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Pressure and Solvent Shifts of Absorption Spectra. II. Intramolecular Charge Transfer Bands[1)]

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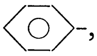
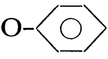
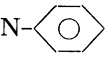
Absorption spectra of intramolecular CT bands of nitrobenzene, *p*-nitrophenol, *p*-nitroaniline, acetophenone, *p*-hydroxyacetophenone, and *p*-aminoacetophenone are observed in several nonpolar solvents at 1 bar, and in heptane up to 4400 bar. The fact that all solvent shifts are linearly red for the function of refractive index (n) of solvents, $(n^2-1)/(2n^2+1)$, consists with the solvent shift theory. On the other hand, the pressure shifts are not straight but convex upward for $(n^2-1)/(2n^2+1)$ and the red shifts by pressure exceeds the solvent shifts. The similar convex pressure shifts are found in ^1L_b bands of several aromatic compounds by plotting the high pressure data of Robertson *et al.* in spite of the straight solvent shifts in these ^1L_b bands measured by us. Therefore the convex pressure shift may be regarded as a general tendency of the electronic spectrum, being ascribed to decrease in the distance between a solute and the surrounding solvents by compression. From comparison with the pressure shift of the intramolecular CT band, it is suggested that, in the pressure shift of the intermolecular CT band of the I_2 complexes shifted to red previously, the effect of decrease in the bond distance between a donor and an acceptor proposed by Offen and Nakashima contributes to not a red shift but a blue shift.

The pressure shifts of the intermolecular charge transfer (CT) bands have been observed to be red,[1–7)] blue,[1,8)] and red to blue.[1,3,4,6)] Offen and Nakashima ascribed these shifts to a sum of two effects of the increase in the dielectric constant (or refractive index) of solvent contributing to a red shift and the decrease in the bond distance between a donor and an acceptor contributing to a red or blue shift,[8)] and their interpretation was supported by us.[1)] Whether the decrease in the bond distance contributes to a red or blue shift in the observed pressure shift may be clarified by eliminating the effect of increase in the dielectric constant of solvent from the pressure shift.

As the binding energy of the covalent bond between a donor and an acceptor in the chromophore of intramolecular CT band is much larger than that of CT interaction of the chromophore of intermolecular CT band (*i.e.*, CT complex), the bond distance between a donor and an acceptor in the chromophore of intramolecular CT band is thought to be far less compressible than that of the CT complex. Therefore, from comparison of the pressure shift between intermolecular and intramolecular CT band, the effect of decrease in the bond distance of CT complex by compression may become clear. In the present study, the pressure and solvent shifts of the intramolecular CT bands were interpreted in comparison with those of π-π^* (^1L_b) band of aromatic compounds, and then compared with those of intermolecular CT bands. Used chromophores of the intramolecular CT band are nitrobenzene, *p*-nitrophenol, *p*-nitroaniline, acetophenone, *p*-hydroxyacetophenone, and *p*-aminoacetophenone. These have well-defined CT bands in the ultraviolet region. In these chromophores, $-NO_2$ and $-\overset{\overset{O}{\|}}{C}CH_3$ (–Ac) correspond to acceptors, and –, HO-–, and H_2N-– correspond to donors.

Experimental

Nitrobenzene and acetophenone were distilled under reduced pressure. *p*-Nitrophenol, *p*-nitroaniline, *p*-hydroxyacetophenone, and *p*-aminoacetophenone were recrystallized from aqueous ethanol. Benzene, toluene, chlorobenzene, phenol, and solvents (pentane, hexane, heptane, cyclohexane, and decalin) were purified by usual method.[9)] The method of measuring the absorption spectra under high pressure was reported.[10)] Refractive indices (n) of the solvents at high pressure were estimated from the dielectric constant (ε) of Refs. 11, 12, and 13 using the relation, $n^2=\varepsilon$.

Results and Discussion

Solvent Shift. Comparison between the solvent and pressure shifts of CT band is important in order to investigate the contribution of the refractive index of solvents to the pressure shifts. Ooshika[14)] and McRae[15)] theoretically proposed Eq. 1 for the estimation of solvent shift of electronic spectrum in nonpolar solvents.

$$\Delta\tilde{\nu} \equiv \tilde{\nu}_s - \tilde{\nu}_0 = C_{solv}\frac{n^2-1}{2n^2+1}, \qquad (1)$$

where $\tilde{\nu}_0$ and $\tilde{\nu}_s$ are wavenumber at absorption maxima in the vapor and the solvent whose refractive index is n, respectively. C_{solv} is a constant and consists of a sum of two terms: one is the dispersive interaction between a chromophore and the surrounding solvents, and the other is the electrostatic interaction between the chromophore permanent dipole and the solvent dipole thereby induced. The values of $\tilde{\nu}_s$ in nonpolar solvents are expected to depend linearly on $(n^2-1)/(2n^2+1)$ of the solvents. Solvent shifts of several intermolecular CT bands in nonpolar solvents have been linear for $(n^2-1)/(2n^2+1)$ of the solvents.[1,16)] In Fig. 1 absorption maxima of intramolecular CT bands are plotted against $(n^2-1)/(2n^2+1)$ of nonpolar solvents. All CT bands shift to red linearly with increase in $(n^2-1)/(2n^2+1)$. Values of the slopes (C_{solv}) in Fig. 1 are shown in Table 1, and are comparable with those of intermolecular CT bands ($C_{solv} \approx 10^4$ cm^{-1}).[1,16)]

Pressure Shift. Figure 2 shows absorption spectra of intramolecular CT band of *p*-nitroaniline in heptane at several pressures. The absorption maximum shifts to red with increasing pressure. Other

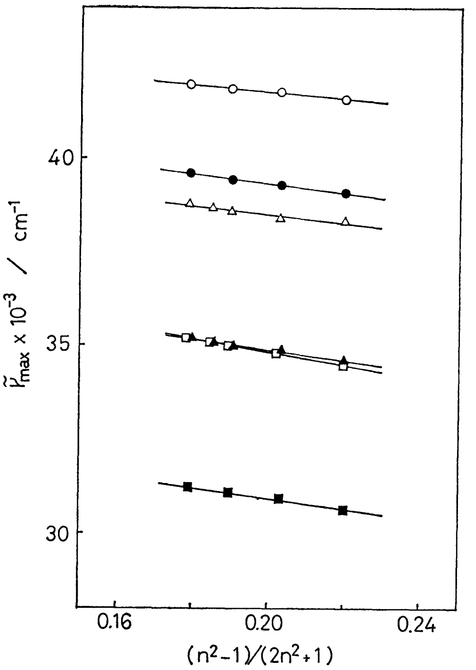


Fig. 1. Solvent shifts of several intramolecular CT bands.
○: ⌬-Ac, △: HO-⌬-Ac,
□: H_2N-⌬-Ac, ●: ⌬-NO_2,
▲: HO-⌬-NO_2, ■: H_2N-⌬-NO_2.
Solvents are pentane ($(n^2-1)/(2n^2+1)=0.179$), hexane (0.185), heptane (0.190), cyclohexane (0.203), and decalin (0.220).

Table 1. Slopes of solvent (C_{solv}) and pressure (C_{press}) shifts of several intramolecular CT bands

	C_{solv} / 10^3 cm^{-1}	C_{press}[a)] / 10^3 cm^{-1}
(A) Nitro compounds		
⌬-NO_2	-13 ± 2	-16 ± 3
HO-⌬-NO_2	-14 ± 2	-22 ± 3
H_2N-⌬-NO_2	-15 ± 2	-25 ± 3
(B) Acetyl compounds		
⌬-Ac	-9 ± 2	-10 ± 3
HO-⌬-Ac	-11 ± 2	-16 ± 3
H_2N-⌬-Ac	-15 ± 2	-19 ± 3

a) Estimated from the straight line through the two points at 1 and 1100 bar in Figs. 3 and 4.

intramolecular CT bands behave similarly. The observed shifts are plotted in Figs. 3 and 4 as a function of $\Delta[(n^2-1)/(2n^2+1)]$ of heptane. All of shifts are not straight for $\Delta[(n^2-1)/(2n^2+1)]$ but convex upward. Values of the initial slopes in Figs. 3 and 4 are shown in Table 1 as C_{press}. The red shift by pressure (C_{press}) exceeds the solvent shift (C_{solv}) in each chromophores.

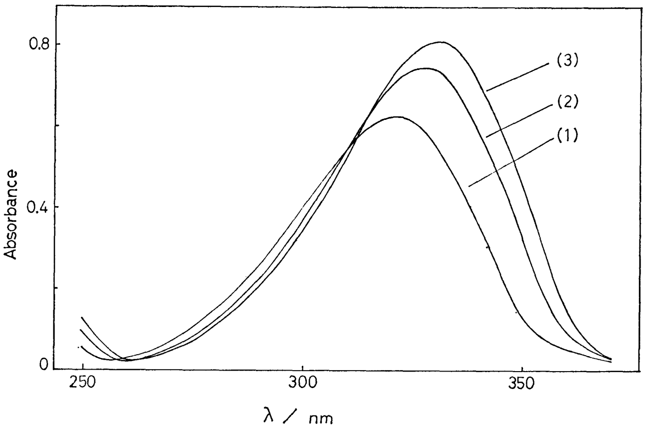


Fig. 2. Absorption spectra of intramolecular CT band of H_2N-⌬-NO_2 in heptane (2.7×10^{-5} mol dm^{-1}). (1) 1 bar, (2) 2.2 kbar, (3) 4.4 kbar. The absorptions are not corrected for compression.

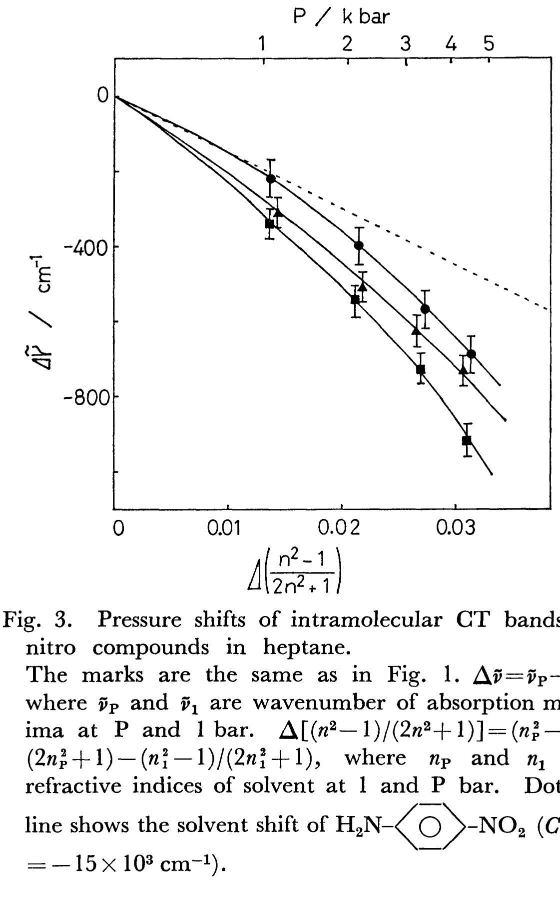


Fig. 3. Pressure shifts of intramolecular CT bands of nitro compounds in heptane.
The marks are the same as in Fig. 1. $\Delta\tilde{\nu}=\tilde{\nu}_P-\tilde{\nu}_1$, where $\tilde{\nu}_P$ and $\tilde{\nu}_1$ are wavenumber of absorption maxima at P and 1 bar. $\Delta[(n^2-1)/(2n^2+1)]=(n_P^2-1)/(2n_P^2+1)-(n_1^2-1)/(2n_1^2+1)$, where n_P and n_1 are refractive indices of solvent at 1 and P bar. Dotted line shows the solvent shift of H_2N-⌬-NO_2 ($C_{\text{solv}}=-15\times10^3$ cm^{-1}).

In the serieses of (A) and (B) of Table 1, the chromophores of larger C_{solv} values have larger C_{press} values. This fact shows that there is a contribution from the refractive index of solvent for the pressure shift of intramolecular CT band. The similar relation between C_{press} and C_{solv} was observed in the intermolecular CT bands of the series of I_2 complexes and tetracyanoethylene (TCNE) complexes (CT complexes with I_2 and TCNE as acceptors, respectively).[1)]

Pressure shifts of the electronic absorption spectra of molecules, such as π-π^* band or intramolecular

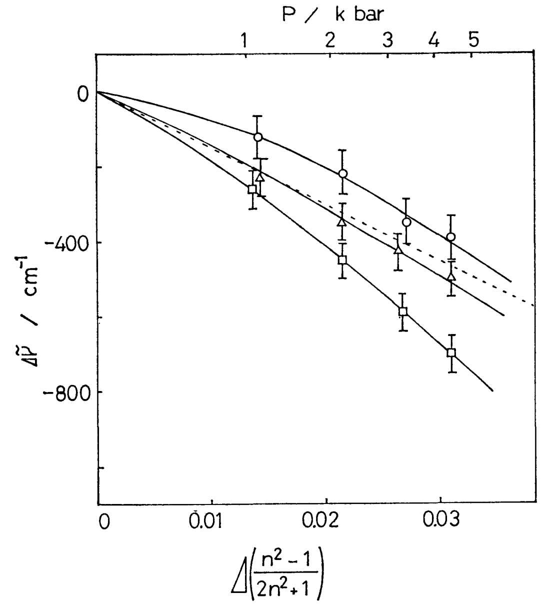
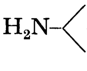


Fig. 4. Pressure shift of intramolecular CT band of acetyl compounds in heptane.
The marks are the same as in Fig. 1. $\Delta\tilde{\nu}$ and $\Delta[(n^2-1)/(2n^2+1)]$ are defined in Fig. 3. Dotted line shows the solvent shift of H$_2$N--Ac ($C_{\text{solv}}=-15\times10^3$ cm^{-1}).

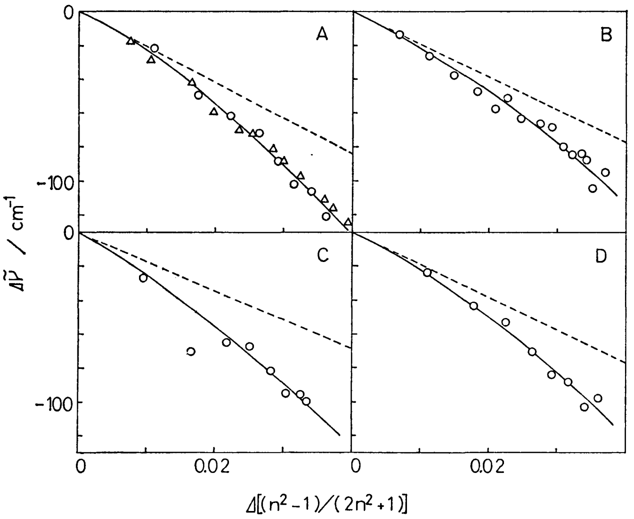


Fig. 5. Comparison between pressure and solvent shifts of ^1L_b band of several aromatic compounds.
A: Benzene at 261 nm, $C_{\text{solv}}=-2100$ cm^{-1}. B: Toluene at 271 nm, $C_{\text{solv}}=-1900$ cm^{-1}. C: Chlorobenzene at 271 nm, $C_{\text{solv}}=-1700$ cm^{-1}. D: Phenol at 277 nm, $C_{\text{solv}}=-1900$ cm^{-1}. Data of pressure shifts (—) in pentane (△) and hexane (○) were cited from Ref. 17 and solvent shifts (----) were estimated in present work as well as in Fig. 1.

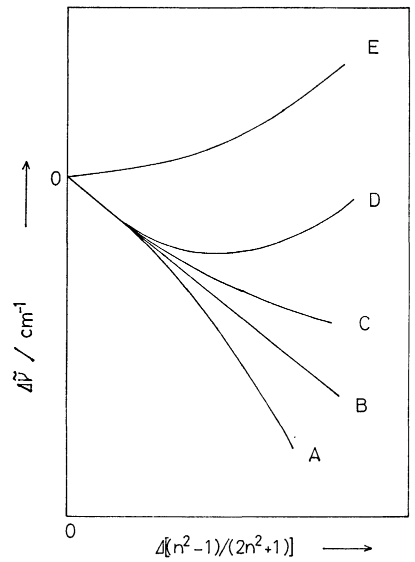


Fig. 6. Several patterns of pressure shift.
A: Convex red shift which should be normal for the pressure shift. Intramolecular CT bands in Figs. 3 and 4 and ^1L_b bands in Fig. 5. B: Straight red shift which is redder than the solvent shift. Benzene- and toluene-I$_2$ complexes. C: Concave red shift. Mesitylene- and Et$_2$O-I$_2$ complexes. D: Inversion shift from red to blue. Hexamethylbenzene-, Et$_2$S-, and Et$_2$Se-I$_2$ complexes. E: Blue shift. Et$_3$N-, n-Pr$_3$N-, and n-Bu$_3$N-I$_2$ complexes.

CT band, have been studied without an attention whether the shift is convex or not for $(n^2-1)/(2n^2+1)$ of solvent. Then the previous data of pressure shifts should be reexamined. As such data, only the table of absorption maxima (λ_{max}) in π-π^* (^1L_b) bands of several aromatic compounds by Robertson *et al.*[17] can be evaluated. The data is plotted in Fig. 5 as a function of $\Delta[(n^2-1)/(2n^2+1)]$ of solvent. All pressure shifts are not straight for $\Delta[(n^2-1)/(2n^2+1)]$ but convex upward as well as those of intramolecular CT bands in Figs. 3 and 4, though the solvent shifts (dotted lines in Fig. 5) measured by us as well as in Fig. 1 are straight for $(n^2-1)/(2n^2+1)$ of solvents. The deviation of pressure shift from the solvent shift is observed.

The solvent shift theory of Ooshika and McRae expressed by Eq. 1 considers the dispersive interaction and the electrostatic interaction between a chromophore and the surrounding solvents. Such interactions are a function of the distance between a chromophore and the solvents, and enhanced with decrease in the distance. Therefore, if the distance decreases by compression, pressure shift should deviate from the shift estimated by Eq. 1 and its deviation should become large with increasing $(n^2-1)/(2n^2+1)$ of solvent (or increasing pressure). The pressure shifts in Figs. 3, 4, and 5 deviated from the solvent shifts may be ascribed to such an effect.

Pressure shifts of intermolecular CT bands of I$_2$ complexes observed in the preceding paper[1] are not convex upward but concave or straight as shown in shifts B, C, D, and E of Fig. 6, where absolute values of the shifts are out of consideration and only the patterns of shifts (*i.e.*, straight, convex, or concave shift) are considered. In comparison with the convex shift (shift A) of the intramolecular CT band, there seems to be a blue shift contribution for the shifts of intermolecular CT bands, not only shifts D and E but also shifts B and C. As such difference in the pressure shifts between the intermolecular and intramolecular CT bands seems to correspond to whether the bond distance between a donor and an acceptor is reducible or not by compression, the contribution to the pressure shift of the I_2 complexes from the decrease in the bond distance is thought to be a blue.

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