

Imaging the predissociation dynamics of the methyl radical from the $3p_z$ Rydberg state

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Synopsis Direct, time-domain measurements are reported for the lifetimes of the lower-lying vibrational levels of the $3p_z$ Rydberg state of the methyl radical. Lifetimes measured are in the region of hundreds of femtoseconds, and show a decrease with increasing vibrational activity. The mechanism is interpreted with the aid of *ab initio* calculations.

The relevance of the methyl radical spans across both applied and fundamental areas of Chemistry, but crucial aspects of its spectroscopy and dynamics are still unknown today.

Due to its planar geometry, many states are spectroscopically dark, since one-photon transitions from the ground state are forbidden. REMPI (resonance-enhanced multiphoton ionization) spectroscopy allowed to obtain information about excited states previously unobserved [1]. Of those, the Rydberg-character $3p_z$ and $4p_z$ states have become widely used in 2+1 REMPI schemes for the detection of the methyl radical. However, it was soon realized that obtaining direct quantitative data on product state distributions of the methyl radical using these schemes was not possible due to predissociation processes that compete favorably with ionization, thus distorting line profiles in the REMPI spectra [2]. There have been no previous attempts to measure predissociation lifetimes in the time domain, or to propose a mechanism for predissociation based on high-level calculations. In this work, we report direct measurements of vibrational-level selective predissociation rates in the $3p_z$ state of the methyl radical. The work is complemented with *ab initio* calculations.

In the experiment, a "synthesis" pulse dissociates CH_3I in a molecular beam, giving rise to methyl fragments in the ground electronic state $\text{CH}_3(X, \nu)$. An ultrashort "excitation" laser pulse around 330 nm excites these methyl fragments by two-photon transitions to the $3p_z$ Rydberg state, $\text{CH}_3(3p_z, \nu)$. A third ultrashort "ionization" laser pulse at 400 nm removes an electron from the Rydberg orbitals. Velocity map images of the resulting CH_3^+ cation are acquired in a

time-of-flight spectrometer. Tuning the excitation laser changes the distribution of excited vibrational states, and channel distinction is possible through energy-resolved detection in the velocity map images. Thus, for a given channel, we obtain a signal that is proportional to the instantaneous population in each vibrational level of the $3p_z$ state, which we map by changing the delay between the excitation and ionization pulses. This is shown in Figure 1, where the inset shows an example image. The results will be discussed under the framework of new *ab initio* calculations on this system.

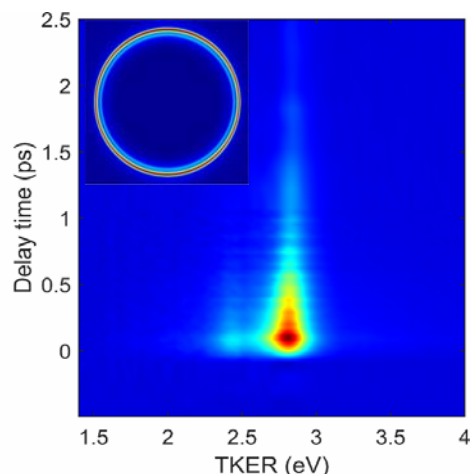


Figure 1. False-color map of the temporal evolution of the total kinetic energy distribution measured for the CH_3 fragment born after CH_3I dissociation. The inset shows a typical Abel-inverted velocity map images.

References

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- [2] J. Zhou *et al* 2003 *J. Chem. Phys.* **119** 2538

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