THE MICROWAVE SPECTRUM OF KETENE

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Abstract

The microwave absorption spectra of the ketene molecules $\text{H}_2\text{C}_2\text{O}$, $\text{H}\text{D}\text{C}_2\text{O}$, and $\text{D}_2\text{C}_2\text{O}$ have been investigated. Reciprocal moments of inertia have been determined for each from the measurements. The centrifugal distortion theory of Hillger and Strandberg has been found valid for both Q and R branches. The structure has been calculated and dipole moment measured; results check and extend the accuracy of values previously determined by other methods. Intensities of satellites of the lightest molecule corresponding to the lowest three vibrational fundamentals have also been measured, and changes in the average reciprocal moments determined. The vibrational frequencies have been calculated and found different from values reported in the literature by infrared workers. References and suggestions for further work are given.
THE MICROWAVE SPECTRUM OF KETENE

Introduction

A. General Properties

Ketene is an organic compound, \( \text{CH}_2\text{C}=\text{O} \), which at room temperature is a colorless, heavy, extremely poisonous (1) gas (Fig. 5). It melts at \(-151^\circ \text{C}\) and boils at approximately \(-50^\circ \text{C}\). Ketene is chemically reactive and a dimer exists at room temperature. There is a large body of literature on the molecule, bearing mainly on its chemical properties. Because its spectrum is difficult enough to be interesting but perhaps simple enough to be precisely analyzed, considerable spectroscopic work has been published. Ketene has \( \text{C}_2\text{v} \) symmetry and an electric dipole moment, and is nearly a prolate symmetric rotor.

B. Early Microwave History

Early in 1948, J. Goldstein of Harvard located four microwave rotational absorption lines of ketene in the 20,000-Mc/sec region, where the \( J = 0 \rightarrow J = 1 \) transition would be expected on the basis of the known structure. At his request, the precise frequencies of those lines were measured in this laboratory, and the Stark coefficients were determined. The higher frequency transitions \( J = 1 \rightarrow 2 \) and \( J = 2 \rightarrow 3 \) were also measured since our laboratory was equipped to work in those regions (40,000 and 60,000 Mc/sec respectively).

Early in 1950, Bak and co-workers at Copenhagen measured the \( J = 0 \rightarrow 1 \) of \( \text{H}_2\text{C}_2\text{O} \), \( \text{D}_2\text{H}_2\text{C}_2\text{O} \), and \( \text{D}_2\text{C}_2\text{O} \) (hereafter briefly referred to as \( \text{H}_2\text{C}_2\text{O}, \text{DHC}_2\text{O} \) and \( \text{D}_2\text{C}_2\text{O} \) respectively) as well as some vibrational satellites (10). The reported absorption frequencies (wavemeter accuracy) check fairly well with our measurements, although some discrepancies amount to 20 Mc/sec. A preliminary report of our work herein described has been given (11).

C. Reason for Interest

The values of the three moments of inertia of \( \text{H}_2\text{C}_2\text{O} \) would enable calculation of thermodynamic gas functions of possible engineering interest; also using those of \( \text{D}_2\text{C}_2\text{O} \) the structure of ketene could be calculated; the combination of Q and R branch transitions that occur would give an interesting check on the theory of centrifugal distortion in asymmetric tops developed in this laboratory (12, 13); the relative intensities of the vibrational satellites which occur would help in the correct assignment of the fundamental vibrational frequencies; and the measurement of the Stark effect would enable accurate evaluation of the dipole moment independent of impurities. Consequently intensive work has recently been begun in this laboratory.

I. Experimental Work

A. Preparation of Ketene and Heavy Ketene

Ketene was made by pyrolysis of acetone using a lamp described by Williams and Hurd (14). Their method was modified in that a vacuum system was used to minimize
Fig. 1 System for ketene synthesis.
loss of the deuterium compounds. With reference to Fig. 1, acetone was cracked at
about atmospheric pressure in subsystem ADCB, and products bled off through capil-

lary F to liquid nitrogen cooled traps GH and rotary vacuum pump I. Acetone in bulb
A was surrounded by a water bath at 55°C. Vapors rising from A cannot pass the drop
condensed in constriction B, so they rise into D and make contact with the dull-red hot
nichrome filament there. Most of the acetone is returned by the water-cooled
condensers C and E to A; ketene, some acetone, and other products pass through
capillary F (1 meter long, 0.4 mm bore) into large cold traps G and H; the pressure on
this side of the capillary is low enough so that the two traps are essentially 100 percent
effective in condensing ketene and less volatile compounds (the second trap condenses
very little). The pump removes at least some of a more volatile product, probably
\( \text{CH}_4 \). Purification of the ketene is carried out by fractional distillation in the following
way. The substance is first triple-distilled at the temperature of dry ice in acetone.
This removes impurities, mainly acetone, less volatile than ketene; they are returned
to A for recycling. The ketene is then placed in a microwave spectroscope and slowly
warmed. The absorption of the effluent vapor at the frequency of the \( J = 0\rightarrow 1 \) line is
monitored as the vapor is being pumped off. When the spectroscope indicates ketene,
and the absorption shows little increase with time, the pump is shut off. This results in
discarding more volatile impurities, roughly 5 to 20 percent of the mixture. The ketene
has been stored in vacuum for months at liquid nitrogen temperatures with no deterio-
ration; some decomposition is noticeable in a week of storage at dry-ice acetone tem-

peratures.

Heavy ketene was made in the same way as the light, but 1.5 cc of 96 percent pure
heavy acetone, supplied to us by R.C. Lord of M.I.T. was used. \( \text{DHC}_2\text{O} \) was made
from a mixture of 50 percent each of heavy and light acetones (attempts to make it by
exchange of light ketene and heavy water were unsuccessful).

B. Systems Used

The spectroscope used for most of this work (15) employed square-wave Stark
modulation at 6 kc/sec, and a 6 kc/sec amplifier, phase detector, and remodulator.
The system bandwidth was roughly 10 cps. Reflex klystrons were used as sources on
this system. Its ultimate sensitivity, used with a two-meter X-band cell of the usual
type, appeared to be between 1 and \( 5 \times 10^{-8} \text{ cm}^{-1} \). A one-meter K-band Stark cell was
used when the system was operated at frequencies above 30,000 Mc/sec. Measurements
in the vicinity of 60,000 Mc/sec and initial measurements at 40,000 Mc/sec were made
with a direct absorption (no Stark) doubling system with superheterodyne detection,
using an X-band cell ten meters long.

C. Observed Spectrum

Table I shows the observed frequencies of the three molecules studied, namely
\( \text{H}_2\text{C}_2\text{O}, \text{DHC}_2\text{O}, \) and \( \text{D}_2\text{C}_2\text{O} \). Lines were identified by Stark effect, intensity and fre-
quency. The identification given is thought to be the only one possible. Figure 2 shows
log intensity plotted against log frequency for the lines of \( \text{D}_2\text{C}_2\text{O} \). Neither instability...
nor dimerization of the sample was serious enough to render the microwave measurements difficult; nevertheless, effects which could be assigned to these actions were observed. In a brass waveguide at room temperature, after ten microns of ketene pressure had been maintained for some time, there was a decrease in peak line intensity of a factor of two in a few hours with an associated drop in Pirani gauge reading. When the waveguide was surrounded by dry ice, the intensity and pressure seemed even more stable. Furthermore, and fortunately for intensity measurement, if at room temperature the pressure were initially high enough (>100 microns) to broaden the line considerably, the peak intensity would not change as the pressure dropped. This indicates that the remaining gas was at least 80 percent pure after an hour. These observations, however, are essentially only approximate.

D. Relative Intensity Measurement

To obtain the vibration frequencies, we measured relative intensities of the \( J = 0 \rightarrow 1 \) transitions in ground and excited vibrational states. With reference to Figs. 4 and 5, the method used was to inject into the 6-kc/sec amplifier of the Stark spectrograph a
signal 180° out of phase with the 6-kc/sec signal from the detector crystal, and adjust
the amplitude of this added voltage to exactly balance out the peak gas absorption signal.
The only factor limiting the precision of this procedure appears to be the presence of
noise. The amplitude uncertainty is roughly equal to the noise voltage present, so the
percentage error in the ratio of ground-state to satellite line is smaller the greater the
signal-to-noise ratio of the line.

The results of about ten independent determinations of the intensity ratio at 27°C
yield the result that the intensities of the four lines in the J = 0→1 region of H₂C₂O are
in the ratio 1:(0.295 ± 7 percent):(0.205 ± 10 percent):(0.121 ± 15 percent). These
errors are limits within which the true intensity ratio is expected to fall.

II. Interpretation of Absorption Frequencies

A. General

The rotational spectrum of a molecule is, to a good first approximation, that of a
rigid rotor. Because of the high resolution of microwave techniques, relatively small
perturbing effects of rotation-vibration interaction must also be considered (16). The
terms "zero-point vibration correction" and "centrifugal distortion correction" are
given to those parts of the effect of vibration on rotation which depend on vibrational
and rotational quantum numbers respectively (there is also a small constant vibration-
rotation interaction term). In addition, rotation-electronic interaction occurs. These
terms are generally very small because of the large mass ratio between electrons and
nuclei.

B. Rigid Rotor

The rigid rotor frequencies were calculated by the methods of King, Hainer and
Cross (17). Their power series in \( \delta \) was used for the R branch, and for Q branch lines
with \( K_{-1} = 1 \); their continued fraction expansion was used for Q branch lines with \( K_{-1} = 2 \).

C. Centrifugal Distortion

The centrifugal distortion correction to the rigid rotor is the only one necessary for
reasonable prediction of the whole microwave spectrum in terms of a selected set of
lines, since the other corrections are independent of rotational quantum numbers. The
problem of making this correction for asymmetric rotors has been treated by Lawrance
and Strandberg (12), and by Hillger and Strandberg (13). There are six "centrifugal
distortion constants" related to the structure of the molecule and the vibrational funda-
mentals. For molecules with \( \delta \ll 1 \), there are general formulas for Q (\( \Delta K_{-1} = 0 \), \( \Delta J = 0 \))
and R (\( \Delta K_{-1} = 0 \), \( \Delta J = +1 \)) branches

\[
Q \text{ branch: } \frac{\nu_{\text{dist}}}{\nu_{\text{rigid}}} = J (J+1) f_1 (K_{-1}) + f_2 (K_{-1}) \tag{1}
\]

\[
R \text{ branch: } \frac{\nu_{\text{dist}}}{\nu_{\text{rigid}}} = (J+1)^2 \frac{4D_J}{b+c} + K_{-1}^2 \frac{D_{JK}}{b+c} \tag{2}
\]

Here, \( \nu_{\text{rigid}} \) is the absorption frequency of the rigid rotor; \( \nu_{\text{dist}} \) is the frequency cor-
rection to be added to \( \nu_{\text{rigid}} \) to get \( \nu_{\text{meas}} \); \( \nu_{\text{meas}} \) is the actual measured absorption
frequency; \( D_J \) and \( D_{JK} \) are two centrifugal distortion constants. \( f_1 (K_{-1}) \) and \( f_2 (K_{-1}) \),
used here temporarily for purposes of discussion, contain the other four centrifugal
distortion constants.

A considerable amount of numerical calculation is involved in determining the six
centrifugal distortion constants from the vibrational fundamentals. In view of some
uncertainty in the assignment of these fundamentals for ketene, we will instead fit the
microwave data to Eqs. 1 and 2.

The fit was attempted in the following way for Q branch lines with \( K_{-1} = 1 \) : for
\( \delta \ll 1 \)

\[
\nu_{\text{rigid}} = k (b-c) \tag{3}
\]

where \( k \) is a constant involving \( \delta \) only in second and higher powers, and \( b \) and \( c \) are the
usual reciprocal moments of inertia. Suppose that an approximate value of (\( b-c \)) is used
to calculate \( \nu_{\text{rigid}} \); we will designate approximate quantities with primes. Then let

\[
(b-c) = (b-c)' (1+\alpha) \tag{4}
\]
whence

\[ \nu'_{\text{rigid}} = \nu'_{\text{rigid}} (1 + a) \]  

(5)

where \( a \) is the fractional correction by which \((b-c)\)' is in error. Then

\[ \nu'_{\text{rigid}} = k (b-c)' (1 + a) \]  

(6)

whence

\[ \frac{\nu'_{\text{meas}} - \nu'_{\text{rigid}}}{\nu'_{\text{rigid}}} = J (J+1) f_1 (1) + f_2 (1) + a . \]  

(7)

From Eqs. 1 and 3, this means that when a value \((b-c)\)' is assumed and the left-hand side of Eq. 7 is plotted against \( J (J+1) \), a straight line should result. This is experimentally found true. The slope of the line is \( f_1 (1) \) and the intercept is \( f_2 (1) + a \), or a combination of \( J \)-independent centrifugal distortion and the necessary fractional correction to the assumed \((b-c)\)'.

Similarly treating the \( K_{-1} \geq 2 \) lines of the Q branch, we may assume a value \( \delta' \) as a first approximation to the true value \( \delta \) of the asymmetry

\[ \nu'_{\text{rigid}} = j (K_{-1}) \delta^{K_{-1}-1} \]  

(8)

where \( j (K_{-1}) \) is a constant involving \( J \) and \((b-c)\) but involving \( \delta \) only as a first-order correction. Writing

\[ \delta = \delta' (1+\beta) \]  

(9)

where \( \beta \) is the necessary fractional correction to the estimated value \( \delta' \), we get

\[ \frac{\nu'_{\text{meas}} - \nu'_{\text{rigid}}}{\nu'_{\text{rigid}}} = J (J+1) f_1 (K_{-1}) + f_2 (K_{-1}) + (K_{-1}-1) \beta . \]  

(10)

Again, this means that when a value of \( \delta' \) is assumed and the left-hand side of Eq. 10 plotted against \( J (J+1) \), a straight line should result. This is experimentally verified for \( K_{-1} = 2 \) with \( D_2C_2O \) and \( HDC_2O \). The intercept of the \( K_{-1} = 3 \) line as well as the \( K_{-1} = 2 \) and \( K_{-1} = 1 \) plots would be required, however, to obtain \( f_2 \) and \( \beta \). Unfortunately, only for \( D_2C_2O \) would such lines be strong enough to be detected, and none of the latter were searched for.

The effect of this situation is to introduce uncertainty into the values of \((b-c)\) and \( \delta \) extrapolated to zero centrifugal distortion of about 1:5000 and 1:1000 respectively; fortunately, the amount of this uncertainty is smaller than the uncertainty in the equilibrium moments of inertia caused by zero-point vibration, and hence has no effect on the accuracy of the structure determination. The limits of error given above are suggested by a definite deviation from linearity in the case of \( D_2C_2O \) of the plot of Eq. 10 for \( K_{-1} = 2 \) when a change of 1:1000 in \( \delta \) is made; \( f_2 (2) \) was estimated in this way. The fitting process described was carried out by least squares.
Values of effective \((b-c)\) and \(\delta\) in the ground vibrational state as well as measured centrifugal distortion constants are given in Table II. The number of significant figures given is much greater than the quoted error because of their empirical value for prediction of lines with \(K_{-1} \leq 2\).

R branch lines pose less of a problem. First we consider lines in the ground vibrational state. For \(\text{H}_2\text{C}_2\text{O}\), values of \((b-c)\) and \(\delta\) found from the Q branch lines were assumed correct, and \(D_J, D_{JK}\) and \((b+c)\) solved for from the many observed R branch lines by the method of least squares. For \(\text{D}_2\text{C}_2\text{O}\), no lines of the group \(J = 2 \rightarrow 3\) were searched for. \(D_J = 0\) was assumed since otherwise it calculated to be a small negative value with an uncertainty greater than its absolute value. For \(\text{DHC}_2\text{O}\), only the \(J = 0 \rightarrow 1\) transition was measured, so calculation of \(D_J\) and \(D_{JK}\) is impossible. This frequency is listed as \((b+c)\).

D. Zero-Point Vibration

There are two well-known methods for finding the equilibrium moments of inertia from the microwave "effective" values, the first from vibrational data and the second from microwave data. In the calculations of the first method, anharmonic force constants which are generally unknown contribute effects of the same order as harmonic force constants so the calculation is seldom feasible. Rough calculations of the harmonic correction can be used to calculate the order of magnitude of the error, however. This idea is later applied to calculation of the error to be assigned to the structure determination. The second method consists of finding rotational transitions of the molecule in each of the fundamental excited vibrational states. The reciprocal moment \(a\) for ketene in a vibrational state characterized by vibrational quantum numbers \(n_1, n_2, \ldots n_9\) is then

\[
a(n_1, n_2, \ldots n_9) = a(0, 0, \ldots 0) + \sum_{i=1}^{9} a_i a_i (n_i + \frac{1}{2})
\]

and similarly for \(b\) and \(c\). Here the \(a\) are interaction constants and \(a(0, 0, \ldots 0)\) is the equilibrium reciprocal moment of inertia, which can then be calculated.

A considerable number of R branch lines of the molecule in excited vibrational states was found. For the \(J = 0 \rightarrow 1\) transition of \(\text{H}_2\text{C}_2\text{O}\), all but one of the interaction lines from vibrations \(v_7, v_8\) and \(v_9\) were measured, enabling calculation of \(a_b^9, a_c^9, a_b^8, a_c^8, a_b^7\) and \(a_c^7\) as well as \(D_{JK}\) for each state. Since we have no knowledge of the other \(a\) values, however, we cannot correct for zero-point vibration. The known values are nevertheless interesting since they give the order of magnitude of this correction. The measured values of \(a\) and \(D_{JK}\) are listed in Table II.

E. Electronic Interaction

There is a small effect on the rotation spectrum caused by the coupling of the electronic motion to the rotation. Recent work by Eshbach and Strandberg (18) has shown how this coupling gives rise to a molecular magnetic moment which can be measured.
We shall now show that the magnetic moment can be used to obtain the effect of the electronic interaction on the rotational frequencies. The hamiltonian of the rigid rotor plus the electrons is (negligible error in calculating the electronic interaction is made here by omitting the vibrational part)

\[ H = H_r + H_e + H' \]  

where

\[ H_r = \frac{1}{2} \sum_{i=a,b,c} \frac{P_i^2}{I_i} \]  

\[ H_e = \frac{1}{2m} \sum_j \sum_{i=a,b,c} \frac{P_{ij}^2}{I_j} + V(a, b, c) \]  

\[ H' = - \sum_{i=a,b,c} \frac{L_i P_i}{I_i} \]  

Here \( N_a, N_b, N_c \) are the components of the nuclear angular momentum \( \vec{N} \) resolved along the nuclear a, b and c principal axes of inertia; \( I_a, I_b, I_c \) are the principal moments of inertia of the nuclear system; \( m \) is the mass of the electron; \( p_{aj}, p_{bj}, p_{cj} \) are the components of linear momentum of the jth electron in a space-fixed system, resolved along the axes a, b and c; and \( V(a, b, c) \) is the potential energy of the electrons. The terms in \( L_i^2/2I_i \), etc. have been neglected. Shift in the center of mass has also been neglected. Also

\[ \vec{P} = \vec{N} + \vec{L} \]  

where \( P_a, P_b, P_c \) are the components of the total angular momentum \( \vec{P} \) of the electrons plus nuclei in a space-fixed system resolved along a, b, c; \( L_{a}, L_{b}, L_{c} \) are the components of the angular momentum \( \vec{L} \) of the electrons in a space-fixed system resolved along a, b, c. Choose now the matrix representation in which \( \vec{P}^2, H_e, \) and \( H_r \) are simultaneously diagonal. This can be done since these operators mutually commute (18).

The eigenvalues of \( H_r \) are the first approximation to the energy levels of the rotational spectrum. The subscript \( n \) labels the eigenvalues \( E_n \) and eigenfunctions \( \psi_n \) of \( H_e \) with \( n = 0 \) corresponding to the lowest state. \( H' \) is a small coupling between \( H_e \) and \( H_r \) which will influence the energy of each rotational level. After diagonalizing \( H \) in \( n \) by second-order perturbation theory, the \( n=0 \) elements of \( H \) are found to be

\[ H = \frac{1}{2} \sum_i \frac{P_i^2}{I_i} - \sum_i \sum_j \frac{P_i P_j}{I_i I_j} A_{ij} \]  

where
\[ A_{ij} \triangleq \sum_n^t \frac{\langle o| L_i | n \rangle \langle n | L_j | o \rangle}{E_n - E_0}. \]  

(18)

In these and later equations, indices \( i, j \) and \( k \) run over \( a, b \) and \( c \).

We define

\[ G_{ij}^e \triangleq -\frac{e}{2\hbar c} \frac{A_{ij} + A_{ji}}{I_j}, \]

(19)

and a symmetric tensor \( G_{ij}^n \) cyclical in \( a, b, c \) of which typical elements are

\[ G_{aa}^n = \frac{e}{2\hbar^2} \sum_k Z_k (b_k^2 + c_k^2) \]

and

\[ G_{ab}^n = -\frac{e}{2\hbar^2} \sum_k Z_k a_k b_k. \]

Eshbach and Strandberg (18) showed for \( ^1S \) states that if \( m_1 \) is the component of the vector rotational magnetic moment \( \vec{m} \) along a principal inertial axis \( i \)

\[ m_1 = \sum_j G_{ij} P_j \]

(21)

where

\[ G_{ij} = G_{ij}^e + G_{ij}^n. \]

(22)

Here, \( e \) is the electronic charge; \( v \) is the velocity of light; \( a_k, b_k \) and \( c_k \) are the coordinates of the \( k \)th nucleus in the principal inertial axis system; and \( Z_k \) is the atomic number of the \( k \)th nucleus.

If \( A_{ij} = A_{ji} \), Eq. 17 can be written

\[ H = \frac{1}{2} \sum_i P_i^2 - \sum_i \sum_j P_i P_j \left( \frac{A_{ij} + A_{ji}}{I_j} \right). \]

(23)

A sufficient condition for this assumption is that \( G_{ij} \) be diagonal. With Eqs. 19 and 22, Eq. 23 becomes

\[ H = \frac{1}{2} \sum_i \frac{P_i^2}{I_i} - \frac{mv}{e} \sum_i \sum_j G_{ij}^n \frac{P_i P_j}{I_i} + \frac{mv}{e} \sum_i \sum_j G_{ij} \frac{P_i P_j}{I_i}. \]

(24)

The second term of the right-hand side of Eq. 24 can be written, using Eq. 20, as
where typical elements of the tensor \( I_{ij}^e \), symmetric and cyclic in \( a, b, c \), are

\[
I_{aa}^e = \frac{1}{2} \sum_k m Z_k (b_k^2 + c_k^2) \\
I_{ab}^e = -\frac{1}{2} \sum_k m Z_k a_k b_k.
\]

That is, \( I_{ij}^e \) is the moment of inertia tensor of the electrons considered concentrated at their respective nuclei, in the nuclear principal axis system. Using Eqs. 24 and 25, we have

\[
H = \frac{1}{2} \sum_i \sum_j \left[ \frac{\delta_{ij}}{I_i} - \frac{I_{ij}^e}{I_i I_j^e} \right] P_i P_j + \frac{\text{mv}}{e} \sum_i \sum_j G_{ij} \frac{P_i P_j}{I_i}
\]

where \( \delta_{ij} \) is the usual Kronecker delta. The quantity in the brackets in Eq. 26 is obviously the reciprocal of a moment of inertia tensor; we will now find the corresponding moment of inertia tensor. The bracketed quantity is nearly diagonal, so its reciprocal will be of the form

\[
\left[ \frac{\delta_{ij}}{I_i} - \frac{I_{ij}^e}{I_i I_j^e} \right]^{-1} = I_i^e \delta_{ij} + \beta_{ij}
\]

where \( \beta_{ij} \ll I_k \) for all \( i, j, k \). Thus

\[
\sum_k \left[ \frac{\delta_{ik}}{I_i} - \frac{I_{ik}^e}{I_i I_k^e} \right] I_k \delta_{kj} + \beta_{kj} = \delta_{ij}
\]

whence

\[
\beta_{ij} = I_{ij}^e
\]

so

\[
H = \frac{1}{2} \sum_i \sum_j \left[ I_i^e \delta_{ij} + I_{ij}^e \right]^{-1} P_i P_j + \frac{\text{mv}}{e} \sum_i \sum_j G_{ij} \frac{P_i P_j}{I_i}
\]

This last equation states that in the limit when the molecular magnetic moment is zero, the case of "perfect slip" which is approached by the large number of inner shell
electrons in molecules made up of heavy nuclei, the effect of electronic interaction is to change the rotational energy from that calculated using nuclear masses to that using atomic masses, the method generally used. Exact correction for electronic interaction can be made from experimental magnetic moment measurements using Eq. 30. This entire derivation is of course based on the assumption $A_{ij} = A_{ji}$ made in connection with Eq. 23; although it covers a very important class of molecules, molecules of very low symmetry are excluded. Generalization appears feasible but more involved.

The tensor $G_{ij}$ has at worst the same symmetry as the nuclear system. For $H_2C_2O$ and $D_2C_2O$, symmetry $C_{2v}$, it is diagonal. An estimate of $G_{ij}$ for $H_2C_2O$ is $G_{aa} = +0.48 \, e/2Mv$, $|G_{bb}| < 0.05 \, e/2Mv$ where $M$ is the proton mass. Use of these figures results in decreasing the H-H distance by $2.45 \times 10^{-4}$ A below the value that results from using atomic masses, and introducing a correction of less than $\pm 4 \times 10^{-5}$ A in the C=C=O distance.

F. Structure

The equilibrium structure is to be calculated from the equilibrium moments of inertia. We do not know the equilibrium moments, so the structure has been calculated from the moments of inertia extrapolated to zero centrifugal distortion. The errors assigned are taken roughly equal to an estimate of the correction resulting from the harmonic force constants, calculated on the assumption of a simple harmonic oscillator.

Unfortunately, the structure of ketene is such that the carbon nucleus is, for all feasible isotopic configurations, so close to the center of gravity of the molecule that its position (+ 0.10 A) has no effect upon the rotational spectrum. Consequently, only three structural parameters can be deduced from this work. First, the H to axis distance can be calculated from $I_A$ of $H_2C_2O$ and $D_2C_2O$. This gives values 0.9399 A and 0.9406 A respectively (uncertainties in extrapolation to zero centrifugal distortion amount to $\pm 0.0010$ A here). Solving the expressions for $I_B$ of $H_2C_2O$ and $D_2C_2O$ simultaneously gives the length of the $C=C=O$ chain and the projection of the C-H bond length along the symmetry axis as 2.4751 A and 0.5210 A respectively. The first of these is to be compared to the electron diffraction result (7) of 2.52 $\pm$ 0.04 A. The inertia defect $\Delta$ in the expression $I_C = I_A + I_B + \Delta$ here amounts to 5 percent and 3 percent of $I_A$ for $H_2C_2O$ and $D_2C_2O$ respectively, so that $I_C$ calculated from this structure is in error by something of the order of 0.2 percent. The measured moments of HDC$_2$O were used as a check, with the result shown in Table III.

These errors are well outside the experimental error; calculations show that the length of the C=C=O chain varies only $6 \times 10^{-5}$ A per Mc frequency change of the $J = 0 \rightarrow 1$ line, and that the component of the C-H distance along the symmetry axis varies $5 \times 10^{-4}$ A per Mc/sec. In this work, Planck's constant times Avogadro's number is taken as $39.9066 \times 10^{-4}$ cgs; the present fractional error in this value (19) of $1:2.3 \times 10^{-4}$, is not the limiting error in the final result, but is of the same order as the electronic correction.

The structure is shown in Fig. 5.
III. Stark Effect and Absorption Intensities

A. Stark Effect

The electric dipole moments determined from the Stark effect of the J = 0→1 transition of each molecule in the ground state, and of H$_2$C$_2$O in excited vibrational states, are listed in Table II. The difference in dipole moment between different isotopic forms is nearly within the experimental error. Some of the vibrational states have dipole moments differing from that of the ground state by more than the experimental error. Errors are estimated limits. Agreement with the more impurity-sensitive method of Hannay and Smyth (9), which yielded 1.45 debye units, seems good.

In general, the Stark effect is quadratic. Because the molecule is nearly symmetric, however, R branch transitions with K$_{-1}$ = 1 have a quadratic Stark at low fields which changes to linear at high fields. R branch lines with K$_{-1}$ > 2 have essentially a linear Stark.

B. Intensities in the Ground Vibrational State

The line breadth parameter was measured on the J = 0→1 line of H$_2$C$_2$O as 19.8 ± 2.0 Mc/mm. Line intensities were then calculated from the Van Vleck-Weisskopf formula, with results consistent with rough estimates of intensity relative to nearby ammonia lines. In particular, the intensity alternation associated with the identical hydrogen nuclei in H$_2$C$_2$O and D$_2$C$_2$O was observed. The specific effect of this nuclear identity on transitions between levels in the ground vibrational state for H$_2$C$_2$O is the increase of transition intensities between levels of odd K$_{-1}$ by a factor of three. Intensities are increased by the same factor for even K$_{-1}$ values in transitions between levels in accessible vibrational states. For D$_2$C$_2$O, ground vibrational state intensities for even K$_{-1}$ are increased by a factor of two; again, transition intensities in accessible excited vibrational states have the opposite dependence on the parity of K$_{-1}$. These facts further substantiate the C$_{2v}$ symmetry of the molecule.

Lines with K$_{-1}$ = 3 are weak. H$_2$C$_2$O lines in K band with K$_{-1}$ = 3 have intensities of 10$^{-9}$ cm$^{-1}$. D$_2$C$_2$O lines in K band with K$_{-1}$ = 3 are about 1.1 × 10$^{-7}$ cm$^{-1}$ in a pure sample, and so could be detected, but K$_{-1}$ = 4 lines are 7 × 10$^{-9}$ cm$^{-1}$. No K$_{-1}$ = 3 lines were searched for, however.

Cooling the waveguide to dry ice temperatures is calculated to give an increase in line strength of a factor of about 4 for low-lying transitions. The vapor pressure of ketene at dry ice temperature was measured as roughly 200 mm of mercury.

Intensities recorded in Table I for H$_2$C$_2$O and D$_2$C$_2$O are calculated on the basis of a pure sample, but for DHC$_2$O, on the basis of a 50 percent pure sample, which is the
maximum easily obtainable.

C. Intensities in Excited Vibrational States

For $\text{H}_2\text{C}_2\text{O}$, the intensity ratio of the ground-state line to the vibration satellites corresponding to vibration fundamentals $v_9$, $v_8$ and $v_7$ is $1:3 \exp\left(-\frac{v_9}{kT}\right): 3 \exp\left(-\frac{v_8}{kT}\right): 3 \exp\left(-\frac{v_7}{kT}\right)$. This involves the highly reasonable assumption that the lowest three modes of vibration are antisymmetric or "B" type. Thus, the intensity measurements already described imply the vibrational fundamentals listed in Table IV. The errors assigned are calculated from the estimated error of the intensity measurement (at room temperature, the frequency error in cm$^{-1}$ is twice the percent error in the intensity).

Figure 6 shows the actual pattern of the $J=0\rightarrow1$ transition of $\text{H}_2\text{C}_2\text{O}$. The solid line connects our measured values, and limits of error assigned to these values are also shown. Intensity points calculated from the vibrational fundamental assignments of Halverson and Williams (3) have also been plotted and connected by a dashed line. Barring an accidental and very unlikely coincidence of the satellites from vibrations $v_6$ and $v_7$, there is a definite disagreement for $v_7$. Although calculation of vibrational fundamentals from rotational relative intensity measurement gives far less accuracy than the usual infrared techniques, the former method has the great advantage of freedom from the confusion of combination bands near the same frequency. The infrared spectrum of ketene has a large number of these which might result in difficulty of assignment of some of the fundamentals.

Fig. 6 $J=0\rightarrow J=1$ pattern of $\text{H}_2\text{C}_2\text{O}$.16.
<table>
<thead>
<tr>
<th>Assignment</th>
<th>Measured Frequency (Mc/sec)</th>
<th>Calculated Frequency (Mc/sec)</th>
<th>Intensity (cm$^{-1}$) (100 percent abundance)</th>
<th>Distortion Correction (Mc/sec)</th>
<th>Vibrational State</th>
<th>Error (Mc/sec)</th>
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<td>$^0_{00} - ^1_{01}$</td>
<td>20.209.20</td>
<td>20.209.15</td>
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Table I

$^1H_2C^12O^{16}$
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<th>Assignment</th>
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<th>Intensity (cm⁻¹) (100 percent abundance)</th>
<th>Distortion Correction (Mc/sec)</th>
<th>Vibrational State</th>
<th>Error (Mc/sec)</th>
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Table I (Continued)

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<th>Assignment</th>
<th>Measured Frequency (Mc/sec)</th>
<th>Calculated Frequency (Mc/sec)</th>
<th>Intensity (cm⁻¹) (100 percent abundance)</th>
<th>Distortion Correction (Mc/sec)</th>
<th>Vibrational State</th>
<th>Error (Mc/sec)</th>
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<td>35,431.86</td>
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<td>35,913.64</td>
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Table II

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<th>D₂C₂O</th>
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<td>20.209.16 ± 0.05</td>
<td>18.821.68 ± 0.15</td>
<td>17.673.46 ± 0.05</td>
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<td>472.421 ± 0.100</td>
<td>568.136 ± 0.100</td>
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<td>δ</td>
<td>0.0013776 ± 0.0000020</td>
<td>0.00254186 ± 0.00000400</td>
<td>0.0042700 ± 0.0002000</td>
</tr>
<tr>
<td>μ, ν₁ = 0, debye</td>
<td>1.414 ± 0.010</td>
<td>1.423 ± 0.015</td>
<td>1.442 ± 0.013</td>
</tr>
<tr>
<td>D₅, Mc/sec</td>
<td>0.0025 ± 0.0020</td>
<td>0.00 ± 0.005</td>
<td>0.353 ± 0.030</td>
</tr>
<tr>
<td>DJK', Mc/sec</td>
<td>0.4766 ± 0.0060</td>
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<td></td>
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<tr>
<td>f₁ (1)</td>
<td>(1.53 ± 0.10) × 10⁻⁶</td>
<td>(1.91 ± 0.10) × 10⁻⁶</td>
<td>(1.66 ± 0.10) × 10⁻⁶</td>
</tr>
<tr>
<td>f₁ (2)</td>
<td>(1.53 ± 0.17) × 10⁻⁶</td>
<td>(2.428 ± 0.033) × 10⁻⁶</td>
<td>(1.375 ± 0.025) × 10⁻⁶</td>
</tr>
<tr>
<td>f₂ (2)</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>ν₉ cm⁻¹</td>
<td>487 ± 15</td>
<td></td>
<td></td>
</tr>
<tr>
<td>ν₈ cm⁻¹</td>
<td>565 ± 20</td>
<td></td>
<td></td>
</tr>
<tr>
<td>ν₇ cm⁻¹</td>
<td>674 ± 30</td>
<td></td>
<td></td>
</tr>
<tr>
<td>μ, ν₉ = 1, debye</td>
<td>1.430 ± 0.012</td>
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<td></td>
</tr>
<tr>
<td>μ, ν₈ = 1, debye</td>
<td>1.387 ± 0.010</td>
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<tr>
<td>μ, ν₇ = 1, debye</td>
<td>1.386 ± 0.010</td>
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<tr>
<td>aₐ + aₐ, Mc/sec ν₉ = 1</td>
<td>57.66 ± 0.05</td>
<td>55.97 ± 0.05</td>
<td>53.27 ±</td>
</tr>
<tr>
<td>ν₈ = 1</td>
<td>10.72 ± 0.05</td>
<td>11.08 ± 0.05</td>
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</tr>
<tr>
<td>ν₇ = 1</td>
<td>22.39 ± 0.05</td>
<td>25.18 ± 0.05</td>
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</tr>
<tr>
<td>aₐ - aₐ, Mc/sec ν₉ = 1</td>
<td>18.39 ± 0.05</td>
<td></td>
<td></td>
</tr>
<tr>
<td>ν₈ = 1</td>
<td>- 27.0 ± 0.05</td>
<td></td>
<td></td>
</tr>
<tr>
<td>ν₇ = 1</td>
<td>- 27.88 ± 0.05</td>
<td></td>
<td>34.66 ± 0.05</td>
</tr>
<tr>
<td>D₅, Mc/sec ν₉ = 1</td>
<td>+ 0.020 ± 0.004</td>
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<tr>
<td>ν₈ = 1</td>
<td>- 0.026 ± 0.004</td>
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<tr>
<td>ν₇ = 1</td>
<td>0.019 ± 0.004</td>
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</tr>
<tr>
<td>DJK', Mc/sec ν₉ = 1</td>
<td>0.505 ± 0.030</td>
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</tr>
<tr>
<td>ν₈ = 1</td>
<td></td>
<td></td>
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</tr>
<tr>
<td>ν₇ = 1</td>
<td>0.550 ± 0.030</td>
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</tbody>
</table>
Table III

Moments of Inertia of HCD₂O, AMU-A²

<table>
<thead>
<tr>
<th></th>
<th>Calculated</th>
<th>Measured</th>
<th>Error</th>
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<tbody>
<tr>
<td>Iₐ</td>
<td>2.5946</td>
<td>2.5914</td>
<td>0.12 percent</td>
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<tr>
<td>Iₐ</td>
<td>52.320</td>
<td>52.377</td>
<td>0.03 percent</td>
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<tr>
<td>Iₐ</td>
<td>54.972</td>
<td>55.089</td>
<td>0.21 percent</td>
</tr>
</tbody>
</table>

Table IV

Comparison of Microwave and Infrared Measurements of Vibration Frequencies, cm⁻¹

<table>
<thead>
<tr>
<th></th>
<th>v₉</th>
<th>v₈</th>
<th>v₇</th>
<th>v₆</th>
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</thead>
<tbody>
<tr>
<td>Microwave</td>
<td>487 ± 15</td>
<td>565 ± 20</td>
<td>674 ± 30</td>
<td>--------</td>
</tr>
<tr>
<td>Halverson and Williams</td>
<td>529</td>
<td>588</td>
<td>909</td>
<td>1011</td>
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<tr>
<td>Drayton and Thompson</td>
<td>540</td>
<td>600</td>
<td>910</td>
<td>995</td>
</tr>
</tbody>
</table>

IV. Conclusion

A more accurate structure evaluation for ketene depends mainly upon correct calculation or measurement of the zero-point vibration interaction. It appears that this would be difficult at present.

Further measurement of the spectrum of D₂C₂O would be extremely interesting as a more complete check on centrifugal distortion theory applied to a molecule with both Q and R branch transitions; besides investigating how well the rotational spectrum can be fitted to the theory, actual calculation of the coefficients from the vibrational fundamentals would be feasible for ketene because of its symmetry. R branch sets measurable are J = 0→1*, 1→2*, 2→3, 3→4 and 4→5; Q branch series measurable have Kₗ = 1*, 2* and 3. Those starred have actually been measured.

Possibly, further work on the vibrational spectrum is also indicated.
References


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