

# Experimental and theoretical progress in time-resolved (e, 2e) electron momentum spectroscopy of photodissociation dynamics of acetone at 195 nm

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**Synopsis** We report on experimental and theoretical progress in time-resolved (e, 2e) electron momentum spectroscopy of photodissociation dynamics of the deuterated acetone molecule at 195 nm. Experimentally, we are conducting a series of measurements to have improved experimental results, compared to the earlier ones, by using a pump laser with higher intensity. Theoretically, we have examined the predicted minimum energy reaction path to investigate whether associated (e, 2e) calculations meet the experimental results. A noticeable difference between the experiment and the calculations has been found at around binding energy of 10 eV, suggesting that the observed difference may originate, at least partly, in ever-unconsidered non-minimum energy paths.

Through many years of intensive studies, electron momentum spectroscopy (EMS) has been established as a powerful means to measure spectral electron momentum density or to look at individual molecular orbitals in momentum space [1, 2]. Extension of the applicability of EMS to transient species is one of the challenges to be tackled, as the change of the electron motion is the driving force behind any chemical reactions. For this purpose, we have recently developed time-resolved EMS (TR-EMS) by combining EMS with a pump-probe technique using femtosecond laser (120 fs) and picosecond electron (1 ps) pulses [3]. The potential ability of TR-EMS has already been demonstrated through orbital imaging of the highest occupied molecular orbital of deuterated acetone (acetone-*d*6) in its short-lived (13.5 ps), second singlet excited ( $S_2$ ) state [4], an EMS study on the electronic structure of the relatively long-lived (86 ns), first singlet excited ( $S_1$ ) state of toluene [5], and an attempt at a product vibrational analysis of a photo-induced chemical reaction that occurs as a deactivation process of acetone-*d*6 in the  $S_2$  state [6].

The purpose of this study is to obtain information about dynamics of the photo-induced chemical reaction of  $S_2$  acetone-*d*6 as a result of a joint experimental and theoretical investigation. Experimentally, we are conducting TR-EMS measurements with improved statistics, compared to the earlier ones [4, 6], by using a pump laser with higher intensity. Our idea here is that although the current time-resolution is limited to  $\pm 35$  ps owing to velocity mismatch effects, information about electron dynamics during the chemical reaction may be left as a trace in the measured TR-EMS spectra. Indeed, we have calculated associated TR-EMS spectra and compared those with the experiments.

The  $S_2$  acetone-*d*6 is known to undergo a three-body dissociation that eventually gives CO and two  $CD_3$  within  $\sim 20$  ps, firstly via rapid dissociation of acetone-*d*6 to acetyl ( $CD_3CO$ ) and  $CD_3$  after electronic relaxation to its  $S_1$  state and secondly via subsequent dissociation of  $CD_3CO$  to CO and  $CD_3$  [7]. We have found, for instance, that the experimental TR-EMS binding energy spectrum measured at a delay time of 0 ps exhibits substantially larger intensities at around 10 eV, compared to the associated theoretical spectrum that was generated by summing up EMS spectra of the initial, intermediate, and final reaction products calculated at their equilibrium geometries with appropriate weight factors determined by their lifetimes. Furthermore, the observed difference in intensity between the experimental and calculated spectra can be reduced by considering contributions of the dissociating acetyl radical in a bent molecular geometry that is far different from the equilibrium geometries along the minimum energy reaction path. We are planning to perform molecular dynamics trajectory simulations, under professional guidance, to resolve the difference.

## References

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