

288. *The Infra-red Spectrum of Keten.*

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The infra-red absorption spectrum of keten vapour has been determined between $2\ \mu$ and $20\ \mu$. Many of the bands show a characteristic contour, and some show partially resolved rotational fine structures, which have been correlated with the molecular dimensions. The results have been used to assign magnitudes to the fundamental vibration frequencies, eight of which are satisfactorily identified, and a probable value is given for the ninth. The values of some thermodynamic properties have been calculated.

THE infra-red absorption spectrum of keten has been measured by Gershinowitz and Wilson (*J. Chem. Physics*, 1937, **5**, 500), although few details were reported by them. The Raman spectrum of the liquid was measured by Kopper (*Z. physikal. Chem.*, 1936, *B*, **34**, 396), but the two sets of data leave much doubt about the assignment of vibration frequencies to the normal modes. With this light molecule, the use of better resolving power than that employed by Gershinowitz and Wilson should reveal rotational contour of the vibrational bands which may be helpful in making the vibrational assignments. We therefore recently re-measured the infra-red spectrum of keten vapour, using single- and double-beam recording prism spectrometers of fairly high resolving power. The results are described below, and discussed in relation to the assignment of vibration frequencies, and to the molecular structure.

Since this work was completed, we learnt in a discussion with Dr. F. Halverson and Dr. V. Z. Williams, at the American Cyanamid Company, Stamford, Conn., that they too had re-measured the spectrum. Our results agree in most essentials with theirs, although, using a prism of lithium fluoride, they were able to obtain rather higher resolution near $3\ \mu$. We may differ, however, in some points of detail in the interpretations. We are much indebted to Drs. Halverson and Williams for allowing us to see their results and for discussions.

EXPERIMENTAL.

Keten was prepared by the pyrolysis of acetone vapour on a heated metal filament in the standard manner. The effluent vapour was passed through two vertical water-cooled condensers, followed by three bottles surrounded by a mixture of ice and salt, then through a trap at -80° , and finally condensed in a liquid-air trap. The product was repeatedly fractionated to remove residual ethylene and traces of acetone, the disappearance of these substances being followed by means of their intense infra-red bands. Reference to the spectrum of diketene previously measured (Whiffen and Thompson, *J.*, 1946, 1005) showed that this possible impurity was absent.

Three spectrometers were used, namely, a single-beam recording instrument with prisms of rock-salt and potassium bromide for the region $6\text{--}20\ \mu$ (Whiffen and Thompson, *J.*, 1945, 268), a double-beam recorder with prism of calcium fluoride for the range $5\text{--}8\ \mu$ (Thompson, Whiffen, Richards, and Temple, in the press), and a Hilger D88 spectrometer with sylvine prism for the region $14\text{--}20\ \mu$. Pressures from 5 to 200 mm. were used in a cell 21 cm. in length. The effective slit widths are shown on the diagram.

Results.—The absorption spectrum is shown in the figure, from which it is seen that the rotational fine structure or contour of the bands between 500 and $1100\ \text{cm.}^{-1}$ is highly complex. The positions of the sub-maxima (cm.^{-1}) between 500 and $800\ \text{cm.}^{-1}$, measured with prisms of potassium chloride or bromide, are given in Table I. The intensities pass through a maximum near $550\ \text{cm.}^{-1}$. By means of a rock-salt prism the region $700\text{--}800\ \text{cm.}^{-1}$ is resolved further.

The sub-maxima in the very complex region $800\text{--}1000\ \text{cm.}^{-1}$ are also given in Table I. The intensities in this region pass through a maximum near $910\ \text{cm.}^{-1}$. The two well-marked maxima at 989 and $1002\ \text{cm.}^{-1}$ appear not to belong to the group centred at about $910\ \text{cm.}^{-1}$.

The remaining bands are listed in Table II. Several are clearly of the type with three sub-maxima, although in some cases the weak central peak is not quite resolved.

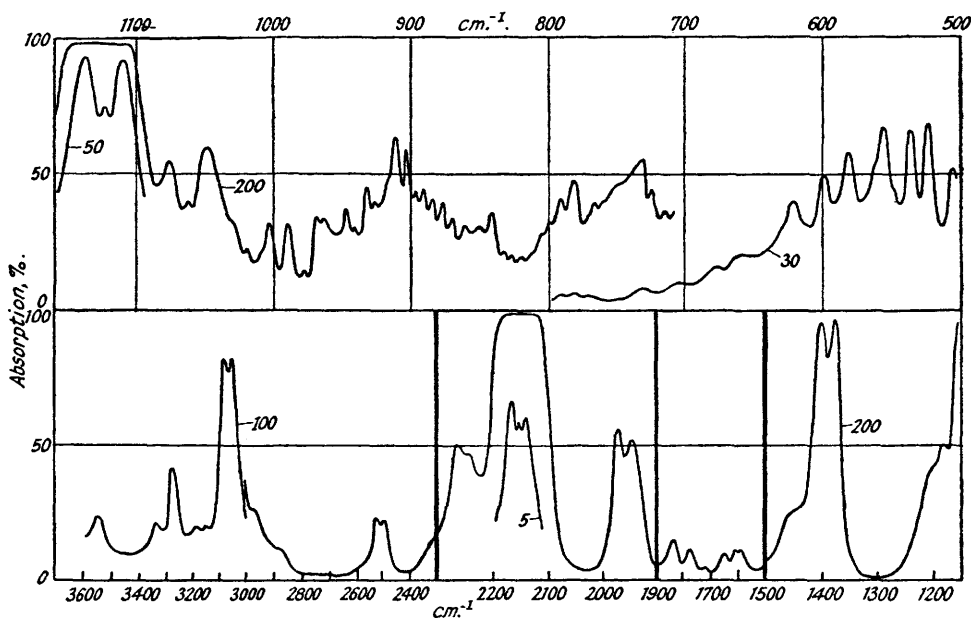
TABLE I.

Region 550 cm^{-1} .				Region 910 cm^{-1} .					
505	563	630	734	818	850	889	922	952	996
523	581	662	784	827	858	896	927	963	1002
536	595	678	790	831	869	902	932	968	1007
556	621	708		835	877	910	940	977	1027
				840	884	916	947	989	

TABLE II.

Position of bands (cm^{-1}).

1047		1456 ?	2140	2965 v. weak
1062	medium	1590	2150	3045 } strong
1072		1604	2160	3070 } strong
1109		1654 v. weak	2240	3130 } v. weak
1122	v. strong	1728 v. weak	2265	3180 } v. weak
1135		1775 v. weak	2495	3264 weak
1190 ?	v. weak	1833 v. weak	2520	3328 v. weak
1375		1944	2873 ?	3532 v. weak
1400	strong	1968		



Discussion.—Keten falls in the symmetry point group C_{2v} . There will be nine fundamentals with the symmetry shown in Table III, C_z being the axis lying along the $\text{C}=\text{C}=\text{O}$ bonds, and σ_x the plane containing all the nuclei.

TABLE III.

Class.	Symmetry w.r.t.			Moment change.	Number.	Form of vibration.
	C_z .	σ_x .	σ_y .			
A_1	s	s	s	M_z	4	ν_1 CH_2 stretching ν_2 CCO stretching ν_3 CCO stretching ν_4 CH_2 deformation
A_2	s	as	as	i	0	
B_1	as	as	s	M_x	2	ν_5 CH_2 bending ν_6 CCO deformation
B_2	as	s	as	M_y	3	ν_7 CH_2 stretching ν_8 CH_2 rocking ν_9 CCO deformation

Beach and Stevenson (*J. Chem. Physics*, 1938, **6**, 75) have given the following dimensions for the molecule: $r_{\text{CO}} = 1.17 \text{ \AA}$, $r_{\text{CC}} = 1.35 \text{ \AA}$. Assuming the very probable values $r_{\text{OH}} = 1.08 \text{ \AA}$,

$\widehat{\text{HCH}} = 120^\circ$, the moments of inertia are 2.9×10^{-40} , 83×10^{-40} , and 86×10^{-40} g.-cm.². The molecule will therefore approximate closely to a symmetrical rotator with moments of inertia 2.9 and 85×10^{-40} . The bands will be of two kinds. The "parallel" type, in which the direction of change of electric moment is parallel to the axis of symmetry C_2 , will have a contour with three sub-maxima, the outer spacing being calculated by the formula of Gerhard and Dennison to be about 24 cm.^{-1} . The central sub-maximum might, if it is weak, be not quite resolved. The individual lines in the P and Q branches will be only about 0.7 cm.^{-1} apart and could therefore not be resolved. Parallel type bands will arise from vibrations in class A_1 . "Perpendicular" type bands, from vibrations in classes B_1 and B_2 , will be expected to consist of a succession of marked Q branches with spacing $\frac{h}{8\pi^2} \left\{ \frac{1}{I_o} - \frac{1}{I_A} \right\}$, *i.e.*, about 19 cm.^{-1} . On the other hand, we may expect to find complications in the perpendicular bands of a molecule like this, arising from interactions between vibration and rotation. This may lead to abnormal and irregular spacings of the Q branches. In the case of allene, a very closely related molecule, such a complication has been discovered and discussed previously (Thompson and Harris, *Trans. Faraday Soc.*, 1944, **40**, 295).

The Raman intervals found by Kopper are listed, together with the infra-red bands given by Gershinowitz and Wilson, in Table IV. Inspection of the band contours found shows that there

TABLE IV.

Raman intervals (Kopper).		Infra-red bands (Gershinowitz and Wilson).	
501 (1 <i>b</i>)	1344 (2)	890 s	1935 s
599 (1/2 <i>b</i>)	1386 (1 <i>b</i>)	1110 s	2160 s
715 (1/2 <i>b</i>)	1895 (1/2)	1185 w	2915 w
801 (1/2 <i>b</i>)	2049 (1/2 <i>b</i>)	1325 w	3058 s
998 (1)	2952 (5)	1350	3165 w
1130 (6 <i>b</i>)	3015 (4 <i>b</i>)	1400 s	
1198 (1)			

is general agreement with those calculated, but the perpendicular bands are complicated severely by interactions. In assigning magnitudes to the fundamentals we may expect a parallelism with allene, $\text{CH}_2=\text{C}=\text{CH}_2$ (Thompson and Harris, *loc. cit.*), and with nitrous oxide, $\text{N}=\text{N}=\text{O}$ (cf. Herzberg, "Infra-red and Raman Spectra", 1945, p. 278). In the former case the stretching vibration frequencies of the CCC skeleton are 1069 cm.^{-1} and 1965 cm.^{-1} ; and in nitrous oxide the corresponding values are 1285 cm.^{-1} and 2223 cm.^{-1} . The bending vibration frequencies of the skeletons are respectively 845 and 589 cm.^{-1} .

With keten we can at once fix the four symmetrical vibrations of class A_1 : ν_2 and ν_3 will be 1122 and 2150 cm.^{-1} , both these bands having parallel-type contour, and the values being close to those in allene; ν_4 the methylene group deformation, will give rise to the parallel band at 1390 cm.^{-1} , and ν_1 the symmetrical stretching vibration of the CH_2 group will be connected with the strong parallel-type band at 3060 cm.^{-1} . These values agree well with the stronger bands given by Gershinowitz and Wilson, but it may be noticed that the Raman intervals found for the liquid at 2049 and 3015 cm.^{-1} , which presumably correspond to ν_3 and ν_1 , are lower than the values just given.

There remain fine fundamentals each of which should give rise to a perpendicular-type band. It is certain that one of these must lie close to 540 cm.^{-1} , the middle of the group of Q branches, and this is assigned to ν_9 . These Q branches are not regularly spaced, although the actual spacings range around the expected value. It seems certain, too, that the complex perpendicular type band centred near 910 cm.^{-1} is due to a fundamental. Neither 540 nor 910 cm.^{-1} could be due to an overtone or combination, but there are no corresponding Raman intervals. It is possible that the Raman interval of 501 cm.^{-1} for the liquid corresponds to the infra-red band of the vapour at 540 cm.^{-1} .

It was remarked above that the Q branches near 995 cm.^{-1} appear not to be connected with the band at 910 cm.^{-1} . If this is so, there must be a fundamental of this value, since no plausible overtone or combination could have a perpendicular-type structure. Also, there is a definite Raman interval of 998 cm.^{-1} . The two values 910 and 995 are therefore assigned to the rocking and bending of methylene groups, ν_8 and ν_5 .

There now remain ν_6 and ν_7 . The latter is the unsymmetrical stretching mode of the CH_2 group, which would be expected to have a value rather higher than that found for ν_1 (3060 cm.^{-1}). There is no Raman interval of the appropriate value, but Gershinowitz and Wilson found a weak

band at 3165 cm.^{-1} , and we have found two very weak bands at 3130 and 3180 cm.^{-1} . The band due to ν_7 should have perpendicular-type structure. It seems probable, and the work of Halverson and Williams confirms, that there is in fact a band at about 3155 cm.^{-1} , and the two sub-maxima at 3130 and 3180 are really unresolved Q branches on either side of the centre. We should not quite resolve these with the instruments used.

As regards ν_6 , the deformation of the CCO skeleton, we should expect a value $500\text{--}700\text{ cm.}^{-1}$. Unfortunately the Raman spectrum gives us no guidance, and although the complexity of the infra-red spectrum in this range may arise, in part, from overlapping of bands due to two vibrations, it does not seem possible to fix the missing values in this way. However, it is seen that a number of the unexplained bands throughout the entire spectrum are well explained as combinations with a fundamental of about 600 cm.^{-1} . There is a Raman interval of about this value, although in view of the other discordance between Raman and infra-red data it might be presumptuous to attach much significance to this. We shall, however, assume that $\nu_6 = 600\text{ cm.}^{-1}$. The combination and overtone bands are then explained as shown in Table V.

TABLE V.

Band (cm.^{-1}).	Interpretation.	Band (cm.^{-1}).	Interpretation.
1062	2×540	1956	$(910 + 2 \times 540) (2 \times 995) ?$
1190 ?	2×600	2252	2×1122
1456 ?	$540 + 910$	2510	$1122 + 1390$
1597	$995 + 600$	2873 ?	$(2 \times 995 + 910) (2 \times 1122 + 600)$
1654	$1122 + 540$	2965	?
1728	$1122 + 600$	3264	$2150 + 1122$
1775	?	3328	$(2150 + 2 \times 600)$
1833	2×910	3532	$2150 + 1390$

Thermodynamic Properties.—Values of some thermodynamic functions have been calculated at a series of temperatures. Although the small uncertainty in both the molecular dimensions and the ninth frequency may lead a slight error, the specific heat will probably be correct to within 0.1 cal., and the values should be useful for most purposes. Values of molar specific heat and heat content function are given in Table VI, and those of the free energy function and entropy in Table VII.

TABLE VI.

Temp., °K.	Spec. heat (cals.),		$(H^\circ - E_0^\circ)/T$, cals.,		$(H^\circ - E_0^\circ)$, kcal.
	$C_{\text{vib.}}$	C_{total}	vib.	total.	
250	2.44	10.39	0.64	8.59	2.148
300	3.51	11.45	1.03	8.98	2.694
400	5.60	13.54	1.90	9.85	3.940
500	7.28	15.22	2.78	10.73	5.365
600	8.71	16.66	3.62	11.57	6.942
700	9.60	17.54	4.40	12.35	8.645
800	10.55	18.50	5.10	13.05	10.44
900	11.39	19.34	5.75	13.70	12.33

TABLE VII.

Temp., °K.	$-(F^\circ - E_0^\circ)/T$, cals.,			S° , cals.,		
	tr. rot.	vib.	total.	tr. rot.	vib.	total.
250	46.43	0.185	46.61	54.38	0.82	55.20
300	47.85	0.328	48.18	55.80	1.36	57.16
400	50.15	0.744	50.89	58.10	2.65	60.75
500	51.93	1.26	53.19	59.88	4.04	63.92
600	53.39	1.842	55.23	61.32	5.46	66.78
700	54.60	2.465	57.06	62.55	6.87	69.42
800	55.66	3.096	58.76	63.61	8.19	71.80
900	56.60	3.737	60.34	64.55	9.49	74.04

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