

The relaxation from linear to triangular Ag_3 probed by femtosecond resonant two-photon ionization

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We present extended NeNePo (negative to neutral to positive) measurements on the ultrafast dynamics in the ground state of neutral, mass-selected Ag_3 molecules. A vibrational wave packet in the neutral molecule is created with an ultrashort laser pulse by photodetachment of the excess electron from the corresponding mass-selected anion. The subsequent molecular rearrangement is probed by photoionization after a selected time delay. Complementary to our previous investigations of this process, we now use two-photon photoionization via a resonant state in the probe step. Here, a bound-bound excitation to a well-known state followed by one-photon ionization is used instead of the nonresonant bound/free transition into the ionic continuum. Using radiation with wavelengths near 370 nm for resonant ionization, we observe a fast bending motion of the initially linear Ag_3 , followed by an ultrafast intramolecular vibrational energy redistribution, interpretable as an intramolecular collision process. The signal shows an apparent loss of vibrational coherence after the collision, which can be explained by the finite temperature of the anionic clusters in our experiment. Additionally, we describe a previously unknown resonance in the linear neutral molecule around 500 nm. © 1999 American Institute of Physics. [S0021-9606(99)01127-7]

INTRODUCTION

Femtosecond NeNePo spectroscopy (negative to neutral to positive) is a powerful method to probe the dynamics of ground-state molecules.¹⁻⁴ It relies on the preparation of a vibrational wave packet in the neutral molecule by photodetachment of the excess electron from the corresponding anion with an ultrashort laser pulse. The evolution of the wave packet is probed by photoionizing the neutral molecule with a second laser pulse after a selected, variable time delay. The method can yield dynamic information when it is applied to molecules with significantly different anionic and neutral geometry. The method allows a straightforward implementation of mass selection of the ions both prior to and after the charge reversal process.

The experimental feasibility of the method has been proven using silver trimers and larger silver clusters as model systems. Since then it has attracted considerable theoretical⁵⁻¹⁰ and experimental⁴ interest. However, a substantial limitation of the original experiments is its restriction to nonresonant two-photon photoionization. The photon energies should be chosen to lie well above the ionization potential of the neutral molecule in order to avoid the interference of molecular Rydberg states or autoionizing resonances. As a recent theoretical analysis has elucidated,⁷ under such conditions the ion yield will only partially mirror the molecular dynamics in the ground state. Much information is lost by the integration over the unknown energy of the free electron.

The authors of Ref. 7 therefore consider combining this method with zero-kinetic-energy (ZEKE) photoionization, in what might naturally be called ZEKE-NeNePo. Here the de-

tection of zero-kinetic-energy electrons in coincidence with the photoions would remove the ambiguity associated with the spectrum of final energies of the photoelectrons. The cation yield in such measurements must reflect faithfully any change in the vertical ionization potential of the molecule along its trajectory on the neutral potential energy surface, as well as the occurrence of internal vibrational relaxation (IVR) at various time scales. However, ZEKE-NeNePo is rather difficult to realize experimentally, so we chose instead to use resonant multiphoton ionization for the probe step. The cross section for the bound-bound transition involved here effectively determines the photoion yield and should be as sensitive to geometry changes in the neutral molecule as the ZEKE photoionization probability. In this contribution we demonstrate the use of resonant two-photon ionization to probe the relaxation of neutral Ag_3 from the linear configuration of its precursor anion to a highly excited, triangular geometry. Following Ref. 7, we discuss our results in terms of a sequence of coherent molecular configuration changes, an intramolecular collision process, and internal vibrational energy redistribution.

EXPERIMENT

Our experiments were performed in a guided ion beam apparatus which consists of a sputtering cluster ion source and four subsequent radio frequency (RF) quadrupole assemblies (Fig. 1).

Four beams of Xe^+ ions are created by a modified cold reflex discharge ion source (CORDIS). This device employs a magnetically confined plasma which is heated directly by tantalum filaments from which the ions are extracted and

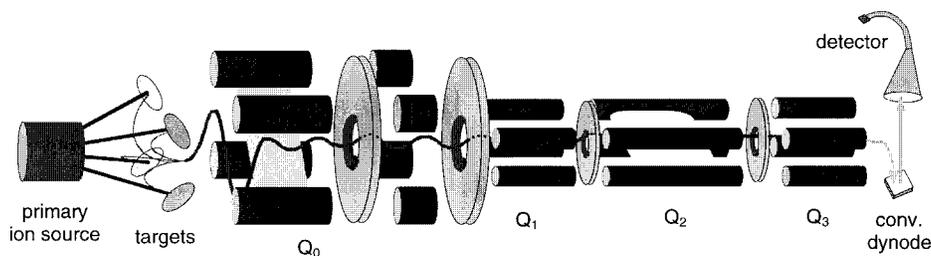


FIG. 1. Schematic diagram of the experimental apparatus.

accelerated by a three-element electrostatic lens. Details and specifications of the original CORDIS are given in Ref. 11. We have modified the extraction electrodes to hold four separate ion lenses in a square arrangement. Thereby we extract four independent ion beams, each of which deviates by an angle of 5° from the axis of the ion source. The highest ion energies and currents obtained are 20 keV and 10 mA per beam. After passing through a differential pumping stage, each of the beams hits a quadratic silver sheet ($l=25$ mm). The particles sputtered from the surface consist of atoms, ions, and neutral and ionic clusters.

Clusters of the desired charge state are collected by an electrostatic lens and introduced into the first RF-quadrupole (Q_0). This ion guide has a large rod diameter of 20 mm and consequently runs at a low frequency of 400 kHz. It is enclosed in a gas cell flooded with He gas to a pressure of 10^{-2} mbar. Here, the clusters which are initially boiling hot and occupy a large volume in real space and momentum space are cooled and moderated by the friction they experience in the gas atmosphere. At the same time they experience the quadratic radial pseudopotential in the ion guide and condense toward the central axis to form a beam of small cross section. By this means the brightness of the source is increased by about a factor of 50 compared to a direct coupling of a mass-selective quadrupole ion guide to a sputtering ion source of our kind. At the same time the temperature of the clusters is reduced to about room temperature.¹²

Subsequently, the cluster ions of interest are selected from the beam by a quadrupole mass filter (Q_1). They are introduced into a long homemade quadrupole ion guide (Q_2) which, for the purpose of the NeNePo experiments, serves as an ion trap. This trapping mode of operation of a quadrupole ion guide was first described by Dolnikowski and Watson.¹³ It employs the electrostatic entrance and exit lenses of the ion guide and an integrated gas cell to confine the ions. The entrance lens is fixed at a potential slightly below the initial kinetic energy of the ions, while the exit lens is held at a higher potential to reflect all ions in the trap. During their first cycle in the trap, injected ions pass twice through the gas cell where they lose kinetic energy by collisions with the helium gas and cannot escape via the entrance lens. They are therefore trapped inside the ion guide and oscillate with decreasing kinetic energy between entrance and exit lens. Hence the ion trap can be filled with a continuous flow of ions without ever pulsing the entrance or exit lens of the trap. The accumulation only ceases when the ion density reaches the space charge limit, which in our case is around 10^8 ions/cm³.

Inside the trap the anions interact with the laser light

which is applied collinearly to the trap axis. Any cationic products are no longer confined inside the trap but are extracted by the entrance and exit lens. The cluster cations leaving the ion trap via the exit lens are mass analyzed in a second quadrupole mass filter (Q_3). Their yield is measured by an off-axis conversion dynode detector as a function of the wavelength, the duration, and the energy of the laser pulses and their respective delays.

Neutral clusters produced from the anions by the pump or the probe pulse but not ionized subsequently, are no longer trapped and leave the quadrupole due to their velocity at the time of neutralization. It may require several hundred microseconds until all neutral molecules have left the ion trap. This limits the repetition rate at which this experiment can be performed. We therefore used a Nd:YLF laser-pumped regenerative titanium:sapphire amplifier running at 1 kHz as a source for the ultrashort laser pulses. It is seeded with the pulses from a titanium:sapphire oscillator and produces pulses of about 110 fs duration and typically 400 μ J per pulse. Fifteen percent of the power is split off each pulse, its diameter is reduced with a telescope to 0.5 mm, and its frequency is doubled before it is sent to the apparatus for photodetachment. The remaining 85% of the power is used to pump an optical parametric generator/amplifier, whose output is tunable between 1570 and 1200 nm. At this point the light beam is either frequency-doubled two times to provide a femtosecond ultraviolet (UV) source tunable between 385 and 300 nm or put into an optical parametric generator for sum-frequency generation between pump and signal pulses to reach the wavelength range between 530 and 475 nm. These pulses, with a duration of about 120 fs, are also collimated to a diameter of 0.5 mm and spatially overlapped with the photodetachment laser beam at 400 nm which is passed through a computer-controlled delay line. Both are introduced collinearly with the quadrupole arrangement through the detector flange of the quadrupole system.

To monitor the temporal and spatial overlap between pump and probe pulse in the region of interaction with the ions, we use a copper electrode which can be positioned in the ion trap under measurement conditions. The photoelectron current from this electrode, produced by two-photon photoemission, is measured with a picoammeter as a function of the delay. It exhibits a pronounced maximum when both pulses overlap spatially and temporally and hereby sets the zero point of the clock. Furthermore, it becomes possible to monitor the cross-correlation function between the shapes of the pump and probe pulse. This measurement is repeated for every probe wavelength, because the optical path length

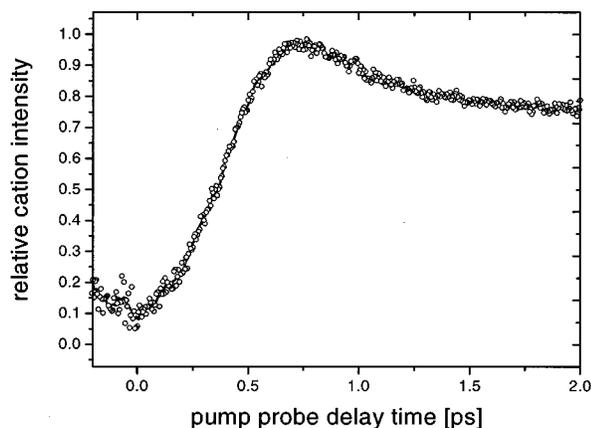


FIG. 2. Ag_3^+ yield from the NeNePo process as a function of the delay time between photodetachment and photoionization at a wavelength of 415 nm.

through the optical parametric generator changes slightly with the wavelength setting.

RESULTS

The silver trimer anion is a linear molecule, while the neutral forms an obtuse triangle. It is therefore a model system for a large amplitude rearrangement of a molecule which starts from a saddle point of the potential energy surface and involves the breaking of the initial $D_{\infty h}$ symmetry.

In earlier experiments¹ we used pump and probe pulses of the same wavelength around 400 nm for photodetachment and ionization. A typical measurement is reproduced in Fig. 2 for reference. It gives the yield of silver trimer cations as a function of the delay time between photodetachment and photoionization. Here we observed no sign of a periodic bending motion of the neutral molecule which would be reflected in an oscillating cation yield. Instead the signal shows a pronounced minimum at zero delay time, a single maximum around $\Delta t = 500$ fs, and then converges to a constant value after a time of about 2 ps. This behavior was interpreted as a consequence of (a) the time-dependent vertical ionization potential of the molecule and (b) a fast conversion of kinetic energy from the initial bending motion into the two remaining vibrational degrees of freedom. The first argument accounts for the minimum at the delay time $\Delta t = 0$ and the rise in signal to a maximum at $\Delta t \approx 500$ fs. The second argument explains why there is no oscillatory behavior visible at delay times $\Delta t > 1$ ps. At that time it was not clear whether this was because of ultrafast loss of the molecular coherence within less than one period of the bending vibration or because the motion remained coherent but the coherence could not be detected due to the nonresonant character of the probe process.

In order to clarify this question we performed new experiments employing resonant two-photon ionization of the neutral silver trimers. Fortunately, a state which lies energetically above half the adiabatic ionization potential of the molecule is known from continuous wave (cw) spectroscopy.^{14,15} It has been tentatively assigned to ${}^2E''$ symmetry and its 0-0 transition lies 26971 cm^{-1} above the

ground state. We therefore used a wavelength of 370 nm as a starting point of our femtosecond investigation.

For this experiment light pulses with a central wavelength of 400 nm, a pulse duration of about 100 fs, and a peak power density of $5 \cdot 10^2 \text{ W/cm}^2$ were used for photodetachment. Under these conditions, almost all Ag_3 anions in the path of the laser are neutralized. The pulses for photoionization had a duration of 120 fs and a power density of about $5 \cdot 10^8 \text{ W/cm}^2$. Cations emerging from the two-color NeNePo process could be detected at probe pulse wavelengths between 385 and 345 nm whereas no cations were detected at higher or lower photon energies. The apparent width of this resonance can be attributed to the large difference between vertical and adiabatic electron affinity, which was calculated to be 0.4 eV.⁷

At zero delay time between pump and probe pulse the center of the resonance is found at 360 nm. It shifts to about 370 nm for delay times longer than 1 ps. In Fig. 2 the delay-time-dependent cation yield is given for various wavelengths of the ionizing radiation. The spectra are normalized to a constant change in signal between $\Delta t = 0$ and $\Delta t = 1$ ps for ready comparison in the time domain. Their overall shape resembles our previous measurements. In all cases the signal exhibits a minimum at $\Delta t = 0$ and rises steeply to a maximum after about 500 fs. Then it converges to a constant value at $\Delta t > 8$ ps. Similar to the measurements with nonresonant ionization, in no case is any oscillatory behavior found. As wavelengths go from longer to shorter, the initially rising slopes of the spectra move gradually to shorter times. The signal reaches half its maximum amplitude after 300 fs in the case of ionization at 384 nm but after only 110 fs in the case of 347 nm. This behavior corresponds to a time-dependent absorption spectrum of the molecule (compare discussion below).

A photon energy of 3 eV for the photodetachment is well above the calculated and measured vertical detachment energy (VDE) of Ag_3^- (2.44 eV). In order to clarify the possible influence of this excess energy we performed a second set of two color pump and probe measurements where one of the light pulses was tuned to 495 nm in order to fit exactly to the VDE of the anion. The second pulse remained at a wavelength of 400 nm. Applying the light of only one of the pulses, the anion signal due to photodetachment showed the same depletion in either pulse, whereas the cation signal resulting from photodetachment and photoionization from the same pulse was ten times higher for 495 than for 400 nm. This strong enhancement of the cation signal was found only in a narrow wavelength region between 495 and 500 nm. A typical pump and probe transient using both colors is given in Fig. 3. Positive delay times denote that the pulse at around 500 nm comes first, serving as pump pulse, and the blue pulse at 400 nm is then used for photoionization. For negative delay times the function of pump and probe pulse is reversed accordingly. In contrast to the previously discussed measurements, we now observe a strong maximum in cation intensity at $\Delta t = 0$. The overall delay-time-dependent signal can be decomposed into the peak at time zero when both pulses coincide and a shoulder at $\Delta t = 500$ fs, as indicated in Fig. 3. The straight line shows the difference between the

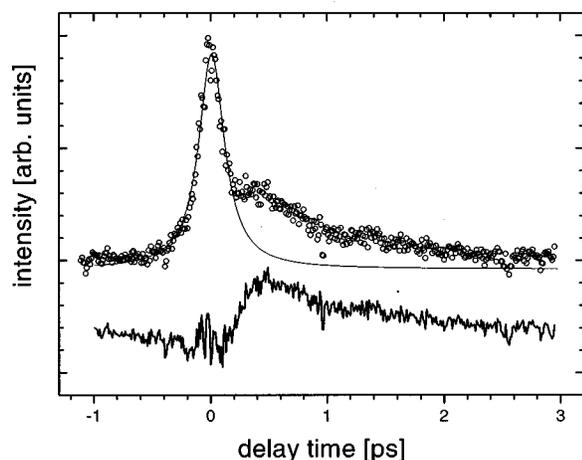


FIG. 3. NeNePo signal of Ag_3^+ obtained at a photodetachment wavelength of 500 nm, and a photoionization wavelength of 400 nm (positive delay times).

measured signal (hollow circles) and a fit to the peak at $\Delta t = 0$, but is shifted vertically for clarification. The resulting transient clearly resembles the time-dependent signal in the one-color experiment mentioned above (refer to Fig. 2).

DISCUSSION

For the set of measurements using the $^2E''$ state as intermediate resonance (Fig. 4), we find a minimum in the ion signal for delay time $\Delta t = 0$. This behavior is similar to the one-color experiments published previously (compare Fig. 2), but for a different reason. In the new experiments we are in a wavelength regime where the energy is sufficient to ionize in a two-photon process, even at time zero. Hence, the modulation of the ion signal with time is due to the change of potential energy difference between the ground state and the $^2E''$ state of the neutral Ag_3 along its coordination path for relaxation. Nevertheless, the spectra show no oscillatory motion of the Ag_3 molecules after the first relaxation. We therefore assume that under our experimental conditions the coherence of the molecular ensemble is destroyed within the first vibrational period.

This conclusion is supported by recent calculations of Bonacic-Koutecky and colleagues,⁷ who modeled the NeNePo investigations of Ag_3 . Among other calculations, they followed bunches of classical trajectories on the *ab initio* potential energy surface of the neutral trimer belonging to a sample of initial conditions at various temperatures of the anionic clusters. Their results confirm the picture of the molecular motion after photodetachment as presented in Ref. 2: The neutral molecule is initially linear and then bends with increasing acceleration to reach the triangular configuration. The initial bending motion follows a narrow valley in the potential energy surface and involves at the same time a slight stretching and subsequent recontraction of the molecule. After a certain time, which depends strongly on the initial temperature of the cluster ensemble, the bending motion of the molecule comes to an abrupt standstill at the turning point when the terminal atoms collide. According to these calculations, the amount of coherence that remains in

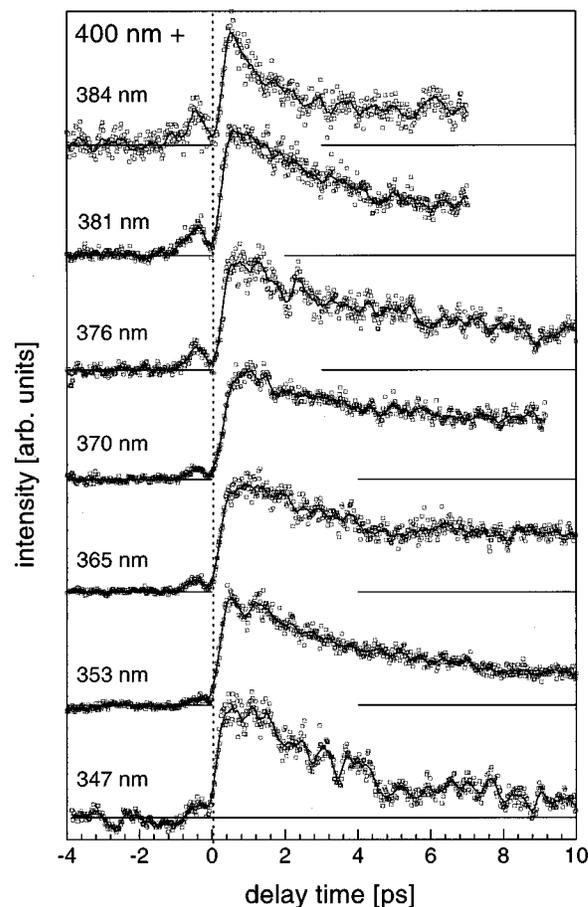


FIG. 4. NeNePo signals of Ag_3^+ obtained using resonant two-photon ionization at various wavelengths.

the system after the collision depends strongly on the initial temperature of the anionic cluster ensemble. At an initial temperature of 50 K, the trajectories stay bundled in space immediately after the collision and the system starts to oscillate predominantly along the stretching coordinate, exhibiting resonant IVR. At 300 K the trajectories diverge substantially and both bending and symmetric stretching vibrations are excited, giving rise to dissipative IVR.

The molecular motion is best rationalized in a one-dimensional cut through the potential energy surfaces (PES) along the bending mode Q_x , (see Fig. 5). The calculated potentials for the three charge ground states are shown in Fig. 5 by solid lines. The dashed lines give a qualitative picture of the resonant states involved in this ionization process and are taken from preliminary calculations. After photodetachment from the anion (bottom slim arrow) a molecular wave packet is formed in the linear configuration of the neutral molecule (at $Q_x = 5.2$ au). Though this configuration appears to be a local minimum of the neutral PES, there is a monotonically decreasing pathway toward the triangular configurations around $Q_x = 0$ which involves a change in the symmetric stretching coordinate. Along this path the molecule bends, so that after a delay time of 500 fs, resonant ionization via the $^2E''$ state of the neutral Ag_3 becomes possible in a large Franck-Condon regime (broad arrows) due to the similar slopes in the PES. This resonant ionization path-

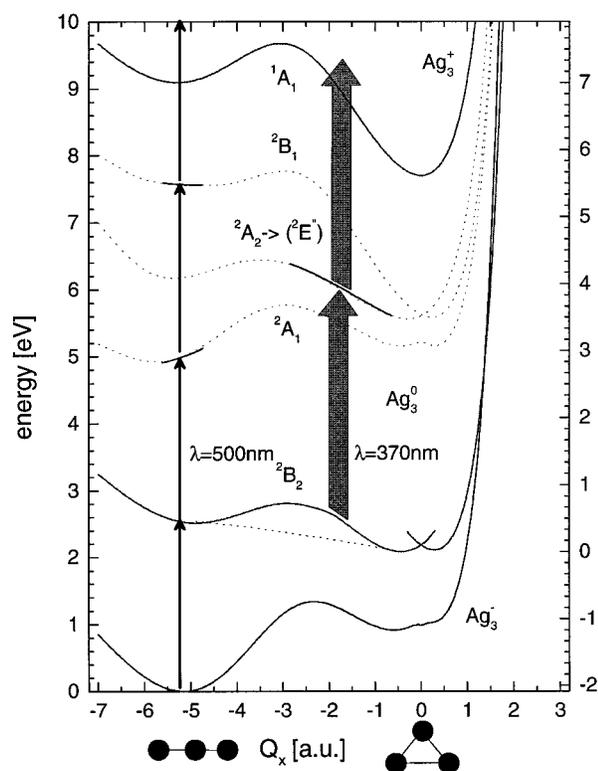


FIG. 5. Cut along the bending coordinate Q_x through the potential energy surfaces of the resonant states of Ag_3 used for the NeNePo experiments. The optical transitions are indicated as arrows.

way gives rise to the spectra given in Fig. 4. As a consequence of the IVR processes discussed above, this part of the PES is not revisited at later times and therefore the signal in Fig. 4 declines at larger delay times.

Tuning the wavelength for one pulse from the UV (370 nm) into the green (500 nm) as done in the second set of measurements (Fig. 3), the picture changes completely. Instead of a minimum we find a maximum in cation intensity for delay time zero. Additionally, a shoulder is found in the cation signal at positive delay times around $\Delta t = 500$ fs. As can be seen from the decomposition of the data performed in Fig. 3, the shoulder clearly resembles the signal obtained in the one-color experiments at 400 nm (cf. Fig. 2). As in both cases the ionization is performed at 400 nm, we conclude that a variation of the photodetachment wavelength from 400 to 500 nm has no marked effect on the subsequent bending dynamics of the neutral molecule. This implies that most of the excess energy of the photodetachment laser is transferred into the photoelectron and does not remain in the molecule. The most prominent feature in the spectrum, however, is the peak around $\Delta t = 0$. For energetic reasons, such an ionization requires the absorption of three photons. Because of the strong enhancement in the ion signal using the pulse at 500 nm compared to the one at 400 nm, we assume that the linear silver trimer can be ionized resonantly at 500 nm. If there was only one resonant state participating in the process, one should expect to observe a wavelength shift of the resonance as the wave packet evolves on the PES. Instead, the signal vanishes at all delay times outside a narrow range around

time zero. This can only be explained if a second resonant state is involved in the ionization process. Such a state is indeed predicted by the calculation, and in Fig. 5 the two proposed participating states are labeled 2A_1 and 2B_1 , respectively. They have opposite slopes along the bending mode Q_x so that only at $\Delta t = 0$ the two transition energies coincide accidentally.

CONCLUSION

We presented extended measurements on the Ag_3 molecule using a bound-bound transition via intermediate resonant states. Two excited states are seen at short delays as a resonance in the linear geometry of the molecule. The strong change of the ion signal close to zero delay time implies large differences in the gradients of the potential energy surfaces involved in the ionization process, particularly in the region near the linear configuration of the molecule. The ${}^2E''$ excited state we believe to contribute to the resonant absorption after partial relaxation of the linear molecule. Here, the maximum in ionization probability was found in the geometry of an obtuse isosceles, nearly equilateral triangle. The lack of oscillation we attribute to fast IVR processes after collision of terminal atoms along the relaxation path. Overall, both the theoretical and the experimental findings reflect the tendency of collisions to enhance the spread in phase space of partially coherent systems and provide a molecular understanding of the fast intermolecular redistribution processes of vibrational energy that can be found in molecules as small as a metal trimer.

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