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The Infra-Red Absorption Spectrum and Vibrational Frequency Assignment of Ketene

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The infra-red absorption spectrum of ketene from 2μ to 15μ has been determined and a complete frequency assignment deduced. All the harmonic bands can be simply interpreted on this assignment. The fine structure of the 925-cm^{-1} band is discussed.

I. INTRODUCTION

KETENE is a simple and interesting molecule and one for which a complete frequency assignment should be possible. In spite of this, there is available very little spectroscopic information for ketene. The Raman spectrum of the liquid has been determined by Kopper¹ and the infra-red spectrum of the vapor under low resolution by Gershinowitz and Wilson.² The lack of more data is probably due to the difficulty of obtaining and maintaining a pure sample of ketene free from the dimer. The 2μ - 15μ infra-red absorption spectrum of ketene (vapor), recorded under higher resolution than the earlier work, is reported here, along with a vibrational frequency assignment.

II. EXPERIMENTAL DETAILS

The sample of ketene used for this study was prepared in these laboratories. The method of preparation was essentially that of Rice, et al.³ The preparation here differed from theirs in that the final purification in a vacuum-jacketed column was omitted. Instead, the product was rapidly vaporized through a long, water-cooled, spiral condenser (to remove unreacted acetone) into a dry-ice acetone-cooled receiver. The above procedure was repeated and about the middle third of the material was collected and used for these studies.

The sample container was kept at dry-ice acetone or liquid-nitrogen temperature except when sampling. Before the first vapor sample was taken into the absorption cell, the sample container was

slowly warmed and the first material to vaporize was discarded until about three-fourths of the sample remained. This was done to eliminate any remaining ethylene dissolved in the ketene. No vapor sample was allowed to remain in the absorption cell for more than about an hour, so that several samples were taken to obtain the complete absorption spectrum.

The spectrograph used was an automatic-recording rocksalt-prism instrument,⁴ evacuated to eliminate CO_2 and H_2O vapor absorption. The length of the absorption cell was 15 cm. The wave-lengths are reproducible to within $\pm 0.01\mu$ for λ greater than 5μ . For wave-lengths shorter than 5μ , the reproducibility is somewhat less, becoming about $\pm 0.02\mu$ at 3μ . These reproducibilities are indicated by calibration check runs on ammonia, ethylene, and carbon dioxide. The absolute accuracy of the wave-lengths depends on the proper correlation of absorption maxima in spectra of these same vapors with published grating values, allowing for the differences in resolution between instruments. Since some effort was made to do this well, it is probable that the absolute error is very nearly the same as the reproducibility error. The spectral intervals subtended by the slits (twice the "spectral-slit widths") are indicated on the spectrum (Fig. 1). The accuracies of the intensities shown may be no better than ± 10 percent in transmission units, but the relative intensities are probably much better. Transmission values shown in Fig. 1 are taken from a single recording at each pressure.

III. EXPERIMENTAL RESULTS

The observed wave-lengths, frequencies, and intensities of infra-red absorption maxima are given in Table I.

⁴ R. R. Brattain, *Phys. Rev.* **60**, 164 (1941).

¹ H. Kopper, *Zeits f. physik. Chemie* **B34**, 396 (1936).

² H. Gershinowitz and E. B. Wilson, Jr., *J. Chem. Phys.* **5**, 500 (1937).

³ F. O. Rice, J. Greenberg, C. E. Waters, and R. E. Vollrath, *J. Am. Chem. Soc.* **56**, 1760 (1934).

The initial spectrum (300 mm) showed bands at 5.74μ and 8.25μ which by their positions and shapes suggested an impurity of acetone, the two strongest bands in the acetone spectrum being at these wave-lengths. A recheck of these regions with a new sample showed the two bands to be much reduced in intensity, but still present. Hence, it is highly probable that the bands arise from adventitious acetone, and the dotted portions of Fig. 1 in the 5.5μ – 6.0μ and 8.1μ – 8.4μ regions indicate the probable absorption curve with the acetone eliminated. The source of this impurity is uncertain, since if acetone were present in the ketene sample it should have remained behind when the ketene was taken off.

Two of the fine-structure peaks, at 9.94μ and 11.22μ , are anomalous in that they are relatively stronger in the 300 mm spectrum than in the 100 mm one. Since the two strongest bands of liquid diketene⁵ are near 9.93μ and 11.43μ , it is probable that these anomalous intensities arise from a trace of this compound which was formed

during the high-pressure run and which distorted the ketene spectrum in these regions. The amount of dimer formed in the lower-pressure runs would be expected to be negligible, assuming second-order kinetics. The probable true absorption curve in the 10μ and 11μ regions due to ketene alone is indicated by the dotted lines in Fig. 1.

The remainder of the spectrum is presumably due to ketene only. In particular, no indications of ethylene or methane are present. Ethylene would show bands near 5.3μ and 6.9μ , and methane near 7.6μ . The strongest band of ethylene has a strong, sharp *Q* branch at 10.52μ , which in principle could account for the peak at this position in the ketene spectrum. However, this peak fits in well with the other maxima in the region and is not anomalously intense, so there is no need to adduce ethylene impurity to explain it.

Although acetylene has never been noted as an impurity of ketene, the moderate band at the unusual position, 3.07μ , was suggestive of this compound. However, lack of absorption at 7.67μ ,

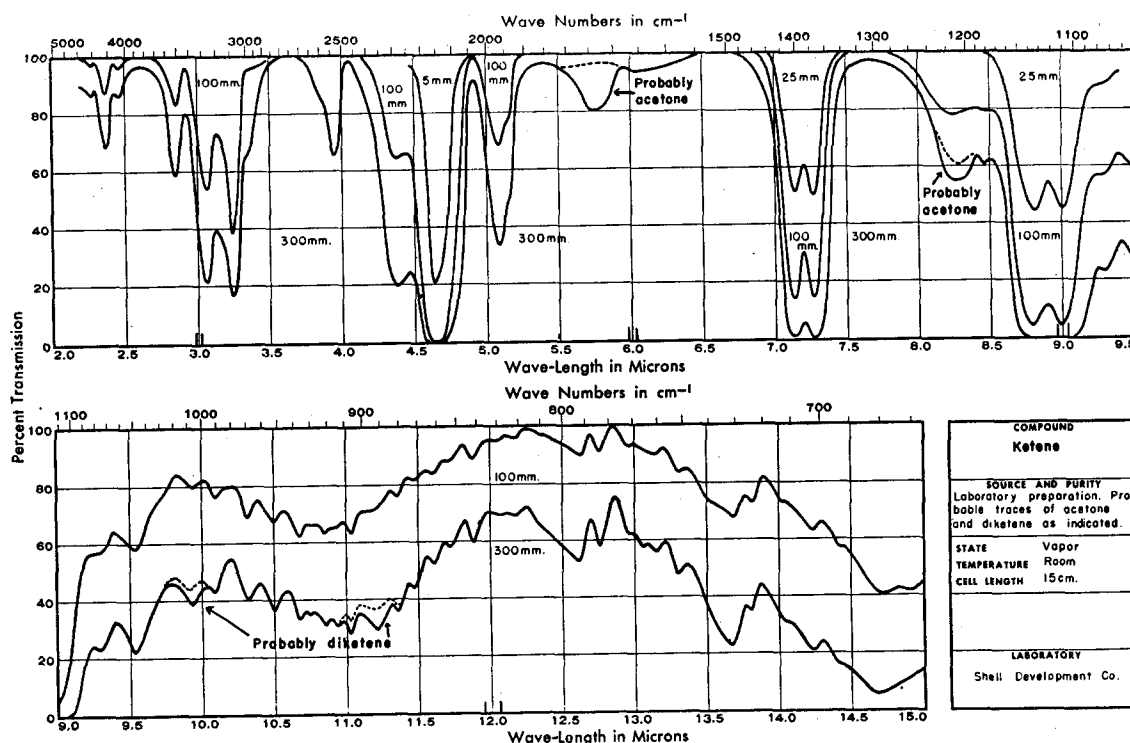


FIG. 1. Absorption spectrum of ketene vapor.

⁵ Unpublished work of this laboratory; also, very recently, D. H. Whiffen and H. W. Thompson, J. Chem. Soc. (Lond.) 1005 (1946).

TABLE I. Wave-lengths, frequencies, and intensities of infra-red absorption maxima of ketene vapor.

$\lambda(\mu)$	$\omega(\text{cm}^{-1})$	Intensity cell: 150 mm press.: 100 mm	$\lambda(\mu)$	$\omega(\text{cm}^{-1})$	Intensity cell: 150 mm press.: 100 mm
2.27	4405	0	9.94***	1006	
2.365	4230	1	10.10	990	
2.455	4075	0	10.33	968	
2.85	3510	1	10.505	952	
3.065	3265	4	10.685	936	
3.245	3080	6	10.75	930	
~3.36	~2975	0	10.86	921	
~3.84	~2605	0s	10.95	913	
3.94	2540	1	11.04	906	
4.37	2290	3s	11.22***	891	
4.64	2155	10	11.36	880	
5.085	1967	3	11.48	871	
~5.15	~1940	1s	11.62	861	
~5.74*	~1740	0	11.73	853	
~6.05	~1655	0	11.89	843	
7.135	1402		12.06	829	
7.265	1376	8	12.18	821	
~8.24**	~1215	2	~12.4	~805	0s
8.46	1182	0	12.62	792	1
8.80	1136		12.765	783	1
9.00	1111	9	12.97	771	
~9.30	~1075		13.07	765	
9.54	1048	3	13.15	760	
~9.72	~1030	0s	13.31	751	
			~13.52	~740	
			13.68	731	
			13.81	724	
			~14.04	~710	
			~14.43	~695	
			14.72	679	
			14.94	669	

* Probably due to acetone.

** Probably due in part to acetone.

*** Probably due in part to diketene.

s shoulder on adjacent stronger band.

and lack of the very sharp Q branch at 13.69μ , precludes explaining the 3.07μ band as due to acetylene.

IV. FREQUENCIES OF KETENE

In accordance with well-understood structural principles, the ketene molecule may be assigned to the symmetry group C_{2v} . That is, there are one two-fold rotation axis and two vertical reflection planes, mutually perpendicular and passing through the axis. The molecular vibrations of ketene then fall into four representations with the symmetry characteristics shown in Table II. Selection rules permit the appearance of all four classes in the Raman and of all but the A_2 class in the infra-red. However, since there are no fundamental vibrations of the ketene molecule of representation A_2 , all the fundamental vibrations should appear in both the infra-red and Raman spectra.

Since the molecule is very nearly a symmetrical

rotator, all vibrations of the A_1 representation correspond to parallel bands, and vibrations of the B_1 and B_2 representations to perpendicular bands. The least moment of inertia is so low⁶ that the parallel-type bands should have nearly the appearance of linear-molecule parallel bands, i.e., show marked P and R branches, but only a very weak Q branch.⁷ The $P-R$ separation should be about 23 cm^{-1} . The perpendicular bands should appear as structureless rounded bands (if unresolved) or as equally spaced P_Q and R_Q branches ($\Delta J=0$, $\Delta K=\pm 1$) with the $\Delta J=\pm 1$, $\Delta K=\pm 1$ transitions furnishing an effectively continuous background (if partially resolved).

For bands short of 6μ , the spectrograph used did not have sufficient resolution to distinguish the true envelopes of the bands. However, of the longer wave-length bands, it is clear that the pairs of peaks at $7.13\mu-7.27\mu$, $8.80\mu-9.00\mu$, and probably also $9.31\mu-9.55\mu$, represent A_1 (parallel) bands. The $P-R$ separations of these are 26, 25, and 27 cm^{-1} , respectively, which are in satisfactory agreement with the value calculated above on the simple theory. The series of peaks between 9.8μ and 12.0μ undoubtedly are attributable to a B_1 or B_2 (perpendicular) band. The region from 12.0μ to 15μ presents a confused aspect, consisting of very irregularly spaced and almost randomly intense maxima. Since there is reason to believe that one of the fundamentals of the perpendicular type lies at 16.7μ (see below), the most reasonable interpretation of this region is that it is a superposition of a weak perpendicular band (of type B_2 and hence with a weak Q branch appearing as the peak at 13.68μ) on the short-wave side of a strong band with center near 16.7μ . The lack of a rudimentary Q branch in the 10.8μ perpendicular band is some indication that this band is of the B_1 type, the dipole change being along the intermediate axis of inertia.

In Table III are shown the infra-red band centers and symmetry types, as discussed above. The centers of the unresolved bands are taken as the absorption maxima, of the parallel bands as the midpoint between the P and R branches,

⁶ The moments calculated from the $\text{C}=\text{C}$ and $\text{C}=\text{O}$ distances given by J. Y. Beach and D. P. Stevenson, *J. Chem. Phys.* **6**, 75 (1938) and the assumption of 120° hydrogen angles and a 1.06 \AA $\text{C}-\text{H}$ distance, are 1.71, 124.0, and $125.7\text{ at.wt. units} \times \text{\AA}^2$.

⁷ S. L. Gerhard and D. M. Dennison, *Phys. Rev.* **43**, 197 (1933).

and of the 11μ perpendicular band as 10.8μ . The Raman spectrum given by Kopper is also shown. The line at 998 cm^{-1} was questioned by Kopper, since it appeared only on one plate. The 801 cm^{-1} shift was thought by Kopper to be due to impurity of acetone. The present authors further question the line at 1344 cm^{-1} . As will be seen below, this cannot be attributed to a ketene fundamental nor to any overtone or combination. Since one of the expected impurities is ethylene, and since the strongest Raman line of ethylene vapor is at 1342 cm^{-1} ,⁸ it is reasonable to attribute the line to this impurity.

V. VIBRATIONAL ASSIGNMENT

In Table IV are given the types and symmetries of the various fundamental vibrations. It is clear that the very strong infra-red band at 2155 cm^{-1} represents one of the double-bond stretching vibrations, since mechanical interaction between the adjacent double bonds should result in a large shift out of the customary double-bond region ($\sim 6\mu$). The analogous band in allene is found at 1980 cm^{-1} .⁹ The lack of a corresponding strong Raman line is somewhat curious. The only Raman line in the vicinity is a weak one at 2049 cm^{-1} , and if this is to be correlated with the 2155 cm^{-1} infra-red band the shift must be attributed to a large liquid-vapor effect. Since the vibration is essentially an antisymmetrical combination of the two stretching vibrations, the weakness of the Raman line must arise from the near equality of the polarizability *vs.* bond-length function for the two bonds, since for a molecule symmetrical in the stretching coordinates the line would be forbidden.

The other double-bond stretching vibration, essentially the symmetrical combination of the

TABLE II. Symmetry designations for ketene.

Representation	Rotation about 2-fold axis	Reflection through plane of hydrogen atoms	Reflection through plane perpendicular to plane of hydrogen atoms
A_1	+	+	+
A_2	+	—	—
B_1	—	+	—
B_2	—	—	+

⁸ See G. Herzberg, *Infra-red and Raman Spectra of Polyatomic Molecules* (D. Van Nostrand Company, Inc., New York, 1945), p. 326.

⁹ J. W. Linnett and W. H. Avery, *J. Chem. Phys.* **6**, 686 (1938).

TABLE III. Infra-red and Raman frequencies (in cm^{-1}) of ketene.

Infra-red ω	(vapor) symmetry	Raman (liquid) ω	Assignment
731(2)	B_2	510(1b)* 599(1/2b) 715(1/2b)	Fundamental Fundamental Fundamental; C=C=O bending
925(3)	Prob. B_1	801(1/2b)	Probably acetone impurity Fundamental; CH ₂ out-of-plane wagging
1062(3)	A_1	998(1)	Probably spurious
1124(9)	A_1	1130(6b)	2 \times 510 = 1020 Fundamental; C=C=O stretching
1182(0)	?	1198(1)	P branch of 1198 2 \times 599 = 1198
1215(2)	?	1344(2)	R branch of 1198
1391(8)	A_1	1386(1b)	Probably ethylene impurity Fundamental; HCH bending
$\sim 1655(0)$?	1895(1/2)	1124 + 510 = 1634 1124 + 731 = 1855 1391 + 510 = 1901 1391 + 599 = 1990**
$\sim 1940(1s)$?	2049(1/2b)	Fundamental; C=C=O stretching
1967(3)	?		1391 + 925 = 2326; 2 \times 1124 = 2248
2155(10)	NR		1391 + 1124 = 2515 1391 + 2 \times 599 = 2589
2290(3s)	NR	2952(5)	Fundamental; A_1 CH stretching**
2540(1)	NR	3015(4b)	Fundamental; B_1 CH stretching**
$\sim 2605(0s)$	NR		2155 + 1124 = 3279
2975(0)	NR		2155 + 1391 = 3546
3080(6)	NR		2965 + 1124 = 4089
3265(4)	NR		3080 + 1124 = 4204;
3510(1)	NR		2 \times 2155 = 4310
4075(0)	NR		2965 + 1391 = 4356;
4230(1)	NR		3080 + 1391 = 4471
4405(0)	NR		

NR = not resolved.

s = shoulder on adjacent stronger band.

* A value of 530 cm^{-1} for the vapor-phase value gives a better fit for the overtones.

** Assignments incorrect; see note added in proof at end of paper.

individual bond stretchings, may be assigned as the 1124 cm^{-1} frequency. This corresponds to the strongest Raman line (1130 cm^{-1}), and the infra-red band is of the correct symmetry. The analogous frequency of allene is at 1069 cm^{-1} .⁹

The HCH-bending frequency, expected to be in the 1400 cm^{-1} region by analogy with other organic molecules, is clearly assignable to the 1391 cm^{-1} infra-red band and 1386 cm^{-1} Raman line. The two CH-stretching frequencies are assignable to the 3080 cm^{-1} infra-red band (B_1) and the infra-red and Raman frequency near 2950 cm^{-1} (A_1). The only Raman line corresponding to the infra-red 3080 cm^{-1} band is that at 3015 cm^{-1} , the large shift being ascribable to an anomalously large liquid-vapor effect. The symmetry characters appended are assumed from the usual observation that the symmetric CH stretching frequencies are lower than the antisymmetric.

The assignment of the remaining vibrations—the two CH₂-wagging and two CCO-bending motions—is not so clearcut. These are all perpendicular motions, and are expected to be of considerably lower frequency than those discussed

above. It is on this basis that the 1344 cm^{-1} Raman line was attributed to an impurity, since it cannot be explained as a fundamental or as an overtone (see discussion of overtones below). There are four observed frequencies capable of being assigned to these fundamentals: the Raman shifts at 510 and 599 cm^{-1} , and the infra-red bands at 731 (Raman: 715 cm^{-1}) and 925 cm^{-1} . The lack of lower frequencies is significant, since if no fundamentals are less than 510 cm^{-1} then none of these four can be interpreted as a harmonic, nor with any probability as a difference band. Hence, the four may be taken as the most reasonable values for the remaining four fundamentals. The frequency at 599 cm^{-1} is the probable source of the infra-red band giving rise to the increasing absorption toward the long-wave end of the spectrum.

Assignment of these four frequencies as the remaining fundamentals receives some confirmation from a consideration of the overtone and combination bands. The 1062 cm^{-1} infra-red band (symmetry A_1) can be assigned as 2×510 . Assuming the symmetries of the 731 and 925 cm^{-1} bands to be B_2 and B_1 , respectively, as discussed earlier, the symmetries of the two lowest frequencies must be B_1 and B_2 , and hence their combination should be inactive (representation A_2). The first overtone of the 599 cm^{-1} frequency fits very well as the 1198 cm^{-1} Raman line and the pair of infra-red maxima at 1182 and 1215 cm^{-1} , assuming these to be the P and R branches of an A_1 band at 1198 cm^{-1} .

On the basis of the set of fundamentals deduced above it is possible to explain satisfactorily all the other overtone bands, as shown in Table III. Only one of these, the very weak shoulder at 3.84μ (2605 cm^{-1}), needs to be assigned as a third harmonic. Since there are relatively few fundamentals, the fact that such an assignment can be

made is good support for the assignment. All the stronger overtones contain at least one component fundamental of high intensity.

One further slight modification in the assignment will be made. As noted above, the 1062 cm^{-1} infra-red band is best accounted for as 2×510 . Since the difference here is much too large to be ascribable to anharmonicity only, it is probable that the fundamental frequency for the vapor molecule is near 530 cm^{-1} , and the difference between this and the observed Raman line at 510 cm^{-1} is a liquid-vapor shift. In this connection, the large liquid-vapor shift on the 2155 cm^{-1} and 3080 cm^{-1} bands may be pointed out (see above). Use of 530 cm^{-1} as the true value of the fundamental gives a much better fit on all the other overtones involving this frequency. Hence, the finally deduced set of fundamental frequencies is: $530(B_1 \text{ or } B_2)$, $599(B_2 \text{ or } B_1)$, $731(B_2)$, $925(B_1)$, $1124(A_1)$, $1391(A_1)$, $2155(A_1)$, $2960(A_1)$, $3080(B_1)$. Using these, all sixteen second harmonic bands assigned in Table III fit the calculated sums to 1 percent on the average, and in the worst case (1895 cm^{-1} assigned as $1124 + 731 = 1855$) to 2.7 percent.

There remains the question as to which pair of the four lowest frequencies (530 , 599 , 731 , 925 cm^{-1}) corresponds essentially to the CCO bending vibrations and which pair to the CH_2 wagging vibrations. As analogous cases for the skeletal bending frequencies of an $\text{X}=\text{C}=\text{Y}$ system, we may consider carbon dioxide and allene. For the former this frequency is at 667 cm^{-1} ,¹⁰ and for the latter 353 cm^{-1} .⁹ The large difference may be due either to differences in the inherent deformability of the $\text{C}=\text{C}$ and the $\text{C}=\text{O}$ systems or to the resonance in CO_2 (resonance structures of the type $(^-\text{O})-\text{C}\equiv\text{O}^{(+)}$). In either case ketene should be intermediate, since from the electron-diffraction determination of the double-bond distances in ketene, considerable resonance with structure $(^+)\text{O}\equiv\text{C}-\text{C}^{(-)}\text{H}_2$ is indicated (Stevenson and Beach, ref. 6). Hence, the pair of frequencies in ketene at 530 and 599 cm^{-1} may be assigned to the skeletal bending vibrations, the splitting being due to the loss of symmetry occasioned by the CH_2 group. The 731 and 925 cm^{-1} bands are then to be assigned to the CH_2 vibrations, and may be compared with the analogous frequencies

TABLE IV. Symmetry classes of vibrations for ketene (C_{2v} symmetry).

Type of vibration	A_1	A_2	B_1	B_2	Expected region (cm^{-1})
1 $\text{C}=\text{C}$ stretching	1	0	0	0	1000-2000
1 $\text{C}=\text{O}$ stretching	1	0	0	0	
2 $\text{C}-\text{H}$ stretching	1	0	1	0	3000
2 $\text{C}=\text{C}=\text{O}$ bending	0	0	1	1	<800
1 HCH bending	1	0	0	0	1400
2 CH_2 wagging	0	0	1	1	700-1000

¹⁰ D. M. Dennison, Rev. Mod. Phys. 12, 175 (1940).

in allene^{9,11} (845 and 1030 cm⁻¹) and in formaldehyde¹² (1165 and 1278 cm⁻¹).

VI. FINE STRUCTURE OF THE 925 cm⁻¹ BAND

The only band whose fine structure is free enough of interference to be discussed is that near 925 cm⁻¹; the 731 cm⁻¹ band is too badly overlaid by the lower-frequency band (599 cm⁻¹) to be interpretable.

Although the resolution is not sufficient for any definitive study of the band, it is clear that the sub-band *Q* branch spacings exhibit the convergence phenomenon first discussed by Nielsen in connection with formaldehyde,¹³ and later beautifully illustrated by Thompson and Harris in the spectrum of allene.¹¹ The spacing at the high-frequency end of the band is about 16 cm⁻¹, and at the low frequency end 9 cm⁻¹, the convergence to low frequencies being due presumably to Coriolis interaction with the nearby 731 cm⁻¹ band. The situation is not so simple as with the allene case, however, where the intermediate spacing near the band center was very nearly that indicated by the simple symmetric-rotator theory, $(I_c^{-1} + I_A^{-1})h/4\pi^2$. For ketene the simple theory predicts a spacing of ~ 19 cm⁻¹ (i.e., about twice that of allene, from the twofold reduction in off-axis hydrogen nuclei). The observed spacing is less than this over the whole band, indicating some further vibration-rotation interaction, which is apparently absent in the allene¹¹ and formaldehyde¹³ spectra. The band is anomalous also in that the intermediate spacing (i.e., that midway between the limiting spacings at the band ends), which is about 13 cm⁻¹, does not occur at the band center as judged by the intensity maximum (925 cm⁻¹), but is displaced to about 890 cm⁻¹.

VII. THE C=C AND C=O BOND-STRETCHING FORCE CONSTANTS

In view of recent interest in the polarities and other bond characteristics of the double bonds in ketene,^{14,15} some consideration has been given to

TABLE V. Double-bond-stretching force constants, in dynes/cm.

Molecule	C=C constant	C=O constant	Interaction constant
H ₂ C=CH ₂	10.87 · 10 ⁵
H ₂ C=C=CH ₂	9.59	...	-0.12 · 10 ⁵
H ₂ C=C=O	9.70	13.43 · 10 ⁵	(-0.12)
H ₂ C=C=O	8.30	15.75	(0.61)
H ₂ C=C=O	7.65	17.26	(1.33)
O=C=O	...	15.52	1.33
H ₂ C=O	...	13.48	...

the bond-stretching force constants. However, it seems clear from the discussion given below that the infra-red spectrum is incapable of furnishing reliable information on the bond orders.

Calculations were made on ethylene and allene (as examples of pure CC double bonds), formaldehyde (as an example of a typical ketonic or aldehydic CO double bond), carbon dioxide, and ketene. The CH₂ group was treated as a point mass of weight 14. Observed fundamental frequencies were used throughout rather than true harmonic frequencies, since sufficient data for determining the latter are not available for all molecules considered. The double-bond stretching frequencies of ethylene (1623 cm⁻¹)⁸ and formaldehyde (1750 cm⁻¹)¹² lead immediately to the force constants shown in Table V. The other three molecules (allene, ketene, and carbon dioxide) are linear and triatomic under the assumptions used. The complete quadratic potential function for the parallel vibrations is then,

$$2V = K_1\Delta r_1^2 + K_2\Delta r_2^2 + 2k\Delta r_1\Delta r_2.$$

For allene and carbon dioxide the molecular symmetry requires $K_1 = K_2$, so that the two constants shown in Table V were determinable from the two observed frequencies (allene: 1071, 1980 cm⁻¹;¹⁶ carbon dioxide: 1337, 2349 cm⁻¹¹⁷). It is seen that the allene C=C constant is less than that of ethylene; whether this represents an actual difference in bond character, or whether it is spurious and the result of ignoring the hydrogen motions, is not known. The interaction constant between the two bonds is satisfactorily small. The C=O constant of CO₂ is appreciably greater than that of formaldehyde, which fact has been often pointed out as evidence for the partial triple-bond character of the bond in CO₂. The

¹¹ H. W. Thompson and G. P. Harris, Trans. Faraday Soc. 40, 295 (1941).

¹² E. S. Ebers and H. H. Nielsen, J. Chem. Phys. 6, 311 (1938).

¹³ H. H. Nielsen, J. Chem. Phys. 5, 818, 822 (1937).

¹⁴ N. B. Hannay and C. P. Smyth, J. Am. Chem. Soc. 68, 1357 (1946).

¹⁵ A. D. Walsh, J. Am. Chem. Soc. 68, 2408 (1946).

¹⁶ See reference 8, p. 339.

¹⁷ See reference 8, p. 173, Table 41.

CO_2 interaction constant is rather large, which is perhaps not unexpected since the participation of the various resonance structures will be altered on changing one of the CO distances, and this in turn will affect the potential energy function of the other bond.

In applying the above potential function to ketene, it is clear that some assumption must be made about the magnitude of the interaction constant k , since the two observed frequencies (1124 cm^{-1} , 2155 cm^{-1}) must be used to determine the principal constants. Furthermore, the principal constants obtained depend strongly on the choice of k . Table V shows this dependence, with k assumed to have the same value as in allene, as in carbon dioxide, and as an average of these. The C=O stretching constant can be made to vary from a value essentially the same as that of formaldehyde to a value greater than that of CO_2 . In the absence of any *a priori* choice for k , about all that can be said is that it is probably stronger than the bond of formaldehyde. The C=C bond turns out to be equal to or more probably weaker than the bond in allene.

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Note Added in Proof: A paper on this same subject by Halverson and Williams¹⁸ appeared after submission of this manuscript. Because of the increased resolution afforded by a lithium fluoride prism, these authors obtained results which necessitate modification of two of the assignments proposed above. However, the assignment of one of the fundamentals by Halverson and Williams in a different manner from that proposed above is felt by the present authors to be questionable, and is discussed below.

The two assignments of our Table III which must clearly be modified are: (1) the B_1 CH stretching frequency must be placed at 3162 cm^{-1} and the A_1 at 3066 cm^{-1} , as assigned

by Halverson and Williams (our resolution was insufficient to disclose the weak perpendicular band at 3162 cm^{-1}); (2) the band at 1967 cm^{-1} cannot be attributed to the combination $1391 (A_1) + 599 (B_1 \text{ or } B_2)$, since Halverson and Williams show this band to be parallel (A_1).

The assignment which remains in question is that of one of the CH_2 wagging vibrations. In the region where the two CH_2 wagging frequencies are to be expected, there occur two noticeable bands (731 and $\sim 925\text{ cm}^{-1}$), the spectrum obtained by ourselves agreeing with that of Halverson and Williams throughout this region. There is agreement that one of these fundamentals is at $\sim 925\text{ cm}^{-1}$ Halverson and Williams explained the 731 cm^{-1} band as due to an impurity, on the basis of the persistence of a band at this position when the ketene was allowed to polymerize on long standing; and placed the other fundamental at 1011 cm^{-1} , principally on the consideration that a band near 1000 cm^{-1} is necessary to account for 1967 cm^{-1} as an overtone of A_1 symmetry. There are, however, three objections to be raised to this assignment. Firstly, the spectrum itself shows no indications of a distinct band near 1011 cm^{-1} , the peaks in the region being ascribable to the fine structure of the $\sim 925\text{ cm}^{-1}$ band. This in itself is not a strong point, since one of the allowed ethylene bands is extremely weak and difficult to observe. Secondly, there exists a Raman line at 715 cm^{-1} which can be correlated with the infra-red 731 cm^{-1} band as a fundamental, but is not explained at all on Halverson and Williams' assignment. Thirdly, the present authors are of the opinion that the 731 cm^{-1} infra-red band is not due to impurity, since particular efforts, which were adequately but not wholly successful, were made to avoid polymers or other impurities. The most likely polymeric impurity, diketene, was either absent or present in only very small amounts as attested by the weakness of bands at positions where diketene has extremely strong bands. Further, the intensity of the 731 cm^{-1} band relative to other ketene bands was constant within our limits of error in the various spectra we obtained, although we never allowed a sample to remain more than about an hour under observation. The finding by Halverson and Williams of a

¹⁸ F. Halverson and V. Z. Williams, J. Chem. Phys. **15**, 552 (1947).

band at this position in a sample of polymerized ketene may easily be a case of coincidence of bands. In view of these considerations, the authors are inclined to assign ~ 925 and 731 cm^{-1} as the two CH_2 wagging fundamentals, as was done in the present paper, and to seek some other explanation of the 1967 cm^{-1} band.

As Halverson and Williams have implied, it is not possible to explain the 1967 cm^{-1} band as an overtone, combination, or difference band (other than in the manner criticized above). Also it does not seem possible to explain it as the $\text{C}=\text{C}=\text{O}$ stretching vibration (fundamental: 2155 cm^{-1}) shifted by interaction with an excited low frequency, i.e. a band of the type $(\nu_{\text{C}=\text{C}=\text{O}} + \nu_{\text{low}}) - \nu_{\text{low}}$. Judging from CO_2 and N_2O ,

the shift to be expected for this reason is only a few cm^{-1} . The most plausible, but not wholly satisfactory, explanation of the 1967 cm^{-1} band is that it is the isotopic analog for the $\text{C}^{12}=\text{C}^{13}=\text{O}^{16}$ molecule of the 2155 cm^{-1} band. The intensity ratio is close to 100:1, exactly as is necessary. However, force-constant calculations based on either the simplified linear-triatomic molecule approximation used in this paper, or on the more extended treatment given by Halverson and Williams, predict an isotopic shift in the neighborhood of 50–100 cm^{-1} instead of the required 200 cm^{-1} shift.

It is clear that further work toward resolving the bands from 700 to 1050 cm^{-1} is needed before an unequivocal assignment can be made.

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Hydrodynamic Properties of Sea Water at the Front of a Shock Wave*

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The Rankine-Hugoniot relations have been applied to appropriate equation-of-state data in order to calculate the propagation velocity, particle velocity, enthalpy increment, Riemann function, etc. at shock fronts of various amplitudes in sea water. One set of tables provides values over a wide pressure range (up to about 80 kilobars) and is principally intended for use in conjunction with theories of propagation of shock waves originated by underwater explosions. A second set of tables contains values which are closely spaced up to pressures of 14 kilobars. These are calculated with somewhat greater precision and are intended for use in connection with experimental measurements of particle and propagation velocities, etc.

I. INTRODUCTION

IT has long been recognized that the velocity of propagation of sound waves of finite amplitude in a fluid medium is a function of the pressure in the wave. Lamb¹ ascribes the early

development of the theory to independent investigations of Earnshaw and Riemann. Qualitatively this work indicated that, since the higher pressure portions of a wave travel with greater velocity, an arbitrarily-shaped pressure pulse of finite amplitude must, during propagation, alter its shape in such a manner as to build up into a shock front. By applying the laws of conservation of mass, energy, and momentum to the transfer of matter across the shock front, Rankine and Hugoniot obtained a set of three relations among the five variables: pressure, density, particle velocity (u), shock front

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¹ H. Lamb, *Hydrodynamics* (Cambridge University Press, London, 1932) 6th Ed., p. 481.