Theoretical analysis of the time-resolved binary (e, 2e) binding energy spectra on three-body photodissociation of acetone at 195 nm

M Yamazaki1, S Nakayama1, C Y Zhu2 and M Takahashi1

1 Institute of Multidisciplinary Research for Advanced Materials, Tohoku University, Sendai 980-8577, Japan
2 Department of Applied Chemistry, Institute of Molecular Science, National Chiao-Tung University, Hsinchu 30050, Taiwan

E-mail: masahiko@tohoku.ac.jp

Abstract. We report on theoretical progress in time-resolved (e, 2e) electron momentum spectroscopy of photodissociation dynamics of the deuterated acetone molecule at 195 nm. 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 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.

1. Introduction

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 [1–8]. Extension of the applicability of EMS to transient species is one of the challenges to be tackled, as the change of electron motion is the driving force behind chemical reactions. To this end, 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 [9]. The inherent ability of TR-EMS has already been demonstrated, for instance through orbital imaging of the highest occupied molecular orbital of deuterated acetone (acetone-d6) in its second singlet excited (S2) state [10] and an attempt at a product vibrational analysis of a photoinduced chemical reaction that occurs as a deactivation process of S2 acetone-d6 [11]. Here, the reason for having chosen the deuterated compound as the target is that lifetime of S2 acetone-d6 is approximately three times longer (13.5 ps [12]) than that of S2 acetone-h6; the measurement may be more feasible with the current status of TR-EMS in terms of unsatisfactory data statistics and time resolution of ±35 ps that is mainly determined by velocity mismatch effects.

The above-mentioned photoinduced chemical reaction of S2 acetone-d6 is known to undergo a three-body dissociation that eventually gives CO and two CD3 within ~20 ps, firstly via rapid dissociation of acetone-d6 to acetyl radical (CD3CO) and CD3 after electronic relaxation to its S1 state and secondly via subsequent dissociation of CD3CO to CO and CD3 [12, 13]. Nevertheless, electron
and nuclear dynamics during the sequential C-C bond cleavage reaction of \( S_2 \) acetone-d\(_6\) still remain as the unresolved issue at the most fundamental level. Although the current time resolution (±35 ps) of TR-EMS is not fine enough to observe in real time the chemical reaction, one may be able to extract some information about electron and nuclear dynamics. This is because such information is expected to be left as a trace in the measured TR-EMS spectra. The purpose of the present study is to test the new possible ability of TR-EMS by making a careful comparison between one of the reported binding energy spectra [10] and associated theoretical spectra.

2. Experiment

Since details of the experiment for \( S_2 \) acetone-d\(_6\) are described elsewhere [10], only a brief account of it is given here. Figure 1 shows a schematic picture of the experimental setup [9]. The 800 nm output of a 5-kHz femtosecond laser (<120 fs, 0.8 mJ) was split into a pump path and an electron-generation path. 90% of the output was used to yield with an optical parametric amplifier the pump laser pulse (195 nm, ~120 fs, 0.8 μJ), which was subsequently used to excite a deuterated acetone molecule in a target gas beam to the \( S_2 \) (n, 3s) Rydberg state after the 5-kHz repetition rate being halved by an optical chopper. On the other hand, 10% of the 800 nm output was frequency tripled (267 nm, <10 μJ) and it was directed toward a back-illuminated photocathode, in order to produce electron pulses via the photoelectric effect. The photocathode was made of a silver film of 40 nm thickness, which was negatively biased to accelerate the electron pulses up to 1.2 keV. The resulting short pulsed electron beam was then used to induce EMS events. Here, in order to keep a moderate overall energy resolution (~5 eV), a limited beam current of 50 pA (~6.2×10\(^4\) electrons/pulse) and a minimum distance of 10 mm between the ionization point and the photocathode surface were employed, because space charge effects significantly broaden not only the temporal width but also the energy spread of the pulsed incident electron beam. In these experimental conditions, a mean-field-model simulation [9] indicates that the temporal width of the electron beam is of the order of a picosecond. The estimated temporal width value is consistent with our previous study on a transient space-charge field created by irradiation of the pump laser on a Ag wire, where kinetic energy distribution of elastically scattered electrons due to interaction of the pulsed electron beam with the Ag wire was measured against delay time \( t_{\text{delay}} \). The above-mentioned EMS events due to ionization of an excited or unexcited target molecule were recorded by an EMS spectrometer for which an exceptionally large spherical analyzer (mean radius of 220 mm) was employed. Note that since the 5-kHz repetition rate was halved only for the pump laser, the TR-EMS apparatus concurrently produced two kinds of EMS data sets. One is data...
that were measured with the pump laser (laser-on). The other is reference data that were measured without the pump laser (laser-off) and hence they are equivalent to traditional EMS data for the unexcited parent, acetone-\(d_6\) molecules in its ground state. The TR-EMS data were therefore obtained by subtracting the laser-off spectrum with an appropriate weight factor from the laser-on spectrum. For the EMS measurements, the symmetric noncoplanar geometry was employed, in which two outgoing electrons having equal energies and making equal scattering angles (\(\theta_1 = \theta_2 = 45^\circ\)) with respect to the incident electron beam axis were detected in coincidence. The binding energy (\(E_{\text{bind}}\)) and momentum (\(p\)) of the target electron, before ionization, can be determined through the following energy and momentum conservation laws [1–8]:

\[
E_{\text{bind}} = E_0 - E_1 - E_2, \quad (1)
\]
\[
p = p_1 + p_2 - p_0. \quad (2)
\]

Here \(E_j\)'s and \(p_j\)'s (\(j = 0, 1, \text{ and } 2\)) are the kinetic energies and momenta of the incident, inelastically-scattered and ejected electrons, respectively. In this kinematic scheme, the magnitude of the target electron momentum \(p\) is given by

\[
p = |p| = \sqrt{\left(p_0 - \sqrt{2} p_1\right)^2 + \left(\sqrt{2} p_1 \sin(\Delta \phi / 2)\right)^2} \quad (3)
\]

with \(\Delta \phi\) being the out-of-plane azimuthal angle difference between the two outgoing electrons.

3. Theoretical calculations
Within the plane wave impulse approximation, the triple differential cross section for EMS ionization is given by [1–8]

\[
\frac{d^3 \sigma_{\text{EMS}}}{d \Omega_1 d \Omega_2 dE_1} = (2\pi)^4 \frac{p_1 p_2}{p_0} f_{\text{ee}} \sum_{\alpha} S'_{\alpha} |\psi_{\alpha}(p)|^2
\]

where \(f_{\text{ee}}\) is the electron-electron collision factor and \(S'_{\alpha}\) is called the spectroscopic factor or pole strength, while the index \(\alpha\) represents here the symmetry of the momentum-space representation of the quasiparticle or Dyson orbital \(\psi_{\alpha}(p)\). \(\sum_{\alpha}\) represents a sum over final and average over initial state degeneracies unresolved in the experiment as well as the spherical averaging due to random orientation, in space, of gaseous target molecules.

To compare with the experimental binding energy spectrum measured at \(t_{\text{delay}} = 0\) ps [10], theoretical calculations have been made in the following manner. Firstly, for electronically excited species (i.e., acetone-\(d_6\) molecules in their \(S_2\) and \(S_1\) states), the Dyson orbitals, their binding energies, and pole strength values were calculated by using the symmetry adapted cluster configuration-interaction (SACCI) method [14] with the 6-31+G* basis set. For the ground state CO and CH\(_3\), their outer valence binding energies were taken from photoelectron spectroscopic studies reported by Fan et al. [15] and Dyke et al. [16], respectively. On the other hand, the inner valence binding energies of CD\(_3\) were calculated by using the SACCI method with the aug-cc-pVTZ basis excluding F- and D-type functions for C and D atoms, respectively, while those of CO were not considered because of their energies being out of range that we experimentally covered. Binding energies of CD\(_3\)CO and pole strength values of CD\(_3\)CO, CO, and CD\(_3\) were calculated by using the outer valence Green’s function method [17] with the 6-311++G** basis set, while approximate Dyson orbitals were calculated at the level of the density functional theory (DFT) using the B3LYP functional [18] with the aug-cc-pVTZ basis set [19]. All the quantum chemical calculations here were performed using GAUSSIAN03 program [20]. The calculated position-space Dyson orbitals were then converted to spherically-averaged electron momentum distributions or electron momentum profiles with the aid of the HEMS program developed by Brion and his coworkers [21]. Next, band intensities were calculated by integrating the theoretical momentum profiles over the covered electron momentum range, after being folded with the instrumental momentum resolution according to the procedure of Migdall et al. [22].
Δφ-angle integrated binding energy spectrum was subsequently generated for each molecular species considered, by summing up contributions of all the ionization transitions involved, each of which was assumed to have a Gaussian-like band profile with a width of the instrumental energy resolution (5 eV), centered at each own binding energy value.

In addition, an intrinsic reaction coordinate (IRC) for the dissociation process of CD₃CO leading to CO and CD₃ was calculated at the level of DFT using the CAM-B3LYP functional [23] with the 6-31+g(d) basis set. Furthermore, a two-dimensional potential energy surface (PES) scan was performed by changing the C-C bond length and the O-C-C bond angle of CD₃CO, while optimizing any other geometrical parameters, at the level of the second-order Møller-Plesset perturbation theory with the 6-311++G** basis set. Influence of structural change of CD₃CO on associated theoretical binding energy spectra was examined at various geometries on the PES and the IRC.

4. Results and discussion

Figure 2 shows the associated theoretical TR-EMS binding energy spectrum of the sequential C-C bond cleavage reaction of S₂ acetone-d₆ obtained here, which has been generated by summing up spectra of the five molecular species, i.e., the S₂- and S₁-acetone-d₆, CD₃CO, CO, and CD₃, calculated at their equilibrium geometries with appropriate weight factors determined by their lifetimes [12, 13]. Also included in the figure is the experimental spectrum of S₂ acetone-d₆ measured at t_delay = 0 ps with the time resolution of ±35 ps [10]. It can be seen from the figure that the experimental spectrum exhibits substantially larger intensities at around 10 eV, compared to the associated theoretical spectrum. If the observation is real, it would indicate that a possible clue for understanding the observed difference may be due to what is obviously lacking in the associated theoretical calculations, that is, contributions of the evolving systems which connect between the initial, intermediate, and final products. Among those, what most likely contributes is that during the dissociation process of CD₃CO, as its lifetime is much longer (3–6 ps or longer [12, 13]) than that of S₁ acetone-d₆ (~0.6 ps [13]) and S₂ acetone-d₆ does not show noticeable intensities at around 10 eV.

![Figure 2](image-url)

**Figure 2.** Experimental and theoretical TR-EMS binding energy spectra of the acetone-d₆ S₂ state obtained at t_delay of 0 ps.

![Figure 3](image-url)

**Figure 3.** Potential energy surface for the dissociation of acetyl radical.
Figure 3 shows the contour map for the ground state PES of CD$_3$CO, in which relative energy to that of the equilibrium structure ($r_{CC} = 1.5\ \text{Å, } \theta_{OCC} = 130.1^\circ$) is shown in eV. It can be seen that as the dissociation proceeds along the IRC, the C-C bond length becomes longer, while the O-C-C bond angle becomes smaller slightly, e.g., $\theta_{OCC} = 100.8^\circ$ when $r_{CC} = 2.9\ \text{Å}$. It can be also seen that there exists a local minimum at ($r_{CC}, \theta_{OCC}$) = (1.5 Å, 60°). This local minimum is energetically accessible because its relative energy (c.a. 2-eV higher than that of the equilibrium geometry) is lower than the maximum available energy of CD$_3$CO (2.8 eV [24]) estimated from a calculated energy difference between the S$_2$ acetone-$d_6$ and the ground-state CD$_3$CO at their equilibrium structures.

Figure 4 (a) compares theoretical TR-EMS binding energy spectra calculated at several geometries along the IRC with that calculated at the equilibrium geometry. Band intensities between 10–15 eV are found to be enhanced when dissociation dynamics along the IRC is taken into account. However, this enhancement is too small to resolve the difference between experiment and theory observed in figure 2. Interestingly, it has been found that the observed difference can be reduced much more by considering contributions from evolution of the acetyl radical at strongly bent geometries which are far different from those along the IRC but are similar to that at the local minimum, as can be seen in figure 4 (b); the smaller the O-C-C angle is and the shorter the C-C distance is, the band intensities at around 10 eV become pronounced. These findings imply that TR-EMS could have probed electron and nuclear dynamics along the non-minimum energy reaction path.

![Figure 4](image)

**Figure 4.** Theoretical TR-EMS binding energy spectra for (a) the structural changes along the intrinsic reaction coordinate and (b) bent geometries of dissociating acetyl radical.

5. Conclusion
We have reported on theoretical progress in TR-EMS of photodissociation dynamics of acetone-$d_6$ at 195 nm. A theoretical EMS investigation of the acetyl radical at various geometries on the potential energy surface has shown that contributions of acetyl radicals at strongly bent geometries are the possible origin of the observed difference between experiment and associated calculations along the IRC. In other words, information about electron and nuclear dynamics during the sequential C-C bond cleavage reaction of S$_2$ acetone-$d_6$ may have been left as a trace in the measured TR-EMS spectrum.

We are now arranging some plans to get deep insight into such electron and nuclear dynamics. Theoretically, it is currently being prepared to perform on-the-fly trajectory simulations of the
sequential C-C bond cleavage reaction of S$_2$ acetone-$d_6$. Experimentally, there is ample room for improvement. For instance, the time resolution of TR-EMS is currently poor and it is limited by velocity mismatch effect that originates from the difference in the propagation speed between the pump-laser and probe-electron pulses. However, it can be improved while avoiding any loss of the signal intensity, if the intensity front of a pump laser pulse is tilted properly [25]. Such an attempt is also now in progress.

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