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The Infra-Red Spectrum of Ketene

FREDERICK HALVERSON AND VAN ZANDT WILLIAMS

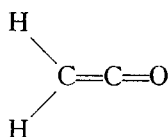
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The infra-red spectrum of gaseous ketene has been studied from 2.5μ to 25μ with a spectrometer using LiF, NaCl, and KBr prisms. A perpendicular band at 3162 cm^{-1} with components relatively free of perturbations has been resolved, and the intensity alternation associated with the twofold axis observed. All fundamental vibrational frequencies have been assigned. A normal coordinate treatment of the general H_2XYZ molecule has been made and reasonable force constants for ketene calculated.

I. INTRODUCTION

FROM chemical evidence and bond theory, ketene is formulated as being a planar molecule with a twofold axis of symmetry, corresponding to the structural formula



Beach and Stevenson¹ made an electron diffraction study of the molecule and found $r(\text{C}-\text{O}) = 1.17 \pm 0.02\text{A}$, and $r(\text{C}-\text{C}) = 1.35 \pm 0.02\text{A}$. Using these measured dimensions and assuming the given structural formula, one can predict the gross structural features to be expected in the infra-red spectrum of such a molecule.

Making the assumption that $r(\text{C}-\text{H}) = 1.08\text{A}$ and $\angle \text{HCH} = 120^\circ$, one calculates $I_A \cong 2.9 \times 10^{-40}\text{ g cm}^2$ (moment of inertia about the twofold axis) and $I_B \cong I_C \cong 85 \times 10^{-40}\text{ g cm}^2$. Consequently, the rotational structure should resemble that of a symmetrical top molecule—vibrations in which the change of electric moment is along the twofold axis giving rise to parallel bands, and the other vibrations giving rise to perpendicular bands. The maxima of the *P* and *R* branches of the parallel bands should have a separation of about 25 cm^{-1} at room temperature; the perpendicular bands should consist of rather widely spaced (*ca.* 19 cm^{-1}) *Q* branches with alternating intensities.

Temporarily neglecting the effect of the hydrogen atoms, one can consider the $\text{C}=\text{C}=\text{O}$ part of

the molecule as being analogous to nitrous oxide, $\text{N}=\text{N}=\text{O}$. The frequencies of the stretching vibrations of this molecule are 1285.0 cm^{-1} and 2223.5 cm^{-1} , and the frequency of the bending vibration is 589 cm^{-1} .² The analogous vibrations of ketene minus the hydrogen atoms should have frequencies of approximately the same magnitude—the stretching vibrations giving rise to parallel bands, and the bending vibration giving rise to a perpendicular band. It is probable, however, that the presence of the hydrogen atoms will release the degeneracy of the bending vibration so that two perpendicular bands with nearly the same frequency will appear.

The presence of the hydrogen atoms should also add five fundamental vibrations, three of which are more or less characteristic of the CH_2 group—a symmetric $\text{C}-\text{H}$ bond stretching and a symmetric CH_2 deformation (parallel bands) and an antisymmetric $\text{C}-\text{H}$ bond stretching (perpendicular band). The frequencies of these vibrations should be similar to those occurring in ethylene or in the vinyl halides ($\text{C}-\text{H}$ stretching in the region $2900\text{--}3200\text{ cm}^{-1}$; CH_2 deformation in the region $1300\text{--}1500\text{ cm}^{-1}$). The other two vibrations—out-of-plane and in-plane wagging of the CH_2 group against the rest of the molecule—should give rise to perpendicular bands, and by analogy with ethylene and the vinyl halides should have frequencies in the region $900\text{--}1050\text{ cm}^{-1}$. It is understood, of course, that the true normal vibrations of the complete molecule are superpositions of these postulated modes of

¹ J. Y. Beach and D. P. Stevenson, *J. Chem. Phys.* **6**, 75 (1938).

² G. Herzberg, *Infra-red and Raman Spectra of Polyatomic Molecules* (D. Van Nostrand Company, Inc. New York, 1945), p. 278.

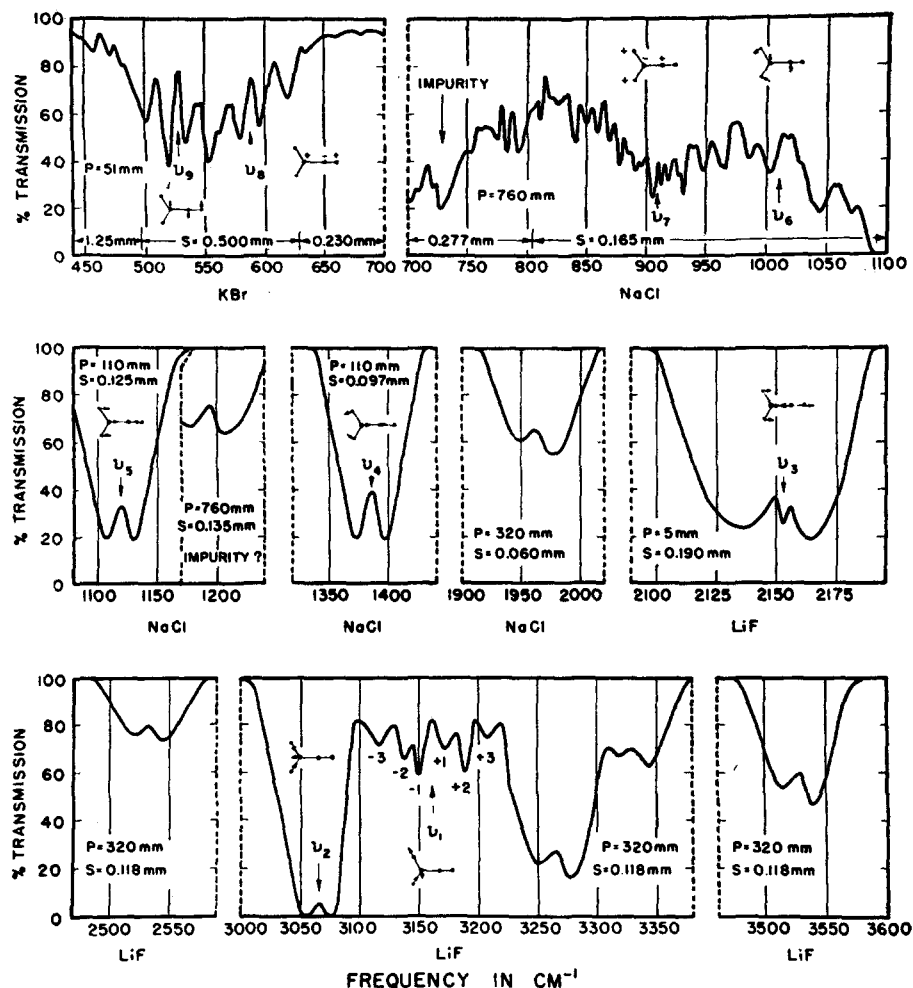


FIG. 1. Infra-red spectrum of ketene.

motion, but it is believed that these simple modes are so chosen that they are almost normal modes.

II. OBSERVED INFRA-RED SPECTRUM^{3,4}

The infra-red spectrum of ketene shown in Fig. 1 was obtained using a Perkin-Elmer spectrometer Model 12A with LiF, NaCl, and KBr prisms. With the exception of the very intense band at 2153 cm^{-1} , a 10-cm Pyrex absorption cell with glyptal sealed KBr windows was used in all regions. Ketene pressures were varied from 50 mm to 760 mm of Hg. In order to obtain the structure of the band at 2153 cm^{-1} , a

5-cm cell was used with ketene at a pressure of 10 mm of Hg. The ketene was prepared in these laboratories by Dr. G. L. Simard and Mr. J. F. Steger by pyrolysis of acetone in a quartz column, and purified by low temperature distillation in a vacuum jacketed still.

Some difficulty was experienced in obtaining the spectrum because of the dimerization of ketene, particularly at the higher pressures. By following the changes over a period of several hours, however, it was possible to correct for the presence of diketene.⁵ This procedure also per-

³ H. Gershinowitz and E. B. Wilson, Jr., J. Chem. Phys. **5**, 500 (1937). They reported some of these bands in a "Letter to the Editor," but did not give any structure for them and made no assignments.

⁴ H. Kopper, Zeits. f. physik. Chemie **B34**, 396 (1936). A report on the Raman spectrum of liquid ketene.

⁵ A 10-cm absorption cell was filled with ketene at an initial pressure of one half atmosphere and allowed to stand for several days, with the infra-red spectrum obtained at regular intervals. The diketene absorption bands appeared within two hours, and increased noticeably in intensity for three days. At the end of seven days the ketene pressure was considerably less than 10 mm of Hg; and by the end of the eighth day, even the intense ketene

TABLE I. Observed ketene-absorption bands 3900–2900 cm^{-1} (LiF prism; 10-cm cell; 320-mm pressure; slit = 0.118 mm).

Frequency	Int	Frequency	Int	No.
3538 <i>R</i>	<i>M</i>	3208	<i>W</i>	+3
3526 <i>Av</i>		3189	<i>S</i>	+2
3515 <i>P</i>				
3343 <i>R</i>	<i>W</i>	3173	<i>W</i>	+1
3330 <i>Av</i>		3151	<i>S</i>	–1
3317 <i>P</i>				
3277 <i>R</i>	<i>S</i>	3137	<i>W</i>	–2
3264 <i>Av</i>		3117	<i>S</i>	–3
3252 <i>P</i>				
3079 <i>R</i>	<i>VS</i>	\perp band		
3066 <i>Av</i>				
3053 <i>P</i>				

II bands

mitted identifying certain bands as probably due to other impurities.

Region from 3900 to 2900 cm^{-1}

There are four parallel bands and one perpendicular band in this region. No *Q* branches are resolved for any of these parallel bands, and so the band centers are taken as the mean of the *P* and *R* branches. The perpendicular band is overlapped on the low frequency side by the very intense parallel band at 3066 cm^{-1} and on the high frequency side by the parallel band at 3264 cm^{-1} . Consequently only six components of the perpendicular band are clearly observed. The adjacent components show a fairly regular intensity alternation, and the intensity maximum of the band appears to fall between the components at 3189 cm^{-1} and 3151 cm^{-1} . Since the spacing of the components is a little irregular, the average of the five spacings available, $\langle \Delta \nu \rangle_{av} = 18.2 \text{ cm}^{-1}$, is considered the normal spacing. Frequencies for the bands in this region are given in Table I.

Region from 2900 to 1100 cm^{-1}

Several parallel bands are observed in this region, one of them being extremely intense with

band at 2153 cm^{-1} did not appear. However, the bands at 722 and 728 cm^{-1} were still present, and so could not be due to ketene. The bands at 773, 783, 792, and 841 cm^{-1} had disappeared, but the rate at which they did made it doubtful that they were ketene bands.

TABLE II. Observed ketene absorption bands 2900–1100 cm^{-1} (LiF prism for 2153 cm^{-1} band; NaCl prism for the rest).

Frequency	Int	<i>P</i> †	Frequency	Int	<i>P</i> †
2540 <i>R</i>	<i>M</i>	320 mm	1398 <i>R</i>	<i>VS</i>	110 mm
2533 <i>Av</i>			1386 <i>Av</i>		
2515 <i>P</i>			1375 <i>P</i>		
2164 <i>R</i>	<i>VVS</i>	*	1205 <i>R</i>	?	760 mm
2153 <i>Q</i>			1191 <i>Av</i>		
2136 <i>P</i>			1178 <i>P</i>		
1974 <i>R</i>	<i>M</i>	320 mm	1132 <i>R</i>	<i>VS</i>	110 mm
1962 <i>Av</i>			1120 <i>Av</i>		
1949 <i>P</i>			1107 <i>P</i>		

* A 5-cm cell with 10-mm ketene pressure was used for this band.
† Column headed *P* is pressure in a 10 cm cell.

a *Q* branch at 2153 cm^{-1} . This band shows practically complete absorption if the ketene pressure in a 10-cm cell is 10 mm of Hg or larger. As shown in Fig. 1, the *Q* branch is very weak relative to the *P* and *R* branches. The positions of all the bands in this region are given in Table II. The very weak bands at 1178 cm^{-1} and 1205 cm^{-1} are real and are believed to be due to ketene, but are listed with a question mark since they were found only at the higher pressures where diketene also formed.

Region from 1100 to 700 cm^{-1}

This region contains a large number of irregularly spaced bands of varying intensities. There

TABLE III. Observed ketene absorption bands 1100–700 cm^{-1} (NaCl prism; 10-cm cell; 760-mm pressure; slit = 0.160 mm).

Frequency	Int	Frequency	Int
703	<i>S</i>	886	<i>W</i>
712	<i>S</i>	891	<i>M</i>
722	<i>S</i> *	896	<i>W</i>
728	<i>S</i> *	907	<i>S</i>
731	<i>W</i>	912	<i>M</i>
752	<i>M</i>	918	<i>M</i>
760	<i>W</i>	927	<i>VW</i>
773	<i>S</i> †	932	<i>S</i>
783	<i>S</i> †	940	?
792	<i>S</i> †	948	<i>S</i>
807	?	963	?
811	<i>W</i>	966	<i>S</i>
819	<i>W</i>	986	<i>S</i>
825	?	1004	<i>S</i>
830	<i>VW</i>	1018	<i>VW</i>
841	<i>S</i>	1028	<i>M</i>
851	<i>W</i>	1044	<i>MS</i>
860	<i>M</i>	1058	<i>VVW</i>
869	<i>M</i>	1070	<i>MS</i>
878	<i>M</i>		

* Definitely due to an impurity.
† Probably due to an impurity.

TABLE IV. Observed ketene absorption bands 700–400 cm^{-1} (KBr prism; 10-cm cell; 110 mm of Hg; slit = 0.500 mm).

Frequency	Int	Frequency	Int
458	<i>W</i>	562	<i>VW</i>
472	<i>W</i>	571	<i>W</i>
482	<i>VW</i>	580	<i>S</i>
501	<i>S</i>	596	<i>S</i>
520	<i>S</i>	620	<i>S</i>
534	<i>M</i>	634	<i>W</i>
539?	<i>VW</i>	658	<i>W</i>
546?	<i>VW</i>	680	<i>W</i>
553	<i>S</i>	698	?

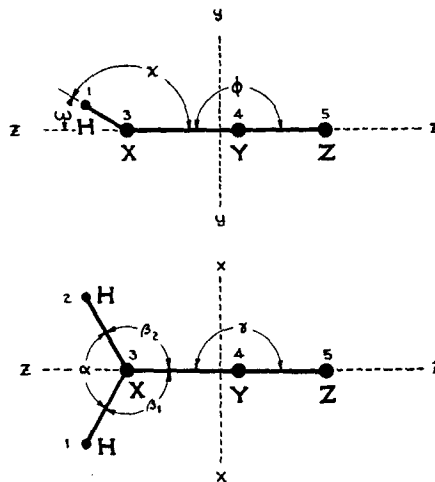
appears to be a parallel band at the upper end of the region—*P*, *Q*, and *R* branches at 1044, 1058, and 1070 cm^{-1} , respectively—with the *Q* branch barely resolved. It is in this region that the dimerization gives the most trouble, since the dimer has rather strong bands at 1009, 1000, 950, 910, 890, 877, and 847 cm^{-1} . When a sample of ketene with an initial pressure of one-half atmosphere in a 10 cm cell was allowed to stand two days, most of the bands in the region 750–900 cm^{-1} disappeared with the exception of diketene bands and weak absorption bands at 773, 783, and 792 cm^{-1} . These bands look like *P*, *Q*, and *R* branches, but the spacing is not correct for ketene, and so they are believed to be the result of some impurity. The band structure in the region 900–1100 cm^{-1} was still apparent, however. The observed bands are given in Table III.

Region from 700 to 400 cm^{-1}

This region contains a series of irregularly spaced intense absorption bands extending from 458 cm^{-1} up to 700 cm^{-1} with the greatest intensity between 520 and 620 cm^{-1} . An intensity alternation is apparent, but not nearly so regular as in the 3164 cm^{-1} band. The system has the appearance of two overlapping perpendicular bands, with the components given in Table IV.

 TABLE V. Symmetry types and characters for point group C_{2v} .

C_{2v}	<i>I</i>	$C_2(z)$	σ_{xz}	σ_{yz}
A_1	+1	+1	+1	+1
A_2	+1	+1	-1	-1
B_1	+1	-1	+1	-1
B_2	+1	-1	-1	+1


 FIG. 2. Structural parameters for H_2XYZ molecule.

III. THEORETICAL CONSIDERATIONS⁶

A molecule H_2XYZ in which the XYZ atoms are collinear, and in which the two H atoms are symmetrically bonded to the X -atom, has nine vibrational degrees of freedom. If the molecule is planar, its symmetry point group is C_{2v} (a two-fold axis with two mutually perpendicular planes through it); if the molecule is non-planar, its symmetry point group is C_s (retaining only the plane of symmetry through the XYZ -atoms which bisects the HXH angle). The representation of the molecular point group which has the vibrational motions as its basis, in the terms of its irreducible components, is $\Gamma_{\text{vib}} = 4A_1 + 3B_1 + 2B_2$ for the C_{2v} molecule, and $\Gamma_{\text{vib}} = 6A' + 3A''$ for the C_s molecule. The symmetry types for point group C_{2v} are given in Table V. We have taken σ_{xz} to be the plane of the molecule. For point group C_s , type A' is symmetric and type A'' is antisymmetric with respect to reflection in the symmetry plane. Ketene is a C_{2v} molecule of this kind, and cyanamide ($H_2N-C\equiv N$) is a corresponding C_s molecule.

The technique of Wilson⁷ was used for setting

⁶ Since an investigation of cyanamide is also in progress, and since there is considerable similarity between the cyanamide and ketene molecules, the first part of this section is made general for any such a pentatomic molecule. Equations for the frequencies of the totally symmetrical vibrations of ketene have been given before [H. W. Thompson and J. W. Linnett, *J. Chem. Soc.* 1384 (1937); H. J. Bernstein, *J. Chem. Phys.* 6, 718 (1938)], but none have been given for the unsymmetrical vibrations or for the non-planar molecule.

⁷ E. B. Wilson, Jr., *J. Chem. Phys.* 7, 1047 (1939); 9, 76 (1941).

	S_2	S_5	S_3	S_4	S_7	S_8
S_2	$\frac{1}{m_1} + \frac{1 \cdot \cos \alpha}{m_3}$	$\frac{\sqrt{2} \cos \beta}{m_3}$	0	$-\frac{\sqrt{2} \epsilon \sin \alpha}{m_3}$	$-\frac{\sqrt{2} \tau \cos \frac{\pi}{2} \sin \chi}{m_3}$	$\frac{\sqrt{2} \tau \cos \frac{\pi}{2} \sin \chi}{m_3}$
S_3		$\frac{1}{m_3} + \frac{1}{m_4}$	$-\frac{1}{m_4}$	$-\frac{2\epsilon \tan \frac{\pi}{2} \cos \beta}{m_3}$	$-\frac{\xi \sin \chi}{m_3}$	0
S_3	A_1		$\frac{1}{m_4} + \frac{1}{m_5}$	0	0	0
S_4				$\frac{2\epsilon^2 + 2\epsilon^2(1 - \cos \alpha)}{m_1 + m_3}$	$\frac{2\epsilon \tau \sin \frac{\pi}{2} \sin \chi}{m_3}$	$-\frac{2\epsilon \tau \sin \frac{\pi}{2} \sin \chi}{m_3}$
S_7					$\frac{\xi^2 + \tau^2 + \xi^2 \tau^2 \xi \tau \cos \chi}{2m_1 m_4 + m_3}$	$-\frac{\tau^2 \tau \xi \cos \chi - \tau(\tau + \delta)}{m_3}$
S_8	(A)				B_2	$\frac{(\tau + \delta)^2}{m_4} + \frac{\tau^2}{m_3} + \frac{\delta^2}{m_5}$

	S_1	S_6	S_9
S_1	$\frac{1}{m_1} + \frac{1 - \cos \alpha}{m_3}$	$-\frac{(\tau - \epsilon \cos \beta)(1 - \cos \alpha)}{m_3 \sin \beta}$	$-\frac{\sqrt{2} \tau \sin \frac{\pi}{2}}{m_3}$
S_6		$\frac{\epsilon^2 + (\tau - \epsilon \cos \beta)^2(1 - \cos \alpha)}{m_1 + \frac{(\tau - \epsilon \cos \beta)^2(1 - \cos \alpha)}{m_3 \sin^2 \beta} + \frac{\tau^2(1 - \cos \alpha)}{m_4 \sin^2 \beta}}$	$\frac{\sqrt{2} \tau \sin \frac{\pi}{2}}{\sin \beta} \left(\frac{\tau - \epsilon \cos \beta}{m_3} + \frac{\tau + \delta}{m_4} \right)$
S_9	B_1 (A')		$\frac{\tau^2}{m_3} + \frac{(\tau + \delta)^2}{m_4} + \frac{\delta^2}{m_5}$

$m_1 = \text{mass of atom 1}$
 $m_3 = \text{mass of atom 3}$

$\epsilon = \frac{1}{r(X-H)}$
 $\tau = \frac{1}{r(X-Y)}$

$\delta = \frac{1}{r(Y-Z)}$
 $\xi = \frac{\epsilon}{\cos \frac{\pi}{2}}$

FIG. 3. G matrix for H_2XYZ molecule (symmetrical about diagonal).

up the secular equation, and it was checked by Eliashevich's⁸ method. The valence force coordinates (VFC) used are indicated in Fig. 2 and Table VI. Factoring of the secular equation is obtained by choosing valence force symmetry coordinates ($VFSC$) which form a basis for irreducible representations of both the C_s and C_{2v} point groups, i.e., are symmetry coordinates for both molecules. In order to do this, the angle χ between the H_2X plane and the XYZ axis is introduced as a structural parameter, and the change in this angle is used as one of the coordinates. For convenience, the $VFSC$ are designated by S_1, S_2, \dots , with a corresponding designation ν_1, ν_2, \dots , for the vibration frequencies, meaning that the vibration of frequency ν_1 involves coordinate S_1 primarily, etc. The $VFSC$ are given in Table VII.

The G matrix ($2T = S'G^{-1}S$) for the $VFSC$ is given in Fig. 3. It contains the atomic masses, internuclear distances, and functions of the vari-

ous bond angles. Blocks are outlined to represent the factoring for symmetry point group C_{2v} (ketene); terms outside the blocks enter only for non-planar molecules ($\chi \neq \pi$). Simplifying relationships which exist for a planar molecule are given in Table VIII.

The F matrix⁹ ($2V = S'FS$) used with the G matrix in obtaining the secular equation, $|GF - \lambda E| = 0$, for the ketene molecule is given in

TABLE VI. Bonds and angles used for VFC .

$\angle H_2XY = \chi$
$\angle HXH = \alpha$
$\angle H_1XY = \beta_1$
$\angle H_2XY = \beta_2$
$\angle XYZ = \begin{cases} \varphi \\ \gamma \end{cases}$
$r(H_1-X) = r_1$
$r(H_2-X) = r_2$
$r(X-Y) = r_{34}$
$r(Y-Z) = r_{45}$

⁹ The most general F matrix can be used with the G matrix of Fig. 3. We have limited ours because of the limited amount of experimental information from which to obtain constants.

⁸ M. Eliashevich, J. Phys. Chem. U.S.S.R. 14, 1381 (1940).

Fig. 4. In this potential system it is logical to expect F_8 and F_9 to have practically the same value (they would have exactly the same value if the $C=C=O$ axis had had fourfold symmetry). The constants F_1 and F_2 differ only by twice the constant representing interaction between the two $X-H$ bonds ($F_1=K_1+k_{12}$; $F_2=K_1-k_{12}$).

The parallel bands which appear in the infra-red spectrum can arise only from transitions whose over-all vibrational symmetry is of type A_1 . Transitions of type A_2 are not allowed to appear in infra-red absorption, and transitions of symmetry species B_1 and B_2 yield perpendicular bands. For transitions of species B_1 , the change of electric moment is along the axis of intermediate moment of inertia ("B"-type bands); for transitions of species B_2 , the change is along the axis of largest moment of inertia ("C"-type bands). In the case of ketene, however, the "B"- and "C"-type bands are practically identical,¹⁰ since $\rho=I_A/I_B$ is of the order of magnitude of 0.035, and $I_B \cong I_C$. In addition, since ρ has such a small value, the ratio of the intensity of the Q branch of a parallel band to that of the P and R branches must be very small.¹¹

IV. ASSIGNMENT OF OBSERVED VIBRATIONAL FREQUENCIES¹²

The strongest parallel band in the 2900–3200 cm^{-1} region is picked as arising from the funda-

TABLE VII. VFSC with symmetry designation.

VFSC	C_{2v}	C_s
$S_2 = 1/\sqrt{2}(\Delta r_1 + \Delta r_2)$		
$S_3 = \Delta r_{45}$		
$S_4 = \Delta \alpha$	A_1	A'
$S_5 = \Delta r_{34}$		
$S_7 = \Delta \chi$		
$S_8 = \Delta \varphi$	B_2	
$S_1 = 1/\sqrt{2}(\Delta r_1 - \Delta r_2)$		
$S_6 = 1/\sqrt{2}(\Delta \beta_1 - \Delta \beta_2)$	B_1	A''
$S_9 = \Delta \gamma$		

¹⁰ Reference 2, p. 480.

¹¹ Reference 2, p. 421.

¹² Thompson and Linnett (see reference 6) assigned the frequencies of the totally symmetrical vibrations on the basis of Kopper's Raman data. T. Y. Wu [*Vibrational Spectra and Structure of Polyatomic Molecules* (J. W. Edwards, Ann Arbor, Michigan 1946), p. 251.] made a partial assignment using Gershonowitz's and Wilson's (see reference 3) and Kopper's (see reference 4) data. His assignment is given in Table IX.

	F	S_2	S_5	S_3	S_4	S_7	S_8	S_1	S_6	S_9
A_1	S_2	F_2	0	0	0					
	S_5	0	F_5	f_{35}	0					
	S_3	0	f_{35}	F_3	0					
	S_4	0	0	0	F_4					
B_2	S_7					F_7	f_{78}			
	S_8					f_{78}	F_8			
B_1	S_1							F_1	0	0
	S_6							0	F_6	f_{69}
	S_9							0	f_{69}	F_9

FIG. 4. Assumed F matrix for ketene molecule.

mental vibration ν_2 , with a band center near 3066 cm^{-1} . Other parallel bands in this region must be combination bands. The only perpendicular band must be ν_1 , and its center is picked at 3162 cm^{-1} . Its components show an intensity alternation which requires the axis of least moment of inertia to be a twofold axis. For Fermi statistics the first component on the low frequency side of the band center must be a strong one ($K'=0 \leftarrow K''=1$), and the band center must be between the strongest lines. Consequently the band center is picked half way between the 3151 cm^{-1} and 3173 cm^{-1} components.

The extremely strong parallel band at 2153 cm^{-1} is assigned to ν_3 . The other stretching vibration of the $C=C=O$ part of the molecule is assigned the frequency $\nu_5=1120 \text{ cm}^{-1}$. ν_4 must be assigned to the strong parallel band at 1386 cm^{-1} . Thus all of the totally symmetrical fundamentals are assigned.

The frequencies ν_8 and ν_9 are expected in the region 500–600 cm^{-1} by analogy with N_2O . In this region there is a set of irregularly spaced bands whose structure is qualitatively in agreement with that discussed by Nielsen¹³ for the rotational bands of slightly anisotropic oscillators. The alternation in intensities for the rotational bands is not nearly so marked as in the perpen-

TABLE VIII. Relationships for a planar molecule.

$\sin \frac{1}{2}\alpha = \sin \beta$
$(1 - \cos \alpha) / \sin \beta = 2 \sin \frac{1}{2}\alpha$
$(1 - \cos \alpha) / \sin^2 \beta = 2$

¹³ H. H. Nielsen, J. Chem. Phys. 5, 818 (1937).

dicular band at 3162 cm^{-1} . Again, however, the first component on the low frequency side of the band center should be strong, and so one center must be very close to 529 cm^{-1} . The other center in this region must be close to 570 , 588 , or 610

TABLE IX. Observations and assignments of vibrations of ketene.

Infra-red—Gas		G and W**	Raman—Liquid	
H and W*			K††	Wu†
$\nu_9(B_1)C=C=O$ bend	529 \perp VS		501 (1b)	ν_8
$\nu_8(B_2)C=C=O$ bend	588 \perp VS		599 (1/2b)	ν_9
			715 (1/2b)	
			801 (1/2b)	
$\nu_7(B_2)H_2-C=C$ bend	909 \perp W	890 S		ν_7
$\nu_6(B_1)H_2-C=C$ bend	1011 \perp W		998 (1)	ν_6
$2\nu_9(A_1)$	1058 \parallel W			
$\nu_8(A_1)C=C=O$ S	1120 \parallel VS	1110 S	1130 (6b)	ν_8
$2\nu_8(A_1)$	1190 \parallel VW?	1185 W	1198 (1)	
		1325 W		
		1350	1344 (2)	ν_4
$\nu_4(A_1)H_2C$ def.	1386 \parallel VS	1400 S	1386 (1b)	
$2\nu_6(A_1)$	1962 \parallel M	1935 S	1895 (1/2)	
$\nu_8(A_1)C=C=O$ S	2153 \parallel VVS	2160 S	2049 (1/2b)	ν_3
$\nu_4+2\nu_8(A_1)$	2533 \parallel M			
		2915 W		
$\nu_2(A_1)C-H$ S	3066 \parallel S	3058 S	2952 (5)	ν_2
$\nu_1(B_1)C-H$ S	3162 \perp W	3165 W	3015 (4b)	ν_1
$\nu_3+\nu_6(A_1)$	3264 \parallel S			
$\nu_3+2\nu_8(A_1)$	3330 \parallel W			
$\nu_3+\nu_4(A_1)$	3526 \parallel M			

* Present paper.

† Wu's¹³ numbering system has been changed to correspond to this paper.

** See reference 3.

†† See reference 4.

cm^{-1} , and we choose 588 cm^{-1} as being the most plausible. This also can account for the overtone at 1190 cm^{-1} if there is interaction between the overtone and ν_6 . (It must be remembered, however, that the 1190 cm^{-1} band may be caused by an impurity.) ν_9 is assigned as 529 cm^{-1} and ν_8 as 588 cm^{-1} . The choice made in this case is dependent on the assignment of ν_6 and ν_7 , since best agreement among force constants is obtained if the higher frequency of this pair arises from a vibration of the same symmetry type as the lower frequency of the similar pair near 900 – 1050 cm^{-1} .¹⁴

By analogy with ethylene and the vinyl halides, ν_6 and ν_7 should fall in the region 900 – 1050 cm^{-1} . There are a number of absorption bands in this region, which appear to start at 810 cm^{-1} and continue up into the strong parallel band at 1120 cm^{-1} . Irregular spacings and intensities make it difficult to pick band centers, however. The parallel band appearing at 1962 cm^{-1} gives some aid, since it must be a first overtone of either ν_6 or ν_7 (parallel bands arising only from transitions

of over-all A_1 symmetry). Thus the fundamental frequency corresponding to this overtone cannot be less than 981 cm^{-1} , and could hardly be greater than 1030 cm^{-1} and still give rise to the overtone at 1962 cm^{-1} . Apparently, the interaction between the overtone and ν_3 is appreciable in liquid ketene since the Raman spectrum⁴ shows the overtone with an intensity comparable to that of ν_3 and presumably displaced in position. If a similar interaction exists in the vapor phase, the fundamental probably lies nearer 1030 cm^{-1} than 981 cm^{-1} . Possible band centers in this region are near 995 cm^{-1} and 1011 cm^{-1} , and we choose 1011 cm^{-1} as the more probable (midway between a strong component at 1004 cm^{-1} and a weak one at 1018 cm^{-1}) and assign it to ν_6 by analogy with formaldehyde.¹⁵ ν_7 is chosen at 909 cm^{-1} , since the over-all absorption seems strongest here and since it places the band center between a strong 907 cm^{-1} component and a weaker 912 cm^{-1} component. This is a little lower than some of the assignments in the vinyl halides,¹⁶ but is higher than others.¹⁷ There is an absorption overlapping the strong 1120 cm^{-1} parallel band, which appears to be a weak parallel band with a Q branch at 1058 cm^{-1} and P and R branches at 1044 cm^{-1} and 1070 cm^{-1} , respectively. This band we assign to $2\nu_8$. Some of the weak bands in the region 750 – 850 cm^{-1} may be the result of the difference bands $\nu_4-\nu_8$ and $\nu_4-\nu_9$, and some of them may be the result of impurities.

The assignment of frequencies, together with a comparison with other observations on ketene, is given in Table IX. Only band centers are listed, and the uncertain bands in the 750 – 850 cm^{-1} region are omitted.

V. FORCE CONSTANTS

Using the assignments given in Table IX it is possible to evaluate a number of the force constants appearing in Fig. 4. Since the number of frequencies available for determining the force constants is nine, and we have listed twelve constants as being of probable importance, some

¹⁵ E. S. Ebers and H. H. Nielsen, J. Chem. Phys. **5**, 822 (1937). (Also, it is in agreement with similar vibrations in ethylene.)

¹⁶ K. S. Pitzer and N. K. Freeman, J. Chem. Phys. **14**, 586 (1946).

¹⁷ P. Torkington and H. W. Thompson, Trans. Faraday Soc. **51**, 236 (1945).

¹⁴ See section V of this paper—"Force Constants."

of the constants must be fixed by analogy with related molecules. For the geometrical parameters in Fig. 3, we have taken $r(\text{C}=\text{C})=1.35\text{\AA}$, $r(\text{C}=\text{O})=1.17\text{\AA}$, $r(\text{C}-\text{H})=1.08\text{\AA}$ and $\angle\text{HCH}=120^\circ$.

The value of F_4 can be fixed in the range 0.46 to 0.52×10^{-11} erg/radian² by estimating extreme values of the ratio F_5/F_3 and solving the resulting cubic equation in F_4 . We expect F_3 to have a rather large value since $r(\text{C}=\text{O})=1.17\text{\AA}$ is considerably shorter than the normal double bond distance. A force constant almost as large as the value 15.5×10^5 dynes per cm for CO_2 ¹⁸ would be very plausible. The $\text{C}=\text{C}$ distance is only very slightly larger than the normal distance, and so F_5 should be close to 9.8×10^5 dynes per cm. A plausible set of constants which reproduce the observed frequencies of the A_1 vibrations within one and one-half percent is: $F_2=5.23$, $F_3=15.5$, $F_5=9.8$, $f_{35}=1.5$ ($\times 10^5$ dynes per cm) and $F_4=0.494$ ($\times 10^{-11}$ erg per radian²).

The constants determining the frequencies of B_1 and B_2 vibrations are perhaps best considered together. We have assumed that F_8 and F_9 should have values rather close together and of the order of magnitude of the bending constant in N_2O , 0.69×10^{-11} erg per radian².¹⁹ One would not expect the bending constant to be as high as in carbon dioxide, 0.78×10^{-11} erg per radian²,²⁰ since the effect of resonance in this case is to give some single bond—triple bond character ($\text{H}_2\text{C}^--\text{C}^+\equiv\text{O}$).¹ By analogy with the calculations of Pitzer and Freeman,¹⁶ the constant F_7 should have a value around 0.23×10^{-11} erg per radian.² Keeping the interaction constants small ($|f| \leq 0.04 \times 10^{-11}$), and assigning $\nu_6=1011\text{ cm}^{-1}$ and $\nu_7=909\text{ cm}^{-1}$ by analogy with formalde-

TABLE X. Force constants for ketene.

$F_1 = 5.23$	$F_4 = 0.494$
$F_2 = 5.23$	$F_6 = 0.49$
$F_3 = 15.5$	$F_7 = 0.21$
$F_5 = 9.8$	$F_8 = 0.75$
$f_{35} = 1.45$	$F_9 = 0.68$
$\times 10^5$ dynes/cm	$f_{78} = +0.04$
	$f_{69} = -0.03$
	$\times 10^{-11}$ erg/radian ²

hyde,¹³ it is necessary to assign $\nu_8=588\text{ cm}^{-1}$ and $\nu_9=529\text{ cm}^{-1}$ in order to obtain values for F_8 and F_9 reasonably close together. The constants obtained by this procedure are ($\times 10^{-11}$ erg per radian²): $F_6=0.49$, $F_9=0.68$, $f_{69}=-0.03$, $F_7=0.21$, $F_8=0.75$, and $f_{78}=+0.04$. These constants reproduce the frequencies within 0.5 percent. If the reverse assignment is made for ν_8 and ν_9 , the closest values of F_8 and F_9 are 0.70×10^{-11} and 0.87×10^{-11} erg per radian.² The value chosen for F_1 is 5.23×10^5 dynes per cm. A plausible set of force constants for the ketene molecule is given in Table X.

VI. MOLECULAR DIMENSIONS

The rotational bands in the ketene spectrum exhibit the same irregularities observed in the formaldehyde spectrum.¹⁵ Unlike formaldehyde, however, ketene shows no discrete bands in the ultraviolet spectrum²¹⁻²³ from which to obtain the rotational constants. Thus we shall use the average spacing of the components in the 3162 cm^{-1} band to obtain the moment of inertia around the twofold axis. This yields a value of $I_A=2.96 \pm 0.50 \times 10^{-40}$ g cm² which is compatible with $r(\text{C}-\text{H})=1.08\text{\AA}$, and $\angle\text{HCH}=120^\circ$.

²¹ Lardy, J. chim. phys. **21**, 353 (1924).

²² R. G. W. Norrish, H. G. Crone, and O. Saltmarsh, J. Chem. Soc. 1533 (1933); J. Am. Chem. Soc. **56**, 1644 (1934).

²³ W. F. Ross and G. B. Kistiakowsky, J. Am. Chem. Soc. **56**, 1112 (1934).

¹⁸ Reference 2, p. 187.

¹⁹ Reference 2, p. 174.

²⁰ Reference 12, p. 147.