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Two-Photon Photoelectron Spectrum of Methyl Iodide through a Dissociative Intermediate State

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The two-photon photoelectron spectrum of methyl iodide was recorded in a magnetic bottle time-of-flight spectrometer. As absorption of the first photon is resonant with the dissociative A-state continuum of methyl iodide, the experiment corresponds to a bound−free−bound transition. A progression in the C−I stretching vibration is observed, which corresponds, in a simplified picture, to the dissociation coordinate. The results agree well with recently published two-photon ZEKE spectra of CH_3I. This similarity has impact on an ongoing discussion about discrepancies between calculated and measured intensities in two-photon ionization spectra.

Introduction

The dynamics of the photodissociation process are an interesting and fascinating area of physical chemistry.[1] Although time-domain techniques are successfully applied to many problems of chemical dynamics, frequency-domain techniques continue to provide considerable insight into the dissociation process. A well-known method is resonance Raman scattering.[2] Here the molecule is excited into a dissociative state. During the dissociation process, a photon is spontaneously emitted and a spectrum of the ground state is obtained with a rich vibrational structure, which reflects the intermediate state dynamics. It was shown recently that the dynamics of a continuum state can also be projected onto the ground state of the ion when the second photon is absorbed rather than emitted.[3] As selection rules are less stringent for ionization and charged particle detection is more sensitive than photon detection, considerable insight into the photodissociation dynamics can be obtained, as shown for several alkyl iodides.[3−6] In those experiments, the molecules are excited into the dissociative A-state band by absorption of the first photon. In the second absorption step the molecules are further excited into very high-lying Rydberg states converging onto the vibrational states of the ion. After field ionization of these states,[7] a high-resolution zero kinetic energy photoelectron (ZEKE) spectrum[8] of the ion is obtained. The wave function of a continuum state has considerable Franck−Condon overlap with a large number of ionic states. Thus the two-photon ionization spectra of CH_3I,[3−5] CD_3I,[5] and C_2H_5I[6] show large and intense progressions that are absent in the one-photon ZEKE-[4] and photoelectron[9,10] spectra. The progressions can be attributed to modes that are involved in the dissociation process.

The effect of a dissociative intermediate resonance modulating electronic spectra was reported already a decade ago.[11] Interest in the technique renewed because important spectroscopic information on regions of the potential energy surface inaccessible directly from the ground state can be obtained this way, as shown, for example, in the Rydberg states of Cl_2,[11] I_2,[12] HI,[13] and CH_3I.[14]

From our prospective, the most interesting feature of two-photon ionization through dissociative states is the possibility to obtain information on the dissociation dynamics in the intermediate state. This, however, requires the extraction of reliable line intensities from the spectra, which have to reflect the intermediate state dynamics. In a recent paper by Abrashkevich and Shapiro,[15] (from hereon referred to as AS) a theory of two-photon ionization via a dissociative intermediate state was developed and applied to the one-color two-photon ZEKE spectrum of CH_3I.[5] Interestingly the calculated line intensities differ drastically from the experimental values obtained by Strobel *et al*.[5] The experimental spectrum is dominated by an intense progression in the C−I stretching vibration ν_3, which peaks at the third overtone, 3^4. In comparison, in the resonance Raman spectra recorded at an excitation wavelength of 266 nm (ref 2) the progression is peaked at 3^2. On the other hand, in the calculations, a progression in ν_3 contributes only to a minor degree to the spectrum, which is instead dominated by combination bands of ν_3 and the CH_3 umbrella mode, ν_2. In addition, AS also calculated most of the intensity for the origin band, whereas in the ZEKE experiments the third overtone appeared with almost the same intensity. To account for the differences, it was suggested that the line intensities in the ZEKE spectra depend on the concentration of external ions, and ionic correction factors were introduced. It can indeed be shown that external ions affect the intensities in ZEKE spectra,[16,17] by inducing m_l-mixing in high-lying Rydberg states, leading to a lifetime enhancement. Nevertheless it would be surprising if that effect should introduce mode-specific order-of-magnitude effects in the ZEKE spectra of CH_3I.

In order to test the hypothesis, an experiment has to be performed which excludes the influence of Rydberg states. Such an experiment is possible if kinetic electrons are detected instead of ZEKE electrons. In the next sections we report the one-color two-photon photoelectron spectrum of methyl iodide, CH_3I. As in the ZEKE experiments, absorption of the first photon excites the molecule into a dissociative state. The second photon of the same frequency ionizes the molecule, and a photoelectron spectrum is recorded, which shows significant vibrational structure. We discuss the relevance of the photoelectron spectra with respect to the difference between the experimental and the calculated two-photon spectra. Although the experiment was originally motivated by those differences, we feel that it is interesting in its own right. It describes an independent and particularly simple experimental approach to the problem of photodissociation dynamics, also based on two-

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photon ionization, which complements ZEKE spectroscopy as well as resonance Raman spectroscopy.

Experimental Section

The experiments were carried out in a magnetic bottle time-of-flight photoelectron spectrometer described previously.[18,19] In this technique an inhomogeneous magnetic field is applied to collect and collimate the electrons. A collection efficiency of >30% is achieved this way. Typically an energy resolution of 15 meV can be obtained for low-energy electrons. Methyl iodide, CH_3I, was purchased from Aldrich and used without further purification. It was diffused into the ionization chamber through a small orifice. Typical pressures during operation were on the order of several 10^{-5} Torr in the ionization region and around 10^{-6} Torr in the flight tube.

The laser system employed was a 10 Hz picosecond ($t = 2.5$ ps) Ti:sapphire laser with a tuning range from 750−840 nm, regeneratively amplified to a millijoule energy level. The details of the setup are published elsewhere.[20] The output was frequency doubled and mixed in KDP crystals to produce radiation with a wavelength close to 250 nm. In order to minimize intensity effects, the energy was attenuated to a few microjoules. The light was focused into the ionization region by means of a 500 mm lens. The wavelength was determined in a Jarrell-Ash 0.25 m monochromator. Its accuracy for the third harmonic is estimated to be ±0.3 nm. Although a short-pulse laser was used in the studies described in this paper, we want to point out that the experiment itself is a pure frequency-domain experiment.

Electrons were collected in a microchannel plate detector for 2000 shots. The data were acquired and averaged in a LeCroy 9450 digital storage scope and transferred to a personal computer. Typical count rates were on the order of 5−10 electrons per shot.

Time-of-flight spectroscopy is linear in time rather than energy. When the spectra were converted to linear-in-energy it was ensured that the area under the peaks is maintained by using the appropriate Jacobians in the transformation.

Results and Discussion

Before we discuss the experimental results we want to point out an important difference between the conventional photoelectron spectra and ZEKE spectra. In a photoelectron spectrum, the excitation energy is fixed and all energetically accessible final ionic states are recorded for this fixed energy. In a ZEKE spectrum, on the other hand, the laser is scanned over all final states. Therefore in the one-color ZEKE experiment discussed in ref 5, the excitation energy is scanned at the same time as the probe energy. Thus the absorption cross section for the first step is continously changing. This is the reason why a comparison between ZEKE and photoelectron spectra has to be restricted to a qualitative rather than a quantitative discussion. On the other hand, this also shows that additional information can be obtained from photoelectron spectra that is not available from one-color ZEKE spectra. It would be possible, however, to get this information from a two-color ZEKE spectrum, in which both lasers are scanned independently.

It is important to establish that the photoelectron spectrum presented below is indeed the one of methyl iodide. This was done by recording mass spectra in our magnetic bottle spectrometer, which is possible with low mass resolution ($m/e \approx 80$) and sensitivity. The focusing conditions were adjusted in such a way that the molecular ion CH_3I^+ dominates the mass spectrum and fragmentation was minimized.

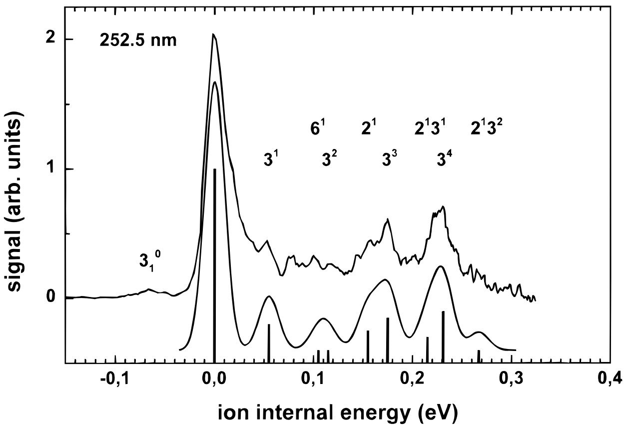

Figure 1. Two-photon photoelectron spectrum of CH_3I, recorded at 252.5 nm. The upper trace shows the experimental spectrum while the lower trace shows a simulation. The values for the intensity I_0 of the different contributions are represented as sticks. The spectrum is dominated by a progression in ν_3, the C−I stretching vibration.

The upper trace of Figure 1 shows the two-photon photoelectron spectrum of CH_3I, recorded at 252.5 nm. Besides an intense 0−0 transition, it shows a rich vibrational structure. In order to check if we identified the important contributions to the spectrum, a simulation was performed (lower trace). The energies of the vibrational states of the ion are known.[5] All relevant transitions were assigned an intensity I_0 and folded with a Gaussian. Then I_0 was varied to achieve optimum agreement with the experimental spectrum. The optimized I_0 values are given as sticks in Figure 1. In principle the spectral resolution depends on the total kinetic energy of the electron. An accurate expression can be found in ref 18. For simplicity we assumed a constant fwhm. A comparison with ref 18 shows that this assumption is reasonable for the energy range ($E_{kin} < 300$ meV) studied here. It turned out that the experimental data could be fitted well with a fwhm of 15 meV. A progression in ν_3, the C−I stretching vibration with a frequency of 478 cm^{-1} (ref 5), is evident. In the simulations it can be identified as the most important mode. Interestingly the intensity of the members of the progression is rising with the vibrational quantum number, maximizing at 3^4. This peak corresponds to an electron kinetic energy of 50 meV, which is close to the detection limit in our spectrometer. The fundamental of ν_2, the CH_3 umbrella mode also shows up in the spectrum. Only if it was included in the simulation could the shape of the band around 160 meV internal energy be reproduced. The lowest combination bands, 2^13^1 and 2^13^2 appear in the shoulders of the 3^4 band. Although the shape of the band could not be fitted without taking the combination bands into account, they are smaller than 3^4, which is also the peak dominating the ZEKE spectrum of Strobel et al.[3,5] So, despite the differences between ZEKE and PES-spectra discussed above, the PES spectrum agrees qualitatively well with the experimental ZEKE spectrum. In conclusion, the simulation shows that taking into account only the ν_3 progression, the fundamentals of ν_2 and ν_6, and the $\nu_2\nu_3$ combination bands, one can reproduce the spectrum very well.

We also identified a ν_3 hot band around −60 meV internal energy. The small size of this band indicates that hot band contributions are of minor importance in the present experiment.

Another interesting peak is the fundamental of ν_6, 6^1, at 106 meV. It appears only with a small intensity but is reproducible. This peak, which correspond to the H_3−C−I bending vibration, was already observed in the ZEKE spectrum. Excitation of this vibration is introduced by the coupling of the $^1Q_1$ and $^3Q_0$ surfaces in the intermediate state[21] and is probably responsible for the unusual distribution of rotational excitation observed in photodissociation experiments.[22] The coupling leads to a

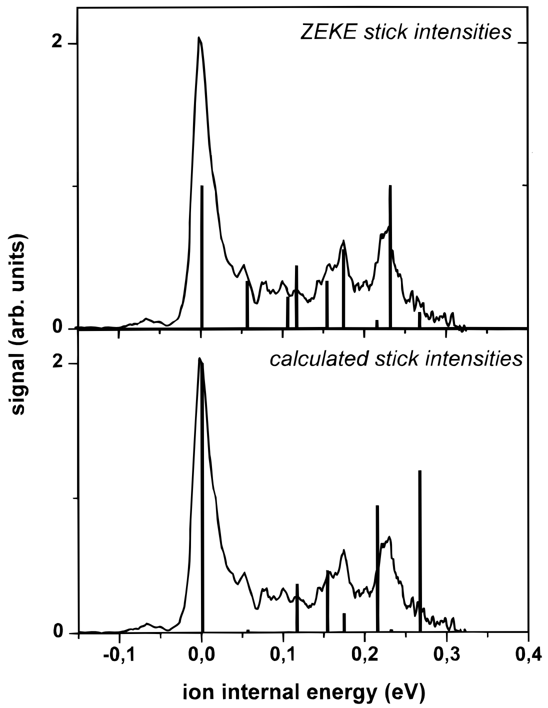

Figure 2. comparison of the photoelectron spectrum from Figure 1 with the stick intensities extracted from the experimental ZEKE spectrum (upper trace, divided by a factor of 2, see text for details) and the calculations (lower trace).

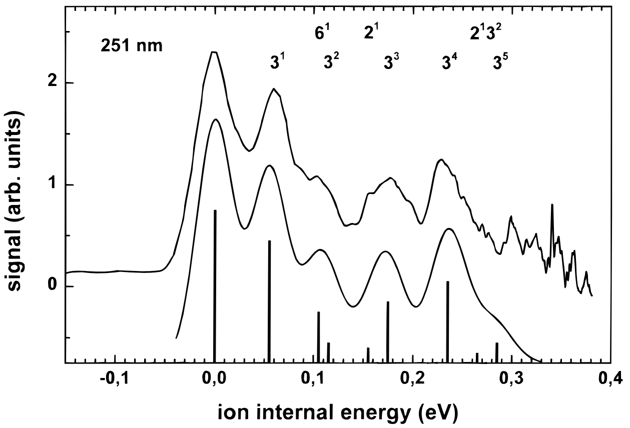

Figure 3. Two-photon photoelectron spectrum of CH_3I, recorded at 251 nm. Due to the inferior resolution and signal-to-noise ratio, the assignments of the bands at the low-energy side have to be considered with care. A simulation of the spectrum is given in the lower trace. The appearance of the spectrum compared with the one recorded at 252.5 nm is surprisingly different, showing how small changes in the intermediate state potential can affect the spectrum.

symmetry reduction in the intermediate state,[23] thus allowing this non-totally symmetric vibration to appear in the spectrum. The observation of this mode in the PES spectrum highlights again how dynamical features of the photodissociation process that are apparent in ionization can be absent in emission, although the reason for the absence of ν_6 in the emission spectra is not clear yet. It also confirms that the appearance of this mode in the ZEKE spectrum is not due to effects in the Rydberg state but reflects true molecular dynamics.

A comparison of the spectrum with the band intensities extracted from the ZEKE-spectrum and from the calculations by AS is given in Figure 2. When compared to the origin band, the intensities for the bands in the progression are consistently larger in the ZEKE spectrum than in the photoelectron spectrum. However, if the ZEKE intensities are divided by a factor of 2 the relative intensities of the bands in the progression are fitted very well (Figure 2, upper trace). An explanation for this factor of 2 is given below. A comparison of the photoelectron spectrum with the band intensities calculated by AS for a laser pulse duration of 1 ps is given in the lower trace of Figure 2. A reasonable fit could be achieved if the intensities calculated for the combination bands would simply be assigned to the ν_3 progression. Therefore labels are omitted in the figure. This issue is also discussed below.

In order to observe as much vibrational excitation as possible we moved the laser wavelength to 251 nm, which is the blue limit of the laser system. The spectrum recorded under these conditions is depicted in Figure 3. Again a simulation of the spectrum is given in the lower trace, this time assuming a fwhm of 18 meV. The optimized I_0 values are shown as sticks. Due to the inferior resolution and signal-to-noise ratio the bands overlap considerably, and the assignments for the low-energy bands have to be considered with care. The overall appearance of the spectrum differs from the one recorded at 252.5 nm. Most notably the fundamental, 3^1, is the most intense member of the progression and shows up with almost the same intensity as the origin band. The overtones 3^3 and 3^4, on the other hand, appear with similar intensity, like in the spectrum recorded at 252.5 nm.

In the following section we will discuss several issues that are relevant for the qualitative comparison between the ZEKE and the PES results. A difference between the ZEKE experiments and the photoelectron spectra described here lies in the bandwidth of the laser system employed. While the ZEKE spectra were recorded with narrow-band nanosecond lasers, the photoelectron spectra were recorded with a picosecond laser with a bandwidth on the order of 20 cm^{-1} fwhm, so an influence of pulse duration or bandwidth is conceivable. The calculations of AS were performed for both the cw case and a pulse duration ranging from $\tau = 10$ fs to 1 ps. The calculations showed that for a pulse duration of more than 50 fs the ionization probability hardly changes, indicating that neither the duration nor the bandwidth of the pulse is expected to have a large effect on the experimental results.

Short-pulse experiments are inherently high-intensity experiments. The typical laser intensities in the present experiment are estimated to be 10^{10} W cm^{-2}. Thus a Rabi period of several 100 fs can be estimated, which is not too different from the time scale of dissociation (<50 fs) in the intermediate state of CH_3I. In order to check for intensity effects, the laser intensity at 252.5 nm was increased over an order of magnitude. This lead to a poorer energy resolution, probably due to Coulomb effects. It was also observed that the relative intensity of the origin transition was slightly higher. This can be understood by assuming a competition between a resonant and a nonresonant pathway, as discussed in ref 6. The nonresonant pathway, *i.e.* simultaneous rather than sequential two-photon absorption, will contribute only to the origin band. It is also favored at higher laser intensities. We want to point out that this is different from saturation, which would tend to equalize vibronic band intensities at high laser intensities. This effect also explains why the origin band is more intense relative to the progression in the PES spectrum than in both the ZEKE[3,5] and REMPI[14] spectra. However, the overall appearance of the spectrum, *i.e.* the relative intensities of the spectral features in the progression, did not change with intensity. Therefore we assume that intensity effects are only of minor importance. The fact that the relative intensities of the bands in the progression do not change with the laser intensity also means that dynamical information can be extracted from them.

In conclusion the dominance of the ν_3 progression instead of the $\nu_2\nu_3$ combination bands in the photoelectron spectra does not support the idea of extra ions influencing Rydberg state lifetimes and thus ZEKE intensities. We therefore have to consider other explanations to account for the discrepancy between the calculated and measured ZEKE spectra. First of all one has to consider that the band assignements given in the calculations are somewhat tentative[24] due to the anharmonic character of the potential energy surface.[25] If one simply assigns the intensities calculated for the combination bands (Figure 2, lower trace) to the corresponding members of the ν_3 progression, the agreement between the experimental and the calculated spectra is much better. Another plausible explanation comes from the fairly large difference between the photoelectron spectra recorded at 252.5 and 251 nm. It demonstrates that even small differences in the intermediate state potential can have an impact on the appearance of the spectrum. Interestingly this difference is most pronounced in the 3^1, whose intensity is significantly underestimated by the calculations. Most of our understanding of the excited states of methyl iodide is based on the resonance Raman spectra recorded at an excitation wavelength of 266 nm. At this energy only two excited states, $^3Q_0$ and $^1Q_1$, are of major importance. At the excitation energies employed in the ionization experiments other states might show a non-negligible coupling with those two states, thus altering the appearance of the spectrum.

To account for small differences in the potential energy surface by calculation is particularly difficult in the case of a ZEKE experiment, where the continuous change in wavelength has to be considered. A calculation of the photoelectron spectrum presented here should be simpler and would clearly be helpful to resolve this issue. In fact, we see it as the great advantage of conventional photoelectron spectroscopy compared to the ZEKE method that it is a fixed-frequency experiment, facilitating a comparison with theory.

Another possible explanation might be the use of an inadequate potential for the ionic state in the calculations. In fact, no reliable data for the ionic equilibrium bond lengths are available either from experiment or from *ab initio* calculations. In this context, a related experiment is of interest in which the 6s Rydberg state of CH_3I was probed by [1+1′+1] REMPI.[14] The first photon, scanned from 254 to 273 nm, was resonant with the dissociative continuum. The spectra showed a strong ν_3 progression in the Rydberg state as well as a number of $\nu_2\nu_3$ combination bands. The lower members of the ν_3 progression appear with an intensity similar to that of the origin band. The combination bands appear with lower intensity than the ν_3 bands. They are, however, more prominent than in the two-photon ZEKE spectrum. The pump wavelength range in the REMPI spectra was very similar to the range in the ZEKE spectra of Strobel *et al*.[5] This suggests that an accurate description of the final state on which the intermediate state dynamics is projected is critical. Nevertheless it is noteworthy that the [1+1′+1] spectra of CH_3I also show a progression in ν_3 as the dominant feature and are thus in agreement with both the results presented here and in the publications by Strobel *et al*.[3,5]

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References and Notes

(1) Schinke, R. *Photodissociation dynamics;* Cambridge University Press: Cambridge, 1993.

(2) Imre, D.; Kinsey, J. L.; Sinha, A; Krenos, J. J. *J. Phys. Chem.* **1984,** *88*, 3956.

(3) Strobel, A; Lochschmidt, A; Fischer, I; Niedner-Schatteburg, G.; Bondybey, V. E. *J. Chem. Phys.* **1993,** *99,* 733.

(4) Zhu, Y. F.; Grant, E. R. *J. Phys. Chem.* **1993,** *97,* 9582.

(5) Strobel, A; Fischer, I.; Lochschmidt, A.; Müller-Dethlefs, K.; Bondybey, V. E. *J. Phys. Chem.* **1994,** *98,* 2024.

(6) Knoblauch, N.; Strobel, A.; Fischer, I.; Bondybey, V. E. *J. Chem. Phys.* **1995**, *103,* 5417.

(7) Reiser, G.; Habenicht, W.; Müller-Dethlefs, K.; Schlag, E. W. *Chem. Phys. Lett.* **1988,** *152,* 119.

(8) Müller-Dethlefs, K; Schlag E. W. *Annu. Rev. Phys. Chem.* **1991,** *42,* 109.

(9) Karlsson, L; Jadrny, R.; Mattsson, L.; Tim Chau, F.; Siegbahn, K. *Phys. Scr.* **1977,** *16,* 225.

(10) Rosenstock, H. M.; Buff, R.; Ferreira, M. A. A.; Lias, S. G.; Parr, A. C.; Stockbauer, R. L.; Holmes, J. L. *J. Am. Chem. Soc.* **1982,** *104,* 2337.

(11) Li, L.; Lipert, R. J.; Park, H.; Chupka, W. A.; Colson, S. D. *J. Chem. Phys.* **1987,** *87,* 6767.

(12) Donovan, R. J.; Lawley, K. P.; Min, Z.; Ridley, T.; Yarwood, A. J. *Chem. Phys. Lett.* **1994,** *226,* 525.

(13) Young, M. A. *J. Phys. Chem.* **1993,** *97,* 13508.

(14) Min, Z.; Ridley, T.; Lawley, K. P.; Donovan, R. J. *J. Photochem. Photobiol.* **1996,** *A100,* 9.

(15) Abrashkevich, D. G.; Shapiro, M. *J. Chem. Phys.* **1996,** *105,* 9493.

(16) Chupka, W. A. *J. Chem. Phys.* **1993,** *99,* 5800.

(17) see *e.g.* Merkt, F. *J. Chem. Phys.* **1994,** *100,* 2623. Vrakking, M. J. J.; Fischer, I.; Villeneuve, D. M.; Stolow, A. *J. Chem. Phys.* **1995,** *103,* 4538 and references therein.

(18) Kruit, P.; Read, F. H. *J. Phys. E: Sci. Instrum.* **1983,** *16,* 313.

(19) Minsek, D. W.; Chen, P. *J. Phys. Chem.* **1990,** *94,* 8399.

(20) Fischer, I.; Schultz, T. *Appl. Phys. B* **1997,** *64,* 15.

(21) Guo, H. *J. Chem. Phys.* **1992,** *96,* 6629.

(22) Ogorzalek Loo, R.; Haerri, H.-P.; Hall, G. E.; Houston, P. L. *J. Chem. Phys.* **1989,** *90,* 4222.

(23) Amatatsu, Y.; Morokuma, K.; Yabushita, S. *J. Chem. Phys.* **1991,** *94,* 4858.

(24) M. Shapiro, private communication.

(25) Shapiro, M. *J. Phys. Chem.* **1986**, *90*, 3644.