Switching the vibrational excitation of a polyatomic ion in multi-photon strong field ionization

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The multiphoton ionization (MPI) of CH₃I has been investigated by angular resolved photoelectron spectroscopy as a function of femtosecond laser excitation intensity. A sudden change in the electron kinetic energy is observed above a specific field strength. The multiphoton excitation at a fixed wavelength of 800 nm becomes vibronically resonant due to Stark shifting of intermediate Rydberg state levels. The present letter gives an experimental evidence for ultrafast optical control of the vibrational excitation in a polyatomic ion by adjusting the intensity of a femtosecond laser pulse.

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1. Introduction

Stark field control of dissociative photochemical processes has been successfully demonstrated [1,2]. Also in high-intensity multiphoton interaction with molecules [3] Stark shifting is a prevalent effect. Measuring the kinetic energy of the emitted electrons and the recoil ions usually meet the demands for investigating a majority of the underlying phenomena. In MPI experiments with high-intensity laser fields, Stark shifting of excited states (e.g. Rydberg states) has been observed in different atomic systems, e.g. Xe [4,5], H [6], Ar [7], and Kr [8]. For molecules, the available excess energy can additionally transfer into rotvibrational excitation of the ion. These additional degrees of freedom complicate the interpretation of electron energy measurements in MPI, substantially [9]. Upon ionization from high lying Rydberg states the vibrational excitation are typically conserved. The nearly parallel potential energy curves of ion and Rydberg states favor transitions with minor vibrational changes. As consequence, the vibrational levels of accidentally populated intermediate Rydberg state in MPI mainly determine the final vibrational excitation of the ion. For molecular hydrogen, a selective vibrational excitation of the H₂⁺ ions due to Stark shifting into specific resonances has been observed [10–12]. This effect however, provides a general tool to control the ultrafast excitation of specific vibrations in molecular ions [12]. Despite of the numerous works (e.g. [13–16]) reported on MPI of polyatomic molecules, investigation of vibrational excitation via Stark shifting are rare and mainly focus on small diatomic molecules [10–12,17–19].

2. Experimental setup

We investigated the intensity dependent ultrafast MPI of the polyatomic CH₃I molecule by photoelectron imaging spectroscopy. The experiments were performed with a home-built double-sided velocity map imaging setup [20]. Briefly, it consists of two time-of-flight (TOF) mass spectrometers, each equipped with a position sensitive detector. The two spectrometers share the same interaction region where a molecular beam is produced by seeding CH₃I (Sigma Aldrich, 99.0% purity) in helium buffer gas (1.5 atm) through a miniature valve (Fa. Gyger) pulsed at a rate of 400 Hz. The near infrared output (at ∼800 nm) of a femtosecond laser system (Clark-MXR CPA-1000) with pulse duration of ∼100 fs was used for MPI of CH₃I.

The beam was focused into the molecular beam chamber by a f = 40 cm lens. The intensity is controlled by adjusting a continuously variable neutral density filter and measured with a power meter. All other optical elements were kept unaltered. The pulse energies measured after the focusing lens, were between 48 μJ and 160 μJ with a 5% uncertainty. Assuming Gaussian beams, the waist in the focal region is approximately 100 μm², which corresponds to intensities between 0.48 and 1.6 × 10¹³ W/cm².

The ions and electrons generated were extracted and accelerated in two opposite directions and imaged [21] onto the detectors, composed with a microchannel plate (MCP)/phosphor screen and a CCD camera.
3. Results and discussion

Photoelectron images (PEI) were acquired at femtosecond laser pulse intensities ranging from $0.48 \times 10^{13}$ to $1.6 \times 10^{13}$ W/cm$^2$ at the intercept with the molecular beam. Two distinct ionization regions are commonly discriminated according to the applied laser intensities at a given wavelength, – the MPI regime for weak electric fields and the tunneling ionization regime at strong fields [12]. The continuous transition from one to the other regime is generally described by the Keldysh adiabaticity parameter $\gamma_K$. The Keldysh parameter [22] can be defined by the square root of the ratio between the ionization energy ($I_p$) and twice the ponderomotive energy $\gamma_K = \sqrt{l_p/2U_p}$ with $U_p = (e^2/(2\epsilon_0 cm_e))(l/\omega^2)$, $l$ is the laser intensity, $m_e$ the electron mass, $e$ the elementary electric charge, $\epsilon_0$ the dielectric constant, $c$ the speed of light and $\omega$ the laser frequency. Tunnel ionization dominates when $\gamma_K < 1$ while for $\gamma_K > 1$ a perturbative approach is thus adequate to describe the m-photon ionization. Our current measurements are in the multiphoton regime with $\gamma_K$ varying from 4.2 to 2. However, the definition of $\gamma_K$ takes no consideration of the actual shape of the potential surfaces. For molecules with extended molecular orbitals, field ionization can occur already at $\gamma_K > 1$, i.e. at relatively low laser intensities. Moreover, accidental resonances due to Stark shifts can enhance the ionization from particular vibrations if specific intermediate states are in resonance with an integer number of the applied photons.

Angular resolved photoelectron spectra are recorded by velocity space imaging as a function of laser pulse energy. Figure 1 shows PEI reconstructed by the basis-set expansion method (BASEX) [23] corresponding to intensities between $0.48$ and $1.60 \times 10^{13}$ W/cm$^2$.

The different photoelectron velocities appear at rings with different radii. As shown in Figure 1, two well-resolved concentric rings are observed in the images related to intensities below $0.8 \times 10^{13}$ W/cm$^2$. With increasing intensity, the contribution of these two rings decreases and at intensities between 0.8 and $1.1 \times 10^{13}$ W/cm$^2$ a new ring arises. This new component then becomes the dominant contribution to the electron image at even higher intensities. The photoelectron kinetic energy (PKE) distributions (as shown in Figure 2) can be inferred from the PEI. For ease of comparison, all PKE distributions are normalized to the strongest signal for all individual pump laser intensities.

According to the CH$_3$I ionization energy of $E_{ion} = 9.54$ eV [24], MPI can be achieved by seven- (or more) photons absorption at $~800$ nm. The black arrow in Figure 2 at 1.31 eV indicates the maximum possible electron energy after the seven-photon ionization. For short pulse and strong field MPI, the involved states reasonably shift in their intrinsic energy. In strong field approximation $\gamma_K < 1$, the AC Stark shifts of Rydberg and continuum states are in the order of the electron ponderomotive energy [25]. The induced Stark shifts of the lowest bound states tend to be smaller in magnitude and thus the effective ionization potential becomes intensity dependent $E_{ion}(I) = E_{ion} + \alpha I$. Accordingly, with increasing intensity the external laser field causes a down shift of the observed electron kinetic energies $E_{kin} = n\hbar\nu_0 - E_{ion} - E_{int}$ in short pulse m-photon MPI. $E_{int}$ denotes the ro-vibrational internal excitation energy of the ion.

At low-range intensities ($<0.80 \times 10^{13}$ W/cm$^2$), our measurements result in two well resolved energy components in the PKE, which are peaked at 0.47 and 1.15 eV (Figure 2a). The energy
The difference between these components is 0.68 eV, what is in good agreement with the energy gap of 0.63 eV between the two \( \tilde{X}E \) spin–orbit states of CH3I* [26]. The apparent peaks at 0.47 eV and 1.15 eV are attributed to the ionic \( \tilde{X}E_{1/2} \) and \( \tilde{X}E_{3/2} \) states, respectively. In CH3I, the \( \tilde{X} \) electronic ground state of neutral CH3I has a \( (1\epsilon)^2 (3\alpha_1)^2 (2\epsilon)^4 \) electron configuration. The final \( \tilde{X}E \) spin–orbit states are produced by the removal of one of the \( 2\epsilon \) electrons. In fact, the emitted electron stems from localized \( 5p_x \) or \( 5p_y \) iodine nonbonding orbitals [27].

As visible in the PKE of Figure 2a \( (I<0.80 \times 10^{13} \text{ W/cm}^2) \) both spin–orbit components broaden and slightly shift to lower energies with increasing laser pulse intensity. The slope of this gradual shift is \( \sim 0.035 \times 10^{-12} \text{ eV/(W/cm}^2) \). At middle-range intensities \( (0.85–1.10 \times 10^{13} \text{ W/cm}^2) \), the intensity of the two \( \tilde{X}E \) related PKE components decreases abruptly while a new peak appears (Figure 2b). At the high-range intensities \( (>1.1 \times 10^{13} \text{ W/cm}^2) \) the new component at 0.78 eV outshines the PKE distribution (Figure 2c). Above the intensity of \( 1.1 \times 10^{13} \text{ W/cm}^2 \) the PKE depicts again a slight down shift, with a gradient comparable to what has been observed in the ‘low’ intensity range. A 2D plot of the photoelectron energy distributions as a function of intensity (Figure 3) visualizes the step-like switch from the \( \tilde{X}E_{3/2} \) related component to a ‘new’ component. The associated energy for the observed step is 0.37 eV which corresponds to \( \sim 3000 \text{ cm}^{-1} \). Photo-excitation of CH3I is commonly described by the \( A, B, C \) and \( D \) absorption bands [28]. A rather weak three-photon \( 5\pi \pi \rightarrow \sigma^* \) transition to the CH3I A-band results in a prompt dissociation, producing CH3 and I fragments on a 100 fs time scale [29]. However, the simultaneous detection of TOF mass spectra at the different intensities demonstrate, that even at the highest intensities only spurious amounts of fragment ions have been observed (Figure 4). The signal ratios of CH3+/CH3I and I+/CH3I are below 5% \( (0.044 \text{ and } 0.027, \text{ respectively}) \). However, dissociation from the \( A \)-band excited states can cause a signal drop, but essentially has no influence on the qualitative analysis of our observation. Hence we neglect the overall contributions to the photoelectron signal from ion fragmentation and dissociation products in the data evaluation. Disregarding the unstructured \( A \)-band absorption, the CH3I Rydberg-states commonly grouped to the \( B, C \) and \( D \) bands are possibly reached by four or five 800 nm photon absorption processes, and thus determine the final ion state, due to the specific intermediate vibronic resonances. The \( B- \) and \( C \)-band transitions involve Rydberg states that are produced by transition of a \( 5\pi \) electron to a \( \sigma \)-type orbital. The remaining three \( 5\pi \) electrons are subject to strong spin–orbit coupling. The spin coupling between the 6s Rydberg electron and the ionic core yields four electronic states, from which two have a \( 2E_{3/2} \) and two have a \( 2E_{1/2} \) ion core [30]. The ensemble of states that is produced by promotion of a \( 5\pi \) electron to the 6p orbital is typically merged to the \( D \)-band.
To give an approximate overview, wavenumber positions of a series of CH$_3$I $^2$E$^+$-Rydberg transitions together with a few vibronic excitations that are in the vicinity of the laser excitation (data from Refs. [23,26,27]).

At ‘low’ intensities one PKE peak is observed at 1.15 eV (Figure 2), which is 1285 cm$^{-1}$ above the expected $^2$E$_{3/2}$ ionization threshold. Neglecting any shifts at such intensities, the internal ion energy approximately matches the energy of the (2$^1$P$^o$) or the (3$^1$D$^o$) vibration modes of the cation [30,31,34]. The second PKE peak was measured 1688 cm$^{-1}$ above the $^3$E$_{1/2}$ cation ground state, which is energetically close to the excitation of one quanta of $v_4$. Effective excitation of $^2$E$_{3/2}$($^1$S) via the 6s(6p)$^2$E$_{3/2}$(0$^0$) Rydberg state has been observed before [30]. Since the ion ground state and the Rydberg-states converging to it have a rather similar geometry, we assume that an unaltered vibronic excitation upon the eventual removal of the Rydberg electron [30] in MPI is preferred. Therefore strong transitions to the ion states are expected from similar vibronic excitations in the intermediate Rydberg states. Following this argumentation and the former energy considerations, we infer for low intensities, $\tilde{X}^2E_{3/2}^+(3^1D_2$ or 2$^1$S) $\rightarrow$ 6p$^2$E$_{3/2}$(0$^0$) $\rightarrow$ X$^1$A$^1$(0$^0$) and the $\tilde{X}^2E_{1/2}^+(1^1S)$ $\rightarrow$ 6p$^2$E$_{1/2}$(0$^0$) $\rightarrow$ X$^1$A$^1$(0$^0$) excitation pathways. The beneficial Frank Condon overlap to the final $\tilde{X}^2E_{3/2}^+$(1$^{11}$D$^2$) ion state yields an increased signal. The energy of the $\tilde{X}^2E_{3/2}^+(1^1S$) state is $\sim$3000 cm$^{-1}$ (0.37 eV) higher compared to the $\tilde{X}^2E_{3/2}^+(3^1D_2$ or $^2^2E_{1/2}^+(2^1S$) states at populated low intensities and as consequence the kinetic energy of the measured electrons downshift accordingly. The observed ‘switch’ in the PKE matches well with the addition of one quanta of $v_1$ in the cation state. However, due to the complexity of the molecular system an ab initio theory for MPI considering all accidentally resonances under strong field conditions is not readily available and the symmetry selection rules hardly impose any restrictions on the photoionization transitions [27]. Nevertheless additional information is preserved from the angular distribution of the detected photoelectrons. The angular distributions are derived from the images by fitting the LIN-BASEX result [35] to an expansion in Legendre polynomials. In the laboratory frame, PADS resulting from seven-photon ionization with linear and parallel polarized pump and probe laser beams can be described by [36]:

\[ I(\theta) \propto \sum_{k=0}^{7} \beta_{2k} P_{2k}(\cos \theta) \]  

(1)

where $\beta_{2k}$ are the anisotropy parameters, $P_{2k}(\cos \theta)$ are Legendre polynomials of rank 2k, and $\theta$ is the angle between the laser polarization direction and the direction of the ejected electron. The fitted anisotropy coefficients (Table 1) are obtained with the LIN-BASEX algorithm [35]. $\beta_2$ is between $-1 \leq \beta_2 \leq 2$ and for a single photon transition $\beta_{-2}=0$. $\beta_2 = 2$ relates to transitions with maximum intensity along the polarization axis while $\beta_2 = -1$ corresponds to perpendicular transitions. $\beta_2 = 0$ reflects an isotropic electron
distribution. Multiphoton transitions successively contribute also to the higher order Legendre polynomials in Eq. (1).

Signals arising from ionization of orbital electrons with similar bonding character are expected to show similarities in the β-values [37]. The PAD’s correlated to the two $\tilde{X}^2E$ spin–orbit states of $\text{CH}_3^+$ significantly differ in their β-values (Table 1) already at the lowest applied intensities. For all $2k\beta_{2k}(E_{1/2}) > \beta_{2k}(E_{1/2})$ has been determined. In particular βy differs by ~10%, while the βy-10-values considerably change by factors of 2–5. The electron configuration of resonant intermediate Rydberg states in MPI has a strong influence on the PAD of the detected electrons. A strong sensitivity for alignment has been observed in the ionization of high lying p-Rydberg states [38]. However, the most striking difference between the low intensity PAD’s is a perpendicular contribution appearing in the $E_{1/2}$ case (Figure 6b), which is not visible for the $E_{1/2}$ component (Figure 6a). The PAD of the ‘new’ appearing high intensity contribution is similar to the $\tilde{X}^2E_1$ component at low intensities, which strongly supports the assumption that these PKE contributions relate to the same electronic state. Care has to be taken by interpretation of anisotropy values upon changing the intensity, since molecules tend to align during the short pulse strong field interaction [39]. The degree of the intensity dependent alignment ($\cos^2\theta$) depends on the rotational temperature and the difference in polarizabilities perpendicular and parallel to the molecular axis. Because $\cos^2\theta$ is expressible in terms of a linear combination of $P_0(\cos\theta)$ and $P_2(\cos\theta)$, the laser induced alignment cannot be disentangled by fitting Legendre polynomials to the PAD’s. Thus alignment signatures are expected to contribute to the PAD’s with increasing intensity. The measured PADs, e.g. concentrate more along the direction of the laser polarization at higher intensities. In our experiments no other significant intensity–dependent features in the PAD’s have been observed by looking at each component separately. It can be seen from Figure 6 and Table 1 that the PAD shape and the β-values of the new component (c) are similar to the second component (b) and considerably different to component (a). We infer that the similarity between (b) and (c) is due to an ionization process that consigns a common final $\tilde{X}^2E_1$/2 ion state. Minor differences between (b) and (c) contribution (Figure 6) are most probably due to the different vibrational excitation. In principle also an 8-photon ionization to the next electronically $\tilde{A}^2A_1$ ion state (onset at ~12.13 eV) with increasing intensity could occur, causing a new contribution in the PKE. Considering the higher order process as being less effective, we do not expect it as dominating contribution in the PE spectrum. In addition, the highly energetic $\tilde{A}^2A_1$ cation state correlates to the removal of a $3\alpha_2^+$ electron from the $\sigma(C-I)$ bonding orbital. As such, the involved transitions differ from the previously discussed 7-photon ionization and one would expect a significant change in the PAD shapes if the new PKE component would be related to this cation state. Thus we interpret the observed switch that is observed in the measured PKE distribution as modification of the vibrational excitation in the $\tilde{X}^2E_1$/2 ion state.

In this letter we have solely concentrated on the power-dependence of the observed photoelectron spectra in one-color multi-photon ionization of a polyatomic molecule. Additional information on intermediate resonances and fragmentation behavior can be expected by complementary wavelength dependent measurements [13].

4. Conclusion

In conclusion, the MPI of $\text{CH}_3I$ induced by ultrafast femtosecond pulse has been investigated by intensity-dependent photoelectron imaging spectroscopy. Intensity-dependent PKE and angular distributions are obtained. Two energy components, corresponding to the two strong spin–orbit coupling ground states of the $\text{CH}_3^+$ ions, $\tilde{X}^2E_1$ and $\tilde{X}^2E_1$, are observed at low range intensities. With increasing intensity, an energy shift ($\Delta E \approx -0.37\text{eV}$) of the second component is clearly discernible. This step-like shift appears at a threshold-intensity and energetically corresponds to the excitation of one additional quanta of the C–H stretching vibration ($v_1$) in the $\tilde{X}^2E_1$ state. The appearance and dominance of this new peak has been interpret by Stark shifted intermediate levels. Due to intermediate resonances the residual vibrational excitation in the ion state could be efficiently changed by intensity adjusted femtosecond laser pulses in MPI. The method offers a possibility for an optical control of the vibrational excitation of polyatomic ions without the application of phase control methods or time delayed pulse sequences.

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References