

Time-Resolved Photothermal Spectroscopy as a Probe for Photofragment Energy Transfer Dynamics: Photodissociation of Iodobenzene at 266 nm

June Sup Lee and Hyun Jin Hwang*

Department of Chemistry, Kyung Hee University, Seoul 130-701, Korea

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Dynamics of energy transfer during and after photodissociation have been subjects of great interest during the last few decades,¹⁻⁶ because it is critical in understanding various photochemical and photophysical processes. Upon photodissociation, excess energy over bond-dissociation energy partitions into translational, rotational, vibrational, and electronic modes of photofragments, in different extents depending on the nature of the potential energy surfaces involved.^{1,2} Following photodissociation, energies deposited in different modes of photofragments relax back into equilibrium with the overall translational temperature of the gas medium *via* intermolecular collision, on different time scales depending on the nature of the energy levels excited.³⁻⁶ Therefore, relaxation dynamics of photofragments reflects various energy transfer processes of photofragments as well as dynamics of the photodissociation process.

In this communication, we report a time-resolved photo-thermal technique that can be used to resolve intermolecular energy transfer processes of photofragments in real time. Provided high sensitivity and time resolution of the technique developed, we were able to resolve V-T energy transfer of the phenyl radical produced from photodissociation of iodobenzene at 266 nm, from T, R-T and E-T energy transfer. To our knowledge, this constitutes the first example of direct monitoring of V-T energy transfer of a photofragment by a photothermal technique.

We have chosen UV photodissociation of iodobenzene as a model system, because its mechanism, leading to a simple C-I bond rupture, is well characterized and the phenyl radical is produced with a large amount of internal (*i.e.*, ro-vibrational) energy. The recent photofragment translational spectroscopy (PTS) experiments⁷⁻¹⁰ reveal that two types of photodissociation take place in iodobenzene: a fast, direct dissociation due to excitation of the repulsive n,σ^* state in the C-I bond and a slower, indirect dissociation due to excitation of the π,π^* state in the phenyl ring which is predissociated by the n,σ^* state. While the former produces an iodine atom in both the ground $I(^2P_{3/2})$ state and the spin-orbit excited $I^*(^2P_{1/2})$ state, the latter dissociates only into the $I(^2P_{3/2})$ state. Due to a strong coupling between the n,σ^* and π,π^* states, the phenyl radical is produced with a large amount of vibrational energy especially in the slower channel. For example, average values of translational, internal (ro-vibrational), and electronic energy of photofragments at 266 nm are $E_T : E_{V,R} : E_E = 24.7 \text{ kcal/mol} : 17.2 \text{ kcal/mol} : 4.6 \text{ kcal/mol}$, respectively.^{9,10} Due to this large contribution to overall relaxation dynamics, one could readily observe V-T energy transfer of the phenyl radical. In addition, as observed in the recent fs real time experiment,¹¹ UV photodissociation of iodobenzene takes place quite rapidly (on

the time scale of ps and sub-ps depending on the dissociation channels), and thus the dynamics of photodissociation is well separated in time from the collisional energy transfer processes of photofragments.

Experimental apparatus used for monitoring the photo-thermal transient is depicted in Figure 1. A gaseous sample of iodobenzene (0.80 Torr) in Ar (500 Torr) is photodissociated by a pulsed excitation laser at 266 nm, and the resulting thermal lensing signal due to intermolecular energy transfer of photofragments is monitored by detecting time-dependent variation of the power of a CW probe laser, which intersects the line-focused excitation laser at a right angle along the long axis of the excitation laser profile. Details of principles for the generation of the thermal lensing signal is described elsewhere.^{4,5} Briefly, collisional energy transfer of photofragments results in translational heating of the gas and this temperature rise causes change in the refractive index. The spatial profile of the refractive index is determined by the spatial profile of the excitation laser where the probe laser intersects, as well as the extents of energy transfer and diffusion processes. Thus, a near Gaussian profile of the refractive index builds up in the early time due to fast energy transfer processes, and it decays in time due to thermal and mass diffusion.

Figure 2 shows a thermal lensing signal obtained for the photodissociation of iodobenzene at 266 nm at a laser pulse

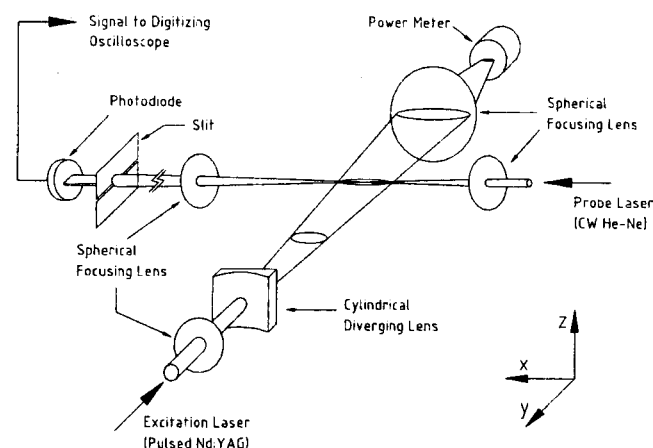


Figure 1. Experimental setup used in the time-resolved photo-thermal technique. A gaseous sample is excited by a line-focused pulsed laser (the fourth harmonic of a Q-switched Nd:YAG laser, Spectra Physics GCR150), and the resulting time-dependent thermal lensing signal is monitored by intersecting the excitation laser with a CW He-Ne laser at a right angle along the long axis of the excitation laser beam profile ($84 \mu\text{m} \times 30 \text{ mm}$ at the intersection).

energy of 270 $\mu\text{J}/\text{pulse}$, corresponding to laser fluence of 1.8 MW/cm^2 . As shown in Figure 3, the photothermal signal around this fluence condition increases linearly as the laser pulse energy, giving a unit slope in the log-log plot. This suggests that the photothermal signal results predominantly from one-photon absorption.

As shown in Figure 2, two rise components are observed well separated in time with comparable intensities, and it is followed by a diffusional decay on a longer time scale. The experimental data are fitted to the following equation derived based on the theory of Sontag and Tam:⁴

$$S = S_0 [1 - r_1 \exp(-t/\tau_1) - r_2 \exp(-t/\tau_2)] (w^2 + 8Dt)^{-3/2} \quad (1)$$

with $r_1 + r_2 = 1$

where r_1 and r_2 are amplitude factors for two rise components with time constants τ_1 and τ_2 , respectively. D denotes the thermal diffusivity and w is the $1/e^2$ radius of the Gaussian excitation beam. The best fit to this equation is depicted in Figure 2, and the fitting conditions and results are summarized in Table 1.

The fast rise component rises instantly within the response time of the apparatus (*ca.* 250 ns as estimated from the detector response time and the acoustic transit time), suggesting that the related energy transfer process takes place on the molecular collision time scale. Therefore, this component can be attributed to T-T and R-T energy transfer of photofragments. The slow rise component shows a rather longer time constant of *ca.* 17 μs . This rise component can be attributed to V-T energy transfer of the phenyl radical. The slow component could contain some contribution from E-T energy transfer of the $\text{I}^*(^2P_{1/2})$ atom. However, collisional relaxation of $\text{I}^*(^2P_{1/2})$ by almost all of

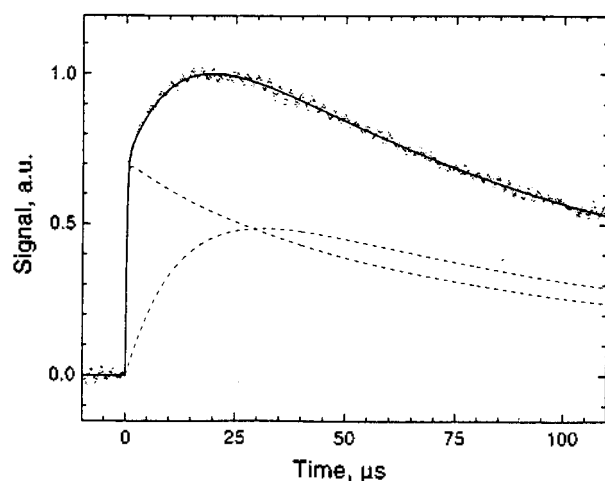


Figure 2. Thermal lensing signal observed for the photodissociation of iodobenzene (0.80 Torr) in Ar (500 Torr) at 266 nm. Theoretical best-fit (solid line) of experimental data (dots) represents that the photothermal transient consists of two rise components with rise times of *ca.* 0.25 and 17 μs . Calculated signals for the two rise components are depicted as dashed lines. The fast rise component is due to relaxation of translational and rotational energies of the photofragments and the slow component is attributed to vibrational relaxation of the phenyl radical. Details of the fitting results and experimental conditions are summarized in Table 1.

the molecules studied to date is known to be very slow ($\tau \geq$ about 100 μs at the present condition).^{2,3} Therefore, unless iodobenzene or phenyl radical has unusually large $\text{I}^*(^2P_{1/2})$ quenching efficiency, the slow rise component must result purely from V-T energy transfer. Unfortunately, no data are available for the $\text{I}^*(^2P_{1/2})$ quenching efficiency of iodobenzene and phenyl radical.

As summarized in Table 1, contributions of the fast and slow components to the total heat release are $r_1:r_2=0.45:0.55$, respectively. Thus, based on our interpretation described above, V-T energy transfer of the phenyl radical accounts for a large fraction (55%) of the total energy released. This feature is consistent with the results of the PTS experiments,⁷⁻¹⁰ confirming presence of a strong coupling between the n,σ^* and π,π^* states leading to high internal excitation of the phenyl radical.

However, in details, our result is in slight disagreement with the PTS results of Freitas *et al.*^{9,10} From their results, we obtain $E_T:E_{V,R}=24.7 \text{ kcal/mol}:17.2 \text{ kcal/mol}=0.59:0.41$. Since rotational energy of the photofragment must relax as quickly as translational energy, the contribution of the slow component would be slightly smaller than 0.41, in contrast to the value of 0.55 observed in the present work. Possible causes of this discrepancy are as follows. E-T energy transfer of the $\text{I}^*(^2P_{1/2})$ fragment might be as fast as V-T transfer

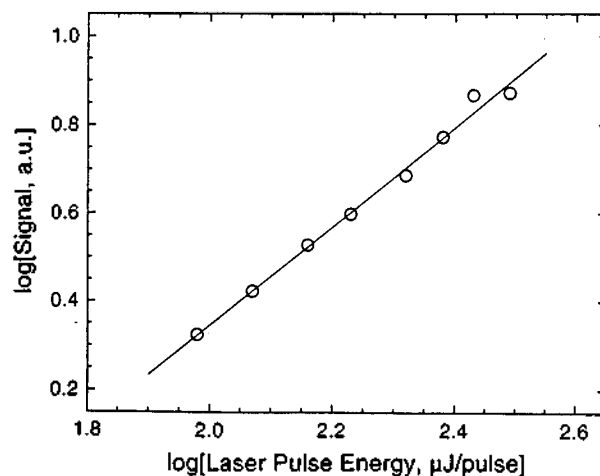


Figure 3. Dependence of the thermal lensing signal on the pulse energy of the excitation laser. The signal at each laser pulse energy is determined at the peak value of the photothermal transient. The slope of the best-fit is 1.1 ± 0.1 , implying that the photothermal signal results predominantly from one-photon absorption.

Table 1. Summary of the fitting results and apparatus constants for the thermal lensing signal shown in Figure 2

	Physical Quantity	Value
Fitting Parameters	r_1	0.45 ± 0.04
	$r_2 = 1 - r_1$	0.55 ± 0.04
	$\tau_2, \mu\text{s}$	17 ± 2
	$D, 10^{-6} \text{ m}^2/\text{s}$	8.5 ± 0.7
Apparatus Constants*	$\tau_1, \mu\text{s}$	0.25
	$w, \mu\text{m}$	84 ± 5

*These values are used as constant parameters in the fitting.

of the phenyl radical, thus giving rise to an additional contribution to the slow component. If this is the case, we would observe $r_1:r_2 \approx E_T:E_{V,R}+E_E=0.53:0.47$, which is in slightly better agreement with the present result. However, as discussed before, this is highly improbable considering available data for the $I^*(^2P_{1/2})$ quenching efficiency of other molecules. Recombination processes between the photofragments could also be considered as a possible candidate for an additional heat source. However, this is not likely the case because as observed in alkyl iodides¹² the recombination processes are known to occur in a much longer time scale (say, ms time domain), which is even longer than the time scale of the E-T energy transfer of $I^*(^2P_{1/2})$. Another possibility is that there might exist additional photochemical or photophysical channels in the fate of the photoexcited iodobenzene, which are not observed in the previous photodissociation experiments.⁷⁻¹¹ Some molecule might survive from dissociation for longer time (say longer than ns) than that can be observed in the PTS experiments⁷⁻¹⁰ and the fs real-time experiment.¹¹ If this happens (likely due to perturbation by Ar atoms in the gas), it must result in more excitation of vibrational energy levels either in iodobenzene or phenyl radical, resulting in a larger contribution to the slow rise component.

In conclusion, we have demonstrated that by use of a time-resolved photothermal technique, one can directly resolve the V-T energy transfer process of photofragments from other energy transfer processes. This enables us not only to study vibrational relaxation of radicals but also to investigate the detailed nature of the photodissociation, *i.e.*, energy partitioning during the photodissociation. More complete accounts for this work, including mechanism of V-T energy transfer of the phenyl radical, will be published in

the future.

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