# INFRARED ABSORPTION OF FORMALDEHYDE AT LOW TEMPERATURES EVIDENCE FOR MULTIPLE TRAPPING SITES IN AN ARGON MATRIX

K. B. HARVEY AND J. F. OGILVIE<sup>1</sup>

The Department of Chemistry, University of British Columbia, Vancouver, British Columbia Received September 22, 1961

#### ABSTRACT

The infrared absorption of formaldehyde in both the polycrystalline and the monomeric form has been measured at  $4^{\circ}$  K. In the latter case the molecules were suspended in an inert matrix of Ar or N<sub>2</sub>. The fine structure of the matrix spectra is discussed from the point of view of rotation of the monomers but this interpretation is ruled out in favor of one based on multiple trapping sites in the matrix.

## INTRODUCTION

In the past few years, the matrix isolation technique has become established as one of the principal aids in the investigation of free radicals and other chemically reactive species (1, 2, 3). More recently, however, interest has arisen in the physical aspects of the matrix environment particularly as related to the spectra of the trapped molecules. Milligan and his co-workers have published infrared evidence for the rotation of  $H_2O_1$  $D_2O$ , HDO (4), and  $NH_3$  (5) in inert-gas matrices and were able in the latter case to assign the rotational transitions. Glasel (6) placed the same interpretation on fine structure observed in the O—H stretching region of H<sub>2</sub>O in matrices of Xe and Ar. In the field of electronic spectroscopy, Robinson and McCarty have explained the spectrum of trapped  $NH_2$  radicals in terms of rotation (7), and have achieved also considerable success in the theoretical interpretation of spectral shifts using a Lennard-Jones (6-12) potential function to represent the interaction between the trapped atoms or simple molecules and the matrix (8). The present high-resolution infrared study was undertaken with a view to providing further information on the interactions which take place between the matrix and trapped molecules. In particular, it provides optical spectroscopic evidence for multiple trapping sites, a feature which has also been investigated by electron spin resonance (9, 10).

#### EXPERIMENTAL

The low-temperature cell constructed for this work is basically of the Duerig-Mador type (11) equipped with optical windows of cesium iodide. The only major modification is a rotatable liquid helium chamber which makes it possible to spray the gaseous sample onto the trapping surface from the side rather than from below. A Au-Cu:Ag-Au thermocouple mounted directly below the cesium iodide trapping surface enables us to measure the approximate temperature of the sample during warmup.

Gaseous mixtures to be investigated were prepared in 5-liter bulbs in ratios determined by the partial pressures of the components. It is interesting that, even though the dilute component was introduced first, proper mixing of the components was not a trivial consideration. It was found necessary to heat parts of the bulb to produce convection currents to ensure effective mixing, and even then care had to be exercised to make certain that no pockets of pure formaldehyde were trapped in side arms etc. No attempt was made to measure absolute flow rates during the deposition of the sample, but reproducible conditions could be obtained through pressure measurements on the low-pressure side of the controlling needle valve.

The formaldehyde vapor was produced by heating paraformaldehyde (polyoxymethylene) until the required pressure of vapor was obtained in the bulb. Considerable care was taken to make certain that the paraformaldehyde contained a minimum of water, as indicated by its infrared spectrum. The purest material was that precipitated from a basic formalin solution (12) and then well dried under vacuum. Absorption in the O—H stretching region was very weak and since the O—H units terminate the chains, we were led to

<sup>1</sup>Present address: Department of Physical Chemistry, University of Cambridge, Cambridge, England.

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#### CANADIAN JOURNAL OF CHEMISTRY, VOL. 40, 1962

the conclusion that the polymer units were quite large. This was further substantiated by the very weak intensity of the band attributable to the C—O stretching mode of the methoxyl group, also at the end of the chain. The matrix materials, Ar and  $N_{2}$ , were analyzed mass spectrometrically and contained less than 40 p.p.m. impurities. They were admitted directly from the gas cylinders, through an evacuated capillary, to the sample bulb to avoid the introduction of impurities through the use of a gas regulator.

Spectroscopic measurements were carried out on a Perkin-Elmer 112G spectrometer with a modified source unit. Calibration was effected through established grating spectra and the reported frequencies are estimated to be precise to  $\pm 2$  cm<sup>-1</sup>. Spectral slit widths are indicated on the individual spectra.

#### RESULTS

In addition to the matrix isolation spectra, we examined the spectrum of polycrystalline formaldehyde at 4° K and 77° K. Figure 1 shows the more interesting spectra, and the



FIG. 1. The fundamentals  $\nu_2$ ,  $\nu_4$ , and  $\nu_6$ . Upper spectra are of normal associated CH<sub>2</sub>O at 77° K and 4° K, lower spectrum is that of monomer dispersed in argon matrix at 4° K.

observed bands are summarized completely in Table I along with the gas phase measurements of Blau and Nielson (13) and previous low-temperature spectra of Schneider and Bernstein (14). Our results differ significantly from those of the latter authors in the fine structure observed in some of the bands, probably because of the higher resolution and lower temperatures used in our work. None of these lines coincide with those of the highertemperature modification reported by Schneider and Bernstein, nor did we observe any effects to indicate the presence of two crystalline forms. On the other hand, our films were probably deposited much more slowly and we did not extensively investigate the effect of temperature on the spectrum. Our primary interest was in obtaining spectra of associated molecules at low temperatures for comparison with the matrix spectra.

With regard to the matrix spectra, our chief concern must be to estimate the degree of isolation attained. This can be done in a number of ways, all of which lead us to the conclusion that the matrix spectra are those of isolated monomers. That little or none of the normal associated species is present is confirmed by an inspection of the fundamentals  $\nu_1$  and  $\nu_2$ . In these cases, the shifts from polycrystalline solid to matrix are quite

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#### HARVEY AND OGILVIE: INFRARED ABSORPTION

## TABLE I

1	nfrared	absorpti	on of	formal	ldehyde	(frequencies	in	cm⁻¹)*	

	Dlass and	d Schneider and		work		
	Neilson	Bernstein				trix
Mode	gas	77° K	77° K	4° K	Ar	N2
					2809.5m 2800.5m	2808w
$\nu_1(\nu CH)a_1$	2766.4	2834s	2829vs 1720sh	2829vs	2796vs	2799s
$v_2(vCO)a_1$	1746.0	1712s	1711vs	1715vs	1742vs 1738s 1732m	1739m 1736.5m
$v_3(\delta CH_2)a_1$	1500.6	1491s	1506sh 1495vs 1490sh	1494vs	1498m	1495
$\nu_4(\nu CH)b_1 \\ \nu_b(\rho CH_2)b_1$	$2843.4 \\ 1247.4$	2890s 1247m	2885s 1250vs 1246s 1239.5w	2885s 1250vs 1246s 1244sh 1241w	2880m 2871w 2862s 1245w 1247vw	2865m
$\nu_6(\omega \mathrm{CH}_2)b_2$	1163.5	1177w	1177s 1174m 1167 5yw	1176sh 1174.5m 1172w	1174vw 1167.5m 1164w	
$\frac{2\nu_2 a_1}{2\nu_2 a_1}$		3414w 2960m	3402w	3404w		
$\begin{array}{c} (\nu_2 + \nu_5)b_1 \\ (\nu_3 + \nu_5)b_1 \end{array}$	3003.3	2997s 2729w	2991vs 2727m	2993m 2727w	2996m 2718w 2721sh	2720w
$(\nu_1 + \nu_2)a_1$			4535vw 4539sh	4545vw		
$(\nu_2 + \nu_4)b_1$			4562w	4562vw		

\*The approximate relative intensities are quoted after the frequencies of absorption according to the following abbreviations: vs = very strong, s = strong, m = medium, w = weak, vw = very weak; sh = shoulder.

large and any associated species in the matrix would be readily detected. The presence of smaller polymer units (dimers, trimers, etc.) was investigated by varying the matrix ratio or rate of deposition, and by observing the spectrum of the deposit as it warmed. The mixture used in most cases was  $Ar/CH_2O = 300$  but if this were reduced below 100 or so, then spectra of the type shown in Fig. 2 were observed. In the warmup spectra, it will be seen that the lines assigned to monomers disappear as the broadened bands due to absorption by polymers grow in intensity. We may, therefore, assume with reasonable certainty that the absorption of interest is due to monomers.

#### DISCUSSION

## Polycrystalline Solid

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There are several possible explanations for the fine structure observed in the spectrum of the crystalline solid. The fundamentals  $\nu_2$  and  $\nu_3$  both become considerably narrower as the temperature is lowered from 77° K to 4° K, suggesting a rotational envelope decreased in width by the depopulation of upper rotational levels. This interpretation is ruled out, however, by the n.m.r. spectrum at 77° K.\* Alternatively, some of the weaker

\*These spectra were very kindly run for us by Mr. D. Gilson on samples of formaldehyde specially prepared by double distillation. The observed doublet splitting was of the order of 7 gauss, much larger than the 3 gauss expected if the proton pair in  $CH_2O$  were rotating.

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CANADIAN JOURNAL OF CHEMISTRY, VOL. 40, 1962



FIG. 2. Behavior of  $\nu_1$  fundamental during warmup of the deposit. Lowest spectrum is that of monomer at 4° K dispersed in argon and uppermost is that of normal associated CH<sub>2</sub>O at 77° K. The middle two are matrix spectra at intermediate temperatures (about 35 and 50° K).

lines may be due to the presence of the isotopic species  $C^{13}H_2O$ , which has a natural abundance of about 1%. The expected shifts may be readily estimated for the two vibrations of species  $b_1$  using the FG matrix method and introducing the appropriate symmetry co-ordinates. The calculated shifts were found to be  $-12 \text{ cm}^{-1}$  and  $-9 \text{ cm}^{-1}$  for  $\nu_4$  and  $\nu_5$  respectively. For the out-of-plane bending mode  $\nu_6$ , the calculated shift was  $-12 \text{ cm}^{-1}$ . It is possible then, that the weak lines at 1167.5 cm<sup>-1</sup> and 1241 cm<sup>-1</sup> are due to the presence of  $C^{13}H_2O$ . The lack of a corresponding line for  $\nu_4$  might be due to the low relative intensity of this mode. On the other hand, even if this assignment to isotopic species is correct, a number of lines remain unassigned. These are likely due to intermolecular effects, but since the crystal structure of formaldehyde is unknown, little can be done in the way of interpretation. They might arise, for example, from the existence of crystallographically non-equivalent molecules in the unit cell.

### Matrix Spectra

Dealing with the argon matrix spectra first, it is noted that for four of the six fundamentals a triplet structure is observed. Only  $\nu_3$  and  $\nu_5$  lack this structure and in these two cases, the shift  $\nu_{solid}$  to  $\nu_{gas}$  is very small. Furthermore, the shapes of these bands are such as to suggest a closely spaced, unresolved fine structure. These observations alone tend to rule out rotation as the cause of the fine structure but this can be shown even more convincingly by considering the spectrum to be expected in the case of rotation. Using the rotational constants of Lawrence and Strandberg (15), and treating the formaldehyde molecule as a prolate symmetric top (16), one may calculate the first few rotational energy levels. These are listed in Table II along with the appropriate Boltzmann

TABLE II Rotational energy levels of formaldehyde

mann factors	Boltzma		
$4^{\circ} \operatorname{K} (A \leftrightarrow B)$	4° K (eq.)	<i>E</i> (cm <sup>-1</sup> )	F(J,K)
$\begin{smallmatrix}1\\0.42\\0.07\end{smallmatrix}$	$\begin{array}{c}1\\0.42\\0.07\\0.01\end{array}$	$ \begin{array}{r} 0 \\ 2.44 \\ 7.32 \\ 10.62 \end{array} $	(0,0) (1,0) (2,0) (1,1)
	$0.42 \\ 0.07 \\ 0.01 \\ 0.01 \\ 0.01$	2.44 7.32 10.63 15.51	(1,0) (2,0) (1,1) (2,1)

factors. If thermal equilibrium obtains, then only the two lowest levels are significantly populated at 4° K so that the number of observable transitions is severely limited. For parallel bands  $(\nu_1, \nu_2, \nu_3)$  the selection rules are:  $\Delta K = 0$ ,  $\Delta J = 0$ ,  $\pm 1$  if  $K \neq 0$  and  $\Delta K = 0$ ,  $\Delta J = \pm 1$  if K = 0; and three transitions R(0,0), R(1,0), and P(1,0) are permitted. In the case of perpendicular bands  $(\nu_4 \text{ and } \nu_5)$ ,  $\Delta K = \pm 1$ ,  $\Delta J = 0$ ,  $\pm 1$  so that a Q branch is allowed and the transitions would be Q(1,0), R(0,0), and R(1,0). The remaining vibration,  $\nu_6$ , while of a different symmetry, may also be considered a perpendicular band in this approximation. Thus, if the trapped formaldehyde molecules were rotating, we might expect to see fine structure, as illustrated in Fig. 3.



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FIG. 3. Calculated rotational structure of parallel and perpendicular bands of  $CH_2O$  in thermal equilibrium at  $4^\circ$  K.

Comparison of the calculated fine structure with that observed reveals no agreement other than the fact that they are both triplets. Not only are the observed spacings far too large, but  $\nu_1$  and  $\nu_2$ , which are of the same symmetry, do not exhibit the same band structure. A number of refinements might be considered in the theoretical treatment but these only serve to worsen the agreement. If, for example, the selection rule ortho  $\leftrightarrow$ para were not violated during the freezing process, then a state of thermal non-equilibrium would be expected in which the (1,1) and (2,1) levels would also have a significant population. (These levels correlate with levels of species *B* in the more accurate asymmetric

89

## CANADIAN JOURNAL OF CHEMISTRY, VOL. 40, 1962

rotor treatment while the (0,0) and (1,0) levels are of species A.) The main effect of this on the calculated spectra would be to introduce a Q branch into the parallel band and a P branch into the perpendicular band, giving more lines than observed. A similar situation would obtain if some of the selection rules were violated or if the rotational temperature were higher than 4° K. Alternatively, if the motion of the molecule were hindered in such a way that rotation about only one axis were allowed, the band structure would be like that of a linear or diatomic molecule. This would be a series of lines with a regular spacing of about 2.5 cm<sup>-1</sup> or 18 cm<sup>-1</sup> depending on the axis of rotation. Such an interpretation, like the others discussed, fails to account for the observed spectra so we must rule out rotation as the cause of the fine structure.

On the other hand, a strong argument can be presented for multiple trapping sites. In the three best-resolved bands,  $\nu_1$ ,  $\nu_2$ , and  $\nu_4$ , it is seen that the strongest lines are nearest to the gas phase absorption frequency while the weaker lines are shifted in the direction of the frequency of absorption in the polycrystalline solid. This suggests that the molecules are trapped in three types of holes of different sizes. The majority of the molecules occupy the largest type of hole and, being least perturbed, absorb at a frequency closest to that observed for the gas. A lesser number of molecules are present in somewhat smaller holes where the packing is more like that existing in the polycrystalline solid. From the small size of the gas-to-solid shifts for  $\nu_3$  and  $\nu_5$  it can be deduced that these vibrations are least perturbed by the close-packed environment of a solid. Hence the triplet splitting in the matrix spectrum should be small in these cases, in agreement with observation.

In speculating on the nature of the trapping sites, it is interesting to compare the present work with that of Foner *et al.*, who reported the trapping of hydrogen atoms on both substitutional and interstitial sites in inert-gas matrices. Specifically, they proposed that in these cubic close-packed structures, hydrogen atoms occupy substitutional sites and octahedral holes in both argon and xenon and possibly also tetrahedral holes in xenon. The sizes of these holes in argon are

$$r_{\rm sub} = 1.88 \text{ Å}, r_{\rm oct} = 0.77 \text{ Å}, r_{\rm tet} = 0.43 \text{ Å},$$

so that a hydrogen atom may apparently squeeze into a hole considerably smaller than its own van der Waals radius (1.2 Å). The fact that the size of the tetrahedral hole in xenon is about the same as that of the octahedral hole in argon suggests that this is about the minimum size of hole which can accommodate a hydrogen atom. Taking into account the much larger size of the formaldehyde molecule it seems extremely unlikely that it could be accommodated in anything smaller than the environment of a substitutional site in argon. The distortion required to accommodate a formaldehyde molecule in an octahedral hole would likely be so large that the site would simply lose its identity as an octahedral hole and become a substitutional site. It is proposed, therefore, that the lines at 2809.5 cm<sup>-1</sup>, 1732 cm<sup>-1</sup>, and 2880 cm<sup>-1</sup> in  $\nu_1$ ,  $\nu_2$ ,  $\nu_4$ , respectively, be assigned to absorption by formaldehyde molecules replacing a single argon atom in the cubic close-packed structure. The remaining lines must be assigned to absorption by formaldehyde molecules occupying larger holes, presumably those in which two and three argon atoms are displaced. The environment of these sites would be such as to prevent rotation while still allowing greater freedom of vibration.

The spectrum exhibited by formaldehyde in a nitrogen matrix is less complex than that in argon. This was not unexpected since others have reported similar phenomena (4) and we have observed it ourselves for H<sub>2</sub>O and D<sub>2</sub>O. On the basis of the observed spectra,

90

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## HARVEY AND OGILVIE: INFRARED ABSORPTION

it would appear that two types of sites are occupied but it is difficult to specify what these might be. In solid  $\alpha$  nitrogen, which is the stable form below 35° K, the arrangement of the molecule centers is face-centered cubic with the axes of the molecules inclined at the tetrahedral angle to one another (17). The cylindrical substitutional site with a radius of about 1.5 Å and a length of approximately 4 Å, could probably accommodate a formaldehyde molecule with a small amount of distortion of the  $N_2$  lattice. The other hole would have to be larger and likely corresponds to the case in which a formaldehyde molecule replaces two N2 molecules.

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## RÉSUMÉ

On a mesuré l'absorption infrarouge de formaldéhyde à 4° K dans l'état polycristallin et de forme monomérique. Dans le dernier cas, les molécules ont été suspendues dans une matrice inerte d'argon ou d'azote. Les fondamentales des monomères ont une structure qui suggère une rotation des molécules, mais cette interprétation est à écarter en faveur d'une explication basée sur l'existence de plusieurs emplacements différents dans la matrice.

#### REFERENCES

1. A. M. BASS and H. P. BROIDA. Formation and trapping of free radicals. Academic Press, New York. 1960.

- 2
- 3.
- 4.
- E. D. BECKER and G. C. PIMENTEL. J. Chem. Phys. 25, 224 (1956).
  G. C. PIMENTEL. Spectrochim. Acta, 12, 94 (1958).
  C. CATALANO and D. E. MILLIGAN. J. Chem. Phys. 30, 45 (1959).
  D. E. MILLIGAN, R. M. HEXTER, and K. DRESSLER. J. Chem. Phys. 34, 1009 (1961). 5.

- 8.
- D. E. MILLIGAN, K. M. HEXTER, and K. DRESSLER. J. Chem. Phys. 34, 1009 (1961).
  J. A. GLASEL. J. Chem. Phys. 33, 252 (1960).
  G. W. ROBINSON and M. MCCARTY. J. Chem. Phys. 30, 999 (1959).
  M. MCCARTY and G. W. ROBINSON. Mol. Phys. 2, 415 (1959).
  S. N. FONER, E. L. COCHRANE, V. A. BOWERS, and C. K. JEN. J. Chem. Phys. 32, 963 (1960).
  F. J. ADRIAN. J. Chem. Phys. 32, 972 (1960).
  W. H. DUERIG and I. L. MADOR. Rev. Sci. Instr. 23, 421 (1952).
  J. F. WALKER. Exercuted budg. Painbald, New York, 1972.
- 10.
- W. H. DUERIG and I. L. MADOR. Rev. Sci. Instr. 23, 421 (1952).
   J. F. WALKER. Formaldehyde. Reinhold, New York. 1953. 11.

13.

- 14
  - 15.
- 16.
- H. H. BLAU and H. H. NIELSON. J. Mol. Spectroscopy, 1, 124 (1957).
  W. G. SCHNEIDER and H. J. BERNSTEIN. Trans. Faraday Soc. 52, 13 (1956).
  R. B. LAWRENCE and M. P. W. STRANDBERG. Phys. Rev. 83, 363 (1951).
  G. HERZBERG. Infrared and Raman spectra. Van Nostrand, New York. 1945.
  L. H. BOLZ, M. E. BOYD, F. A. MAUER, and H. S. PEISER. Acta Cryst. 12, 247 (1959).