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Solvent Effects on the Absorption and Emission Spectra of *p*-Aminoacetophenone

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The absorption and emission spectra of *p*-aminoacetophenone (PAAP) were measured in various solvents at different temperatures. Several interesting facts have been revealed: PAAP, which is non-fluorescent in other solvents, fluorescences strongly in the ethanol matrix at 77°K; the ratio of the intensity of fluorescence to that of phosphorescence varies according to the wavelength of the exciting light; the phosphorescence band shifts largely by changing the temperature. Explanations for these observed results have been given by considering that the lowest $^1(\pi\rightarrow\pi^*)$ level and the $^1(n\rightarrow\pi^*)$ level lie fairly close to each other in this molecule and a reversal of the energy levels occurs by changing the solvent and the temperature. The lowest triplet state of PAAP is concluded to be $^3(\pi\rightarrow\pi^*)$ and not $^3(n\rightarrow\pi^*)$.

It is known that *p*-disubstituted benzenes having the electron accepting and donating groups show characteristic ultraviolet absorption bands in the near ultraviolet region which shift largely by changing the solvent.¹⁾ Experimental and theoretical researches have shown that these absorption bands are characterized to be the

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1) W. D. Kumler, *J. Am. Chem. Soc.*, **68**, 1184 (1946).

intra-molecular charge-transfer (CT) spectrum.[2] These molecules are therefore believed to have strongly polar structures and hence large electric dipole moments in the excited states. The large spectral shift may be attributed mainly to the stronger interaction of the excited molecule with the solvent.

Aromatic ketones, such as acetophenone and benzophenone, generally show no fluorescence, but fairly strong phosphorescence at the low temperature. In these molecules, both the lowest excited singlet and triplet states are believed to be the $(n\rightarrow\pi^*)$ states, where an electron from the lone pair orbital of the oxygen atom is excited into a vacant π^* molecular orbital. By substituting an amino group or any other electron-donating group at the para-position, the triplet $(\pi\rightarrow\pi^*)$ level becomes the lowest, leading to a strong change in the phosphorescence lifetimes and the photochemical reactivities of these molecules.[3]

We present here a new example of the reversal of the electronic excited states induced by the solvent effect, found from the study of the absorption and emission spectra of *p*-aminoacetophenone (abbreviated as PAAP hereafter). Somewhat similar phenomena of the reversal of levels caused by the solvent effect have been reported for *N*-heterocycles.[4,5]

Experimental

Apparatus. The absorption spectra were measured with a Cary spectrometer Model 15 using 1 cm and 10 cm quartz cells. Low temperature absorption spectra were measured by using a qualtz Dewar vessel and a cylindrical cell of 1.5 cm diameter.

The emission spectra and its excitation spectra were measured with an Aminco-Bowman spectrophotofluorimeter. The solutions were degassed by the freeze-thaw technique. The lifetimes of the triplet states were determined from the decay curves of the phosphorescence intensities traced by the oscilloscope.

Materials. *p*-Aminoacetophenone (PAAP) was recrystallized from ethanol, washed with ether and *n*-heptane, and then sublimed in vacuum. *p*-Aminobenzoic acid and *p*-nitroaniline were purified by recrystallization from ethanol followed by sublimation in vacuum.

Solvents used for the emission study (ethanol, ether and isopentane) were dried and distilled. These solvents showed no fluorescence or phosphorescence at the level of the sensitivity used. Other solvents used for the measurements of absorption spectra (*n*-heptane, benzene, chloroform, carbon tetrachloride, dimethylformamide and formamide) were the special reagent grade and were used without further purification. Water used was distilled and passed through an ion exchange column to remove heavy metal ions.

Results and Discussion

Absorption Spectra. The solvent shifts of the absorption spectra of PAAP are shown in Fig. 1. The longest-wavelength band has a strong intensity, $\varepsilon=(1-2)\times10^4$, and is certainly assigned to be an allowed $\pi\rightarrow\pi^*$ band. The solvent shift is abnormally large compared to those of the ordinary aromatic compounds. One may recognize a weak tail in the absorption spectrum of a concentrated *n*-heptane solution which is most probably assigned to the $n\rightarrow\pi^*$ band of PAAP. The $\pi\rightarrow\pi^*$ band shifts further by lowering the temperature down to 77°K as shown in Fig. 2.

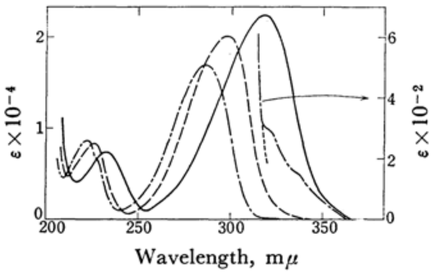
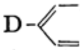
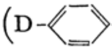
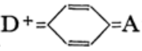


Fig. 1. Absorption spectra of PAAP at room temperature.
—— in ethanol —— in EP
---- in *n*-heptane

We have confirmed that PAAP is practically non-fluorescent in *n*-heptane or in EP (a mixture of 4 vol ether and 1 vol isopentane). This suggests that the lowest excited singlet state is $^1(n\rightarrow\pi^*)$ in these solvents. The result is compatible with the assignment of the weak tail found in the concentrated heptane solution to the $n\rightarrow\pi^*$ band.

As mentioned previously, compounds of the D--A type have a typical intense absorption band in the near-ultraviolet region. The transition corresponding to this absorption band is qualitatively represented as being from the ground state (D--A) to the CT excited state (D⁺==A⁻). The two states therefore have dipole moments differing widely from each other. In polar solvents, therefore the upper state receives a large dipole-dipole interaction between solute and solvent molecules and will show a large solvent shift. In the present case, three different types of solute-solvent interactions should be taken into account: (1) hydrogen-bonding, (2) dipole-dipole interaction (including small higher-order electrostatic interactions) and (3) electronic polarization

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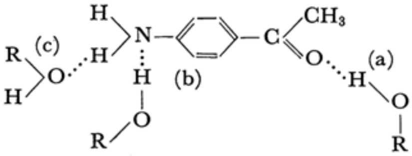
[2] J. Tanaka, S. Nagakura and K. Kobayashi, *J. Chem. Phys.*, **24**, 311 (1956).

[3] G. Porter and P. Suppan, *Trans. Faraday Soc.*, **61**, 1664 (1965).

[4] N. Mataga and S. Tsuno, This Bulletin, **30**, 368 (1957); N. Mataga, *ibid.*, **31**, 459, 487 (1958).

[5] V. L. Ermolaev and I. P. Kotlyar, *Opt. and Spectry.*, **9**, 183 (1960).

effect of the solvent.[6,7] As for the hydrogen-bonding, three types may be considered to take place as shown below.



In the 'vertical' or 'Franck-Condon' excited state, the configurations of the solvent molecules relative to a solute molecule should remain unchanged. At this state, type a) and c) hydrogenbondings are thought to stabilize the upper state more than the ground state and hence to cause the red shift, while type b) hydrogen-bonding should cause the blue shift, because it is unstable in the upper state. The dipole-dipole interaction should cause a red shift for the case of PAAP, because, in this case, the direction of the dipole moment of the molecule in the upper state is the same as that in the ground state. The electronic polarization effect of the solvent should always cause the red shift. This red shift must be of the same order whether the solvent is polar or nonpolar.

From these considerations it may be deduced that, as the solvent becomes polar, the net solute-solvent interactions will lead to the red shift of the first absorption peak of PAAP. This conclusion is in accordance with the results shown in Table 1.

TABLE 1. THE WAVELENGTHS OF THE FIRST AND THE SECOND INTENSE $^1(\pi\rightarrow\pi^*)$ ABSORPTION PEAKS OF PAAP IN VARIOUS SOLVENTS AT ROOM TEMPERATURE

Solvent	The second peak, mμ	The first peak, mμ	Dielectric constant* (20°C)
(Vapor)	215	270	1.00
n-Heptane	223	283	1.924
Carbon tetrachloride	—	293	2.238
EP	226	297	—
Benzene	—	298	2.284
Ether	227.6	301	4.335
Chloroform	—	301	4.806
Acetonitrile	228	303.5	37.5**
Dimethylformamide	—	314	36.7
Formamide	—	316	109.5
Ethanol	233	318	24.30**
Methanol	231	317	32.63**
Water	230	311	80.37

* A. Weissberger, ed., "Organic Solvents," 2nd Ed., Intersci. Publ., Inc., New York (1955).
** At 25°C.

The reason why the band shifts further to the red in EP and ethanol solutions by lowering the temperature (Fig. 2) may also be explained by taking into account the enhanced hydrogen-bonding and orientation of the solvent molecules at the low temperature. The abnormally large magnitude of this temperature effect in this case may be attributed to the large change in the dipole moments between upper and lower states.

Emission Spectra. As it has already been pointed out, PAAP in *n*-heptane and EP solutions is practically non-fluorescent. However, we have found that it shows a fairly strong emission band with the maximum at 350 mμ in ethanol solution at 77°K, together with the phosphorescence band (Fig. 2A). There is no doubt that the emission band is the fluorescence band of PAAP, namely, due to the transition from the $^1(\pi\rightarrow\pi^*)$ state to the ground state, because it is in a good mirror-image relation with the absorption spectrum. This emission band decreases in intensity as the temperature is raised, but is observable even at room temperature. A very weak fluorescence band is also observed in the EP solution at 77°K (Fig. 2B). From its position, the band may be assigned to the same fluorescent transition of PAAP as observed in the ethanol solution. In this case, the band is so weak at room temperature that no definite evidence for its existence was obtained.

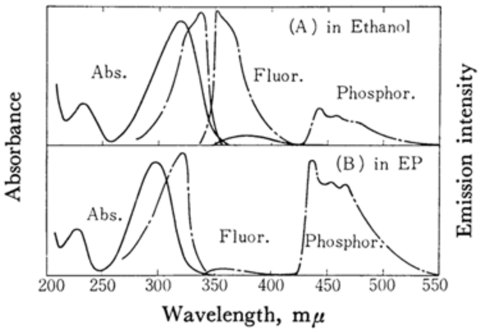


Fig. 2. Absorption and emission spectra of PAAP.
---- at 77°K, —— at room temperature

Generally speaking, the intensities of the fluorescence bands of organic molecules are not much changed by the temperature, though a small amount of intensification at low temperature is sometimes experienced which is probably due to the depression of radiationless deactivation. In order to see how much this amounts to in the present case, several compounds which have similar structures as PAAP are chosen and their emission spectra have been measured. *p*-Aminobenzoic acid, as an example, shows both fluorescence and phosphorescence bands at 77°K, and the intensity of the former is almost the same as that at room temperature. The excitation spectra for the

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[6] Y. Ooshika, *J. Phys. Soc. Japan*, **9**, 594 (1954).
[7] E. G. McRae, *J. Phys. Chem.*, **61**, 562 (1957).

phosphorescence and fluorescence bands of *p*-aminobenzoic acid agree with each other.

We have found an interesting fact that the relative fluorescence to phosphorescence intensity ratio [F/P] varies with the wavelength of the exciting light. In general, the conversion from a singlet state to a triplet state (inter-system crossing) is slower than the internal conversion between singlet states, and, hence, the former usually occurs through the lowest singlet excited state. The ratio [F/P] of ordinary organic compounds, therefore, does not vary by the excitation wavelength. This means that identical excitation spectra are usually obtained for the fluorescence and phosphorescence. In the case of PAAP, the excitation spectra of the fluorescence and phosphorescence are quite different as shown in Fig. 3. From the comparison of these with low temperature absorption spectra in Fig. 2, it is seen that the excitation spectrum for the phosphorescence in the EP matrix corresponds to the absorption spectrum, and in the ethanol matrix the excitation spectrum for the fluorescence corresponds to the absorption spectrum. The excitation spectrum for the phosphorescence in the ethanol matrix has its peak at the shorter wavelength than the absorption peak. The weak fluorescence in the EP matrix is observable only when the sample is excited at the longest wavelength end of the absorption.

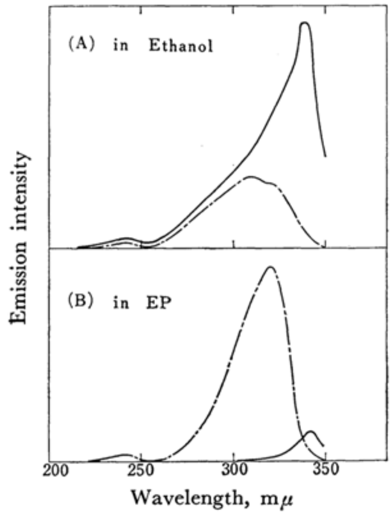
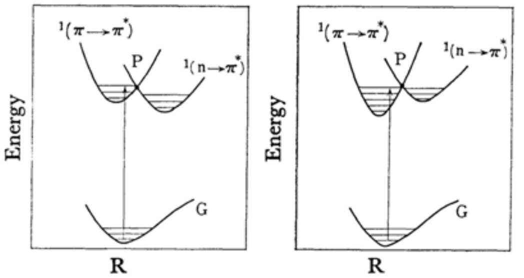


Fig. 3. Excitation spectra for the fluorescence, ——, and for the phosphorescence, –·–·–, of PAAP at 77°K. Concn. 10^{-5} mol/*l*

A tentative explanation for these rather peculiar observed results will be given below. Firstly, as seen from the absorption spectra of PAAP in various solvents and temperatures, the $^1(\pi\to\pi^*)$ level of this molecule is stabilized largely in polar solvents, and further stabilized at 77°K. The 'vertical' $^1(n\to\pi^*)$ state of this molecule, on the other hand, is not stabilized or even destabilized in EP and ethanol solutions compared to the cases in nonpolar solutions. In nonpolar solvents, the $^1(\pi\to\pi^*)$ level is a little higher than the $^1(n\to\pi^*)$ level as is the case for acetophenone. Consequently, it may be assumed that in the EP solution at 77°K and in the ethanol solution at room temperature, the two levels come very close to each other (we call it an intermediate case), and in 77°K ethanol, the $^1(n\to\pi^*)$ state becomes higher than the $^1(\pi\to\pi^*)$ state. Schematic diagrams are drawn to explain the energy relations of these states as shown in Fig. 4. Here, the abscissa is of a very complex nature representing the configurational of the solvent molecules around a solute molecule. The energy curves show qualitatively that the upper and lower electronic levels have energy minima at certain points in the configurational coordinate R. The transition probability from G to $^1(\pi\to\pi^*)$ is overwhelmingly large compared to that from G to $^1(n\to\pi^*)$. Hence when the exciting photons have energies lower than the 'crossing point' P, the probability for the tunnelling to the non-fluorescent $^1(n\to\pi^*)$ level may be of a comparative order to the probability for direct fluorescent transition to G.[*2] But when photon energy is higher than P, the excitation energy transfers mostly to the $^1(n\to\pi^*)$ level, and no fluorescence should appear. This mechanism explains the reason why a very weak fluorescence is observed for the EP solution at 77°K and for the ethanol solution at room temperature. It also explains why the excitation spectrum for the fluorescence of the EP solution lies near the longest-wavelength limit of the absorption bands. For the ethanol solution at 77°K, the energy of the $^1(\pi\to\pi^*)$ state is lower than that of the $^1(n\to\pi^*)$ (Fig. 4B). In this case, most of the excitation energy can be emitted as fluorescence.



(A) Intermediate case (B) Inverted case

Fig. 4. Schematic energy diagrams for the electronic states of PAAP with respect to the configuration coordinate.

[*2] Actually, the configurational coordinate R is a multidimensional coordinate, and so we cannot define a 'crossing point' P. The statement here should be taken to represent only that the rate of tunnelling is the smaller, the lower the photon energy.

TABLE 2. THE LIFETIMES AND THE WAVELENGTHS OF THE PHOSPHORESCENCE BANDS OF SUBSTITUTED BENZENES

Solute	Solvent	Temperature °K	Lifetime sec	The short wave-length limit,* mμ
PAAP	Ethanol	77 and 90	1.0	425
		100 — 150	1.4**	460
	EP	77	0.7	420
	9 vol ethanol + 1 vol 1 N HCl_{aq}	77	1.0*** <0.1***	425 375
Acetophenone	Ethanol	77	0.008	375
	EP	77	—	377
Aniline	Ethanol	77	4.6	350
	EP	77	5.5	360
p-Aminobenzoic acid	Ethanol	77	3.1	400
	EP	77	3.0	395
Benzoic acid	Ethanol	77	2.3	355
p-Nitroaniline	Ethanol	77	0.4	485

* The values change slightly by the slit width. We made all measurements with the same slit width in order to see the correct relative values.

** This value corresponds to that for the shifted phosphorescence in Fig. 5. In spite of the higher temperature, the lifetime becomes longer than at 77°K.

*** In this solvent, there are two components of the phosphorescence; one is that of PAAP and the other seems to be that of *p*-acetylanilinium ion because of its spectral similarity to that of acetophenone.

The Mechanism of the Inter-system Crossing. In Table 2, the lifetimes of the phosphorescence emission of PAAP and related compounds measured in various conditions are tabulated. The lifetimes of PAAP are of the order of a second in all conditions measured, suggesting that the phosphorescence is due to the transition from the ${}^3(\pi\rightarrow\pi^*)$ state, not from the ${}^3(n\rightarrow\pi^*)$, for, if the latter is the case, the emission would have a lifetime of the order of 1 msec.[*3]

Now, the observed result that the excitation spectrum for the phosphorescence in the case of 77°K ethanol solution has a peak at a shorter wavelength than the absorption peak is a rather strange one and seems to be explained only by assuming that the rate of the inter-system crossing is large when the photon energy is higher than the 'crossing point' P. If this is true, the inter-system crossing occurs mostly through the following course:

$$G \underset{(3)}{\rightleftarrows} {}^1(\pi\rightarrow\pi^*) \xrightarrow{(1)} {}^1(n\rightarrow\pi^*) \xrightarrow{(2)} {}^3(\pi\rightarrow\pi^*)$$

It has already been pointed out that the process (1) is the more efficient with photons of the higher energy. The process (2) may have a fairly high rate,[8] which will easily surmount that for the radiationless decay of the ${}^1(n\rightarrow\pi^*)$ state.

On the other hand, if the photon energy is lower than P, the step (1) occurs rarely and most of the excitation energy is dissipated very rapidly by the emission of fluorescence (step (3)).

In most other cases, the energy relation is like that shown in Fig. 4A, so that the excitation energy is mostly transferred to ${}^1(n\rightarrow\pi^*)$. Hence in such cases the excitation spectra for the phosphorescence should agree with the absorption spectrum, in accord with observed results. The above-mentioned explanation inevitably implies that the rate of transfer from ${}^1(\pi\rightarrow\pi^*)$ to ${}^3(\pi\rightarrow\pi^*)$ or ${}^3(n\rightarrow\pi^*)$ is very small. The reason why the transfer from ${}^1(\pi\rightarrow\pi^*)$ to ${}^3(\pi\rightarrow\pi^*)$ is slow may be explained by El-Sayed's theory. We cannot specify at present the reason why the transfer from ${}^1(\pi\rightarrow\pi^*)$ to ${}^3(n\rightarrow\pi^*)$ is slow.

Anomalous Temperature Effect upon the Phophorescence Spectrum of PAAP. We have found a very peculiar change of the phosphorescence spectrum of PAAP by the temperature. At 77°K, the phosphorescence band has some substructures with the maximum at 440 mμ. As the temperature is raised from 100°K to 130°K, this 440 mμ component decreases in intensity and another component centered at 480 mμ appears (Fig. 5). Above 150°K, the shape of the spectrum does not change and only the intensity decreases. When the sample is recooled to 77°K, the phosphorescence spectrum of PAAP has been found to return to the original curve. The lifetimes of both the 440 mμ and 480 mμ components are found to

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[*3] The results in Table 2 also indicate that the lowest triplet levels of *p*-aminobenzoic acid and *p*-nitroaniline are not ${}^3(n\rightarrow\pi^*)$ but ${}^3(\pi\rightarrow\pi^*)$, because their lifetimes are also of one second. Although these results have no direct connection with the present discussion, they are included in the table, because they seem to give some interesting informations concerning the relative height of various excited states in substituted aromatics.

8) M. A. El-Sayed, *J. Chem. Phys.*, **38**, 2834 (1963).

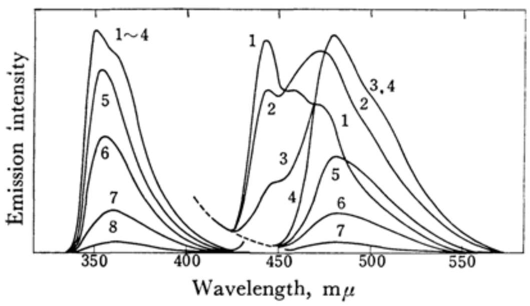

Fig. 5. The effect of temperature upon the emission spectra of PAAP in ethanol. The curves are numbered in the order of rising temperature: 1. 77—90°K; 2—4. 100—150 °K; 8. 200°K.

be of the same order. In the EP matrix, on the other hand, the phosphorescence spectrum weakens normally as the temperature is raised from 77°K.

This anomalous behavior of the phosphorescence spectrum of PAAP in ethanol may be explained by taking the solvent effect into consideration as follows. In the low temperature ethanol matrix, the solvent molecules are oriented around the PAAP molecule so that the hydrogen-bonding and other solute-solvent interactions are the strongest. When the phosphorescent $^3(\pi\rightarrow\pi^*)$ state is reached by the photo-excitation, the solvent molecules still stay at positions not much different from those in the ground state, because the gross movements of the solvent molecules are inhibited in the rigid matrix. As the matrix is warmed, the solvent molecules become free to move and reorient themselves so as to take the equilibrium configuration for the $^3(\pi\rightarrow\pi^*)$ state during its lifetime, leading to a new phosphorescence band at the longer wavelength. The same change is expected to take place in the EP matrix, but with much smaller magnitude. Other explanations, for instance, a transient dimer-formation, might also be possible. But we prefer the former explanation at the present stage, because of the fact that this phenomenon only occurs in ethanol.

The authors wish to express their sincere thanks to Professor Noboru Mataga for helpful discussions. Our thanks are also due to Dr. Katsumi Kimura for his kind suggestion upon the electronic structures of the benzene derivatives.