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Dynamic Stark shift of the 3R_1 Rydberg state of CH_3I

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Abstract. Stark shift of the 3R_1 Rydberg state of CH_3I is measured for different Stark field intensities. Photodissociation products, generated after predissociation of the state, were detected when the molecules were excited with photons resonant with the energy difference between the ground and the shifted 3R_1 state, allowing the shift to be quantified. Qualitative agreement has been found with a 1D model.

1 Introduction

The Stark effect consists of the shift of the energy levels of an atom or molecule under the influence of an electric field. If the field oscillates rapidly the shift does not follow each cycle adiabatically, but its intensity envelope instead. Typically, the intensities that can be achieved in this manner are significantly higher than with dc fields. Dynamic Stark shift (DSS) has a measurable effect on biological systems[1][2] and laser generation itself[3] or the control of chemical reaction dynamics [4], among other applications.

In the present work, the DSS of the 3R_1 state of CH_3I by a picosecond duration, near infrared intense laser pulse is studied. The B absorption band of CH_3I consists of a discrete set of lifetime broadened peaks that correspond to different vibrational levels of the 3R_1 state. Electronically, this bound state is of Rydberg character but is crossed by a valence, dissociative state at a point near the bottom of the potential well. Therefore, it undergoes predissociation yielding mostly $\text{CH}_3 + \text{I}^*(^2P_{1/2})$. A method that is sensitive to the presence of these fragments can be used as a test of the strength of the absorption to the B band in the parent CH_3I molecule, as has been done in this work.

2 Material and methods

The experimental setup has been described previously [5]. Three laser pulses are required for this experiment. The first one, with a wavelength of ≈ 200 nm, pumps the CH_3I molecule to the 3R_1 Rydberg state in its vibrationless level. A 333.45 nm probe pulse is employed for 2+1 resonance enhanced multiphoton ionization (REMPI) of the CH_3 fragments generated after predissociation. In temporal overlap with the pump pulse, an infrared (≈ 800 nm), temporally stretched pulse using a pair of diffraction gratings to a duration of around 4 ps is used as the Stark field. The three pulses are generated in a chirped-pulse amplified Ti:Sapphire laser by harmonic generation or after optical parametric amplification. All beams are focused with a 25 cm focal length lens onto a pulsed molecular beam. The ions generated in the interaction region are mass separated in a time-of-flight mass spectrometer and detected by velocity map imaging (VMI) [5].

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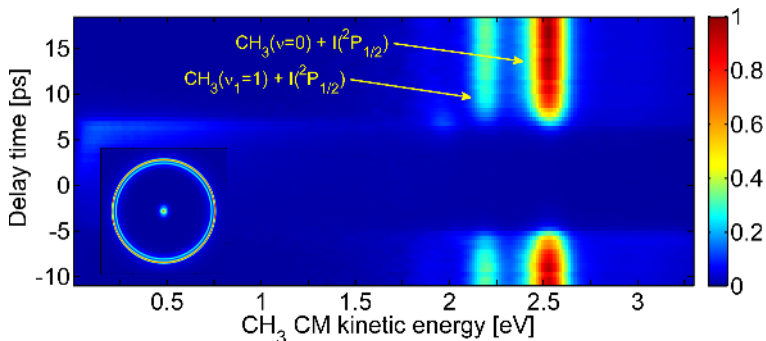


Fig. 1. 2D intensity map showing the kinetic energy distribution of the CH_3 fragments as a function of the delay time between the pump (201.2 nm) and the Stark (800 nm) pulses. The Stark pulse is temporally gaussian shaped with a pulse energy of 300 μJ and a FWHM of 3.9 ps. Inset: Abel inverted ion image corresponding to a delay time of 15 ps. CH_3 fragments are ionized with a 333.45 nm laser (2+1 REMPI) and VMI is employed to image the projection of the ion spheres. After Abel inversion and angular integration, kinetic energy distributions used for the main figure are obtained.

The methodology employed to measure the Stark shift is based on retuning the pump laser wavelength to recover the resonance between the vibrationless ground and 3R_1 states. First, CH_3 fragments are detected in a pump-probe experiment, where the probe pulse is sufficiently time delayed (typically, tens of picoseconds, *i.e.* much longer than the 3R_1 state lifetime). The Stark pulse is then introduced in temporal overlap with the pump pulse, producing a decrease of the fragment signal due to absorption suppression generated by the Stark shift of the state. Finally, the pump wavelength is retuned until fragment ion signal is recovered. The magnitude of the change in the pump photon energy corresponds to the dynamic Stark shift of the state for a given Stark field intensity.

In order to theoretically evaluate the Stark shift, wave packet propagations in reduced dimensionality (one dimension corresponding to the C-I distance) were performed using the Split Operator technique with Fast Fourier Transform [6]. The potential energy surfaces, dipole moments and diabatic couplings were obtained using *ab initio* calculations at MRCI level (including singlet and doublet excitations) over a state average CAS(6,5)/ANO-RCC. The spin-orbit coupling was calculated considering the AMFI approximation [7]. The ground state wavepacket, multiplied by the transition dipole moment, was propagated around 30 ps under the effect of a cw laser of 800 nm. The spectrum was obtained by Fourier transform of the autocorrelation function, at different laser field strengths, and the resonance was extracted from it.

3 Experimental results

Without an external Stark field applied, predissociation of the 3R_1 state occurs following absorption of a 201.2 nm photon (0_0^0 transition) and CH_3 fragments are generated in correlation with $\text{I}^*(^2P_{1/2})$. An example of images obtained in these conditions is presented in the inset of figure 1. The three almost isotropic rings –the inner one is only barely seen– correspond to CH_3 fragments in different vibrational states ($\nu_1 = 0, 1, 2; \nu_2 = 0$) [5].

In order to explore the effect of the Stark pulse, a pump-Stark delay scan was carried out with a 0.3 mJ Stark pulse. This energy corresponds to a situation where the suppression of the resonance is complete. Figure 1 shows a 2D map with the kinetic energy distribution of the CH_3 fragments as a function of delay time. For a delay interval between -5 and 5 ps, the signal disappears completely since the Stark pulse intensity is high enough to shift the 3R_1 state beyond the bandwidth of the pump pulse.

Calibration of the Stark shift with the energy of the applied field was carried out as described in section 2. Special care was taken when retuning the pump photon to always excite the vibrationless

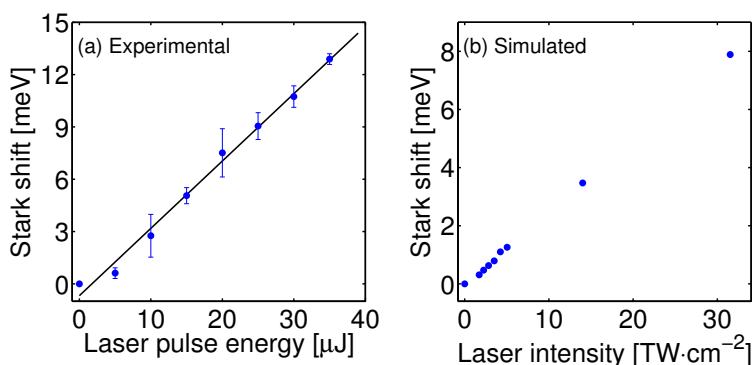


Fig. 2. (a) Measured Stark shift as a function of the energy of the Stark field and linear regression of the data (solid line). Error bars correspond to standard deviation. (b) Theoretical Stark shift as a function of laser intensity.

3R_1 state. During the retuning, the pump pulse was fixed at the time of the maximum intensity of the Stark pulse. Calibration points are shown in figure 2(a). The relationship between the energy of the field and the Stark shift produced is found to be linear. The energy of the 3R_1 state shifts to higher values up to 13 meV for the highest Stark pulse energies of 30 μJ used here.

Figure 2(b) shows the theoretical shift in the maximum of the simulated spectrum as a function of the employed laser field strength. Two issues are of importance in the comparison with experiment. It is worth noting that the direction of the shift is predicted correctly to higher photon energies. However, the predicted magnitude of the shift is considerably lower than that observed, which may well result from the limitations of the 1D model employed.

4 Conclusions and outlook

Dynamic Stark effect on the 3R_1 Rydberg state of CH_3I has been measured. An intense infrared pulse shifts the 3R_1 potential energy surface, thus avoiding absorption and suppressing photodissociation of the molecule. Absorption is retrieved when the wavelength of the pump laser is retuned to the resonance energy between the ground state and the shifted 3R_1 state. This fact was exploited to calibrate the efficiency of the effect. A 1D theoretical calculation shows qualitative agreement with the data, obtaining the correct direction of the shift, although predicting a lower shift than that measured. Due to the extreme sensitivity of the predissociation dynamics of the 3R_1 state with the spatial details of the wavefunction –excitation to different vibrational levels leads to predissociation lifetimes that differ by around an order of magnitude– dynamic Stark control could become a good candidate to control the photofragmentation dynamics of CH_3I after excitation in the B absorption band.

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