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Tagging multiphoton ionization events by two-dimensional photoelectron spectroscopy

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Two-dimensional photoelectron spectroscopy has been used to supply process-specific labels to multiphoton ionization events. Employing these tags, the authors can construct excitation and photoelectron spectra along predefined excitation routes in the neutral manifold and ionization routes to the ionic manifold from one single two-dimensional photoelectron spectrum. These results offer a novel way to elucidate the vibronic and dynamic properties of excited and ionic states. © 2007 American Institute of Physics. [DOI: 10.1063/1.2738465]

I. INTRODUCTION

Multiphoton ionization–photoelectron spectroscopy (MPI-PES) is a powerful tool to accurately determine energies of excited states and ionization potentials, as well as to probe excited state properties. A MPI-PES experiment is traditionally performed in two steps. In the first step, an excitation spectrum is recorded by scanning the wavelength of a laser focused into a gaseous sample and measuring the total yield of photoelectrons. If the laser flux is so high that nonresonant n-photon absorption leads to appreciable ionization, one generally observes a step in the ionization yield when the excitation frequency is scanned over the n-photon ionization threshold. From this step the ionization potential of the molecule can be determined directly. On the other hand, if at the n’-photon level resonance occurs with an excited vibronic state and the molecule is ionized in a sequential n’+m absorption process, the ionization probability is enhanced and the photoelectron yield increases. Peaks in the excitation spectrum thus correspond to resonances with excited vibronic states of the neutral molecules. In the second step, the laser is tuned to a specific vibronic resonance in the excitation spectrum and the distribution of photoelectron kinetic energies is determined, resulting in a photoelectron spectrum that can be considered as a fingerprint of the excited state.

Unfortunately, more often than not the situation is not so straightforward. It is not always clear what process is associated with a particular multiphoton ionization event: How many photons are involved in the excitation and ionization steps (in the case of resonance enhanced ionization)? Is it the molecule that is ionized or a fragment? To what extent do superexcited states above the ionization threshold play a role? etc. Often, one is able to resolve these issues in due course by very careful and fastidious experimentation, for example, by using various excitation wavelengths, precise calibration, multicolor ionization schemes, and photoelectron-photoion coincidence measurements. However, this requires a lot of time and experimental effort. In this paper, we present two-dimensional photoelectron spectroscopy (2D-PES) as a fast, simple, and efficient tool that enables direct visual recognition of the processes responsible for multiphoton ionization events. We show that the wealth of information contained in these 2D spectra can be analyzed in a straightforward way to efficiently map out the vibrational manifolds of both excited neutral and ionic states. Previously, 2D-PES combined with one-photon ionization has been applied with great success for the study of above-threshold processes such as autoionization and postcollision interactions. We will demonstrate that the comprehensive nature of 2D-PES is particularly valuable in multiphoton ionization experiments.

II. EXPERIMENTAL DETAILS

The experimental setup used has been described in detail elsewhere. The light from an excimer pumped dye laser is focused into the ionization chamber of a magnetic bottle spectrometer by a quartz lens with a focal length of 175 mm. Samples are introduced into the ionization region of the spectrometer as an effusive beam. The photoelectrons formed in the ionization region are parallelized by a strongly diverging magnetic field, and they enter a 0.5 m flight tube where a homogeneous magnetic field guides them to a pair of stacked microchannel plates (MCPs). It is often useful to
use a small electric field to push slow photoelectrons toward the flight tube. For this purpose, two copper electrodes are mounted in the ionization region. The ac signal of the MCPs is recorded and averaged by a 500 MHz digital oscilloscope that is read out by a personal computer for further analysis.

### III. RESULTS AND DISCUSSION

The essence of 2D-PES is simple. In the conventional two-step process described in I, dispersed photoelectron spectra are recorded in a separate experiment for selected peaks in the excitation spectrum. In 2D-PES, instead, we record the entire dispersed photoelectron spectrum at all steps of a continuous excitation wavelength scan, and then plot the results, as shown in Fig. 1. The major advantage of this approach is that signals are now not only characterized by excitation and photoelectron energies but also by a slope. This slope is effectively a label that tells us what process is responsible for the signal.

In order to quickly and efficiently record the photoelectron spectrum at all steps of the excitation scan, the time-of-flight spectra recorded on the oscilloscope are directly converted to a linear energy scale by application of the following formula:

\[
E = \frac{1}{2} m_e \frac{l^2}{l - t_0} e,
\]

where \( E \) is the photoelectron energy in eV, \( m_e \) the mass of the electron, \( l \) the distance from the ionization region to the detector, \( t \) the flight time, \( t_0 \) the moment of ionization, and \( e \) the elementary charge. In practice \( t_0 \) and \( l \) are fitted to a known spectrum (typically that of xenon). The disadvantage of retrieving photoelectron spectra in this way is that, because of the limited time resolution of the measurement, the resolution is lower for faster photoelectrons. When recording a standard one-dimensional PES, we use a scanning retardation voltage and convert only the high resolution part of the time-of-flight spectrum. In this way, a uniform (high) resolution can be obtained. By using a direct conversion of the time-of-flight spectrum and sacrificing resolution, we, however, gain in 2D-PES access to the full photoelectron spectrum at every excitation wavelength.

In the following, we will demonstrate the effectiveness of 2D-PES by its application to the indole molecule. From a single 2D-PE spectrum we will determine straightaway (i) the ionization potential (IP), (ii) the vibronic structure of the cation, (iii) the term values of two Rydberg states, and (iv) their vibrational structure. For the simultaneous determination of these particular properties, a one-color three-photon MPI scheme is well suited, and is therefore applied here. In general, however, the 2D-PES technique can be used with any \((n+m)\) one- or multicolor MPI scheme, the choice for a particular scheme depending only on the process(es) one would like to study.

Figure 1 shows the three-photon 2D-PE spectrum for an effusive beam of indole for excitation energies from 20 500 cm\(^{-1}\), just below the three-photon ionization threshold, to 24 500 cm\(^{-1}\). At the three-photon threshold of about 20 860 cm\(^{-1}\), photoelectrons with zero kinetic energy are detected. As the excitation energy is increased, so is the kinetic energy of the photoelectrons (PKE). In the 2D-PE spectrum this leads to what we will call a ridge with a characteristic slope of \(\Delta \text{PKE}/\Delta h\nu\). Obviously, for the ridge resulting from three-photon ionization to the vibrational ground state of the ion the slope is 3. Since it is associated with ions with zero vibrational energy, the ridge is marked in Fig. 1 as ZVE. We define the ZVE spectrum as the integral \(\int_{\text{ZVE}(x)} PKE(x)dy\) of the photoelectron yield, \(x_0\) is the \(x\) coordinate at the onset of the ridge, and \(\delta\) is the width defined by the lines indicated in Fig. 1. This ZVE spectrum, displayed in Fig. 3(a), contains the three-photon ionization threshold corresponding to an IP of 7.760 ± 0.005 eV, a value that is in excellent agreement with the most accurate literature value of 7.7602 ± 0.0006 eV. The other features present in the ZVE spectrum will be discussed below.

Apart from the energy of the vibrational ground state level of the ion, the 2D-PE spectrum also provides information on vibrationally excited levels of the ion. Figure 2 is a zoom in of the low-energy part of the 2D-PE spectrum of Fig. 1. At various energies above the three-photon threshold, ridges with a slope of 3 can be observed. These ridges are associated with nonresonant three-photon ionization to vibrationally excited states of the ion. The most direct way to extract a vibrational spectrum of the ion is to integrate the signal of the photoelectrons with near-zero energy between the lines marked by “Z” in Fig. 2, a procedure that, in fact,
close the Condon approximation and assuming that the
electronic transition moment is independent of the photoelectron
energy and the vibrational wave function of the electronic ground state
of the neutral and that of the ion. Figure 4(d) displays such a
Franck-Condon simulation based on the equilibrium geometries and
associated force fields calculated with density functional theory, using the B3LYP exchange correlation
functional11–13 and a triple-

basis set augmented with polar-
correction terms of CASPT2 calculations16 that predicted vertical excitation energies of 43 230 and 43 310 cm−1 for the 3
states, the first two resonant states was calculated at a lower energy
(42 020 cm−1) and is therefore a less likely candidate.

The third resonant feature in the ZVE spectrum—the broad band centered around a one-photon energy of 23 130 cm−1—is harder to explain. One might be tempted to assign it to—in that case lifetime-broadened—the 3
Rydberg state, but such an assignment would imply that the
CASPT2 calculations predicted an incorrect ordering of the 3
manifold, and would be inconsistent with the lack of branching into a ridge with a slope of 1 at 23 130 cm−1. The latter observation also argues against nondiagonal ionization from the R2 Rydberg state as a possible explanation for the appearance of the 23 130 cm−1 feature.

Vibrionic spectra of the two 3p Rydberg states can be extracted from the 2D-PE spectrum by integration over the R1 and R2 ridges using the integrals

\[ f_{R}(x) = \int_{0}^{\infty} S(x+y/3)(x+y/3)dy, \]

with \( x_{R} \) and \( y_{R} \) the \( x \) and \( y \) coordinates of the maximum of the ridge \( R \) in the 2D-PE spectrum. The spectra, shown in Figs. 4(b) and 4(c), closely re-

properties very similar to those of the ion. Based on their quantum defect of 0.55 and 0.52, respectively, we therefore assign the resonant states to members of the 3p Rydberg manifold. Such an assignment is completely in line with the results of CASPT2 calculations16 that predicted vertical excitation energies of 43 230 and 43 310 cm−1 for the 3p, and 3p, states. The 3p state was calculated at a lower energy (42 020 cm−1) and is therefore a less likely candidate.

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seem the spectrum obtained for nonresonant three-photon ionization [Fig. 4(a)] and its simulation [Fig. 4(d)]. This provides further confirmation of the assignment of the resonant states as Rydberg states. Redshifted from the origin band in Fig. 4(b), a small peak is visible. We assign this peak to a hot band, i.e., a transition from a thermally excited vibrational level in the ground state to the vibrationless Rydberg state.

The applicability of 2D-PES is further illustrated in Fig. 5, which shows the three-photon 2D-PE spectrum of 5-fluoro-3-methyl indole. An obvious difference with the experiments on indole is that here the laser is not scanned over the actual three-photon threshold. Nevertheless, the IP can readily be determined from an extrapolation of the ridge with a slope of 3 to zero photoelectron kinetic energy, and is determined as 7.70±0.01 eV. The 2D-PE spectrum gives evidence for two close-lying Rydberg states at 43 000 and 44 740 cm−1. Based on their quantum defects of 0.61 and 0.49, respectively, and the analogy with indole, we assign these two states to the 3p_x and 3p_y Rydberg states.

IV. SUMMARY AND CONCLUSIONS

We have shown that two-dimensional photoelectron spectroscopy offers unique possibilities to tag multiphoton ionization events. The labels provided by the technique enable one to read off directly from the 2D-PE spectrum the photophysical process responsible for the appearance of a particular subset of photoelectrons. As a result, various types of excitation spectra of intermediate, resonance enhancing, neutral states and of ionic states, as well as photoelectron spectra can be extracted unambiguously from a single 2D-PE spectrum. In the present study, we have successfully employed the technique to disentangle various multiphoton ionization pathways and to determine the excitation energies of the 3p_x and 3p_y Rydberg states of indole and 5-fluoro-3methyl indole. In a forthcoming paper, we will show the significant advantages the technique offers to elucidate the singlet-triplet coupling between the lower-lying excited states of acetylene.

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9 The modern implementation of ZEKE involves pulsed field ionization of highly excited Rydberg states. This greatly increases the resolution of the experiment, see, for example, Ref. 10.
18 A conceptually similar method—but based on “Rydberg tagged” H atoms—has been used to accurately determine bond dissociation energies. In that case, the kinetic energy release as a function of the excitation energy is extrapolated back to zero (see, for example, Ref. 19).