

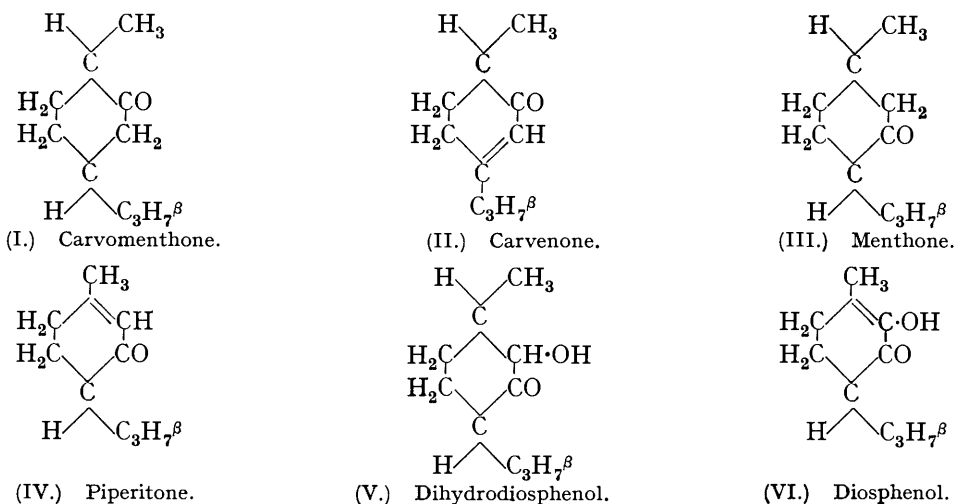
**318.** *The Rotatory Dispersion of Organic Compounds. Part XXVIII.  
The Ultra-violet Absorption of Ketones.*

By T. M. LOWRY and R. E. LISHMUND.

THE mathematical form of the absorption band of an optically active ketone is important because it may be related in a very simple way to the form of the curve of circular dichroism, which in turn determines the partial rotation contributed by the ketonic group. The

present paper therefore contains an account of experiments made in order to determine how far the form of the absorption band of a ketone can be expressed by the various equations that have been proposed for this purpose. Confirmation has thus been obtained of the curious observation (Lowry and Hudson, *Phil. Trans.*, 1933, A, 232, 117; Hudson, Wolfrom, and Lowry, J., 1933, 1179) that the absorption curves of organic compounds are often steeper on the side of longer wave-lengths, but not on the side of shorter wave-lengths, and that as a limiting case the curves are often symmetrical on a scale of wave-lengths, but never on a scale of frequencies. Observations are also recorded on the strength,  $f$ , of the absorption bands of the different ketones, on the influence of chlorine and hydroxyl radicals on the position and strength of the ketonic band, and on the effects produced by cooling to the temperature of liquid air.

*Form of the Absorption Bands.*—In order to provide data for mathematical analysis, measurements were made (with a Hilger Spekker-photometer) of the ultra-violet absorption bands of a number of ketones, many of which were provided by the Chemical Department of the University of St. Andrews. The formulæ of the principal compounds are set out below :



Absorption bands which were approximately symmetrical on a scale of wave-lengths were given by (i) the simple alicyclic ketones, namely, *cyclohexanone*, *menthone*, and *carvomenthone*; (ii) ketones possessing one alcoholic hydroxyl group, namely, *4-hydroxypentan-2-one* and *dihydrodiosphenol*; (iii) the enolic diketones, *acetylacetone* and *diosphenol*. On the other hand, bands which were steeper on the side of longer wave-lengths were given by (i) the simple aliphatic ketones and their chlorine derivatives; (ii) *camphor*; (iii) *piperitone*, and probably the isomeric *carvenone*.

The former were represented by the equation (ii) below of Lowry and Hudson (*loc. cit.*), and the latter by Hudson's general equation (iii) (Thesis, Cambridge, 1933, 162); but, since there is no theoretical reason for their exclusion, fractional values were used for the constant  $n$  in the latter equation.

There seems to be no fixed rule connecting the lack of symmetry with molecular structure, but it is noticeable that the introduction of an alcoholic hydroxyl group renders the band more symmetrical. The constants of the symmetrical and the unsymmetrical bands are summarised in Tables I and II respectively. Agreement between experimental and theoretical curves is almost perfect for *cyclohexanone* in *cyclohexane*; this band is remarkable for its large half-width, and the  $f$ -value is correspondingly high, as compared with other bands of similar intensity. In several cases, however, the experimental curve is expanded at the base and pinched at the top as compared with the calculated curve. This effect is specially prominent in *4-hydroxypentan-2-one*. Since it cannot be attributed to experimental error, we are obliged to conclude, either that equation (i) is only an approximation

to the true form of the symmetrical curves, or that these absorption bands are composite, with a narrow and a wide component of similar wave-length superposed on each other. A similar expansion and pinching was observed at the base and top of the unsymmetrical bands, which otherwise showed an equally close agreement between the experimental and the calculated curves.

*Strength of the Absorption Bands.*—Born ("Optik," 1933, p. 487) has shown that the strength  $f$  of an absorption band is given by :

$$f = \frac{n' mc}{\pi e^2} \cdot \frac{1}{N} \cdot \int_{-\infty}^{+\infty} \mu d\nu \quad \dots \quad (i)$$

where  $m$  and  $e$  are the mass and charge of the electron,  $c$  the velocity of light, and  $N$  the number of molecules in unit volume,  $\mu$  is the absorption coefficient given by  $I/I_0 = e^{-\mu l}$  at frequency  $\nu$ , and  $n'$  is the index of refraction of the solution at the frequency of maximum absorption. In order to calculate the strength of an absorption band, therefore, it is necessary to express the absorption curve by an equation which can be integrated. The equation (ii) of Lowry and Hudson,

$$\epsilon = \epsilon_{\max.} e^{-\left(\frac{\lambda - \lambda_0}{\theta}\right)^2} \quad \dots \quad (ii)$$

where  $\theta$  is obtained from the half-width  $\lambda'$  of the band by the relation  $\lambda' = 1.6651\theta$ , and Hudson's general equation (iii),

$$\epsilon = \epsilon_{\max.} e^{-\left(\frac{\lambda_0}{\lambda}\right)^n \left(\frac{\lambda - \lambda_0}{\theta}\right)^2} \quad \dots \quad (iii)$$

where  $n$  is an integer, 1, 2, 3 . . . . , lead to the equations (iv) for the strength of a symmetrical band, and (v) for an unsymmetrical band to about 2% as follows :

$$f = \frac{0.4609 \lambda' \epsilon_{\max.} n'}{\lambda_0^2} \left[ 1 + 0.54 \left(\frac{\lambda'}{\lambda_0}\right)^2 \right] \quad \dots \quad (iv)$$

$$f = \frac{0.4609 \lambda' \epsilon_{\max.} n'}{\lambda_0^2} \left[ 1 + \frac{\lambda'^2}{\lambda_0^2} \{0.54 + 0.54n + 0.34n^2 - 0.135n(n-1)\} \right] \quad (v)$$

Values deduced from these equations are set out in Tables I and II.

TABLE I.  
*Symmetrical Bands.*

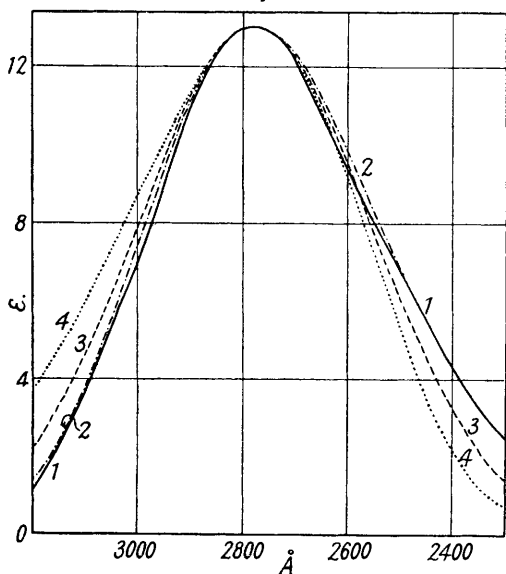
Substance.	Solvent.	$\lambda_{\max.}$ (Å.).	$\epsilon_{\max.}$	$\lambda'$ (Å.).	$f$ .
<i>cyclo</i> Hexanone	<i>cyclo</i> Hexane	2833	16.5	633	$9.6 \times 10^{-4}$
Menthone	"	2920	20.3	448	$7.2 \times 10^{-4}$
"	Alcohol	2867	24.6	433	$8.3 \times 10^{-4}$
Carvomenthone	<i>cyclo</i> Hexane	2886	19.5	454	$7.1 \times 10^{-4}$
"	Alcohol	2841	22.3	351	$6.2 \times 10^{-4}$
4-Hydroxypentan-2-one	"	2706	171	399	$6.0 \times 10^{-3}$
Dihydrodiolsphenol	"	2745	128	476	$5.2 \times 10^{-3}$
Acetaldehyde	<i>cyclo</i> Hexane	2903	16.5	503	$6.6 \times 10^{-4}$
Acetylacetone	Alcohol	2730	9,450	374	0.302
Diosphenol	"	2725	11,150	376	0.367

TABLE II.  
*Unsymmetrical Bands.*

Substance.	Solvent.	$\lambda_{\max.}$ (Å.).	$\epsilon_{\max.}$	$\lambda'$ (Å.).	$n$ .	$f$ .
Acetone	<i>cyclo</i> Hexane	2775	13.0	527	1.72	$6.5 \times 10^{-4}$
Methyl ethyl ketone	"	2785	15.4	475	1.53	$6.7 \times 10^{-4}$
"	Alcohol	2720	17.9	454	1.64	$7.4 \times 10^{-4}$
Diethyl ketone	<i>cyclo</i> Hexane	2799	18.3	488	2.64	$8.6 \times 10^{-4}$
Monochloroacetone	"	2919	31.0	561	3.40	$1.7 \times 10^{-3}$
<i>sym.</i> -Dichloroacetone	"	2994	40.6	491	1.76	$1.6 \times 10^{-3}$
Camphor	Alcohol	2883	29.9	416	3.57	$1.1 \times 10^{-3}$
Piperitone	"	3191	48.8	551	3.00	$1.9 \times 10^{-3}$
Carvenone	"	3119	49.0	575	—	$2.1 \times 10^{-3}$

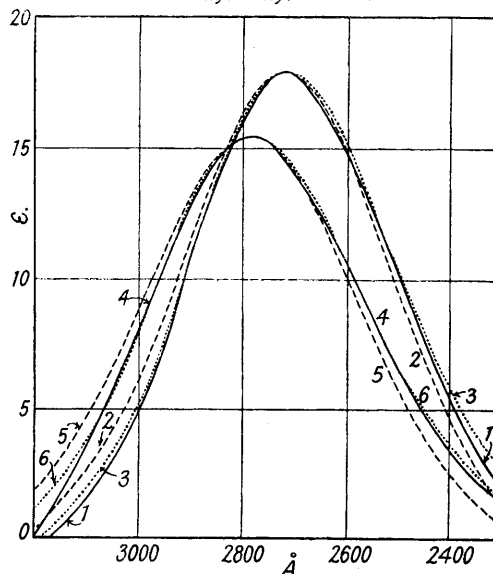
*Influence of Chlorine and Hydroxyl Radicals.*—It is interesting to compare the effects produced on the carbonyl band by the introduction into the molecule of chlorine atoms and

FIG. 1.  
Acetone in cycloHexane.



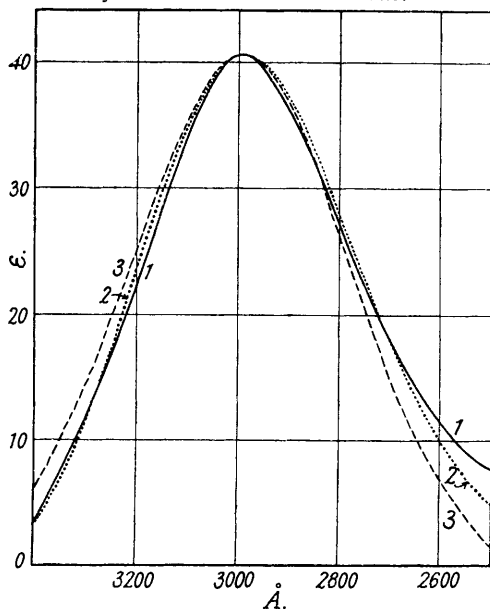
1. Exp. 2. Modified L.H.  
3. L.H. 4. Kuhn.

FIG. 2.  
Methyl Ethyl Ketone.



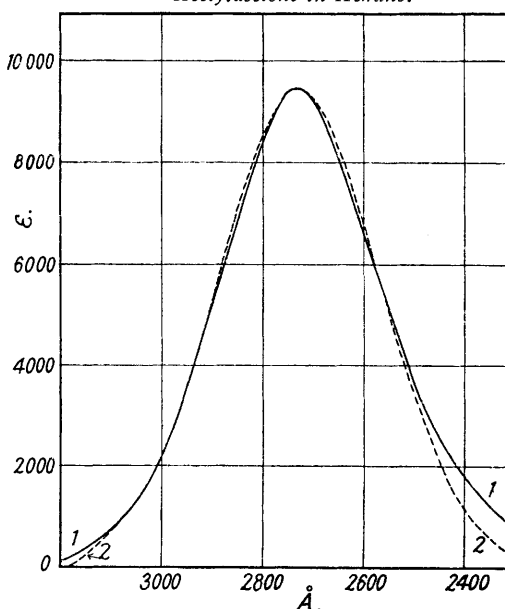
1. Abs. in alcohol. 4. Abs. in cyclohexane.  
2. L.H. 5. L.H.  
3. Modified L.H. 6. Modified L.H.

FIG. 3.  
sym.-Dichloroacetone in Hexane.



1. Exp. 2. Modified L.H. 3. L.H.

FIG. 4.  
Acetylacetone in Hexane.



1. Exp. 2. L.H.

hydroxyl groups. Herold (*Z. physikal. Chem.*, 1932, B, 18, 265) found a displacement of the band towards the visible region in both cases, and assumed that this was due to the in-

fluence of the dipole moment between the substituent and the carbon atom to which it was attached, rendering the carbon atom more positive. His data for the chloroacetones are confirmed by the measurements recorded in Table II; but opposite effects are shown by the hydroxy-ketones in Table III. Thus, on comparing the carbonyl bands of 4-hydroxypentan-2-one,  $\text{CH}_3\cdot\text{CO}\cdot\text{CH}_2\cdot\text{CH}(\text{OH})\cdot\text{CH}_3$ , and dihydrodiosphenol with those of methyl propyl ketone and menthone respectively, it is evident that the displacement caused by the introduction of the hydroxyl group is *towards the extreme ultra-violet region*. Measurements were also made of the absorption of deoxybenzoin,  $\text{C}_6\text{H}_5\cdot\text{CH}_2\cdot\text{CO}\cdot\text{C}_6\text{H}_5$ , and benzoin,  $\text{C}_6\text{H}_5\cdot\text{CH}(\text{OH})\cdot\text{CO}\cdot\text{C}_6\text{H}_5$ . The long wave-length band may be ascribed to the carbonyl group and the displacement from 3256 to 3160 Å. is again towards the extreme ultra-violet. A displacement in the same direction has also been recorded by Lowry and Baldwin (this vol. p. 704), who have recently shown that the absorption band of acetoin in cyclohexane has a maximum at 2726 Å., whilst the corresponding maximum in methyl ethyl ketone is at 2785 Å., in direct opposition to the effect recorded by Herold in hydroxyacetone.

The introduction of a chlorine atom or hydroxyl group also increases the intensity of maximum absorption. In dihydrodiosphenol the exaltation factor is *five* and in 4-hydroxypentan-2-one it is *eight*.

TABLE III.  
*Absorption of Hydroxy-ketones.*

Substance.	Solvent.	$\epsilon_{\text{max.}}$	$\lambda_{\text{max.}}$	$\delta\lambda_{\text{max.}}$ (Å.).
{ Methyl ethyl ketone	<i>cyclo</i> Hexane	15.42	2785	} — 59
{ Acetoin *	"	13.67	2726	
{ Methyl propyl ketone †	Alcohol	21.2	2770	} — 44
{ 4-Hydroxypentan-2-one	"	171	2706	
{ Deoxybenzoin	<i>cyclo</i> Hexane	129	3256	} — 95
{ Benzoin	"	250	3160	
{ Menthone	Alcohol	24.6	2867	} — 122
{ Dihydrodiosphenol	"	128	2745	

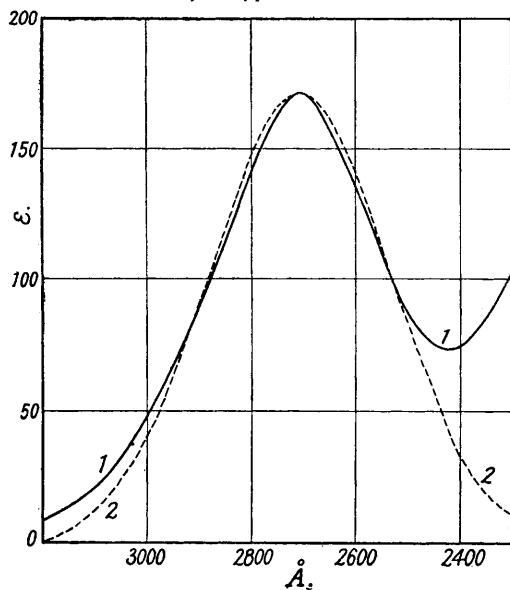
\* Lowry and Baldwin, this vol., p. 704.

† Rice, *J. Amer. Chem. Soc.*, 1920, **42**, 727.

*Absorption at the Temperature of Liquid Air.*—Pringsheim (*Physikal. Z.*, 1926, **27**, 856) and Croup (*Physical Rev.*, 1934, **40**, 345) have shown that at low temperatures the absorption bands of benzene and other aromatic compounds are sharpened, with the development of a vibrational fine structure, as given by the vapour at the ordinary temperature. Similarly, Arnold and Kistiakowsky (*J. Amer. Chem. Soc.*, 1932, **54**, 1713) have observed that at 80° K the carbonyl band of acetaldehyde splits up into seven components. At such low temperatures the motion of the molecules is diminished and the blurring of the vibrational bands by the Stark effect of their electric fields is minimised. Bowden and Morris, however (*Proc. Roy. Soc.*, 1934, *B*, **115**, 274), have pointed out that, when the upper state of the electronic transition corresponds to dissociation or "predissociation," no vibrational fine structure can appear, however low the temperature.

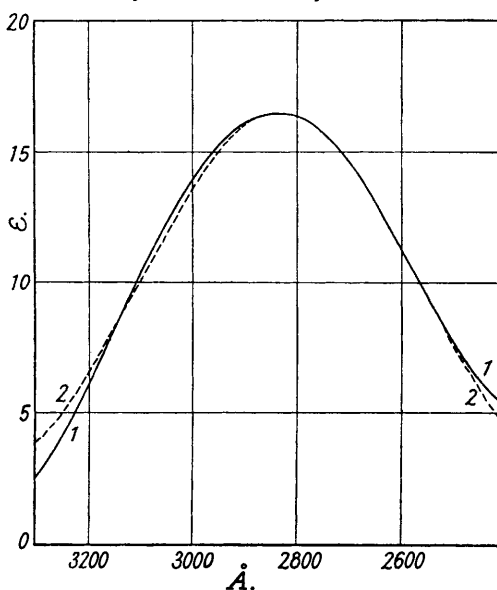
During the present research, quantitative measurements of absorption at the temperature of liquid air were made, apparently for the first time, in the case of a few of the above ketones, Henri's method being used ("Etude de Photochimie," 1919). Contrary to expectation, the increase in the intensity of maximum absorption at the temperature of liquid air was always small and in two cases a decrease was actually observed. On account of the experimental difficulties, however, the value of the intensity of absorption at  $-190^\circ$  can only be taken as approximate. No evidence of band-splitting was obtained. The most striking result is the displacement of the band-head by about 50 Å. towards the extreme ultra-violet region, whereas the suppression of the higher vibrational states at  $-190^\circ$  would be expected to produce a small displacement towards the visible region. The observed displacement in the opposite direction is probably an intensification of the solvent shift, which displaces the carbonyl band through about 60 Å. towards the extreme ultra-violet when the solvent is changed from *cyclohexane* to alcohol. This is regarded as a Stark effect, resulting from the interaction of the dipoles of solvent and solute; the further displacement at low temperatures is attributed to a diminution in the vibration of the molecules and consequent stabilisation of their electric fields.

FIG. 5.  
4-Hydroxypentan-2-one.



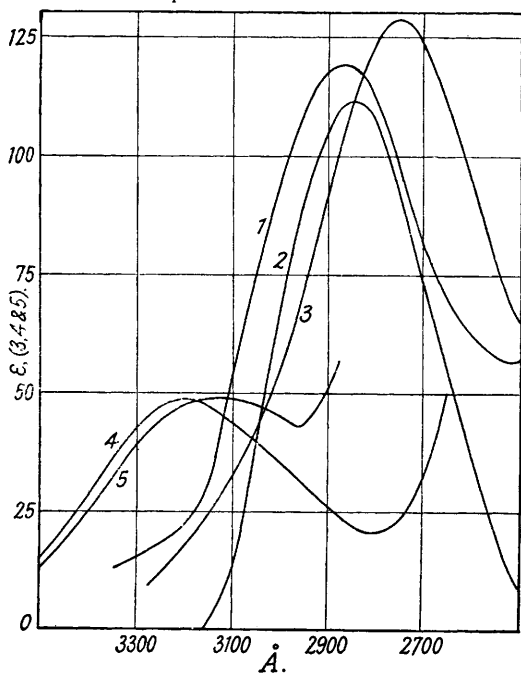
1. Exp. 2. L.H.

FIG. 6.  
cycloHexanone in cycloHexane.



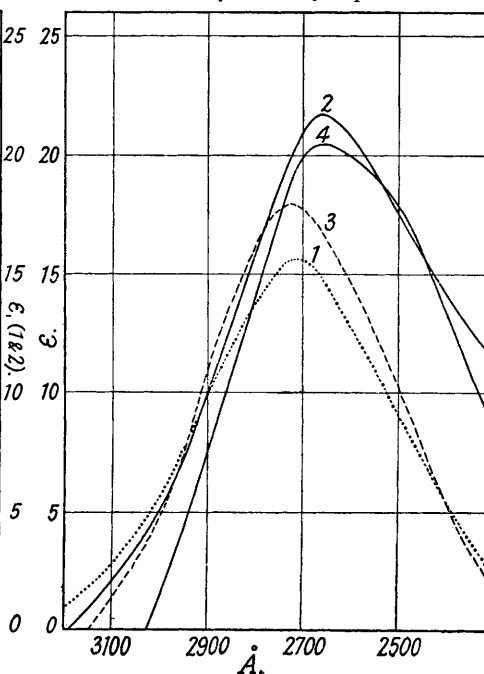
1. Exp. 2. L.H.

FIG. 7.  
Terpene Ketones in Alcohol.



1. Menthone. 2. Carvomenthone.  
3. Dihydroxyphenol. 4. Piperitone.  
5. Carvenone.

FIG. 8.  
Absorption of Acetone and Methyl Ethyl Ketone  
at the Temperature of Liquid Air.



1. Acetone (ord. temp.).  
2. Acetone (-190°).  
3. Methyl ethyl ketone (ord. temp.).  
4. Methyl ethyl ketone (-190°).

TABLE IV.

*Absorption of Ketones at the Temperature of Liquid Air.*

Substance.	Ordinary temperature.		Temperature of liquid air.	
	$\lambda_{\max.}$ (Å.).	$\epsilon_{\max.}$	$\lambda_{\max.}$ (Å.).	$\epsilon_{\max.}$
Acetone	2710	15.4	2655	21.7
Methyl ethyl ketone	2720	17.9	2660	20.4
Menthone	2867	24.6	2820	21.2
Carvomenthone	2841	22.3	2780	25.0
Camphor	2883	29.9	2850	27.0

## SUMMARY.

1. Quantitative measurements of the absorption bands of a series of ketones have shown that bands which are symmetrical on a scale of wave-lengths are given by three alicyclic ketones, two hydroxy-ketones, and two enolic diketones. Bands which are steeper on the side of longer wave-lengths are given by simple aliphatic ketones and their chloro-derivatives, as well as by camphor and piperitone. Bands symmetrical on a scale of frequencies, or steeper on the side of shorter wave-lengths, have not been observed.

2. The ketonic absorption band is displaced towards the visible region when hydrogen is replaced by chlorine, but towards the further ultra-violet when it is replaced by hydroxyl.

3. Cooling to the temperature of liquid air displaces the head of the band by about 50 Å. towards the extreme ultra-violet region, but has no great effect on the intensity of the band.

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