

# Time-dependent Picosecond Transient Absorption Spectra of 9-Acetylanthracene, Benzophenone and Acridine in Solution

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*(Received June 22, 1983)*

The transient absorption spectra of the title compounds in solutions at room temperature have been measured on the picosecond time scale. For 9-acetylanthracene and acridine there were measurable changes of the spectral shapes in the first picosecond region, while no spectral change was observed for benzophenone.

## INTRODUCTION

Recently, Hochstrasser *et al.*<sup>1</sup> reported on the time-dependent picosecond transient absorption spectra of a number of compounds in solution at room temperature. All the spectra, at different delay times, were normalized to the same peak height to facilitate comparison of the band shapes. The spectra obtained by this procedure suggest that vibrationally unrelaxed molecules are present in the solutions for times up to tens of picoseconds after optical excitation. In some cases new information was obtained about the electronic states whose spectra had been unobserved by that time. One should note, however, that such a normalization procedure for comparison

of the band shapes is liable to amplify errors in weak absorption bands by the multiplication of small errors, such as baseline drifts.

In the present study, we observed the transient absorptions of 9-acetylanthracene, benzophenone and acridine at a given delay time by changing the sample concentration or the intensity of excitation light, and weak spectra were normalized with reference to the corresponding strong ones. Taking into account the errors caused by the normalization, we observed the transient absorptions at different delay times to see whether the essential spectral narrowing and shift were present in the first picosecond region.

## EXPERIMENTAL

9-Acetylanthracene was synthesized by the method of Hawkins.<sup>2</sup> G.R.-grade benzophenone (Wako) was recrystallized three times from ligroin. Zone-refined acridine (Tokyo Kasei) was used without further purification. The solvents (acetonitrile, *n*-heptane, *n*-hexane) were of spectral grade (Dojin) and were used without further purification. Sample solutions in a cell of 2 mm pathlength were not deaerated. The transient absorption spectra were measured at room temperature.

The details of our picosecond transient absorption spectrometer have been given elsewhere.<sup>3</sup> The second harmonic (347.2 nm) from a mode-locked ruby laser was used to excite the sample. The mean pulse width (26 ps) and the time-zero point,  $t=0$ , were determined from the overlap of excitation and probe pulses by measuring the buildup of  $T_n \leftarrow T_1$  absorption of benzophenone (in *n*-heptane) at 530 nm. A double-beam optical arrangement was adopted, and absorption spectra in the 200 nm scanning region were measured with two multichannel photodiode systems. The three most probable spectra were averaged.

## NORMALIZATION OF SPECTRA

The reproducibility and stability of a mode-locked ruby laser were not stated to have been well controlled. Since our absorption spectrum was obtained by two laser shots, small errors such as baseline drifts were inevitable in the calculation of a double-beam absorption spectrum, i.e., the channel-by-channel subtraction.

Thus, the following two procedures were carried out in the normalization of the weak absorption spectrum (Spectrum B) to a strong one (Spectrum A) due to the same species.

(1) Normalization I. Let the true absorbances of Spectra A and B be  $I_A(\lambda)$  and  $I_B(\lambda)$  with systematic drifts of  $\Delta_A$  and  $\Delta_B$  in the baseline, respectively, where  $\lambda$  is the wavelength for a given absorption. When the band maximum of Spectrum B is normalized to that of Spectrum A at  $\lambda = \lambda_1$ , one obtains

$$\alpha[I_B(\lambda) + \Delta_B] = I_A(\lambda) + \Delta_A + (\alpha\Delta_B - \Delta_A) \left[ 1 - \frac{I_A(\lambda)}{I_A(\lambda_1)} \right] \quad (1)$$

where  $\alpha$  is the normalization factor, i.e.,

$$\alpha = [I_A(\lambda_1) + \Delta_A] / [I_B(\lambda_1) + \Delta_B]$$

Since each baseline is nearly horizontal, and  $\Delta_A$  and  $\Delta_B$  are less than  $\pm 0.02$  absorbance units for our system, Eq. (1) gives two normalized spectra depending on the positive and negative values of  $(\alpha\Delta_B - \Delta_A)$ , i.e., Spectra C and C' in Figure 1-I.

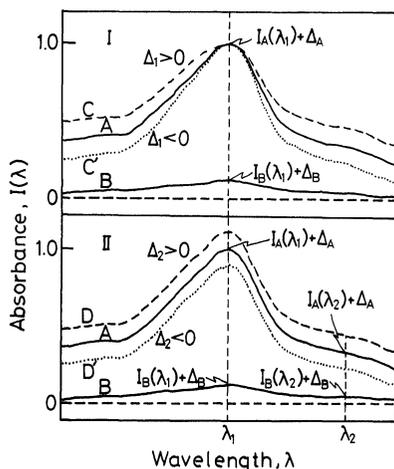


FIGURE 1 Normalization of a weak absorption (B) with reference to that of a strong one (A). (C) or (C'), normalized by Normalization I; (D) or (D'), normalized by Normalization II;  $\Delta_1 = \alpha\Delta_B - \Delta_A$ ;  $\Delta_2 = \beta\Delta_B - \Delta_A$ .

(2) Normalization II. Let a normalization factor  $\beta$  be defined as follows:

$$\beta = \frac{[I_A(\lambda_1) + \Delta_A] - [I_A(\lambda_2) + \Delta_A]}{[I_B(\lambda_1) + \Delta_B] - [I_B(\lambda_2) + \Delta_B]} = \frac{I_A(\lambda_1) - I_A(\lambda_2)}{I_B(\lambda_1) - I_B(\lambda_2)} \quad (2)$$

where  $\lambda_2$  denotes an appropriate wavelength other than  $\lambda_1$  at the band maximum. Since  $I_A(\lambda)$  and  $I_B(\lambda)$  represent the true absorbances of Spectra A and B, respectively, the intensity ratio  $I_A(\lambda)/I_B(\lambda)$  should be independent of  $\lambda$ , so that  $I_A(\lambda)/I_B(\lambda) = I_A(\lambda_1)/I_B(\lambda_1) = I_A(\lambda_2)/I_B(\lambda_2)$ . It then follows from Eq. (2) that  $\beta = I_A(\lambda)/I_B(\lambda)$ . Therefore, one obtains

$$\beta[I_B(\lambda) + \Delta_B] = I_A(\lambda) + \Delta_A + (\beta\Delta_B - \Delta_A) \quad (3)$$

Eq. (3) gives two normalized spectra as illustrated in Figure 1-II (Spectra D and D'), depending on the positive and negative values of  $(\beta\Delta_B - \Delta_A)$ . The basic difference between the two types of normalizations is that Normalization I always gives spurious absorptions at  $\lambda \neq \lambda_1$ , especially in the region of very weak absorption, while Normalization II gives Spectrum A by a vertical shift of  $(\beta\Delta_B - \Delta_A)$  in absorbance units after multiplication of Spectrum B by  $\beta$ . Namely, in the case where strong and weak absorptions are thought to belong to the same species, Normalization II should, in principle, provide smaller errors than Normalization I.

## RESULTS AND DISCUSSION

Figures 2-I and II show the transient absorptions of 9-acetylanthracene ( $2.0 \times 10^{-4}$  M) in acetonitrile at a delay time of 320 ps. The lowest trace in Figure 2-I shows a typical three-cycle baseline spectrum. The systematic deviation from zero is everywhere less than 0.02 absorbance units. Spectra A and B (solid lines), taken with the usual ( $I_e$ ) and attenuated ( $0.15 \times I_e$ ) excitation-light intensities, respectively, can be assigned to the  $T_n \leftarrow T_1$  absorption of vibrationally relaxed 9-acetylanthracene.<sup>4</sup>

When the band maximum of Spectrum B is normalized to that of Spectrum A at 423 nm by Normalization I, Spectrum C (dotted line) is obtained. On the other hand, Spectrum C' (dotted line) is obtained by Normalization II, in which case the normalization factor  $\beta$  is

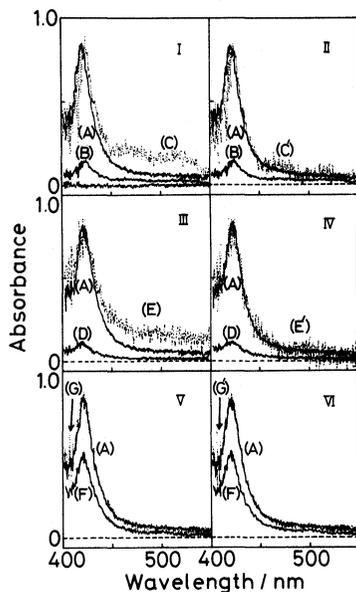


FIGURE 2 Transient absorptions of 9-acetylanthracene in acetonitrile at a delay time of 320 ps. (A), by a usual condition; (B), by attenuating the excitation-light intensity to 15% of (A); (D) and (F), by reducing the sample concentration to 1/10 and 1/2 of (A), respectively; (C), (E) and (G), normalized at 423 nm by Normalization I; (C'), (E') and (G'), normalized at 423 and 500 nm by normalization II. The lowest solid line in (I) is the experimental baseline spectrum taken with no excitation.

calculated using the absorbances at 423 and 500 nm of Spectra A and B. Spectrum C gives errors resulting in weak spurious absorptions above 450 nm and a spectral shift at the band maximum, whereas these errors are much smaller in Spectrum C'.

Nearly the same results are obtained in Figures 2-III and IV, where a weak absorption (D) was taken with a sample diluted to one-tenth of the original concentration instead of attenuating the excitation-light intensity. However, Normalization I caused no significant error when the sample concentration was one-half the original one (Figures 2-V, VI). This implies that the error caused by Normalization I is inessential if the weak absorption has a sufficient intensity.

In Figure 3, we display the transient absorptions of 9-acetylanthracene taken at various delays. The spectrum taken at  $-30$  ps and

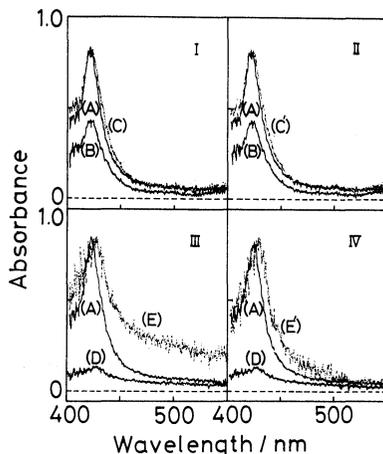


FIGURE 3 Transient absorptions of 9-acetylanthracene in acetonitrile taken at various delays. (A), (B) and (D), at 320, -10 and -30 ps, respectively; (C) and (E), normalized by Normalization I; (C') and (E'), normalized by Normalization II.

processes by Normalization II shows the essential spectral broadening and shift in comparison with that at 320 ps. Since the spectral change for 9-acetylanthracene is very similar to that for benzophenone observed by Hochstrasser *et al.*,<sup>1</sup> this change might be due to vibrationally unrelaxed 9-acetylanthracene.

Figures 4-I and II show the results obtained with benzophenone ( $1.0 \times 10^{-2}$  M) in *n*-heptane at a delay time of 320 ps. Spectra A and B (solid lines) were taken with the usual ( $I_e$ ) and attenuated ( $0.1 \times I_e$ ) excitation-light intensities, respectively. Since Spectrum A is very similar to the  $T_n \leftarrow T_1$  absorptions of benzophenone at longer times,<sup>1,6-8</sup> we conclude that the absorption with  $\lambda_{\max} = 530$  nm is due to the  $T_n \leftarrow T_1$  absorption of vibrationally relaxed benzophenone. Spectra C and C' obtained by Normalization I and II are essentially identical. Nearly the same results were obtained in the normalization of the weak absorption taken by reducing the sample concentration to one-tenth.

Hochstrasser *et al.*<sup>1</sup> have observed that the transient absorption of benzophenone shows spectral narrowing and shift over the first 50 ps. However, our normalized spectra taken at -20 ps (Spectra E and E' in Figures 4-III and IV) show no essential spectral broadening and

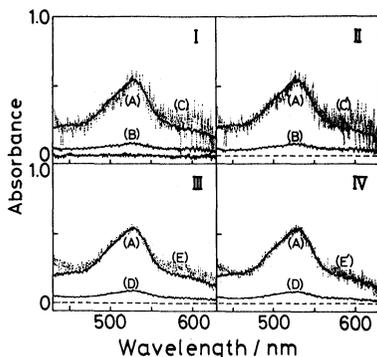


FIGURE 4 Transient absorptions of benzophenone in *n*-heptane at various delays. (A) and (B) at 320 and (D) at  $-20$  ps, respectively. (B), by attenuating the excitation-light intensity to 10% of (A); (C) and (E), normalized at 530 nm by Normalization I; (C') and (E'), normalized at 530 and 600 nm by Normalization II. The lowest solid line in (I) is the experimental baseline spectrum taken with no excitation.

shift in comparison with that at 320 ps. Therefore, Spectra E and E' do not appear to be vibrationally unrelaxed benzophenone.

Figures 5-I and II show the spectra of acridine ( $2.6 \times 10^{-4}$  M) in *n*-hexane at 320 ps delay. Spectra A and B (solid lines) were again taken with the usual ( $I_e$ ) and attenuated ( $0.15 \times I_e$ ) excitation-light

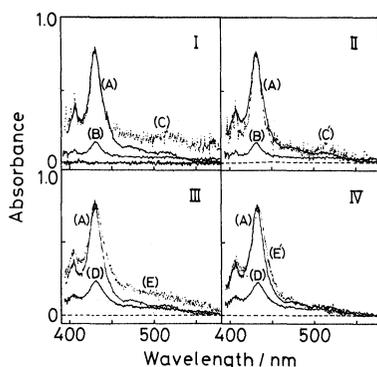


FIGURE 5 Transient absorptions of acridine in *n*-hexane at various delays. (A) and (B) at 320 and (D) at  $-10$  ps, respectively. (B), by attenuating the excitation-light intensity to 15% of (A); (C) and (E), normalized at 433 nm by Normalization I; (C') and (E'), normalized at 433 and 500 nm by Normalization II. The lowest solid line in (I) is the experimental baseline spectrum taken with no excitation.

intensities, respectively. The absorption spectra in the range of 400–460 nm (with  $\lambda_{\text{max}}$  at 433 and 407 nm) are similar to the  $T_n \leftarrow T_1$  absorptions at longer times<sup>9–12</sup> in regard to the positions of the absorption bands and the intensity distribution. The weak absorption above 450 nm in Spectrum C obtained by Normalization I does not appear in Spectrum C' obtained by Normalization II. A similar result was obtained by normalization of the weak absorption measured by reducing the sample concentration to one-tenth of the original one.

Apart from this weak absorption above 450 nm, the normalized spectra at –10 ps (Spectra E and E' in Figures 5-III and IV) evidently show broadening and shifts to a longer wavelength in comparison with that at 320 ps. Since no essential spectral narrowing and shifts are observed in Spectra C and C' within experimental error, changes in the time-dependent spectral shape below 450 nm might be due to vibrationally unrelaxed acridine, as suggested for benzophenone by Hochstrasser *et al.*<sup>1</sup>

The weak absorptions of acridine observed above 450 nm in Spectra C and E are very similar to that observed in the first picosecond region, i.e., at 14 ps by Hochstrasser *et al.*, who have assigned this spectrum to that of a transition between  $n\pi^*$  configurations in the singlet states. However, we suspect that this weak absorption is a spurious one as a result of normalization analogous to Normalization I. This is based on the following reasons: (1) No such weak absorptions are observed by Normalization II. (2) From the normalized spectrum at 14 ps reported by Hochstrasser *et al.*, one can estimate the ratio of the absorbance at 520 nm to that at 433 nm to be 0.48. By contrast, our Spectrum E at –10 ps indicates that the ratio is 0.15, which is nearly equal to those estimated from published spectra<sup>1,9,13</sup> measured at longer times, though the value 0.15 is smaller than the error arising from Normalization I, i.e., 0.23 in Spectrum C. (3) If these authors' suggestion is acceptable, one should observe an absorption of much higher intensity above 450 nm, because we have clearly observed the absorption peak at 407 nm whose relative intensity to that at 433 nm is 0.46–0.58.

As we have demonstrated in the present paper, time-dependent spectral changes in the first picosecond region sometimes depend on the procedure of spectral normalization. In spite of these circumstances, the spectral changes which might be due to vibrationally unrelaxed triplet states were observed in 9-acetylanthracene and

acridine, whereas no spectral change was observed in benzophenone. No strong evidence has been provided which supports the results of Hochstrasser *et al.* in regard to the presence of  $S_1$  absorption of acridine at 14 ps.

### Acknowledgement

This research was financed by a grant-in-Aid for Scientific Research from the Japanese Ministry of Education, Science and Culture (No. 470006).

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