

PICOSECOND LASER STUDIES OF THE PHOTODISSOCIATION OF I₂-AROMATIC COMPLEXES AND THE FORMATION OF I ATOM-AROMATIC COMPLEXES IN SOLUTION

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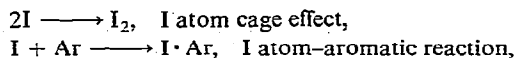
The dynamics of the photodissociation of I₂-aromatic complexes, cage effect phenomena, and the formation of iodine atom-aromatic complexes in solution are reported. Using picosecond laser methods these various processes were investigated in the neat liquids benzene, mesitylene, and *p*-xylene and in solutions of CCl₄ and these aromatics.

1. Introduction

The laser induced photodissociation of I₂ molecules in solution can be used as a method to study not only the dynamics of collision induced predissociation and atom recombination processes [1, 2] but also to investigate atom-molecule reactions in liquids. In a previous study [2], picosecond light pulses at 530 nm were used to excite I₂ molecules in solution and to probe the evolution of the perturbed system. In this way, the dynamics of the collisionally induced predissociation of the excited I₂ molecule leading to a pair of ground state 2P_{3/2} iodine atoms and the dynamics of the subsequent geminate atom recombination (cage effect) or escape were obtained. In the inert solvents carbon tetrachloride and hexadecane the atom recombination process is the dominant one. However, if there are molecules present in the solution with which the I atoms can react, then a

competition between the atom recombination reaction and the atom-molecule reaction can occur. In the present study the aromatic molecules benzene, mesitylene and *p*-xylene, either in the neat form or in CCl₄, were used as the reactive molecules.

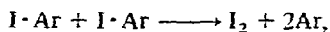
Although iodine atoms are known to form transient charge transfer complexes with these aromatics [4-7], the intrinsic rates of formation of the complexes are not known. At a low concentration of the aromatic the rate of complex formation is determined by the time required for the reacting partners to diffuse to some reaction distance. This diffusion limited rate can be circumvented by photolyzing I₂ in the neat aromatic liquid. Thus by measuring the time dependent appearance of the absorption characteristic of the atom-molecule complex [4-7] a number of different processes can be examined. These include the competition between the cage recombination of the atoms and the atom-molecule reaction,



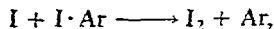
the cage reaction of a pair of atom-aromatic complexes,

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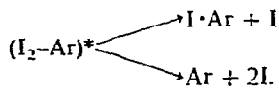
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and a mixed cage effect,



and the possible effect of the I₂-aromatic complex on the photodissociation process, e.g.



2. Experimental

A mode-locked neodymium glass laser was used throughout the experiments. A schematic of the experimental arrangement is shown in fig. 1. A single pulse was selected from the train of 1.06 μ light pulses, amplified and then frequency doubled. The major fraction of the resulting 530 nm pulse was used to excite the iodine samples of 1 mm path-length. A small fraction of the pulse was split off the main beam, optically delayed with respect to the exciting pulse and used to probe the transmission of the samples. The mesitylene samples were

additionally probed by light from stimulated Raman emission at 627 nm, which was generated by focusing the green probe light into a cell containing ethanol. In some of the measurements a polarizer in the probe beam was used to obtain simultaneously the parallel and perpendicular transmissions with respect to the polarization of the exciting pulse. Using the two-photon fluorescence technique, the full width at half-maximum of the laser pulse was found to be less than 10 ps.

A number of measurements (10–15) at each time delay were made and the average was calculated with reference to variations in excitation intensity.

Spectrophotometric grade solvents and sublimed iodine were used in the experiments. The concentration of the iodine in the solutions was fixed at 1×10^{-2} M. All experiments were carried out at room temperature.

3. Results and discussion

The actual structure of the ground state I₂-aromatic complex is unknown, but the binding interaction is presumed to be charge transfer in nature [8, 9]. In inert solvents [2] (no ground state

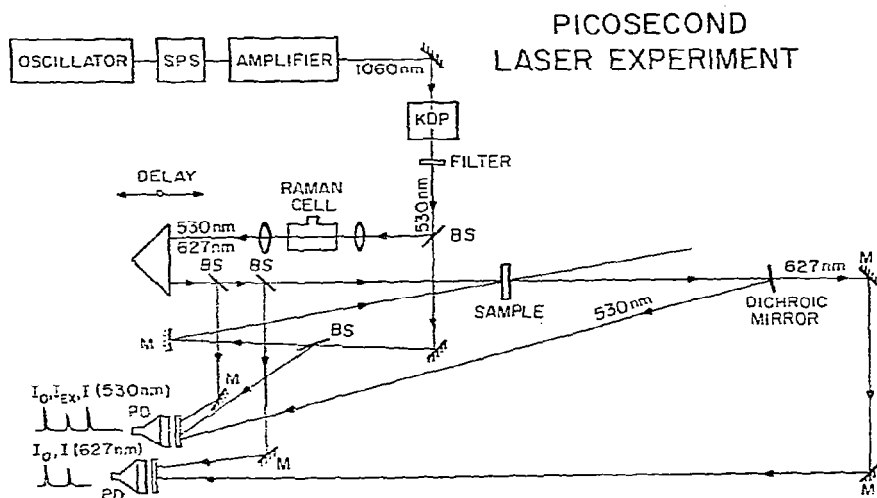


Fig. 1. Schematic of the picosecond laser experimental arrangement. SPS is the single pulse selector, KDP is the frequency doubling crystal and PD is the photodiode.

complex) the iodine is reorienting more rapidly than the time resolution of our experiments (≈ 5 ps). This was determined by establishing that the transmission of probe light was not dependent on its polarization. Similarly, for the time dependent measurements of the atom-molecule complex, no polarization dependence was observed. This can be due to the I₂ molecule reorienting more rapidly than we can time resolve, as in the inert solvents, or to a random orientational distribution of the atom-molecule complexes initially formed, or to the lack of a well defined transition moment direction for the atom-molecule complex.

In inert solvents the absorption of I₂ was found [2] to decrease following excitation due to the destruction of the I₂ molecules. In the aromatic solvents used in this study the formation of the I atom-aromatic complexes produced an increase in absorption at the 530 nm probe wavelength which more than compensated for the decrease due to the loss of I₂ molecules. This enhanced absorption is a

result of the absorption coefficient of the I atom-aromatic complex [4, 6] being greater than the I₂ molecule at 530 nm, and to the net increase in the number of absorbers since the loss of each I₂ molecule produces two I atom-aromatic complexes. It was possible to separate the dissociation of the I₂ molecules from the formation of I atom-aromatic complexes for the case of I₂ in mesitylene since the I atom-mesitylene complex has a strong absorption in the red whereas the I₂ does not. Using a picosecond probe pulse at 627 nm, the kinetics of formation of the I atom-mesitylene complex in neat mesitylene and in CCl₄ were obtained (fig. 2). Since the lifetime of the complex is orders of magnitude longer [4-7] than the events considered here, the transmission appears constant following the initial rapid formation of the complex. The strong similarity of the collision induced predissociation rate of I₂ in inert solvents with the rate of formation of the I atom-mesitylene complex ($> 10^{11}$ s⁻¹) indicates that the rate determining step

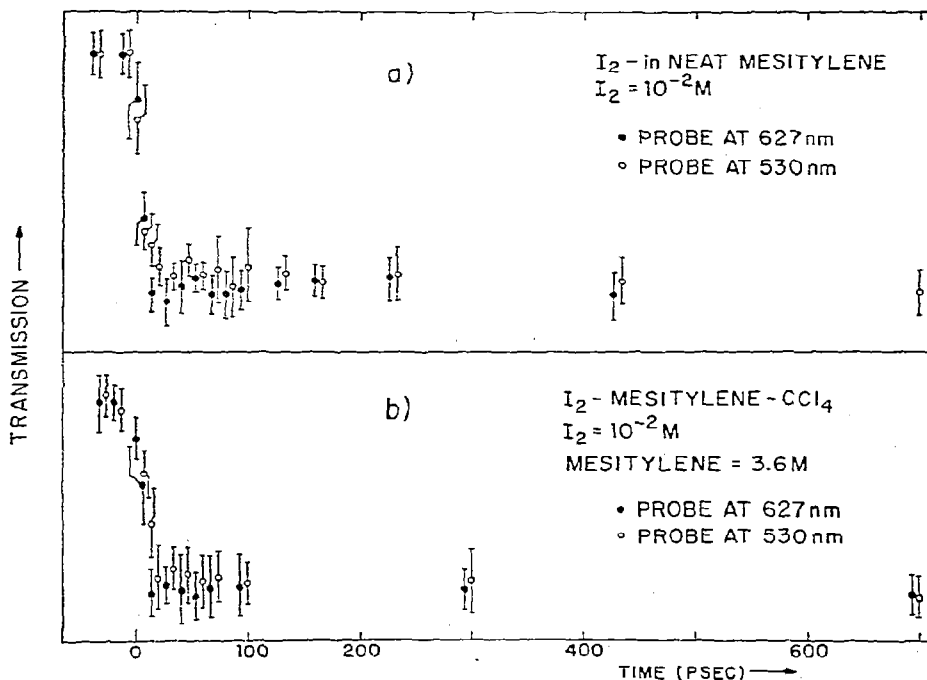


Fig. 2. (a) Optical transmission (arbitrary units) of 10^{-2} M I₂ in neat mesitylene. (b) Optical transmission (arbitrary units) of 10^{-2} M I₂ in 3.6 M mesitylene and CCl₄.

in this latter case is also the collision induced predissociation rate of the excited I_2 molecule. Accordingly, the rate of reaction of the iodine atom with mesitylene must be significantly faster ($\gg 10^{11} \text{ s}^{-1}$) than the collision induced predissociation rate of the excited iodine molecule. Although these results indicate that the I_2 -mesitylene complex (about 85% of the I_2 is bound to mesitylene) [8] does not alter the rate of the dissociation process relative to I_2 in inert solvents, we could not establish whether the photodissociation yielded $I \cdot \text{Ar} + I$ or $\text{Ar} + 2I$.

The cage effect which is clearly observed in the picosecond kinetic studies in inert solvents is found to be absent in mesitylene, not clearly resolvable in *p*-xylene and small in benzene. The rise in absorption, indicative of the formation of the I atom-aromatic complex in the neat aromatic solvents, is very rapid ($< 10 \text{ ps}$) compared with the cage recombination times ($> 100 \text{ ps}$) observed [2] in the more viscous inert solvents studied. We conclude from this that the atom-aromatic reaction in the neat and concentrated aromatic solutions efficiently quenches the possible cage recombination involving free iodine atoms. The constancy of the I atom-mesitylene complex absorption out to relatively long times (700 ps) also shows that there is no I atom-mesitylene cage effect nor mixed cage effect.

By varying the concentration of benzene in CCl_4 the competing effects of geminate iodine atom

recombination and the iodine atom-benzene reaction can be seen (fig. 3). The transmissions of the four different cases shown in fig. 3 are initially the same, i.e., approximately the same transmissions at times prior to the excitation pulse. At the low benzene concentration of 0.1 M the transmission initially increases due to the destruction of I_2 , followed by a decrease in transmission due to a cage recombination of a fraction of the free I atoms. The remaining free I atoms escape and will subsequently either react with other free I atoms (non-geminate recombination) or with the more abundant benzene molecules. This non-geminate recombination occurs on a time scale orders of magnitude greater than the events observed in these experiments. For this reason the transmission appears constant following the completion of the various cage processes. In 2 M benzene the destruction of I_2 is still the dominant process at early times and leads to an increase in transmission. The magnitude of the increase is relatively small due to the growing importance of number of transmission decreasing processes. All of these reactions are in turn competing with each other. They include the iodine atom cage effect (the only important effect at early times for the 0.1 M case), the iodine atom-aromatic complex formation (dependent on the benzene concentration), and the mixed cage effect. At concentrations of benzene (5 M) and mesitylene (3.6 M) iodine atom-molecule formation reactions are dominant relative to cage

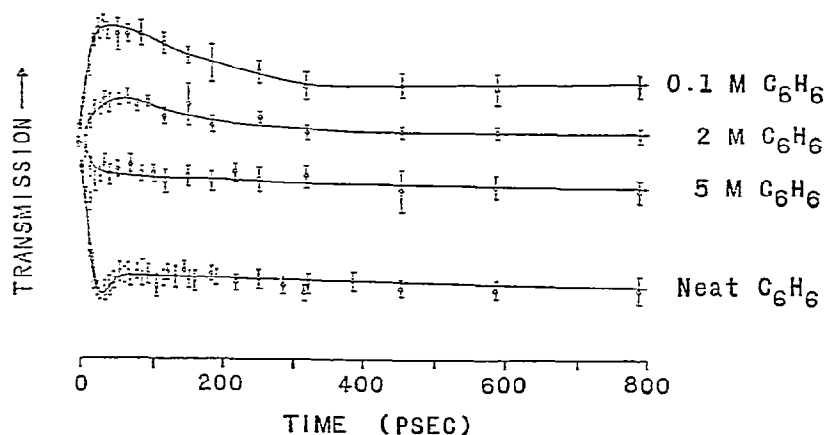


Fig. 3. Optical transmission (arbitrary units) of $10^{-2} \text{ M } I_2$ in various mixtures of C_6H_6 and CCl_4 .

effects and a decrease in transmission occurs. For the neat benzene case we note an initial rapid drop in transmission. Following the formation step a small increase in transmission indicates that a cage effect involving the geminate recombination of the two I·Bz complexes is occurring. The total duration of the cage recombination is approximately 40 ps. The short duration and small magnitude of this cage process relative to the recombination of free I atoms in neat solvents can be due to the stability of the complex and the steric requirements for the reaction between complexes.

The observation of the atom-aromatic cage process in benzene, but not in the other aromatic solvents, is most likely due to its lower stability. This is in line with the view that the stabilities of the complexes are due to charge transfer interactions. Thus benzene, having a higher ionization potential than the other aromatics, would contribute less to the charge transfer bonding. The relative stabilities would then be in the same order as found for the I₂-aromatic series [8, 9].

In summary we have found that the rate of photodissociation of I₂ is not affected by the fact that the I₂ is weakly bound to an aromatic. We have also determined that the reaction between the iodine atom and aromatic to form the transient I·Ar complex is extremely rapid ($> 10^{11} \text{ s}^{-1}$) and competes effectively with the I atom cage effect in the neat aromatic liquids. In addition a cage effect involving the geminate recombination of I·Ar

complexes is small but observable in benzene but not in the complexes of iodine atom with *p*-xylene or mesitylene.

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