381. *The Carbonyl Doublet in the Infrared Spectrum of Cyclopentanone.*

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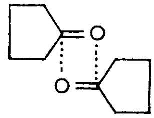
The doublet in the carbonyl region of the infrared spectrum of cyclopentanone has been investigated. Examination of cyclopentanone in a range of solvents and as a liquid film at various temperatures eliminated all but two explanations for the doublet. The absence of the lower-frequency component of the doublet in deuterated cyclopentanone showed that Fermi resonance coupling is responsible for the presence of this band in normal cyclopentanone.

AMONG saturated ketones cyclopentanone is unusual in that its Raman and infrared spectra exhibit doublets in the carbonyl stretching region.[1] Suètaka [2] has suggested that the lower-frequency band arises from a hydrogen-bonding effect, but Jones and Sandorfy [1] have pointed out that the doublet may arise from interaction of the normal C=O stretching vibration with an overtone of a lower-lying vibration. Although many explanations can be envisaged, it seems probable that the cyclopentanone doublet is caused by (i) association through hydrogen bonding of type $>CH_2 \cdots O{=}C$,[2] or (ii) association through dipole–dipole interaction leading to an equilibrium involving the associated form shown,[3] or (iii) the occurrence of a " hot transition " (in which a low frequency vibration is excited from both the ground and the upper states) in addition to the normal carbonyl band, or (iv) the operation of Fermi resonance interaction between the fundamental carbonyl band and a neighbouring overtone (or combination band) of the correct species arising from lower frequency absorption,[1] or (v) absorption from different configurational isomers of cyclopentanone. The results of the present study exclude four of these possibilities and provide confirmatory evidence for the remaining explanation. [To avoid repetition the letter " r " (see Tables 1 and 2) is used in the following discussion to denote the relative intensities of the components of the carbonyl-region doublet. The r value, which varies with different conditions of examination, is the intensity of the higher-frequency component (~1745 cm.$^{-1}$) divided by that of the lower-frequency band (~1730 cm.$^{-1}$).]



Examination of cyclopentanone as a liquid film and as a dilute solution in non-polar solvents such as carbon disulphide led to markedly different r values (Table 1). If the existence of configurational isomers were responsible for the second band in the carbonyl region, doublets showing corresponding intensity variations would be expected to appear elsewhere in the spectra: the observed absence of such bands between 4000 and 650 cm.$^{-1}$ excludes the configurational isomer theory [explanation (v)].

TABLE 1. *Values of r for cyclopentanone doublet at 25°.*

[r is the intensity of the higher-frequency component (~1745 cm.$^{-1}$) divided by that of the lower-frequency band (~1730 cm.$^{-1}$).]

Solvent	1% Soln.	10% Soln.	Solvent	1% Soln.	10% Soln.
Carbon disulphide ...	4·30	3·50	Dioxan	1·84	1·68
Benzene	2·66	2·52	(Liquid film)	1·33	
Furan	1·92	1·81	Acetonitrile	0·96	0·95
			Chloroform...........	0·78	0·81

From the data in Table 1 it appears that, while the r values vary widely in different solvents, the value for a particular solvent is not appreciably affected by dilution.

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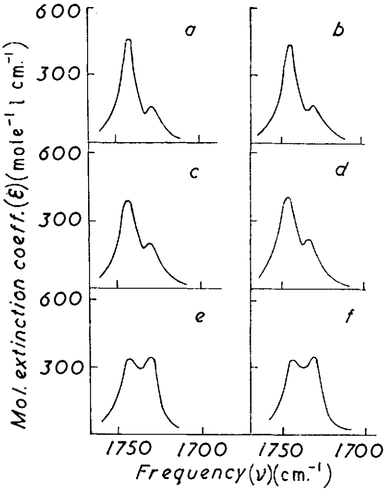
[1] Jones and Sandorfy, " Techniques of Organic Chemistry, Vol. IX, Chemical Applications of Spectroscopy," Interscience Publ. Corp., New York, 1956, p. 487.

[2] Suètaka, *Gazzetta*, 1952, **82**, 768.

[3] Bernstein and Schneider (*Trans. Faraday Soc.*, 1956, **52**, 13) have discussed a similar effect in connection with the infrared spectrum of solid formaldehyde.

Association of cyclopentanone molecules by hydrogen-bonding or dipole–dipole interaction [explanations (i) and (ii)] is therefore unlikely. Comparison of the r values for a liquid film and various solutions (Table 1 and Fig.) leads to a second reason for rejecting these explanations. To accommodate the variation in r with solvent polarity on either association theory it must be assumed that the 1730 cm.$^{-1}$ component arises from the associated form. From this it follows that the intensity of the lower-frequency component should decrease relative to that of the higher-frequency component as the temperature is raised. The temperature-dependence observed with liquid films was in fact small, and in the opposite direction (Table 2).



Carbonyl region for cyclopentanone solutions at 25°.

Benzene, (*a*) 1%, (*b*) 10%; *furan,* (*c*) 1%, (*d*) 10%; *acetonitrile,* (*e*) 1%, (*f*) 10%.

The remaining possibilities, the occurrence of a " hot transition " or Fermi resonance interaction, are not clearly distinguished by the results described so far. However, the very marked intensification of the lower-frequency component in chloroform and acetonitrile is unusual if this band arises from a hot transition. Further, the variation in the r values over a 75° range is much smaller than would be expected on this theory, whereas the r value of a doublet originating in Fermi resonance would normally show little or no temperature dependence. (In a hot transition r is proportional to $[\exp h\nu/kT - 1]$, where ν is the frequency of the band associated with the hot transition, h = Planck's constant, k = Boltzmann's constant, and T = absolute temperature.)

TABLE 2. *Values of r for liquid films of cyclopentanone.*

Temp.	25°	55°	80°	100°
r	1·33	1·33	1·30	1·22

TABLE 3. *Carbonyl region bands* (*cm.*$^{-1}$) *of cyclohexanone and cyclopentanone in different solvents.*

Solvent	Cyclohexanone	Cyclopentanone		Solvent	Cyclohexanone	Cyclopentanone	
Cyclohexane	1724	1750	1729	Benzene	—	1746	1731
Tetrachloroethylene	1720	1748	1730	Acetonitrile	1709	1745	1732
Toluene	1719	1747	1728	Nitromethane	1709	1745	1731
Carbon tetrachloride	1719	1747	1731	Methylene dichloride	1708	1744	1729
Carbon disulphide	1717	1747	1732	Chloroform	—	1743	1728
Dioxan	1716	1746	1732	Aniline	1702	1742	1725
(Liquid film)	1713	1746	1732	Bromoform	1701	1741	1725
Furan	—	1746	1731				

A crucial distinction between the two explanations was made by examining the spectrum of partially deuterated cyclopentanone. (This compound was prepared as described below and it seems probable that most of the hydrogen in the product was introduced during the oxidation of the hexanediol with aqueous chromic acid in acetone. The isotopic impurity of the cyclopentanone does not affect the following discussion.) The deuterated material in a variety of solvents showed only a single carbonyl band (1745 cm.$^{-1}$ for a solution in carbon tetrachloride). This result is to be expected from the Fermi resonance theory, since deuteration should move the interacting overtone or combination band from its original position (~1730 cm.$^{-1}$) to lower frequency, thereby eliminating the resonance effect. However, from the hot-transition theory an intensification of the lower-frequency band would have been predicted. (This follows from the relationship for r given previously, together with the reasonable assumption that the frequency of the hot transition would be lower in the heavier molecule.)

The conclusion that Fermi resonance is responsible for the cyclopentanone doublet is supported by the data in Table 3, which show that the frequency of the carbonyl stretching band of cyclopentanone (the higher-frequency component) is not influenced by solvent polarity to the usual extent. (With a normal ketone, such as cyclohexanone, increasing solvent polarity causes a greater shift in the carbonyl frequency.) The carbonyl-region doublets recently reported for ethylene carbonate[4] and certain cyclopentenones[5] have also been attributed to Fermi resonance interaction, and with ethylene carbonate the intensity and frequency changes observed with solvents of different polarity are similar to those found here for cyclopentanone.

The vibrational spectrum of cyclopentanone has not been sufficiently well analysed for the interacting absorption (~1730 cm.$^{-1}$) to be identified with certainty. However, combination bands suitable for resonance with the C=O stretching vibration could arise from (*a*) 1155 cm.$^{-1}$ [Raman and infrared (very strong)] and 581 cm.$^{-1}$ (Raman), or (*b*) 890 cm.$^{-1}$ (Raman, very strong) and 836 cm.$^{-1}$ (infrared, very strong).

EXPERIMENTAL

Spectrography.—Spectra were recorded on a Perkin-Elmer double-pass grating spectrophotometer, model 112G. The values of the mechanical slit widths were selected to give a spectral slit width of less than 2 cm.$^{-1}$ throughout the 4000—600 cm.$^{-1}$ range. The intrument was flushed with dry nitrogen at such a rate that the water vapour bands (1900—1400 cm.$^{-1}$) did not exceed 15% of the absorption. All solvents were purified, dried, and fractionated before use.

Cyclopentanone.—Commercial material (B.D.H.) was converted into the sodium hydrogen sulphite adduct, which was crystallised four times from ethanol-water (4 : 1). The adduct (60 g.) and sodium carbonate (60 g.) were dissolved in hot water, and the solution distilled in steam. Saturation of the distillate with salt, extraction with benzene, and evaporation of the dried benzene solution gave material which was distilled through a Vigreux column fitted with a condensing still-head (reflux ratio 40 : 1). Cyclopentanone was collected as the fraction with b. p. 130—130·5°; its homogeneity was confirmed by gas-phase chromatography.

Cyclohexanone.—Purification as above, except that the bisulphite adduct was crystallised from water, gave material with b. p. 155—155·5°.

Deuterated Cyclopentanone.—A solution of hexa-2,4-diyne-1,6-diol (4 g.) in purified ethyl acetate (150 c.c.) was shaken with Adams catalyst (0·5 g.) for 5 hr. in an atmosphere of deuterium (generated by electrolysing 99·7% deuterium oxide containing sulphur trioxide). After the removal of catalyst and solvent, the residue was chromatographed on alumina (200 g.; Grade H). Ether eluted deuterated hexan-1-ol (0·4 g.) which was discarded. Elution with ether-methanol (19 : 1) afforded deuterated hexane-1,6-diol (3·1 g.) as a colourless oil.

8N-Chromic acid (40 c.c.) was added during 10 min. to a solution of the deuterated diol (3·1 g.) in acetone (80 c.c.) at 10°. The mixture was kept at 10° for a further 30 min. and then poured into water (800 c.c.). Continuous extraction of the aqueous solution with ether (250 c.c.) for 12 hr., followed by removal of the solvent, gave deuterated adipic acid (1·1 g.), m. p. 150—151° after crystallisation from ethyl acetate.

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[4] Bellamy and Williams, *Trans. Faraday Soc.*, 1959, **55**, 14.

[5] Yates and Williams, *J. Amer. Chem. Soc.*, 1958, **80**, 5896.

A solution of the deuterated acid in deuterium oxide (10 c.c.) was kept at 60° for 2 hr. and then evaporated at 15 mm. After the addition of barium carbonate (50 mg.) the mixture was distilled at 300° for 3 hr. The upper layer (largely deuterated cyclopentanone) of the distillate was separated from the lower layer (largely deuterium oxide), washed with 10% sodium carbonate in deuterium oxide, and dried ($MgSO_4$). Distillation in a small fractionating apparatus gave deuterated cyclopentanone (300 mg.), b. p. (bath-temp.) 143—147°, in which the absence of impurities was established by gas-phase chromatography. Mass-analysis showed the product to contain 61 atoms % of deuterium.

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