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Solvent Effects on the Intensities of Forbidden Bands of Molecules. Absorption Spectra of Acetone and Cyclopentanone[1)]

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The near ultraviolet absorption spectra of acetone and cyclopentanone have been studied in various fluid solutions at room temperature. The intensity enhancements observed are ascribed to perturbation of dispersion forces between solute and solvent molecules. The results are parallel to those of the Ham effect in benzene. No correlation was found between the intensity increments and solvent polarities. This is at variance with the correlation that has been reported in the $S_1(L_b)$—S_0 transition spectra of pyrene and coronene.

Many investigations have been reported on solvent effects for electronically forbidden transitions of molecules[2—14)] since the first finding of the "Ham bands" in the 260 nm absorption spectrum of benzene in a solid solution containing 7% CCl_4.[12)] From a systematic study on the $S_1(L_b)\leftarrow S_0$ absorption spectra of benzene, naphthalene, and phenanthrene in solid glasses at 83 K, Durocher and Sandorfy have suggested that the environmental perturbation causing the Ham effect of benzene is essentially the same for the others.[6)] One of the authors (M. K.) has derived the formulas by which the absorption enhancements of benzene and naphthalene are closely correlated with solvent polarizabilities and solute-solvent intermolecular distances.[9)]

An interesting example of solvent perturbations was demonstrated in the absorption and fluorescence spectra of pyrene and coronene in polar solvents by Nakajima.[11,15)] The intensity enhancements of the origin bands in the S_1—S_0 spectra of pyrene and coronene were found closely correlative with solvent polarities rather than with solvent refractive indexes. This correlation is at variance with the Ham effect in benzene and similar effects in the other aromatic compounds.[7,10)] Very recently, Nakajima also proposed that quadrupole-dipole interactions should be taken into account[15)] besides dipole-dipole interactions which have been employed for the explanation of the Ham effect by Koyanagi.[9)] On the other hand, Lianos and Georghiou have suggested on the basis of the IR studies that a weak complex is formed between pyrene and a certain polar solvent.[16)] By studying the $S_2(L_a)\leftarrow S_0$ absorption spectra in several polar solvents, we have also confirmed the validity of their suggestions.[17)]

In the present work we studied the $S_1(n\pi^*)\leftarrow S_0$ absorption spectra of acetone and cyclopentanone in various solvents and found that the correlation of the absorption increments with solvent properties is very similar to those in benzene and naphthalene.

Experimental

Materials and Apparatus. The solutes, acetone (Dotite Spectrosol) and cyclopentanone (a reagent from Wako Pure Chemical Industries, Ltd.), were distilled *in vacuo* after drying over anhydrous potassium carbonate and anhydrous sodium sulfate, respectively. The solvents employed were of spectroscopically pure grade (Dotite Spectrosol) except benzonitrile and perfluorohexane (GR grade reagents from Wako Chemical Industries, Ltd. and Tokyo Kasei Co. Ltd., respectively). Almost all of the solvents were thus used without further purification. The exceptions are for benzene, toluene, and benzonitrile. Since these aromatics in the atmosphere have well been known to give poor transparency below 350 nm due to formation of transient complexes with oxygen, *i.e.*, the so-called contact charge transfer complexes,[18,19)] nitrogen gas was bubbled into the solvents prior to use.

Absorption spectra were observed at room temperature using a Shimadzu Multipurpose Spectrometer type MPS-50 and/or a Hitachi Perkin-Elmer 139 UV-VIS Spectrometer. Cells employed were of 1.0 cm in optical path. The other experimental conditions are similar to those given previously.[5)]

Intensity Measurements. The *f*-values of the absorption spectra of two ketones were determined by means of the usual expression of the integrated absorption intensity:[20)]

$$f = 4.317 \times 10^{-9}\int_{pq} \varepsilon(\tilde{\nu})\mathrm{d}\tilde{\nu},$$

where the integral denotes the area under a plot of molecular extinction coefficients ε in $dm^3\ mol^{-1}\ cm^{-1}$ units *versus* $\tilde{\nu}$ in cm^{-1} units. The alphabetical indexes p and q limit the wavenumber range within which the $S_1(n\pi^*)\leftarrow S_0$ absorption of light in effect takes place. The substantial absorptions of acetone and cyclopentanone extend, in many cases, from 29800 to 45400 cm^{-1} and 28000 to 43500 cm^{-1}, respectively (for example, see Figs. 1—4). Unfortunately, however, several solvents showed poor transparency in the short wavelength region of the absorption spectra in question and only a part of each absorption system was measurable in these solutions. The *f*-value of each ketone in such a case was then obtained by comparing the partial absorption area in the solution with the corresponding area in cyclohexane used as a standard solvent: On an assumption that a change in the frequencies of the prominent vibrations in the spectra of the ketones is little with a change in solvents, the wavelength truncation in these solutions was carried out at an equal wavenumber position from the absorption maximum in the case of acetone and also at an equal wavenumber position from one of the prominent vibronic peaks in the case of cyclopentanone. The solvents treated in this way are $CHCl_3$, CCl_4, benzene, toluene, and benzonitrile.

Molecular Radii and Other Molecular Properties. The molecular radii employed were calculated using molecular weights and densities available for the liquid states, on an assumption that all the molecules are spherical. No correction factor was taken for the assumption of the spherical volume. The polarizability data[21)] is summarized in Table 1 together with other properties of solvents.[22,23)]

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TABLE 1. SOLVENT PROPERTIES[a]

Solvent	Mol wt	Density / 10^3 kg m^{-3}	R[b] / Å	$\bar{\alpha}$[c] / 10^{-31} m^3	D[d]	n[e]
C_6F_{14}	338[f]	1.695[f,g]	4.292	125.5[h]	—	1.2514[i]
C_6H_{14}	86.18	0.65937	3.728	118.4[h]	1.890	1.37486
C_6H_{12}	84.16	0.7791	3.499	108.7	2.023	1.42623
CCl_4	153.8	1.63195	3.343	105	2.238	1.46030
$CHCl_3$	119.4	1.4892	3.168	82.3	4.806	1.44858[j]
CH_2Cl_2	84.93	1.3266	2.938	64.8	9.08	1.4246
CH_3CN	41.05	0.77683[g]	2.757	48.6	37.5	1.34411
C_6H_6	78.12	0.87865	3.279	103.2	2.284	1.50112
$C_6H_5CH_3$	92.14	0.86694	3.480	123.1[h]	2.379[g]	1.49693
C_6H_5CN	103.1	1.0051	3.439	124.4[h]	25.20[g]	1.5282

a) Data at 20 °C unless mentioned otherwise. b) Molecular radius. c) Mean molecular polarizability. d) Dielectric constant. e) Refractive index at the sodium D line. f) Taken from the catalog of Tokyo Kasei Co. Ltd. g) Data at 25 °C. h) Calculated from refractive index and molar volume. i) Taken from Ref. 7. j) Data at 15 °C.

Results and Discussion

In their electronic ground states, both acetone and cyclopentanone can be treated as a nonrigid species belonging to a point group isomorphous with C_{2v}. No matter what it may be, however, the $S_1(n\pi^*)\leftarrow S_0$ absorption transition of each molecule is considered to be essentially electric dipole forbidden.[24–26] The very small oscillator strengths observed confirm that this is the case.

The absorption spectra of acetone and cyclopentanone were studied in various solvents at room temperature. Some representative spectra are shown in Figs. 1 and 2, respectively. The spectra of acetone do not show any prominent vibronic band, but only a broad band maximum around 36000 cm^{-1}. This broadness in the spectra is assumed to come from (i) a low energy barrier to rotation of the methyl group about the bond to the C=O chromophore (*e.g.*, $\approx$3.15 kJ mol^{-1} in the vapor[27]) and (ii) active participation of several low frequency modes as has been demonstrated in the $n\pi^*$ spectra of acetones.[28] The greater enhancement of the absorption intensity is found in solvents with the greater molecular polarizability. For example, the relative ratios of the band areas in Fig. 1 are 1.00 : 1.21 : 1.25 : 1.32 : 1.41 : 1.57 in C_6F_{14}, CH_3CN, C_6H_{12}, CH_2Cl_2, $CHCl_3$, and CCl_4, respectively. As for C_6F_{14}, it is well known that spectra in perfluoro-hydrocarbons generally give *quasi*-vapor spectra.[7,13]

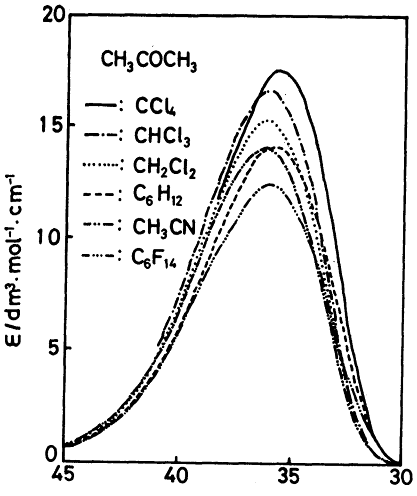

Fig. 1. The $S_1(n\pi^*)\leftarrow S_0$ absorption spectra of acetone in several solvents at 20 °C.

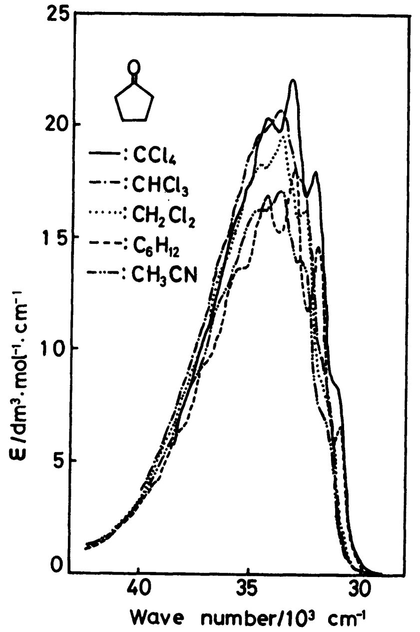

Fig. 2. The $S_1(n\pi^*)\leftarrow S_0$ absorption spectra of cyclopentanone in several solvents at 20 °C.

Another spectral aspect is found in Fig. 3 which displays the spectral behavior in a binary solvent system of CCl_4 and hexane. The intensity enhancement of the overall band system seems to almost satisfy an additivity rule between the respective solvents. This fact never supports an idea that the intensity enhancement might closely be related with some complex formation between the solute and solvent molecules.[5,17] Similar additive properties in the spectral behaviors are also found in many other binary solvent systems employed.

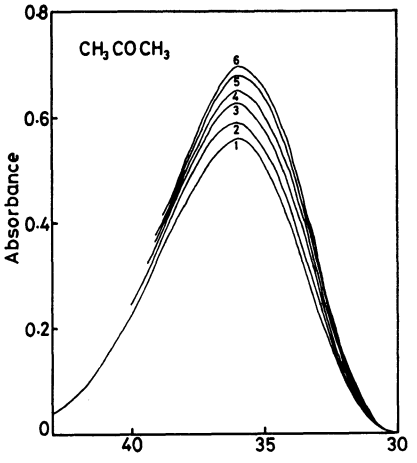

Fig. 3. The absorption spectra of acetone in CCl_4–C_6H_{14} binary mixed solutions at 20 °C. Concentration of CCl_4 in mol dm^{-3} units: (1) 0; (2) 2.1_2; (3) 4.2_4; (4) 6.3_7; (5) 8.4_9; and (6) $10._6$.

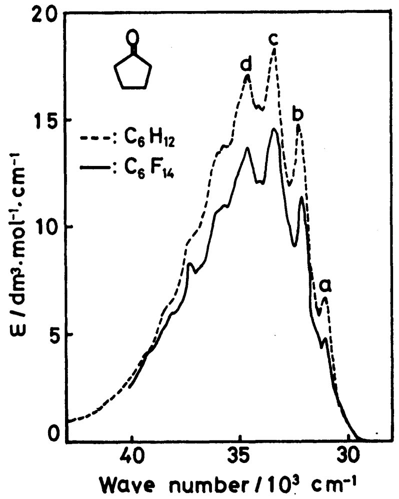

Fig. 4. The absorption spectra of cyclopentanone in cyclohexane and perfluorohexane at 20 °C.

In contrast with the acetone case mentioned above, the absorption spectra of cyclopentanone show several prominent vibrational structures in the vapor and in most fluid solutions (Fig. 2). For a further advance in discussion, the absorption spectra in cyclohexane and perfluorohexane solutions are chosen and demonstrated in Fig. 4. Here four characteristic bands are designated as *a*, *b*, *c*, and *d*. The detailed vibrational assignment of the absorption bands in the vapor and some comments on the spectra in solutions have been given by Howard-Lock and King.[29] Since one-to-one band correspondence between the spectra in fluid solutions and in the vapor is quite inferior to those in the cases of benzene and naphthalene because of great inhomogeneous broadening and participation of several intense sequence bands in the case of cyclopentanone, it is very difficult to definitely identify the origin band in the spectra of cyclopentanone in such fluid solutions. However, comparison of a very low resolution spectrum in the vapor with the spectra in solutions enables us to predict a probable location of the origin band in the solutions around the band *a* (Fig. 4).

In the vapor a cold *pseudo*-origin band of 25^1_0 due to the inversion doubling splitting along to the b_1 out-of-plane vibrational coordinate has been observed close to the undetected 0-0 band (see Ref. 30 for the vibrational notation and assignment of cyclopentanone in the ground state): The splitting has been established to be extremely small, say, less than 0.2 cm^{-1}.[29] Furthermore, there appear several sequence bands with considerable intensity in the neighborhood of the origin band. For these reasons, it is also very difficult to fully estimate the intensity contribution of the origin band in these solutions.

Despite the obscured assignment of the origin band, it is favorable to see that intensities of almost all of the "bands," *e.g.*, those of bands *a*—*d* shown in Fig. 4, are enhanced in a proportional ratio when solvents are changed from perfluorohexane to cyclohexane (see Fig. 4). This proportionality in the intensity enhancement is possibly of an apparent feature, originating mainly in the inhomogeneous broadening of these solution spectra superimposed on the vibrationally tangled band system in the spectrum of cyclopentanone. Similar intensity increments are also found to take place in the other solvent systems (see Fig. 2).

The total intensity of each solute is thus taken as a measure of the environmental effects about which some discussion will be given below. First let us apply the treatments of environmental effects given by Nakajima[11] to our ketone cases. For the explanation of the anomalous $S_1(L_b)$—S_0 spectra of pyrene in polar solvents, he has introduced a new solvent parameter f'. The parameter is rewritten as follows:

$$f' = (D-1)/(2D+1) - x(n^2-1)/(2n^2+1),$$

where D denotes the dielectric constant, n the refractive index of the solvent, and x an adjustable dimensionless parameter. Although the physical meaning of f' is not necessarily clear, his treatments with a partial success seem to give a correlation between f' and ε_p, where ε_p means the molar extinction coefficient of the $S_1 \leftarrow S_0$ absorption origin band of pyrene. In Fig. 5 the oscillator strength of cyclopentanone, f, is plotted against the

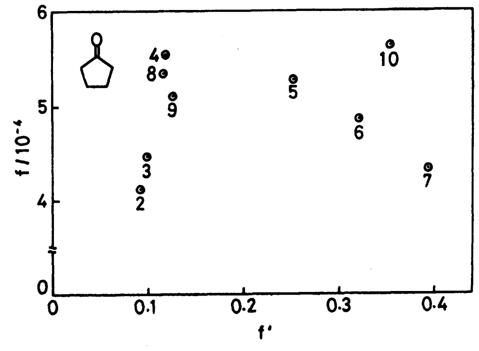

Fig. 5. Plots of the oscillator strength of cyclopentanone, f, against the solvent parameter given by Nakajima (Ref. 11), $f'=(D-1)/(2D+1)-0.5\,(n^2-1)/(2n^2+1)$. The numbering of the plots is as follows: (1) C_6F_{14}; (2) C_6H_{14}; (3) *cyclo*-C_6H_{12}; (4) CCl_4; (5) $CHCl_3$; (6) CH_2Cl_2; (7) CH_3CN; (8) C_6H_6; (9) $C_6H_5CH_3$; and (10) C_6H_5CN.

solvent parameter f' with $x=0.5$, the value which Nakajima has employed for the elucidation of the environmental effect in the S_1—S_0 spectra of pyrene. However, we could not find any straightforward correlation between f and f'. This was never improved for the other solute, acetone; no settled correlation was obtained between f and f' in the case of acetone, either. It seems thus that the Nakajima-like treatments[31] are not valid for the explanation of the environmental intensity enhancement in the $S_1(n\pi^*)\leftarrow S_0$ spectra of acetone and cyclopentanone in fluid solutions.

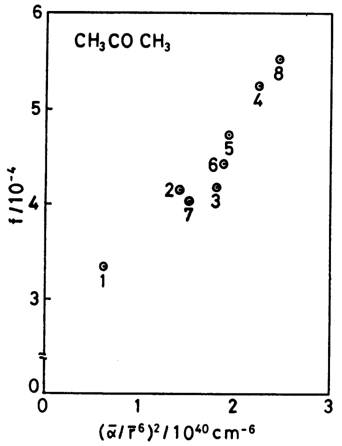

Fig. 6. A correlation diagram between the oscillator strength of acetone, f, and the squared value of the relative dispersion energy of solvents, $(\bar{\alpha}/\bar{r}^6)^2$. For the numbering of the plots, see the caption given in Fig. 5.

Next let us adopt another treatment given by one of the authors (M. K.) who has succeeded in explaining the Ham effect in terms of other solvent properties.[9] In Fig. 6 the oscillator strength of acetone, f, is plotted as a function of the squared value of a relative dispersion energy between the solute and solvent molecules, $(\bar{\alpha}/\bar{r}^6)^2$. Here $\bar{\alpha}$ denotes the mean molecular polarizability of the solvent and $\bar{r}$ the mean molecular distance between the solute and solvent molecules. Despite roughness in the approximation for $\bar{r}$, the observed oscillator strengths of acetone show an approximately linear increase with an increase in $(\bar{\alpha}/\bar{r}^6)^2$. A similar correlation is also found to hold for cyclopentanone (see Fig. 7).

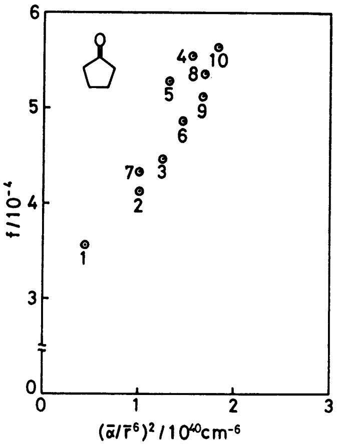

Fig. 7. A correlation diagram between the oscillator strength of cyclopentanone, f, and the squared value of the relative dispersion energy of solvents, $(\bar{\alpha}/\bar{r}^6)^2$. For the numbering of the plots, see the caption given in Fig. 5.

With the help of the perturbation theory, we shall here give a qualitative explanation and a comment on the environmental intensification observed. Now let us take a model that one solute molecule is surrounded by n solvent molecules. The total Hamiltonian H is then given by

$$H = H_0 + H', \tag{1}$$

where H_0 is the zeroth order Hamiltonian, that is, the intramolecular terms of the free molecules, and H' is the total perturbation sum between the solute and n solvent molecules.

$$H' = \sum_{a}^{n}\sum_{i}\sum_{j} h_a(\xi_i, \eta_{aj}), \tag{2}$$

where ξ_i denotes i-th charge(electron) coordinates of the solute, η_{aj} j-th electron coordinates of a-th solvent molecule, and $\sum_i \sum_j h_a(\xi_i, \eta_{aj}) \equiv \phi_a$ represents interactions between the solute and the a-th solvent molecule. For the intermolecular interactions of neutral molecules the terms ϕ_a are generally described by a two-center expansion of reciprocal intermolecular distance r^{-1} in terms of spherical harmonics:[33]

$$\phi_a = \sum_{k=1}^{\infty} (b_{k+2}/r^{k+2}). \tag{3}$$

Here the first term in Eq. 3 represents the so-called dipole-dipole interactions. A further detailed description for them is found in Ref. 33.

If Ψ_0°, Ψ_1°, $\cdots$, Ψ_S° are the electronic wavefunctions for the free solute molecule, the k-th wavefunction of the solute in a fluid solution can be described as follows:

$$\Psi_k = \sum_{j}^{s} C_{jk}\Psi_j^\circ, \tag{4}$$

where the absolute values of coefficients, $|C_{jk}|_{j\neq k}$, are much smaller than unity and their magnitudes are evaluated by off-diagonal matrix elements, $\langle\Psi_j^\circ|H'|\Psi_k^\circ\rangle$, and energy differences between the respective states, ΔE_{jk}.

In general, environmental interactions may mix Ψ_j° with Ψ_k°. The coefficients C_{jk} will then be related to solvent properties as follows:

$$\begin{aligned} C_{jk} = \sum_{q,q'}^{X,Y,Z}\sum_{\hat{q},\hat{q}}^{x,y,z} \{ & A_q(\mu_{\hat{q}}/r^3) + B_{qq'} + (\mu_{\hat{q}}/r^4) + B'_{q'} \\ & \times (Q_{\hat{q}\hat{q}'}/r^4) + C_{qq'}(Q_{\hat{q}\hat{q}'}/r^5) \\ & + D_{qq'}(\alpha_{\hat{q}\hat{q}}/r^6) + \cdots \}. \end{aligned} \tag{5}$$

Here A, B, B', C, $\cdots$ denote intramolecular integrals of the solute multiplied by appropriate proportional constants; each of the subscripts q and q' represents one component of the Cartesian coordinates (X,Y,Z) of the solute and each of $\hat{q}$ and $\hat{q}'$ one component of the Cartesian coordinates (x,y,z) of the solvent; and μ, Q, α are the dipole moment, quadrupole moment, molecular polarizability of the solvent molecule, respectively.

Here it should be noted that only a small number of the terms are effective for the intensity borrowing mechanism: This contrasts with the solvent shift mechanism for which many terms with large matrix elements in Eq. 5 generally play an important role. In the case of a high symmetry molecule such as benzene, for example, the transition-dipole selection rule severely restricts the number of effective perturbation terms in Eq. 5. The terms D_{XX} and D_{YY} have thus been shown to be most important and predominant in the benzene 260 nm absorption case.[9] At present *a priori* we can offer no quantitative explanation for the observed intensity enhancement of acetone and cyclopentanone, because the treatments employed in an explanation of the Ham effect of benzene can not be applied to lower symmetric guest and host molecules without further revision and extention. However, *a posteriori* we may postulate, in the present cases,

$$C_{j1} \propto (\bar{\alpha}/\bar{r}^{6}), \tag{6}$$

where j may possibly be taken as $^1\pi\pi^*$. Supposing that the electronic transition $1 \leftrightarrow 0$ is forbidden in the free molecule, we may then relate the borrowed intensity of the transition in the fluid solutions to the squared value of C_{j1}. Thus we obtain for the intensity of the origin band:

$$I_{0-0} \propto (\bar{\alpha}/\bar{r}^{6})^{2}. \tag{7}$$

In conclusion the intensity enhancement of the $S_1(n\pi^*) \leftarrow S_0$ absorption spectra of acetone and cyclopentanone in fluid solutions is qualitatively interpreted in terms of dispersion force interactions unless solvents have no strong chemical interactions such as hydrogen bondings and charge transfer interactions with the solute molecules.[34,35] Although we strongly believe the dispersion force interactions play a main role also in the intensifications of many other aliphatic carbonyls,[36,37] careful check must be required for further generalization.

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