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Infra-Red Absorption Bands in the Spectrum of Deutero-Formaldehyde

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The spectrum of deutero-formaldehyde in the infra-red has been studied from 2.0μ to 13.0μ and seven absorption bands have been found. With these data and the data on the spectrum of the ordinary formaldehyde available it has been possible, making use of the product relations of Redlich, to identify with considerable certainty the fundamental frequencies of the H₂CO and D₂CO molecules, respectively, as: $\nu_1 = 2780 \text{ cm}^{-1}$, $\nu_2 = 1750 \text{ cm}^{-1}$, $\nu_3 = 2875 \text{ cm}^{-1}$, $\nu_4 = 1503 \text{ cm}^{-1}$, $\nu_5 = 1278 \text{ cm}^{-1}$, $\nu_6 = 1165 \text{ cm}^{-1}$, and $\nu_1' = 2056.4 \text{ cm}^{-1}$, $\nu_2' = 1700 \text{ cm}^{-1}$, $\nu_3' = 2160.3 \text{ cm}^{-1}$, $\nu_4' = 1106.4 \text{ cm}^{-1}$, $\nu_5' = 990.2 \text{ cm}^{-1}$ and $\nu_6' = 938.0 \text{ cm}^{-1}$. With this identification the valence force constants for the formaldehyde molecules have been computed.

I. INTRODUCTION

 \mathbf{I}^{N} a recent publication² we have discussed the measurements made by us on two of the fundamental absorption bands in the spectrum of ordinary formaldehyde vapor. With these data one may make a reasonable assignment of the fundamental frequencies for that molecule, but since some controversy has existed concerning these we have considered it of sufficient importance to measure also the spectrum of the deuterium formaldehyde. If the six bands which we desire to assign as the fundamentals are correctly chosen we should expect to find in the spectrum of this isotopic molecule six corresponding bands; the frequencies of these latter six bearing definite and well-known relationships³ to the frequencies of the former six. To establish the existence of these would serve as a convincing check on our identification and in this communication we wish to report on measurements which we have made on the absorption bands in the spectrum of D₂CO.

II. EXPERIMENTAL

A. Preparation of the D_2CO

The samples of D_2CO used in this investigation were made in the same manner as those used for measurements on the ultraviolet bands due to this molecule.⁴ The method, which will be described in detail in that paper, consisted essentially of a photochemical union between deuterium and carbon monoxide under irradiation from a quartz mercury arc. The gaseous formaldehyde formed in this manner was liquefied and distilled three times to remove glyoxal. The colorless liquid remaining was allowed to polymerize slowly. This polymer was then introduced into our cells in weighed amounts whereafter the cells were evacuated and heated to a temperature sufficiently high to vaporize completely the sample.

Except for the preparation of the D_2CO the experimental procedure has here been almost identical to that in the measurements made and reported by us on two fundamental bands in the spectrum of the ordinary formaldehyde. The absorption cells were identical in length and construction to those used there and for the preliminary survey of the spectrum the same Wadsworth prism spectrometer was used. In this preliminary survey (Fig. 1) intense absorption was found near 4.3μ , 6.0μ , and in the region from 8.0 μ to 13.0 μ . For the high dispersion measurements on these regions the same prismgrating spectrometer referred to in our earlier work was utilized. Three different diffraction gratings were necessary; one ruled with 3600 lines per inch for the region near 4.3μ , a second ruled with 2000 lines per inch for the region near 6.0μ , and a third with 900 rulings to the inch for the region 8.0μ to 12.0μ . The slit widths used throughout these measurements included in each case approximately 1 cm⁻¹ and deflections were taken with the cell in the beam and with the cell removed from the beam at equivalent intervals on the circle so that the data might be plotted as percent absorbed.

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² E. S. Ebers and H. H. Nielsen, J. Chem. Phys. 5, 822 (1937).

³O. Redlich, Zeits. f. physik. Chemie **B28**, 371 (1935). ⁴ To be published soon.



B. The 4.3µ region

This region corresponds to the region near 3000 cm^{-1} in the spectrum of H₂CO measured by one of us⁵ and like that region it consists also of three badly overlapping bands which, however, have been sufficiently well resolved so that their characteristics may be identified. Two of them are of the type containing, P, Q and R branches while the third is of the type arising from oscillations of the electric moment perpendicular to the axis of symmetry. The centers of these have respectively been chosen to be 2056.4 cm⁻¹, 2209.0 cm⁻¹ and 2160.3 cm⁻¹. The asymmetry of the molecule appears in this case to be great enough so that much of the sharpness of the rotation lines of the bands of the first type has been destroyed. An estimate of what here must be regarded as the spacing yields a value of about 1.85 cm⁻¹. In the second type of band, however, especially some distance from the center, one readily identifies a regularity of structure, the separations between the most prominent lines being about 7.6 cm⁻¹. In Fig. 2 is shown the absorption pattern characteristic of this region. The principal lines and their frequency positions are tabulated in Table I.

C. The 6.0µ region

This band is of the type with single P, Q and R branches and would seem to correspond to the ⁶ H. H. Nielsen, Phys. Rev. 46, 117 (1934).

region near 1750 cm⁻¹ in the spectrum of ordinary formaldehyde. Unfortunately the band overlaps so badly with the intense water vapor fundamental of this region that it has been impossible to obtain any accurate data concerning the actual rotational structure of the branches. An envelope of this region obtained with widened spectrometer slits yields the curve shown in Fig. 3. The center appears to be very near to 1700 cm^{-1} .

D. The region 8.0µ to 12.0µ

This region has been sufficiently well resolved to show that it also is made up of three different bands that badly overlap each other. That of highest frequency is clearly of the type with single P, Q and R branches and must undoubtedly correspond to the similar band in H₂CO which lies near 1500 cm⁻¹. The remainder of this region must correspond to that in the spectrum of H₂CO reported by us in the work referred to in the introduction. It is clearly due to the oscillations of the electric moment normal to the axis of symmetry of the molecule and as in the case of H₂CO many of the spacings between the principal lines appear larger than the corresponding ones found in the band of similar character near 2160 cm⁻¹. These spacings are here equal approximately to 10 cm^{-1} , or about 25 percent larger than the former. In Fig. 4 is shown the absorption pattern of this region as determined by these measurements and in Table II will be found the frequency positions of many of the principal lines.

III. DISCUSSION OF THE EXPERIMENTAL RESULTS

With the completion of these measurements, fairly accurate information concerning the bands



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in the spectra of the formaldehyde is available and it seems possible now to make an assignment of the fundamental frequencies with a good deal of certainty. In making these assignments one may be guided by the fact that there are certain product relationships, which, as Redlich has shown, the frequencies belonging to any one symmetry class must fulfill. Our assignment of fundamental frequencies in the case of H₂CO and D₂CO is given in Table III using the notation of Dennison and Sutherland.⁶ As we shall verify in the following paragraph, this assignment is consistent with the requirements derived by Redlich.

For H₂CO and D₂CO the normal oscillations divide up into three symmetry classes which include respectively, the frequencies ν_1 , ν_2 , ν_4 ; ν_3 , ν_5 ; and ν_6 . In terms of these the product relations of Redlich may be written in the following manner:

TABLE I. Frequency positions of lines in the 4.0µ region.

$\begin{array}{c} -21\\ -20\\ -19\\ -18\\ -17\\ -16\\ -15\\ -14\\ -13\\ -12\\ -11\\ -10\\ -9\\ -8\\ -7\\ -6\\ -5\\ -4\end{array}$	2011.2 2014.0 2015.3 2015.3 2020.0 2022.4 2025.5 2028.1 2038.0 2038.2 2033.1 2035.0 2038.6 2038.2 2040.3 2044.8 2044.6 2047.8 2049.4 2049.4	1 2 3 4 5 6 7 8 9 10 11 12 13 14 15 16	2119.0 2127.2 2134.8 2139.2 2149.6 2151.3 2157.0 2160.3 2166.3 2170.9 2174.8 2180.6 2187.1 2193.9 2202.0 2210.8	$ \begin{array}{r} -3 \\ -2 \\ -1 \\ 0 \\ 1 \\ 2 \\ 3 \\ 4 \\ 5 \\ 6 \\ 7 \\ 8 \\ 9 \\ 10 \\ 11 \\ 12 \\ 13 \\ 14 \\ 14 \\ 14 \\ 14 \\ 14 \\ 14 \\ 14 \\ 14$	2051.0 2052.6 2054.3 2056.4 2064.0 2065.7 2067.3 2069.0 2070.6 2070.6 2077.8 2073.9 2075.6	15 16 17 18 19 20 21 22 23 24 25 26 27 28 29 30 31	2081.7 2083.3 2085.5 2086.2 2089.5 2091.7 2094.0 2096.8 2099.3 2101.6 2103.9 2106.4 2108.4 2108.4 2110.7 2112.4 2115.9
-5 -4	2047.8 2049.4			13 14	2077.8 2080.0	31	2115.9

6 G. B.	B. M. Sutherland	and D.	М.	Dennison,	Proc.
Roy. Soc.	148A, 250 (1935).				

 $(\nu_{1}\nu_{2}\nu_{3}/\nu_{1}'\nu_{2}'\nu_{3}')^{2} = (m_{D}^{2}m_{C}m_{O}/m_{H}^{2}m_{C}m_{O})(M_{H_{2}CO}/M_{D_{2}CO}),$ $(\nu_{4}\nu_{5}/\nu_{4}'\nu_{5}')^{2} = (m_{D}^{2}m_{C}m_{O}/m_{H}^{2}m_{C}m_{O})$ $\times (A/A')(M_{H_{2}CO}/M_{D_{2}CO}),$ $(\nu_{6}/\nu_{6}')^{2} = (m_{D}^{2}m_{C}m/m_{H}^{2}m_{C}m_{O})$ $\times (B \cdot C/B' \cdot C')(M_{H_{*}CO}/M_{D_{2}CO}),$ (1)

where ν_i and ν_i' are the frequencies of oscillation of the H₂CO and D₂CO molecules; A, B, C and A', B', C' their principal moments of inertia; $m_{\rm H}$, $m_{\rm C}$, m_{0} , etc., the masses of the component atoms and where $M_{\rm H_2CO}$ and $M_{\rm D_2CO}$ are the molecular masses of the two molecules. In order to make use of these relations to verify our assignment of frequencies it is necessary to know the values of A, B, C, A', B' and C'. The values A, B and C have been determined for H₂CO in the ground state, with considerable accuracy by Dieke and Kistiakowsky⁷ who give the following values expressed in g cm²: $A = 24.33 \times 10^{-40}$, $B = 21.39 \times 10^{-40}$, $C = 2.941 \times 10^{-40}$. These same

TABLE II. Frequency positions of lines in 11µ region.

1	841.3 cm ⁻¹	15	977.8 cm ⁻¹
2	852.9	16	981.1
3	859.2	17	990.2
4	864.9	18	997.9
5	875.9	19	1002.1
6	887.8	20	1009.1
7	893.3	21	1014.4
8	906.4	22	1023.3
9	938.5	23	1033.3
10	949.1	24	1043.4
11	958.5	25	1053.8
12	962.4	26	1066.4
13	968.0	27	1103.8
14	974.5		

⁷ G. H. Dieke and G. B. Kistiakowsky, Phys. Rev. 45, 4 (1934).



FIG. 4.

values are also found to be consistent with the infra-red absorption data. The bands in the spectrum of D_2CO , in particular those due to oscillations of the electric moment along the axis of symmetry, are hardly well enough resolved to make a complete rotational analysis feasible and hence, very accurate values for A', B', and C' cannot be determined from the data here presented. An estimate of the values of A', B', and C' can, however, be arrived at which is sufficiently accurate for use in Eqs. (1). We shall make use of the bands near 4.5μ which are probably as well resolved as any, to make these estimated values of A', B' and C'.

If we approximate the rotational motion of the D₂CO molecules by that of an equivalent symmetric rotator with the moments of inertia \overline{A} , \overline{B} and \overline{C} related to the actual moments of inertia A', B' and C' in the following manner $1/\overline{A} = 1/\overline{B} = \frac{1}{2}(1/A'+1/B')$ and $\overline{C} = C'$ one obtains for the separations between principal lines in the bands arising from oscillations of the electric moment parallel and perpendicular to the axis of symmetry, respectively, the following values:

 $\Delta \nu_1 = (h/4\pi^2) \frac{1}{2} (1/A' + 1/B')$ and $\Delta \nu_2 = (h/4\pi^2) \lceil 1/C' - \frac{1}{2} (1/A' + 1/B') \rceil$.

These assumptions are clearly less valid here than for H₂CO for here the asymmetry will be appreciably greater than for H₂CO, but still sufficiently good, when spacings not too near the center are considered to make the above test. For $\Delta \nu_1$ we have taken the value 1.85 cm⁻¹ and for $\Delta \nu_2$ the value 7.6 cm⁻¹ seems best. These values lead to $\tilde{A} = \bar{B} = 30.1 \times 10^{-10}$ g cm² and $\bar{C} = 5.84 \times 10^{-10}$ g cm². Bearing in mind that $(1/\bar{A} + 1/\bar{B}) = (1/A' + 1/B')$ and that C' = A' - B'we obtain the values $A' = 33.0 \times 10^{-40}$, B' = 27.2 $\times 10^{-40}$ and $C' = 5.84 \times 10^{-40}$ for the moments of inertia for the D_2CO molecule expressed in $g \text{ cm}^2$.

For convenience we insert Table IV which sets forth the values of $\Pi(\nu_i/\nu_i')^2$ as computed from Redlich's Eqs. (1) as compared with the values determined from the experimental measurements. We feel the agreement is a satisfactory one when one considers that Redlich's derivation applies strictly speaking only when the oscillatory motion is harmonic, and offer it in support of our assignment of frequencies given in Table III. Certain writers have preferred the assignment $\nu_1(H_2CO) = 2974$ cm⁻¹ and $2\nu_4(H_2CO)$ =2780 cm⁻¹ to the one given by us. We cannot but feel that the frequency 2780 cm^{-1} is much too intense to be given the assignment $2\nu_4$ and that the much less intense band at 2974 cm⁻¹ would fit much more consistently with this assignment. This opinion is supported also by the measurements made on the corresponding bands in the spectrum of the isotopic molecule. This question cannot definitely be settled, however, by resorting to Redlich's equation since either assignment gives agreement between experimental and computed values of $\Pi(\nu_i/\nu_i')^2$.

If the above assignment of frequencies be adopted as correct, we may make use of it to derive information concerning the forces binding the atoms of the molecule together. Certain assumptions are, in general, necessary concerning the nature of these forces and the one which here

TABLE III. Assignment of frequencies in H₂CO and D₂CO.

H₂CO	D ₂ CO
$\begin{array}{c} \nu_1 & 2780 \text{ cm}^{-1} \\ \nu_2 & 1750 \\ \nu_3 & 2875 \\ \nu_4 & 1503 \\ \nu_5 & 1278 \\ \nu_6 & 1165 \\ 2\nu_4 & 2974 \end{array}$	$\begin{array}{c} 2056.4 \text{ cm}^{-1} \\ 17002160.3 \\ 1106.0 \\ 990.2 \\ 93822092 \end{array}$

TABLE IV. Values of $\Pi(\nu_i/\nu_i')^2$.

Computed values Experimental values	1.48 1.5	2.8 2.9	3.7 3.6

shall be made is that the actual interatomic forces may to a good approximation be replaced by valence forces. This assumption which has proved itself useful in a great many cases is a convenient one since the quantities which then may occur in the potential energy function are ones readily interpretable in chemical and physical theory. Using such forces, Lechner⁸ has considered the oscillational motion of the XYZ_2 type of molecule in its own plane and has derived the following relations:

$$\nu_{3}^{2}\nu_{5}^{2} = f_{13}\alpha'A,$$

$$\nu_{3}^{2} + \nu_{5}^{2} = f_{13}B + \alpha'C,$$

$$\nu_{1}^{2}\nu_{2}^{2}\nu_{4}^{2} = f_{12}f_{13}\alpha D,$$

$$\nu_{1}^{2} + \nu_{2}^{2} + \nu_{4}^{2} = f_{12}H + f_{13}I + \alpha K,$$

$$\nu_{1}^{2}\nu_{2}^{2} + \nu_{1}^{2}\nu_{4}^{2} + \nu_{2}^{2}\nu_{4}^{2} = f_{12}f_{13}E + f_{12}\alpha F + f_{13}\alpha G$$

where f_{12} , f_{13} , α and α' are to be regarded as force constants and A, B, C, D, E, F, G, H, I, and K are constants depending upon the masses of the atomic nuclei, the interatomic distances and the YZ_2 bond angle. f_{12} and f_{13} are, respectively, the force constants to be associated with displacements of the X, Y and Y, Z particles along the valence arm joining them together;

⁸ F. Lechner, Wien Bericht. 141, 633 (1932).

TABLE V.

	Computed Frequencies		Measured Frequencies		
Force Constants	H2CO	D ₂ CO	H ₂ CO	D ₂ CO	
$\begin{array}{l} \alpha = \ 1.46 \pm .03 \\ \alpha' = \ .57 \pm .01 \\ f_{12} = 12.06 \pm .03 \\ f_{13} = \ 4.22 \pm .14 \end{array}$	$\nu_1 = 2780 \\ \nu_2 = 1840 \\ \nu_3 = 2825 \\ \nu_4 = 1470 \\ \nu_5 = 1267$	$\nu_1 = 2138 \\ \nu_2 = 1625 \\ \nu_3 = 2118 \\ \nu_4 = 1115 \\ \nu_5 = 997$	$\nu_1 = 2780 \nu_2 = 1750 \nu_3 = 2875 \nu_4 = 1500 \nu_5 = 1278$	$\nu_1 = 2056 \nu_2 = 1700 \nu_3 = 2160 \nu_4 = 1106 \nu_5 = 990$	

 α and α' the valence force constants associated with the deformation of the XZ_2 and the XYZbond angles, respectively.

The interatomic distances may be computed from the values of the moments of inertia, the XZ_2 bond angle having been assumed to be tetrahedral or about 109°. The constants f_{12} , f_{13} , α and α' have then been evaluated from the above equations of Lechner using the fundamental bands observed for the H₂CO and the D₂CO molecules. The values obtained for these constants from the two isotopic molecules are in good agreement; in Table V the average value of these being set down together with the actually observed fundamental frequencies and a set of frequencies, computed by substitution of these average value force constants into the above equations of Lechner, for comparison.

The values seem to be in satisfactory agreement when one considers that the Lechner derivations are valid, in reality, only when the oscillational motion is harmonic.