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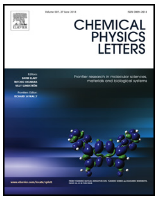

Switching the vibrational excitation of a polyatomic ion in multi-photon strong field ionization

Yuzhu Liu, Thomas Gerber, Peter Radi, Yaroslav Sych, Gregor Knopp*

Paul Scherrer Institute, 5232 Villigen, Switzerland

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ABSTRACT

The multiphoton ionization (MPI) of CH_3I 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.

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 rovibrational 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 $H_2{}^+$ 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 CH_3I molecule by photoelectron imaging spectroscopy. The experiments were performed with a home-built doubled-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 CH_3I (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 CH_3I.

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 μm^2, which corresponds to intensities between 0.48 and 1.6×10^{13} W/cm^2.

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.

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* Corresponding author.
E-mail address: gregor.knopp@psi.ch (G. Knopp).

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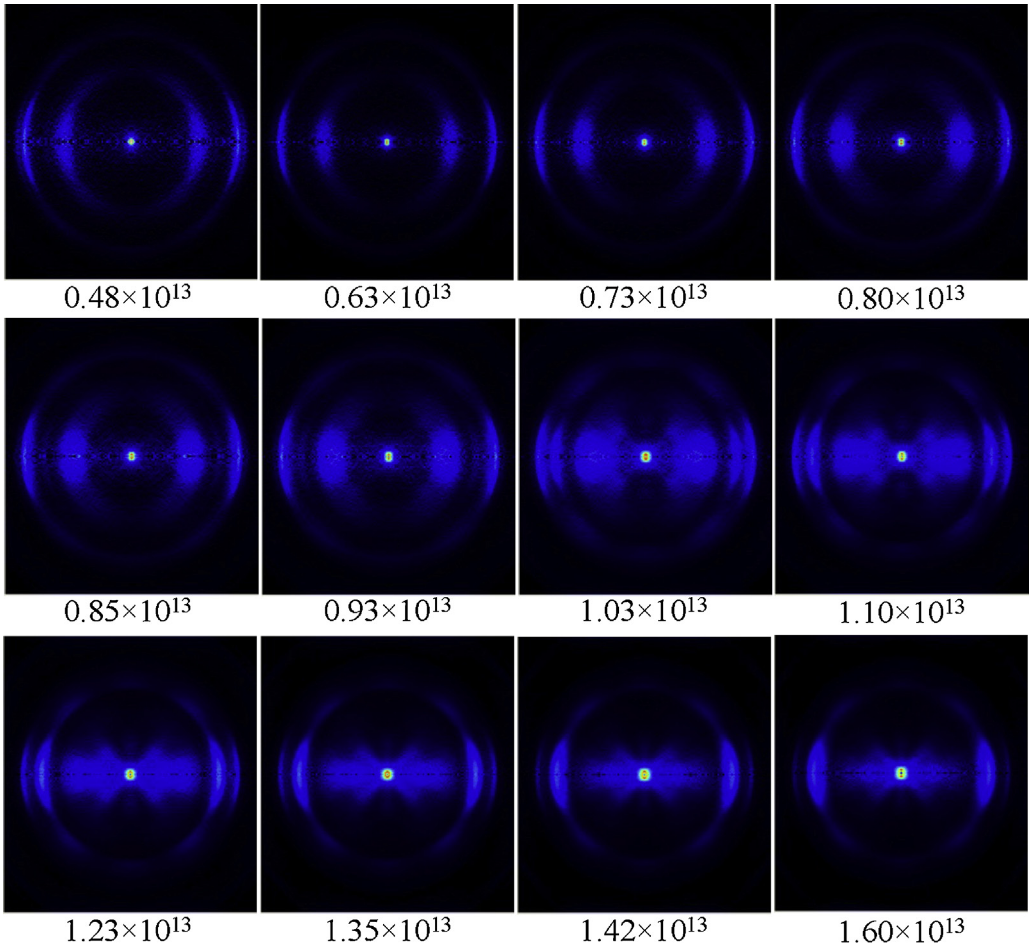

Figure 1. A series of intensity-dependent PEI. The linear polarization of the ionization laser is aligned horizontal in the plane of the figure.

3. Results and discussion

Photoelectron images (PEI) were acquired at femtosecond laser pulse intensities ranging from 0.48 to 1.6×10^{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 γ_K. The Keldysh parameter [22] can be defined by the square root of the ratio between the ionization energy (Ip) and twice the ponderomotive energy $\gamma_K = \sqrt{Ip/2Up}$ with $Up = (e^2/(2\varepsilon_0 c m_e))(I/\omega^2)$. I is the laser intensity, m_e the electron mass, e the elementary electric charge, ε_0 the dielectric constant, c the speed of light and ω 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 γ_K varying from 4.2 to 2. However, the definition of γ_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 map 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 1.60×10^{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 0.8×10^{13} W/cm^2. With increasing intensity, the contribution of these two rings decreases and at intensities between 0.8 and 1.1×10^{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 $E_{\text{ion}} = 9.54$ 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 $\tilde{E}_{\text{ion}}(I) = E_{\text{ion}} + \alpha I$. Accordingly, with increasing intensity the external laser field causes a down shift of the observed electron kinetic energies $E_{\text{kin}} = nh\nu_0 - \tilde{E}_{\text{ion}} - E_{\text{int}}$ 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