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Vacuum-UV Three-Photon Chemical Reaction via Vibrationally Hot Molecules: Decomposition of Triphenylmethane

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A VUV (vacuum-UV) three-photon hot molecule reaction is demonstrated in this study for gaseous triphenylmethane (TPM). A TPM radical was derived from vibrationally hot TPM, which sequentially absorbed the second and third photons within a laser pulse. In the condensed phase, TPM radical was formed by the deprotonation of a cation radical, which was formed by the two-photon ionization. The multiphoton reaction via a hot molecule is a special case which can produce a neutral radical directly. This study also shows that more than two high-energy photons (VUV) can be absorbed and accumulated as vibrational energy. It should be emphasized that an internal conversion is not a useless photophysical process, but a very interesting process for forming an important intermediate in multiphoton laser chemistry.

Introduction

Recently, the study of nonradiative transition theory has been refined and is in a new stage. As a result of recent theoretical work, the fast internal conversion process is explained in terms of a conical intersection between the initial and final states.[1] Vacuum-UV (VUV) ultrafast laser spectroscopy clearly has shown that an internal conversion occurs on the order of femtoseconds and picoseconds for molecules such as benzene,[2] benzene dimer,[3] benzene−ammonium complex,[4] pyrazine,[5] ethylene, and chloroethylene.[6] An internal conversion, i.e., a vibrationally hot molecule formation process, is a dominant deactivation pathway of highly excited gaseous aromatic hydrocarbons. The various chemical reactions of hot molecules have been studied.[7] One can expect efficient reactions at a specific energy for hot molecules because very high internal energy, which is nearly equal to the photon energy absorbed, was accumulated as vibrational energy of the electronic ground state.[8] However, the absorption of a single photon is not always enough to induce chemical reactions, because if the molecular size or the reaction activation energy is large, the reaction rate cannot compete with the collisional deactivation rate. The accumulation of energy that results from the absorption of a second photon by hot molecules does much to induce intractable chemical reactions. Given that hot molecules have relatively long lifetimes and large molar extinction coefficients, the multiphoton reaction would take place in the gas phase. Two-laser two-color experiments on cycloheptatriene have demonstrated the specific rate of the isomerization reaction of hot molecule by observing C_2 fragment formed by the combination of nonresonant (visible laser) and resonant (UV laser) multiphoton process.[9] The infrared multiphoton reaction could be defined as an another example of multiphoton hot molecule reaction. A CW argon laser can induce multiphoton chemistry of azulene.[10] The examples of multiphoton hot molecule reactions within a single laser pulse were found in 1987 for toluene[11] and azulene,[12] and, subsequently, we have found examples of two-photon hot molecule reactions.[13] No multiphoton reaction involving more than VUV two photons has yet been found experimentally, although the nature of reactions involving more than two photons was discussed in the original papers on this subject.[11,12] The decomposition of triphenylmethane (TPM) is the first experimental demonstration of a VUV three-photon reaction via a hot molecule.

Experimental Section

TPM (Nacarai, 99%) was purified by recrystallization from ethanol with charcoal followed by sublimation. Nitrogen gas was purchased from Osaka Sanso, and the stated purity was 99.99%. The experimental setup is similar to that described in a recent paper[13] and therefore will be explained briefly. Gaseous TPM, which was vaporized at 433 or 443 K, was photolyzed with an ArF laser (Lambda Physik Compex102,193.3 nm, 14 ns/fwhm, 1−40 mJ cm^{-2}). Transient species were monitored by a pulsed Xe flash lamp (EG&G FX 425) with a perpendicular beam against the laser beam. The transmittance light was focused into a monochromator (Jovin-Yvon HR320) that was connected to a photomultiplier tube (Hamamatsu Photonics R758). Data were collected by a digital oscilloscope (Sony Tektronix TDS 620B), and analyzed on a Power Macintosh. The sample and cell were renewed with every laser shot in order to avoid any effects resulting from the accumulation of photoproducts.

Results and Discussion

Figure 1a shows the transient absorption spectra of TPM in the presence of 585 Torr of nitrogen. The fully relaxed spectrum (○) was identified as TPM radical by an analogy with the condensed phase result.[14] The initial spectrum (●) originated in hot TPM and hot TPM radical. The region around 320 nm of the initial spectrum, which was broad and slightly red-shifted compared to the relaxed spectrum, was understood to be hot TPM radical. In the short-wavelength region, the spectra of hot TPM and hot TPM radical overlapped each other. Other transients, such as a triplet state[15] and cation radical[16] as well

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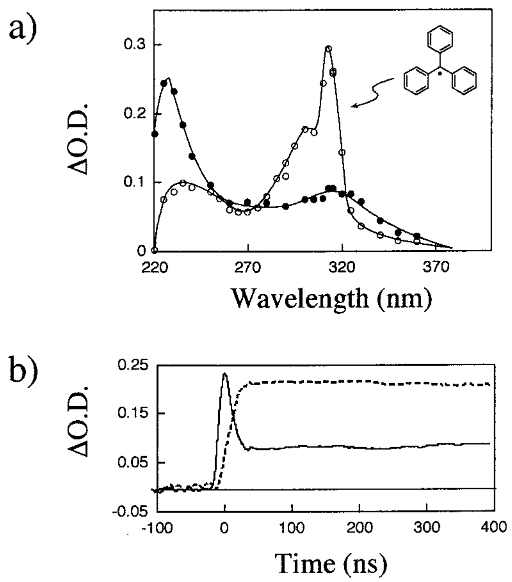

Figure 1. (a) Transient absorption spectra of TPM at 0 s (●) and 400 ns (○) after the laser pulse in the presence of 585 Torr of nitrogen at 433 K. Laser fluence was 16.0 ± 0.1 mJ cm^{-2}. (b) Transient time profiles of TPM at 230 nm (solid line) and at 315 nm (dotted line).

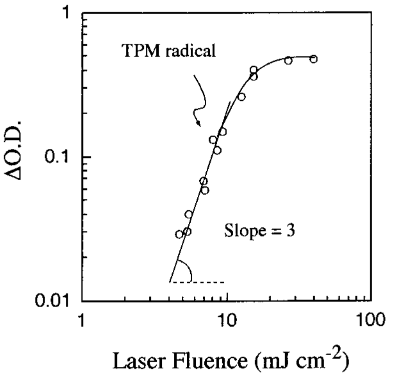

Figure 2. Correlation between the absorbance of TPM radical and laser fluence. TPM radical (315 nm) was observed at 400 ns after the laser pulse in the presence of 600 Torr of nitrogen at 443 K. The solid line has a slope of 3.0.

as fluorescence, were not observed in the wavelength region up to 700 nm. Figure 1b shows the transient time profiles at 230 and 315 nm. The time profile at 230 nm consisted of a sharp hump, which represents the formation and collisional deactivation of hot molecule, and the stable absorption of TPM radical. Under these experimental conditions, the collisional frequency with nitrogen was on the order of 10^{10} s^{-1}. Therefore, the hot TPM should have been quenched, and the yield of TPM radical suppressed, by nitrogen.[17] On the basis of the experimental results and the reported photophysical properties of TPM in the liquid phase,[18] we concluded that the dominant deactivation pathway of TPM in an electronic excited state is internal conversion, and that TPM radical was derived from vibrationally hot TPM.

Figure 2 shows the correlation between the absorbance of TPM radical and laser fluence. The result clearly shows that the formation of TPM radical is a three-photon process. Interestingly, the TPM radical formation was saturated. The saturation behavior observed in the absorbance was mainly due to the depletion of the ground state. Moreover, the decay of TPM radical was observed in the laser fluence region above 20 mJ cm^{-2}, while TPM radical seemed to be stable in the lower laser fluence region, as shown in Figure 1b. The decay rate of TPM radical was estimated to be 1.0×10^6 s^{-1} at 40 mJ cm^{-2}. Such a slow decay should not correspond to the hot molecule reaction in the presence of 600 Torr of nitrogen. The TPM radical is known to be a stable radical in the deoxygenated inert solvent. An intermolecular coupling of TPM radical is difficult due to the steric hindrance.[19] We concluded that the TPM radical−H recombination process may be responsible for the slow decay as in the case of benzyl radical studied by Damm et al.[20]

The reaction rate constants could be predicted by the statistical reaction theory if the reaction occurred thermally. The rate constants have been well applied to alkylbenzenes[21] and olefins.[22] The dissociation rate constants of TPM were estimated on the basis of RRKM theory.[23] Assuming that the internal energy of hot TPM consisted of the photon energy and vibrational energy at the experimental temperature, the maximum amounts of energy accumulated by photon absorption were 1300 (2 $h\nu$), and 1920 (3 $h\nu$) kJ mol^{-1}. These reaction rate constants were then calculated to be 6.4×10^7 (2 $h\nu$) and 4.4×10^{10} s^{-1} (3 $h\nu$).[24] These results indicate that it is necessary to accumulate at least three photons in order to compete with the collisional relaxation rate by nitrogen.

However, the rise time of TPM radical (9.3×10^7 s^{-1}, 315 nm) was slower than the estimated value (4.4×10^{10} s^{-1}) for the three-photon process.[25] The slow rise can be explained in terms of the delay that consequentially occurred in the sequential multiphoton hot molecule mechanism. The three-photon-absorbed species should appear after the formation of the two-photon-absorbed species, although the reaction rate of the three-photon-absorbed species is very fast. In addition, the rise time was apparently not affected either in the presence or in the absence of nitrogen. The product rise time may therefore not always be coincident with the absolute reaction rate in the sequential multiphoton processes. The delay of TPM radical formation is, however, another strong piece of evidence that a hot molecule mechanism is involved, because if a predissociation reaction had taken place, such a long delay would not been observed.

The multiphoton chemistry of alkylarenes has also been studied in the condensed phase;[26] however, the reaction mechanism in the condensed phase was very different from that in the gas phase. In the condensed phase, TPM radical was formed by the deprotonation of a cation radical, which was formed by the two-photon ionization.[14] The lifetime of an electronic excited state is a key factor in determining the mechanisms. Recent ultrafast experiments showed that very fast internal conversion occurred in the gas phase with VUV excitation. For example, the lifetime of the benzene S_2 state was determined to be 50 fs, which corresponds to the internal conversion rate.[3] For the following reasons, hot molecules are good intermediates in multiphoton reactions: (1) they were formed instantaneously after the laser excitation; (2) they have relatively long lifetimes compared to the electronic excited state; and (3) they have large molar extinction coefficients. In the condensed phase, the second photon will be absorbed by (1) the lowest electronic excited state, and then ionize, or (2) the vibrational ground states, which are in the electronic ground state, and in which photon energy was not accumulated. Although the multiphoton reaction is one of the most important advantages of laser-induced reactions,[27] ionization is the most probable process in the condensed phase. The multiphoton reaction via a hot molecule is a special case. A simple summation of photon energy exceeds the ionization potential, however, the energy was distributed over the whole vibrational modes (99 in the case of TPM). If the photon energy was distributed equally to each vibrational modes, the energy was only 6.9 kJ mol^{-1} per vibrational mode. Therefore, the absorption of second photon is not enough to ionize the molecule. As a result of photoexcitation−internal conversion sequences, the photon energy was accumulated as vibrational energy. Hot molecule reaction would be important in multiphoton laser chemistry because a neutral radical, not a cation radical, is obtained, even though a multiphoton reaction takes place. The multiphoton hot molecule reactions have also been applied to molecules that have been deemed to be photoinert, such as biphenylene.[28] The present study extends the area of the multiphoton hot molecule mechanism, and finds that the accumulation of energy from absorbing more than two photons would induce more intractable chemical reactions in large molecules. It should be emphasized that an internal conversion is not a useless photophysical process, but a very interesting pathway for forming an important intermediate in multiphoton chemistry.

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