# Low Energy Dissociative Electron Attachment to Ozone

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The production of $O^-$ and $O_2^-$ by dissociative electron attachment to ozone is reported for incident electron energies between 0 and 10 eV. A previously unobserved sharp structure is observed in the formation of $O^-$ ions at zero incident energy. This large additional cross section peak has important consequences for the role of ozone in the anion formation processes in the ionosphere. [S0031-9007(99)09373-4]

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The discovery of the "ozone hole" above Antarctica by Farmer and co-workers in 1985 has led to a major international research program to study the chemical reactions of ozone responsible for such dramatic ozone loss [1]. The catalytic destruction of ozone by halogen free radicals is now largely understood, and the major mechanisms by which ozone is destroyed in the stratosphere have been identified [2]. The role of ozone in the $D$ region in the ionosphere is, however, less well established. The physics and chemistry of the $D$ layer of the ionosphere are dominated by ion-molecule reactions and, in particular, by the formation rates of $CO_3^-$, $HCO_3^-$, and $NO_3^-$ anions [3]. Current models of the $D$ layer [3] assume that the major negative ion formation process in this region arises from the exothermic nondissociative three-body electron attachment to molecular oxygen [4], i.e.,

$$e + O_2 + O_2 \rightarrow O_2^- + O_2, \qquad (1)$$
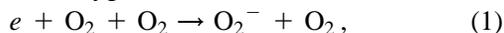
with $CO_3^-$, $HCO_3^-$, and $NO_3^-$ anions being formed subsequently in a complicated sequence of reactions involving neutral constituents [5]. The dissociative electron attachment reaction to molecular oxygen is not considered in these models since the cross section is significant only at electron energies above about 4 eV [6].

Conversely, electron impact dissociative attachment to ozone may also form significant concentrations of oxygen anions at about thermal energies. Two possible dissociative attachment channels first observed by Curran [7] exist,

$$e + O_3 \rightarrow O^- + O_2, \qquad (2a)$$

$$e + O_3 \rightarrow O + O_2^-. \qquad (2b)$$
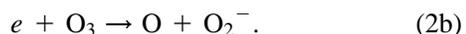
The product oxygen anions may then be subsequently lost either by associative detachment with atomic or molecular oxygen or by charge transfer reactions with ozone. The $O_3^-$ anions produced in these charge transfer reactions may then undergo further reactions with H, $CO_2$, and $NO_2$ to form $HCO_3^-$, $CO_3^-$, or $NO_3^-$. Current ionospheric models [3] have used the rate coefficients estimated from the early experiments of Curran [7] and Stelman *et al.* [8] (see also [9]) to compare the anion formation rate from electron attachment to ozone via the exothermic reaction (2a) with the three-body attachment to molecular oxygen via reaction (1). They concluded that the electron

attachment process (2a) is only a minor contribution to the total oxygen anion production. Nevertheless, several groups [10–14] have recently reported new results on the mechanism of dissociative electron attachment to ozone and ozone clusters [15] which suggest that the role of dissociative electron attachment to ozone in the ionosphere should be reevaluated.

Similarly the role of low energy electron attachment in those electrical discharges used to produce ozone in commercial apparatus (so-called "ozonizers") should be reappraised. Ozonizers are remarkably inefficient instruments producing only a few percent (often less than 1%) of the required product. Models of such electrical discharges have suggested that the product yield should be much greater [16–18] but, to date, it has not been possible to obtain such calculated yields. Low energy electron attachment may provide a mechanism for the destruction of nascent ozone within the discharge, since there is a preponderance of low energy electrons in such discharges, and therefore explain the low yields achieved by such devices.

It is therefore important to study low energy dissociative electron attachment to ozone and quantify the magnitude of the cross section for the formation of both $O^-$ and $O_2^-$ anions. As part of a continued investigation of electron scattering studies from aeronomic molecules we have therefore reinvestigated low energy dissociative electron attachment to ozone. In particular, we have studied those processes leading to the dissociation of ozone at low energies (less than 2 eV) with high energy resolution. In this Letter we report, for the first time, the presence of a large peak close to zero eV in the formation cross section for $O^-$ anions via reaction (2a). The large measured cross section for the formation of $O^-$ anions at such thermal energies suggests that, in contrast to present assumptions, the production of oxygen anions by electron attachment to ozone via reaction (2a) is a major anion formation process in the $D$ layer and not three-body electron attachment reaction (1) to molecular oxygen.

The high resolution trochoidal electron spectrometer used in these studies has been described previously [19,20] allowing one, in principle, to produce electron beams with a resolution of better than 5 meV FWHM. The attachment

reaction occurs in a small collision chamber from which the anions are extracted by a weak electric field into a quadrupole mass spectrometer. The mass-selected ions are detected in a single-ion pulse counting mode using a channeltron. Data acquisition during the measurements was controlled by a personal computer. The electron energy scale and electron energy spread are calibrated and determined throughout the experiment using $CCl_4$ and $SF_6$ as test gases (for details, see [20]).

Because of the high reactivity of ozone on surfaces and in order to quantify any charge transfer processes or ion-molecule reactions (which may result in erroneous signals being recorded), two ozone samples were used of greatly different purities. High purity sources of ozone (>80%) were prepared using a mobile ozone generator [21] in which low concentrations of ozone were produced using a commercial Fischer ozonizer prior to being collected on silica gel cooled to $-80\,°C$. Subsequent desorption from the silica gel allowed high purity samples of ozone to be collected in a five liter glass bulb prior to insertion into the electron spectrometer. Low concentrations of ozone ($\approx 1\%$) were produced with a negative corona discharge ozonizer, with the effluent being passed directly into the spectrometer without further purification. The cross sections for anion production from ozone were found to be independent of the ozone concentration, production method of ozone, and the geometry and construction materials of the gas inlet system.

Figure 1(a) shows the measured $O^-$ anion cross section as a function of incident electron energy in the low energy region up to 2 eV. A broad peak centered at 1.3 eV
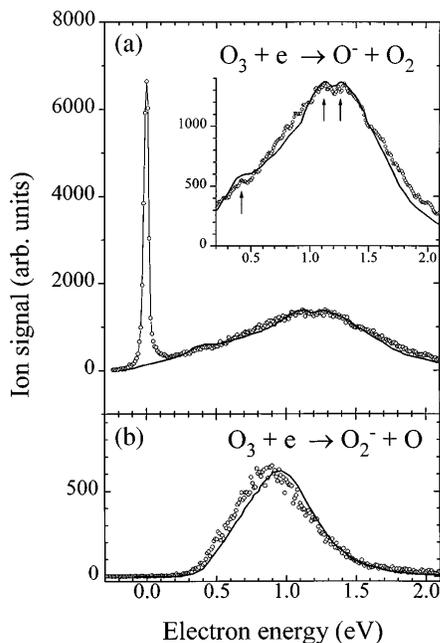
is observed in excellent agreement with the earlier high resolution data of Allan et al. [11] and those of other recent experiments [10,12,14], not shown in Fig. 1(a) for the sake of clarity. Fine (vibrational) structure is observed [see inset in Fig. 1(a)] superimposed upon the peak in close agreement with [11] and has been used to renormalize the energy scale of Allan et al. (a shift of 20 meV). This structure [arrows in Fig. 1(a)] has been attributed to the opening of dissociation channels with a vibrationally excited $O_2$ fragment [11]. However, evidence for dissociative excited states of $O_3^-$ in this energy range has also been reported in laser photodissociation studies [22], and thus this structure could arise from complex curve crossings between the $O_3^-$ anion and $O_3$ ground state of the neutral molecule. Figure 1(b) shows the measured $O_2^-$ anion yield as a function of incident energy. A single structureless peak is observed peaking around 1 eV, in excellent agreement with the data of Allan et al. [11] and other recent experiments [10,12,14], not shown in Fig. 1(b) for the sake of clarity.

Figure 2 compares the present $O^-/O_3$ cross section curve with the cross section of Allan et al. [11] (normalized to Skalny et al. [10]) and the recent absolute results of Rangwala et al. [14] in the energy range up to 10 eV. The present cross sections are in good agreement for energies less than 1.3 eV but are lower than those of [14] at the high energy side of this peak (see inset in Fig. 2). This difference may be ascribed to the observation by Rangwala et al. [14] of a high energy shoulder between 2 and 4 eV. Allan et al. [11] and Walker et al. [12] have shown that $O^-$ anions arising from the resonant region between 2 and 4 eV have high kinetic energies. This will lead to a loss of these ions in the present study, because our apparatus is optimized for the detection of near zero energy anions with high energy resolution by using a near zero extraction field [20,23]. Rangwala et al. [14], in contrast, are able to apply higher



FIG. 1. Upper part $O^-$ cross section for dissociative electron attachment to ozone and lower part $O_2^-$ cross section for dissociative electron attachment to ozone: open circles, present results; solid line, data by Allan et al. [11]. Inset, see text.
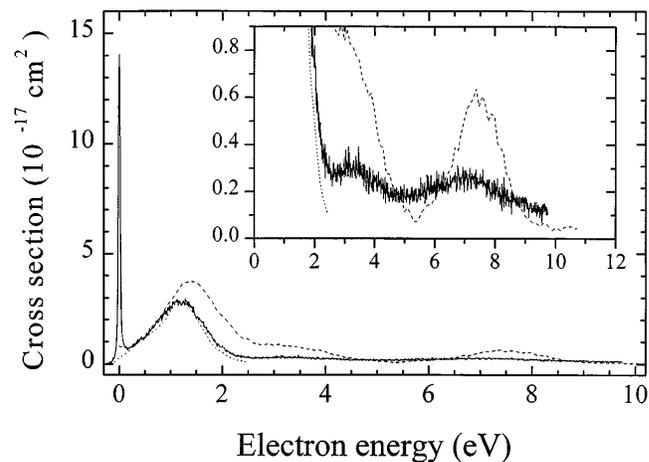


FIG. 2. Comparison of present results (solid line) for $O^-$ cross section for dissociative electron attachment to $O_3$ with those of Allan et al. [11] designated by dotted line and those of Rangwala et al. [14] designated by dashed line.

extraction fields preventing such kinetic discrimination and therefore provide a more realistic measure of the absolute yield of those anions produced with high kinetic energies. Similarly between 6 and 8 eV the $O^-$ anions are produced with high kinetic energies and are therefore partially lost to our detector but are observed by Rangwala *et al.* [14].

The major observation in the present results is that in contrast to the earlier measurements we observe (see Fig. 1 upper part and Fig. 2), a rather large and sharp peak in the $O^-$ cross section at or close to zero energy. Observation of this unexpected "zero energy" peak (see Fig. 3) is dependent upon the incident electron energy resolution as determined from the half width at full maximum of this sharp peak; see below. At apparent resolutions in excess of 100 meV the feature is broadened such that it can no longer be distinguished from the background. Therefore it is not surprising that those earlier experiments having electron beam resolutions of more than 100 meV were unable to observe this structure. Only Allan *et al.* [11] has similar nominal resolution to the present work (with typical resolutions used of 30 meV) but did not report this feature. We were therefore extremely careful to check the present apparatus for any experimental artifacts that could give rise to such a structure. The nonobservation of any such structure in the simultaneously recorded $O_2^-$ cross section [Fig. 1(b)] and the absence of such structure in studies on, for instance, NO [23] and $N_2O$ [24] excluded any apparatus artifact. In order to probe any interfering ion-molecule or surface interaction the experiment was repeated over the course of several months with ozone sources of greatly different purities and with different gas inlet systems [25]. In each case the observation of this feature was found to be solely a function of the actual incident electron beam resolution (as determined by the width of this feature in ozone). It should be mentioned, moreover, that we have observed a strong deterioration of the energy resolution (of

about more than a factor of 2) when changing from $CCl_4$ (used in each experimental run first as test gas to determine the nominal resolution of the monochromator via the width of the $Cl^-$ zero energy peak [20]) to ozone. This is a likely explanation for the nonobservation in previous studies.

Therefore we believe the new structure observed here in the $O^-$ cross section for electron attachment to ozone at zero energy is correct. Furthermore a plot of the cross section against the incident electron energy on a log/log scale, Fig. 4, reasonably follows the $E^{-1}$ behavior predicted by the de Broglie $s$-wave cross section [26]. Such an $s$-wave mechanism is found for several molecules and clusters that capture free electrons at low energies (e.g., $SF_6$ [27,28], $CCl_4$ [20,29], $O_2$ clusters [19], and NO cluster [30]), and there it is not perhaps surprising that ozone should show a similar behavior. However, $s$-wave attachment to the ground state of ozone is forbidden by symmetry rules and therefore such an observation may be attributed to electron attachment to vibrationally excited ozone. The deviation from $E^{-1}$ behavior below 30 meV is due to the finite resolution (approximately 40 meV) in the experimental run shown in Fig. 4 of the electron beam. In turn such a low energy $s$-wave cross section behavior can be used to estimate the electron energy distribution from the width of the zero energy peak (for details, see [20]). This has enabled us (see above) to obtain the important information that the resolution of the trochoidal monochromator is strongly decreased when studying ozone.

The present results have some significant consequences for the role of direct electron impact dissociative excitation of ozone within the $D$ layer of the ionosphere and in commercial ozonizers. At present the production of anions by electron attachment to ozone is neglected in the ionospheric models [3] as it was thought to be only a minor contribution to the total anion production compared
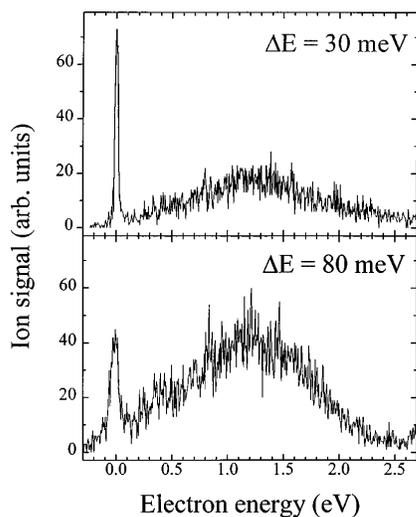


FIG. 3. The $O^-$ cross section (arb. units) for dissociative electron attachment to ozone measured at the two electron energy resolutions of 30 and 80 meV.
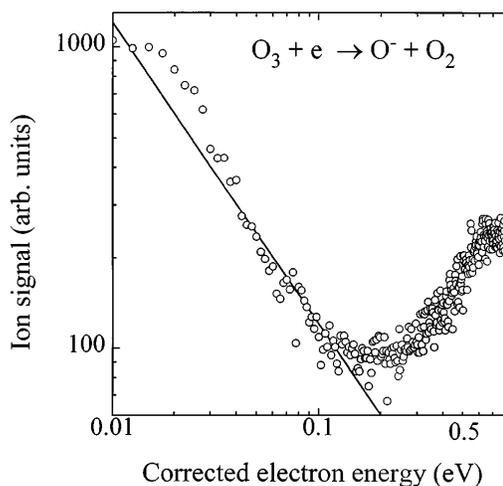


FIG. 4. A logarithmic plot of the present $O^-$ yield (open circles) against electron energy. At low energies the cross section shows de Broglie $s$-wave character [26], i.e., the cross section is proportional to $E^{-1}$ (designated by solid line).

to the three-body attachment reaction (1). If, however, the present cross sections for the production of $O^-$ are converted to rate constants (taking into account that these constants usually refer to thermodynamic equilibrium, while in the present case the internal energy of the target is unknown), the dissociative attachment reaction to ozone becomes a major formation process for $O^-$ ions in the $D$ layer of the ionosphere. In addition, there are also important consequences of such a large dissociative attachment rate constant for the production of ozone in negative corona discharges in commercial ozonizers. Such discharges have a large flux of low energy electrons ($<1$ eV). Should the cross section for electron dissociative attachment be large, it is possible that a sizable proportion of the nascent ozone formed in the discharge region is subsequently destroyed by electron collisions, thus producing the low yields obtained from such devices. Hence to increase the yield of ozone it would be necessary to broaden the electron distribution within the discharge and/or reduce the number of low energy electrons.

In conclusion, using a high resolution electron monochromator to study electron attachment cross sections to ozone, we have been able to observe, for the first time, an additional sharp peak in $O^-$ formation close to zero incident energy. Present measurements suggest that the production cross section for $O^-$ from $O_3$ at about zero energy is approximately 4 times that of the 1.2 eV peak and since it is resolution dependent it may, in fact, be even greater. This may have important consequences for the interpretation of the role of dissociative attachment to ozone in commercial ozonizers and in the ionosphere.

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