Energy transfer of highly vibrationally excited biphenyl

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The energy transfer between Kr atoms and highly vibrationally excited, rotationally cold biphenyl in the triplet state was investigated using crossed-beam/time-of-flight mass spectrometer/time-sliced velocity map ion imaging techniques. Compared to the energy transfer of naphthalene, energy transfer of biphenyl shows more forward scattering, less complex formation, larger cross section for vibrational to translational (V→T) energy transfer, smaller cross section for translational to vibrational and rotational (T→VR) energy transfer, larger total collisional cross section, and more energy transferred from vibration to translation. Significant increase in the large V→T energy transfer probabilities, termed supercollisions, was observed. The difference in the energy transfer of highly vibrationally excited molecules between rotationally cold naphthalene and rotationally cold biphenyl is very similar to the difference in the energy transfer of highly vibrationally excited molecules between rotationally cold naphthalene and rotationally hot naphthalene. The low-frequency vibrational modes with out-of-plane motion and rotationlike wide-angle motion are attributed to make the energy transfer of biphenyl different from that of naphthalene. © 2010 American Institute of Physics. [doi:10.1063/1.3495766]

I. INTRODUCTION

Collisonal energy transfer of molecules containing chemically significant amounts of energy has been studied for several decades. It is one of the important processes in chemistry. In thermal unimolecular reactions, the energies needed for reactions 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.

Lindermann\(^1\) first discovered the importance of molecular energy transfer in thermal unimolecular decomposition in 1921. In Lindermann’s theories, each collision suffered by the activated molecules was considered to be strong. A strong collision is assumed to transfer as much as 30 kcal/mol or more in a single collision. Although Lindermann’s theory provides a model to explain the pressure dependence of unimolecular reactions, experiments from early unimolecular reaction rate coefficients in the low-pressure and fall-off regions shows significantly difference from theoretical prediction.\(^2\) Those experiments indicated that instead of strong collision, average energy transfer in each collision is very small. Energy transfer of highly vibrationally excited diatomic molecule, KBr, has been investigated using crossed-molecular-beams. Large amount of energy transfer from vibration to translation was observed.\(^3\)–\(^6\) On the other hand, new experimental techniques have been developed to directly measure the average energy per collision of highly vibrationally excited polyatomic molecules in the past three decades.\(^7\)–\(^15\) They confirmed the suggestion from unimolecular reaction rate coefficient measurements, i.e., the average vibrational energy transfer per collision is generally less than a few kcal/mol and may be less than 0.1 kcal/mol. Despite the wealth of energy-transfer studies of highly vibrationally excited molecules, little experimental information about the energy transfer distribution and energy transfer mechanism is available. This is because all these experiments have been performed under bulk conditions. Their results are averages of the outcomes of individual collisions over an ensemble of colliding molecules. Detail information about the result of single collision is easily washed. Consequently, this is a major bottleneck in understanding the energy transfer of highly vibrationally excited molecules.\(^16\),\(^17\)

Recently we have studied the energy transfer between rare gas (Ar and Kr) and highly vibrationally excited molecules (azulene, naphthalene, methyl-naphthalene) using crossed-beam/time-of-flight mass spectrometer/time-sliced velocity map ion imaging techniques.\(^18\)–\(^22\) Some details of energy transfer distribution and mechanism were obtained. For example, we have demonstrated that at low enough translational collision energies complex with lifetime longer than rotation period can be formed. Although the lifetime of this complex is longer than most of the other collision durations, energy does not transfer from highly vibrationally excited molecules to translational energy. Instead, energy is transferred from translation into vibration and/or rotation of the highly vibrationally excited molecules. Increasing translational collision energy not only increases large amounts of vibration to translation (V→T) energy transfer, but also enhances the translation to vibration-rotation (T→VR) energy transfer. The increase of T→VR energy transfer is much larger than that of V→T energy transfer as the translational collision energy increases. As a result, it does not help to stabilize the highly vibrationally excited molecule. On the other hand, rotation was found to be a gateway to transfer...
large amount of vibrational energy to translational energy. Increasing the initial rotation energy increases the \( V \rightarrow T \) energy transfer probability, but decreases the \( T \rightarrow VR \) energy transfer probability. Rotation also enhances the large \( V \rightarrow T \) energy transfer probabilities, termed supercollisions. Energy transfer of highly vibrationally excited molecules between rotationally cold naphthalene and 2-methylnaphthalene does not show observable difference, indicating the motion of methyl group does not play an important role.

In this work, we report the collisional energy transfer between Kr and highly vibrationally excited, rotationally cold biphenyl \((C_6H_5C_6H_5)\) in the triplet state. Comparison to the energy transfer of naphthalene shows that low vibrational frequency modes of biphenyl, such as out-of-plane motions and the rotationlike wide-angle motions, greatly enhance the vibration to translation energy transfer. This kind of vibration makes the energy transfer of biphenyl very different from that of naphthalene.

II. EXPERIMENT

The experimental apparatus includes a pulsed uv laser set at 266 nm, one vacuum ultraviolet (vuv) laser at 157 nm, a differentially pumped crossed-beam vacuum chamber and a time-of-flight mass spectrometer with a time-sliced velocity-map ion imaging system. The schematic for the apparatus is shown in Fig. 1. The details have been described in the previous studies. Only a brief description is described here.

The vacuum system that we employed consisted of two source chambers, a differentially pumped chamber, and a main chamber. In one source chamber, biphenyl molecular beam was formed as the carrier gas (Ar, 60 psi) flowed through a reservoir filled with biphenyl at temperature 120 °C and then expanded through a high temperature (180 °C) pulsed nozzle. A Kr atomic beam was created in the other source chamber by expanding ultrapure Kr at a pressure of 200 psi through a pulsed nozzle maintained at temperature of 180 °C. These two beams crossed each other at a fixed angle (25°) and at a position 4 mm below the center of the ion optics. A pulsed uv laser set at 266 nm (25 mJ/cm²) crossed the biphenyl molecular beam 16 mm upstream from the crossing point of the atomic and molecular beams. Biphenyl molecules in the molecular beam were excited to the \( S_1 \) state after absorbing a single 266 nm photon. Highly vibrationally excited biphenyl in the triplet state was produced after intersystem crossing. Molecules which absorbed more than one uv photon either dissociated into fragments quickly (estimated to be within nanosecond) or became cations. Fragments have no interference on the experimental measurement because we only probed the parent mass in the time-of-flight mass spectra. Cations created by 266 nm multiphoton ionization arrived at the detector about 20–30 μs earlier than the cations generated from 157 nm photoionization. They can be easily discriminated from the arrival time and they have no effects on the measurement either.

Collision probability between atomic and molecular beams was only about 5%. Scattered excited biphenyl molecules were ionized by 157 nm laser beam. The 157 nm photon energy is only large enough to ionize biphenyl in the triplet state. It is not large enough to ionize biphenyl molecules in the ground state. However, unscattered excited biphenyl molecules in the molecular beam were also ionized by the 157 nm laser beam. These ions having the same velocity as the molecular beam were focused by the ion optics into a small spot on the microchannel plate (MCP) detector. In order to avoid saturation and possible damage to the detector, a stainless-steel pin located 5 cm in front of the detector was used to block these ions. Most of the scattered biphenyl molecules have velocities different from that of the molecular beam. They were not affected by the stainless-steel pin. Only a small portion of scattered biphenyl molecules in the forward direction was obscured by the stainless-steel pin. The images with Kr atomic beam and the images without Kr beam were taken alternately after every 27 000 laser shot accumulation. The final image presented in this work, accumulated from a total of 162 000 laser shots, was taken from the images with Kr beam after the subtraction of the images without Kr beam.

We have studied the energy transfer between highly vibrationally excited naphthalene and Kr.20–22 Here, naphthalene under the same experimental conditions as biphenyl was investigated again for comparison.

III. RESULTS AND DISCUSSIONS

A. Generation and detection of highly vibrationally excited biphenyl in the triplet state

The electronic spectrum of biphenyl has been investigated extensively in vapor,23–28 solid,24,29 and crystal phases.24,28 The electronic absorption spectrum of biphenyl is broad and structureless at its lowest energy band due to the excitation of low-frequency torsional vibrational modes. The electronic absorption spectrum in vapor phase at 340 K28 show three bands around 4.6, 5.2, and 6.41 eV associated with the \( \pi-\pi^* \) valence transition to the \( S_1 \), \( S_2 \), and \( S_3 \) states, respectively.30 The \( S_1 \rightarrow S_0 \) 0–0 transition band is located at...
The main fluorescence parameters are experimentally studied and the Franck–Condon factor for the 0–0 transition is small. The 174315-3 Energy transfer of biphenyl J. Chem. Phys. 133, 0258.0 cm−1 (4.37 eV), which has been identified by supersonic jet laser spectroscopy.31–34 The lowest triplet state was measured by high-resolution electron energy-loss spectroscopy, where biphenyl was deposited on a thin film of Ar solid.35 The spectrum shows a structureless band with onset around 3 eV and maximum peak at 3.5 eV. The phosphorescence spectrum of biphenyl in n-heptane at 77 K shows the 0–0 transition from ground state to the lowest excited triplet state located at 2.84 eV.36–37 Phosphorescence spectra in solid neon host studied by Baca et al. illustrates the T1 → S0 transition at 2.86 eV.38 Both theoretical calculations and experimental evidences confirmed that the geometry of biphenyl at the ground state is twisted around the central C–C bond.39,40 however, it becomes a nearly planer structure at both singlet (S1)41–43 and triplet states (T1).43–46 Therefore, the Franck–Condon factor for the 0–0 transition is small. The main fluorescence parameters are experimentally studied and analyzed in diluted cyclohexane solution.47–50 The fluorescence quantum yield is measured to be 0.17 ± 10% with short decay time (16 ± 5% ns). The properties of biphenyl in triplet excited state has also been studied in cyclohexane solution51 proclaiming the intersystem crossing quantum yield from the S1 to T1 state is 0.84. The T1 state has much longer lifetime (130 μs) compared to the S1 state lifetime.

Highly vibrationally excited biphenyl molecules with vibration energy of 41.8 kcal/mol can be generated by absorption of one 266 nm photon, corresponds to the excitation to the S1 state, followed by intersystem crossing to the T1 state. The ionization potential of biphenyl is about 8.3 eV (191 kcal/mol).52 Biphenyl in the triplet state can be ionized using 157 nm photons (182 kcal/mol). The photon energy is much larger than the ionization threshold of the triplet state 5.5 eV (127 kcal/mol) that the ionization cross section is expected to be not sensitive to the small change of vibrational energy in the triplet state. On the other hand, this photon energy is not enough to ionize the biphenyl on the electronic ground state. This allows us to detect the biphenyl on the triplet state without interference from the molecules on the ground state. The large ionization cross section difference between biphenyl in the ground state and the triplet state at 157 nm is shown in Fig. 2. No ion was observed when biphenyl molecular beam was not irradiated by 266 nm photons. Only biphenyl excited by 266 nm photons can be ionized by 157 nm laser beam. The 157 photon energy is also low enough that the highly vibrationally excited biphenyl generated in the triplet upon absorption of 266 nm photons would not dissociate into smaller ionic fragment upon ionization by 157 nm photons.53 This allowed us to have mass-selective detection and the measurement would not be interfered by multiphoton absorption.

### B. Energy transfer distributions

Figure 3 shows the image of scattered biphenyl by Kr atoms. The image of scattered naphthalene by Kr atoms is also shown for comparison. The translational collision energies are 330 and 320 cm−1 for biphenyl and naphthalene, respectively. The rectangular blank area in the upper right-hand corner is the portion of the image blocked by the stainless-steel pin located in front of the MCP detector. Figures 3 also illustrates the respective Newton diagrams, including the initial naphthalene and biphenyl molecular beam velocities, initial Kr beam velocities, center-of-mass velocities, relative velocities, and elastic collision circles. The portion of image inside the elastic collision circle represents the decrease of biphenyl or naphthalene velocity in the center of mass frame after collision by Kr atoms, corresponding to the energy up, ΔE_v, translation to vibration and rotation T → VR collisions. The portion of image outside of the circle represents the increase of biphenyl or naphthalene velocity after collision, corresponding to the energy down, ΔE_v, vibration to translation V → T collisions. Notice that the energy transfer for energy down collisions includes the change of vibrational energy to rotational energy as well as the change of vibrational energy to translational energy. However, we can only detect the energy transfer to the translational degrees of freedom.

If complex is formed during the collision and lifetime of the complex is longer than the complex rotation period, the formation of complex can be recognized from the pattern of image intensity distribution, i.e., the large intensities in the forward and backward directions with forward-backward symmetry. The intensity from the complex in the forward direction is overlapped with the large direct forward scattering intensity in this inelastic scattering experiments. Therefore the intensity symmetry is broken. However, the forma-
tion of complex still can be easily identified from the backward intensity peak. For naphthalene, the intensity of the backward peak can be clearly observed and the central position of the backward peak is located inside the elastic scattering circle. It indicates the corresponding energy transfer is energy up $T \rightarrow VR$ collisions. On the other hand, the backward peak in biphenyl scattering is not as strong as that of naphthalene, indicating the biphenyl-Kr complex formation probability is smaller than that of naphthalene-Kr. However, the position of the backward peak remains inside the elastic circle, suggesting the energy transfer of the biphenyl-Kr complex is also from translational energy to vibrational and rotational energy.

The final velocity distribution of scattered biphenyl was obtained directly from the image intensity distribution. From the conservation of momentum

$$M_{\text{bip}} \times V_{\text{bip}} = M_{\text{Kr}} \times V'_{\text{Kr}}$$

(1)

(where $M_{\text{bip}}$, $M_{\text{Kr}}$, $V_{\text{bip}}$, and $V'_{\text{Kr}}$ represents the masses of biphenyl, Kr, and the velocity in the center-of-mass frame before and after collision, respectively) the velocity of the corresponding scattered Kr atom after collisions can be determined from the measured scattered biphenyl velocity. The amount of energy transfer for each collision therefore can be calculated from the conservation of energy.

$$E_{\text{int}} + \frac{1}{2} M_{\text{bip}} \times V_{\text{bip}}^2 + \frac{1}{2} M_{\text{Kr}} \times V'_{\text{Kr}}^2 = E'_{\text{int}} + \frac{1}{2} M_{\text{bip}} \times V'^2_{\text{bip}} + \frac{1}{2} M_{\text{Kr}} \times V'^2_{\text{Kr}}.$$ 

(2)

$E_{\text{int}}$ and $E'_{\text{int}}$ represent the internal energy of biphenyl before and after collision, respectively. The internal energy of biphenyl before collision depends on the initial internal energy of the biphenyl and the uv photon energy. Due to the supersonic expansion, biphenyl molecules in the molecular beam before absorbing uv photons are rotationally and vibrationally cold. Therefore, the internal energy before uv excitation can be neglected. By combining a molecular beam with a narrow bandwidth laser, internal energy distribution of biphenyl before collision, $E_{\text{int}}$, is almost equal to photon energy which is quite narrow and well defined. $V_{\text{bip}}$ and $V_{\text{Kr}}$ represent the biphenyl and Kr velocity in the center of mass frame before collision, respectively. They can be obtained from the velocity of each molecular beam. Energy transfer, defined as $\Delta E = E'_{\text{int}} - E_{\text{int}}$, therefore can be obtained from the image. The same analysis method was used for the collisions between naphthalene and Kr.

The angle-resolved energy transfer probability density functions are shown in Fig. 4. The side and backward energy transfer probability density functions shown in Fig. 4 are multiplied by additional factors such that they and forward probability density functions have the same value at $\Delta E = 0$. This makes it easy for the comparison of the shapes of these density functions. For naphthalene, the multiplied factors are smaller than that of biphenyl, indicating that side and backward scatterings for biphenyl are smaller than that of naphthalene. Both biphenyl and naphthalene show that the probability of forward scattering is large, and most of the forward scatterings turn out to be small energy transfer collisions. However, the ratios of large energy transfer to small energy transfer in energy down collisions, $\Delta E_{\text{fr}}$, increases as the scattering angles increase from forward to sideway and backward directions. These ratios of biphenyl are larger than that of naphthalene, indicating more energy transfer for biphenyl in energy down collisions. Significant difference between biphenyl and naphthalene was found not only in the shape of angle-resolved energy transfer probability density functions, but also in the maximum $V \rightarrow T$ energy transfer. The maximum $V \rightarrow T$ energy transfer of energy down collisions for biphenyl is close to 2000 cm$^{-1}$, which is much larger than that for naphthalene (less than 1500 cm$^{-1}$). On the other hand, although the density functions for biphenyl and naphthalene in energy up collisions are not the same, both of them reach the maximum available energy. This indicates the energy transfer in energy up collisions is very efficient for both molecules.

Figure 5 shows the angle-resolved relative cross section of $V \rightarrow T$ energy transfer and $T \rightarrow VR$ energy transfer for naphthalene and biphenyl, respectively. As the molecule changes from naphthalene to biphenyl, the $V \rightarrow T$ energy transfer cross section increases and the $T \rightarrow VR$ energy transfer decreases. Unlike naphthalene which most of the collisions with Kr end up as $T \rightarrow VR$ energy transfer, more collisions between biphenyl and Kr become $V \rightarrow T$ energy transfer.

The total energy transfer probability density function was obtained directly from the summation of the probability distribution functions at various scattering angles, as shown in Fig. 6. It shows that naphthalene has a little larger prob-
ability at small $T \rightarrow VR$ energy transfer, and biphenyl has a little larger probability at large $V \rightarrow T$ energy transfer. In Fig. 6, the total cross section was normalized to be one separately for each molecule so that we can compare the shapes of the energy transfer probability density functions. In order to compare the energy transfer efficiency between these two molecules, the curves in Fig. 6 need to be scaled so that the area under each curve is proportional to the relative total collisional cross sections. The total collisional cross section $\sigma_{\text{coll}}$ is related to the ion image intensity $S_{\text{image}}$, the intensity of rare gas beam $I_{\text{rare}}$, molecular beam intensity, $I_{\text{mole}}$, uv absorption cross section $\sigma_{266}$, uv laser intensity $I_{266}$, and intersystem crossing quantum yield $\Phi_{\text{IS}}$, the ionization cross section of molecule in the triplet state by 157 nm photons, $\sigma_{157}$, and the 157 nm laser intensity $I_{157}$

$$S_{\text{image}} = I_{\text{rare}} \times I_{\text{mole}} \times \sigma_{266} \times I_{266} \times \Phi_{\text{IS}} \times \sigma_{\text{coll}} \times \sigma_{157} \times I_{157}. \quad (3)$$

In addition to the measurement of the ion image intensity for the excited molecules in collisions with rare gases, we also measured the naphthalene and biphenyl ion intensities without rare gas atomic beam. The ion intensity measured in such conditions is simply proportional to the number of molecules in the triplet state, the ionization cross section at 157 nm, and the 157 nm laser intensity

$$S_{\text{ion}} = I_{\text{mole}} \times \sigma_{266} \times I_{266} \times \Phi_{\text{IS}} \times \sigma_{157} \times I_{157}. \quad (4)$$

The ratio of the total cross sections for naphthalene and biphenyl can be expressed by the following equation:

$$\frac{\sigma_{\text{coll}(\text{bip})}}{\sigma_{\text{coll}(\text{nap})}} = \frac{S_{\text{image}(\text{bip})}}{S_{\text{image}(\text{nap})}}. \quad (5)$$

This equation shows that the uv laser intensity, uv absorption cross section, intersystem crossing quantum yield, vuv laser intensity, and vuv ionization cross section are all cancelled. We do not need to measure those parameters directly. We only need to measure the scattered image intensity and the ion intensity without atomic beam. This largely reduces the uncertainty in the measurement. During the experimental measurement, we kept the rare gas atomic beam the same. Meanwhile, we put both naphthalene and biphenyl in the molecular beam so we can measure ion image intensity $S_{\text{image}}$ and ion intensity $S_{\text{ion}}$ for naphthalene and biphenyl alternatively in a relatively short period of time in order to reduce the systematic error. The result shows that the ratio of the absolute total collision cross sections for Kr and naphthalene to Kr and biphenyl is 1: 1.17 ± 0.1. In Fig. 6, one of the biphenyl probability curves has been multiplied by 1.17 for comparison. Although the multiplied factor is not large, it reduces the difference between naphthalene and biphenyl in small $T \rightarrow VR$ energy transfer, but enlarges the difference in large $V \rightarrow T$ energy transfer.

### C. Energy transfer mechanism

The mechanism of collisional energy transfer between a highly vibrationally excited polyatomic molecule and a monatomic gas has been investigated for benzene-rare-gas system by carrying out both vibrational close-coupling, infinite-order sudden quantum-scattering computations, and classical trajectory calculation.\(^{54}\) It showed that only the three modes with the smallest frequencies give vibrational relaxation cross sections of appreciable magnitude. These three modes are the out-of-plane vibrations, $\nu_{16}$ (frequency 398 cm\(^{-1}\)) and $\nu_{13}$ (frequency 672 cm\(^{-1}\)), and in-plane vibration $\nu_{5}$ (frequency 606 cm\(^{-1}\)). The results show that it is the multiquantum transitions out of modes with the lowest vibrational frequencies that are giving rise to the largest energy transfer, not the smaller quantum transitions out of modes of higher frequencies. The vibrational relaxation cross sections for benzene-rare-gas are $\sigma(\nu_{16}) > \sigma(\nu_{5}) > \sigma(\nu_{13})$. However, if the in-plane vibration $\nu_{5}$ was given the same frequency as the out-of-plane vibration $\nu_{16}$, the cross sections for $\nu_{16}$ are still much larger than those for $\nu_{5}$. It suggested that low-frequency vibration modes, particularly if it is an out-of-plane motion, are prominent in transferring significant amounts of energy. The other classical trajectory calculations for benzene-rare-gas system showed that rotations are gateway for vibrational energy transfer. Molecules with large initial rotational energy are more efficient in $V \rightarrow T$ energy transfer than those with small initial rotational energy.\(^{55}\)
No theoretical calculations have been performed for the collisions between biphenyl (or naphthalene) and Kr. However, the energy transfer mechanism of benzene-rare-gas systems investigated from calculations may be applied to biphenyl (or naphthalene) and Kr due to the similar molecular structures, i.e., collisions between an atom and a molecule with a planar aromatic structure. Table I lists the triplet state vibrational frequencies of biphenyl and naphthalene. The number of low-frequency vibrational modes for biphenyl is larger than that of naphthalene, especially for the frequency below or close 100 cm$^{-1}$. The motions of these low-frequency vibrational modes happen to be the wide-angle vibration. The vibrational motions of the first three low-frequency vibrations are shown in Fig. 7. The first one is the relative rotation of two aromatic rings along C–C bond axis. The second and the third vibrations are both out-of-plane bending motions of two aromatic rings. The motions of these vibrations are very similar to the rotation of aromatic rings.

In the previous studies of collisions between Kr and naphthalene, we showed that energy transfer properties change significantly as the initial rotational temperature of naphthalene changes from $\sim 10$ to 350 K. The changes of energy transfer properties due to the change of rotational temperature include less complex formation, larger V $\rightarrow$ T cross section, smaller T $\rightarrow$ V cross section, and more supercollisions. These changes happen to be the same as difference between highly vibrationally excited but rotationally cold naphthalene and biphenyl. We suggest that these low-frequency rotationlike vibrations are the most likely factors which make the difference between biphenyl and naphthalene. They must play an important role in the enhancement of V $\rightarrow$ T energy transfer and supercollisions. Further theoretical calculations on this system and similar experimental examples will be helpful to investigate the mechanism we proposed.

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FIG. 7. Motions of the first three low-frequency vibrations of biphenyl in the triplet state T$_1$. 

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