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# Solvent Effects on the $n\rightarrow\pi^*$ Absorption Intensities of Acetone and Cyclopentanone

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**Synopsis.** The recently proposed theory [*J. Chem. Phys.* **78**, 5175 (1983)] for the solvent effect on the absorption intensity has been successfully applied to the $n\rightarrow\pi^*$ bands of acetone and cyclopentanone in various organic solvents observed by Nakashima, *et al.* [*Bull. Chem. Soc. Jpn.* **55**, 415 (1982)].

Nakashima *et al.*, in their recent paper,[1] correlated the intensities of the $n\rightarrow\pi^*$ absorption bands of acetone and cyclopentanone in various organic solvents to $(\bar{\alpha}/\bar{r}^6)^2$ of the solvents, $\bar{\alpha}$ being the mean molecular polarizability of the solvent and $\bar{r}$ the mean distance between the solute and solvent molecules.[2] The $n\rightarrow\pi^*$ absorption of ketones is usually observed as very weak bands. It is electric-dipole forbidden, but is vibrationally induced.[3,4]

Recently we[5] have shown that the energy density of light acting on the solute molecule is different from that outside of the solution and that the ratio of the observed oscillator strength ($f''$) to the *true* oscillator strength ($f$) of the solute molecule is given by

$$f''/f=[s(n^2-1)+1]^2/n. \tag{1}$$

In this expression, $n$ is the refractive index of the medium, and $s$ is a shape parameter between zero and unity depending upon the shape of the cavity in which the solute molecule is supposed to lie and upon the relative direction of the transition moment in the cavity. Eq. (1) may also be written as

$$\sqrt{nf''}=\sqrt{f}\,s(n^2-1)+\sqrt{f}, \tag{2}$$

which expresses a linear relationship between $\sqrt{nf''}$ and $(n^2-1)$.

Nakashima *et al.*, measured absorption spectra at room temperature. The observed oscillator strengths ($f''$) of acetone and cyclopentanone in various solvents were estimated from Figs. 6 and 7 in their paper.[1] These values are listed in Table 1. Also listed are the refractive indices ($n_{20}^{\mathrm{D}}$) of these solvents measured[6] at 20 °C with the Na-D line. Using these values for $n$ in Eq. (2), we plotted $\sqrt{nf''}$ *vs.* $n^2-1$ in Figs. 1 and 2. The least-squares fittings give $s=0.88$ and $f=1.80\times10^{-4}$ for acetone and $s=0.71_5$ and $f=2.27\times10^{-4}$ for cyclopentanone.

These values of $s$ are reasonable since the transition moments of the vibrationally induced $n\rightarrow\pi^*$ transitions of these molecules are supposed to be perpendicular to the plane of the sp$^2$-hybrid planar structure in the carbonyl group. Note that $s=1$ if the flat molecule is very large compared with the size of the solvent molecules and that $s=1/3$ when the cavity is spherical.[5]

The relation Eq. (1) or (2) was derived in Ref. 5 on the assumptions (i) that both solute and solvent are nonpolar and mutually innert and (ii) that the absorption band is strong enough so that the imaginary part of the polarizability in the frequency region of the absorption is well approximated by this absorption band alone. These conditions are not strictly satisfied here, but the reasonable results obtained here imply that these conditions are fairly well satisfied. It may be interesting to compare the values of $f$ with the gas-phase oscillator strengths ($f°$). Values of $f°$ are, however, not known for the $n\rightarrow\pi^*$ transitions of these molecules.

Solvent effects on the absorption intensity are of two-fold:[5] (a) The effective density of radiation energy "seen" by the solute molecule is different from the energy density when the dielectric medium is eliminated, and (b) the transition moment and the absorption frequency of the solute molecule are different from one solution to another and also different from those of the isolated molecule because of the solute-solvent interaction in the solution systems. In the present paper, only the solvent effect of type (a) was considered. On the other hand, the effect considered

TABLE 1. OBSERVED OSCILLATOR STRENGTHS[a] ($f''$) AND THE QUANTITIES $\sqrt{nf''}$ OF THE $n\rightarrow\pi^*$ TRANSITIONS OF ACETONE AND CYCLOPENTANONE IN VARIOUS SOLVENTS

| Solvent[b] | $n$[c] | $n^2-1$ | Acetone | | Cyclopentanone | |
|---|---|---|---|---|---|---|
| | | | $f''/10^{-4}$ | $\sqrt{nf''}/10^{-2}$ | $f''/10^{-4}$ | $\sqrt{nf''}/10^{-2}$ |
| (1) $C_6F_{14}$ | 1.2514 | 0.5660 | $3.33_5$ | $2.04_3$ | $3.56_7$ | $2.11_3$ |
| (7) $CH_3CN$ | $1.3441_1$ | $0.806_6$ | $4.03_9$ | $2.33_0$ | $4.34_3$ | $2.41_6$ |
| (2) $C_6H_{14}$ | $1.3748_6$ | $0.890_2$ | $4.15_7$ | $2.39_1$ | $4.15_0$ | $2.38_9$ |
| (6) $CH_2Cl_2$ | 1.4246 | $1.029_5$ | $4.43_3$ | $2.51_3$ | $4.87_4$ | $2.63_5$ |
| (3) $C_6H_{12}$ | $1.4262_3$ | $1.034_1$ | $4.18_9$ | $2.44_4$ | $4.47_2$ | $2.52_5$ |
| (5) $CHCl_3$ | $1.4485_8$ | $1.098_4$ | $4.73_2$ | $2.61_8$ | $5.29_5$ | $2.77_0$ |
| (4) $CCl_4$ | $1.4603_0$ | $1.132_5$ | $5.26_8$ | $2.77_4$ | $5.55_1$ | $2.84_7$ |
| (9) $C_6H_5CH_3$ | $1.4969_3$ | $1.240_8$ | | | $5.13_8$ | $2.77_3$ |
| (8) $C_6H_6$ | $1.5011_2$ | $1.253_4$ | $5.55_1$ | $2.88_7$ | $5.37_4$ | $2.84_0$ |
| (10) $C_6H_5CN$ | 1.5282 | $1.335_4$ | | | $5.64_6$ | $2.93_7$ |

a) Estimated from Figs. 6 and 7 in Ref. 1. b) The numbering of solvents coincides with that of Ref. 1. Here, solvents are in the order of increasing $n$. c) Refractive indices of solvents, $n_{20}^{\mathrm{D}}$ taken from Ref. 6.

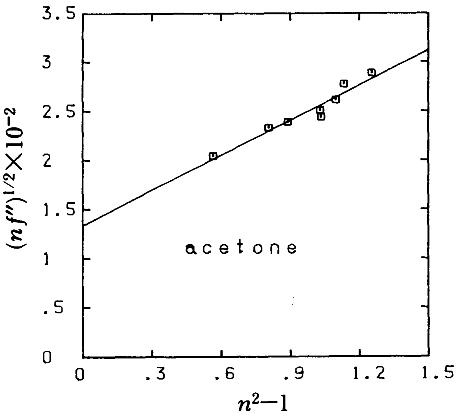

Fig. 1. Plot of $\sqrt{nf''}$ *vs.* $n^2-1$ for the $n\rightarrow\pi^*$ transition of acetone in various organic solvents. The solid line indicates the least-squares fitted Eq.(2) with $s$= 0.884 and $f$=$1.80_1\times10^{-4}$.

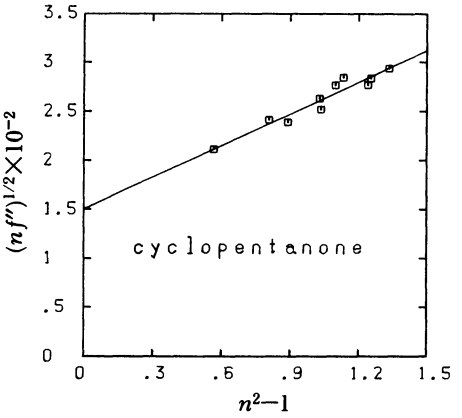

Fig. 2. Plot of $\sqrt{nf''}$ *vs.* $n^2-1$ for the $n\rightarrow\pi^*$ transition of cyclopentanone in various organic solvents. The solid line indicates the least-squares fitted Eq. (2) with $s$=0.715 and $f$=$2.27_0\times10^{-4}$.

by Nakashima *et al.*[1] is of type (b). The fact that the linearity of Eq. (2) has been observed fairly well as shown in Figs. 1 and 2 indicates that the effect of type (a) is significant in the solution systems studied here. This, however, does not exclude the possibility that $f$ may be significantly different from $f°$ as the result of the solvent effect of type (b). It is therefore desirable to have experimental values of $f°$ for the $n\rightarrow\pi^*$ transitions of acetone and cyclopentanone.

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