The energy-transfer dynamics between highly vibrationally excited azulene molecules and Kr atoms in a series of collision energies (i.e., relative translational energies 170, 410, and 780 cm⁻¹) was studied using a crossed-beam apparatus along with time-sliced velocity map ion imaging techniques. “Hot” azulene (4.66 eV internal energy) was formed via the rapid internal conversion of azulene initially excited to the S₄ state by 266-nm photons. The shapes of the collisional energy-transfer probability density functions were measured directly from the scattering results of highly vibrationally excited or hot azulene. At low enough collision energies an azulene-Kr complex was observed, resulting from small amounts of translational to vibrational-rotational (T-VR) energy transfer. T-VR energy transfer was found to be quite efficient. In some instances, nearly all of the translational energy is transferred to vibrational-rotational energy. On the other hand, only a small fraction of vibrational energy is converted to translational energy (V-T). The shapes of V-T energy-transfer probability density functions were best fit by multiexponential functions. We find that substantial amounts of energy are transferred in the backward scattering direction due to supercollisions at high collision energies. The probability for supercollisions, defined arbitrarily as the scattered azulene in the region 160° < θ < 180° and ΔE_J > 2000 cm⁻¹ is 1% and 0.3% of all other collisions at collision energies 410 and 780 cm⁻¹, respectively. © 2006 American Institute of Physics. [DOI: 10.1063/1.2150468]

I. INTRODUCTION

The collisional energy transfer of highly vibrationally excited molecules (known colloquially as “hot” molecules) is one of the important processes in chemistry. In thermal unimolecular reactions, the energies needed for reaction are accumulated via collisions with bath atoms or molecules, whereas in chemical activation, recombination reactions, and various photochemical processes, collisions can stabilize these highly excited intermediate species.

Collisional deactivation of molecules containing chemically significant amounts of energy has been studied for several decades. Some of the early gas-phase experiments uncovered evidence, albeit indirect, for the collisional quenching of activated molecules from unimolecular rate coefficients in the low-pressure and falloff regions. More recently, experimental techniques have been developed to measure fundamental energy-transfer properties of highly vibrationally excited polyatomic molecules. For example, the average energy transferred (ΔE) per collision along with its dependence on the internal energy E of high-energy molecules has been obtained from several such techniques. Despite the wealth of energy-transfer studies of hot molecules, only scarce information of the collisional energy-transfer probability density function P(E′, E) has been obtained experimentally. Consequently, this is a major bottleneck in these experiments. Most experiments yield averaged quantities such as the first and second moments (i.e., ⟨ΔE⟩ and ⟨ΔE²⟩) of P(E′, E) or the experimental data must be fitted to a chosen empirical formula (e.g., step, monoeponential, biexponential, or Gaussian-type function) from which it becomes impossible to extract the “true” identity of the probability function. Experiments that provide for a direct determination of P(E′, E) as a function of ΔE are needed for a more complete understanding of energy-transfer processes.

Classical trajectory calculations have been employed to examine collisions between rare-gas atoms and hot molecules. These studies confirmed the early experimental result, which revealed that a small number of collisions transferred large amounts of energy and that the energy-transfer mechanism differed from that of normal energy transfer. The calculations suggest that these unusual collisions do not belong to the high-energy tail of the normal energy-transfer distribution, but are in fact, supercollisions and are dynamically constrained. Because the probability for supercollisions is small, buried perhaps in the high-energy tail of the normal energy-transfer distribution, experiments that can elucidate the dynamical constraints will provide a greater opportunity to identify supercollisions than those that depend solely on the energy-transfer probability density function. In this investigation, we combine crossed-beams and time-sliced velocity-map ion imaging techniques to study the energy transfer between Kr atoms and hot azulene.
Azulene molecules at several collision energies (i.e., relative translational energies). The shape of the probability density function $P(E', E)$ from selected initial $E$ to final $E'$ energies is measured directly from the velocity distribution for the scattered azulene molecules. Evidence for supercollisions is reported.

II. EXPERIMENT

A. Method

The experimental apparatus includes a pulsed UV laser set at 266 nm, two pulsed VUV lasers, one at 157 nm and the other at 118 nm, a differentially pumped crossed molecular-beam vacuum chamber and a time-of-flight mass spectrometer (TOF-MS) with a time-sliced velocity-map ion imaging system. A schematic for the apparatus is shown in Fig. 1. The vacuum system that we employ consists of two source chambers, a differentially pumped chamber and a main chamber. In one source chamber, azulene (Az) vapor formed as a carrier gas flowed through a reservoir filled with Az at room temperature. Carrier gases included ultrapure (99.999%) Ar, Ne, and mixtures of Ne (66%) and He (34%) at total pressures of 35, 75, and 95 psi, respectively, for the different collision energies. The Az and rare-gas mixtures were expanded through a pulsed nozzle (0.2-mm-diameter orifice) to form the molecular beam. The molecular beam was collimated by two skimmers (1.0-mm diameter), one in the source chamber and the other in the differentially pumped chamber, before entering the main chamber. A Kr atom beam was created in the other source chamber by expanding ultrapure Kr (99.999%) at a pressure of 400 psi through a pulsed nozzle. The Kr beam passed through two skimmers (2.0-mm diameter) before entering the main chamber. Both the molecular beam and the Kr atom beam were positioned perpendicular to the time-of-flight axis of the mass spectrometer. The two beams crossed each other at a fixed angle of $25^\circ$ and at a position 4 mm below the center of the ion optics. The pulse duration for azulene beam and Kr beam were measured using a fast ionization gauge (Beam Dynamics Inc., model FC-1) and were approximately 31 and 60 µs (full width at half maximum), respectively. Turbo molecular pumps of 2000, 400, 300, and 300 l/s were used to pump the source chamber of the Kr beam, the source chamber of the azulene beam, the differential pumped chamber, and the main chamber, respectively. Gas pressures in the differentially pumped and main chambers remained at $8 \times 10^{-6}$ and $5 \times 10^{-7}$ Torr, respectively, when both nozzles were operated at 30 Hz.

A pulsed UV laser set at 266 nm (area $2.5 \times 25$ mm, intensity $32$ mJ/cm$^2$, and pulse duration 4 ns) crossed the azulene molecular beam 16 mm upstream from the crossing point of the atomic and molecular beams. Azulene molecules in the molecular beam were excited to the $S_4$ state after absorbing a single 266-nm photon. Hot azulene was produced after fast internal conversion (IC) to the ground electronic state within a subnanosecond. Relative concentrations for unexcited and hot azulene in the molecular beam were characterized using VUV laser beams fixed at 157 and 118 nm, respectively. Details for the characterization procedure are described in another publication. For the section of the molecular beam irradiated by the UV laser, 73% of the cold azulene molecules absorbed a single UV photon in their transformation to hot azulene. Approximately 19% of cold azulene molecules absorbed multiple UV photons. They either isomerized to naphthalene and dissociated into fragments within a few nanoseconds, or became cations. Fragments have no effect on the experiment because we only probed the parent mass. These azulene cations were repelled out of the molecular beam by an electric field before entering the collision region. As little as 8% of the azulene molecules did not absorb any UV photon and remained as cold azulene.

After colliding with the Kr atom beam, azulene molecules were ionized by a 157-nm pulsed laser sheet (GAM laser, Inc., model EX50, 2-ns time jitter). The laser was focused by a cylindrical MgF$_2$ lens ($f=40$ cm) before passing through the center of the ion optics. The laser beam’s size in the ionization region was 10 mm wide and less than 0.4 mm thick. The large beam size of the 157-nm laser provides near homogeneous detection sensitivity for the different velocities of the scattered azulene molecules. The delay between the 266- and 157-nm laser pulses was about 20–50 µs and was dependent on the molecular-beam velocity. The delay was adjusted so that the 157-nm laser pulse reached the ionization zone directly after the largest portion of hot azulene molecules passed through the atomic and molecular beam crossing point. We also note that the photon energy of the 157-nm laser is sufficiently large to photoionize both hot and cold azulene. However, the photon energy is still low enough so that these photoionized molecules do not break into ion fragments.

The kinetic energy and angular distributions of the scattered azulene molecules were measured by a TOF-MS that incorporates time-sliced velocity-map ion imaging techniques. The ion optics consisted of 29 concentric electrodes, with each electrode having an inner and outer diameter of 60 and 90 mm, respectively. The electrodes were mounted on eight ceramic rods. Ceramic spacers were inserted to keep the distance between adjacent electrodes. The field-free region of the TOF-MS was about 67 cm. The weak extraction field produced by the ion optics was used to widen the ion turnaround time to several hundred nanoseconds, permitting greater resolution for the selection of the longitudinal velocity. While maintaining conventional two-dimensional velocity mapping, a third velocity component was mapped.

![FIG. 1. Schematic diagram of the crossed molecular-beam apparatus.](Image)
B. Energy calibration and energy resolution

The energy resolution of this experiment is restricted by two main factors: (1) ion optics and the detection system, and (2) the molecular-beam velocity distribution. The energy resolution and calibration of the ion optics and detection system is performed using the photodissociation of I$_2$ and I$_2^+$ at 532 nm. The energy resolutions at 67, 155, 317, 1168, and 2208 cm$^{-1}$ are about 22% (15 cm$^{-1}$), 15% (23 cm$^{-1}$), 8% (26 cm$^{-1}$), 3.5% (41 cm$^{-1}$), and 3% (67 cm$^{-1}$), respectively. The azulene velocity distributions in the molecular beam were measured directly from the azulene ion image using a computer. We utilized a real-time ion-counting method featuring a threshold algorithm to discriminate low-level noise from the CCD. Spatial resolution was further improved by recording only the center pixel of each light spot produced by ions hitting the microchannel plate assembly.

Unscattered azulene monomers in the molecular beam were also photoionized by the 157-nm laser beam. Ions having the same velocity as the molecular beam were focused by the ion optics into a small spot on the MCP detector. In order to avoid saturation and possible damage to the detector, a 2 × 25-mm stainless-steel pin located 5 cm in front of the detector was used to block these ions. Scattered azulene molecules with velocities different from that of the molecular beam were not affected by the stainless-steel pin.

The images with 266-nm irradiation on the azulene molecular beam and the images without 266-nm irradiation were taken alternately after every 20 000 laser shot accumulation. The final image presented in this work was accumulated from a total of 800 000–1 000 000 laser shots, depending on the signal-to-noise ratio.

C. Sensitivity calibration

In crossed-beam experiments, two beams cross each other on a time scale of at least several microseconds. Products with relatively high velocities in the laboratory frame tend to fly away from the detection zone during the crossing period, unlike slower moving products, which tend to accumulate and therefore have a higher probability of being ionized by a probe laser. A “density-to-flux” transformation is required to account for the nonuniform detection sensitivity.

A computer program was written to simulate the detection sensitivity. Spatial and temporal intensity profiles for the pulsed atomic and molecular beams were generated. The scattered product is proportional to the overlap of the respective beam intensity profiles. A spatial profile for the scattered products was derived from the time evolution of the products according to their respective velocities. Because the ionization process in our experiment is one-photon absorption, ionization sensitivity in the direction of laser propagation (X direction) remains uniform. Therefore detection sensitivity is dependent only in the perpendicular direction (Y direction). Overlap of the two-dimensional (2D) ionization laser sheet and the product’s spatial distribution at the time that the probe laser pulse’s arrival corresponds to the detection sensitivity. The parameters used in the simulation include the atomic and molecular-beam velocities, the spatial and temporal profiles for both beams, and the area of the laser sheet. All of these parameters were measured experimentally.

III. RESULTS AND DATA ANALYSIS

Figure 2 shows the spatial distribution for the azulene molecular beam and some of the scattered products at the time the 157-nm laser pulse arrives. The relative concentrations for azulene molecules absorbing zero, one, or multiple 266-nm UV photons as measured by the VUV laser beams set at 157 and 118 nm are also shown. The leading part of the molecular-beam pulse is not irradiated by the UV laser and therefore contains primarily cold azulene. Most of the scattered cold azulene molecules from this portion of the beam fly away from the detection region before the arrival of the VUV ionization laser sheet and therefore are not detected. On the other hand, nearly all of the Azulene molecules confined to the middle portion of the molecular-beam pulse absorb a single UV photon and after rapid IC become hot molecules. Only a small fraction of azulene molecules will absorb zero photons and remain as cold azulene or will become cations or fragments via a multiphoton process. These azulene cations are repelled out of the molecular beam by an electric field before the arrival of the VUV ionization laser pulse. Much of the scattered azulene from this part of the molecular beam stays within the detection region. Consequently, the detection sensitivity for this portion of scattered azulene is high. The trailing part of the molecular beam, like the leading part of the beam, is also not irradiated by the UV laser. Therefore most of the azulene molecules in this portion of the molecular-beam pulse remain as cold molecules that have not yet crossed the Kr atom beam when the VUV ion-
The original cold azulene intensity along the molecular-beam axis (without 266-nm laser, measured by a 1-mm-wide 157-nm laser beam) is given by the area between the curve of intensity profile of Az beam and the line of Az beam direction. The relative intensities for azulene molecules absorbing zero, one, or multiple photons upon irradiation with the 266-nm laser are represented by the following enclosed areas: (1) area between the line of Az beam direction and curve of zero photon represents zero-photon absorption, (2) area between the curve of zero photon and the curve of one photon represents one-photon absorption, (3) area between the curve of one photon and the curve of intensity profile of Az beam represents multiphoton absorption. The molecular beam’s position and scattered azulene’s position are shown at the time the 157-nm laser beam pulse arrives. The firing of the 266-nm laser beam preceded this by 20–50 μs, depending on the molecular-beam velocity. The circles represent the positions of elastic scattered azulene from three different positions of azulene beam. For the scattered azulene molecules that originated from the lead portion of the molecular-beam pulse (represented by the largest circle), most are not within the 157-nm laser ionization region. Consequently, they do not contribute to the image intensity and are represented by the dotted circle. Most of the scattered azulene molecules coming from the middle portion of the molecular-beam pulse, represented by the two smaller circles, remain within the ionization region and are represented by the solid circles.

In each sensitivity in our experiments can be attributed to the large area crossed by the ionizing laser sheet. This significantly reduces the experimental uncertainty in the density-to-flux transformation. The detection sensitivity for cold azulene with the irradiated molecular beam, $S_c(v_x,v_y)$, is much lower than that for hot azulene $S_h(v_x,v_y)$. This is due primarily to the low concentration of cold azulene remaining in the middle part of the molecular-beam pulse. The high detection sensitivity for cold scattered azulene with the unirradiated molecular beam, $S_{c0}(v_x,v_y)$, is due to the large intensity of cold azulene in the molecular beam.

Figures 4(a), 5(a), and 6(a) show the raw images of scattered azulene molecules from collisions with Kr atoms at collision energies of 170, 410, and 780 cm$^{-1}$, respectively. The scale is shown in the number of ion counts. The number reaches ~1000 at the largest intensity, and it is only 0–3 at the background noise level. The rectangular blank in the upper right-hand corner is the part of the image blocked by the stainless-steel pin positioned in front of the MCP detector. The images of Figs. 4(a), 5(a), and 6(a) contain both scattered hot and cold azulene. They are represented by the terms on the right-hand side in the following equation:

$$E_{av}(v_x,v_y) = S_h(v_x,v_y) \times I_h(v_x,v_y)$$

$$E_{av}(v_x,v_y) + S_c(v_x,v_y) \times I_c(v_x,v_y).$$

$E_{av}(v_x,v_y)$ represents the experimental raw image intensity at velocities $v_x,v_y$, with the UV laser irradiating the molecular beam. $I_h(v_x,v_y)$ and $I_c(v_x,v_y)$ are the “true” image intensities at velocities $v_x,v_y$, for scattered hot and cold azulene, respectively. $I_h(v_x,v_y)$ is the image intensity we seek. As shown by Eq. (2), $I_c(v_x,v_y)$ can be obtained from the experimental raw image $E_{av}(v_x,v_y)$, with the unirradiated molecular beam,

$$E_{av}(v_x,v_y) = S_{c0}(v_x,v_y) \times I_c(v_x,v_y).$$

Images resulting from the small amount of scattered cold azulene in the molecular beam, $S_{c0}(v_x,v_y) \times I_c(v_x,v_y)$, are shown in Figs. 4(b), 5(b), and 6(b). In general, this image intensity accounts for about 11% of the raw image intensity, $E_{av}(v_x,v_y)$. Much of of the raw image intensity in Figs. 4(a), 5(a), and 6(a), comes from the scattering of hot azulene, $S_h(v_x,v_y) \times I_h(v_x,v_y)$. The image intensity of $E_{av}(v_x,v_y)$ mainly contributed from hot azulene largely reduces the experimental uncertainty. The “true” image of scattered hot azulene, $I_h(v_x,v_y)$, is obtained from Eq. (1), whereby
$S_1(v_x,v_y) \times I_1(v_x,v_y)$ is subtracted from the raw image intensity $E_{uv}(v_x,v_y)$ before being normalized by the hot azulene sensitivity matrix, $S_0(v_x,v_y)$. The results are illustrated in Figs. 4(c), 5(c), and 6(c).

Figures 4(c), 5(c), and 6(c) also include the respective Newton diagrams, initial azulene, and Kr beam velocities, center-of-mass velocity, relative velocity, and elastic collision circle. The elastic collisions are distributed along the elastic collision circle according to their deflection angles. The elastic collisions that have small deflection angles are obscured by the stainless-steel pin and cannot be detected. The image inside the elastic collision circle represents the energy up $\Delta E_{up}$, translation-vibration and rotation (T-VR) collisions, whereas the image outside of the circle represents the energy down $\Delta E_{dp}$, vibration-translation (V-T) collisions. All of these images (for the different collision energies) share a similar feature, a strong intensity distribution in the forward scattering direction. Additionally, there is a backward scattering peak with small intensity inside the elastic collision circle. With increasing collision energy, this peak shifts further inward and its intensity decreases. Outside of the elastic collision circle, the intensity in the forward scattering direction decreases rapidly with increasing $\Delta E_a$. The backward scattering intensity is not as large and also does not decrease as fast as that for forward scattering at collision energies 410 and 780 cm$^{-1}$, respectively.

The shapes of energy-transfer probability density functions at various scattering angles can be obtained from the images presented in Figs. 4(c), 5(c), and 6(c). The component of relative velocity uncertainty at each angle is taken into consideration for the data analysis. The final results, illustrated in Figs. 7 and 8, show the shapes of energy-transfer probability density functions after the deconvolution from relative velocity distribution. The energy-transfer prob-

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**FIG. 4.** (Color) Images and Newton diagrams for collision energy 170 cm$^{-1}$: (a), (b), and (c) represent the raw images $E_{uv}(v_x,v_y)$, the scattered cold azulene image $S_1(v_x,v_y) \times I_1(v_x,v_y)$ and the “true” scattered hot azulene image $I_h(v_x,v_y)$, respectively. (a), (b), and (c) are plotted on the same scale.

**FIG. 5.** (Color) Images and Newton diagrams for collision energy 410 cm$^{-1}$: (a), (b), and (c) represent the raw images $E_{uv}(v_x,v_y)$, the scattered cold azulene image $S_1(v_x,v_y) \times I_1(v_x,v_y)$ and the true scattered hot azulene image $I_h(v_x,v_y)$, respectively. (a), (b), and (c) are plotted on the same scale.
abilities for both energy down V-T and energy up T-VR collisions are shown. Note that the azulene in the molecular beam before collisions is rotationally cool. The contribution from initial rotational energy can be neglected. For the energy down V-T collisions, the shapes of the energy-transfer probabilities are nearly identical for forward, side, and backward scattering at the lowest collision energy (170 cm\(^{-1}\)), although the magnitudes are different. As the collision energy increases to 410 cm\(^{-1}\), the shapes of the probability

FIG. 6. (Color) Images and Newton diagrams for collision energy 780 cm\(^{-1}\): (a), (b), and (c) represent the raw images \(E_{\text{ex}}(v_x,v_y)\), the scattered cold azulene image \(S_{\text{ex}}(v_x,v_y)\) \(\times I_{\text{sc}}(v_x,v_y)\) and the true scattered hot azulene image \(I_{\text{sc}}(v_x,v_y)\), respectively. (a), (b), and (c) are plotted on the same scale.

FIG. 7. The shapes of energy down \(\Delta E_{\text{u}}\) V-T probability density functions at various scattering angles: (a) collision energy 170 cm\(^{-1}\); thin solid line: forward scattering \((40 < \theta < 50)\); dotted line: sideways scattering \((80 < \theta < 100)\); the thick solid line: backward scattering \((160 < \theta < 180)\). (b) Collision energy 410 cm\(^{-1}\); thin solid line: forward scattering \((30 < \theta < 40)\); dotted line: sideways scattering \((80 < \theta < 100)\); thick solid line: backward scattering \((160 < \theta < 180)\). (c) Collision energy: 780 cm\(^{-1}\); thin solid line: forward scattering \((20 < \theta < 40)\); dotted line: sideways scattering \((80 < \theta < 100)\); the thick solid line: backward scattering \((160 < \theta < 180)\).

FIG. 8. The shape of energy up \(\Delta E_{\text{u}}\) T-VR probability density functions at various scattering angles. (a) Collision energy: 170 cm\(^{-1}\); thin solid line: forward scattering \((40 < \theta < 50)\); dotted line: sideways scattering \((80 < \theta < 100)\); the thick solid line: backward scattering \((160 < \theta < 180)\). (b) Collision energy: 410 cm\(^{-1}\); thin solid line: forward scattering \((30 < \theta < 40)\); dotted line: sideways scattering \((80 < \theta < 100)\); thick solid line: backward scattering \((160 < \theta < 180)\). (c) Collision energy: 780 cm\(^{-1}\); thin solid line: forward scattering \((20 < \theta < 40)\); dotted line: sideways scattering \((80 < \theta < 100)\); the thick solid line: backward scattering \((160 < \theta < 180)\).
functions for both forward and side scattering remain nearly the same. However, there is a tail in the high-energy region for backward scattering and transferred energies as large as 500–5000 cm\(^{-1}\) have been observed. The contribution from the high-energy tail in the backward scattering increases as the collision energy increases to 780 cm\(^{-1}\). It also spreads out somewhat to side-way scattering. For energy up collisions, the respective shapes for forward, side, and backward scattering all differ. The small increase in the probability as \(\Delta E_u\) increases in the backward scattering direction at collision energies of 410 and 780 cm\(^{-1}\) is partly due to the existence of the backward scattering peak.

We noticed that molecular-beam velocity distribution affects the shape’s energy-transfer probability density functions. Although the effect is small due to the high-speed ratio \((V/\Delta V)\) of the molecular beam, it is angle and collision-energy dependent. Therefore it is worthwhile to understand the effect in order to make sure that the difference we observed at different collision energies are not simply due to the different speed ratios of molecular beams at different collision energies. The angle between azulene velocity and relative velocity is very small (about \(-20^\circ\)) at collision energy of 780 cm\(^{-1}\). However, this angle becomes large (\(-60^\circ\)) at the collision energy of 170 cm\(^{-1}\). On the other hand, the angles between Kr velocity and relative velocity are always close to 90° (from \(-95^\circ\) to \(-130^\circ\)). Both velocity distributions of azulene and Kr therefore give rise to the distribution (or uncertainty) of the relative velocity. However, the effect of the azulene velocity distribution on the relative velocity is larger at high collision energy than that at low collision energy, and the effect of the Kr velocity distribution on the relative velocity is small at all collision energies. The final effect is that the distribution of the relative velocity results in slightly overestimating the amount of energy transfer in the forward direction at high collision energy. As a result, the difference between the energy-transfer probability density functions at forward and backward directions should be slightly larger than that in raw data. Since the difference between the energy-transfer probability density functions at forward and backward directions in raw data at large collision energy is already larger than that at small collision energy, the deconvolution of velocity distribution simply further enhances our observation, i.e., the backward scattering contains more high-energy tail than that in the forward scattering at high collision energy.

The shapes of total energy-transfer probability density function and the energy-transfer density function for energy down collisions are quite different. They cannot fit to multiexponential functions.

### IV. DISCUSSION

The images for scattered hot azulene reveal important details about the energy-transfer mechanism. For energy up T-VR collisions, we observe a strong forward scattering peak along with a weak backward scattering peak, which indicates the formation of a short-lived azulene-Kr complex. A complex that results in small \(\Delta E_u\) transfer. However, the intensities of the backward peak decrease and move further toward inside the elastic collision circle as the collision energy increases. The decrease of the backward peak intensity with the increase of initial relative translational energy can be understood from the fact that the Az and Kr are not easily trapped by the van der Waals potential well complex when the relative velocity is large. The corresponding T-VR energy-transfer values of the backward peaks are 0, 100, and 500 cm\(^{-1}\) for collision energies 170, 410, and 780 cm\(^{-1}\), respectively. The shapes of the energy-transfer probability density functions obtained in this experiment for T-VR energy transfer are very different from the exponential functions that have been used in thermal energy experiments or in most computer simulations. The difference can be attributed mainly to the Maxwell-Boltzmann distribution of translational energies and Boltzmann distribution of internal and rotational energies in thermal experiment.
On the other hand, only a small percentage of vibrational energy is converted to translational energy in these collisions. The maximum vibrational energy released to translational energy is only about 3%, 10%, and 13% of the available vibrational energy at the respective collision energies 170, 410, and 780 cm$^{-1}$. However, the amount of transferred energy is not small. The energy transferred as large as 4000–5000 cm$^{-1}$ was observed at large collision energies. Although the resulting energy-transfer probability density functions can be described using multienvelopes, the corresponding energy-transfer mechanisms for each component in the multienvelope function are found to differ for the different collision energies. For example, at the lowest collision energy 170 cm$^{-1}$, all of the exponential functions have nearly the same contribution from the various scattering directions. This can be seen in Fig. 7(a) in which the shape of probability function is the same in the forward, side, and backward scattering directions. However, contributions from the different scattering directions to each component in the multienvelope function differ for collision energies 410 and 780 cm$^{-1}$. The contribution from scattering in the backward direction to these components describing the high-energy tail in the probability density increases at high collision energies. This large energy transfer observed in the reverse scattering direction and at higher collision energies suggests that the energy-transfer mechanism is likely to be supercollisional in nature.

Although supercollisional models have been proposed to describe the unusual energy-transfer dynamics of hot molecules, supercollisions remain an important problem in the field of energy transfer. In addition to the large amounts of energy transferred, classical trajectory calculations suggest that supercollisions have special dynamical constraints and are not simply associated with the high-energy tail of the normal energy-transfer distribution. For example, classical trajectory calculations by Gilbert and co-workers were undertaken to examine supercollisions between highly excited azulene molecules and Xe atoms. They showed that large amounts of energy are transferred to Xe, when during the collision, the hydrogen atom from azulene is “squashed” between Xe and the azulene carbon skeleton, causing a strong interaction on the repulsive wall of the intermolecular potential.

The supercollisions that we observe only in the backward scattering direction and at large collision energies indicate that these collisions must occur at small impact parameters with large enough collision energy. The probability for supercollisions, defined arbitrarily as the scattered azulene in the region 160° < $\theta$ < 180° and $\Delta E_\text{in}$ > 2000 cm$^{-1}$, is about 1% and 0.3% of all other collisions at collision energies 410 and 780 cm$^{-1}$, respectively. Although the probability is small, the effect of supercollisions on the properties, such as reaction rates, which depend nonlinearly on the amount of energy transferred, is large.

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