Identification of water fragmentation channels utilizing phase shifts under ω/2ω fs laser field irradiation

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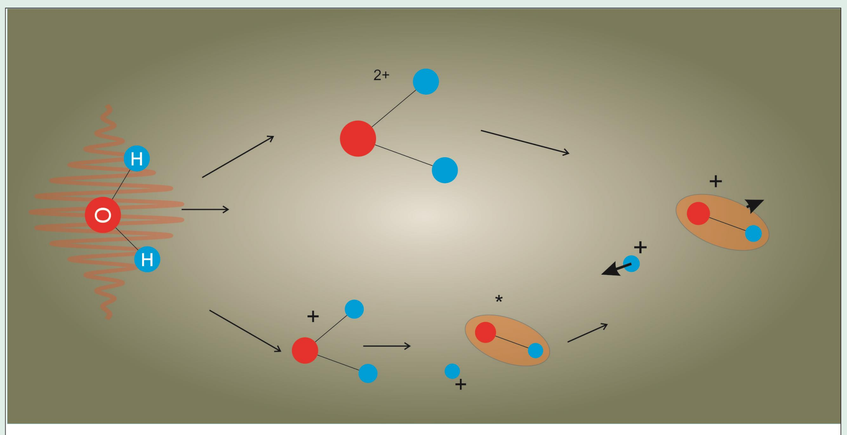
Study and control of unimolecular reactions is feasible by laser irradiation using two frequencies (ω/2ω) [1].

Ionization of molecules using strong ω/2ω asymmetric fields can among other things:

1. Alter the branching ratio between two dissociative channels [2]
2. Shed light on ultrafast phenomena like hydrogen migration [2,3]
3. Distinguish between dissociative states that release similar fragments [4].

In the present work, we have studied the two-body fragmentation H_2O^{2+} according to the reaction:

$H_2O^{2+} \rightarrow H^+ (E_{Kin} = 4.8\ eV) + OH^+ (E_{Kin} = 0.3\ eV)$.



Two body fragmentation routes of water leading to $H^+ (E_{kin} = 4.8\ eV) + OH^+ (E_{kin} = 0.3\ eV)$ (a)

- Water dications' fragmentation was investigated at two ω/2ω wavelength regions 1250/625nm and 1400/700nm, generated by an Optical Parametric Amplifier (seeded by a 20 fs Ti: Sapphire laser) and an additional BBO crystal.
- The phase between the ω and 2ω components 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.

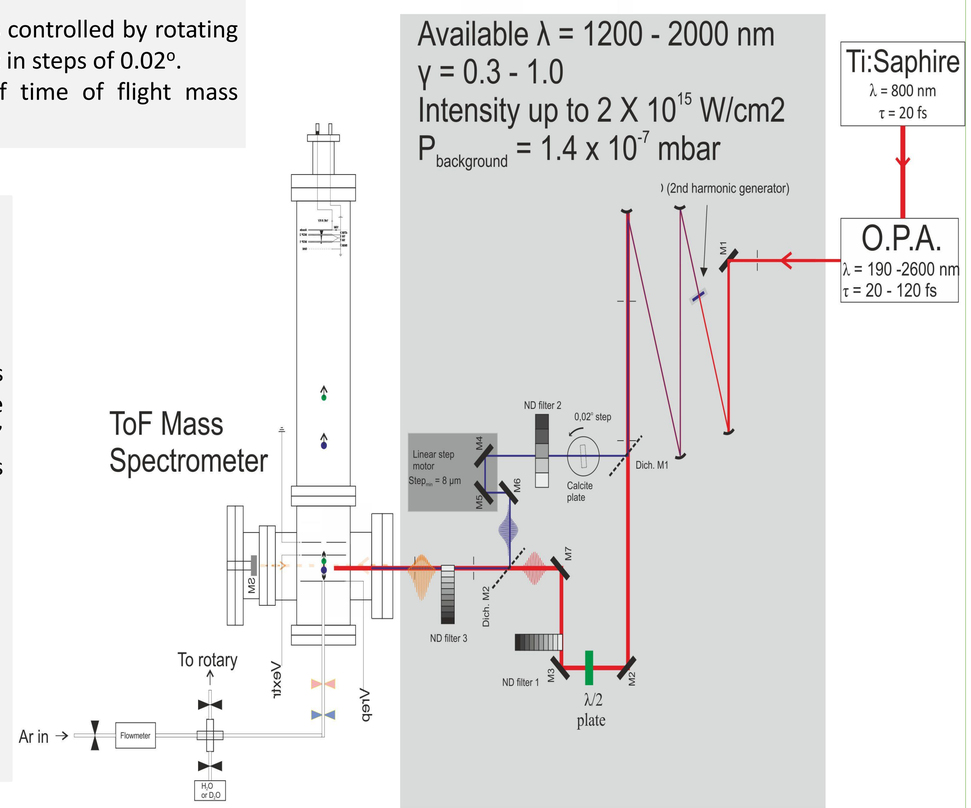
The composed field is mathematically described as:

$$E_{tot}(t,\phi) = E_0(t)[\cos(\omega t)+\gamma\cos(2\omega t+\phi)],$$

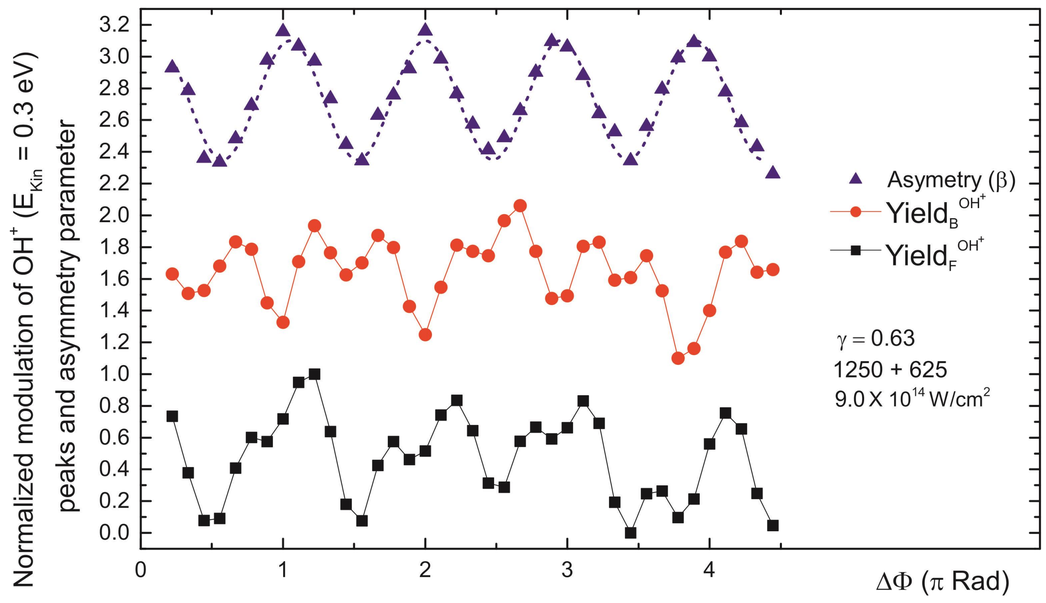
where γ is the ratio of the 2ω and ω electric fields and ϕ is the phase between the two beams. One useful parameter that is indicative of the fragments' ejection direction is the asymmetry parameter and is defined as

$$\beta = \frac{Yield_{Forward} - Yield_{Backward}}{Yield_{Forward} + Yield_{Backward}}$$

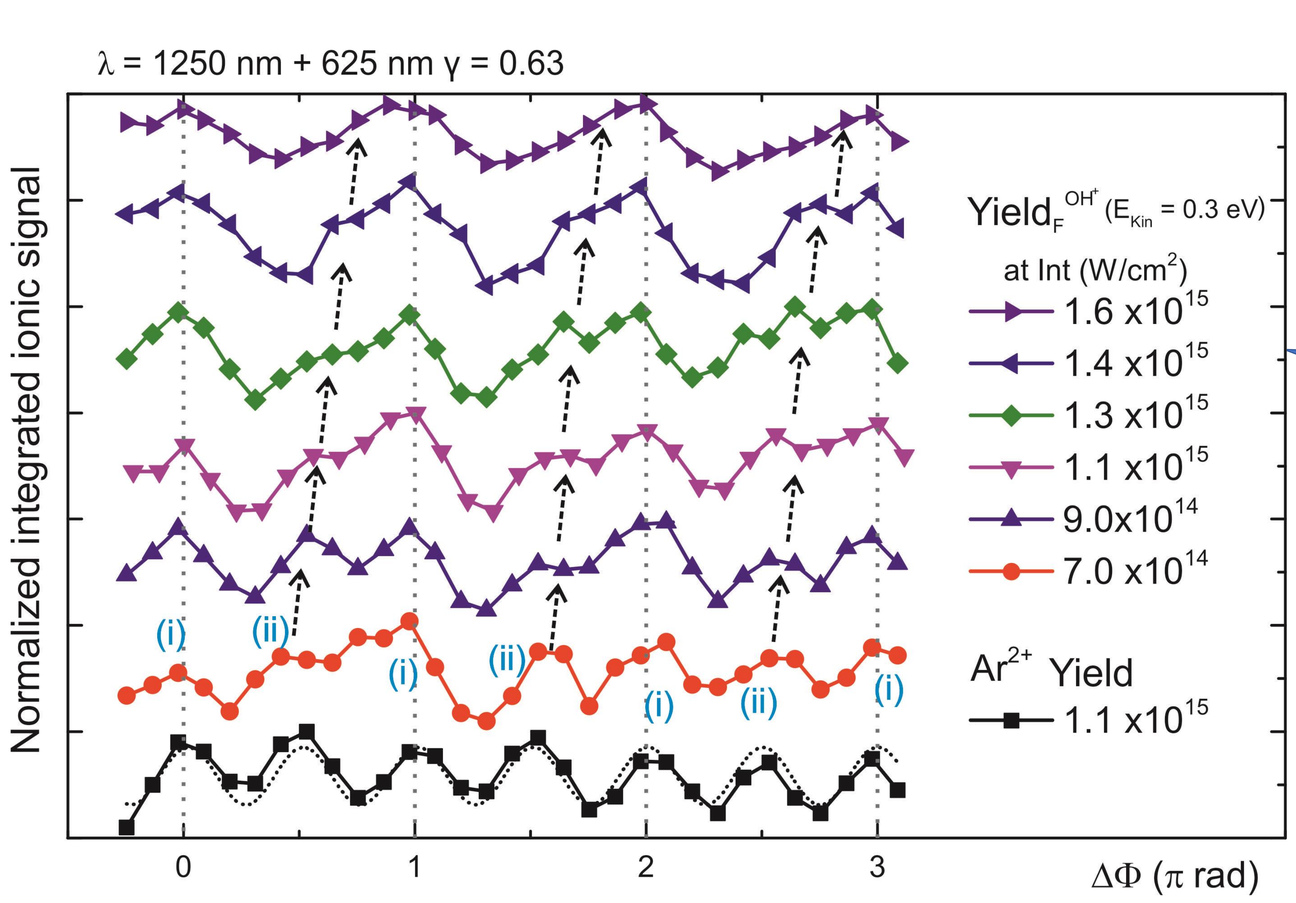
Experimental Setup (ω/2ω)

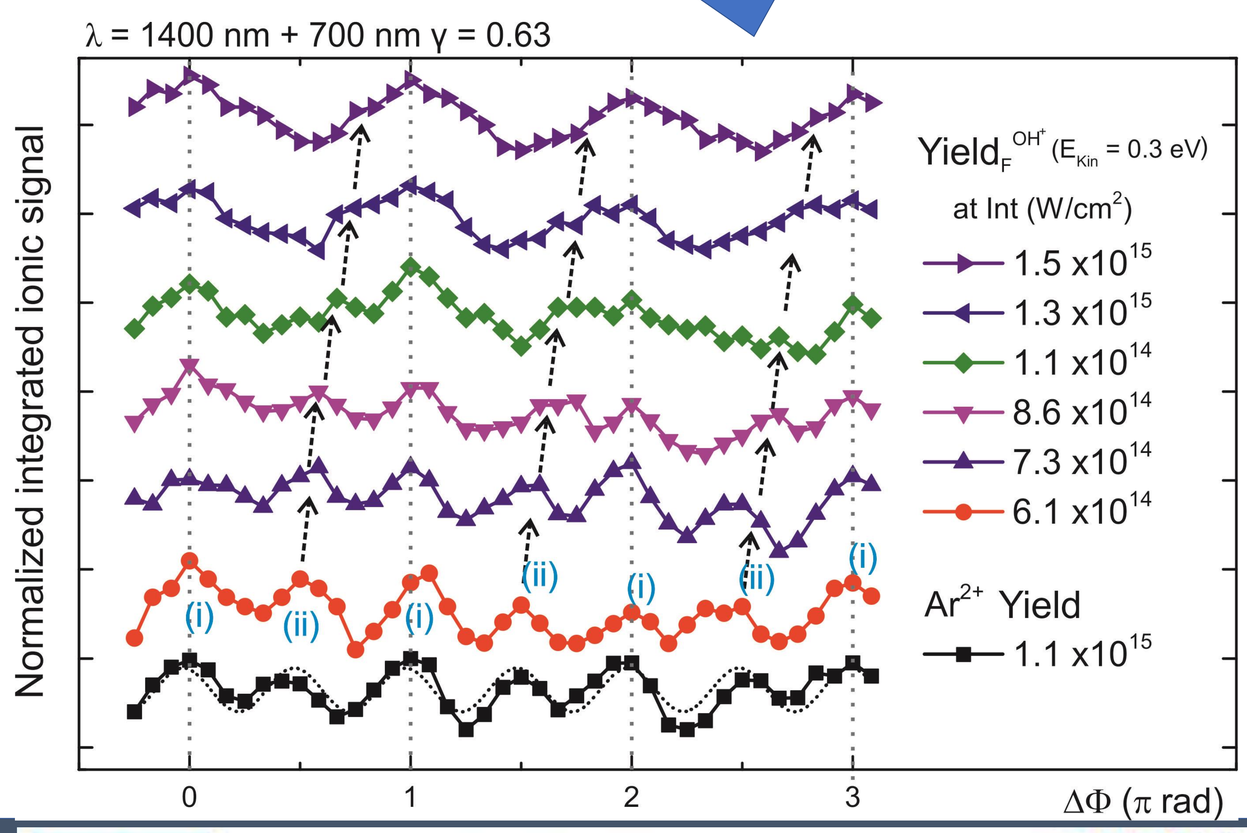


- A phase difference φ=π between Y_F^{OH+} and Y_B^{OH+} components was observed while the phase difference with respect to the components of the H^+ (E_{Kin} =4.8 eV) peak was also φ=π [2]. This observation, in conjunction with momentum conservation confirms that these fragments are released from H_2O^{2+}.
- 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^{OH+} and Y_B^{OH+}) show a dependence on the double frequency (2ω behavior).



- Ar^{2+} peak is monitored for phase calibration
- The phase difference between the OH^+ peak components ((i) and (ii)) is dependent of the laser's intensity and is perceived like a phase shift as the intensity rises
- This shows that two precursor dissociative states lead to these OH^+ fragments, despite the fact that they are ejected with the same (within the experimental error) kinetic energy.





- Two dissociation channels release similar fragments. The first 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 (rescattering) 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.

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