

Identification of water fragmentation channels utilizing phase shifts under $\omega/2\omega$ fs laser field irradiation

Emmanouil Kechaoglou¹, Katerina Ferentinou¹, Spyridon Kaziannis¹ and Constantine Kosmidis^{1*}

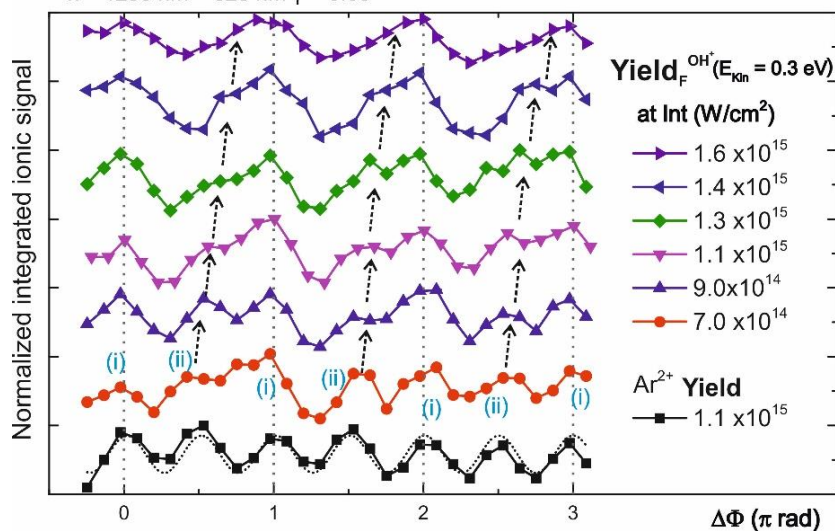
1. Department of Physics, Atomic and Molecular Physics Laboratory, University of Ioannina, University Campus, Ioannina GR-45110, Greece

Abstract

Distinction between two dissociative channels of H_2O^{2+} releasing alike fragments of similar kinetic energy is achieved by utilizing strong near-IR $\omega/2\omega$ asymmetric fields.

Irradiation using two laser frequencies ($\omega/2\omega$) has been proposed and utilized as a way of controlling unimolecular reactions [1]. Strong $\omega/2\omega$ asymmetric fields have been applied for controlling the branching ratio between two dissociative channels [2] and to gain information on ultra-fast phenomena like hydrogen migration [2,3]. Furthermore, by observing the fragments' yield dependence on the phase difference between the ω and 2ω components of the asymmetric field, there is the ability in some cases to distinguish between two dissociative states that result in the same fragments with similar kinetic energies [4]. In the present work, we have studied the two-body fragmentation H_2O^{2+} according to the reaction: $\text{H}_2\text{O}^{2+} \rightarrow \text{H}^+$ ($E_{\text{kin}} = 4.8$ eV) + OH^+ ($E_{\text{kin}} = 0.3$ eV).

$\lambda = 1250$ nm + 625 nm $\gamma = 0.63$



Water dications' fragmentation was investigated at two $\omega/2\omega$ wavelength regions: 1250/625nm and at 1400/700nm generated from an Optical Parametric Amplifier (seeded by a 20 fs Ti: Sapphire laser) and an additional BBO crystal. The composed field is mathematically described as: $E_{\text{tot}}(t, \phi) = E_0(t)[\cos(\omega t) + \gamma \cos(2\omega t + \phi)]$, where γ is the ratio of the 2ω and ω electric fields and ϕ is the phase between the two beams. The latter is controlled by rotating a Calcite plate in the path of the second harmonic in steps of 0.02° . The ionization signal is recorded by means of time of flight mass spectrometry. One useful parameter that is indicative of the fragments' ejection direction is the asymmetry parameter and is defined as $\beta = (\text{Yield}_F - \text{Yield}_B) / (\text{Yield}_F + \text{Yield}_B)$, where $\text{Yield}_{(i)}$ is the

signal of fragments ejected towards (Y_F) and backwards (Y_B) of the detector.

By recording the signal of the $Y_F^{\text{OH}^+}$ and $Y_B^{\text{OH}^+}$ components of the OH^+ peaks ($E_{\text{kin}} = 0.3$ eV) a phase difference $\phi = \pi$ was observed while the phase difference with respect to the components of the H^+ ($E_{\text{kin}} = 4.8$ eV) peak ($Y_F^{\text{OH}^+} / Y_F^{\text{H}^+}$ and $Y_B^{\text{OH}^+} / Y_B^{\text{H}^+}$) was also $\phi = \pi$. This observation, in conjunction with momentum conservation confirms that these fragments are released from H_2O^{2+} . Moreover, we found that although the asymmetry parameter (β) of the OH^+ peak exhibits a sinusoidal modulation that is dependent on the asymmetric field's direction (ω behavior), the individual OH^+ peak components ($Y_F^{\text{OH}^+}$ and $Y_B^{\text{OH}^+}$) show a dependence on the double frequency (2ω behavior). Furthermore, by increasing the laser intensity the phase difference between these OH^+ peak components varied. In order to have an internal calibration, Ar atoms were introduced in the interaction region offering thus phase reference by monitoring the Ar^{2+} peak. The different dependency of the two OH^+ components on the phase of the $\omega/2\omega$ laser field as the intensity increases, is manifested in the above Figure as phase shift. Unambiguously this implies that the precursor dissociative states leading to these OH^+ fragments are different, despite the fact that they are ejected with the same (within the experimental error) kinetic energy. We propose that the first dissociation channel takes place in a dication's state while the second one via an energetically lower lying autoionizing state of H_2O^+ , which after deprotonation, fragments to OH^* leading finally to OH^+ [5]. Direct ionization (non-sequential) is favored at relatively lower laser intensities (peak (i)), while the contribution of the sequential process is increased with laser intensity (peak (ii)). For the higher laser intensities applied, the phase difference between the individual OH^+ peak components is small to be distinguishable and the ω behavior dominates.

References

- [1] P. Brumer and M. Shapiro, *Chem. Phys. Lett.*, 126, 1986, 541.
- [2] E. Kechaoglou, S. Kaziannis, C. Kosmidis, *Phys. Chem. Chem. Phys.*, 21, (2019), 11259-11265.
- [3] N. Kotsina, S. Kaziannis and C. Kosmidis, *Chem. Phys. Lett.*, 2014, 604, 27-32
- [4] N. Kotsina *et al.*, *J. Chem. Phys.*, 139, 2013, 104313.
- [5] D. Reedy *et al.*, *Phys. Rev. A*, 98, (2018), 053430

Acknowledgments

"This research is co-financed by Greece and the European Union (European Social Fund- ESF) through the Operational Programme «Human Resources Development, Education and Lifelong Learning 2014- 2020» in the context of the project "Selective dissociation induced by asymmetric laser fields: The case of H_2O " (MIS 5047636)."