) for ortho states (odd values of ζ), i being the nuclear spin of the identical nuclei, where E" is the rotational term value of the ground level $J_{T''}$, k the Boltzmann constant and T the absolute temperature). The absolute intensity is proportional to the number of molecules in the absorbing path in the ground vibrationless state, the line width, the slit width, the frequency, and a factor representing the effective change of dipole moment in the vibrational transition. In scans of the same small spectral region in one experimental trial, all the forementioned factors should be approximately constant, so that only relative intensities are relevant for the purpose of comparison.

The relative intensities calculated (31) for water at 4°K. with the room temperature ortho-para ratic but otherwise in a normal thermal distribution are as indicated in table 5 after the calculated frequencies. Comparing the observed intensities, frequencies and shifts for the symmetric vibrations, one can see that the experimental results are guite consistent in that the lines at 1624. 1593 and 3651 cm⁻¹ are the most intense of the respective groups, in disagreement with the calculated intensity pattern, and in that the shifts are similar for the corresponding sets of frequencies of each vibration. The observed intensities for v_3 transitions are less at variance with the calculated intensities if one assumes a Coriolis interaction, a perturbation of a rotation-vibration level of v_1 by a close-lying one of v_3 ; such a perburbation of a pair of levels of the same quantum number J and the same total symmetry properties would result in a displacement, perhaps small, of the frequencies and much higher intensity (16) for the v_1 transition. As seen in the interacting bands, 3699 and 3708 cm⁻¹, are not completely resolved, each line tending to appear more intense than it really is.

An examination of the spectra obtained by Shurvell (29) of heavy water (D_2O) in argon, krypton and nitrogen reveals similar trends, in that the observed frequencies are consistent with the calculated, allowing for matrix shifts, but that the observed intensities, while self-consistent, are in disagreement with the calculated.

If three different trapping sites, the substitutional site

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and the octahedral and tetrahedral interstitial sites, were available to a water molecule, and if the water molecule were able to execute fairly free rotation in two of the sites but not in the third, the observed spectral frequencies would be explained. If the molecules were in a normal thermal distribution of rotational levels except that the ortho-para ratio is of some value between those of 4°K. and room temperature. then the observed intensities would be explained. (Glasel (3) has noticed that his line corresponding to 3757 cm⁻¹ of this work has decreased more rapidly than the other monomer lines at 20[°]K., indicating a slow ortho-para conversion.) The set of rotational lines of lesser shift from the gas phase frequencies would originate from molecules in the largest trapping sites and consequently of least interaction with the matrix--probably the substitutional lattice sites. The single lines observed in both argon and nitrogen matrices would be pure vibrational transitions of non-rotating molecules in the smallest--tetrahedral interstitial--sites. The other set of lines would then be due to molecules rotating in the octahedral interstitial sites. Not all observed lines are accounted for by these hypotheses, nor all calculated transitions observed, but the recorded spectra are best explained by such hypotheses.

Other hypotheses to interpret the water spectra are a nonequilibrium population of rotational levels, violation of normal selection rules due to distortion of the molecule in the lattice or lattice interactions, and a combination of the forementioned hypotheses. None of these explain the observed

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spectra as well as the preceding argument; however, that strong lines are observed near the zero lines for both H_2^0 and D_2^0 in all matrices tried hints that still another theory may be needed.

The spectra of formaldehyde in argon should also be capable of similar interpretation if rotation is occurring. Since however this molecule is larger than water, rotation is not as likely, and pure vibrational transitions may then be expected. The formaldehyde molecules could still be trapped in different lattice sites, and the vibrational transitions thus resulting would differ slightly in frequency, depending on trapping site. The presence of three lines at the C-H and C-O stretching frequencies indicates that three possible sites are available in argon, but two lines, two sites in nitrogen. The experimental intensities indicate that the substitutional lattice sites are much more favoured by formaldehyde molecules for occupancy than interstitial sites. The gas-matrix shifts of frequency are small for the fundamentals of formaldehyde except for the C-H stretching frequencies, in which cases the shifts are of +30 and +19 cm⁻¹ for v_1 and v_4 in argon, and 33 and 22 cm⁻¹ respectively in nitrogen. The shifts here are similar to those observed for NH_2 (30) but are of opposite sign to those for water (see above, table 5). These shifts may be due to dielectric effects (13) in which case all shifts would be expected to tend to decreasing frequency) or to some more specific electronic effect, perhaps a dipole-induced dipole interaction. In the latter case the average shift would be expected to increase with increasing atomic number of inert gas, an observed-effect (29);

the magnitude and direction of the shift would require very specific calculation. Attempts to explain the formaldehyde matrix spectra by considering both free and hindered rotation have not been generally successful (31).

III-8 Miscellaneous notes.

Despite Nielsen's assurances to Herzberg (23), no band at 2081 cm⁻¹ was observed in this work in the gas phase spectrum of formaldehyde. This band may be due to glyoxal.

The accuracy of frequencies (given in this study in reciprocal centimetres corrected for vacuum) is ± 2 cm⁻¹

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APPENDIX. The structure and Symmetry of Formaldehyde and Water I The structures

The structure assumed for water is a symmetrical, non-linear molecule. The symmetry point group is therefore C_{2v} , and the three unequal moments of inertia make the water molecule an asymmetric top for the purpose of rotational analysis.

The structure and dimensions of formaldehyde assumed in this work are as indicated in figure 10. The values shown were taken from (11). They are considered to be the best available because they are calculated from accurate physical measurements, electron diffraction date (10) for the carbonoxygen distance, and microwave spectra (9) and ultraviolet spectra (8) for the moments of inertia. The latter two calculations are in good agreement with each other and the rotational calculations of (11).

II The symmetry of formaldehyde

The formaldehyde molecule belongs to the C_{2v} point group and the elements of this group are E, C_2 , $\sigma_{\tilde{v}}$ and $\sigma_{\tilde{v}}$. The plane of the molecule is the (x,z) plane with the C_2 axis in the z-direction. The character table for this group is table 6. Table 6. Character table for C_{2v} .

| Al A2 Bl B2 | | E 1 1 1 | C2 1 -1 -1 -1 | b v. -1 1 -1 | ∀ √ 1 -1 -1 1 | Tz Rz Tx; Ty; | Ry Rx | n 4 1 3 | Infra-1 3 0 2 1 | red | |
|----------------------|------|------------------|---------------------------|------------------------------|----------------------------------|------------------------|----------|------------------|-----------------------------|------|-----|
| Xr | | 12 | -2 | 4 | 2 | | | | | | |
| X _r i | nt. | 6 | 0 | 4 | 2 | | | | | | |
| Sinc | e 3n | L — 1 | 6 = 6 | funda | mentals | s are | e poss | ible | (where | n is | the |



number of atoms in a non-linear molecule), all the fundamentals are infra-red active.

The internal co-ordinates chosen for the symmetry analysis in section III-2 were as follows:

$$R_{1} = \Delta r_{1}$$

$$R_{2} = \Delta r_{2}$$

$$R_{3} = \Delta r_{3}$$

$$R_{4} = \Delta \alpha_{1} r_{1} \alpha$$

$$R_{5} = \Delta \alpha_{2} r_{2} \alpha$$

$$R_{6} = \Delta \alpha_{3} r_{3} \alpha$$

The symmetry co-ordinates used to factor the secular determinant were as follows:

$$\begin{array}{rcl}
\mathbb{Q}_{1} &= & \mathbb{R}_{1} \\
\mathbb{Q}_{2} &= & \frac{1}{\sqrt{2}} (\mathbb{R}_{2} + \mathbb{R}_{3}) \\
\mathbb{Q}_{3} &= & \frac{1}{\sqrt{2}} (\mathbb{R}_{2} - \mathbb{R}_{3}) \\
\mathbb{Q}_{4} &= & \mathbb{R}_{4} \\
\mathbb{Q}_{5} &= & \frac{1}{\sqrt{2}} (\mathbb{R}_{6} + \mathbb{R}_{5}) \\
\mathbb{Q}_{6} &= & \frac{1}{\sqrt{2}} (\mathbb{R}_{5} - \mathbb{R}_{6})
\end{array}$$

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Since the six internal co-ordinates were all in the plane of the molecule, and since there are only five in-plane vibrations, there is one redundant co-ordinate, of species A_1 .

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