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Two-photon photodissociation of gaseous azulene at 325 nm

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The two-photon photodissociation of gaseous azulene at 325 nm is reported. Acetylene is the major photodissociation product. The quantum yields for acetylene produced by irradiation of neat azulene at its normal vapor pressure and as a function of argon bath gas pressure are reported. The quantum yield of acetylene produced from irradiated azulene at its normal vapor pressure (~ 10 mTorr) is $\sim (5.85 \pm 1.46) \times 10^{-6}$. Using a mechanism by which internal conversion precedes the absorption of the second photon, the two-photon absorption cross section is calculated.

I. INTRODUCTION

Because of its characteristic photophysical properties,[1–6] azulene is used in collisional energy transfer,[7–23] spectroscopic, and photophysical studies.[1–6] Following electronic excitation, fast internal conversion (IC) produces vibrationally highly excited molecules in the ground electronic state.[1–3] Internal conversion from S_1 and S_2 to S_0 occurs with lifetimes of picoseconds and nanoseconds, respectively, and quantum yields close to unity.[4,5] Excitation to higher states such as S_3 or S_4 converts rapidly to S_2 followed by internal conversion to S_0.[6]

Highly vibrationally excited azulene in the ground electronic state, prepared by IC, is used extensively by several groups to study collisional energy transfer.[7–23] The collisional deactivation of excited azulene by various bath gases has been studied by Hippler, Troe, and coworkers[9–12] using time-resolved ultraviolet absorption spectroscopy (UVA).[13–15] and by Barker and coworkers[16–21] using time-resolved infrared fluorescence (IRF).[16] Jalenak *et al.*[22] have studied the vibration-to-vibration energy transfer from highly excited azulene molecules to CO_2 by diode laser absorption spectroscopy. Hassoon *et al.*[23] used azulene as the hot donor in their collision-induced sensitization method for studying supercollisions. Lim and Gilbert,[24] using classical trajectory calculation techniques, obtained collisional energy transfer parameters of azulene colliding with a series of monatomic bath gases.

Recently, the unimolecular isomerization of azulene to naphthalene under thermal activation and selective photoexcitation has been studied by Brouwer *et al.*[25] and by Damm *et al.*[26] The thermal isomerization of azulene was studied in a shock tube in the temperature range of 1300–1900 K.[25] Single and multiphoton UV excitation with a nanosecond pulsed excimer laser at 193 (Ref. 26), 248 (Ref. 26), and 308 nm (Ref. 10) were used in the photoisomerization studies. It was shown that the isomerization process is a "clean" unimolecular reaction with 1:1 conversion of azulene to naphthalene. By comparing the measured rate constants from the photoexcitation experiment and those from the thermal isomerization data fit to Rice–Ramsberger–Kassel–Marcus (RRKM) calculations, these workers conclude that only at the short wavelength (193 nm) does azulene undergo a one-photon photoisomerization. However, in the longer wavelengths (248 and 308 nm), two- and three-photon excitation is needed to induce reaction.[10,26] In the present work, we found that 325 nm excitation of azulene, in addition to photoisomerization, also leads to photodissociation in a two-photon absorption process.

Typically photodissociation of organic molecules does not occur under one-photon irradiation unless very short wavelengths are used,[27,28] however, multiphoton absorptions result in dissociation over a wide range of wavelengths. Normally, UV multiphoton excitation coupled with very fast internal conversion produces high vibrational excitation of molecules in their ground electronic state. Dissociation, as well as ionization, unimolecular isomerization, and collisional energy transfer processes can then be studied. Two methods are used in these studies: (a) time-resolved methods using intense and ultrashort pulses for both excitation and probe; or (b) continuous-wave methods measuring yields as a function of light intensity and gas pressure. The UV multiphoton dissociation of toluene, ethylbenzene, and *n*-butylbenzene was studied by Nakashima *et al.*[29] Using 193 nm excitation under conditions where the one-photon dissociation process was completely quenched by collisions, they found that the yields of benzyl radical produced increased linearly with the square of the laser intensity. On going to higher intensities, the yield did not depend any more on the square of the laser intensity, but decreased, and this was attributed to the destruction of benzyl radical by absorption of a third photon. Hippler *et al.*[30] studied the multiphoton dissociation of toluene, ethylbenzene, and cycloheptatriene. The yields of benzyl and methyl radicals and other final products were measured as a function of the laser intensity and the bath gas pressure. They have also found that the observed yields indicated a two-photon absorption process. However, they have suggested a spontaneous fragmentation of the highly excited radicals produced by the initial two-photon excitation of the parent molecule instead of an absorption of a third photon, as suggested by the former work as the reason for the decline in the product yield.

In this work, we explore a new channel—the dissociation of azulene producing acetylene as the main final product along with other minor products. This dissociation occurs at relatively modest laser intensities compared to those intensities used in earlier work reported above.

II. EXPERIMENT

Gas samples of pure azulene at its room temperature vapor pressure (near 10 mTorr) and diluted with argon as inert bath gas (up to 20 Torr) were irradiated at 325 nm. A helium–cadmium cw laser (Omnichrome, Series 74) was used with a maximum power of 40 mW and beam diameter of 1.2 mm. The laser power was monitored by a calibrated Scientech 365 power meter with the UV-360001 calorimeter head. The irradiation cell was a Pyrex cylinder (22.5 cm length, 1.3 cm inside diameter) outfitted with two Brewsters angle quartz windows.

The yield of acetylene was measured as a function of laser intensity and as a function of the added inert gas pressure at a constant intensity of 23.5 mW. Neutral density filters were used to vary the laser light intensity. The amount of azulene in the irradiation cell was kept constant and equal to its vapor pressure during the 1 h irradiation. A broadband laser beam expander (Ealing, expansion ratio X5) was used for some of the runs.

After irradiation, the samples were analyzed by a HP 5890 gas chromatograph equipped with a flame ionization detector and 3392A integrator. Quantitive analysis was performed for acetylene only using a 12 ft×1/8 in. stainless steel column packed with Chromosorb 104, 80/100 mesh (Alltech Associates). The column temperature was maintained at 100 °C with a He carrier gas flow rate of 30 ml/min. Retention time of 1.6 min was obtained.

Azulene (Aldrich, >99%) was purified by pumping on the sample with the vacuum line. The argon (Matheson, >99.998%) was used without further purification, but it contained a very small quantity of acetylene. Blank runs at each pressure of argon were used in order to correct for this residual acetylene present in the argon bath gas.

III. RESULTS AND DISCUSSION

The linear dependence of the amounts of acetylene produced in the irradiation of neat azulene vapor pressure as a function of the square of the laser intensity is shown in Fig. 1. When the laser beam was expanded by a beam expander, no acetylene was detected. Moreover, using collimated light from a 200 W high pressure mercury lamp with intensities comparable to those of the laser (10 nm bandwidth centered at 325 nm), no acetylene was observed.

In Fig. 2, the inverse quantum yields of acetylene produced by the photodissociation process is plotted against the argon pressure in the cell. As the pressure increased, the quantum yield Φ_d decreased due to collisional deactivation as expected in photolysis experiments in the gas phase. At pressures higher than 10 Torr, the quantum yield became very low. The measured Φ_d at the normal vapor pressure of azulene is $(5.85 \pm 1.46) \times 10^{-6}$. The large error (~25%) in the quantum yield values results from difficulty in measuring accurately the small amount of laser intensity absorbed by the azulene needed to calculate the number of photons absorbed.

Three other products, in addition to the isomerization product naphthalene, were observed in the irradiated samples. One of these products was identified as phenylacetylene, however, it is produced in very small quantities (less than one-fifth the yield of acetylene) making a quantitative

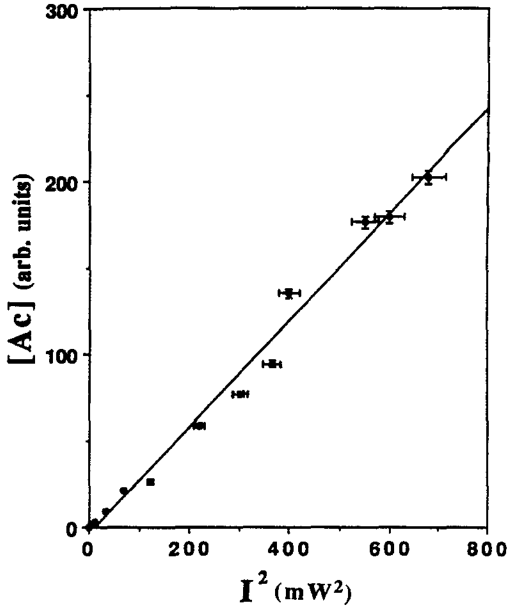

FIG. 1. The relative amounts of acetylene produced after irradiation of azulene as a function of the square of the laser intensity (one arbitrary unit $= 3.07 \times 10^{11}$ molecules).

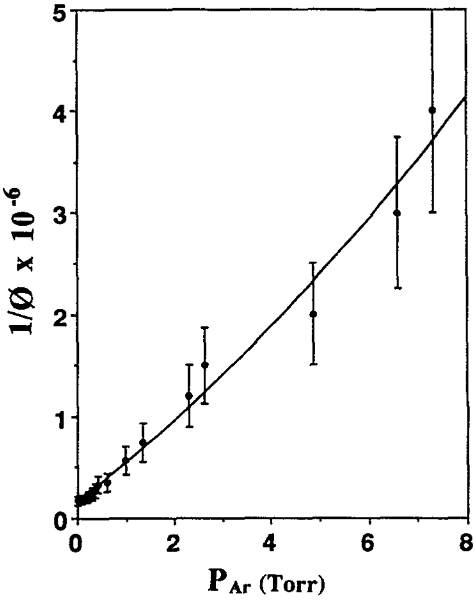

FIG. 2. The inverse quantum yields of acetylene produced as a function of the added bath gas pressure.

analysis impossible. The other two unidentified products were also produced in very small amounts. Probably these two unidentified products are not C_8H_6-type compounds, such as pentalene or benzocyclobutadiene, which are unstable in the present experimental conditions.

A. Mechanism for the two-photon absorption and azulene dissociation

The linear dependence of the acetylene yield on the square of the laser intensity, as shown in Fig. 1, indicates a two-photon absorption process. Our proposed two-photon dissociation mechanism rests also on the following facts:

(1) Toluene and other molecules[29,30] excited by one photon produce, after fast internal conversion, highly vibrationally excited molecules in the ground electronic state. The hot molecules possess a broad and strong absorption spectrum in the UV region[12,13] for facile absorption of a second photon leading to dissociation.

(2) The pressure-dependent dissociation quantum yield obtained in the present work and the two color time delayed multiphoton ionization (MPI) experiments[31] support a reaction mechanism[10] in which azulene photoexcited to S_2, undergoes internal conversion to an internally hot S_0^* which absorbs an additional photon, and internally converts again to the ground electronic state S_0^{**} before dissociating.

The following mechanism for the excitation and decomposition reaction is proposed:

$S_0+h\nu\rightarrow S_2$	one-photon absorption σ_1,
$S_2\rightarrow S_0^*$	internal conversion $(\tau_{\mathrm{IC}}^2)^{-1}$,
$S_0^*+M\rightarrow S_0+M$	deactivation $\beta\omega$,
$S_0^*+h\nu\rightarrow S_n^*$	second-photon absorption σ_2,
$S_n^*\rightarrow S_0^{**}$	internal conversion $(\tau_{\mathrm{IC}}^n)^{-1}$,
$S_0^{**}+M\rightarrow S_0+M$	deactivation $\beta\omega$,
$S_0^{**}\rightarrow \mathrm{Ac}+\mathrm{Products}$	decomposition k_d,
$S_0^{**}\rightarrow \mathrm{Na}$	isomerization k_i,

where S_n indicates an electronic level of azulene, Ac and Na are acetylene and naphthalene, respectively, and M indicates a deactivating collider.

Making the usual steady state assumption and allowing for the fact that $(\tau_{\mathrm{IC}}^2)^{-1}$, $(\tau_{\mathrm{IC}}^n)^{-1}\gg$ all other processes, one obtains the general expressions for acetylene formation and the number of photons absorbed per unit time and unit volume

$$(\mathrm{Ac})=\frac{\sigma_1\sigma_2 k_d I_0^2\Delta t(\mathrm{Az})}{(\beta\omega+k_d+k_i)(\beta\omega+\sigma_2 I_0)}, \tag{1}$$

$$I_{ab}=\frac{\beta\omega\sigma_1 I_0(\mathrm{Az})+2\sigma_1\sigma_2 I_0^2(\mathrm{Az})}{\beta\omega+\sigma_2 I_0}. \tag{2}$$

Δt is the irradiation time and (Az) is the number of azulene molecules per cm^3. β is the collision efficiency and ω is the collision frequency. Two collision partners must be considered, so we take

$$\beta\omega=\beta_1\omega_1+\beta_2\omega_2, \tag{3}$$

where the subscript 1 indicates Az–Az collisions and 2 indicates the Az–Ar collisions. The collision frequencies are given by

$$\omega_1=Z_1^{\mathrm{LJ}}P_{\mathrm{Az}} \quad\text{and}\quad \omega_2=Z_2^{\mathrm{LJ}}P_{\mathrm{Ar}}, \tag{4}$$

where Z_i^{LJ} is the Lennard-Jones collision number. The quantum yield is defined as

$$\Phi=[d(\mathrm{Ac})/dt]/I_{ab} \tag{5}$$

and the following general expression for the inverse quantum yield is obtained:

$$\Phi^{-1}=\left[\frac{\omega_1^2+(k_i+k_d)\omega_1}{\sigma_2 I_0}+2(\omega_1+k_i+k_d)\right]\frac{1}{k_d}+\left(\frac{k_i+2\omega_1}{\sigma_2 I_0}+2\right)\frac{\beta_2\omega_2}{k_d}+\frac{\beta_2^2\omega_2^2}{k_d\sigma_2 I_0}. \tag{6}$$

It can be seen that Eq. (6) takes the pressure P dependent form

$$\Phi^{-1}=a+bP_{\mathrm{Ar}}+cP_{\mathrm{Ar}}^2. \tag{7}$$

The mechanism predicts a nonlinear dependence of the quantum yield on the argon pressure which is the case in Fig. 2.

B. Estimation of parameters

The absorption cross section for the second photon σ_2 can be calculated by using appropriate values of the various parameters in Eqs. (1), (2), and (6). The value of $\omega_1=Z_1^{\mathrm{LJ}}P_{\mathrm{Az}}$ is estimated by taking[9,17] $Z_1^{\mathrm{LJ}}=3.3\times10^7$ $\mathrm{Torr}^{-1}\,\mathrm{s}^{-1}$ and $P_{\mathrm{Az}}=10$ mTorr. Z_2^{LJ} is equal to 1.69×10^7 $\mathrm{Torr}^{-1}\,\mathrm{s}^{-1}$ (Ref. 9). The value of the unimolecular rate coefficient for isomerization to naphthalene at 61 540 cm^{-1} (two 325 nm photons) is[10] $k_i=1\times10^7\ \mathrm{s}^{-1}$, good to within a factor of 2 of the correct value.[10] The dissociation rate of azulene to acetylene plus other products k_d can be obtained using the following equation:

$$k_d=k_i\frac{\Phi_d}{\Phi_i}. \tag{8}$$

The value of $\Phi_d\sim5\times10^{-6}$, the quantum yield for dissociation which we measured, and $k_i\sim10^7\ \mathrm{s}^{-1}$ and $\Phi_i\sim4\times10^{-2}$, for isomerization from Ref. 26, yield a value of $k_d\sim10^3\ \mathrm{s}^{-1}$. We use σ_1 of $5.4\times10^{-18}\ \mathrm{cm}^2$ given by Barker *et al.*[32] and Sabal and Carr.[31] Damm *et al.*[10] report σ_1 at the shorter wavelength of 308 nm as $3.3\times10^{-18}\ \mathrm{cm}^2$ similar to the one used here. I_0 for our experiments at constant power and variable pressure was 3.4×10^{18} photon $\mathrm{s}^{-1}\,\mathrm{cm}^{-2}$. The value of β_1 for collisions between azulene molecules is taken to be unity and the collisional efficiency for azulene–argon collisions is estimated from the equation[10]

$$\frac{\beta_2}{1-\beta_2^2}\approx\frac{-\langle\Delta E\rangle S^*}{E-E_0}, \tag{9}$$

where $\langle\Delta E\rangle$ is 210 cm^{-1} (Ref. 9), $S^*\sim9.26$, $E_0\sim22\,000$ cm^{-1} (Ref. 10), and E is 61 540 cm^{-1}. The collisional efficiency thus obtained is $\beta_2=0.05$. A detailed comparison of the quantum yield expression containing β with detailed fine grain master equation calculations show[10] that β can be used instead of the master equation in expressions such as Eqs. (1), (2), and (6).

C. Simplified expressions

With the above values in mind, we can make some simplifying assumptions to obtain simplified expressions for Eqs. (1) and (6) and for the constants *a*, *b*, and *c* in Eq. (7). From the values given above, $\beta_1=1$, $\omega_1=3.3\times10^5$ s^{-1} at the normal vapor pressure of azulene and $k_d \ll k_i$. Given the values of σ_2 obtained by multiphoton ionization experiments[31,33] ($\sim10^{-21}$ cm^2), two-photon isomerization experiments of azulene to naphthalene[10] ($\sim10^{-17}$ cm^2) and emission studies of azulene[34] ($\sim10^{-18}$ cm^2), it can be seen that $\beta_1\omega_1 \gg \sigma_2 I_0$. Since it is also true that $k_i \gg \beta_1\omega_1 \gg k_d$ Eq. (1) can be simplified to

$$(\mathrm{Ac})=\frac{3.24\times10^{16}\sigma_1\sigma_2\Delta t k_d V I_0^2}{k_i Z^{\mathrm{LJ}} A^2}, \tag{10}$$

where V is the volume of the irradiated sample and A is the cross section of the beam.

This simplified expression can be used to evaluate σ_2 from our data of the production of acetylene from neat azulene as a function of the laser power shown in Fig. 1. We obtain $\sigma_2=7.2\times10^{-22}$ cm^2, which from the estimate of our error is probably good to a factor of 2.

Similar consideration leads to the evaluation of *a*, *b*, and *c* of Eq. (7) as follows:

$$a=\omega_1 k_i/\sigma_2 I_0 k_d, \tag{11}$$

$$b=\beta_2 Z_2^{\mathrm{LJ}} k_i/\sigma_2 I_0 k_d, \tag{12}$$

$$c=(\beta_2 Z_2^{\mathrm{LJ}})^2/\sigma_2 I_0 k_d. \tag{13}$$

Equations (11)–(13) enable the evaluation of σ_2 from the pressure-dependent data shown in Fig. 2. The values for σ_2 obtained from the values of *a*, *b*, and *c* of the pressure-dependent quantum yield equation are 1.6×10^{-18}, 2×10^{-18}, and 3.5×10^{-18} cm^2, respectively. These values are self-consistent and in agreement with those values obtained from the isomerization experiments.[10] However, there is a discrepancy with the value obtained from Eq. (10).

D. Evaluations and comparisons

The results reported and analyzed above show very convincingly that the dissociation of azulene to acetylene and other products is a two-photon process which is affected by bath gas collisions. The two-photon absorption cross section is obtained by two different experiments represented by Figs. 1 and 2 and are in good agreement with values reported in the literature.

Multiphoton ionization (MPI) experiments give 6×10^{-21} cm^2 (Ref. 31) and 4.4×10^{-21} cm^2 (Ref. 33) for σ_2, which were obtained using the value of σ_1 of 5.4×10^{-18} cm^2 (Ref. 31) also used in our calculations. Two-photon isomerization of azulene to naphthalene[10] at 308 nm gives $\sigma_2=1.1\times10^{-17}$ cm^2, where σ_1 is given as 3.3×10^{-18} cm^2. From emission studies of azulene[34] at 347.2 nm, σ_2 was determined to be 1.2×10^{-18} and 6×10^{-18} cm^2, where σ_1 was 1×10^{-19} and 5×10^{-19} cm^2.

The values of σ_2 in the isomerization[10] and in the spectroscopic[34] experiments indicate that $\sigma_2>\sigma_1$. This increase in cross section is attributed[10] to the increase in absorption of the hot molecule. On the other hand, MPI experiments[31,33] indicate $\sigma_2<\sigma_1$, contrary to the findings in isomerization or spectroscopic experiments. Our results show that either $\sigma_2<\sigma_1$ [Eq. (10)] or $\sigma_2\sim\sigma_1$ [Eqs. (11)–(13)] which is closer to the MPI results.

The possibility of one-photon isomerization of azulene to naphthalene which then absorbs the second photon and dissociates does not exist. The absorption threshold of naphthalene is 313 nm, a shorter wavelength than the 325 nm photons used in the present experiments. Moreover, even at shorter wavelengths, it was shown[9,25,26] that one-photon isomerization does not occur at 308 and 248 nm excitation due to the low energy of the photon. In addition, the acetylene was obtained at pressures up to 10 Torr, where collisional deactivation is expected to cool any hot naphthalene produced, so any secondary dissociation of naphthalene is ruled out.

The ionization potential of azulene is 59 846 cm^{-1}, less than the two 325 nm photon energies of 61 538 cm^{-1}. Hence, ionization of azulene should be considered. Lubman *et al.*[33] have studied the multiphoton ionization (MPI) of naphthalene and azulene in a crossed laser–molecular beam experiment. They claim that the MPI of azulene proceeds via resonant or near-resonant autoionizing states. A two-color excitation overlapped in space, but delayed in time showed no ionization of azulene. In the present experiment, ionization of the naphthalene produced during the irradiation does not take place because its absorption threshold is at shorter wavelength than the one used. Sabol and Carr[31] have also studied the MPI of azulene using a pulsed two-color experiment. They find that in addition to one-color, two-photon excitation which they assign to two-photon resonance enhanced ionization via S_2, they see an enhancement of the ionization signal in the two-color spatially overlapped-time delayed experiment. They explain the disagreement with the Lubman *et al.* work by claiming a much higher ion detection sensitivity. Both experiments showed none or very low levels of ionization and were performed with pulsed lasers with orders of magnitude of higher power than used in the current experiment. It is safe to conclude therefore that no MPI is obtained in the current studies.

IV. CONCLUSIONS

The photodissociation of azulene by UV multiphoton excitation occurs at relatively long wavelength (325 nm) and low laser intensity. This effect was probably present in the previous studies of the photophysics and photochemistry of the azulene molecule. The yields for acetylene, the main photodissociation product, as a function of the laser intensity show that the dissociation is a two-photon absorption process. The pressure dependence of the acetylene yield indicates a deactivation process of the hot ground electronic state of azulene. The two-photon absorption cross section is obtained from the dependence of acetylene produced on the square of the laser intensity (Fig. 1) and from the pressure dependence of the quantum yield (Fig. 2) in the dissociation experiments. The values obtained agree with previously reported values.

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