

Research Article

Ultrafast Dynamics of 1,3-Cyclohexadiene in Highly Excited States

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The ultrafast dynamics of 1,3-cyclohexadiene has been investigated via structurally sensitive Rydberg electron binding energies and shown to differ upon excitation to the 1B state and the 3p Rydberg state. Excitation of the molecule with 4.63 eV photons into the ultrashort-lived 1B state yields the well-known ring opening to 1,3,5-hexatriene, while a 5.99 eV photon lifts the molecule directly into the 3p-Rydberg state. Excitation to 3p does not induce ring opening. In both experiments, time-dependent shifts of the Rydberg electron binding energy reflect the structural dynamics of the molecular core. Structural distortions associated with 3p-excitation cause a dynamical shift in the p_x - and p_y -binding energies by 10 and 26 meV/ps, respectively, whereas after excitation into 1B, more severe structural transformations along the ring-opening coordinate produce shifts at a rate of 40 to 60 meV/ps. The experiment validates photoionization-photoelectron spectroscopy via Rydberg states as a powerful technique to observe structural dynamics of polyatomic molecules.

1. Introduction

The photochemical ring-opening reaction of 1,3-cyclohexadiene (CHD) is widely studied due to its important role as a prototype for important reactions in chemistry as well as in biological systems [1, 2]. Upon excitation to the 1B valence state, the reaction path carries the molecule within about 140 fs along the ring-opening coordinate through the 1B/2A and 2A/1A conical intersections back to the ground state [3–7]. But even while these curve-crossing transitions are now well understood, numerous questions remain. Of particular interest are the geometric changes occurring in the molecule after excitation into the 1B-valence state and as the molecule travels through the electronic states, as such structural motions have eluded direct experimental observation. As has been pointed out, [5, 6, 8, 9] the wave packet remains quite narrow during the reaction, implying that “structure” is a well-defined quantity even though it rapidly evolves. Moreover, it is unknown if higher-lying electronic states follow ring-opening pathways similar to that

following the 1B excitation, or if other unique mechanisms emerge. Because the dynamics is determined by the rapid motions of wave packets on intricately sculptured surfaces [8], a dependence on the excitation energy is to be expected.

The observation of structural dynamics, that is, structural changes during chemical reactions, is one of the grand challenges, not only in the investigation of the CHD ring-opening reaction, but for the field of chemical reaction dynamics in general. While historically static structure determination methods, such as electron diffraction, have been adapted to fast time scales, there are some limitations, for example, relating to the size of the molecular system [10–14]. Rydberg fingerprint spectroscopy (RFS) takes advantage of the fact that the binding energies of electrons in Rydberg states are sensitive towards the arrangement of atoms in the ion core [15–19]. Because the structure in a Rydberg state most often closely resembles that of the ion state, the spectra of these states feature sharp peaks without vibrational broadening [20–22]. High time resolution of the method is obtained by using ultrafast, pulsed lasers in a pump-probe

scheme [10, 21]. Importantly, the complexity of the Rydberg spectra does not scale with the size of the molecule.

The present work demonstrates that RFS is able to observe not only kinetic transitions between populations of molecules in different energy wells, as has been done in the past [7], but also the time-dependent dynamical motions in essence, the technique captures the geometrical aspect of the time-propagating wave packet and thereby serves as a method to measure ultrafast structural dynamics. While the computation of Rydberg electron binding energies is not yet sufficiently advanced to invert spectra to derive and determine molecular structures, the experiments on CHD show that RFS is a viable method to measure ultrafast structural dynamics.

2. Results and Discussion

Figure 1 shows the time-resolved Rydberg electron binding energy spectra of CHD, observed by photoelectron spectroscopy, using two different excitation schemes. The spectrum of (a) was obtained upon multiphoton ionization with a 5.97 eV pump photon ($\hbar\omega_4$), followed by a temporally delayed 3.00 eV ($\hbar\omega_2$) probe photon (the “4 + 2” experiment). In the spectrum of (b) a 4.63 eV pump ($\hbar\omega_3$) was followed by a 3.12 eV ($\hbar\omega_2$) probe photon (the “3 + 2” experiment). Any one-color background signals were subtracted, so that only the two-color ionization signal is shown. The contour plots map the electron binding energy E_B (obtained by subtracting the measured photoelectron energy E_e from the energy of the ionizing probe photon) as a function of the pump-probe time delay. Comparison with absorption spectra shows that excitation at the wavelength of the $\hbar\omega_4$ photon should yield a $1A_1 \rightarrow 3p$ transition, identifying the intense band around 2.3 eV in the (4 + 2)-spectrum as the 3p Rydberg state [3]. While the admixture of valence states to 3p is not yet known, it has been suggested that 3s mixes with the doubly excited 2A state that plays an important role in the ring-opening mechanisms [4].

The 2.3 eV band is also seen in the (3+2)-spectrum, along with a progression of Rydberg peaks at lower binding energies. Previous studies revealed the reaction path associated with the $\hbar\omega_3$ excitation. The 4.63 eV photon places CHD on a steeply repulsive part of the 1B potential energy surface, which accelerates it along the ring-opening coordinate, yielding 1,3,5-hexatriene (HT). Along this reaction path the wave packet bypasses a cusp in a symmetry-breaking direction and enters the $2A_1$ surface, from where it decays to the electronic ground state [4–7]. Ionization out of $2A_1$ by two $\hbar\omega_2$ probe photons passes through the Rydberg states that are seen in the spectrum [7].

The Rydberg peaks at lower binding energies, between 0.5 and 1.7 eV, are inaccessible by any $\hbar\omega_3$ - or $\hbar\omega_4$ -one-color excitation from the ground-state. While a single $\hbar\omega_3$ - or $\hbar\omega_4$ -photon would not have sufficient energy to access those states, two resonant $\hbar\omega_3$ - or $\hbar\omega_4$ -photons would directly ionize the ground state structure. Consequently, the one-color spectra do not contain any of the lower binding energy Rydberg peaks. Therefore, it can be concluded that, with exception of the 3p state that can be excited directly by a

$\hbar\omega_4$ -photon, the Rydberg progression can only be populated out of the $2A_1$ state making it an indicator that the molecule indeed follows the previously suggested reaction path.

In the (4 + 2)-spectrum, only two peaks of the lower binding energy Rydberg progression are observed. Both are very weak and temporally delayed with respect to the 3p peak. While the origin of the band at $E_B = 1.1$ eV could again not be identified, the peak near $E_B = 1.5$ eV has a quantum defect of 0.98, identifying it as the previously observed 4s Rydberg state [7].

The somewhat broadened band around 1.7 eV is likely due to the Rydberg 3d manifold. A temporal delay of the lower binding energy progression from the 3p peak suggests that the 3p state is directly excited in the (4 + 2) experiment, rather than via the relaxation on the 1B and 2A surfaces as is the case in the (3 + 2) experiment. It is impossible to exclude, however, a population of the 3p state by $\hbar\omega_4$ via a very quickly decaying valence state. From the low intensity of the Rydberg progression in the (4+2)-spectrum, we infer that only a very small fraction of the wave packet travels along the 2A surface. The majority of the excited molecule appears to undergo a direct conversion to the ground state.

Figure 2 focuses on the 3p state in the (4 + 2) experiment, where the band exhibits a fine structure with an approximate 0.05 eV spacing. Since the center positions of those fine structure bands depend differently on the time delay (see below), we exclude the possibility that they arise from a vibrational progression. Instead, their likely origin is from the different magnetic quantum number components of 3p, that is, the $3p_x$, $3p_y$, and $3p_z$ levels. The intensity ratio of 1 : 0.8 for the two most dominant peaks matches the ratio of the oscillator strengths for the p_x (2.24 eV) and p_y (2.29 eV) (Since the binding energies of the p-states shift in time, the binding energies given here correspond to the peak centers at the time of maximum electronic state population.) transitions as previously determined in a CASPT2 calculation by Merchán et al. [3]. The transition to the p_z state is symmetry forbidden in the one-photon excitation, and therefore much weaker [3]. The orientation of the 3p states is such that the p_z state lies along the C_2 symmetry axis, where the p_y - and p_x -states are perpendicularly within and out of the plane of the molecule, respectively. In the (3 + 2) experiment, the 3p signal is not sufficiently resolved to distinguish the components of the 3p manifold.

Closer inspection of the time-resolved electron binding energy spectra reveals that the peak centers shift towards higher binding energies with increasing delay times. Figure 3 shows the binding energies of select peaks in the (3 + 2)- and (4 + 2)-spectra as a function of time. The peak centers at each time-point were obtained by fitting the signals to Voigt profiles [23] without deconvolution with the instrument function in the time domain. While the resolution of the experiment is limited by the full width at half maximum of the probe pulse, which is in the order of 37 meV, the peak centers, and therefore the peak shifts, can be determined with a much higher accuracy. The broad bandwidth of the femtoseconds pulses used in this experiment contributes to the spectral resolution but by itself does not induce a peak shift.

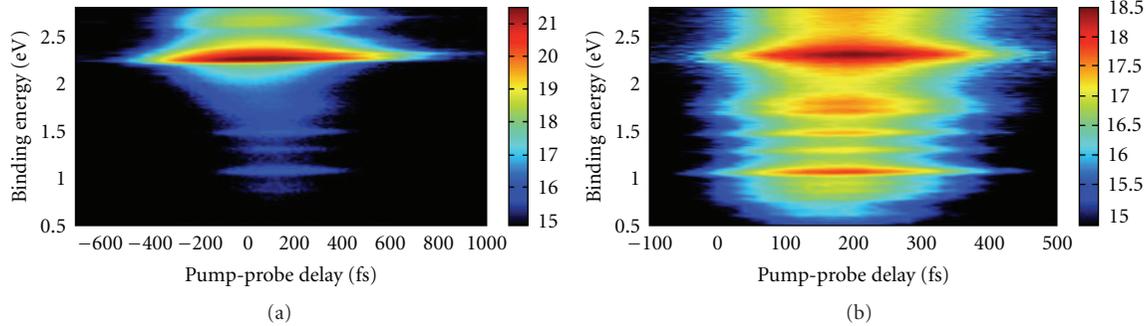


FIGURE 1: Time-resolved binding energy spectra of CHD. (a) shows the spectrum with 207 nm excitation and (b) represents the result with 268 nm excitation. The color encodes the intensity on a (natural) logarithmic scale.

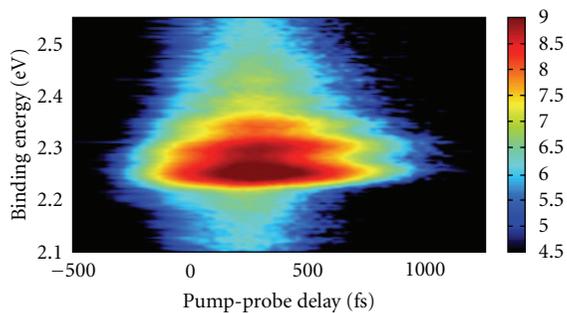


FIGURE 2: Time-resolved binding energy spectrum of the 3p manifold in the (4+2) experiment. At least 3 peaks are visible as part of a 0.05 eV fine structure. The color encodes the intensity on a (natural) logarithmic scale.

Various optics in the experimental setup cause a chirp in the laser pulse, that is, a slight dependence of the photon energy on the time. Due to its shorter wavelength, this effect is more prevalent in the pump pulse. The observed binding energies are, however, measured as the kinetic energy of the electron that is released when the molecule is taken from its initial state to the ion surface. The observed binding energies are therefore not affected much by chirp in the pump pulse. The probe pulse energy on the other hand does determine the kinetic energy of the ejected electron. In particular at the negative times, when the “late” part of the probe overlaps with the “early” part of the pump, could the observed binding energy be influenced by chirp. But because we observe different rates of change in the binding energies for different peaks, we conclude that the observed peak shifts must be a molecular property rather than an artifact of the laser. Since mostly the chirp in the $\hbar\omega_2$ probe pulse affects the observed binding energies, the significantly different magnitudes of peak shifts in the (3+2) and (4+2) experiments can be trusted to be real effects as well. At this time, the exact quantities and shapes of the shifts in peak maxima should, however, be viewed as qualitative and relative parameters rather than absolute molecular ones.

For the (4+2) experiment, the time-dependent binding energies of the two most intense peaks in the 3p manifold are shown. They are found to shift with a slope of 10 meV/ps for

the p_x peak at 2.24 eV and 26 meV/ps for the p_y peak starting at 2.28 eV.

For the (3+2) experiment, Figure 3(b) shows that the 3p levels shift at 52 meV/ps. Since this spectrum does not resolve the magnetic sublevels, we cannot itemize this shift between p_x and p_y . The 4s peak and the unidentified signal starting at 1.06 eV shift at rates of 63 meV/ps and 43 meV/ps, respectively. These shifts in 3p are a factor of 2 to 6 larger than those of the p_x and p_y states observed in the (4+2) experiment. Because the Rydberg electron binding energy is sensitive to the molecular structure, the shifts in binding energy represent the rate of change of the molecule’s geometrical structure. We therefore conclude that the structural rearrangement upon excitation to the 3p level, while not vanishingly small, is nevertheless much smaller than that incurred upon excitation to the lowest excited state that leads to the well-known ring-opening reaction. CHD appears to be structurally stable in the 3p Rydberg state.

Previously, we have found that multiphoton ionization from the ground electronic state via the Rydberg states reveals the ultimate outcome of the ring opening reaction [7]. However, that work focused solely on excitation to the 1B state. Building upon our past findings, we can now expand this to cover excitation to the Rydberg states. From the absorption spectrum ($\epsilon = 4800$ L/mol/cm at 207 nm) [24] and the pump laser pulse energy, it can be calculated that at least 10% of the CHD molecules should be excited to the 3p state in the (4+2) experiment. If CHD underwent ring opening upon excitation at 207 nm, this fraction of CHD would be unavailable for excitation via the same Rydberg level and therefore cause a depletion in the CHD spectrum. Such a depletion has previously been observed in a (3+2) investigation [25]. Figure 4 shows the two-color spectra with time delays before and after the ring opening, as well as a difference spectrum in the (4+2) experiment. There are no new spectral features and no depletion of the CHD peak, consistent with the previous conclusion that the ring does not open when the molecule is excited at 207 nm. We conclude that the structural dynamics are sensitively dependent on the excited electronic state. Two different aspects of the time-resolved Rydberg spectra lead to this conclusion: the time evolution of the intensity of certain spectral features provides information about the ultimate

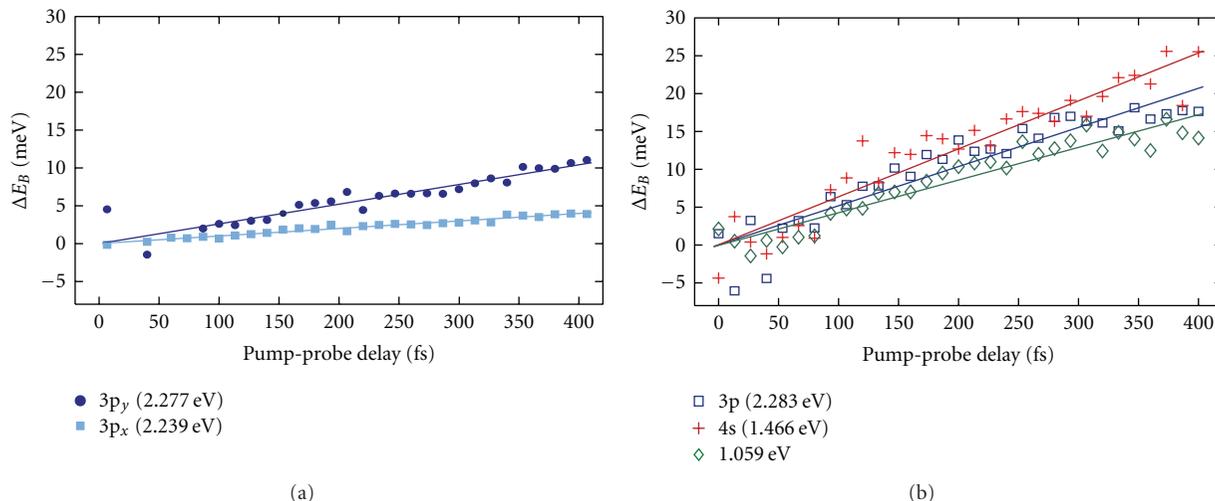


FIGURE 3: Shifts of peak maxima as a function of time. (a) $(4 + 2)$ ionization: the peak centers of the p_x (light blue squares) and p_y (dark blue circles) signals. Linear fits are included as solid lines in the respective colors. (b) $(3 + 2)$ experiment: the shifts of peak centers of the $3p$, the $4s$, and the 1.06 eV peaks as a function of delay time. Linear fits are included as solid lines in the respective colors. The numbers in parentheses denote the binding energies at zero pump-probe delay, as determined by a linear fit to the temporal development of the binding energies of each peak. These binding energies have been used as the starting point against which the shifts are measured.

outcome of the reaction, while the time evolution of the Rydberg binding energy results from structural distortions as the molecule moves along the reaction paths leading to the products.

The results gained from this experiment are surprising in the present case as one would have expected that the $3p$ Rydberg state rapidly decays into the lower, reactive valence state. Further, one could speculate that the $3p$ state decays first into $3s$, which in turn is suspected to evolve into the doubly excited state that opens the ring. None of those mechanisms appear to be at work in CHD. The question now is what relaxation path facilitates the extremely fast decay of the $3p$ Rydberg state in the $(4 + 2)$ excitation and what the structural distortions are, that go along with it.

3. Conclusion

In summary, time-resolved RFS studies of 1,3-cyclohexadiene with excitation at 268 and 207 nm reveal that the structural dynamics of this system is sensitively dependent on the excited electronic state. While 268 nm excitation into the 1B valence state opens the ring to form hexatriene, little evidence for this reaction is found upon excitation with 207 nm even though the molecule contains 1.36 eV more energy. While the very weak peaks at small binding energy could relate to a relaxation path through the 1B state and into the ring-opening coordinate, the very low intensity of those peaks suggests that the largest part of the wave packet bypasses the reactive electronic surfaces and goes directly to the ground electronic state. The difference in the photochemical activity of the two states is also reflected in the different time dependencies of the Rydberg electron binding energies. The photochemically stable state shows a fairly modest variation of the binding energy with delay time,

while the opening of the ring is associated with a much larger binding energy shift. It is noteworthy that broadening of the Rydberg lines during the time window of observation is not seen in either experiment. However, the $3p$ Rydberg signal in the $(3 + 2)$ experiment is broadened compared to that arising from direct excitation. Previous work has associated the spectral width to dispersion of molecular structure [26]. This is consistent with the theoretically derived notion that the wave packet remains well focused during the transition to the ground state [8]. Challenges in the near future include the time and energy-deconvoluted analysis of the peak shifts in order to get the true molecular binding energy variations. These could then be compared to wavepacket dynamics calculations such as those conducted by Schönborn et al. [8].

RFS as a tool to measure structural dynamics can be compared to ultrafast electron diffraction. In electron diffraction, one typically does not invert the observed diffraction pattern to obtain the distribution of molecular distances and then the molecular structures. Instead, diffraction patterns are calculated for different hypothetical structures and compared to experimental scattering patterns, a process that is iterated until the optimal structure is found. To use RFS as a structure determination method, a similar procedure can be used once it is possible to calculate Rydberg electron binding energies of molecules with specific structures. While the required theoretical method remains a formidable computational challenge, attempts to develop it are being made [10]. Regardless, the present experimental investigation establishes that RFS is an experimental technique that, upon development of its theoretical counterpart, has unique utility as a structural dynamics probe.

The time resolution of the RFS method is limited only by the duration of the laser pulses. While other methods, like ultrafast electron diffraction, can in principle provide

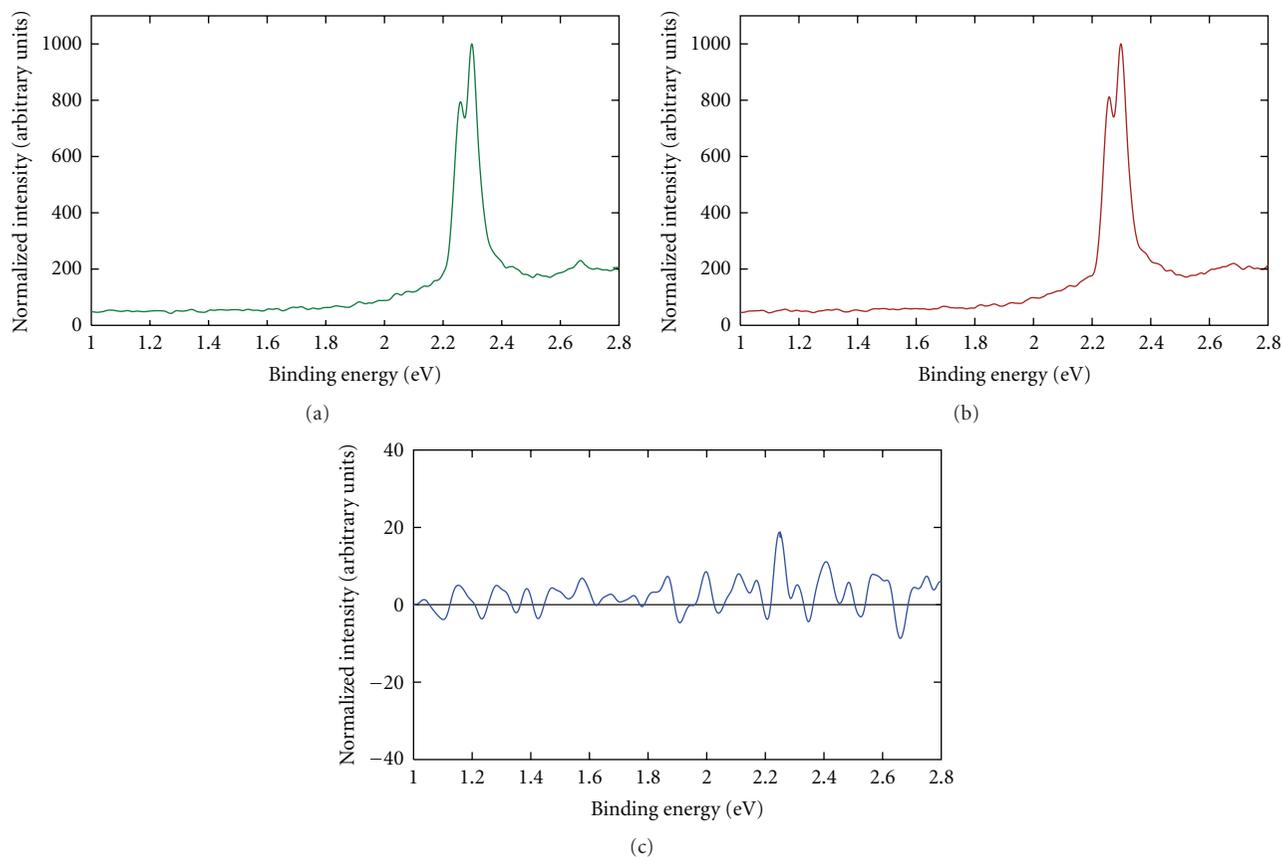


FIGURE 4: Rydberg electron binding energy spectra of CHD. (a) Projection of the nonbackground-subtracted spectrum onto the binding energy coordinate at pump-probe delays of more than 800 fs before the time zero. (b) Projection of the nonbackground-subtracted spectrum onto the binding energy coordinate at pump-probe delays over 13.6 ps after the time zero. (c) Difference photoelectron spectra. The spectra used to obtain the difference spectrum were slightly smoothed and are normalized to the maximum peak intensity.

information about specific atom-atom distances, ultrafast time-resolved analysis with such methods is difficult and limited to small- and medium-sized molecules. The large amount of internal energy inherent in the molecule as ring-opening occurs, or as the molecule transitions to the ground state, likely affects the diffraction signals more severely than RFS, which might make success of scattering experiments difficult to achieve on this system. Rydberg fingerprint spectroscopy as a complementary technique is inherently able to time-resolve ultrafast structural processes, while being sensitive to global molecular structure. Upon development of accurate computational techniques to calculate Rydberg electron binding energies, Rydberg fingerprint spectroscopy will be a powerful tool to “watch” ultrafast structure changes in molecules.

4. Experimental Methods

The experimental design used in this study has been described previously [26–30]. Briefly, CHD was cooled to 0°C, seeded into a stream of helium carrier gas, and expanded through a 100 μm nozzle orifice and a 150 μm skimmer. Ultrafast laser pulses cross the molecular beam

perpendicularly. The laser system consists of a regenerative amplifier (Spitfire, Spectra-Physics) seeded by a Ti:sapphire laser (Tsunami, Spectra-Physics) and pumped by a 5 kHz Nd:YLF laser (Evolution 30, Coherent). The output power of the system was about 800 mW for the near-IR fundamentals. For the (4 + 2) experiments, the fundamental beam was frequency doubled and quadrupled by two separate 0.1 mm thick BBO crystals, yielding second ($\hbar\omega_2$, 413 nm, 3.00 eV) and fourth ($\hbar\omega_4$, 207 nm, 5.99 eV) harmonics at band widths of 1 nm (24 meV) and 3 nm (23 meV), respectively. Through appropriate focusing, the intensities at the focal spots within the interaction region were kept below about 10^{12} W/cm² and 10^{10} W/cm², respectively. The duration of the pump-probe overlap was about 306 fs.

For the (3+2) experiment, second ($\hbar\omega_2$, 398 nm, 3.12 eV) and third ($\hbar\omega_3$, 268 nm, 4.63 eV) harmonics were obtained by frequency doubling and tripling the 800 nm output, using a set of 0.1 and 0.3 mm thick BBO crystals. The band widths were 2 nm (40 meV) for the third and 5 nm (37 meV) for the second harmonic. The intensities at the focus were on the order of 10^{12} W/cm² ($\hbar\omega_2$) and 10^{11} W/cm² ($\hbar\omega_3$). The duration of the pump-probe overlap was about 220 fs.

Photoelectrons were collected by a time-of-flight photoelectron spectrometer.

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