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Earle S. Ebers and Harald H. Nielsen

III. Selection Rules and the Question of Intensities

The final conclusions of the previous section may be confirmed quantitatively by a study of the selection rules and the intensity relations. The rules of transition may be arrived at by examination of the nonvanishing matrix components of the electric moment as the molecule executes a transition from the ground state to one of the two characterized either by $\Psi(+1)$ or $\Psi(-1)$. Since the method is an obvious one, we shall not here derive them, but content ourselves merely by stating what they are. When a transition from the zeroth vibration state to one of the two upper states takes place the selection rule for K will in general be $\Delta K = \pm 1$, lines in the spectrum occurring at the following corresponding frequency positions:

$$\nu = (\nu_1 + \nu_2)/2 \mp (Kh/4\pi^2 A) \\ \pm \{(\nu_1 - \nu_2)^2/4 + (K\zeta h/4\pi^2 A)^2\}^{\frac{1}{2}}. \quad (10)$$

From this it will be seen that when $\Delta \nu$ is large compared with $K\zeta h/4\pi^2 A$ the spacing between rotational lines approaches the normal value $h/4\pi^2 A$, but as K increases, taking like signs in (10), the spacing approaches $(1+\zeta)h/4\pi^2 A$; taking opposite signs in (10), a value approaching $(1-\zeta)h/4\pi^2 A$ prevails. Examination of the matrix components verifies, moreover, that when the molecule executes an oscillational transition from the ground state to the state $+1$, the probability of the rotational transition $K = K' + 1$ in the lower to $K = K'$ in the upper state increases at the expense of the transition $K = K' - 1$ to $K = K'$, as K increases. Similarly, when the molecule makes a transition from the ground state to the oscillational state -1, the transition $K = K' - 1$ to $K = K'$ increases in probability at the expense of the other.

This result is again consistent with the work of Teller and Tiza in which they showed that for a two dimensional isotropic oscillator rotating in its own plane, ζ being taken as unity, the rotational structure would collapse into a single line, i.e., the spacing between two adjacent lines would be zero. This is virtually what happens in our case as $Kh/4\pi^2 A$ becomes large compared to $\Delta \nu$.

In conclusion we shall simply summarize the derived results. In certain molecules when oscillations occur which are only slightly anisotropic interactions between rotation and oscillation may occur, not wholly unlike those that take place in completely symmetric molecules. The effect upon the spectrum will be a rapid convergence of the rotational lines in the halves of the two bands adjacent to each other toward a limiting value of the spacings $(1-\zeta)h/4\pi^2 A$, while on the other sides the spacings between lines rapidly approach a value $(1+\zeta)h/4\pi^2 A$. The intensities of the former set of lines will at the same time be enhanced at the expense of the latter set of lines.

The author desires to express his gratefulness to Professor E. Teller and to Professor D. M. Dennison with whom he has had occasion to discuss this problem and who have made suggestions distinctly helpful in deducing the results in the present formulation.

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Two infrared bands of the type arising from oscillations of the electric moment normal to the axis of symmetry have been measured under high dispersion and identified as the two oscillations which are at right angles to each other and which in Sutherland and Dennison's notation are ν_5 and ν_6. Their centers are respectively at 1278 cm^{-1} and 1165 cm^{-1}. The anomalous spacing between the principal rotation lines is accounted for on the basis of an interaction between rotation and the two oscillations which are only slightly anisotropic.

I. INTRODUCTION

IT has been possible by measurements on the absorption by formaldehyde vapor in the ultraviolet[2] and infrared regions[3] of the spectrum to accurately determine the magnitudes of the moments of inertia of this molecule. Concerning what are to be taken to be the fundamental vibration frequencies, however, considerable ambiguity has existed, for while the five bands in the region 3.0μ to 7.0μ may definitely be identified, no such identification for the remaining bands from 7.0μ on has until now seemed possible. Neither has it been possible to enlist any aid in this matter from the Raman spectrum which has only been investigated for formaldehyde in solutions. Four investigators[4] of the Raman spectrum of formaldehyde in solution following different methods of procedure, draw the unanimous conclusion that the standard 40 percent water solution cannot give rise to the fundamental frequencies characteristic of H_2CO, but that the lines observed must be attributed to products of hydration or of polymerization—a conclusion supported also by other physical evidence.[5] Certain authors have drawn upon the results of a fifth investigator[6] of the Raman spectrum of formaldehyde in solution for the purpose of assigning vibration frequencies to the H_2CO molecule, apparently without too close scrutiny of its validity for the purpose. The measurements are reported to be on an 80 percent solution but which we are inclined to interpret as a misprint intended to·read 30 percent. Our belief is based upon the experience of one of us in an attempt to make Raman measurements on pure liquid formaldehyde and on concentrated solutions as well (all of which were maintained at $-78.5°C$ and illuminated by radiation of wave-length 4358A only) which failed because of the too rapid polymerization of the formaldehyde at the walls of the Raman tube.

Even if the solution in the above were of a concentration of 80 percent we do not feel that these frequencies may unequivocally be assigned to the formaldehyde molecule for of the six lines reported, all except the one at 1768 cm^{-1} fall at positions coincident with lines, reported also by the other four investigators, concerning which there is general agreement. It seems only natural to ascribe these lines also to products of hydration or polymerization since it is difficult to believe that such products would not also be present in a solution of formaldehyde in 80 percent concentration.

To help clarify what are the actual facts concerning the fundamental bands due to the formaldehyde molecule we have remeasured the entire spectrum of the vapor from 1.0μ to 15.0μ using a prism spectrometer of the Wadsworth-Litrow type. In addition the entire spectral range 7.0μ to 12.0μ has been investigated under high dispersion using a prism-grating spectrometer.

II. EXPERIMENTAL

An important advance in the experimental technique over that of other attempts is the improved absorption cell here used in making these measurements. This cell was actually developed in preparation for the measurements which we proposed to make on the isotopic formaldehydes.[7] The small amounts of these compounds which were available prevented employing the older method of displacing the air in the cell by formaldehyde vapor and necessitated constructing a cell which would remain vacuum tight up to 200°C. This was accomplished, however, by sealing the joints which the polished rocksalt windows make with the ground ends of the glass tube of which the cell was made with glyptal (No. 1201). These cells were eminently satisfactory and have been operated at temperatures as high as 250°C without any signs of deterioration. No difficulty was experienced from the unequal expansion of the glass and the rocksalt during the raising of these cells to their desired temperatures since the glyptal takes an appreciable time to lose its elasticity. On cooling, however, strains were produced which frequently cracked the halite windows or broke it loose from the glass tube.

[1] Fellow of the Royal Society of Canada.

[2] G. H. Diecke and G. B. Kistiakowsky, Phys. Rev. 45, 4 (1934).

[3] Harald H. Nielsen, Phys. Rev. 46, 117 (1934).

[4] Kohlrausch and F. Köppl, Zeits. f. physik. Chemie 24, 370 (1934); P. Krishnamurti, Ind. J. Phys. 6, 309 (1931); James H. Hibben, J. Am. Chem. Soc. 53, 2418-9 (1931); B. Trumpy, Klg. Norske Videnskab Selskabs Skrifter 9, 1-20 (1935).

[5] Frederic Walker, J. Phys. Chem. 35, 1104 (1931); V. Henri and A. Schou, Zeits. f. Physik 49, 774 (1928).

[6] N. Pal and Sen Gupta, Ind. J. Phys. 5, 24 (1930).

[7] To be published soon.

The cells of the above type were 7 cm long and 5 cm in diameter. They were evacuated and tested before a weighed sample of para-formaldehyde sufficient to yield enough formaldehyde vapor to produce the desired absorption (generally enough to produce formaldehyde vapor to a pressure of about 20 cm Hg) was introduced. The cell was then evacuated, sealed off and raised to a temperature above that required for complete sublimation.[8] Besides economizing on the material a cell such as that described above possesses the other obvious advantage of insuring that no oxidation of the formaldehydes could take place. This cell was used for all the measurements made with the prism spectrometer and for many of the high dispersion measurements as well.

It is clearly desirable, if possible, to make the high dispersion measurements at room temperature. It was found possible to do this in the following manner. To a cell similar to the one described above, 27 cm long was joined a trap which in turn was joined to a reservoir containing polymerized formaldehyde which had been purified according to the method of Spence and Wild.[9] The entire system was evacuated and sealed off and then the formaldehyde was sublimed over into the trap where it was collected as a liquid by a freezing bath kept at a temperature of −78.5°C. At this temperature the liquid formaldehyde, which is monomeric, has a vapor pressure of 22 mm[9] Hg. The 27 cm cell filled with formaldehyde vapor at this pressure offers a path length of sufficient magnitude for the absorption measurements to be readily made. Polymerization of the vapor on the walls and

windows of the cell occurs slowly at this pressure and the cell may be used with confidence for about four hours. The cells were then taken apart and completely rebuilt. The measurements obtained using this cell were found to duplicate those obtained when the heated cell was used except that in the former case the lines were noticeably sharper and more details in the absorption pattern were discernible. For the exploratory prism work, a prism spectrometer of the Wadsworth-Litrow type was available. It was used only to verify the results obtained in the earlier investigation and to extend the exploration from 11.0μ to 15.0μ. The spectrometer used to make the high dispersion measurement was the same used in other experiments carried out in this laboratory and is capable of resolving lines separated by frequency intervals of less than 1 cm^{-1}. Two gratings were used in making the measurements from 7.0μ to 12.0μ, one ruled by R. W. Wood with 800 lines per inch and another with 1200 lines per inch. The latter was most generously loaned to us by Professor H. M. Randall for these measurements.

III. EXPERIMENTAL RESULTS

The absorption spectrum of formaldehyde as determined prismatically is shown in Fig. 1 and confirms in general appearance the prism curve of Nielsen although the present one seems to indicate more continuous absorption from 7.5μ on. This may be due in part to the somewhat better resolving power of the prism instrument used in the earlier experiment. Regions of intense absorption occur near 3.5μ, 5.7μ, 6.7μ and 7.5μ to nearly 10μ, but beyond these no evidence of any absorption bands could be found.

The region from 7.5μ to 10μ was found to consist of two rather intense and overlapping bands, having the characteristics of oscillations

[8] A rough determination of the vapor pressure of paraformaldehyde yielded the following results:

T°C	30	65	80	90	100	110	120
P mm Hg	0	156	246	331	372	401	586

[9] R. Spence and W. Wild, J. C. S. 507 (1935); R. Spence and W. Wild, J. C. S. 338–40 (1935).
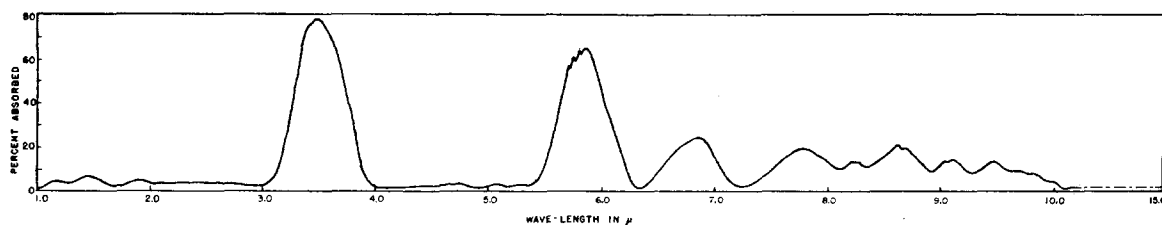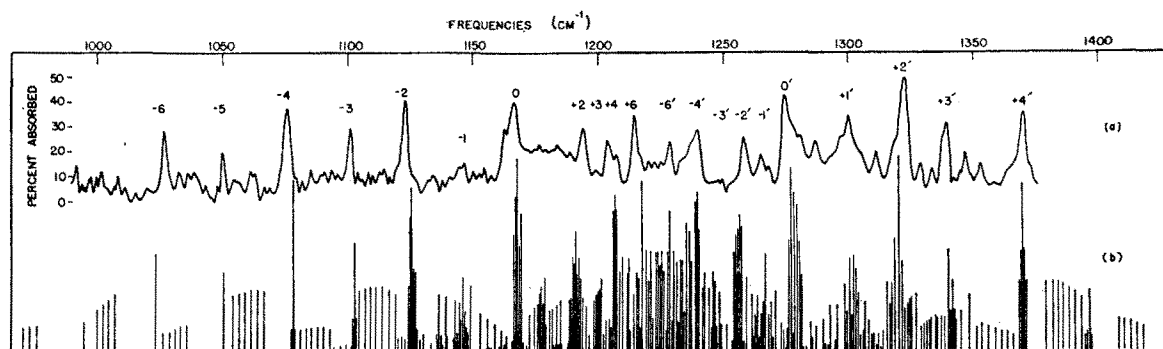

FIG. 1.

FIG. 2.

perpendicular to the axis of symmetry. From 7.5μ to beyond 8.0μ the region duplicates almost exactly the data reported by Nielsen, except that with the cell operated at room temperatures considerably more detail was to be found. As reported in our preliminary communication,[10] the data from this point on was entirely different from those of Nielsen. The band reported by him was of the type arising from an oscillation parallel to the axis of symmetry of the molecule while that which here is found is another band of the type where the electric moment oscillates perpendicular to this axis. It is probably to be concluded that the earlier reported band was due to some impurity present, perhaps some product of oxidation, but certainly not to formaldehyde. It is to be noted also that the spacings between the lines of this band reported in the earlier work are slightly less than those in other bands of this type. In all events the measurements on this region have been repeated a great many times and under varied conditions, but the pattern has consistently repeated itself. In Fig. 2 (a) is reproduced the absorption pattern of this region as it was observed with the cell operated at room temperature. Our Fig. 2 (a) embraces the region 9.6μ reported by Nielsen to and including the lines given by him in his Fig. 5. One additional line has been added to this latter group. In Table I are given the frequency positions of the principal lines in the band. The convergence of these so noticeable in Nielsen's Fig. 5 is here shown by the additional detail we have observed to be only an apparent one. The fact that the spacings between the

rotational lines in the extremities of the two bands is something over 23 cm⁻¹ or nearly 50 percent larger than those in the similar type of band near 3.5μ in the spectrum of formaldehyde is a detail worthy of some note.

IV. DISCUSSION OF THE RESULTS

These rather intense bands comprising the region from 7.5μ to 10μ and here measured under high dispersion must undoubtedly be taken to be the so-called "deformation" frequencies which in Sutherland's and Dennison's[11] notation are ν_5 and ν_6. As to which is which of the two frequencies is more difficult to ascertain, however. Our most likely avenue of successfully identifying these is by a study of the rotational structure. The formaldehyde molecule, considered as a rotating body, is a slightly asymmetric top so that these two oscillations which are both normal to the axis of symmetry (i.e., the one is perpendicular to the plane of the molecule while the other remains in the plane) might be expected to produce bands whose rotational structure would in a general way be similar except near the centers. These lines near the center which are the only ones really affected by the asymmetry become split up into components here too closely spaced for spectroscopic resolution and would appear rather as broadened lines. The manner in which this broadening takes place, however, is different for the two lines nearest the center in each of the two bands. For the oscillation out of the plane the two central lines converge toward each other giving an apparent spacing between these something less

[10] E. S. Ebers and H. H. Nielsen, J. Chem. Phys. 5, 84 (1937).

[11] G. B. B. M. Sutherland and D. M. Dennison, Proc. Roy. Soc. 148A, 250 (1935).

than that between any of the other lines in the band, while for the oscillation remaining in the plane, the central lines converge away from each other producing a spacing between them larger than that between other lines in the band.

The two bands lie, moreover, very close together; separated from each other by an interval $\Delta\nu$ of only slightly more than 100 cm^{-1}. The frequencies are therefore only slightly anistropic and interactions between rotation and oscillation may therefore be expected to occur of the type discussed by one of us.[12] We shall assume further that this type of interaction does not here materially alter the asymmetry of the molecule so that the energies of the molecule rotating and oscillating in these modes may to a good approximation be written:

$$E=\frac{h}{2}(\nu_5+\nu_6)+\left(\frac{h^2}{8\pi^2}\right)\frac{J(J+1)}{2}\left(\frac{1}{A_x}+\frac{1}{A_y}\right)$$
$$-\frac{Wh^2}{8\pi^2}\left[\frac{1}{2}\left(\frac{1}{A_x}+\frac{1}{A_y}\right)-\frac{1}{A_z}\right] \quad (1)$$

for the ground state and:

$$E=h(\nu_5+\nu_6)+\frac{h^2}{8\pi^2}(J(J+1)-W)(1/2A_x+1/2A_y)$$
$$+\frac{(W+\zeta^2)h^2}{8\pi^2A_z}\pm h\left[\left(\frac{\nu_5-\nu_6}{2}\right)^2+W\left(\frac{h\zeta}{4\pi^2A_z}\right)^2\right]^{\frac{1}{2}} \quad (2)$$

for the first excited states where W are the roots of the Wang-Klein[13] secular determinant for the eigenvalues of the asymmetric rotator and which may perhaps most readily be obtained from the

TABLE I. *Frequencies of principal absorption lines for the region 7.0μ–10μ.*

Line No.	Frequencies in cm^{-1}	Line No.	Frequencies in cm^{-1}
−6	1027.0	−6′	1229.1
−5	1051.0	−4′	1239.3
−4	1075.9	−3′	——
−3	1099.7	−2′	1259.0
−2	1121.8	−1′	1265.3
−1	1146.3	0′	1275.2
0	1165.7	+1′	1300.8
+1	——		1312.3
+2	1093.4	+2′	1323.0
+3	——	+3′	1339.4
+4	1204.6		1347.0
+6	1213.8	+4′	1370.5

[12] Harald H. Nielsen, J. Chem. Phys. **5**, 818 (1937).
[13] S. C. Wang, Phys. Rev. **34**, 243 (1929); O. Klein, Zeits. f. Physik **58**, 730 (1929).

equations of Nielsen.[14] In our case these will approximately be equal to K^2, K taking all integral values from zero to J, the quantum number of total angular momentum. An approximate value for the constant ζ occurring in the above equation has been calculated in reference 12 on the basis of a model where the CH$_2$ triangle remains rigid and may be seen to have an involved dependence on the normal modes of the oscillations. Replacing W by K^2 in (1) and (2) and observing that in the case of a symmetric top that the strong lines in a perpendicular band like the ones here observed which protrude above the background are obtained when the molecule executes a transition of the type $\Delta J=0$, $\Delta K=\pm1$, one obtains the following approximate relation for the frequency positions of the lines in the two bands:

$$\nu=(\nu_5+\nu_6)/2+(h/8\pi^2)(\tfrac{1}{2}(1/A_x+1/A_y)$$
$$+(\zeta^2-1)/A_z)+(Kh/4\pi^2)(\tfrac{1}{2}(1/A_x+1/A_y)$$
$$-1/A_z)\pm((\nu_5-\nu_6)^2/4+(Kh/4\pi^2A_z)^2), \quad (3)$$

K taking the values 0, ±1, ±2, etc. the effect of this interaction on the spectrum will be seen from (3) to be, to give spacings between the principal rotational lines in the extremities of the bands farthest away from each other and in the sides nearest each other, the values $(h/4\pi^2)$ $\times(\tfrac{1}{2}(1/A_x+1/A_y)-(1\pm\zeta)/A_z)$, respectively. It will be seen that the spacings actually observed between these principal lines ultimately reached here would perhaps be about 26 cm^{-1}. Actual quantitative agreement between predicted lines and experimentally observed lines is approached when one takes

$$\nu_5+(h/8\pi^2)(\tfrac{1}{2}(1/A_x+1/A_y)+(\zeta^2-1)/A_z)$$

and,

$$\nu_6+(h/8\pi^2)(\tfrac{1}{2}(1/A_x+1/A_y)+(\zeta^2-1)/A_z),$$

respectively, equal to 1278 cm^{-1} and 1165 cm^{-1}, $(h/4\pi^2)(1/A_z-\tfrac{1}{2}(1/A_x+1/A_y))=16.2$ cm^{-1} and ζ equal to about 0.80. Applying the approximate value of ζ computed in reference 12 to the molecular model of formaldehyde proposed by

[14] Harald H. Nielsen, Phys. Rev. **38**, 1432 (1931). In the equations for W given in this paper, several errors occur, some of which are misprints and others which apparently are due to errors in copying from the original manuscripts. Corrections to these may be found in a paper by Randall, Dennison, Ginsberg and Weber, Phys. Rev. **52**, 160 (1937).

Diecke and Kistiakowsky where the $H-C-H$ bond angle is taken to be tetrahedral one obtains a value of ζ equal to about 0.6. Considering the approximations made in these calculations this value seems in satisfactory agreement with the experimentally determined value. In computing the energies (1) and (2) from which the predicted lines are calculated, actual W values, and not merely the approximate ones $W=K^2$ were used. The W values actually employed were the same determined by Nordsieck[15] in calculations made by him on the appearance of the infrared bands of formaldehyde.

The alternating intensities of the principal lines as observed in the two bands are readily accounted for when one considers the presence of the two identical hydrogen atoms each with a nuclear spin $\frac{1}{2}(h/2\pi)$. This serves to divide the molecular energy states into a symmetric and an antisymmetric classification in the following manner. The complete wave function Ψ for a state will be a product of the following functions; the electronic wave function Φ, the oscillational wave function $R(v_1, v_2, v_3, v_4, v_5, v_6)$, the rotational wave function $\Theta(J, \tau, M)$ and the nuclear spin function S. The number τ occurring in Θ is the parameter introduced by Dennison[16] and takes the $2J+1$ values $-J$ to J, the state of lowest energy for any value of J being that characterized by $\tau=-J$.

The symmetry character of Φ for an interchange of the two identical hydrogen nuclei is unknown to us; R, however, is a symmetric function when all the v's are zero, but antisymmetric when either v_5 or v_6 becomes one, all the others remaining zero. The symmetry character of the function Θ for a molecule like H_2CO where the axis of the least moment of inertia bisects the bond angle of the carbon has been discussed by Dennison and is independent of J. For any value of J, it is alternatingly symmetric, antisymmetric; antisymmetric, symmetric beginning always as symmetric for $\tau=-J$. Applying the general exclusion principle for protons which states that only such energy states are permitted to exist where the entire Ψ function is antisymmetric for an interchange of these, we see that the rotational levels will be divided

into two groups, those having a symmetric and those having an antisymmetric nuclear spin function. Of these the first have a weight factor 3 as compared to a weight factor 1 for the second. Having determined

$$\nu_5+(h/8\pi^2)[\tfrac{1}{2}(1/A_x+1/A_y)+(\zeta^2-1)/A_z],$$
$$\nu_6+(h/8\pi^2)[\tfrac{1}{2}(1/A_x+1/A_y)+(\zeta^2-1)/A_z],$$

respectively, to be 1278 cm^{-1} and 1165 cm^{-1}, bearing in mind that the lines occurring at these points arise from transitions $J=J$, $\tau=-J+1$ $\to J=J$, $\tau=-J$ or $J=J$, $\tau=-J+2\to J=J$, $\tau=-J$ (i.e., $J=J$, $K=1\to J=J$, $K=0$ in the case of the symmetric top) and noting, moreover that these lines are *strong* lines, we have also determined that the levels $J=J$, $\tau=-J+1$, $\tau=-J$ $+2$ have in the ground state a symmetric spin function. Thus the spin function (and as well the weight factor) to be associated with any level in the ground state has uniquely been determined. In the first excited states this classification will be just completely reversed because the function R is here antisymmetric. It may be seen, moreover, that the electronic part of the wave function must be symmetric for an interchange of the two identical hydrogen nuclei. From the above it becomes clear that the principal lines in the bands should be expected to occur alternately strong and weak on either side beginning with an intense line for the transition $J=J$, $\tau=-J+1$, $-J+2\to J=J$, $\tau=-J$.

The lines predicted by the permitted transitions between the energy levels computed from (1) and (2), using J values up to and including $J=10$, have for the sake of convenient comparison been plotted with their appropriate intensities in Fig. 2 (b) directly below the experimentally observed spectrum. While certainly additional lines will arise from levels of J value greater than 10, they will serve principally to fill out the background of the band which is here experimentally unresolved. The additional labor involved in computing the values of W has not seemed justifiable considering what might be gained in the actual agreement to be had between theory and experiment. In general we feel the agreement between the theoretically predicted spectrum and the experimentally observed spectrum as shown in Figs. 2 (a) and 2 (b) to be a satisfactory one when one considers the approximations that have been made.

[15] A. Nordsieck, Phys. Rev. **45**, 133–4 (1934).
[16] D. M. Dennison, Rev. Mod. Phys. **3**, 280 (1931).