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Competitive ionization processes of anthracene excited with a femtosecond pulse in the multi-photon ionization regime

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To clarify the ionization mechanism of large molecules under multi-photon ionization conditions, photo-electron spectroscopic studies on anthracene have been performed with electron imaging technique. Electron kinetic energy distributions below a few eV reveal that three kinds of ionization channels coexist, *viz.,* vertical ionization, ionization from Rydberg states, and thermionic hot electron emission. Their relative yield is determined by the characteristic of the laser pulse. The duration in particular influences the ratio between the first two processes, while for higher intensities the last process dominates. Our results provide strong evidence that internal conversion plays an important role for the ionization of the molecule. © *2011 American Institute of Physics*. [doi:10.1063/1.3663618]

I. INTRODUCTION

Multi-photon ionization of atoms and molecules using a short intense pulse has been studied intensely for a long time. "Multi-photon" denotes the laser intensities below those where field ionization (see below) is not yet active. Observation of photo-electron kinetic energy distribution of atoms, in particular rare gases, has provided a tremendous amount of information about the ionization mechanisms, one of the most spectacular of which is above threshold ionization (ATI) which was first observed in photo-electron spectra of xenon.[1]

One of the key parameters of the atom-light interaction is the ponderomotive energy, U_p, which is the kinetic energy that a free electron acquires in the rapidly oscillating laser field. This effective interaction raises the ionization energy of a target, *IE*, and hence the photo-electron energy shifts to lower values when laser intensity increases, provided that the ionization occurs predominantly at the peak of a laser pulse. Also, it is well known that the energy levels of the Rydberg states vary in parallel with the *IE* with changing light intensity. This induces a resonance-enhanced ionization process at a specific intensity for a given wavelength (Freeman resonance[2]).

At still higher intensities, the laser field becomes comparable to or larger than that of the atomic nucleus and causes emission of electrons by the classical motion in the strong field or by tunneling through the potential barrier created by the external laser field and the nuclear electric field. In this case, photo-electron spectra are expected to be smooth, of approximately exponential shape and displaying no ATI peaks. The transition between multi-photon and field ionization is determined by the Keldysh parameter, $\gamma = \sqrt{IE/2U_p}$. This parameter defines the probability of tunneling ionization for a zero-range potential of a target.[3] At low intensities, its value is much higher than unity and multi-photon ionization is dominant, while field ionization prevails for values far below unity.

The situation is much less clear for *molecules*. A number of attempts have been made to fully understand molecular ionization behavior and it has been found that it is much more complicated than atomic ionization. The ionization of three kinds of alcohols, for example, has revealed that the evolution of photo-electron spectra are similar to those for an atom when using a 800 nm pulse, while excitation with 400 nm light gives results that are sensitive to the molecular geometries.[4] Also, ion yield measurements have shown that organic molecules are more difficult to ionize than xenon when the reduced ionization energy is taken into account.[5] These results suggest that there is a transition from atomic to molecular ionization processes, and that it is highly desirable to understand the effect of molecular properties for the short laser pulse ionization behavior.

One possible contributing factor that makes a difference is the presence of other ionization channels for the molecules. Two other ionization mechanisms have been reported, both effective below field ionization intensities. One is ionization due to quasi-thermal electron emission from a hot electron subsystem, that is, the absorbed photon energy is stored in incoherent electronic excitations and the ionization occurs thermally before the energy is coupled to the molecular vibrations.[6] This mechanism has been found to be active for fullerenes,[7] for sodium clusters[8] and for large polycyclic aromatic molecules,[9] and produces a smooth photo-electron distribution, similar to the one predicted for field ionization.

The other is ionization of a molecule via its Rydberg states. Unlike Freeman resonance of atoms and some very small molecules,[10,11] earlier works have suggested that the detection of these states results from the internal conversion (IC) of so-called super excited states.[12] The mechanism only requires that a Rydberg state is populated, from which the ionization occurs via one or multi-photon absorption. This may also happen in a thermal population of hot electrons. The detection of Rydberg states requires careful choice of the laser pulse as demonstrated by studies on fullerenes.[13] In particular, a pulse with an appropriate duration and with relatively low intensity gives a well-resolved structure.

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Two questions remain to be answered: What factor(s) cause(s) the difference in ionization mechanisms between atoms and large molecules and why does ionization of the latter depend on the pulse characteristic?

Our previous work was concerned with the size-dependent ionization of some poly-aromatic hydrocarbons.[9] The ionization of coronene ($C_{24}H_{12}$) took place only through the quasi-thermal process, whereas that of anthracene ($C_{14}H_{10}$) was significantly different and showed a transition from ATI to a smooth spectrum as the laser intensity increased. This result suggests that anthracene is a good target to be studied in more detail for solving the questions mentioned above.

For this purpose, anthracene was excited with relatively low intensity pulses on the order of 10^{12} W cm^{-2} at different pulse durations. Compared to the previous work, we performed measurements with higher resolution, gained by improving the acquisition software. This allowed us to observe peak shifts in the electron spectra on the order of 0.01 eV.

Three different ionization channels contributed to the measured photo-electron spectra: the vertical multi-photon ionization, i.e., direct ionization from the ground state without any relaxation, single or multi-photon ionization of the (electronically or thermally) populated Rydberg states, from where photons may be absorbed, and finally the thermal emission. The branching into these different channels could be monitored by the electron yield at different energies, corresponding to whether or not the peaks shift with laser intensity, and the smooth part of the spectrum. Their relative yields were found to depend on the characteristic of the laser pulse, and our results show that rapid IC plays a central role for the ionization behavior of such a large molecule.

II. EXPERIMENT

The details of the experimental setup have been described previously,[14] and we will only give a brief summary here. The anthracene was commercial (Sigma Chemical Co., purity 98%) and was used without any further purification. An effusive beam from an oven was intersected at right angle with a focused laser pulse with a wavelength of 775 nm (1.60 eV) or 388 nm (3.20 eV). The generated electrons were accelerated in an electrostatic field under focusing condition[15] and detected with a chevron configuration micro-channel plate detector in combination with a phosphor screen. The phosphor screen luminescence was monitored with a charge coupled device camera without synchronization with the laser shots. One laser shot produced 0.05–20 electrons depending both on the molecular source intensity, i.e., oven temperature which was between 300 and 370 K, and on the laser pulse characteristic. The raw images resulting from typically 400 000 to 3 000 000 laser shots were then inverted with the procedure reported in Ref. 16. An example of a raw and the corresponding inverted image is shown in Figure 1.

After inversion, the amplitude of the signal is plotted as a function of the square of the distance from the center of the image and then calibrated by means of the separation of the ATI peak separation that was identified with the photon energy, to produce the photo-electron spectrum (PES). Some peaks shift with intensity and to minimize fitting errors we therefore used a spectrum for an intensity which makes the shifting peak (see below) appear at almost the same energy as the non-shifted peak centered at 0.45 eV (for instance, 4.9 × 10^{12} W cm^{-2} in Figure 2). The same calibration parameters were applied to the other data.

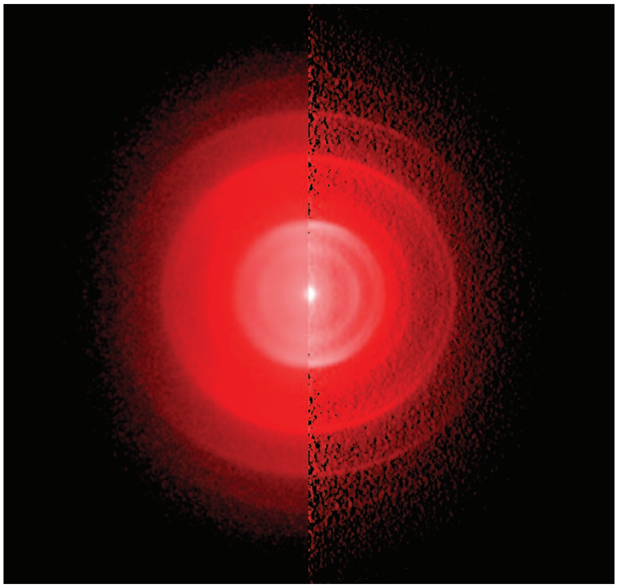

FIG. 1. An example of an experimental raw image (left half) and the corresponding inverted image (right half). The color scale is logarithmic and covers four orders of magnitude. The laser intensity is 4.5 × 10^{12} W cm^{-2} and the duration is 150 fs. The laser polarization is in the vertical direction, defined with a polarizer.

The laser intensity was determined by measuring the Freeman resonance on xenon under the same condition as the

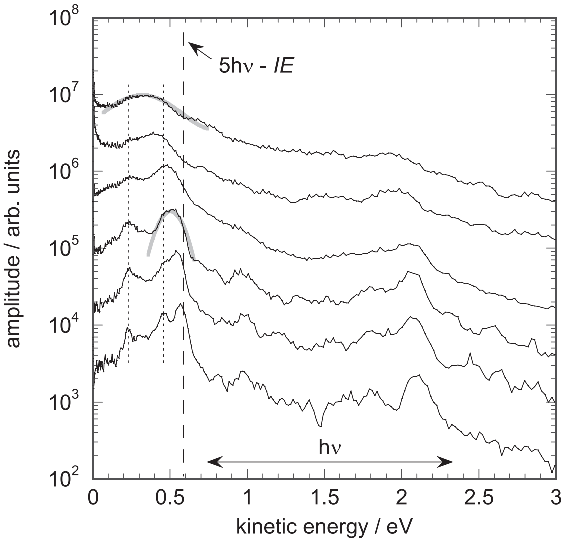

FIG. 2. Semi-log plot of angle-integrated PES in the region up to 3 eV for the pulse duration 150 fs. The laser intensities are 8.4, 6.9, 4.9, 4.0, 3.0, and 2.0 × 10^{12} W cm^{-2} from top to bottom. The length of the horizontal arrow corresponds to one photon energy (1.60 eV). The vertical dotted lines are guides to the eye and indicate that the peak positions are not shifted. The spectra are scaled vertically for display purposes. The curves at 0.5 and 0.3 eV at the intensities 4.0 and 8.4 × 10^{12} W cm^{-2}, respectively, are the fitted peak shapes.

measurement on anthracene. The shortest pulse duration of the laser is 150 fs, and the duration was varied by adjusting the optical pulse compressor in the laser. The duration of a stretched pulse was evaluated also with a xenon photoelectron spectrum assuming that the size of the focal point is independent of the duration.

The value of *IE* is 7.41 eV, as measured in gas phase with a helium lamp.[17] Thus, the ionization requires at least five photons. This *IE* gives $\gamma = 2.6$ for the laser intensity 1×10^{13} W cm^{-2} ($U_p = 0.56$ eV), which all but rules out field ionization throughout the present study.

We did not use any result of mass spectrometry here, mainly because we cannot rule out, as also mentioned in Ref. 18, that the cations will continue to absorb light after ionization and that the conclusions drawn from the mass spectra will be influenced by these effects.

III. RESULTS AND DISCUSSION

A. General features

The evolution of the angle-integrated PES for the wavelength of 775 nm and for the duration of 150 fs is shown in Figure 2, illustrating that the spectral structure depends strongly on the laser intensity. The spectrum agrees well with our previous work, apart from the improved resolution in the present work, and a minor difference in the slope of the high energy part of the spectrum because of an improved background subtraction. For the lowest intensity, the spectrum contains three pronounced peaks below the energy $5h\nu - IE$, centered at 0.22, 0.45, and 0.58 eV. As the intensity increases, the last of these shifts to lower energy and its width increases, while the first two show no shift and decreases in magnitude. The smooth distribution always contributes to the spectra and, especially at the higher intensity, it dominates the count rate.

The origin of these features will be discussed below, followed by a detailed discussion of the ionization mechanism.

B. Excitation of Rydberg states

We assign the peaks that do not shift with laser fluence to electrons that originate in Rydberg states for the following reason. Within the atomic ionization picture, the U_p induces a shift of both the *IE* and of the Rydberg states. In other words, the energy difference between the *IE* and each Rydberg state is constant regardless of the laser intensity. When the origin of the peaks is a direct photo-ionization process, the peaks will therefore shift with the U_p, and conversely, the absence of a shift indicates that the Rydberg states are populated differently. The only possible mechanism is the population of the states by a rapid IC, effective at the time scale of the laser pulse or shorter, and resulting in the preparation of the target molecule in any of a larger number of Rydberg states. This is consistent with the fact that the electron energy of the non-shifted peak observed is lower than $5h\nu - IE$. Consequently, each of the states is detected in a specific energy determined by $h\nu$ and its energy difference from the *IE*, independent of the intensity.

To our knowledge, anthracene does not absorb at 775 nm in one-photon processes, and no information on the multi-photon absorption band is available at present. It is notable that, however, its photo-absorption spectrum in the gas phase shows a broad background together with sharp bands around 6.4 eV,[19] which corresponds to $4h\nu$ for the laser used here. In addition, a strong peak centered at 6.26 eV has been observed and the corresponding electron kinetic energy emitted from this state is 0.45 eV, consistent with the energy of our (non-shifting) strongest peak. This fact supports our analysis that the non-shifted peaks can be assigned to the Rydberg states.

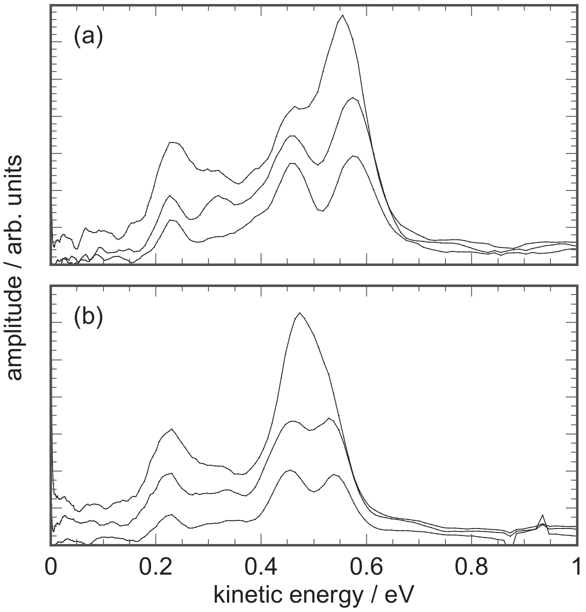

FIG. 3. Linear scale plot of angle-integrated PES in the region less than 1 eV for the pulse duration of (a) 150 and (b) 300 fs. In each of the spectra, the intensities are 2.5, 1.5, and 0.99 × 10^{12} W cm^{-2} from top to bottom. The spectra have been scaled vertically for display purposes.

C. Vertical multi-photon ionization

The peak that shifts with laser fluence, on the other hand, can be assigned to an ionization process without IC, i.e., vertical ionization. To test this assignment, we ionized with a stretched pulse, with the motivation that a pulse of longer duration gives rise to IC more efficiently. In this situation we expect that the ratio of the two kinds of peaks will change, with a relatively higher yield of the peaks that require IC. The result using low intensity pulses to distinguish between the two peaks is shown in Figure 3. Focusing the attention on the amplitude of these two peaks around 0.5 eV, it is clearly seen that the spectral shape is significantly different for the different pulses even for the same intensity. With the shorter pulse the shifting (high energy) peak grows faster than the other peaks with increasing laser intensity, while for the longer pulse, these amplitudes remain similar before they merge at the highest fluence. These tendencies confirm the assignment to direct vs. IC-assisted ionization. In addition, we conclude that the IC rate is shorter or similar to the duration of the shortest pulses used here.

For a better understanding of the vertical process, important for the understanding of the different ionization behavior of atoms and large molecules, the peak position and

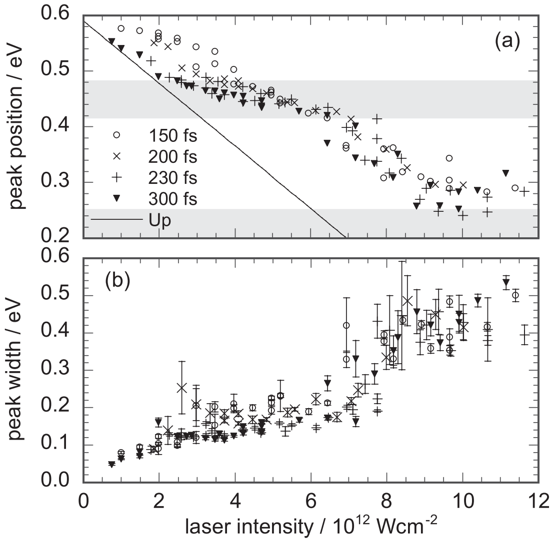

FIG. 4. (a) The position of the shifting peak from angle-integrated PES against the laser intensity, for various pulse durations (circles: 150 fs, crosses: 200 fs, daggers: 230 fs, and triangles: 300 fs) and fluences. The line indicates the shift due to U_p at the maximum intensity. The shaded area illustrates the energy region where the Rydberg peaks are observed. (b) Peak widths (full width at half maximum) corresponding to the data in (a).

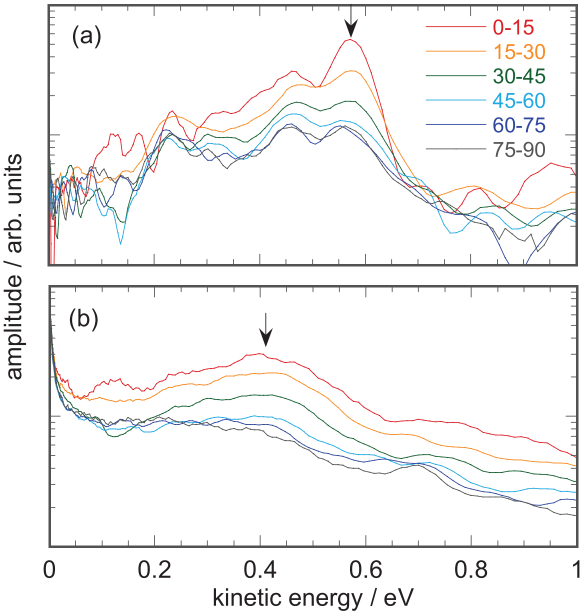

FIG. 5. Semi-log plot of angle-resolved PES in the region below 1 eV for every 15° with respect to the laser polarization direction. The laser intensities are (a) 3.0 and (b) 6.9 × 10^{12} W cm^{-2} and the duration is 150 fs. The arrows point to the peaks we focus attention on. The division of 0°–15° has lower statistic because the inversion process generates noise around 0°, and a band around this angle is therefore excluded from the analysis.[16]

its width are extracted by fitting them with Gaussian functions. The positions and widths from the fits are shown in Figures 4(a) and 4(b). The overall tendency is that higher intensity moves the peak to lower energy and broadens it, independent of the duration. This independence is reasonable because the level shift is described in terms of the laser intensity. Around the peak position 0.45 eV, the peak coincides with one of the non-shifting Rydberg peaks, as mentioned above, and the fit results are less reliable in this region. At higher intensity, the data points are relatively scattered. The reason is that, in addition to the broadening, the peak amplitude is reduced, as seen in Figure 2.

An interesting question is whether or not the observed shift can be described in terms of the theoretical U_p shift, similar to the atomic ionization case. An agreement suggests that the vertical ionization does occur predominantly at the peak of a laser pulse. The comparison is also shown in Figure 4(a). The calculated U_p shift is seen to be larger than the observed shift in the peak position, except at the smallest fluences and longest pulses. In this connection it is important to note that the PES of xenon gas measured under identical experimental condition shows Freeman resonance consistent with the calculated U_p shift at maximum intensity and known Rydberg state energies. The mismatch of the theoretical and experimental curves is not due to an uncertainty in the *IE*, because an uncertainty in this number would only cause a parallel shift in the theoretical line. We conclude from this comparison that the vertical multi-photon ionization occurs at an intensity less than the peak value of the pulse, presumably prior to the peak of the pulse, and at about half the peak intensity.

In order to conclude the above discussion, we should mention the possibility that the value of *IE* changes in a strong laser field. Apart from the ponderomotive energy, which adds a potential energy relative to the vacuum level, the *IE* may change for two other reasons. One is related to the classical effect of the instantaneous electric field. The laser intensity used in the present study is on the order of 10^{12} W cm^{-2} and this is too low to induce field ionization. However, the intensity might be high enough to reduce the *IE* by about 0.2 eV if one considers the size of the molecule and the maximum amplitude electric field. This energy is also the difference between the experimental and the calculated values at about 7 × 10^{12} W cm^{-2} (see Figure 4(a)). To investigate whether this is an important factor or not, we have performed an analysis of the angle dependence of the spectra. The angle resolved spectra contains information about variations of the *IE* because the peak position will shift systematically to lower energy at larger angles relative to the laser polarization direction if the *IE* is changed in the laser field. The results for two different intensities at the duration of 150 fs are shown in Figure 5.

The lower laser intensity in Figure 5(a) shows that the amplitude of the peak centered at 0.55 eV becomes systematically lower with increasing angle, reaching a lowest amplitude five times smaller than the highest. The position, however, does not change with angle, in sharp contrast to the observed change with laser intensity. The same tendency is clearly displayed also for the higher intensity, shown in Figure 5(b), concerning the peak centered at about 0.41 eV. We therefore conclude that the change in the *IE* due to electric fields of the magnitude used in the present study is negligibly small, apart from that of the ponderomotive potential.

The third possible reason for a change of *IE* is that excited electronic states that accompany multiphoton excitation have a different, presumably more extended charge distribution than the ground state molecule and the effective potential will be different because the screening of the nuclear charge will be reduced. This would add a positive contribution to the shift predicted by U_p. As seen in Figure 4(a), the shift is less than that of the U_p and there is little room for this effect in the data.

D. Assigning the high energy electrons

Let us now consider the smooth electron distribution seen in Figure 2. This part of the distribution represents a significant part of the count rate at the higher laser intensities, and it must be attributed to a strong contribution of either field ionization or quasi-thermal hot electron emission. The possibility of distinguishing these two different channels has been discussed previously in connection with the ionization of larger molecules, see, e.g., Ref. 9 where several pieces of evidence were presented that showed that hot electron emission is the far more likely explanation for these molecules. However, it has been suggested[20] that the smooth distribution of anthracene could results from tunneling ionization, based on a modified γ parameter.

To distinguish these two ionization paths, it is helpful to study the symmetry of the photo-electron images relative to the laser polarization direction. For field ionization, the emission occurs predominantly in the polarization direction,[21] while the hot electron emission produces a spherically symmetrical distribution due to its thermal nature.[14] A complication arises because the laser field influences the emitted electrons as well,[22] and an asymmetric image arises even for the thermal process. The effect of the post ionization electric field can be suppressed by irradiating the molecule with a wavelength for which the photo-absorption cross section is large.[9] This will cause ionization at a lower intensity if the process is inherently thermal, because in that case only the amount of absorbed energy matters, provided that it is absorbed within a short enough time, and consequently the effect of the field will be suppressed. The result obtained with frequency-doubled light is shown in Figure 6. The scatter between the 15° curves is small enough to consider this image to be a symmetric one, demonstrating the thermal nature of the electron emission. The smooth distribution can therefore be safely assigned to thermally emitted electrons.

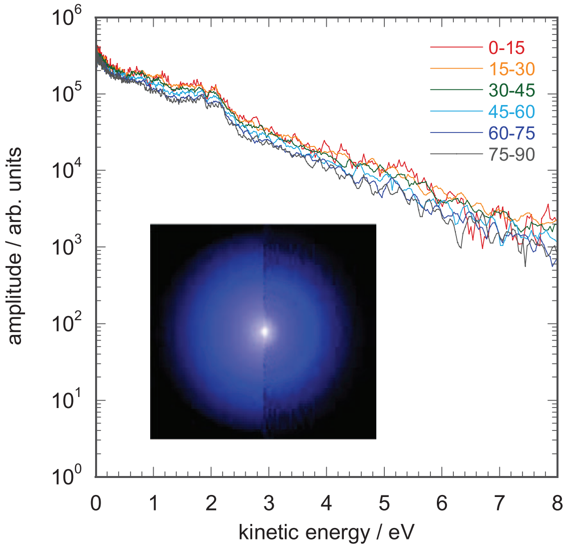

FIG. 6. Semi-log plot of angle-resolved PES in the region up to 8 eV for every 15° relative to the polarization direction produced with a frequency-doubled pulse (388 nm). The laser intensity was about 2×10^{12} W cm^{-2}, which gives $U_p = 0.028$ eV. No scaling was applied. The inset is the corresponding raw and inverted images shown in the same manner as in Figure 1. The hump around 2 eV is due to the Rydberg states. Because of a small ATI amplitude, the energy calibration has an overall uncertainty of about 5%.

E. Discussion of the ionization mechanism

Putting these results together, we can draw several conclusions about the ionization mechanisms. First of all, we can claim that the vertical ionization does not occur predominantly at the peak of a laser pulse. Since large molecules in general have a high number of states, energy level shift in a laser field results in the generation of a quasi-continuum of excited states.[23,24] In fact, the width of the shifting peak seen in Figure 4(b) dramatically broadens as intensity increases, indicating that the ionization is induced resonantly at various intensities. This is one important contrast to the atomic case where the resonant ionization occurs only at specific intensities.

Two questions remain to be answered. One is why the switching of the dominant ionization process is observed. The other is the reason that the shift of the high lying peak is less than expected from the U_p. Resonant photo-absorption occurs at any laser intensity used in the present study, and if a quasi-continuum of resonant states is present, one would expect that ionization occurs at the maximum intensity and that the U_p and consequently the shift will be as predicted for the maximum intensity.

To answer these questions, the following three points are important. First, the contribution of the rapid IC efficiently opens the other ionization channels which compete with the vertical one. Second, the channels' relative strengths are functions of the intensity. Third, the thermal process also occurs during the irradiation, as has been suggested from the observation of asymmetric photo-electron distributions mentioned above. Thermal emission can in fact occur with time constants far shorter than the pulse duration, see, e.g., Ref. 25

Based on these points, the answers to both questions are found in the number of photons that are needed for ionization through the two different types of channels. Ionization via the Rydberg states and the vertical process require as few as five photons, while the thermionic process requires significantly more. Thus one must expect that higher intensities favor the thermal ionization, consistent with the experimental results shown in Figure 2.

Also when considering the reduced peak shift does the competition of the ionization paths play a role. Ignoring the ionization via the Rydberg state for simplicity, we note that if the ionization occurs before the peak intensity is reached, the vertical process will tend to be a major channel while if it occurs at the peak the thermal emission will be relatively more prominent. The maximum of ionization probability for the vertical process is therefore not at the peak intensity if this peak intensity is high enough to give rise to the thermal process. As a consequence, higher intensity suppresses the vertical process more effectively, and this is why the peak shift is lower than that expected. We want to make clear that this explanation does not imply that the electron emission at the peak intensity prevents the emission of electrons at an earlier time. The mean peak shift is determined by the average laser intensity of all electron emission. We can illustrate the point with a simple model describing the competition between the two channels. The model is very simplified and cannot be considered a quantitative description of the situation but will serve to illustrate our point. Assume that the total ionization rate is given by the expression

$$k_{tot} = \sigma_v I^n + \sigma_{th} I^m \equiv k_v + k_{th}, \tag{1}$$

where I is the laser intensity and the σ's are constants. The subscripts refer to vertical and thermal ionization, the latter of which is assumed to be delayed with a negligible amount from the excitation. The number of molecules in the ground state p is depleted according to

$$\frac{dp}{dt} = -pk_{tot} \rightarrow p = p(-\infty)e^{-\int_{-\infty}^{t} k_{tot}(t')dt'}. \tag{2}$$

The average shift is given by the average intensity:

$$\langle I \rangle = \frac{\int_{-\infty}^{\infty} I k_v p(t')dt'}{\int_{-\infty}^{\infty} k_v p(t')dt'}. \tag{3}$$

This value can be estimated as the I of the time where the distribution peaks, i.e., the I at the time

$$\frac{dk_v p}{dt} = 0. \tag{4}$$

Solution of this equation gives

$$n\frac{\dot{I}}{I} = k_{tot} \Rightarrow -\frac{nt}{\tau^2} = \sigma_v I^n + \sigma_{th} I^m, \tag{5}$$

for a gaussian time dependence of the intensity centered on zero time, $I = \exp(-t^2/2\tau^2)$. From this expression we see that the emission rate peaks before the peak of the laser intensity. For sufficiently small intensities the shift in peak time approaches zero, as it should, whereas at higher peak fluences the peak emission rate is displaced towards lower relative fluences, consistent with the experimental data. A comparison of the peak emission time for a given fluence with and without the term $\sigma_{th} I^m$ present shows that the presence of this term shifts the peak emission to lower intensities. The contribution to the thermal yield peaks at a value of the fluence similar to that given by Eq. (5), except that the factor n is replaced by the higher value m. This displaces the thermal ionization to shorter times. As a first approximation, one can assume that the thermal yield is given by the same intensity as the one that solves Eq. (5). Then the ratio of thermal to direct ionization is approximately $\sigma_{th} I^{m-n}/\sigma_v$, which grows with peak intensity.

This effect is important for the detection of the Rydberg states as well, because the suppression of the thermionic process can be achieved by using a low intensity pulse, leaving space for the observation of well-resolved Rydberg structures in the spectra.[13]

IV. SUMMARY

We have discussed the ionization mechanism of anthracene excited with short, intense 775 and 388 nm pulses using a photo-electron imaging apparatus. In the multi-photon regime three ionization processes occur competitively: vertical ionization, excitation of Rydberg states, and thermal electron emission. Their relative yields depend on the characteristics of the laser pulse. In particular the duration has a strong influence on the ratio of the first two process, and the intensity determines the relative probability of the third process. It is noteworthy that the rapid internal conversion from the quasi-continuum states after the photo-absorption plays a key role in suppressing the vertical ionization and thus renders the ionization behavior of a large molecule significantly different from that of an atom.

As mentioned in the Introduction, it is not known what roles the molecular properties plays in the different ionization mechanisms. This work suggests that the presence of an intermediate photo-absorbing state and its relaxation dynamics is decisive for the ionization dynamics.

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