Dissociative electron attachment to polyatomic molecules

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Abstract. Dissociative electron attachment (DEA) to molecule plays a key role in atmosphere, interstellar space and ionization damages of biological tissue. Experimental DEA studies of polyatomic molecules in gas phase provide the dynamics details that are the fundamentals to establish the physicochemical models of the electron-induced reactions in complicated environments. Since 2012, we successively set up two ion-velocity-map-imaging apparatuses, and accomplished a series of experimental studies of the DEA dynamics. Here is a brief review about our progresses on polyatomic molecules.

1. Introduction
Essential roles of DEA to molecule are well known during the past decades, such as the bond cleavage of the biological molecules in ionization irradiation damages [1] chemical reactions in interstellar space [2], oxygen origin in Earth’s primitive atmosphere [3]. Rich information about the DEA dynamics has been revealed by introducing the ion momentum imaging technique in the experiments [4–9]. This technique as well as its developed mode, ion velocity map imaging (VMI) [6,10], enables us to efficiently obtain the momentum distribution of the anionic product Y⁻ of the DEA to molecular XY, e⁻ + XY \rightarrow XY⁻ \rightarrow X + Y⁻.

Quantum scattering theory has been successfully applied for elucidations of the DEA dynamics of diatomic molecules [11–13], in particular, providing an analytic formula to fit the angular distributions of Y⁻ recorded using the conventional turn-table detection [14] or the ion imaging technique. Recently, coherent interferences of the intermediate CO⁻ resonant states [15–17] and interference of two DEA pathways of H₂ [18] have been reported, which enriches the basic knowledges about DEA dynamics. If the two-body dissociation of the resonant-state anion for a polyatomic molecule is fast enough, the axial-recoil approximation [11–13] is applicable to interpret the angular distribution of the anionic product [19–23]. However, the axial-recoil approximation is invalid if the anion fragment recoil axis is allowed to rotate within the dissociation time or the anion fragment is produced in a multi-stepped many-body dissociation process. Moreover, with the improvements of energy resolution, the vibrational-state resolved angular distributions challenge the current quantum scattering calculations in which the ro-vibrational states of the products are not considered explicitly [11–13].

2. Experimental developments
Full angular and kinetic energy distributions of the anionic product can be obtained simultaneously from an ion momentum image recorded with the VMI technique [6], and dynamic information about electron attachment and the resonant-state properties of the intermediate XY⁻ can be further derived. Therefore,
it is essential to record a clear momentum image. In 2012, we established an ion VMI apparatus in which the electrons were emitted from a thermal filament and had an energy spread about 0.5 eV [6]. Recently, to investigate the molecular vibrational effects, we set up a high-resolution VMI apparatus by introducing trochoidal electron monochromator (TEM). In this machine, the energy spread of the incident electrons is reduced to 100 meV or less, thus the DEA dynamics study can be achieved at the molecular vibrational state level [24].

2.1. Application of ion velocity map imaging
According to the VMI working principle [10], the ion velocity (or momentum) image has the higher signal-to-noise ratio and the better momentum resolution than those of the image recorded with the ion image technique [4]. The double (spatial and velocity) focusing conditions are prerequisite in the VMI technique [10], while that are not critical for the regular ion imaging [4]. To realize the double focusing, we should confine the reactions to happen in a volume as small as possible; in practice, the volume with a size of 2×2×2 mm³ is acceptable [6]. Without the specifically designed VMI lenses, the ion momentum image is doomed to be blurred for the larger reaction volume.

As discussed previously [16], the double focusing length is fixed in a designed VMI system, thus the time-of-flight tube cannot be arbitrarily elongated, and otherwise the momentum resolution also becomes worse. Meanwhile, the ion Newton sphere should not be distorted (compressed in the parallel or perpendicular direction) during the flight. The VMI design should be practiced carefully, to have the Newton sphere as large as possible for the central time-slicing [10]. Furthermore, a clear ion momentum image also benefits both from the narrow widths of the incident electron pulse and the time-slicing.

![Figure 1. Schematic overview of our high-resolution experimental setup.](image)

2.2. High-resolution apparatus
The TEM was used in the DEA studies several decades ago, primarily to record the production efficiency curves of the anionic yields. Overcoming the difficulties in combined usage of the TEM and VMI techniques, we successfully set up a high-resolution apparatus. An overview of the experimental arrangement is depicted in figure 1, where the key components are shown in an amplified panel. The electrons emit from a thermal filament, then they are pulsed and energetically monochromized with a homemade TEM (in which a homogenous magnetic field about 70 Gauss is produced with a pair of Helmholtz coils). This monochromator is set perpendicular to the continuous supersonic molecular beam
MB) in the horizontal (x-y) plane. A retarding field analyzer and a Faraday cup installed at the downstream of the TEM are used to determine the electron energy spread (typically about 100 meV) and monitor the current of the monochromized electrons, respectively. Each bunch of the fragment anions produced in the DEA process goes through the VMI lens system which is perpendicular to the electron (along the y axis) and molecular (along the x axis) beams (sometime an effusive MB is set below the pusher lens and along the z axis), then these anions are detected with a pair of microchannel plates (MCPs) and a phosphor screen. A charge-coupled-device (CCD) camera is used to record the images.

The voltages on the VMI lenses are optimized for various anions with different velocities. The kinetic energy resolution (ΔE/E) is about 2% for the O¯ anions with the kinetic energies less than 3.5 eV, but ΔE/E reaches 5.5% at the very low kinetic energy (0.1 eV). This is better than our previous design (ΔE/E = 5% when E ≤ 1.0 eV) [6]. In our experiments, the width of a typical time-slicing pulse applied on the rear MCP is 30 - 45 ns which is thin enough to get a clear sliced image. When this apparatus is operated under the anion mass spectrometry mode, the DC high voltages are applied on the anion detector, while the pulsed voltage height of the pusher lens is larger than that used in the VMI mode, to improve the mass resolution.

3. Recent progresses

Using the low-resolution apparatus [6], we carried out a series studies for polyatomic molecules CO2 [3,19], N2O [20], OCS [25], NF3 [22], CF4 [26], CFC13 [21] and ethanol and acetaldehyde [27]. The DEA processes to the vibrational ground-state (cold) CO2 (see figure 2) and vibrationally excited (hot) CO2 [24] were investigated with the high-resolution apparatus. The following parts are classified with the different molecules.

![Figure 2](image)

**Figure 2.** Production efficiency curves (a) and time-sliced momentum image (b) of the O¯ yield of the DEA to CO2. In (a), the present result (solid circles) is compared with that obtained by Cicman et al. [28] after renomalizations. In (b), the image is recorded at 4.55 eV, the electron incident direction (along y axis) is from top (backward) to bottom (forward) and through the image center, and the image size is scaled with the pixel numbers of the CCD camera.

### 3.1. Triatomic molecules

**CO2.** Below the electron attachment energy of 10 eV, there are two resonant states of CO2¯ related to DEA processes of CO2 [19]. Firstly, we examined the DEA of CO2, e¬ + CO2 → CO2¯ → CO + O¯, around the second resonance 3Πg state at 8.2 eV of CO2¯, and found a dynamic Renner-Teller effect on the angular distributions of the fast O¯ product [19]. The slow O¬ ions may be produced together with
CO at the high-lying vibrational states. Secondly, around the first resonance $^3\Sigma_u^+$ state at 4.4 eV of CO$_2^-$, there were arguments about the assignments to the O$^-$ production efficiency curve, namely, using the vibrational states of the intermediate CO$_2^-$ or the product CO [28]. As shown in figure 2(a), we compare the production efficiency curves and find a good agreement between ours (recorded with the high-resolution apparatus) and that by Cicman et al. [28]. Furthermore, in the O$^-$ image at the electron energy of 4.55 eV (see figure 2(b)), we find the fine structures in the forward-backward direction, namely, the outside signals correspond to CO at the vibrational state $n_v = 1$ while the inner ones are attributed to CO at $n_v = 2$ state. This image is much clearer than that reported previously [9], owing to the present higher resolution. The present assignment with CO vibrational states is in agreement with a previous conclusion [29], deserving further elucidations on its DEA dynamics.

At the electron energies around 18 eV, two DEA processes, e$^- +$ CO$_2$ $\rightarrow$ 2O + C$^-$/O$_2$ + C$^-$, could compete with each other, but the latter pathway was identified for the first time in our VMI measurements [3]. This work not only revealed the interesting DEA mechanisms but also demonstrated an important role of DEA in the origin of molecular oxygen on the planets and the early Earth [3]. The O$_2$ molecules produced in the above DEA process are populated at the high-lying vibrational states, which triggers our explorations of the molecular vibrational effects using the high-resolution apparatus.

Around the resonance $^2\Pi_u$ state of CO$_2^-$, the vibrational excitation of CO$_2$ is a competitive channel of DEA. Owing to the high cross sections and the mode selections of the CO$_2$ vibrational excitations nearby the resonant state, the high DEA cross sections are still observed below the threshold of e$^- +$ CO$_2$ $\rightarrow$ CO + O$^-$, and the angular distribution also indicates the strong dependences of the vibrational states of CO$_2$ [24]. Those are completely different from what we observed in figure 2 for the vibrational ground-state target.

N$_2$O & OCS. In the DEA process e$^- +$ N$_2$O $\rightarrow$ N$_2$ + O$^-$, we observed the evolution of momentum distributions of the O$^-$ fragment in terms of the electron attachment energy, and attributed it to a competition between two distinctly different indirect pathways, namely, climbing over and bypassing the energy ridge after the molecular structure bending. These two pathways prefer leaving the N$_2$ fragment in the high vibrational (at the higher electron energies) and rotational (at the lower electron energies) states, respectively [20]. Trimodal speed distributions of S$^-$ ion were found in e$^- +$ OCS $\rightarrow$ CO + S$^-$ in the electron attachment energy range of 6.2-7.0 eV, which arose from the different populations of the ro-vibrational states of CO fragment [25].

3.2. Other polyatomic molecules

**NF$_3$.** Dissociation dynamics of temporary NF$_3^-$ was investigated in the electron attachment energy range of 0.5 - 4.5 eV. Six pathways can be accessed in energetics, but three of them were explored. The kinetic and angular distributions of the F$^-$ yield indicated that this fragment was produced via two-body and three-body fragmentations, at the higher electron attachment energies. The anisotropic distributions of the fast F$^-$ ions arose from the two-body dissociations and was relevant to the $^2\Sigma$ resonant state of NF$_3^-$, whereas the slow ions were produced via various three-body dissociations [22].

**CF$_4$.** The DEA processes e$^- +$ CF$_4$ $\rightarrow$ CF$_3$ + F$^-$ / CF$_3^-$ + F are two complementary pathways at a common energy (5.5- 6.0 eV). Although CF$_4$ is an apolar molecule, the electron attachment prefers to proceed along the local polar C-F bond, then the impulse dissociation of CF$_4^-$ leads to the backward-distributed F$^-$ (together with the forward-distributed CF$_3$) or the forward-distributed CF$_3^-$ (together with the forward-distributed F). This spatial orientation characteristics was observed in the momentum images of F$^-$ and CF$_3^-$ anionic yields [26].

**CFCl$_3$.** The momentum images of the F$^-$ ions produced in e$^- +$ CFCl$_3$ $\rightarrow$ CCl$_3$ + F$^-$ indicated image pattern evolutions with the electron attachment energy in a range of 2.0–7.0 eV. The angular and kinetic energy distributions of this anion were interpreted with two shape-resonant states of CFCl$_3^-$, while the F$^-$ ions with the lower kinetic energies at higher attachment energies could be produced via three-body dissociations or due to the co-production of CCl$_3$ at an electronically excited state (A*) [21].

**Ethanol (CH$_3$CH$_2$OH) & Acetaldehyde (CH$_3$CHO).** In the DEA processes, the dominant anionic fragments were O$^-$ and OH$^-$ ions for ethanol while O$^-$ and CH$_3^-$ ions for acetaldehyde. Interestingly,
we found that the O¯ production in the DEA to ethanol was achieved via a cascade process, namely, experiencing the intermediate species (CH3CHO)¯ formed by the double dehydrogenations [27]. This is quite similar to the alcohol dehydrogenases in human body.

3.3. Theoretical simulations
Since it is still a challenge in theory to describe the nuclear motions and internal energy disposals of the molecular anion prior to the dissociation, we developed a theoretical simulation strategy. Although most processes do not start in the lowest anionic state, the applicability of our method is based on the following assumptions: the DEA dynamic evolution finally undergoes on the potential energy surface of the lowest anionic state, if the ground-state fragments are produced in the asymptotic region; the coupling between the high and lowest anionic states is accomplished quickly after the vertical electron attachment. The DEA processes of N2O [20], ethanol [27] and dialanine [30] have been qualitatively interpreted well, using our molecular dynamics simulations.

The computations with sophisticated quantum scattering methods are time-consuming, and the convergence is frequently problematic for the anionic resonant states of polyatomic molecules. We utilized a simplified quantum scattering method, the single-center expansion potential scattering, to study the shape resonant states formed in the electron attachments to cysteine and cystine. We found that the resonant states showed the novel selectivity in the bond cleavages, and the S–S bond cleavage of cystine anion was highly favored [31].

4. Remarks
During the past decades, different groups including ours made a lot of efforts to explore the DEA dynamics. There are some long-standing arguments about the spectral assignments of the anionic production efficiency curve, namely, using the vibrational states of the neutral target XY, the resonant-state XY¯ or the polyatomic fragment X (or Y¯). Owing to the combination between VMI and TEM techniques, we can observe the molecular vibrational effects, not only of the products (as shown in figure 2(b)) but also the target molecules [24]. Further theoretical developments to reveal the nuclear motions induced by electron attachment are highly demanded.

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