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Nanosecond Laser Photolysis of *N*-Methylindole in Acetonitrile

Nobuaki KANAMARU and Jiro TANAKA
Department of Chemistry, Faculty of Science, Nagoya University, Furo-cho, Chikusa-ku, Nagoya, Aichi 464
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Nanosecond laser photolysis (nslp) of *N*-methylindole (NMI) was investigated using XeCl laser (308 nm) so that excitation is performed at the red edge of the first absorption band. At least three transient absorptions were observed i.e. those to be ascribed to $S_n \leftarrow S_1$, $T_n \leftarrow T_1$ transitions and ion-pair like species with peaks at ≈ 700 nm, ≈ 460 nm, and ≈ 380 nm, respectively. The transient absorptions were found to be produced by monophotonic processes. The lifetimes of the triplet state and the ion pair were determined to be ≈ 3.1 μs and ≈ 29 μs, respectively, in degassed solutions. Transient photoconductivity (tpc) measured on the same system indicated that there are both rise and decay components. Its fastest decay component of ≈26 μs is close to that of the transient absorption ascribed to the ion pair. This result provides another example of monophotonic electron ejection through fluorescent states of aromatic amines in polar solvents, such as, acetonitrile.

Potophysics and photochemistry (especially photoionization) of indole and its derivatives including tryptophan have been the subjects of intensive research. As for photophysics, the nature of fluorescent states in polar solvents has been discussed by many people and recent consensus on assignment is to an ^1L_a/CT state,[1] where a CTTS (charge transfer to solvent) state[2-4] seems to be involved. This seems to be related to a red edge excitation effect[5] in photophysical behaviors which indicates a strong interaction of a solute molecule with solvent molecules in the excited states. Although phenomena of this kind are usually interpreted by a solvent cage effect,[5,6] possible contribution of the CTTS state[2] cannot be neglected. As for photochemistry, photoionization i.e., electron ejection from indoles to the solvent, was of a great concern. This phenomenon has partly been connected with biological interests.[7]

In this labolatory, photoionization mechanisms of aromatic amines in polar solvents such as acetonitrile (AN) have been studied for years.[8] In the case of 8-anilino-1-naphthalenesulfonate (1,8-ANS), a biphotonic ionization mechanism was elucidated where the CTTS state is suggested to be an intermediate state.[9] In case of *N,N,N',N'*-tetramethyl-*p*-phenylenediamine (TMPD) in acetonitrile (AN), a monophotonic ionization through a fluorescent level was confirmed where a major product is an ion pair between $TMPD^+$ and AN^-.[10] The latter conclusion is made on the basis of the following three kinds of experiments: fluorescence lifetime measurements (including solvent and temperature effects), ns and ps laser photolysis (nslp and pslp), and the transient photoconductivity measurements.

Recently, there are several publications concerning the monophotonic ionization of aromatic amines in polar solvents. Nogami et al.[11] have studied monophotonic ionization of *N,N,N',N'*-tetramethyl-1,6-pyrenediamine (TM-1,6-PDA) in acetonitrile by nslp and tpc measurements, and therefrom, proposed the existence of a long-lived ion pair based on the slow rise time (several μs) of photocurrent, in spite of the rapid (≲50 ns) appearence of a cation-like absorption. Hirata et al.[12] did more detailed experiments on the acetonitrile solution of bis(dimethylamino)tetrahydropyrene (BDATP) by using a ps laser. In this case, the rise time of cation-like absorption was found to be ≈2 ns in agreement with the lifetime of fluorescence, while the rise time of photocurrent was found to be ≈9 ns. Thus, monophotonic ionization from fluorescent level through an ion-pair state was proposed. Experiments on *N,N,N',N'*-tetramethylbenzidine (TMB) were also performed by Hirata et al.[13] In this case, the lifetime of the ion pair was ≈ 4.5 μs. The same group[14] also published the results on TMPD in acetonitrile which gave almost the same data as ours[10] but with some different interpretations.

The photophysical and photochemical schemes proposed in the studies mentioned in the above two paragraphs were not conclusive, e.g., as regards to the mechanism of the ion-pair formation. For instance, in comparing the time dependence of photocurrents with that of transient absorptions, the heterogeneity of the electrode reactions had to be taken into account, i.e., the mobilities of the charge carriers and also the electrode potential working on the ion pair.[10] As for the transient photoconductivity in polar solvents, no established theory is available in contrast to the case of nonpolar solvents.[15]

The aim of the present study is to add more data on this subject so that a clearer identification of the ion pair could be made. A new aspect is that the molecules are excited at the red edge of the 0, 0 band of NMI. Since a fluorescent level is directly excited, a possible mechanism of direct monophotonic ionization before vibrational relaxation may be eliminated.

Experimental

Apparatus and Procedure. The experimental methods of nslp are practically the same as those described in the previous paper[10] except for the fact that a XeCl laser (Lumonics TE 430-2, λ=308 nm and τ=≈ 8 ns, used at ≈ 20 mJ output) replaced a N_2 laser. In case of tpc the size of electrodes was 5×5 mm^2, the separation between them being 2 mm, so that a wider area was illuminated to avoid a biphotonic ionization due to a strong laser light. A 5.1 kΩ

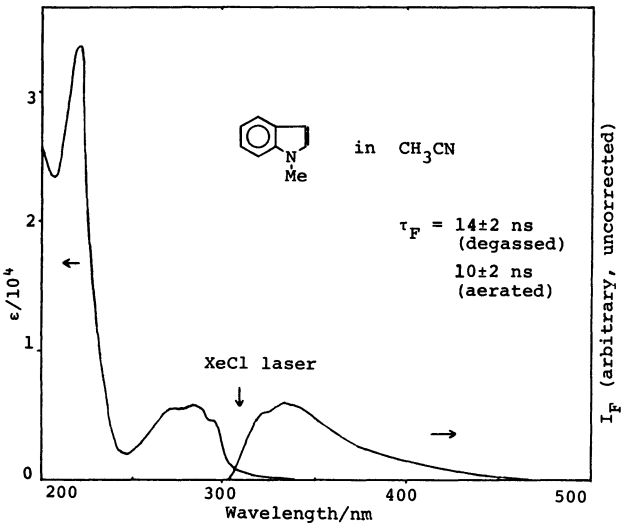


Fig. 1. Absorption and fluorescence spectra of *N*-methylindole in acetonitrile.

termination had to be used because of a small current yield. This caused ≈ 0.5 μs rise time of the system. All the experiments were done at ≈ 25 °C.

Materials. NMI purchased from Tokyo Kasei was vacuum distilled. Spectrograde acetonitrile from Nakarai Chem. was used without further purification.

Results and Discussion

Absorption and Fluorescence. Figure 1 shows the absorption and fluorescence spectra of NMI in acetonitrile. The first peak at ≈ 295 nm is ascribed to the 0, 0 band of the S_1 (^1L_b)←S_0 transition,[1] while the fluorescence is ascribed to the S_1'(^1L_a/CT)→S_0 transition.[1] Also shown in the figure is the location of excitation by the laser which is exactly at the red edge of the first absorption band. Namely, only molecules which are in the solvent cages similar to those of the emitting levels S_1'(^1L_a/CT) are selected by the laser light. Therefore, practically no vibrational relaxation, and little solute-solvent relaxation is required for the optically prepared excited state to reach the fluorescent state. The fluorescence lifetimes in the degassed and aerated solutions were determined to be τ_F°=14±2 ns and τ_F=10±2 ns, respectively. The difference is ascribed to the diffusion-controlled quenching of the fluorescing S_1' state by oxygen: $k_q \approx 10^{10}M^{-1}s^{-1}$ by $k_q[O_2]$=$(k_F+k_{nr}+k_q[O_2])-(k_F+k_{nr})=1/\tau_F-1/\tau_F^\circ=1/(10\times10^{-9})-1/(14\times10^{-9}) \approx 3\times10^7$ (s^{-1}) with [O_2] assumed to be $\approx10^{-3}$ M[†] (The solubility data is not available for the AN solution.). Here, k_F and k_{nr}, respectively, are the radiative and nonradiative decay rates of the S_1' state.

Nanosecond Laser Photolysis. Typical result of nslp on the degassed solution of NMI (6.5×10^{-3}M) is shown in Fig. 2. Time-resolved spectra at t=0, 50 ns and 0.1, 0.5, 4, 16 μs after laser excitation are given by dashed lines in the figure. The shorter-wavelength portions (≤610 and ≤410 nm) of the spectra at t=0 and 50 ns are not available due to interference by the scattered light mainly of fluorescence. The decay curve at each wavelength was represented by the sum of three exponential curves from which "component" spectra i.e., pre-exponential factors, A_s, A_m, and A_ℓ as functions of wavelengths were obtained as shown by the solid lines in the figure with lifetimes τ_s, τ_m, and τ_ℓ, respectively. The component spectra A_m and A_ℓ are similar to those of T_n←T_1 absorptions and of the cation radicals of indole derivatives, respectively, given in the literatures.[3,7,16] Therefore, the former is safely ascribed to the T_1 state of NMI, while the latter is ascribed to the ion pair between NMI^+ and AN^- rather than a free NMI^+, because its decay is described almost by a single-exponential curve. Oxygen effects are also explained by these assignments. The lifetime of the short-lived component has a wide distribution around the mean value of 40 ns compared to the other two, with the minimum value corresponding to the fluorescence lifetime. This fact indicates the existence of species other than S_1' state of NMI. A possible candidate for this species might be (free) AN^-[17] as in the case of TMPD.[10] However, the spectral shapes of the short-lived components could not be determined uniquely, so that any decisive assignment is not presented. Therefore, the spectra at 0 ns may be regarded as the sum of $S_n^{(\nu)}$←S_1' absorption and that of the other species, and the A_s spectra should be taken as a difference spectrum between those of before and after decay of the short-lived species.

The transient absorption intensity depends upon the intensity of the laser (I_{exc}): The plots at the wavelengths and times where the absorbance (A) exceeds 0.01, showed that A is proportional to I_{exc} in the region of $0.2\times I_{max} \leq I_{exc} \leq 0.7\times I_{max}$($I_{max}\approx$20 mJ), while for $I_{exc}>0.7\times I_{max}$, a saturation effect was observed. However, the spectral shapes and the shapes of the decay curves did not depend on I_{exc}. Therefore, all the species observed can be safely regarded to be produced monophotonically. Generally speaking, even if $A \propto I_{exc}$, under the condition that the molar absorption coefficient (ε) at the exciting wavelength of the sample is very small (in this case $\varepsilon<10^3$ at 308 nm) we can not completely deny the possibility of a biphotonic process if ε of a possible intermediate for the process is very large. However, assignment to the ion pair instead of NMI^+ would rule out this possibility, because no report is available which indicates the biphotonic formation of an ion pair through the S_1 state.

The effect of aeration on the same solution was observed as that shown in Fig. 3. The presentation is practically the same as that in Fig. 2. Comparison of the components between Figs. 2 and 3 indicate that apparently the yields of the major species (S_1' and T_1 states and the ion pair) are not influenced by the introduction of air (oxygen) and only lifetimes are shortened by O_2. Small changes in the yields may not be

† 1 M=1 mol dm^{-3}.

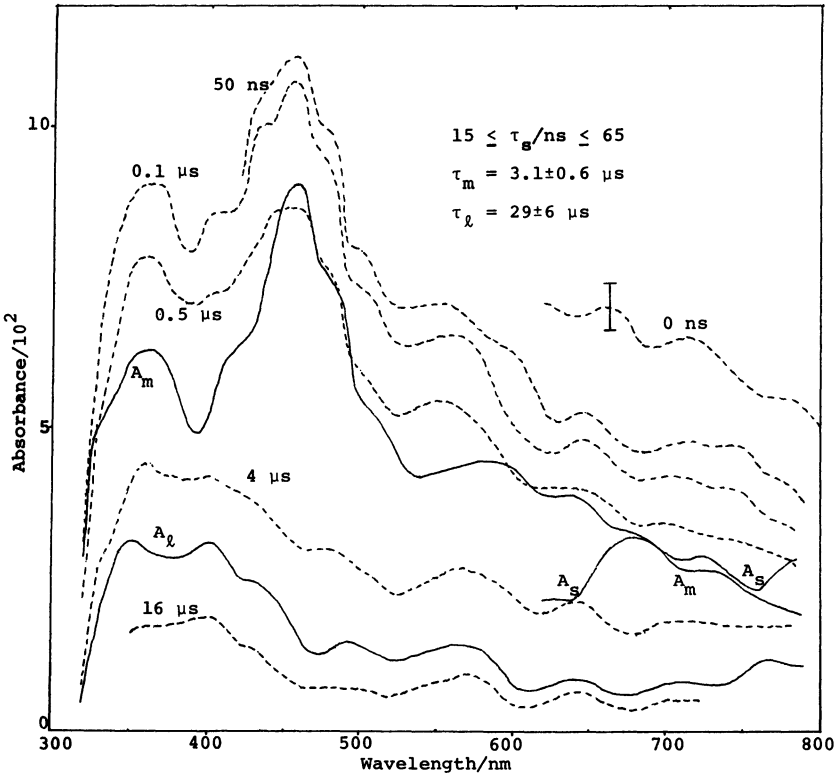


Fig. 2. Nanosecond laser photolysis of a degassed acetonitrile solution (6.5×10^{-3} M) of *N*-methylindole: Time-resolved and decomposed spectra.

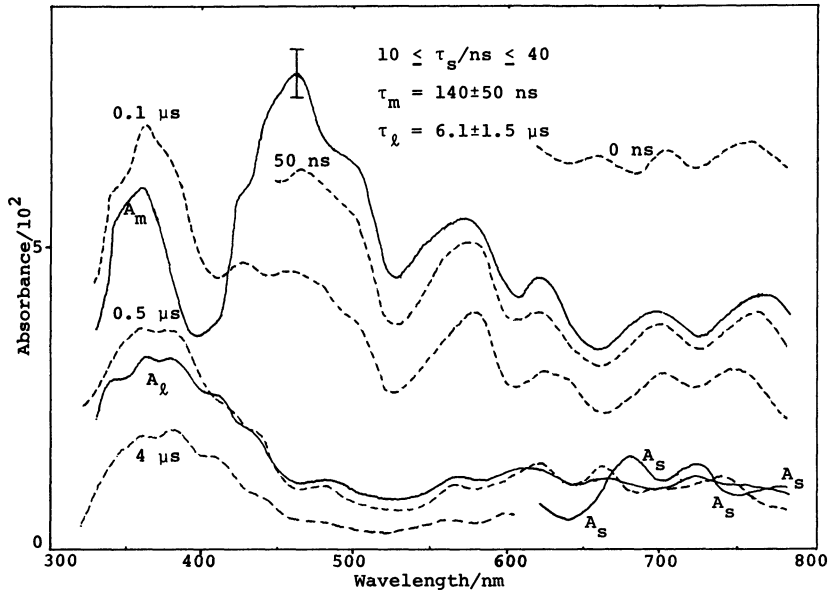


Fig. 3. Nanosecond laser photolysis of an aerated acetonitrile solution (6.5×10^{-3} M) of *N*-methylindole: Time-resolved and decomposed spectra.

consistent with fluorescence-lifetime shortening by oxygen. This fact, however, is rationalized if we assume that both intersystem-crossing and electron-ejection rates increased to the same extent (≈40%). Namely, the ion pair formed in the aerated solution might be due to the ion pair between NMI^+ and O_2^- possibly formed through an exciplex, $NMI^+\cdots O_2^-$ rather than that between NMI^+ and AN^-. There are some discrepancies between the two figures in the wavelength region of $\lambda>500$ nm. These may be interpreted by assuming another component with a lifetime of ≈ 100 ns in the case of the aerated solution. However, a spectral shape for this component is difficult to be determined uniquely because its lifetime is very close to that of the triplet state. The decreased lifetime of the short-lived component is interpreted as (diffusion-controlled)

Table 1. Time Behavior of Photoconductivity of 2×10^{-3} M NMI in N_2 Bubbled and Aerated(in Parenthesis) Acetonitrile Solutions, Respectively

	r	d_1	d_2	d_3
τ_j/μs	1.6±0.3	26±5	400±100	$>10^3$
	(1.3±0.3)	(8±2)	(180±40)	($>10^3$)
$i_j^\circ/\sum_k i_{d_k}^\circ$	−1.00±0.10	0.60±0.10	0.12±0.02	0.28±0.06
	(−0.95±0.10)	(0.60±0.10)	(0.15±0.03)	(0.25±0.05)

quenching of the S_1' state (vide supra) and another species like AN^- by oxygen. The quenching rate of the T_1 state, $k_q'[O_2]=(k_{nr}'+k_q'[O_2])-k_{nr}'=1/\tau_m-1/\tau_m^\circ=1/(140\times10^{-9})-1/(3.1\times10^{-6})=7\times10^6$ (s^{-1}) is just reasonable. Here $\tau_m^\circ=1/k_{nr}'$ is an intrinsic lifetime of the T_1 state. The decay rate of the long-lived component can be interpreted by two alternative schemes or their compromises (e.g. by assuming an equilibrium between them); (1) as the decay rate $k_d=1/\tau_\ell\approx1.6\times10^5$ (s^{-1}) of the ion pair, $NMI^+\cdots O_2^-$, or (2) by the quenching rate, k_q'' of $NMI^+\cdots AN^-$ by oxygen with $k_q''[O_2]=1/\tau_\ell-1/\tau_\ell^\circ=1/(6.1\times10^{-6})-1/(29\times10^{-6})\approx1.3\times10^5$ (s^{-1}). Both these numbers are not unusual for these processes. Although quenching (lifetime shortening) of the ion pairs by oxygen was not clearly demonstrated for the other systems,[11-14] nslp experiments on aminonaphthalenes (naphthalenamines and naphthalenediamines)[18] and *N,N,N',N'*-tetramethyl-2,7-pyrenediamine[19] done in this laboratory presented similar results.

Transient Photoconductivity. In order to obtain more and complementary informations on the scheme, transient photoconductivity was measured for the nitrogen-bubbled and air-saturated acetonitrile solutions of NMI. Its time profile was analyzed as a sum of one or two exponential rise and three exponential decay curves:

$$i_p(t)=\sum_j i_j^\circ e^{-t/\tau_j};\ \{j\}=(c, r, d_1, d_2, d_3).$$

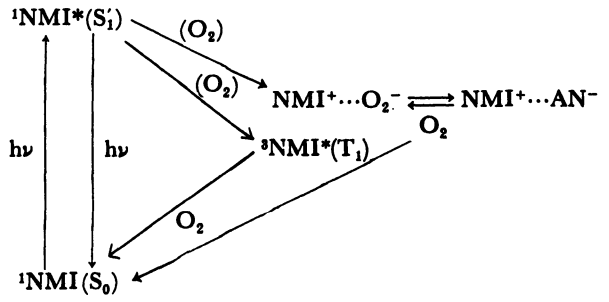
Here, τ_c corresponds to the time constant of the detection system ($\approx$ 0.5 μs). i_p values were proportional to I_{exc} in the region $0.2\times I_{max}\lesssim I_{exc}\lesssim I_{max}$ indicating that the chemical species responsible for the photoconductivity is ascribed to that formed by a monophotonic process. The yield of photocurrent i.e., that of the radicals was estimated to be $\Phi_i\approx0.05$ which is more than one order of magnitude lower than that of TMPD ($\Phi_i\approx0.8$), but comparison was not easy due to large difference and a possible contribution of the biphotonic process in the latter case. The photocurrent yields were almost the same for the nitrogen-bubbled and air-saturated solutions. i_j°, normalized for $i_{d_1}^\circ+i_{d_2}^\circ+i_{d_3}^\circ\equiv1$, and τ_j values for $j=r$, d_1, d_2, and d_3 are given in Table 1, while $i_c^\circ=1-i_r^\circ$ with $\tau_c=0.5$ μs. Since the analysis was made by assuming the sum of five (or four) exponential functions (no deconvolution was made), the actual τ_r values are expected to be slightly less than those given in the table but definitely more than τ_c. This kind of facts have been usually taken as evidences of the ion pairs formed by photo-irradiation and then dissociated with time constants τ_r's (The process with τ_r was not found in nslp experiments and it has been explained by a resemblance of the spectra of the cation and the ion pair.).[11-13] If we apply the above judgement to the present system, the decay portion of the photoconductivity has to be ascribed to the decay behaviors of free ionic species such as NMI^+, AN^-, and some scavengers' anions (X_i^-). However, we regard the process with τ_r rather as the evidence of the formation of the ion pair which dissociates at electrode surfaces by the applied field: The major decay portion of the photoconductivity is governed by the decay of the ion pair existing in the liquid phase which is the origin of the transient absorption in the nslp experiment. This assessment is supported by the following facts: (1) Long-lived (with O_2 effect) transient species (identified to the ion pair) were observed in both nslp (nearly single exponential τ_ℓ component) and tpc (non-exponential but $\tau_{d_1}\sim\tau_\ell$) experiments. (2) Rises (τ_r) were observed in the case of tpc [correspondent to the dissociation rate(s) of the ion pair at the electrode(s) ($1/\tau_r$) which is larger than the intrinsic decay rate of the ion pair ($1/\tau_\ell$)]. (3) The yield of the ion pair $\Phi_{i.p.}$ is estimated to be $\approx$0.1 by this assessment from $\Phi_i\approx0.05$ which is consistent with $\Phi_{i.p.}\approx0.2$ as is estimated from nslp data assuming $\varepsilon_{TT}\approx\varepsilon_{i.p.}$ and $\Phi_F\approx0.1$. (4) Therefore, the longer-lived portion of tpc (τ_{d_2} and τ_{d_3}) has to be ascribed to the heterogeneity of the tpc experiment, i.e., differences in the diffusion rates of the ionic species (freed at the electrodes) and so on.

The above judgement underscores the need of careful examinations of the complementary experimental data of nslp and tpc experiments for elucidating the photoionization mechanisms including ion pairs.

Since presence of the ion pair as a unique chemical species is well established, some comments will be added on the results of TMPD photolysis in acetonitrile solutions[10] which have some differences from those of the present system: (1) The 0.7 μs decay component in the transient photoconductivity ascribed to free $TMPD^+$ is absent in the transient absorption. This fact can be interpreted by assuming that the charge of AN^- taken at the anode is compensated by the $TMPD^+$ arrived at the cathode with the time constant of 0.7 μs. (2) The decrease in the photocurrent corresponding to the ion pair by aeration can be easily explained if we assume that an ion pair with O_2 is formed which

may be less dissociative at the electrodes. This kind of O_2 effect was not observed for NMI solutions because dissociation of $NMI^+\cdots AN^-$ is less feasible ($\tau_r \lesssim 1.6\,\mu s$) than that of $TMPD^+\cdots AN^-$ ($\tau_r < 10\,ns$).

In concluding this paper, one candidate for the scheme of the aerated system is given below:



The scheme for the oxygen-free system is almost obvious.

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