

## Solvent Intensification Effects on the $S_1(n\pi^*) \leftarrow S_0$ Absorption Spectra of Benzaldehyde in Fluid Solutions

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**Synopsis.** The near ultraviolet absorption spectra of benzaldehyde have been studied in various fluid solutions at room temperature. The intensity enhancements observed are explainable in terms of perturbation of dispersion forces between solute and solvent molecules.

Recently we showed that the environmental intensity enhancements of the near ultraviolet absorption spectra of aliphatic ketones such as acetone and cyclopentanone are parallel to those of the Ham effects in benzene.<sup>1)</sup> Despite many studies of solvent effects on the electronic transition energies of aromatic carbonyls,<sup>2)</sup> there has, to the best of our knowledge, been reported no work on their quantitative intensity correlation. One of the reasons is due to some experimental difficulty in discriminating between overlapping  $S_2(\pi\pi^*) \leftarrow S_0$ / $S_1(n\pi^*) \leftarrow S_0$  electronic transition absorptions for the evaluation of the oscillator strength,  $f[S_1(n\pi^*) \leftarrow S_0]$ . Another is possibly in their chemical and photochemical reactivities. In the present work we studied the absorption spectra of a prototype aromatic carbonyl molecule, benzaldehyde, and found that a like solvent correlation also held. The employment of this molecule is advantageous because the  $S_1(n\pi^*) \leftarrow S_0$  absorption spectrum in a certain solution shows a banded structure even at room temperature and there are somewhat detailed available vibronic data on it.<sup>3)</sup>

### Experimental

Benzaldehyde (a reagent from Wako Pure Chemical Industries, Ltd.) was purified through several vacuum distillations. It was stored in a sealed-off glass tubing *in vacuo*. In order to avoid oxydation into benzoic acid, the tubing was located in the dark at 77 K. The solvents employed were of spectroscopically pure or reagent grade. They were deoxygenated by nitrogen gas bubbling before measurements and used without further purification. Absolute oscillator strengths for the solutions are difficult to obtain from integrated intensities because there is almost always some overlap between the  $S_1(n\pi^*) \leftarrow S_0$  and  $S_2(\pi\pi^*) \leftarrow S_0$  absorptions. Integration over only part of the band should give correct relative oscillator strengths as long as there are no changes in the Franck-Condon factors and as long as there are no specific intramolecular interactions whose matrix elements are beyond the order of the ordinary Boltzmann energy,  $\approx kT$ . In almost all cases we employed the band maxima  $0+2\nu(C=O)$  as the upper wave number limit of the integration. The exceptions are for several high polar solvents such as nitriles, chloroform, and dichloromethane; for these solution systems the integrations were taken up to the band maximum of each spectrum and then the integration values were compared with the intensity integration over wave numbers to the band at  $\approx 30200\text{ cm}^{-1}$ .

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in a standard solvent, hexane. The other experimental details are similar to those described previously.<sup>1)</sup>

### Results and Discussion

In the  $S_1(n\pi^*) \leftarrow S_0$  absorption system of benzaldehyde, both allowed and forbidden characters are important because of the breakdown of the local ( $C=O$  group)  $C_{2v}$  symmetry. This is in contrast with the  $S_1(n\pi^*) \leftarrow S_0$  absorption spectra of acetone and cyclopentanone. Despite this geometrical difference, however, the transition still remains substantial forbidden character. The very small oscillator strengths observed confirm

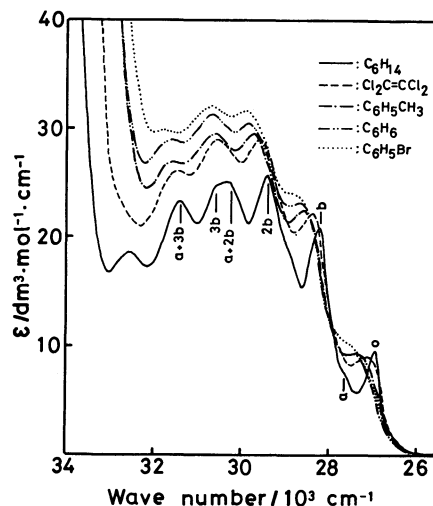


Fig. 1. The  $S_1(n\pi^*) \leftarrow S_0$  absorption spectra of benzaldehyde in several solvents at 20 °C.

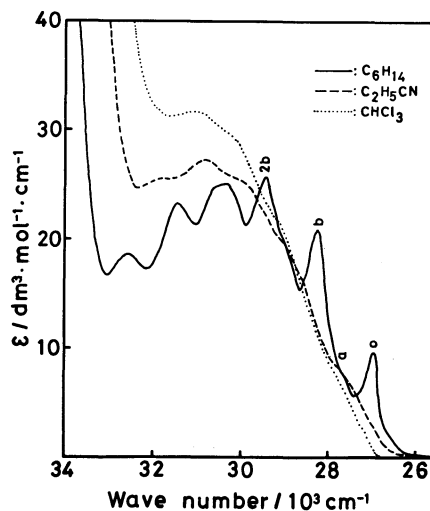


Fig. 2. The  $S_1(n\pi^*) \leftarrow S_0$  absorption spectra of benzaldehyde in polar solvents at 20 °C.

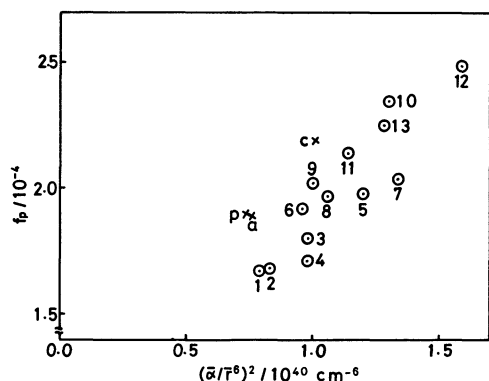


Fig. 3. A correlation diagram between the partial oscillator strength of benzaldehyde,  $f_p$ , and the squared value of the relative dispersion energy of solvents,  $(\bar{\alpha}/\bar{r}^6)^2$ . The numbering of the plots is as follows: (1)  $\text{C}_6\text{H}_{14}$ ; (2)  $i\text{-C}_8\text{H}_{18}$ ; (3) *cyclo*- $\text{C}_6\text{H}_{12}$ ; (4)  $\text{C}_6\text{H}_{11}\text{CH}_3$ ; (5)  $\text{CCl}_4$ ; (6)  $\text{CH}_2\text{Cl}_2$ ; (7)  $\text{C}_2\text{Cl}_4$ ; (8)  $\text{CH}_2\text{Cl}-\text{CH}_2\text{Cl}$ ; (9)  $(\text{CH}_3)_2\text{NCHO}$ ; (10)  $\text{C}_6\text{H}_6$ ; (11)  $\text{C}_6\text{H}_5\text{CH}_3$ ; (12)  $\text{C}_6\text{H}_5\text{-Br}$ ; (13)  $p\text{-(CH}_3)_2\text{C}_6\text{H}_4$ ; (p)  $\text{C}_2\text{H}_5\text{CN}$ ; (a)  $\text{CH}_3\text{CN}$ ; and (c)  $\text{CHCl}_3$ .

that this is the case.

The absorption spectrum of benzaldehyde was studied in various solvents at room temperature. Some typical spectra are shown in Figs. 1 and 2. The spectra in nonpolar or weakly polar solvents (*cf.* Fig. 1) give somewhat prominent vibronic bands. Although the  $n\pi^*$  spectra of benzaldehyde at  $\approx 300$  K are generally accompanied by several sequence bands relevant to CHO-group localized vibrations in the gas phase<sup>3)</sup>, *i.e.*,  $36_i^j$  ( $i=1-4$ ),  $35_j^j$  ( $j=1,2$ ), and  $25_k^k$  ( $k=1-3$ ), almost all of the "bands" in Fig. 1 are essentially assignable in terms of the band groups of  $0_g^g$  (designated as  $o$  in Fig. 1) and  $31_b^b$  ( $a$ ), and in terms of the  $7_n^n$  ( $nb$ ) progression bands ( $n=1-3$ ) thereof.<sup>4)</sup>

The spectral bands in high polar solvents such as chloroform and propionitrile, on the other hand, become considerably broad and shift toward the shorter wavelengths in contrast to the longer wavelength shifts of the  $S_2(\pi\pi^*) \leftarrow S_0$  bands (see Fig. 2). It has been known that these solvents form stoichiometric complexes with several aromatic carbonyl compounds.<sup>5)</sup> We confirmed this is also true for the present benzaldehyde case.<sup>6)</sup> As for these complex-forming solvent systems, it is extremely difficult to discriminate between the spectra of non-complex-forming benzaldehyde and complex-forming one because of weakness in their complex formation forces and little knowledge on the Franck-Condon factors of the complexes' spectra.

In Fig. 3 the partial oscillator strength of benzaldehyde,  $f_p$ , 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 intermolecular distance between the solute and solvent molecules. Nevertheless roughness in the approximation for  $\bar{r}$ , the observed intensities plotted by circles show an approximately linear increase with an increase in  $(\bar{\alpha}/\bar{r}^6)^2$ . This behavior is parallel to those in benzene<sup>7)</sup> and aliphatic ketones.<sup>1)</sup> For comparison, the data on the relative intensities in complex-forming solvents are also plotted by crosses. These intensities are presumed to be of overestimation because of considerable band overlap with the close lying  $S_2(\pi\pi^*) \leftarrow S_0$  absorption. Only a little intensity enhancements, however, were found; it should be noted that this contrasts with a characteristic correlation reported in the  $S_1(L_b) \leftarrow S_0$  spectra of pyrene.<sup>8)</sup>

We have also observed similar environmental enhancements in the  $S_1(n\pi^*) \leftarrow S_0$  absorption spectra of benzophenone and acetophenone. However, each band system was so diffuse that we found some difficulty in obtaining an appropriate intensity for it.

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## References

- 1) K. Nakashima, K. Uchida-Kai, M. Koyanagi, and Y. Kanda, *Bull. Chem. Soc. Jpn.*, **55**, 415 (1982).
- 2) E. Vander Donoekt and C. Vogels, *Spectrochim. Acta, Part A*, **28**, 1969 (1972) and references cited therein.
- 3) For the vibrational numbering, see: M. Koyanagi and L. Goodman, *Chem. Phys.*, **39**, 237 (1979).
- 4) J. Smalarek, R. J. Zwarich, and L. Goodman, *J. Mol. Spectrosc.*, **43**, 416 (1972); M. Koyanagi and L. Goodman, *ibid.*, to be published.
- 5) R. S. Becker, *J. Mol. Spectrosc.*, **3**, 1 (1959).
- 6) In binary mixed solvent systems of each of these polar solvents and hexane, we could observe several isosbestic points. Assuming 1 : 1 complex formation between benzaldehyde and each of these polar molecules, we obtained some equilibrium constants; *i.e.*,  $K = 1.03 \pm 0.15 \text{ dm}^3 \text{ mol}^{-1}$  for chloroform and  $K = 0.5 \pm 0.2 \text{ dm}^3 \text{ mol}^{-1}$  for propionitrile.
- 7) M. Koyanagi, *J. Mol. Spectrosc.*, **25**, 273 (1968).
- 8) A. Nakajima, *Bull. Chem. Soc. Jpn.*, **44**, 3272 (1971).