Generation and characterization of highly vibrationally excited molecular beam

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A simple method to generate and characterize a pure highly vibrationally excited azulene molecular beam is demonstrated. Azulene molecules initially excited to the $S_1$ state by 266-nm UV photons reach high vibrationally excited levels of the ground electronic state upon rapid internal conversion from the $S_1$ electronically excited state. VUV laser beams at 157 and 118 nm, respectively, are used to characterize the relative concentrations of the highly vibrationally excited azulene and the rotationally and vibrationally cooled azulene in the molecular beam. With a laser intensity of 34 mJ/cm$^2$, 75% of azulene molecules absorb a single 266-nm photon and become highly vibrationally excited molecules. The remaining ground-state azulene molecules absorb two or more UV photons, ending up either as molecular cations, which are repelled out of the beam by an electric field, or as dissociation fragments, which veer off the molecular-beam axis. No azulene without absorption of UV photons is left in the molecular beam. The molecular beam that contains only highly vibrationally excited molecules and carrier gas is useful in various experiments related to the studies of highly vibrationally excited molecules. © 2006 American Institute of Physics. [DOI: 10.1063/1.2150467]

I. INTRODUCTION

Highly vibrationally excited molecules contain significant amounts of energy. Consequently, the chemical behavior of these vibrationally “hot” molecules is expected to be very different from that of molecules at room temperature. The structure, spectroscopy, energy transfers, and reactive properties of hot molecules are interesting both from an experimental and theoretical point of view.

Energy transfer to and also from a highly vibrationally excited molecule is important in a number of chemical processes. For example, in thermal unimolecular reactions the energy required for reaction is accumulated from thermal collisions with bath molecules, whereas in chemical activations, recombination reactions, and assorted photochemical processes, collisions can stabilize highly excited intermediates. Although energy transfer of highly vibrationally excited molecules has been studied for many years, a number of important questions remain unanswered. One such question concerns the direct experimental measurement of the shape of the energy-transfer probability distribution function.\footnote{Also at Department of Chemistry, National Taiwan University, Taipei 10617, Taiwan.} Accurate information is generally unavailable because the majority of these experiments have been performed in bulk systems. Bulk collision experiments suffer from extensive averaging over thermal velocity distributions, population distributions, and multiple collisions, thus washing out much of the details. Consequently, only averaged quantities, such as the first moment $\langle \Delta E \rangle$ (i.e., the mean energy lost per collision) and the second moment $\langle \Delta E^2 \rangle$ of energy-transfer probability distribution function, or a crude distribution, are possible. By contrast, scattering experiments incorporating molecular beams offer single-collision conditions and narrower velocity distributions. This translates into more precise energy distributions and therefore more accurate information concerning energy-transfer probability function in energy-transfer reactions. Fewer energy transfer experiments involving highly vibrationally excited molecules have been performed using molecular-beam techniques. One possible reason for this may be due to a general lack of intense hot molecular beams. When the relative concentration of hot molecules in the beam is low, background noise from the original rotationally cooled beam molecules reduces the signal-to-noise (S/N) ratio, making measurements more demanding. A pure, intense highly vibrationally excited molecular beam offers the experimenter improved S/N ratios, thus allowing for enhanced measurement capabilities and increasing the usefulness of this technique for studies in spectroscopy and chemical reaction dynamics.

There are a variety of methods available for generating highly vibrationally excited molecules. Collisions with the walls of a high-temperature vessel is one such way of accomplishing this task.\footnote{Also at Department of Chemistry, National Taiwan Normal University, Taipei, Taiwan.} Hot molecules can also be made in shock tube experiments, whereby the rapid increase in vibrational energy results from kinetic to vibrational (TV) energy transfer.\footnote{Also at Department of Chemistry, National Tsing Hua University, Hsinchu 30013, Taiwan.} CO$_2$ lasers have been employed to pump molecules to high internal energy levels of the ground electronic state via multiphoton absorption.\footnote{Also at Department of Chemistry, National Taiwan University, Taipei, Taiwan.} This technique is especially useful with molecules containing C–F bonds.
Unfortunately, all of these methods end in wide internal energy distributions. An efficient way of preparing hot molecules, possessing very narrow internal energy distributions, involves excitation with UV photons to high electronically excited levels followed by their rapid internal conversion to high vibrational levels of the electronic ground state. In this case, the width of the internal energy distribution depends only on the initial internal energy of the molecule and the UV photon energy. By combining a molecular beam with an intense UV laser beam to saturate the absorption of molecules in the molecular beam. Hot molecules are generated by exciting the molecule under investigation should possess the following properties: (1) It must have a large UV absorption cross section of the first UV photon. A large absorption cross section ensures that every molecule absorbs at least one photon under the largest available laser intensity. (2) The quantum yield of internal conversion must be large, whereas the quantum yield for photon emission must be small. If the quantum yield for photon emission is sufficiently large, then most of the excited molecules will decay via photon emission. (3) If the UV photon energy is larger than the dissociation barrier, then the dissociation rate of the hot molecule needs to be very slow. In other words, long dissociation lifetimes ensure that chemical bond cleavage does not occur before detection. (4) Cross sections for absorption of a second UV photon must be sufficiently small. It is imperative that most of the molecules absorb only one photon in order to generate high concentrations of hot molecules. (5) Molecules absorbing multiple UV photons must either dissociate rapidly into neutral fragments or ionize. Because molecular fragments tend to fly off of the molecular beam axis due to their recoil velocity, fragment concentrations decrease rapidly along the molecular-beam axis. Consequently, these fragments can be neglected if the detection system is positioned far enough downstream of the excitation zone. Additionally, the molecular fragments will not produce a background if the detector is mass-selective. Ions generated from multiphoton absorption are repelled by the appropriate electric field (placed before the detection system) and therefore do not contribute to background.

II. EXPERIMENT

A. Overview

Our approach to generating a highly vibrationally excited molecular beam is similar in scope to one of the methods described above, namely the UV excitation and fast internal conversion. However, we have developed a method to determine and optimize the relative concentrations between the highly vibrationally excited and cold molecules. We use an intense UV laser beam to saturate the absorption of molecules in the molecular beam. Hot molecules are generated upon internal conversion to the ground state. In order to generate a “pure” highly vibrationally excited molecular beam, the molecule under investigation should possess the following properties: (1) It must have a large UV absorption cross section of the first UV photon. A large absorption cross section ensures that every molecule absorbs at least one photon under the largest available laser intensity. (2) The quantum yield of internal conversion must be large, whereas the quantum yield for photon emission must be small. If the quantum yield for photon emission is sufficiently large, then most of the excited molecules will decay via photon emission. (3) If the UV photon energy is larger than the dissociation barrier, then the dissociation rate of the hot molecule needs to be very slow. In other words, long dissociation lifetimes ensure that chemical bond cleavage does not occur before detection. (4) Cross sections for absorption of a second UV photon must be sufficiently small. It is imperative that most of the molecules absorb only one photon in order to generate high concentrations of hot molecules. (5) Molecules absorbing multiple UV photons must either dissociate rapidly into neutral fragments or ionize. Because molecular fragments tend to fly off of the molecular beam axis due to their recoil velocity, fragment concentrations decrease rapidly along the molecular-beam axis. Consequently, these fragments can be neglected if the detection system is positioned far enough downstream of the excitation zone. Additionally, the molecular fragments will not produce a background if the detector is mass-selective. Ions generated from multiphoton absorption are repelled by the appropriate electric field (placed before the detection system) and therefore do not contribute to background.

Cross sections for absorption of the first UV photon and fluorescence quantum yields can generally be found in the literature. They can also be easily measured. Low fluorescence quantum yields are achieved by the proper selection of molecular species and UV photon wavelength. For example, most aromatic molecules have large fluorescence quantum yields after absorbing UV photons in electronic transitions to low vibrational levels of the $S_1$ excited state. Interestingly, fluorescence quantum yields decrease rapidly with increasing photon energy and internal conversion usually becomes the dominant process for the higher energy levels of aromatic molecules. The slow dissociation rate criteria for highly vibrationally excited molecules as outlined in this experiment can readily be achieved if the UV photon energy is smaller than the energy needed for the lowest dissociation barrier. It can also be satisfied when UV photon energies just exceed the dissociation barrier if large polyatomic molecules (~10 to 20 atoms) are chosen. For example, the dissociation lifetimes ($\tau$) for benzene and toluene are greater than $\tau = 300 \mu$s, after excitation with 248-nm photons. Unfortunately, cross sections for absorption of a second UV photon are not generally known. Consequently, a diagnostic tool to characterize the relative concentrations of molecules absorbing zero, one, or multiple UV photons is required. It will enable us to adjust the UV laser intensity and optimize and characterize the concentration of the highly vibrationally excited molecules in the molecular beam.

In this work we choose azulene and UV wavelength at 266 nm as an example to generate a pure highly vibrationally excited molecular beam. The photophysical and photochemical properties of azulene are well known. Azulene has been employed as a hot molecular species in various studies. Absorption cross sections for azulene at 266 nm are as large as $1.7 \times 10^{-16}$ cm$^2$. Absorption of a 266-nm photon corresponds to excitation to the $S_1$ excited state. The first UV photon absorption can easily be saturated using the fourth harmonic (266 nm) of a commercial Nd:YAG laser. The fluorescence quantum yield from the excited state is very small and internal conversion to the ground electronic state dominants. C–H bond cleavage has the lowest dissociation threshold, approximately 113 kcal/mol, which is greater in energy than a 266-nm photon energy. Therefore azulene does not dissociate into fragments after absorption of a single 266-nm photon. Large absorption cross sections, low fluorescence quantum yields, and slow dissociation rates satisfy the requirements for the molecular properties associated with highly vibrationally excited molecules.

The respective ratios for azulene molecules absorbing zero, one, or multiple 266-nm photons are obtained via the VUV photoionization of azulene at 157 and 118 nm. This is illustrated using the following set of reactions:

$$Az + h\nu(266 \text{ nm}) \rightarrow Az^*(S_4) \rightarrow Az^4(S_0),$$

$$Az + h\nu(157 \text{ nm}) \rightarrow Az^+ + e^-,$$

$$Az^4(S_0) + h\nu(157 \text{ nm}) \rightarrow Az^+ + e^-,$$

$$Az + h\nu(118 \text{ nm}) \rightarrow Az^+ + e^-,$$
\[ \text{Az}^+(S_0) + h\nu(118 \text{ nm}) \rightarrow \text{C}_8\text{H}_6^+ + \text{C}_3\text{H}_2 + e^- . \]  

(5)

Reaction (1) describes the excitation to the \( S_1 \) state with subsequent fast internal conversion to high vibrationally excited levels of the ground state. Both 157- and 118-nm photons are sufficiently energetic to ionize azulene and this is shown in reactions (2) and (4). The difference between 118- and 157-nm photoionization is shown in reactions (3) and (5). Hot azulene molecules, \( \text{Az}^+(S_0) \), ionized by 157-nm photons do not crack into smaller cations. However, these same molecules may dissociate into smaller ionic fragments after being photoionized by 118-nm photons. In fact, there are many possible cationic dissociation channels. Reaction (5) is one of the major channels and we use it here to represent all cationic dissociation channels.\(^\text{18}\)

The amount of hot azulene in the molecular beam is determined using the following four-step procedure. (1) The molecular beam is not irradiated by 266-nm UV laser photons. The azulene ion intensity \( I_1 \) (mass-to-charge ratio \( m/e = 128 \)) obtained from the 157-nm photoionization (as shown by reaction 2) represents the initial cooled azulene intensity. (2) The molecular beam is irradiated by 266-nm laser photons. The ion intensity \( I_2 \) (\( m/e = 128 \)) obtained at 157 nm represents the sum of the unexcited and excited (single UV photon absorption) azulene intensities in the molecular beam. The difference in ion intensities between steps 1 and 2 is due to the loss of azulene molecules, which absorbed two or more UV photons and became fragments or azulene cations. These cations are repelled out of the molecular beam by an electric field before the arrival of the 157-nm VUV laser pulse. (3) Similar to step 1, the molecular beam is not irradiated by 266-nm UV laser photons. The azulene ion intensity \( I_4 \) (\( m/e = 128 \)) obtained from the 118-nm photoionization (reaction 4) also represents the initial cooled azulene intensity. However, \( I_1 \) and \( I_4 \) differ due to the different ionization cross sections for azulene at the respective VUV wavelengths. (4) The molecular beam is once again irradiated by 266-nm laser photons. The ion intensity \( I_3 \) (\( m/e = 128 \)) obtained from the 118-nm photoionization represents the azulene molecules, which did not absorb UV photons. This is because the molecules, which absorbed one 266-nm photon, were cracked into smaller ionic fragments by the 118-nm photoionization process. Azulene molecules that absorbed two or more photons became fragments or cations that were repelled out of the molecular beam by the electric-field interaction before the VUV laser pulse arrived. From the set of ion intensities \( I_1, I_2, I_3, \) and \( I_4 \), the respective probabilities \( P_0, P_1, \) and \( P_2 \), for azulene molecules absorbing zero, one, or multiple UV photons under 266-nm laser irradiation can be obtained using the following set of equations:

\[ P_0 = I_4/I_3, \]  

(6)

\[ P_2 = 1 - I_2/I_1, \]  

(7)

\[ P_1 = 1 - P_0 - P_2 = I_2/I_1 - I_4/I_3. \]  

(8)

B. Method

In the present work, the ion intensities for reactions 2–5 were obtained using a time-of-flight mass spectrometer. The apparatus, as shown in Fig. 1, consisted of a 266-nm laser beam, a 157-nm laser beam, a 118-nm laser beam, a differential pumped molecular beam machine with ion optics, ion detector, and signal processing electronics.

The ion optics were formed by 29 concentric electrodes with outer and inner diameters of 90 and 60 mm, respectively. The ion optics were originally designed for the velocity map ion image.\(^\text{19}\) However, here we changed the voltages applied on the optics such that they work in the time-of-flight mode, i.e., we adjusted the voltages so that the width of time-of-flight peak was minimized.

The 266-nm laser beam was provided from the fourth harmonic of a Q-switched Nd:YAG laser (Spectra Physics Lab 190, pulse duration: \( \sim 5 \) ns). The diameter of the laser beam was 3 \( \times 8 \) mm after it passed through a rectangular iris. The 157-nm laser beam was generated from an excimer laser (GAM laser EX50 with 2-ns time jitter). It passed through an iris (2-mm diameter) and was focused by a lens (\( f=40 \) cm). The laser-beam diameter was less than 1 mm at the ionization region. The 118-nm laser beam was generated by frequency tripling of the third harmonic of the other Q-switched Nd:YAG laser in a rare gas cell. A 355-nm laser beam with 30 mJ/pulse from the third harmonic of a Nd:YAG laser (Spectra Physics GCR190, 30 Hz, \( \sim 6 \) ns pulse duration) was focused by a lens (\( f=25 \) cm) into a rare-gas cell filled with 20 Torr of Xe to generate 118.24-nm VUV photons. After the generation of the VUV laser beam in the rare-gas cell, the coaxial UV and VUV laser beams were sent to a home-made vacuum monochromator which separated the VUV laser beam from the UV laser beam. The distance between the laser focal point in the rare-gas cell and the grating in the vacuum monochromator was set to be 100 cm. A concave grating with 600 l/mm and radius of 98.5 cm (Richardson Grating Laboratory) was used in the monochromator. The concave grating refocused the expanding VUV radiation into the molecular beam, which was 100 cm away from the grating. The separation distance between the VUV laser beam from the UV laser beam at the ionization region was very large (\( \sim 4 \) cm) and only the VUV laser beam was sent to the

FIG. 1. Schematic diagram of the experimental apparatus.
ionization region. The grating was set in the near-normal incidence ($20\degree$) and the first order of the 118-nm radiation from the grating was used. Since the VUV laser bandwidth ($<9$ cm$^{-1}$) was much smaller than the spectral resolution of the monochromator, the VUV beam size at the ionization region was not affected by the dispersion of the grating. It only depended on the UV laser-beam size and the focal lengths of both the concave grating and the lens in front of the rare-gas cell. We estimated that the VUV beam diameter was less than 0.5 mm in the ionization region.

The differential pumped molecular-beam machine consisted of a source chamber, a differential pumped chamber, and a main chamber. Azulene vapor was formed by flowing ultrapure He at a pressure of 1.1 atm through a reservoir filled with azulene sample at room temperature. The azulene/He mixture was then expanded through a pulsed nozzle (Even Lavie pulsed valve, 0.2-mm orifice diameter, 30 Hz) to form a molecular beam in the source chamber. It was then collimated by two skimmers (1.5-mm diameter), and entered the main chamber. The pressure of the main chamber remained at $4 \times 10^{-8}$ Torr when the nozzle was operated at 30 Hz.

The molecular beam, VUV laser beam (157 or 118 nm), and the flight axis of TOF mass spectrometer were perpendicular to each other. The 157-nm laser beam and 118-nm laser beam propagated in the opposite direction. The 266-nm laser beam propagated in the plane formed by molecular beam and VUV laser beam, but the angle between 266-nm laser beam and VUV laser beam was about $10\degree$. All laser beams crossed the molecular beam at the center of the ion optics. The delay time between UV and VUV laser pulse was 1 $\mu$s. A chevron microchannel plate (MCP) detector was used to detect these ions. After amplification of the signal by a fast preamplifier (Phillips Scientific, model 6954), the mass spectrum was recorded with a digital oscilloscope (Tektronix TDS 5054). The spectrum was averaged for 2000 laser shots at each UV laser intensity.

III. RESULTS AND DISCUSSION

The ion intensity ratios, $I_4/I_3$ and $I_2/I_1$, were measured as a function of UV laser fluence. The results are shown in Fig. 2 and indicate that $P_0$ decreases rapidly with increasing UV laser fluence. When the laser fluence reached 34 mJ/cm$^2$, $P_0$ approached zero, suggesting that all of the azulene molecules in the molecular beam absorbed at least one photon. The number of azulene molecules absorbing more than one photon also increases with increasing laser fluence, but the rate of increase is not as steep as the rate of decrease in $P_0$. As a consequence, the probability of azulene absorbing only one photon also increases with increasing laser fluence before $P_0$ reaches zero. The maximum value for $P_1$ was 75% at laser fluence of 34 mJ/cm$^2$. Under these conditions, the amount of cold azulene molecules remaining in the molecular beam is less than 1%, which is below the sensitivity of our detection system.

We have attempted to measure the dissociation lifetime of azulene after its absorption of two or more UV photons in order to assure ourselves that these molecules dissociate quickly before the arrival of the VUV probe laser pulse. No product growth within a time window of 100 ns to 20 $\mu$s was observed under high UV laser fluence. The dissociation lifetime for azulene after its excitation by a single 193-nm photon is approximately 20 $\mu$s. Therefore the dissociation lifetime for azulene after absorption of two 266-nm photons is expected to be very short. Recent results using Rice-Ramsperger-Kassel-Marcus (RRKM) theory indicate that the dissociation rate after absorption of two UV photons is four orders of magnitude greater than that at 193 nm. In all likelihood, the dissociation rate for azulene upon absorption of two UV photons is simply too fast to be observed at this time. Another possibility is that most of the molecules absorbing multiple UV photons become cations and therefore few neutral dissociation products are produced. The generation of cations coupled with the fast dissociation of azulene molecules absorbing multiple photons indicates that the signal we observe from reactions 2–5 is not interfered with by the possible slow dissociation rate from multiphoton absorption.

There are a number of molecules with similar molecular properties to azulene that would satisfy the requirements described in this study and could therefore be used to generate pure highly vibrationally excited molecular beams. The VUV wavelengths required to characterize the relative concentration of hot molecules in a molecular beam would need to be carefully adjusted for each molecule investigated. The VUV photon energies for the two different photoionization pulses (e.g., 157 and 118 nm) need to be high enough to ionize cooled molecules, but not too high such that these same molecules crack into smaller ionic fragments after photoionization. In other words, the VUV photon energies for both pulses should be between the ionization potential (IP) and the appearance potential (AP) of the first ionic fragment. It is important that the photon energy for one of the VUV pulses (e.g., 157 nm) be low enough, such that hot molecules do not
crack into ionic fragments after photoionization. It is equally important that the photon energy of the other VUV pulse (e.g., 118 nm) is large enough in order for hot molecules to quickly crack into fragments after photoionization. This particular set of requirements ensures that the relative concentration of hot molecules in the molecular beam can be measured accurately using Eqs. (6)–(8). The recommended choice for the two VUV laser pulses is such that the photon energy of one pulse is slightly above the IP of the molecule and that the photon energy of the other pulse is slightly below the AP of the molecule. The energy difference between AP and IP is indeed the maximum UV laser photon energy that can be utilized to excite these molecules. If the UV photon energy exceeds the energy difference between AP and IP, hot molecules will be made sufficiently energetic to crack into smaller ionic fragments after photoionization at either VUV wavelength. As a result, the molecules need to have a large UV absorption cross section below this maximum value for the UV photon energy. The larger the difference is between a molecule’s IP and AP, the wider the range of UV wavelengths available. A wide UV wavelength range provides a greater chance that the proper UV wavelength can be chosen such that the UV absorption cross section is large and the fluorescence quantum yield is small. This greatly increases the concentration of highly vibrationally excited molecules.

We have demonstrated that a concentrated hot azulene molecular beam can be generated and characterized using the proper selection of UV and VUV photon energies. We find that in addition to hot azulene and the carrier gas, only a small proportion of molecular cations (due to multiphoton ionization and dissociation) exist in the final molecular beam. Cations are repelled out of the beam by an electric field before the detection. A “pure” highly vibrationally excited molecular beam will be very useful in a wide variety of molecular-beam experiments. We have incorporated this type of molecular beam into our research concerning the energy transfer from highly vibrationally excited molecules in a crossed molecular-beam experiment. The results will be published separately.21

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