Energy transfer of highly vibrationally excited azulene. II. Photodissociation of azulene-Kr van der Waals clusters at 248 and 266 nm

Hsu Chen Hsu, a) Chen-Lin Liu, b) Jia-Jia Lyu, c) and Chi-Kung Ni d)  
Institute of Atomic and Molecular Sciences, Academia Sinica, P.O. Box 23-166, Taipei, 10617 Taiwan  

(Received 15 November 2005; accepted 26 January 2006; published online 5 April 2006)

Photodissociation of azulene-Kr van der Waals clusters at 266 and 248 nm was studied using velocity map ion imaging techniques with the time-sliced modification. Scattered azulene molecules produced from the dissociation of clusters were detected by one-photon vacuum ultraviolet ionization. Energy transfer distribution functions were obtained from the measurement of recoil energy distributions. The distribution functions can be described approximately by multiexponential functions. Fragment angular distributions were found to be isotropic. The energy transfer properties show significantly different behavior from those of bimolecular collisions. No supercollisions were observed under the signal-to-noise ratios $S/N=400$ and 100 at 266 and 248 nm, respectively. Comparisons with the energy transfer of bimolecular collisions in thermal systems and the crossed-beam experiment within detection limit are made. © 2006 American Institute of Physics. [DOI: 10.1063/1.2178296]

I. INTRODUCTION

The photodissociation of van der Waals clusters has been studied extensively. Typically two types of experiments have been performed. One is in the infrared region and the other is in the UV-Vis region. In a typical infrared photodissociation experiment, a single infrared photon is absorbed in some well defined monomer’s vibrational mode within a van der Waals cluster. The binding energy of a van der Waals bond is so low that even a single vibrational excitation of a component molecule can easily exceed the dissociation limit. The excited state dissociates in a finite lifetime. This process has been referred to as vibrational predissociation. The infrared absorption line shapes and monomer product speed and angular distributions have been reported for various molecular systems. 1–5

In the UV-Vis experiments, aromatic molecules are frequently involved in the clusters. In these studies, the aromatic members of the clusters are excited by UV-Vis photons to a low lying vibronic level of the first excited singlet state. Following predissociation, the vibrational distribution of free aromatic members are monitored by UV-Vis fluorescence or multiphoton ionization. 6–12 Recently, velocity map ion imaging technique and velocity resolved time-of-flight mass spectrometry have been applied to determine the photofragment recoil energy distribution of van der Waals clusters following predissociation. 13–17 In all studies, only the molecules in the electronic excited state were probed. No products can be detected if they are populated in the ground electronic state. The internal vibrational/rotational excitation energies in the highly vibrationally excited molecules in all previous studies are relatively low. Most of them are less than 4000 cm$^{-1}$, although some of them are extended up to 8600 cm$^{-1}$.

If the van der Waals clusters can be generated in a highly vibrationally excited level and the fragments in the ground electronic state can be detected, then dissociation of highly vibrationally excited van der Waals clusters can provide the information about energy transfer of highly vibrationally excited molecules. 18 Although the energy transfer in full collisions depends strongly on the orientation of the colliding pair, on the rotational energy, and on the relative kinetic energy of the colliding pair, these parameters are fixed in half collisions. However, since the potential energy surfaces involved in the half collisions and full collisions are the same, it is interesting to find the energy transfer mechanisms for these two processes.

In a previous work, we reported the energy transfer from highly vibrationally excited azulene to Kr atoms using a crossed-beam apparatus. Large energy transfer in the backward scattering, resulting from supercollisions, was observed. 19 The present study reports the dissociation of azulene-Kr clusters. Basically, the azulene molecule in the azulene-Kr van der Waals cluster, $\text{Az} \cdot \text{Kr}$, was photoexcited by a UV photon into the electronic excited state. Scattered azulene molecules produced from the dissociation of clusters were detected by one-photon vacuum ultraviolet (VUV) ionization. The energy transfer distribution was obtained from the measurement of the azulene recoil velocity distribution using time-of-flight (TOF) velocity map ion imaging techniques. Comparisons with the bimolecular collision experiments from thermal systems and crossed-beam experiment are made.

a) Also at Department of Chemistry, National Taiwan University, Taipei, 10617 Taiwan.

b) Also at Department of Chemistry, National Tsing Hua University, Hsinchu, 30013 Taiwan.

c) Also at Department of Chemistry, National Taiwan Normal University, Taipei, 11677 Taiwan.

d) Author to whom correspondence should be addressed. Also at Department of Chemistry, National Tsing Hua University, Hsinchu, 30013 Taiwan; Electronic mail: ckni@po.iams.sinica.edu.tw
II. EXPERIMENT

A. Method

Photodissociation of Az·Kr in a molecular beam was performed by a polarized UV photolysis laser at 266 or 248 nm. The photofragment product, azulene, was ionized by one-photon VUV photoionization. The azulene recoil velocity distribution was measured using TOF velocity map ion imaging techniques.

\[
\text{Az} \cdot \text{Kr} + h\nu(266 \text{ or } 248 \text{ nm}) \rightarrow \text{Az}^* + \text{Kr},
\]

(1)

\[
\text{Az}^* + h\nu(157 \text{ nm}) \rightarrow \text{Az}^+ + e^-.
\]

(2)

The delay time between UV and VUV laser pulses was 1 μs. It was long enough such that the dissociation is complete before the VUV laser pulse arrived. In addition, any azulene produced in the electronic excited state from the dissociation was already in the ground electronic state through internal conversion (internal conversion lifetime \(\tau_{IC} \approx 5\ \text{ns}\)). The VUV wavelength was 157 nm, a photon energy which is high enough so that azulene molecules in the electronic ground states can be ionized. The VUV photon energy is also low enough that azulene with large internal energy would not fragment after ionization. Because of the conservation of energy and momentum, energy transfer from the vibrational energy of azulene to the transnational energy of both azulene and Kr can be obtained easily from the recoil velocity of azulene.

The experimental apparatus is similar to that in our previous study of I\(_2\) photodissociation. The schematic diagram is shown in Fig. 1. A 266 nm laser beam with a pulsed duration of \(\approx 5\ \text{ns}\) was provided from the fourth harmonic of a Nd:YAG (yttrium aluminum garnet) laser (Spectra Physics Lab 190). Both 248 nm laser beam (Lumonics PM-884 with 18 ns pulse duration) and 157 nm laser beam (GAM laser EX50 with 10 ns pulse duration and 2 ns time jitter) were generated from excimer lasers. The differentially pumped molecular beam machine consisted of a source chamber, a differential pumped chamber, and a main chamber. Azulene vapor was formed by flowing the mixture of 3% of Kr in Ne at a pressure of 60 psi through a reservoir filled with azulene sample at room temperature. The Az/Kr/Ne mixture was then expanded through a pulsed nozzle (0.2 mm orifice diameter, 50 μs pulse duration) to form a molecular beam in the source chamber. It was then collimated by two skimmers (1.5 mm orifice diameter), and then entered into the main chamber. The pressure of the main chamber remained at 4 \(\times 10^{-8}\) Torr when the nozzle was operated at 30 Hz.

Both the photolysis laser beam and the VUV laser beam crossed the molecular beam at the center of the ion optics. The molecular beam, VUV laser beam, and flight axis of the TOF mass spectrometer were perpendicular to each other. The UV laser beam propagated in the plane formed by the molecular beam and VUV laser beam, but the angle between the photolysis laser beam and VUV laser beam was about 10°. The polarization direction of the UV laser beam was parallel to the plane of the detector (or the plane formed by the UV laser beam and molecular beam). The UV laser beam size after passing through a rectangular iris was about 2 \(\times 8\ \text{mm}^2\) at the ionization region, and the intensity was about 6 mJ/cm\(^2\) for each laser shot. The corresponding power densities were 1.2 and 0.3 MW/cm\(^2\) for 266 and 248 nm, respectively. The VUV laser beam size was about 0.4 \(\times 3\ \text{mm}^2\) at the ionization region after it passed through a rectangular iris and focused by a cylindrical lens. The energy was about 10 μJ per pulse. We understand that the direction of the molecular beam perpendicular to the time-of-flight axis is not the best choice. This is because in such a geometry the energy resolution is easily affected by the molecular beam velocity distribution. However, in order to make a direct comparison of the transnational energy distribution with that obtained from the crossed-beam study, we kept the direction of the molecular beam the same as that in the crossed-beam experiments.

Since there were a lot of azulene monomers in the molecular beam, the 157 nm laser beam also ionized these molecules and generated a large amount of ions. These ions with the same velocity (molecular beam velocity) were then all focused by the ion optics into a small spot on the detector. In order to avoid saturation and possible damage of the detector, a 2 \(\times 25\ \text{mm}^2\) stainless pin located 5 cm in front of the microchannel plate (MCP) detector was used to block these ions. However, most of the azulene molecules from the dissociation of Az·Kr clusters having velocities different from that of the molecular beam were not obscured by the stainless steel pin.

The kinetic energy and angular distributions of the scattered azulene were measured by time-of-flight mass spectrometer using velocity map ion imaging techniques with the
time-sliced modification.20,21 Basically, the ion optics was formed by 29 concentric electrodes with outer and inner diameters of 90 and 60 mm, respectively. A weak extraction field produced from the ion optics was used to spread the ion turnaround time to several hundred nanoseconds, which permitted good resolution for selection of the longitudinal velocity. While maintaining conventional two-dimension velocity mapping, the third velocity component was mapped linearly to the ion time of flight. A z stack microchannel plate detector (diameter of 40 mm) with a fast decay phosphor (decay to 10% in <5 ns) was used to detect ions and generate the image of ion intensity distribution. Time-sliced images were obtained by a fast gated (10 ns) intensifier (Proxitronic Inc., model BV2581TZ5N). Images from the intensifier were recorded by a video charge coupled device (CCD) camera, and were accumulated in the computer. We used a real time ion-counting method with threshold algorithm to discriminate the low level noise from the video CCD camera. Spatial resolution was further improved by only recording the center pixel of each light spot produced by each ion hitting a microchannel plate assembly.22

In order to make sure that Az·Kr was the major cluster in the molecular beam, the relative concentrations of various clusters were measured by VUV (157 nm) photoionization. Figure 2 shows the TOF mass spectrometry. The relative ion intensities of Az·Kr: Az2: Az·Kr2 are about 17.5:0.9:1. No other clusters were observed.

B. Energy calibration and energy resolution

Since the average energy transferred is very small, a high energy resolution and a good energy calibration in a small energy region are necessary in order to obtain an accurate energy transfer distribution. Energy calibration and energy resolution of the apparatus were performed by measuring I atom recoil velocity from the photodissociation of HI at 266.05 nm, I atom from photodissociation of I2 at 532 nm, and I+ recoil velocity from the photodissociation of I2 at 532 nm. The details have been described in a previous study.20 The energy resolutions at 67, 155, 317, 1168, and 2208 cm−1 due to the ion optics and detection system were found to be 4% (15 cm−1), 15% (23 cm−1), 8% (26 cm−1), 3.5% (41 cm−1), and 3% (67 cm−1), respectively. The molecular beam velocity distribution is about ΔV/V=7%. As a result, the overall energy resolution is about 200 cm−1. However, if the fragment velocity distribution is measured from

the part of the image in which fragment recoil velocity (in the center-of-mass frame) is 90° relative to the molecular beam velocity, the effect due to the molecular beam velocity distribution can be reduced.20 The energy resolution from this part of the image is very close to the resolution limited only by the ion optics and detection system.

III. RESULTS AND DATA ANALYSIS

Before we analyze the images, we need to make sure that the images result mainly from reactions (1) and (2). There are several possible reactions that may contribute to the images and therefore produce background in the image. One is the effect from the multiphoton absorption of 266 or 248 nm photons. The dissociation lifetime of azulene at 193 nm is about 20 μs, and the major channel is H atom elimination.23 Absorption of one 248 or 266 nm photon does not produce any fragment within the delay time (1 μs) between pump and probe laser pulses.24 However, absorption of two or more photons results in fast dissociation or multiphoton ionization. Azulene cations produced from UV multiphoton ionization are generated 1 μs earlier than the azulene cations from VUV photoionization; therefore they can be easily discriminated by the different arrival time in TOF mass spectrum. The dissociation lifetime of two-photon absorption is about four orders of magnitude shorter than that at 193 nm.24 Fragments generated from multiphoton dissociation also can be easily distinguished by the TOF mass spectrometer due to different masses, except for the fragment of azulene due to H atom elimination from the 13C isotopomer of azulene.

\[
\text{Az}^{(13}\text{C isotopomer, } m=129) + n\nu(266 \text{ or } 248 \text{ nm}) \rightarrow (\text{Az} - 1)(m = 128) + \text{H}.
\]

The ratio between m/e=129 and 128 was found to be 0.1, suggesting m/e=129 totally from 13C isotopomer due to the natural abundance of 13C. However, no ion signal at m/e =127, corresponding to H atom elimination from normal azulene (m=128) due to multiphoton absorption, was observed. It indicates that either the amount of products from this channel is too low to be detected at the UV laser intensity we used or the fragment ionization potential is too high to be detected by the VUV photons. Therefore the interference from reaction (3) can be neglected.

The other effect is the possible “slow” dissociation processes of cations. If there is any dissociation process that occurs after the ions leave the TOF acceleration region (~1 μs), the generated ionic fragments which have different masses will arrive at the detector at the same time as that of azulene ion. However, these ionic fragments having recoil velocity obtained from the dissociation process will produce the background in the image. They cannot be discriminated by the arrival time in the TOF mass spectrometer. This slow dissociation process of cations includes the dissociative ionization of hot azulene by 157 nm photons.
pulse. For the UV laser intensity of 6 mJ/cm², the result is as follows:

\[ \text{Az} + h\nu(266 \text{ or } 248 \text{ nm}) \rightarrow \text{Az}^+ , \]  
(4)

\[ \text{Az}^+ + h\nu(157 \text{ nm}) \rightarrow C^+ + D + e^- . \]  
(5)

\( C \) and \( D \) represent the possible azulene fragments. In fact, the apparent potential (AP) of azulene is large enough such that reaction (5) cannot occur.\(^{25}\) As a result, the image we obtained only corresponds to reactions (1) and (2), and the following reaction:

\[ \text{Az} \cdot \text{Kr} + h\nu(157 \text{ nm}) \rightarrow \text{Az}^+ + \text{Kr} . \]  
(6)

The image intensity distribution corresponding to reactions (1) and (2) can be obtained from the following equation:

\[ [\text{Image}] = [\text{Image}]_{\text{on}} - R[\text{Image}]_{\text{off}} . \]  
(7)

\([\text{Image}]\) represents the image from reactions (1) and (2). This is the image we want to obtain. \([\text{Image}]_{\text{on}}\) represents the raw image when the molecular beam is irradiated by both the 266 (or 248) and 157 nm laser beams. It corresponds to reactions (1), (2), and (6). The contribution from reaction (6) needs to be subtracted from \([\text{Image}]_{\text{on}}\). The corresponding contribution from reaction (6) is represented by the second term on the right hand side of Eq. (7). \([\text{Image}]_{\text{off}}\) represents the image when the molecular beam is irradiated by the 157 nm laser beam only. The intensity of \([\text{Image}]_{\text{off}}\) totally results from reaction (6). \( R \) is a constant from experimental measurement. It represents the percentage of \( \text{Az} \cdot \text{Kr} \) left in the molecular beam after irradiation by the photolysis 266 (or 248 nm) laser pulse. The percentage of \( \text{Az} \cdot \text{Kr} \) left after irradiation by the UV laser beam can be measured directly from the TOF mass spectrum using the 157 nm laser pulse with and without UV photolysis laser pulse. For the UV laser intensity of 6 mJ/cm², the result obtained by integrating over the individual peaks in Fig. 3 shows that about 55% of \( \text{Az} \cdot \text{Kr} \) dissociates into fragments, and only 45% of \( \text{Az} \cdot \text{Kr} \) remains in the molecular beam. Therefore, \( R \) is 0.45.

The images of azulene from the \( \text{Az} \cdot \text{Kr} \) cluster dissociation are illustrated in Fig. 4. The recoil energy distribution obtained from the angle integrated image intensity profiles are shown in Fig. 5. The image was integrated from the angle of 65° to 115° and from 245° to 295° relative to the molecular beam direction in order to keep good energy resolution. For energy smaller than 45 cm⁻¹, the image was blocked by the pin in front of the detector. This part of the image was not considered in the data analysis. The distributions can be fitted to multieponential functions.

The translational energy dependence of the fragment angular distribution was obtained when the polarization of the photolysis laser was parallel to the plane of the MCP detector. It was found that the distribution is isotropic.

**IV. DISCUSSION**

Absorption of a 700 nm photon corresponds to the excitation of azulene to the \( S_1 \) state. The lifetime of the \( S_1 \) state has been determined to be less than 1 ps using femtosecond laser pulses.\(^{26}\) Gas phase linewidth measurement shows an increase of the internal conversion rate with the excess vibrational energy.\(^{27-30}\) No fluorescence was observed in the \( S_1 \)
state. The second excited singlet state has a fluorescence quantum yield \( \Phi(S_2 \rightarrow S_0) = 0.04 \).\(^{31}\) The energy dependence of \( S_2 \rightarrow S_0 \) fluorescence of azulene vapor suggests that the radiationless decay is almost exclusively internal conversion through \( S_2 \rightarrow S_1 \) at low vibrational energy, but the \( S_2 \rightarrow S_0 \) internal conversion becomes the dominant photophysical process with the increase of \( S_2 \) vibrational energy.\(^{31-33}\) The lifetime of the \( S_4 \) state was found to be about 3.4 ns at zero excess energy and it decreases with the increase of vibrational energy.\(^{32-34}\) The locations of the \( S_3 \) and \( S_4 \) states are at 34 110 and 35 510 cm\(^{-1}\).\(^{35}\) Excitation to \( S_3 \) and \( S_4 \) shows very broad excitation fluorescence spectra. The fluorescence quantum yield of \( S_4 \) is much smaller than that of the \( S_2 \) state. Excitation to the higher electronic states \( S_1 \rightarrow S_4 \) also produces highly vibrationally excited \( S_0 \) azulene by IC (internal conversion) via the \( S_2 \) state.\(^{35,36}\)

The remarkably fast nonradiative relaxation of the excited state and the low fluorescence quantum yields make azulene itself easily prepared as the highly vibrationally excited molecule in the ground electronic state. Energy-selected highly vibrationally excited azulene over a relatively wide range of energy was produced through internal conversion from the electronically excited singlet state populated by UV/Vis absorption. These molecules were frequently used in the study of energy transfer.\(^{36-39}\) It is assumed that most of the azulene molecules excited with photons will quickly end up as vibrationally excited molecules in the ground electronic state before collisions occur. This assumption can be achieved easily in full collision experiments as long as the mean collision time is much longer than the excited state lifetime. However, it is not necessarily true that the dissociation of \( \text{Az} \cdot \text{Kr} \) van der Waals molecules occurs after the internal conversion to the ground electronic state.

Although we do not have the van der Waals cluster dissociation rate and internal conversion rate of the azulene-Kr complex at 266 or 248 nm for comparison, the following information suggests that after absorption of 266 or 248 nm photons some, if not all, \( \text{Az} \cdot \text{Kr} \) clusters become highly vibrationally excited molecules in the lower electronic states before dissociation occurs. We estimate the lifetime of the \( S_4 \) origin to be about several hundreds of picoseconds from the absorption linewidth and fluorescence quantum yield.\(^{35}\) Absorption of 266 and 248 nm photons corresponds to the excitation to vibrational excited levels of the \( S_4 \) state. The lifetime is estimated to be shorter than that of \( S_4 \) origin from the low fluorescence quantum yield and broad linewidth.\(^{35}\) On the other hand, the fragment isotropic distribution suggests that dissociation of the van der Waals cluster is not a prompt process. The dissociation lifetime must be longer than the rotation period. Quasiclassical trajectory calculation also shows that the dissociation lifetimes of aromatic molecule–Ar clusters are about 100 ps, depending on the vibrational energy. For example, the lifetimes of pyrazine-Ar are 132 and 81 ps for vibrational energies of 4000 and 8500 cm\(^{-1}\), respectively.\(^{40}\) Since the absorption of 266 or 248 nm corresponds to the excitation of azulene to the \( S_4 \) state with excess vibrational energies of 2084 and 4812 cm\(^{-1}\), respectively, the van der Waals cluster dissociation rate in the \( S_4 \) state is expected to be longer than 130 ps due to the reduced vibrational energy in the \( S_4 \) state. At least some of the \( \text{Az} \cdot \text{Kr} \) clusters must have the opportunity to become highly vibrationally excited molecules in the lower electronic states before dissociation occurs.

The other evidence that dissociation occurs after internal conversion is the maximum translational energy. Note that the translational energy shown in Fig. 5 does not take the dissociation energy of van der Waals bond into account. If the total vibrational deactivation energy is considered, the dissociation energy must be added to these values. We do not have the van der Waals bond energy of azulene-Kr at this moment. However, it must be in the same order of magnitude as, or even slightly larger than that of benzene-Ar, which is 590 cm\(^{-1}\).\(^{41}\) The maximum translational energy reaches about 1600 cm\(^{-1}\), as shown in Fig. 5. The total vibrational deactivation therefore is more than 2200 cm\(^{-1}\). It is larger than the available vibrational energy of azulene in the \( S_4 \) state at 266 nm. As a result, at least some of the azulene must become highly vibrationally excited azulene in the lower electronic excited state before dissociation occurs.

The energy gap law and momentum gap law have been used to explain the vibrational predissociation of van der Waals clusters.\(^{42,43}\) The general energy gap law or momentum gap law behavior was observed here, i.e., the distribution has a peak at zero energy and monotonically decreases with energy. Large vibrational energy changes are disfavored. However, the recoil energy distributions are best described by multieponential functions. It turns out that these are the functions that are frequently used as an empirical formula for the simulation of the experimental data in energy transfer experiments. The small vibrational energy released.
to the translational energy and the monotonic decrease of the probability with increase of translational energy are similar to the observation of the other molecular systems.\textsuperscript{13-15} The large probability of translational energy at $E=0$ means that the orbital angular momentum for most of the dissociation fragment pairs is close to zero. Since the initial rotations of the clusters from supersonic expansion are almost zero, we can conclude that the rotational distribution of azulene fragments must peak at zero due to the conservation of angular momentum. This kind of distribution is similar to the rotational distribution from the quasiclassical trajectory calculation of pyrazine-Ar clusters.\textsuperscript{40}

The deactivation of highly vibrationally excited azulene in collisions with Kr has been studied using infrared fluorescence and UV absorption methods at room temperature. The average energies transferred per collision at vibrational energies of 17 500 and 30 600 cm\textsuperscript{-1} were found to be 228 and 230 cm\textsuperscript{-1}, respectively, using UV absorption method.\textsuperscript{37} It shows no vibrational energy dependence on the average energy transferred in this region. On the other hand, the average energies transferred per collision at vibrational energies of 16 666 and 29 670 cm\textsuperscript{-1} were found to be 117 and 171 cm\textsuperscript{-1}, respectively, using infrared fluorescence technique.\textsuperscript{38} It shows strong vibrational energy dependence on the average energy transferred. Recent azulene–rare gas (He, Ar, Xe) energy transfer experiment using two-color kinetically controlled selective ionization (KCSI) shows that the average energy transferred increases linearly with the azulene internal energy. The average energies transferred are 112, 225, and 233 cm\textsuperscript{-1} for azulene with internal energy of 30 000 cm\textsuperscript{-1} in collision with He, Ar, and Xe, respectively.\textsuperscript{36} Compared with the thermal experiments, our experimental values from cluster dissociation show that the average photofragment translational energies at 266 and 248 nm are 186±20 and 210±20 cm\textsuperscript{-1}, respectively. The experimental uncertainties were estimated from the apparatus energy resolution.\textsuperscript{39} Note that these values were obtained under the situation that the energy distributions less than 43 cm\textsuperscript{-1}, which were obscured by the stainless steel pin, were extrapolated by the multiplexponential functions from the distributions of the large energy transfer region. If the total vibrational deactivation energy is considered, the van der Waals bond energy must be added to these values, then the energies transferred that we measured from the dissociation of Az\textperiodcentered{}Kr clusters are larger than that from thermal experiments.

In our previous azulene-Kr crossed-beam studies, inordinate amounts of energy transferred from highly vibrationally excited azulene due to supercollisions were observed.\textsuperscript{19} The scattered azulene due to supercollisions are mainly distributed in the backward direction and energy transfer is as large as 2000–5000 cm\textsuperscript{-1}. However, supercollisions were observed only at large collision energies. In the present work, the maximum amount of kinetic energy released is less than 1600 cm\textsuperscript{-1}. If the van der Waals bond energy ($\sim590$ cm\textsuperscript{-1}) is taken into consideration, the maximum vibrational deactivation energy is still much less than the kinetic energy released in supercollisions. We can conclude that no supercollisions were observed in this work. This can be understood from the fact that the initial relative velocity between Az and Kr in the van der Waals cluster is too small to cause supercollisions to occur. In addition, the orientation between Kr and azulene in the van der Waals cluster may not be in such geometry that supercollisions can occur easily. These make the energy transfer distribution different from that of crossed-beam experiment.

**ACKNOWLEDGMENT**

The work was partly supported by the National Science Council, Taiwan, under Contract No. NSC 93-2113-M-001-007.