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Short communication

Dissociative electron attachment to ozone at very low energies revisited

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Abstract

The formation of O^- and $O_2{}^-$ following electron impact to O_3 in the energy range between 0 and 3 eV is revisited using a newly designed trochoidal electron monochromator. The previous observation of a very sharp peak in the O^- ion yield at an energy close to zero eV [Phys. Rev. Letters 82 (1999) 5028] is interpreted as an artefact due to multiple reflection of very low energy electrons in the collision chamber of the spectrometer.

Keywords: Electron attachment; Ozone; Negative ion; Dissociative electron attachment

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Ozone is an important constituent in the atmosphere preventing the UV (B) part of the solar spectrum to reach the earth's surface [1]. Low energy electron impact to O_3 has attracted considerable attention within the last decades in order to unravel the chemical reactions behind the loss of ozone in the stratosphere and the phenomenon of the ozone hole in the Antarctica [2,3].

Dissociative electron attachment (DEA) to ozone has been studied by several groups [4–9] mostly by means of beam experiments. Under single collision conditions, the fragments O^- and $O_2{}^-$ are formed within two intense low energy DEA resonances peaking near 1.0 and 1.2 eV, respectively, with O^- as the dominant channel [9]. The corresponding reactions can be expressed as

$$e^- + O_3 \rightarrow O_3{}^{-\#} \rightarrow O^- + O_2 \qquad (1)$$

$$e^- + O_3 \rightarrow O_3{}^{-\#} \rightarrow O_2{}^- + O \qquad (2)$$

where $O_3{}^{-\#}$ assigns the transient negative ion formed upon a Franck-Condon transition. Based on the well-established bond dissociation energies ($D(O\text{–}O_2) = 1.05 \pm 0.02$ eV [10], $D(O\text{–}O) = 5.17$ eV [11]) and the accurately known electron affinities $EA(O^-) = 1.46$ eV, $EA(O_2{}^-) = 0.44$ eV [11] reaction (1) becomes exothermic by −0.41 eV and reaction (2) endothermic by 0.61 eV.

At higher pressure (beyond single collision conditions) the parent negative ion $O_3{}^-$ is additionally observed at low impact energies with a resonance profile resembling that of the dominant DEA product O^- [5]. $O_3{}^-$ is formed by collisional stabilisation of the transient anion. The adiabatic electron affinity of ozone is 2.108 eV [12].

In a recent high resolution experiment a very narrow but intense resonance close to zero eV was observed on the O^- channel [8]. From its relatively large intensity (approximately four times of that of the 1.2 eV peak at an electron energy resolution of 30 meV) it was suggested that this phenomenon might have important consequences for the role of DEA in commercial ozonisers and the role of ozone in the ionosphere. This result, however, could not be confirmed by a later study measuring the thermal rate coefficient for electron attachment to ozone by means of the FALP (flowing afterglow Langmuir probe) method [13].

In the present contribution we revisit DEA to ozone using a newly constructed trochoidal electron monochromator (TEM) taking advantage of an extended analysis of its operational principle [14].

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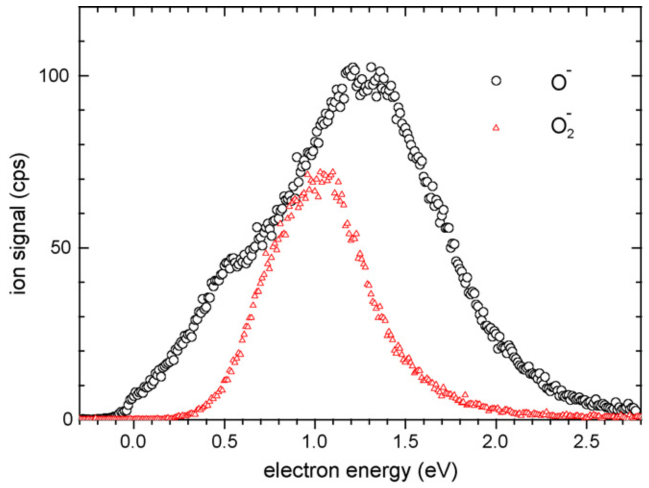

Fig. 1. Ion yields for O_2^- and O^- formation observed with the new instrument at an energy resolution of 45 meV.

Fig. 1 shows the ion yields obtained at an energy resolution of 45 meV indicating that no sharp peak close to zero eV could be observed with this new device. The present results are in excellent agreement with an earlier high resolution beam experiment by Allan and coworkers [5]. In order to search for an explanation for the previous observation of the zero eV peak we compare the two devices and analyse the electron trajectories in the collision chamber. Fig. 2 presents a comparison between the previous monochromator and the newly designed instrument. Apart from a series of modifications which are extensively described in Ref. [14], the new instrument uses a larger exit hole for the electron beam leaving the collision region CC (1 mm instead of 0.5 mm). The analysis (below) shows that in the case of the previous monochromator at very low collision energies electrons may no longer be transmitted through the exit aperture, but be reflected at the exit electrode which can cause an enhanced signal below a particular critical electron energy ε_c. For the analysis we briefly recall some basics for the operation of the TEM.

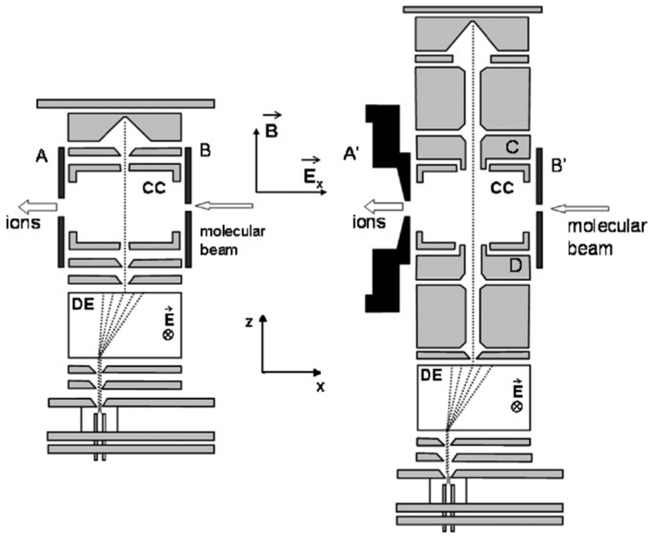

Fig. 2. Schematic of the old monochromator (left) and the newly constructed instrument (right), see the text.

In the instrument a magnetic field is used to guide the electron beam. Energy selection of the electrons emitting from a hot filament is achieved by the application of a homogeneous electric field perpendicular to the magnetic field defining the dispersive element (DE). The electric field is established by two parallel plates along the paper plane in Fig. 2. Under the influence of the combined electric (E) and magnetic field (B) the electrons describe a *trochoidal* or *cycloidal* motion (depending on the injection conditions into the crossed field region) associated with a motion of its guiding centre with the constant velocity along the x-direction given by

$$v_x = \frac{E}{B} \tag{3}$$

This results in a deflection of the electrons according to their z-velocity component and hence a spacial dispersion according to their energy. As a result, only electrons within a particular energy window will be transmitted through the exit hole (displaced with respect to the entrance hole). These energy selected electrons will subsequently be transferred to the collision chamber (after acceleration/deceleration) to the appropriate collision energy (ε).

Accordingly, once the electrons enter the collision chamber (CC) they are subjected to an ion draw out field E now oriented along the x-direction. This results (like in the dispersive element) in a superimposed constant drift of the electrons, now along the y-direction. Note that the electrons drift along a plane of constant electric potential, i.e., application of an extraction field does not affect the electron energy and (in a first approximation) the energy resolution. For that reason a TEM can be operated in a continuous mode instead of pulsing the electron beam and the ion draw out field as frequently applied in electrostatic beam devices.

This deflection along a plane of constant electrical potential, on the other hand, results in a situation that at sufficiently low electron energy (dependent on the strength of the ion extraction field and the magnetic field), the beam will no longer be transmitted through the exit aperture. Instead, reflection at the exit electrode (eventually followed by multiple reflections between entrance and exit electrode within the collision chamber) can occur resulting in an enhancement of the signal below that critical energy. The electron reflection coefficient at a metal surface is a delicate problem which strongly depends on the surface covering and the presence of charges at the surface. For iron we find an electron reflection coefficient of 66% [15] which may also apply for non-magnetic stainless steel, the material from which the previous TEM was machined. For electrons at very low energies, however, reflection from the surface is easily possible even by moderately charged surfaces resulting in multiple reflections.

The critical electron energy (ε_c) below which the beam is no longer transmitted through the exit aperture can be expressed as

$$\varepsilon_c = \frac{m}{2}\left(\frac{l}{B}\right)^2\left(\frac{E}{R}\right)^2 \tag{4}$$

where m is the mass of the electron, l the length of the collision chamber, E the ion extraction field and R is the radius of the exit hole. This equation is easily rationalised by comparing the time an electron of energy ε takes to cross the distance l of the col-

Table 1
Critical electron energy (ε_c) below which the electron beam is no longer transmitted through the exit aperture of the collision chamber calculated for different extraction fields

Extraction field E (V/cm)	ε_c (meV) new TEM $R = 1$ mm	ε_c (meV) old TEM $R = 0.5$ mm
0.1	1.1	4.6
0.3	10.3	41
0.5	28.5	114
1.0	114	456

lision chamber ($l/(m/2\varepsilon)^{1/2}$) and the additional (perpendicular) distance it travels during that time due to the superimposed drift velocity along the y-direction given by Eq. (3).

In both the old and new device the magnetic field was kept at 5 mT while the extraction field was varied between 0.1 and 1 V/cm. From the numerical evaluation of Eq. (4) one obtains

$$\varepsilon_c\,(\text{meV}) = 114\left(\frac{E}{R}\right)^2$$

when E is expressed in V/cm and R in mm.

Table 1 presents a few values for the old and new device illustrating that in the new device reflection is limited to a very narrow energy range.

The *zero eV* peak on the exothermic channel (1) can then be understood as ion intensity arising from multiple reflected electrons. Since the intensity of the O^- signal is non-zero close to threshold, multiple reflected ions can increase this signal. In the case of a larger exit hole the critical energy is significantly reduced and for a given energy resolution, the overall electron intensity in the critical region may then be neglected. We hence conclude that the narrow peak observed on the O^- signal with the old TEM was an artefact due to multiply reflected electrons at very low energies.

It should finally be mentioned that recording processes directly in the threshold region is experimentally an extremely challenging problem as very small disturbances like field inhomogeneities, or surface charging, etc. can have dramatic effects on the intensity of the electrons present in the collision zone.

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