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## An attempt at a product vibrational analysis of a photo-induced chemical reaction by means of time-resolved (*e*, 2*e*) electron momentum spectroscopy

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**Abstract.** We report on a new attempt at an analysis of the vibrational state distributions in the products of a photo-induced chemical reaction. The experiment was performed by using time-resolved electron momentum spectroscopy (TR-EMS) for the products produced by the three-body photodissociation dynamics of the deuterated acetone molecule at 195 nm. It has been found from a comparison between the experiment and associated theoretical calculations that future TR-EMS measurements with improved statistics could be useful for the vibrational analysis of reaction products, in cases when effects of molecular vibration on their electron momentum densities are large enough so as to be noticeable in the binding energy spectra.

### 1. Introduction

Over the last four decades, electron momentum spectroscopy (EMS), also known as binary (*e*, 2*e*) spectroscopy, has been developed as a powerful means to study the spectral momentum densities in matter or to look at individual electron orbitals in momentum space [1-8]. In spite of its potential, however, application of EMS to molecules has long been limited to stable targets in their ground electronic state. In order to make a breakthrough in this limitation, we have very recently developed an advanced form of EMS, which is called time-resolved EMS (TR-EMS) and employs ultrashort laser and electron pulses in a pump-probe scheme [9]. Although the data quality is currently low, it has been demonstrated with the deuterated acetone molecule ((CD<sub>3</sub>)<sub>2</sub>CO) in its second excited singlet *S*<sub>2</sub> (*n*, 3*s*) Rydberg state with a lifetime of 13.5 ps that TR-EMS measurements on short-lived molecular excited states are feasible, opening the door to time-resolved orbital imaging in momentum space [10].

The present work is an attempt to broaden the range of application of TR-EMS. We have chosen as the target an analysis of the vibrational state distributions in the products (CO + 2CD<sub>3</sub>) of the three-body photodissociation reaction of the deuterated acetone molecule at 195 nm, as this reaction is the subsequent decay process of the above-mentioned *S*<sub>2</sub> (*n*, 3*s*) Rydberg state. The idea here is based on the findings of traditional EMS studies [11-13] that molecular vibrations, even in their vibrational ground state, can change the electron momentum density distributions and hence EMS binding energy spectrum of a molecule at the equilibrium nuclear geometry through deformation of the molecular orbital patterns.



In general, the knowledge of the reactant and product vibrational distributions is of great importance in the study of reactive system dynamics [14]. Issues as important as mode selectivity are closely related to this information [15]. Indeed, product vibrational analysis of the three-body photodissociation reaction of acetone has intensively been carried out by using several kinds of spectroscopic methods. For instance, Trentelman *et al.* [16] employed vacuum-ultraviolet laser-induced fluorescence and multiphoton ionization time-of-flight mass spectrometry to probe the CO and CH<sub>3</sub> products respectively, which were produced by 193 nm photolysis of normal acetone ((CH<sub>3</sub>)<sub>2</sub>CO). They have reported a Boltzmann distribution for each product, with characteristic temperatures  $T_{\text{vib}}$  of 2700 K for CO and 800 K for CH<sub>3</sub>. The subsequent study of Hall *et al.* [17] used diode laser transient absorption/gain spectroscopy to monitor time-dependent populations of the CD<sub>3</sub> fragments formed in the photodissociation of deuterated acetone at 193 nm. In contrast to the result of Trentelman *et al.* [16], they have concluded that only about 15% of the nascent CD<sub>3</sub> population is formed in the vibrational states they detected ( $v_2 = 1$  and 2,  $v_3 = 1$ , and the vibrationless state) and most of the nascent CD<sub>3</sub> population should be spread among many undetected vibrational states. This controversy justifies the need of further study on the vibrational analysis of the CO and CD<sub>3</sub> products by means of a different spectroscopic method.

In this paper, we report on an attempt at an analysis of the vibrational state distributions in the products of the photodissociation of deuterated acetone at 195 nm by means of TR-EMS. The experiment has measured an EMS binding energy spectrum for the (CO + 2CD<sub>3</sub>) products, by setting the time delay between the pump laser and probe electron pulses to be large enough so as to avoid contributions of the reactant and reaction intermediates and to pick up only those of the reaction products. Associated theoretical calculations have been made and used to analyze the experimental data. From a comparison between experiment and theory, the potential ability of TR-EMS to conduct a product vibrational analysis of a photo-induced chemical reaction will be discussed.

## 2. Experiment

The experiment on the CO and CD<sub>3</sub> fragments formed in the photodissociation of deuterated acetone at 195 nm was carried out using the TR-EMS apparatus. Since details of the experiment are described elsewhere [10], only a brief account of it is given here. Figure 1 shows a schematic picture of the experimental setup. 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  $\mu$ J), which was subsequently used to excite deuterated acetone molecules 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 by a third harmonic generator and it was directed toward a back-illuminated photocathode, after being attenuated as required (267 nm, <10  $\mu$ J), 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 ultrashort pulsed electron beam (1.2 keV, ~1 ps, ~50 pA) was then used to induce EMS events. Since the photodissociation reaction is known to be ultrafast, yielding the reaction products within a few tens of picoseconds [18], the delay time between the arrival of the pump laser pulse and the probe electron pulse was set to be 100 ps in order to ensure that the measured TR-EMS data were governed by the reaction products, CO and CD<sub>3</sub>. The EMS events 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, deuterated acetone 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.

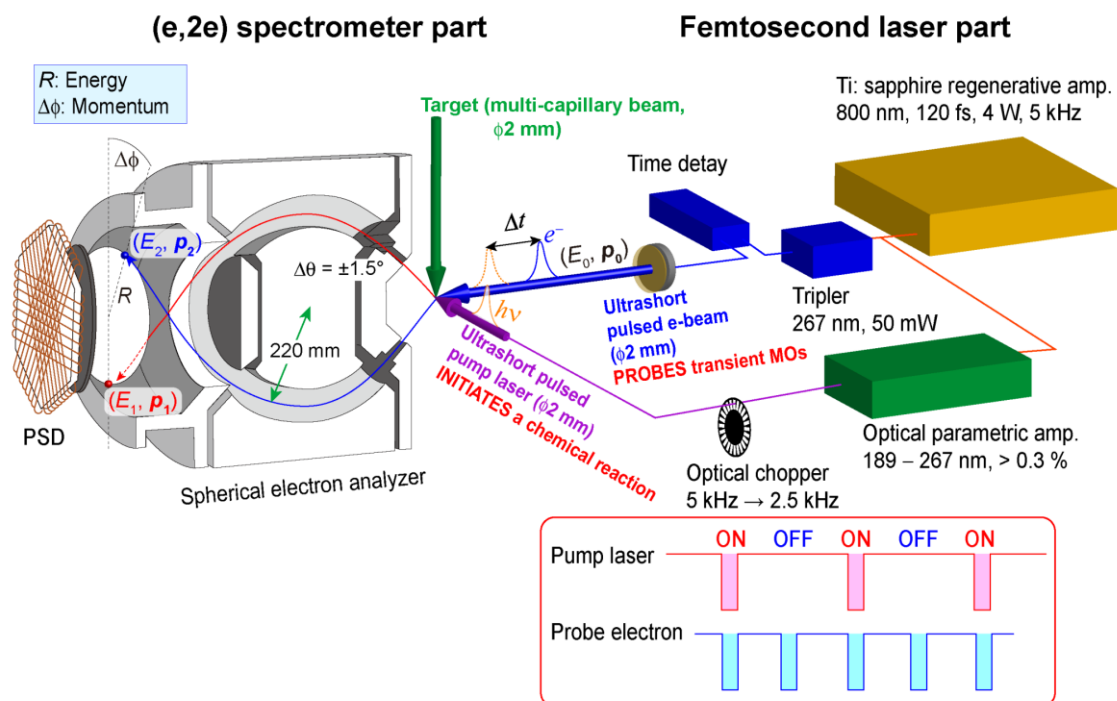


**Figure 1.** A schematic representation of time-resolved electron momentum spectroscopy apparatus. Abbreviations are: PSD for position sensitive detector,  $E_j$  and  $p_j$  ( $j = 0, 1$  and  $2$ ) for the kinetic energies and momenta of the incident, inelastically-scattered and ejected electrons, respectively.

For the EMS measurements, the symmetric noncoplanar geometry was employed (Fig. 2), 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]:

$$E_{\text{bind}} = E_0 - E_1 - E_2, \quad (1)$$

$$p = p_1 + p_2 - p_0. \quad (2)$$

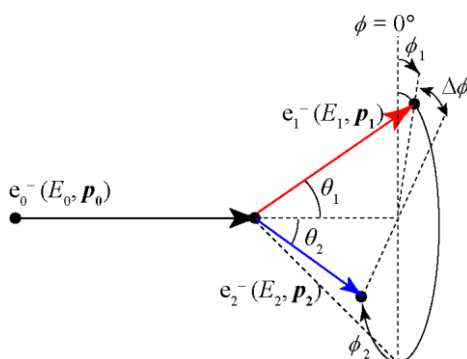


**Figure 2.** Symmetric noncoplanar geometry for the study of the binary ( $e, 2e$ ) reaction.

Here  $E_j$ 's and  $\mathbf{p}_j$ 's ( $j = 0, 1$  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

$$p = |\mathbf{p}| = \sqrt{(p_0 - \sqrt{2}p_1)^2 + (\sqrt{2}p_1 \sin(\Delta\phi/2))^2}, \quad (3)$$

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

### 3. Theoretical calculations

Within the plane wave impulse approximation, the triple differential cross section for EMS ionization is given by [1-8]

$$\sigma_{\text{EMS}} = \frac{d^3\sigma}{d\Omega_1 d\Omega_2 dE_1} = (2\pi)^4 \frac{p_1 p_2}{p_0} f_{\text{ee}} \sum_{\text{av}} M(p), \quad (4)$$

where  $f_{\text{ee}}$  is the electron-electron collision factor and  $\sum_{\text{av}}$  represents a sum over final and an average over initial degeneracies.  $M(p)$  is the structure factor and  $\sum_{\text{av}} M(p)$  represents the spherically-averaged electron momentum density or electron momentum profile. Since the currently achieved energy resolution of EMS cannot resolve vibrational structures in binding energy spectra, the structure factor to be considered is a quantity that are obtained by summing up all the contributions from each vibrational level and it can be expressed, within the harmonic oscillator approximation, as [11-13]

$$M_{i \rightarrow f}(p) = \frac{1}{4\pi} S_f(\mathbf{0}) \int |\psi_f(\mathbf{p}, \mathbf{0})|^2 d\Omega_p + \sum_L \langle \xi_{vL} | \rho_f(p, Q_L \hat{\mathbf{e}}_L) - \rho_f(p, \mathbf{0}) | \xi_{vL} \rangle. \quad (5)$$

Here,  $Q_L$  and  $\hat{\mathbf{e}}_L$  denote the displacement from the equilibrium geometry along the normal coordinate of the  $L$ -th mode and a unit vector along the coordinate, respectively.  $\psi_f(\mathbf{p}; Q)$  is the momentum space representation of the normalized Dyson orbital that is defined as the direct overlap between the  $N$ -electron initial and  $(N-1)$ -electron final ion wave functions, and  $\rho_f(p, Q)$  is the electron momentum profile at a given molecular geometry  $Q$ .  $S_f(Q)$  is spectroscopic factor that is a probability of finding one-hole configurations in the final ion state. Note that the first term of the right-hand side of Eq. (5) is the electron momentum profile at the equilibrium geometry and it is the second term that is responsible for effects of molecular vibration on the electron momentum profile through deformation of molecular orbital patterns.

Theoretical calculations associated with the experiment have been made in the following manner. Firstly, vibrational normal coordinates  $Q_L$  and frequencies  $\nu_L$  were calculated for the electronic ground state of CO and CD<sub>3</sub> at the level of the density functional theory (DFT) using the B3LYP functional [19] with the aug-cc-pVTZ basis set [20].  $\rho_f(p, Q)$ 's were then calculated at several nuclear geometries distorted from the equilibrium along each normal coordinate. In this calculation, Kohn-Sham orbitals, obtained at the same level of theory employed for  $Q_L$  and  $\nu_L$ , were used as the normalized Dyson orbitals. Here, position-space wave functions of CO and CD<sub>3</sub> were generated using the GAUSSIAN09 program [21] and they were subsequently converted to  $\rho_f(p, Q)$  with the aid of the HEMS program developed by Brion and his co-workers [22].  $S_f(Q)$ 's were obtained using the outer valence Green's function method with 6-311++G\*\* basis set, while assuming  $S_f(Q)$  to be unchanged against small changes in  $Q$ .

Secondly, to simulate experimental band intensities, all the theoretical electron momentum profiles were folded with the instrumental momentum resolution according to the procedure of Migdall *et al.* [23]. Band intensities were then calculated by integrating the momentum profiles over the entire electron momentum range covered for each ionization transition of CO and CD<sub>3</sub>.

Lastly, several  $\Delta\phi$ -angle integrated binding energy spectra were created for the CO and CD<sub>3</sub> reaction products. Two are theoretical spectra for the products at their equilibrium geometries. These two spectra were generated 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. Here, for the outer valence region, experimental binding energies for CO and CH<sub>3</sub>, reported by Fan *et al.* [24] and Dyke *et al.* [25] respectively, were taken. On the other hand, for the inner valence region, theoretical values were used, which were predicted by the symmetry-adapted cluster configuration interaction (SACCI) method [26] with the aug-cc-pVTZ basis excluding F- and D-type functions for C and D atoms, respectively. Likewise, similar theoretical spectra were created for the CO and CD<sub>3</sub> reaction products, but with vibrational effects being involved. Here, for CO, we have created a thermally-averaged spectrum by summing up each spectrum at  $v = 0, 1, 2$  with a weight ratio determined by the Boltzmann distribution having  $T_{\text{vib}}$  of 2700 K, reported by Trentelman *et al.* [16]. For CD<sub>3</sub>, we have generated spectra of the product at selected vibrational levels  $v = 0, 4, 7$ , under an assumption that the product is populated equally over all the vibrational modes.

## 4. Results and discussion

### 4.1. Theoretical binding energy spectra

Figure 3(a) shows a  $\Delta\phi$ -angle integrated binding energy spectrum generated by summing the theoretical spectra for CO and CD<sub>3</sub> at their equilibrium geometries, with a weight ratio of 1:2. Blue and green colored vertical bars indicate the band intensities for CO and CD<sub>3</sub>, calculated in the manner described in Sec. 3. Figures (b) and (c) show  $\Delta\phi$ -angle integrated spectra for CO populated at  $v = 0, 1, 2$  and CD<sub>3</sub> at  $v = 0, 4, 7$ , respectively, in which vibrational effects have been involved.

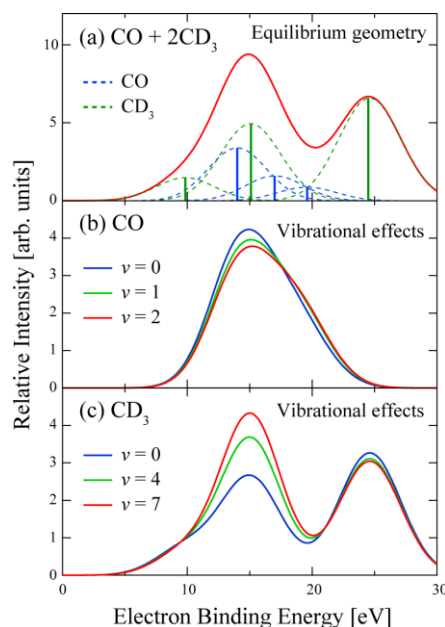


**Figure 3.**  $\Delta\phi$ -angle integrated binding energy spectra for (a) CO + 2CD<sub>3</sub> at their equilibrium geometries, and (b) CO populated at  $v = 0, 1, 2$  and (c) CD<sub>3</sub> at  $v = 0, 4, 7$ .

It can be seen from Fig. 3(a) that the poor instrumental energy resolution does not allow the spectral peaks to be identified. Only the inner valence band of CD<sub>3</sub> at around  $E_{\text{bind}} = 25$  eV, which can be attributed to ionization of the C 2s electron, is well separated from others. Figure 3(b) suggests that vibrational effects on the binding energy spectrum is small for CO. Figure 3(c) indicates, on the other hand, vibrational effects are evidently noticeable for the outer-valence region of CD<sub>3</sub>, while those in the inner-valence region is minimal.

#### 4.2. Comparison between experiment and theory

Figure 4 compares the experimental binding energy spectrum measured for the CO and CD<sub>3</sub> products with associated theoretical spectra. These theoretical spectra, labeled by  $v = 0, 4, 7$ , simulate the experiment in cases CD<sub>3</sub> is populated at  $v = 0, 4, 7$ , respectively, while CO is thermally populated over  $v = 0, 1, 2$  at  $T_{\text{vib}}$  of 2700 K. All the experimental and theoretical spectra are height-normalized at around  $E_{\text{bind}} = 25$  eV, where vibrational effects are predicted to be minimal.

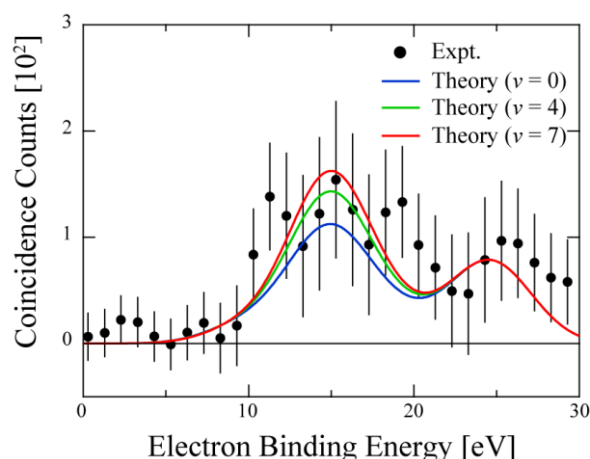


**Figure 4.** Comparison of the experiment with  $\Delta\phi$ -angle integrated binding energy spectra for CO + 2CD<sub>3</sub>. See text for the details.

It can be seen from Fig. 4 that the theoretical spectrum changes its spectral feature in the outer valence region between 10 and 20 eV, depending on the vibrational state distribution. Although it may appear that either of the  $v = 4$  and  $v = 7$  theoretical spectra reproduces the experiment more closely than the  $v = 0$  spectrum, we are not convinced that it is real as the difference in intensity between the theoretical spectra are within the experimental uncertainties. If real, it would support the result of Hall *et al.* [17] that population inversion occurs in the vibrational states of the CD<sub>3</sub> reaction product. However, poor statistics of the present experimental data make it difficult to discuss such a product vibrational analysis and hence we have to leave this issue for later experiments with improved statistics. Another promising direction for the use of TR-EMS in the product vibrational analysis would be to simulate the experiment while involving vibrational effects beyond the harmonic oscillator approximation employed here, because nonharmonic effects (anharmonicities in the vibrational potentials, couplings between vibrations and rotations, etc.) may become more significant at a higher vibrational level. Such calculations are now possible for EMS, as already demonstrated by Deleuze and others [27] who have developed a different approach that employs molecular dynamics simulation on the Born-Oppenheimer potential energy surface.

## 5. Conclusion

We have reported on the attempt to broaden the range of application of TR-EMS, through the analysis of the vibrational state distributions in the products of the photodissociation of deuterated acetone at 195 nm. The associated theoretical calculations were made for CO and CD<sub>3</sub> while vibrational effects being involved within the harmonic oscillator approximation. They have suggested that TR-EMS would be useful for the vibrational analysis of reaction products, at least to some extent, in cases when vibrational effects are large enough so as to be noticeable in the binding energy spectra. At the same time, the theoretical calculations have indicated the need of substantial improvement of experimental data, mainly in the signal-to-background ratio. Such a project to improve the apparatus and the technique of TR-EMS is now in progress.

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