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Fermi Resonance in the Carbonyl Band of Cyclopentanone

R. E. DAVIS and KWANG SUP KIM*

Department of Chemistry, Purdue University, West Lafayette, Indiana 47907

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The relative carbonyl stretching frequency shifts in the infrared spectra of cyclopentanone (CP) and O^{18}-CP have been measured in various solvents. The plot of these shifts versus those of acetophenone shows that the doublet in the carbonyl stretching region of CP is caused by Fermi resonance and the splitting does not take place in O^{18}-CP. In the vapor phase no doublet was observed in CP or O^{18}-CP.

Using these results, the vibrational energy diagrams of CP and O^{18}-CP are proposed and the energy difference between the unperturbed resonating levels (δ^0) and interaction terms (H_{ij}) were obtained. These values agree well with those obtained from the intensity data.

Die relativen Frequenzverschiebungen der Carbonylstreckschwingung im Infrarotspektrum des Cyclopentanons (CP) und O^{18}-CP werden in verschiedenen Lösungsmitteln gemessen. Beim Auftragen dieser Werte gegen die des Acetophenons zeigt sich, daß das Dublett im Bereich der Carbonylstreckschwingung des CP durch Fermiresonanz hervorgerufen wird und bei O^{18}-CP keine Aufspaltung stattfindet. In der Dampfphase wurde weder bei CP noch bei O^{18}-CP ein Dublett beobachtet.

Aufgrund dieser Ergebnisse wird ein Schwingungsenergiediagramm von CP und O^{18}-CP vorgeschlagen und die Energiedifferenz zwischen den ungestörten Resonanzzuständen (δ^0) und den Wechselwirkungstermen (H_{ij}) erhalten. Diese Werte stimmen mit den aus Intensitätsmessungen erhaltenen gut überein.

The carbonyl stretching region of the infrared and Raman spectra of cyclopentanone (CP) contains a doublet band. This splitting has been investigated [1, 2] extensively by examining the effects of solvent, concentration, and temperature on the doublet and by comparing the infrared and Raman spectra of CP and $CP-\alpha:\alpha:\alpha':\alpha'-d_4$. It was concluded that the doublet is caused by Fermi resonance and does not involve conformational isomerism, dimolecular association through hydrogen bonding, dipole-dipole interaction or enolization of the ketone. According to a microwave study, CP has one major conformational structure of C_2 symmetry in the ground state [3]. Although the dimeric association by a dipole-dipole interaction in CCl_4 was reported recently [4], its contribution to the doublet is not significant as confirmed in previous works [1, 2].

In the course of a study of the infrared carbonyl bands of various ketones, we have had occasion to synthesize and study the infrared absorptions of O^{18}-CP in comparison with those of O^{16}-CP. With these spectral data in the carbonyl stretching region, the Fermi interaction of CP and O^{18}-CP has been studied using its solvent perturbation.

Several O^{18}-labelled ketones such as benzoyl chloride [5, 6], *p*-benzoquinone [7] and tetramethylcyclobutane-1,3-dione [8] have been used for study of the

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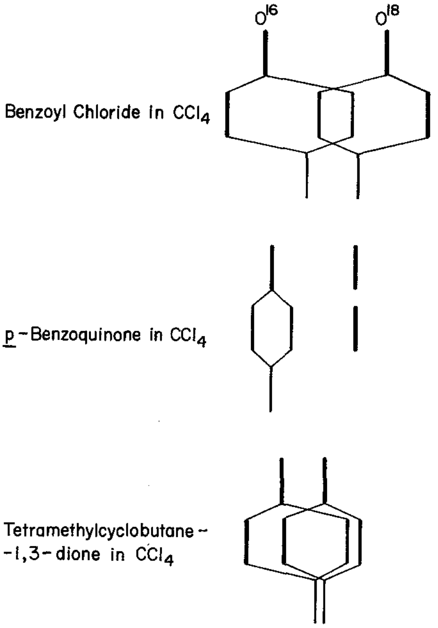

Fig. 1. Schematic interacting energy levels in the carbonyl stretching region of benzoyl chloride, *p*-benzoquinone and tetramethylcyclobutane-1,3-dione

doublet splittings of their normal ketones in the carbonyl stretching region. The interacting energy levels can be represented by the schematic diagram (Fig. 1). The energy levels and the intensities of O^{18}-ketones depend on the degree of the relative shifts of the resonating carbonyl and overtone or combination levels caused by O^{18}-substitution. The overtone or combination bands of benzoyl chloride are effected very much by O^{18}-substitution while those of *p*-benzoquinone and tetramethylcyclobutanedione (TMDO) remain at the almost same locations. This information is useful for the vibrational assignment with group-theoretical considerations and selection rules for TMDO [8]. However, this kind of consideration is not successful for CP because of many numerically possible combinations and its low molecular symmetry.

CP in solvents is similar to *p*-benzoquinone due to the large separation of the resonating levels by O^{18}-substitution (see Fig. 2). In the vapor phase the carbonyl band is shifted to a higher level; the interaction in O^{16}-CP is weakened significantly and it may be negligible (Fig. 3). The same behavior is observed in O^{18}-CP. The half-band width and the relative locations of three sub-bands are almost equal to those of O^{16}-CP (Fig. 3 and Table 1). If there is interaction in the vapor phase, the band would be complex and broad due to the contribution from rotational states. These behaviors are shown schematically in Fig. 4.

With different solvents, the carbonyl band can be shifted. In Fig. 5, the relative frequency shifts ($\Delta\nu/\nu$) calculated on the basis of the vapor state frequency are plotted against those of acetophenone [9]. In the case of O^{16}-CP in which the

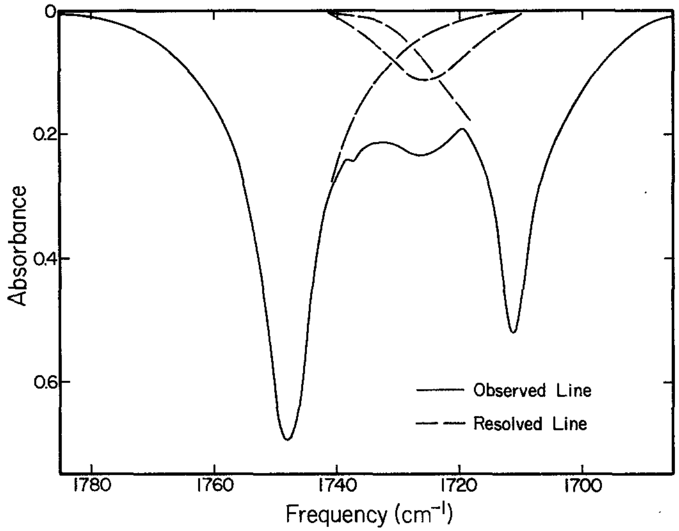

Fig. 2. Infrared spectrum of partially O^{18}-substituted cyclopentanone in the carbonyl stretching region, 0.04 cc/cc CS_2, 0.05 mm thick matched KBr cell

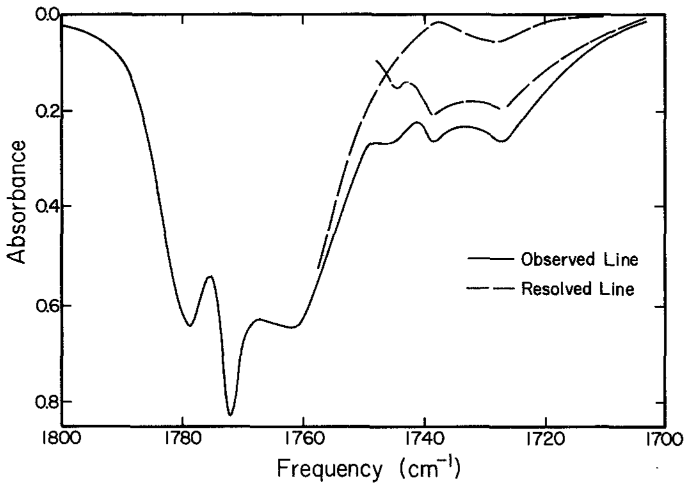

Fig. 3. Infrared spectrum of partially O^{18}-substituted cyclopentanone in vapor phase in the carbonyl stretching region, 15 mm Hg, 10 cm cell with CsBr windows

resonating levels are very close, the carbonyl level can be lower and higher than the other level interacting with it. The latter level depends only weakly upon the nature of solvent. Therefore, the stronger band has been assigned as the carbonyl absorption O^{18}-CP gives a good straight line as ketones do whose carbonyl band does not involve Fermi resonance [9]. O^{16}-CP shows the same tendency as O^{18}-CP in the low and high relative shifts ($\Delta\nu/\nu$). However, the line is not connected in the middle region (the broken line of Fig. 5). This effect takes place in solvents

Table 1. Infrared data in the carbonyl stretching region of O^{16}- and O^{18}-cyclopentanones and the calculated parameters

Point No.	Solvent	ν_{16}	ν_c	ν_{18}	ϱ	δ	δ^0	H_{ij}	a
	Vapor	1776 1771[a] 1759		1743 1738[a] 1725					
1	Cyclohexane	1753	1724	1714	13.78	29	17	11.7	0.89
2	Carbon disulfide	1747	1725	1709	5.77	22	12	9.2	0.88
3	Nitromethane	1733	1747	1706	1.49	14	2	6.9	0.76
4	Chloroform	1729	1745	1703	1.30	16	2	7.9	0.75
5	Bromoform	1726	1743	1703[b] 1699	1.49	17	1	8.5	0.73
6	Benzene	1747	1728	1710	4.73	19	11	7.7	0.89
7	Carbon tetrachloride	1749	1726	1711	5.2	23	13	8.9	0.89
8	Acetonitrile	1746	1733	1707	1.06	13	1	6.5	0.73

[a] Used as standard.

[b] Doublet of equal intensities. Average value was used.

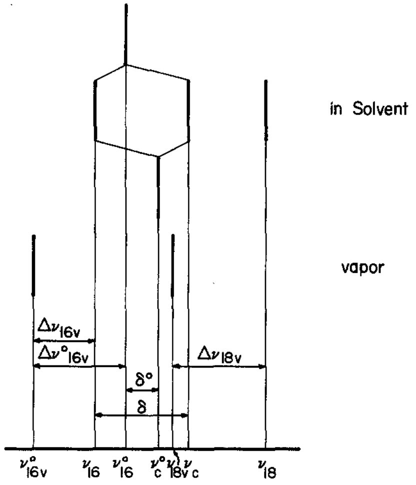

Fig. 4. Schematic interacting energy levels of O^{16}- and O^{18}-cyclopentanones in solvent and vapor phase in the carbonyl stretching region

which would be expected to lower the resonating carbonyl level to the overtone or combination level. The shift ($\Delta\nu^0_{16v}$) of O^{16}-CP can be assumed to be equal to $\Delta\nu_{18v}$, and the frequencies of the resonating levels (ν^0_{16} and ν^0_c) can be determined (Table 1). The extrapolation to $\delta^0 = 0$ in a plot of ϱ against δ^0 gives $\varrho = 1$ (Fig. 6(a)) (ϱ = the intensity of strong band/that of weak band). These two behaviors are those which can be expected from the Fermi resonance scheme which is shown in Fig. 4.

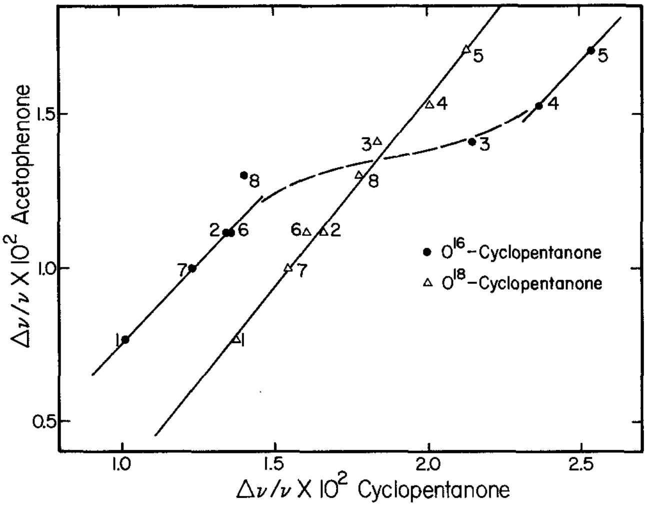

Fig. 5. Plot of the relative frequency shift of O^{16}- and O^{18}-cyclopentanones versus that of acetophenone

If the resonating levels (ψ_i^0 and ψ_j^0) have very nearly the same energy, the effect can be calculated from the first-order perturbation theory. The solution may be written as [10, 11]

$$E_{i,j}=\tfrac{1}{2}(E_i^0+E_j^0)+\tfrac{1}{2}\sqrt{(E_i^0-E_j^0)+4|H_{ij}|^2}\,, \tag{1}$$

where

$$E_i^0=\langle\psi_i^0|\hat{H}|\psi_i^0\rangle$$

$$E_j^0=\langle\psi_j^0|\hat{H}|\psi_j^0\rangle$$

and

$$H_{ij}=\langle\psi_i^0|\hat{H}|\psi_j^0\rangle$$

$\hat{H}$ includes the perturbation operator.

The eigenfunctions after interaction are

$$\psi_i=\boldsymbol{a}\psi_i^0-\boldsymbol{b}\psi_j^0$$

$$\psi_j=\boldsymbol{b}\psi_i^0+\boldsymbol{a}\psi_j^0\,, \tag{2}$$

where

$$a=[\delta+\delta^0/2\delta]^{1/2}$$

and

$$b=[\delta-\delta^0/2\delta]^{1/2}\,.$$

Subscripts i and j indicate the carbonyl and overtone or combination band respectively. If the resonating overtone or combination level (ψ_j^0) is assumed to have negligible intrinsic intensity [12],

$$\varrho=I_i/I_j=\boldsymbol{a}^2/\boldsymbol{b}^2 \tag{3}$$

and combining Eqs. (2) and (3),

$$\delta^0=\delta(\varrho-1)/(\varrho+1)\,. \tag{4}$$

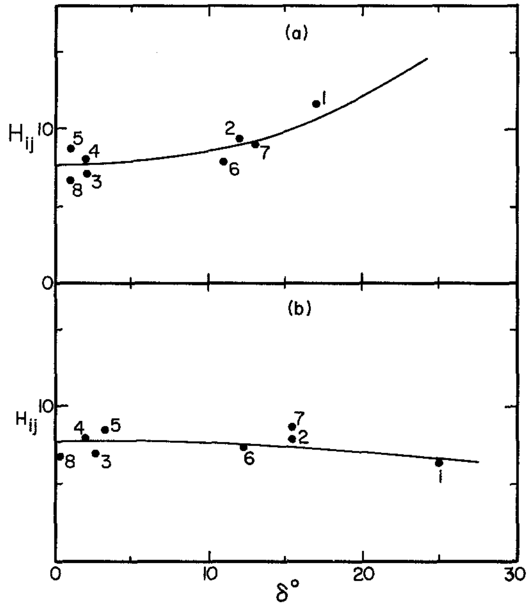

Fig. 6. Plot of H_{ij} versus δ^0. *a* was obtained from the scheme in Fig. 4 and *b* from the intensity data

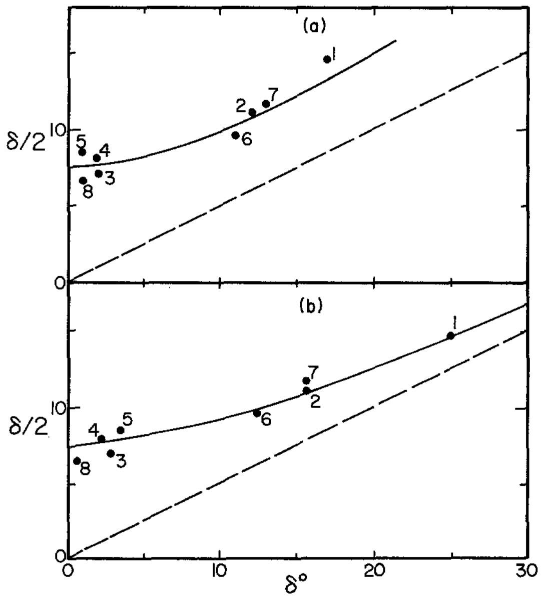

Fig. 7. Plot of $\delta/2$ versus δ^0. *a* was obtained from the scheme in Fig. 4 and *b* from the intensity data

Using these equations, δ^0, H_{ij} and $\boldsymbol{a}$ can be calculated (Table 2). These values are plotted in (b) of Figs. 6 and 7, in comparison with those (a) obtained from the scheme in Fig. 4. They agree well, but discrepancies are found when δ^0 is large, e.g. in nonpolar solvents. According to Fermi resonance theory, H_{ij} will decrease

Table 2. Calculated parameters from intensity data

Point No.	Solvent	δ^0	H_{ij}	a
1	Cyclohexane	25.1	6.2	0.97
2	Carbon disulfide	15.5	7.8	0.92
3	Nitromethane	2.8	6.9	0.77
4	Chloroform	2.1	7.9	0.75
5	Bromoform	3.4	8.3	0.77
6	Benzene	12.4	7.2	0.91
7	Carbon tetrachloride	15.6	8.5	0.92
8	Acetonitrile	0.4	6.5	0.72

(Fig. b) and $\delta/2$ will approach to the broken line (Fig. 7) as δ^0 increases. Therefore the values from ϱ data give a better agreement when δ^0 is large. That is, the postulated energy scheme (Fig. 4) may not be completely valid in the nonpolar solvent because ν_{18} get close to ν_c^0 and the interaction may take place between them.

Experimental

Preparation of O^{18}-CP: O^{16}-CP was sealed in a glass tube with dry tetrahydrofuran, "normalized" (low deuterium content) H_2O^{18} and perchloric acid as catalyst. This mixture was heated for 10 h on a steam bath. CP was isolated in purity of 99.5% or better by gas chromatography (6 ft. column of 20% diisodecylphthalate on 60–80 Chromosorb P). The exchange reaction were carried out by D. Samuel of the Weizmann Institute of Science, Rehovoth, Israel. This product was found to contain 38.2% O^{18}-CP by mass spectrometric analysis.

Spectrography: Spectra were measured on a Perkin-Elmer Model 421 spectrophotometer with a dual grating interchange. Solvent absorptions were removed by using matched KBr cells, 0.05 mm thick. The calibration was performed by using water vapor. Overlapped bands were resolved by a graphical method on an assumption of their symmetric shapes to determine the location and the relative absorbance of each band. For ϱ, the maximum relative absorbance of each band was used.

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Dr. David Samuel provided the O^{18} water and Mrs. I. Wassermann performed the exchange reaction.

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Prof. Dr. R. E. Davis
Department of Chemistry
Purdue University
West Lafayette, Indiana 47907, USA