Intermolecular Charge-Transfer Spectra. II. Pressure Effect on the Characteristic Absorption Spectra of Molecular Complexes

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Previously, Gibson and Loeffler studied the absorption of visible light by solutions of amins in nitrobenzene under large hydrostatic pressures, and observed the significant change of absorption as a function of pressure.[1] Recently, Shuler presented a free electron model to explain the characteristic absorption spectra of molecular complexes, especially the above-mentioned pressure effect on these spectra.[2] According to our opinion, however, Shuler's theory is not a suitable one for the explanation of the present problem, at least in its original form. In the following discussion, we show that the kinetic consideration of Gibson and Loeffler combined with Mulliken's theory[3] may probably be sufficient to explain the observed pressure effect.

Discussion on Shuler's Theory

The essence of Shuler's theory can be summarized as follows. When two one dimensional conjugated molecules, A and B, ap-

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[1] R. E. Gibson and H. Loeffler, *J. Am. Chem. Soc.* **62**, 1324 (1940); See also, **61**, 2877 (1939).

[2] K. E. Shuler, *J. Chem. Phys.*, **20**, 1865 (1952).

[3] R. S. Mulliken, *J. Am. Chem. Soc.*, **74**, 811 (1952).

proach sufficiently close, the potential for π-electrons can be expressed by the idealized model as shown in Fig 1. Then, the penetration of the central potential barrier by π-electrons produces a splitting of energy levels in the resulting two minimum potential. It was difficult, however, to obtain these splittings quantitatively for the unsymmetrical potential as described above, and Shuler assumed the simplified symmetrical potential as shown in Fig. 2. For this model, each original energy level of the free molecule splits into two, and this situation is shown in Fig. 3. On account of the assumption of symmetrical potential, one has the simple relationship

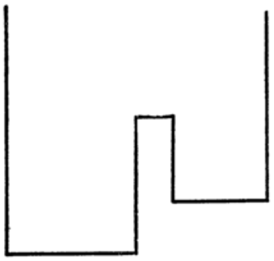


Fig. 1—One-dimensional unsymmetrical potential model for molecular complex.

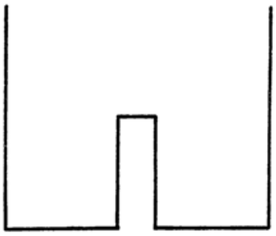


Fig. 2.—Simplified symmetrical potential model which is assumed by Shuler for molecular complex.

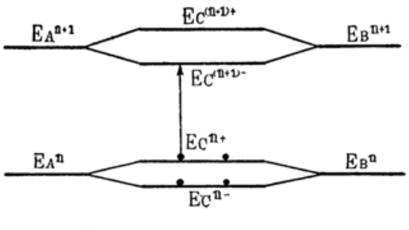


Fig. 3.—Splitting of energy levels by complex formation in case of symmetrical potential

$$E_A{}^n = E_B{}^n \tag{1}$$

for all the energy levels of the conjugated molecular partners. Taking the splitting of each level into account, the energy levels E_C of the complex which correspond to the energy levels $E_A{}^n$ and $E_B{}^n$ of A and B can be expressed as follows:

$$E_C{}^{n+} = E_A{}^n + \varepsilon^n \tag{2}$$

$$E_C{}^{n-} = E_A{}^n - \epsilon^n \tag{3}$$

where $2\epsilon^n$ is the delocalization energy for the n the level. If $E_C{}^{n+}$ is the highest filled level of the complex, the main absorption band is then due to the transition

$$\mathrm{E}_C{}^{n+} \longrightarrow E_C{}^{(n+1)-}$$

where

$$E_C{}^{(n+1)-} = E_A{}^{(n+1)} - \epsilon^{(n+1)} \tag{4}$$

and the wavelength λ_C of this absorption peak is given by

$$\lambda_C = \frac{hc}{\varDelta E} = \frac{hc}{[E_A{}^{(n+1)} - E_A{}^n] - [\epsilon^{(n+1)} + \epsilon^n]} \tag{5}$$

Now, Shuler postulated that the effect of pressure reduced the width and height of central potential barrier corresponding to the closer approach of both components. This situation produces an increase of delocalization energy ϵ on account of easier penetration by π-electrons through the barrier. Consequently, as is seen in Eq. (5), the increase of ϵ produces an increase of λ_C, so long as one assumes the constancy of $[E_A{}^{(n+1)} - E_A{}^n]$. Thus, Shuler's theory predicts the shift of main absorption band towards the longer wavelength side at higher pressure.

We must emphasize, however, that the assumption of symmetrical potential is not adequate to amine-nitrobenzene complexes. In these cases, the potentials are rather unsymmetrical as shown in Fig. 4. And so, the condition of Eq. (1) becomes no longer valid. Then, Eqs. (2), (3), (4) and (5) lose their validity. According to Mulliken's theory, the characteristic absorption band of molecular complex (A B) corresponds essentially to the transition, as follows.

$$(\mathrm{A\,B})^{\cdot} \longrightarrow (\mathrm{A}^- \!-\! \mathrm{B}^+)$$

That is, one electron is transferred from B to A in the process of optical transition. In a free electron model, this situation should be expressed by the transfer of a π-electron from level N_B to level $(M+1)_A$ as shown in Fig. 4. Further, in the case of an unsymmetrical model, the delocalization energy may be mainly due to the small amount of penetration of π-electron from level N_B to

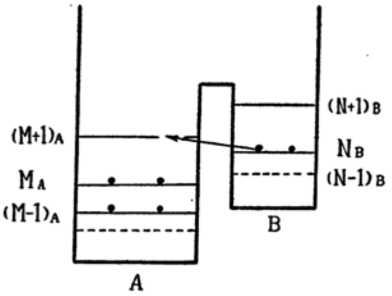
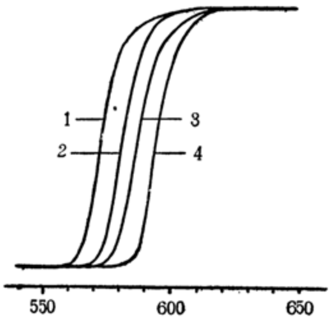


Fig. 4.—Expected relative height of energy level in case of unsymmetrical potential. (In the present case, component A and B corresponds to nitrobenzene and dimethylaniline respectively).

level $(M+1)_A$ through the potential barrier. Thus, the application of Shuler's model may probably be limited to the self-complex such as benzene-benzene complex.

Discussion on Absorption Intensity

The typical experimental results of Gibson and Loeffler are shown in Fig. 5 for 50% solution of dimethylaniline in nitrobenzene at 45°. The results are given as transmission curves. Curve 1 and 3 is the case of solution in 0.5 cm. cell at 1 bar and 1000 bars respectively. Curve 2 and 4 is the case of solution in 0.9 cm. cell at 1 bar and 1000 bars respectively. It must be emphasized that these curves are nothing but a very small portion of the complete absorption band, and the behaviours at the region of absorption maximum under the influence of pressure are not observed. Then, we cannot conclude directly the shift of absorption bands towards the longer side so long as the data are limited to the above mentioned ones.



Wave length, mμ (approx.)

Fig. 5.—Transmission curves for 50% solution of dimethylaniline in nitrobenzene at 45°

1, solution in 0.5 cm cell at 1 bar;
2, solution in 0.9 cm cell at 1 bar;
3, solution in 0.5 cm cell at 1000 bars;
4, solution in 0.9 cm cell at 1000 bars.

Moreover, the comparison between curves 1 and 2 suggests that the pressure effect is mainly due to the intensification of light absorption. In case of curve 2, the absorbing layer is increased 1.8-fold in thickness compared with curve 1. Consequently, we can expect that the degree of light absorption is also increased by the same amount. This situation appears in Fig. 5 as if the absorption band is pushed towards the longer wavelength side, although the location of the absorption band should be the same in either case. If we assume that the pressure effect is only due to the intensification of light absorption, the distance between curves 1 and 3 or curves 2 and 4 requires that the absorption intensity is 2.5~3.5-fold increased under the pressure of 1000 bars, at least in the region of the observed wavelength.

At the present stage, we cannot give any conclusion whether the wavelength at absorption maximum shifts towards the longer or shorter side, or remains at the same position under the effect of pressure. On the other hand, however, we can give a rather definite explanation of the intensification of light absorption, as follows.

Gibson and Loeffler assumed that the absorption of visible light by the solution was proportional to the average time the active groups of unlike molecules spent very close to each other, i.e., to the probability of finding two unlike molecules at very short distances apart and suitably oriented in the solution. Using kinetic consideration and some empirical relations which were obtained by them, they showed that the above hypothesis was sufficient to explain the intensification of light absorption due to the increase of pressure at constant temperature or the elevation of temperature at constant volume. Then, the remaining task is to base the hypothesis of Gibson and Loeffler by Mulliken's theory on intermolecular charge-transfer spectra.

According to Eq. (12) in Part I, the dipole moment of charge-transfer spectra is approximated by the formula

$$\mu_{EN} \simeq e_{ab}(\vec{r}_B - \vec{r}_A) \qquad (6)$$

were

$$b/a \simeq -H_{01}/(W_1 - W_0) \qquad (7)$$

As has been discussed in Part I, dipole moment μ_{EN} is sensitive to the value of H_{01}. Since absorption intensity f_{EN} is proportional to the square of μ_{EN}, f_{EN} is much more sensitive to the value of H_{01}. Further, as can easily be seen from Eq. (6) in Part 1, the value of H_{01} is very sensitive to the overlap between the wavefunctions (in the present case, between that of π-electron systems) of both components. The degree of overlap depends very much on the distance and relative orientation between both components. Consequently, the increase of the probability of finding two unlike molecules, A and B, at very short distances apart and suitably oriented in a solution makes the absorption intensity much larger. Thus, the hypothesis of Gibson and Loeffler is based by the theory of intermolecular charge-transfer spectra.

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