

Multiphoton photoelectron spectroscopy: watching molecules dissociate

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Threshold photoionization spectroscopy [zero kinetic energy (ZEKE), pulsed field ionization (PFI), mass analysed threshold ionisation (MATI)] usually takes advantage of multiphoton excitation through bound intermediate states, but we show that excellent quality, high-resolution spectra can also be obtained in one-color experiments using two- and three-photon ionization. An enhancement similar to resonance Raman yields changed spectra if the excitation proceeds via continuous intermediate states. A molecule which after absorbing a photon started to dissociate is stabilized on the ionic surface by a delayed second photon, with the observed spectra reflecting geometry changes due to this arrested dissociation process. Using two colors, the technique should be applicable to almost any molecule, and yield a detailed insight into its dissociation dynamics.

The classical photoelectron spectroscopy originally developed in the 1960s by Turner *et al.*^{1,2} was very useful in providing information about ionization potentials and the electronic structure of atoms and molecules, but its low resolution was a severe limitation. Unlike optical spectroscopy where a resonant transition between two bound states occurs at a specific frequency or energy, ionization is a threshold process, it will take place not just when the energy needed to accomplish the process is reached, but also for all higher energies. Whereas in optical spectroscopy one detects photons whose frequency is not changed by lenses or mirrors, focusing electrons produced in the ionization step onto a detector changes their energy, the property one needs to measure in order to interpret the spectra and derive the information of interest, and this is the cause of the low resolution of the technique. This drawback of photoelectron spectroscopy was partially eliminated by the development of various methods detecting selectively electrons produced by ionization at or near the threshold, and thus obviating the necessity of measuring the electron energy: zero kinetic energy (ZEKE),^{3,4} pulsed field ionization (PFI)⁵ or mass analysed threshold ionisation (MATI).⁶

Since tunable far UV lasers, which would be needed for ionizing most stable molecules by a single photon, are still not commonplace in laboratories, most of the high-resolution photoelectron studies of this type are “two-color” experiments. They use one laser to access resonantly an excited bound electronic state of the neutral, and complete the ionization process by a second, independently tunable laser.⁷ Compared with the simpler, direct single photon ionization, the two-color experiment has an added advantage: in the first, resonant state, one can select a specific state of the molecule or atom under study.

Even though at the time some experts expressed doubt as to whether the experiment can work, we have several years ago been able to show that even without an intermediate state the threshold ionization can be accomplished also by two photons of the same color;⁸ using a single tunable laser source we have obtained excellent quality photoelectron spectra.^{8–16} In a one-color experiment one loses the ability of state selection, but

this drawback is usually not serious, since the experiments are mostly done on molecules in cold supersonic beams, where only very few quantum states are thermally populated.¹⁷ Furthermore, the resolution of the experiment is sufficient to fully resolve the rotational structure for very small molecules such as NO,⁹ so that no information is lost; for larger molecules one is limited by the $\approx 0.2\text{--}1\text{ cm}^{-1}$ resolution of the photoelectron spectroscopy anyway, so that there is little to be gained by state selection.

Our studies have shown, however, that if the two-photon ionization proceeds via an absorption continuum of an intermediate state, it can yield additional useful information, which would not be easily obtainable either by a single photon ionization, or by the usual “two-color” threshold spectroscopy through a bound electronic state.^{12–14} More specifically, the ionization mediated by a dissociative continuum allows populating ionic levels which would (due to poor Franck–Condon factors) not be accessible in direct single photon ionization, and perhaps even more importantly, provides useful insight into the dissociation dynamics of the neutral precursor molecule, as exemplified by methyl iodide, whose potential diagram is shown in Fig. 1.

The ionization of this molecule removes an electron from a nonbonding orbital, and the potentials of the cation^{18,19} are therefore very similar to that of the neutral molecule. The unchanged geometry is also reflected in the conventional photoelectron spectrum,²⁰ which contains, as shown in Fig. 2 (upper trace) only two very strong lines, origins of transitions into the fine structure components of the doublet ionic ground state, with very little indication of vibrational structure. CH₃I is known to exhibit a strong continuous absorption in the UV range at about half the energy needed for its ionization,²¹ which is due to a pair of dissociative states usually denoted ³Q₀ and ¹Q₁,²² so that any attempt to ionize the molecule by two photons of the same color will necessarily involve excitation into one of these states.

In the experiments to be described below about 300 mbar of methyl iodide vapor are mixed into a high-pressure (≈ 20 bar) helium gas, and expanded at a stagnation pressure of 4 bar via a pulsed piezo valve into ultra high vacuum. The cold molecular beam is crossed by a pulsed tunable dye laser (13 ns, 1.8 mJ, 900 mm focusing (two photons)/4.1 mJ, 150 mm focusing (three photons)) pumped by a Lambda Physik xenon chloride excimer laser. The CH₃I molecules excited by the absorption of two (or three) photons to very high Rydberg states within a few cm^{-1} of the ionization limit are then, after about a 2 μs delay field-ionized by an applied pulsed electric field ($\approx 4\text{ V cm}^{-1}$).¹⁶ By detecting the current due to electrons produced by the ionization as a function of laser frequency, the threshold photoionization spectra are obtained.

Ordinarily a molecule excited optically into a dissociative continuum should dissociate in a single vibrational period on a subpicosecond time scale.²³ Some fraction of the excited

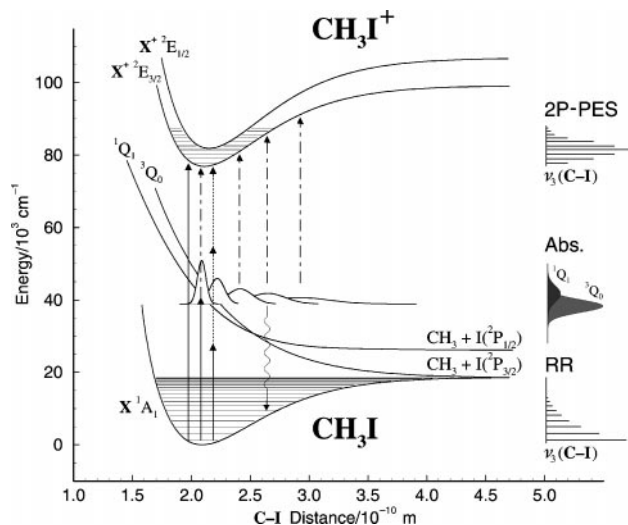


Fig. 1 Schematic potential energy diagram of methyl iodide (CH_3I). In the case of one-photon ionization (long solid arrow) the dissociative continuum (represented by the repulsive states $^1\text{Q}_1$ and $^3\text{Q}_0$) is skipped. If the molecule is excited into the dissociative continuum (medium solid arrow) then the dissociation process starts, but can be stabilized by emitting a photon (swung downward arrow) leading to the schematic resonance Raman (RR) spectrum of the I-C stretching mode ν_3 aside. In our experiments, where the molecule is still in the intense laser field, it is stabilized by absorbing a second photon anytime where the dissociation based, changed geometry Franck-Condon factors become non-negligible (dot-dashed arrows). The appropriate photoelectron spectrum (PES) now shows a maximum. For complementary data by overjumping the dissociative continuum we performed for the first time non-resonant, three-photon threshold photoionization (first photon: short solid arrow, second and third photons: dotted arrows).

molecules, however, may escape this fate: before the dissociation can be completed, they are stabilized by emitting a photon.²⁴ Since, however, between the time of excitation and the time of the photon emission the molecule has already started on the path to dissociation, the $\text{H}_3\text{C-I}$ bond was

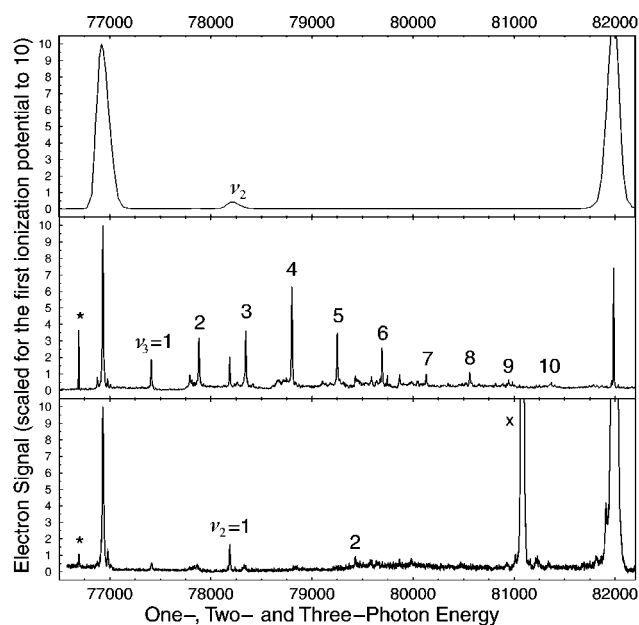


Fig. 2 Comparison of the conventional, one-photon photoelectron spectrum of Karlsson *et al.*²⁰ (upper trace) with the two- (middle trace) and three- (lower trace) photon threshold photoelectron spectra of our group. The two-photon spectrum clearly shows the influence of the dissociative continuum. The peaks labeled with asterisks mark the $\text{I}^+(\text{}^3\text{P}_2) \leftarrow \text{I}^*(\text{}^2\text{P}_{1/2})$ resonance of atomic iodine and the peak labeled with an x denotes a resonance due to CH_3I .

lengthened, the geometry and the Franck-Condon factors have changed. As is well-known to spectroscopists, methyl iodide is one of the classical molecules for observing so-called resonance Raman spectra, exhibiting a long progression in the C-I stretching frequency.²⁴

In our ionization experiment, where the molecule excited by a photon is still in the radiation field of the intense, 13 ns laser pulse, it has an alternative means of avoiding dissociation. Instead of emitting a photon it can, in a process similar to the resonance Raman, adsorb a second photon, and be stabilized by being promoted onto the bound ionic surface.¹²⁻¹⁴ Again, however, the incipient dissociation process between absorption of the first and second photon has changed the geometry and the Franck-Condon factors, and the photoionization spectrum^{12,13} shown in Fig. 2 (middle trace) is observed, which can be contrasted with a conventional (one photon) photoelectron spectrum²⁰ in Fig. 2 (upper trace). Besides the much sharper lines and higher resolution characteristic of the ZEKE-PFI technique, unlike the one-photon spectrum, it exhibits an intense, extensive vibrational structure, where similar to the Raman spectrum a long progression in the C-I stretching frequency ν_3 is clearly observed.

The dissociative processes of this kind can in principle be nicely simulated by semiclassical wave-packet propagation methods. Abrashkevich and Shapiro²⁵ have recently obtained in this way a good agreement with the observed Raman spectrum,²⁴ but express surprise that the intensity distribution for the ionization process is somewhat different, and does not quite agree with our experiment. Actually, in spite of similarities, there is a considerable difference between the resonance Raman, and the one-color two-photon ionization experiments, and one would not necessarily expect identical intensity distributions. In the former experiment the laser wavelength is constant, and the molecule once excited by a photon starts to dissociate. While it can in principle emit a photon at any time during the dissociative process, classically the probability is maximum at the early stages of dissociation, when the fragments being accelerated by the steeply descending repulsive potential, start only slowly to move apart. In the ionization experiment the situation is considerably more complex, while the laser is continuously being tuned, as one records the spectrum. Unlike the Raman process, the second photon absorption, and observation of a threshold ionization event cannot occur at any time, but only when the two-photon energy is in resonance with one of the vibrational levels of the ion, and at specific delays when in the course of the dissociation process the appropriate Franck-Condon factors become non-negligible. The delayed absorption of the ionizing photons then provides a "snapshot" of the dissociating molecule. The complex geometry changes, which take place in the dissociation, are evidenced by the observation of all six vibrational modes of the ion in the experimental spectrum.^{12,13} Besides stretching the C-I bond, also the I-C-H angles must change as the roughly tetrahedral methyl iodide dissociates to yield a planar methyl radical, CH_3 , and it is thus not surprising that a model treating CH_3I as a linear triatomic molecule did not reproduce quantitatively the experimental spectrum.

In order to be able to model the dissociation and the effect of the intermediate state more satisfactorily, it would be quite desirable to also obtain "threshold" one-photon ionization data for CH_3I . Unfortunately, we have a single tunable source available, which cannot even approach the 75000 cm^{-1} range which would be needed, but it occurred to us that one might also move away from the intermediate resonance in a similar, three-photon one-color experiment, since our laser operates satisfactorily in the needed $25000\text{--}28000\text{ cm}^{-1}$ range. The breakup of methyl iodide requires some 18800 cm^{-1} , so the laser wavelength in the three-photon experiment still lies above the dissociation limit of the ground state but very far

from resonance and from the strong 260 nm ($\approx 39\,000\text{ cm}^{-1}$) absorption. In spite of initial doubts that the three-photon cross-section might be too small, and that complete fragmentation rather than ionization will take place, the idea indeed functioned well, as can be seen in Fig. 2 (lower trace) showing the first non-resonant, three-photon threshold photoionization spectrum of methyl iodide.

Similar to the conventional photoelectron spectrum²⁰ in Fig. 2 (upper trace), and in contrast with the resonant continuum mediated two-photon threshold spectrum^{12,13} in Fig. 2 (middle trace), the two 0–0 electronic origin bands are dominant and the vibrational structure is relatively weak. The strongest bands are no longer due to the C–I stretching frequency, but rather to ν_2 , the symmetric CH₃ bending, and even though the ν_3 progression is still observable, it is short and much weaker than in the two-photon spectrum. In the two-photon spectrum (middle trace of Fig. 2) weak bands due to ν_1 , the CH stretch, as well as the overtone of ν_5 , the asymmetric CH₃ bending mode, and more surprisingly also ν_6 , the asymmetric rock, suggest that also a distortion of the three-fold C_{3v} symmetry takes place during the dissociation. This asymmetry is also evidenced by the observation that photodissociation of CH₃I yields rotationally highly excited methyl radicals.^{26–30}

As noted above, the single photon frequency in the three-photon experiment lies far below the onset of CH₃I absorption, and the two-photon energies ($51\,200\text{--}54\,400\text{ cm}^{-1}$) lie well above its maximum. They are in a wavelength range where discrete spectra of the so called X–C and X–D transitions are known to occur, and interaction with states in this region may have some influence upon the observed spectrum. Clearly further more detailed theoretical modelling of the multiphoton processes, and additional experimental studies of methyl iodide dissociation would be extremely interesting. In particular, two-color experiments would permit more flexibility in the choice of photon energies, and a complete separation of the initial excitation from the ionization step. With the first photon one could thus select any desired energy excess above the dissociation threshold, and by tuning the second laser source ionize the molecule and obtain a picture of the dissociation process.³¹ Such a two-dimensional study would greatly facilitate the theoretical analysis of the results, and provide an insight into the geometry changes occurring during the dissociation in unprecedented detail. As already mentioned, this ionization mediated by a dissociative state also allows excitation of numerous vibrational levels of the ion, which would be completely inaccessible otherwise. Thanks to this process, CH₃I⁺¹² (as well as the corresponding deuteride¹³) is perhaps the only larger ion, for which all six of its vibrational frequencies are known.

In summary, we have demonstrated that obtaining excellent quality, high resolution threshold ionization spectra in a one-color experiment is entirely feasible not only by two, but also three and possibly more photons. A study of methyl iodide has permitted us for the first time to compare spectra obtained by one-, two-, and three-photon ionization, and demonstrated clearly the drastic changes in the spectrum due to the resonant mediation of an intermediate state. The experiments confirm that the two- or multiphoton ionization technique *via* dissociative continua, in particular if two different colors could be used, has the potential for providing detailed insight into the dynamics of molecular dissociation. While it has in the recent years become possible to study the dynamics of fast processes in real time using femtosecond laser pulses, such experiments always involve a tradeoff between time- and energy-resolution. The two-photon ionization provides complementary information without having to make this tradeoff. Obviously, the technique is not applicable only

to methyl iodide, but since every molecule has dissociative continua, the use of two independently tunable sources could be extended to essentially any system.

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References

- 1 D. W. Turner and M. I. Al-Joboury, *J. Chem. Phys.*, 1962, **37**, 3007.
- 2 M. I. Al-Joboury and D. W. Turner, *Diss. Chem. Soc.*, 1963, **Part V**, 5141.
- 3 K. Müller-Dethlefs, M. Sander and E. W. Schlag, *Z. Naturforsch.*, 1984, **39**, 1089.
- 4 K. Müller-Dethlefs, M. Sander and E. W. Schlag, *Chem. Phys. Lett.*, 1984, **112**, 291.
- 5 G. Reiser, W. Habenicht, K. Müller-Dethlefs and E. W. Schlag, *Chem. Phys. Lett.*, 1988, **152**, 119.
- 6 L. Zhu and P. Johnson, *J. Chem. Phys.*, 1991, **94**, 5769.
- 7 E. W. Schlag, *ZEKE Spectroscopy*, Cambridge University Press, Cambridge, UK, 1998.
- 8 I. Fischer, A. Strobel, J. Staecker, G. Niedner-Schatteburg, K. Müller-Dethlefs and V. E. Bondybey, *J. Chem. Phys.*, 1992, **96**, 7171.
- 9 A. Strobel, I. Fischer, J. Staecker, G. Niedner-Schatteburg, K. Müller-Dethlefs and V. E. Bondybey, *J. Chem. Phys.*, 1992, **97**, 2332.
- 10 I. Fischer, A. Lochschmidt, A. Strobel, G. Niedner-Schatteburg, K. Müller-Dethlefs and V. E. Bondybey, *J. Chem. Phys.*, 1993, **98**, 3592.
- 11 I. Fischer, A. Lochschmidt, A. Strobel, G. Niedner-Schatteburg, K. Müller-Dethlefs and V. E. Bondybey, *Chem. Phys. Lett.*, 1993, **202**, 542.
- 12 A. Strobel, A. Lochschmidt, I. Fischer, G. Niedner-Schatteburg and V. E. Bondybey, *J. Chem. Phys.*, 1993, **99**, 733.
- 13 A. Strobel, I. Fischer, A. Lochschmidt, K. Müller-Dethlefs and V. E. Bondybey, *J. Phys. Chem.*, 1994, **98**, 2024.
- 14 N. Knoblauch, A. Strobel, I. Fischer and V. E. Bondybey, *J. Chem. Phys.*, 1995, **103**, 5335.
- 15 A. Strobel, N. Knoblauch, J. Agreiter, A. M. Smith, G. Niedner-Schatteburg and V. E. Bondybey, *J. Phys. Chem.*, 1995, **99**, 872.
- 16 B. Urban, A. Strobel and V. E. Bondybey, *J. Chem. Phys.*, 1999, **111**, 8939.
- 17 C. Y. Ng, *Adv. Chem. Phys.*, 1983, **52**, 263.
- 18 R. Weinkauff, K. Walter, U. Boesl and E. W. Schlag, *Chem. Phys. Lett.*, 1987, **141**, 267.
- 19 K. Walter, R. Weinkauff, U. Boesl and E. W. Schlag, *J. Chem. Phys.*, 1988, **89**, 1914.
- 20 L. Karlsson, R. Jadrny, L. Mattsson, F. T. Chau and K. Siegbahn, *Phys. Scr.*, 1977, **16**, 225.
- 21 A. Hantzsch, *Ber. Dtsch. Chem. Ges.*, 1995, **53**, 612.
- 22 R. S. Mulliken, *J. Chem. Phys.*, 1940, **8**, 382.
- 23 R. Schinke, *Photodissociation Dynamics*, Cambridge University Press, Cambridge, UK, 1993.
- 24 M. O. Hale, G. E. Galica, S. G. Glogover and J. L. Kinsey, *J. Phys. Chem.*, 1986, **90**, 4997.
- 25 D. G. Abrashkevich and M. Shapiro, *J. Chem. Phys.*, 1996, **105**, 9493.
- 26 R. O. Loo, H.-P. Haerri, G. E. Hall and P. L. Houston, *J. Chem. Phys.*, 1989, **90**, 4222.
- 27 D. W. Chandler, J. W. Thoman, Jr., M. H. M. Janssen and D. H. Parker, *Chem. Phys. Lett.*, 1989, **156**, 151.
- 28 M. Zahedi, J. A. Harrison and J. W. Nibler, *J. Chem. Phys.*, 1994, **100**, 4043.
- 29 Y. Amatatsu, K. Morokuma and S. Yabushita, *J. Chem. Phys.*, 1991, **94**, 4858.
- 30 Y. Amatatsu, S. Yabushita and K. Morokuma, *J. Chem. Phys.*, 1996, **104**, 9783.
- 31 T. Schultz and I. Fischer, *J. Phys. Chem. A*, 1997, **101**, 5031.