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## ELECTRON ATTACHMENT TO MOLECULES AND CLUSTERS OF ATMOSPHERIC RELEVANCE : OXYGEN AND OZONE<sup>#</sup>

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**Abstract:** Highly monochromatized electrons are used in a crossed beams experiment to investigate electron attachment to oxygen clusters  $(O_2)_n$  at electron energies from approximately zero eV up to 2 eV. At energies close to zero the attachment cross section for the reaction  $(O_2)_n + e \rightarrow O_2^-$  varies inversely with the electron energy, indicative of s-wave electron capture to  $(O_2)_n$ . Peaks in the attachment cross section present at higher energies can be ascribed to vibrational levels of the oxygen anion. The vibrational spacings observed can be quantitatively accounted for. In addition electron attachment to ozone and mixed oxygen/ozone clusters has been studied in the energy range up to 4 eV. Absolute attachment cross sections for both fragment ions anions,  $O^-$  and  $O_2^-$ , from ozone could be deduced. Moreover, despite the initially large excess of oxygen molecules in the neutral oxygen/ozone clusters the dominant attachment products are undissociated cluster ions  $(O_3)_m^-$  including the  $O_3^-$  monomer while oxygen cluster ions  $(O_2)_n^-$  appear with comparatively low intensity.

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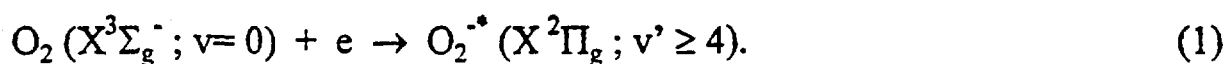
## Introduction

Electron attachment studies are of fundamental importance to the understanding of electron-molecular interactions and the mechanisms of negative ion formation [1,2]. In addition these studies are of practical value for the design of industrial gas discharge devices (such as high voltage switches, refrigerators, plastic foam and propellant gas production) [3] and for the elucidation of atmospheric processes [4,5]. For instance the atmospheric abundance of chlorofluorocarbon (CFC) gases has been growing rapidly in the past decades due to human activities and it has been recognized that CFC gases are involved on the one hand in the destruction of the ozone in the lower stratosphere and on the other hand may be efficient green house gases [6]. Besides this catalytic destruction, ozone is also subject to dissociation by photons and electrons. Whereas under stratospheric conditions dissociation of ozone is initiated predominantly by photons, in the D-region of the ionosphere (and also in gas discharges) electron attachment plays an important role in dissociating  $O_3$  [5,7]. The ensuing fragment anions  $O^-$  and  $O_2^-$  thus produced are either lost by associative attachment with atomic or molecular oxygen or in charge transfer reactions with ozone (note that these primary anions may be also produced via interaction of electrons with oxygen and oxygen clusters). The ozone anion produced is then lost in further reactions leading to the formation of the most important atmospheric negative ions  $NO_2^-$ ,  $NO_3^-$  and  $CO_2^-$  [5].

The recognition of the importance of ozone in the stratosphere in reducing biologically harmful UV radiation that would otherwise reach the earth's surface, has attracted great scientific attention and led to many studies concerning the physics and chemistry of these reactions [6]. As electron attachment and the properties of the anions produced are involved in these processes we have studied the attachment cross sections of some of the these

molecules and their respective clusters using a recently developed high resolution electron monochromator (with an energy spread of a slow as about 5 meV [8,9]). In particular, we will summarize here results concerning ozone, oxygen clusters and mixed oxygen/ozone clusters (for more details see also Ref. [10-13]). For results concerning some of the CFC gases see Ref. [9,14-16].

Electron attachment to a single ground state oxygen molecule proceeds in the energy range from 4.4 to 10 eV via a dissociative channel, whereas at low energies (below 1eV) attachment to O<sub>2</sub> (which has a positive adiabatic electron affinity of EA = 0.440 ± 0.008 eV [4]) results in a non-dissociative resonance process [17,18]



Because the bond length of the neutral molecule is much smaller than for the anion [19] and O<sub>2</sub> has a positive EA, the incoming electron cannot induce a Franck-Condon transition to the ground state of the anion. Instead only vertical transitions to the fourth and higher vibrational levels are possible, the fourth vibrational level lying about 90 meV above the first vibrational level of the neutral [20]. The molecular anion formed via reaction (1) is unstable with a predicted [21] lifetime towards autodetachment of about 10<sup>-10</sup> s. In a high pressure environment this anion can be stabilized collisionally to a vibrational level v' < 4 which lies below the v = 0 level of the neutral thereby making autodetachment impossible. According to Spence and Schulz [17] and McCorkle et al. [18] the „effective“ cross section for this „three-body attachment“ process (proceeding via the low-lying <sup>2</sup>Π<sub>g</sub> compound state) shows pronounced structure with energy coinciding with the positions of the vibrational states of the O<sub>2</sub><sup>-</sup> compound state with v' ≥ 4. Recently, electron attachment to oxygen clusters was studied in crossed beams experiments

showing at low energies a broad „zero energy“ peak for the production of  $O_2^-$  and higher homologues, i.e., the stoichiometric  $(O_2)_n^-$  anions [22,23] (the production of non-stoichiometric cluster anions was found to closely follow the energy dependence of the  $O^-$  production from the monomer). The position of this zero energy resonance was reported in the earlier measurements (using electron beams with an energy distribution of 0.5 eV FWHM) to lie close to 0 eV [22], whereas in the later experiments using an electron monochromator with a 0.2 eV FWHM the maximum was found to lie at around 0.7 eV [23] (it is conceivable that this difference could be due to a distinctly smaller average cluster size in the later experiment, see below). As no anions have been observed previously in electron/ $O_2$  crossed beam experiments under single collision conditions at these low energies the question remained (besides the observed discrepancy in the peak position) what is the exact attachment mechanism leading to the production of these ions at thermal energies - an attachment reaction of importance in low temperature and high pressure swarm experiments [2].

The dissociation of ozone by photon impact is well known and has been studied in detail [24]. Conversely, there exist only few experimental studies at present time [25], dealing with the interaction of electrons with ozone, in particular concerning the dissociative attachment of electrons by ozone. This lack of experimental data is very likely due to the chemical activity of ozone in contact with metal and other surfaces which makes it difficult to control the ozone concentration of neutral  $O_3$  targets.

The existence of two dissociative attachment channels





was first observed by Curran [26] using an ion source (equipped to use the RPD method to improve the energy resolution of electron beam) in conjunction with a mass spectrometer. Due to single collision conditions in the ion source it is clear that these ions can only be produced by reaction (2) and (3) and not by any other secondary reactions (see below), reaction (2) being exothermic by 0.43 eV and reaction (3) being endothermic [27]. Relative attachment cross section have been measured by Curran [26] with an electron distribution of 0.2 eV FWHM from zero up to about 3 eV and from these curves appearance energies for the  $\text{O}^-$  and  $\text{O}_2^-$  production via reaction (2) and (3) of about 0 eV and 0.42 eV have been deduced. Moreover a very crude estimate of the absolute cross sections, given by the author, is that they lie in the region of  $10^{-18}$  and  $10^{-17}$   $\text{cm}^2$  which is in line with unpublished results of Chantry and Phelps [28]. Later data concerning the dissociative attachment of electrons to ozone studied by swarm techniques have been reviewed by Phelps [29], Caledonia [27] and Massey [30]. In all of these studies, rate coefficients  $k$  [ $\text{cm}^3 \text{s}^{-1}$ ] or attachment coefficients  $\eta = k/v_d$  [ $\text{cm}^{-1}$ ] (usually normalised to the ozone density  $n(\text{O}_3)$  [ $\text{cm}^{-3}$ ],  $\eta' = \eta/n(\text{O}_3)$  [ $\text{cm}^2$ ]) for dissociative attachment of electrons via processes (1) and/or (2) were measured and reported. Because of the lack of absolute cross section data and the lack of reliable reaction rate coefficients at higher electron energies new studies have been performed using a negative corona discharge ozonizer for the production of the ozone target [10]. In addition first studies on negative ion formation following electron interaction with a beam of clusters containing oxygen and ozone molecules has been carried out and will be presented here.

## Experimental

In principle free electron attachment can be investigated either by swarm techniques yielding information on the attachment rate constant  $k$  as a function of electron and/or gas temperature or by crossed beam experiments yielding information on the attachment cross section  $\sigma$  as a function of electron energy and gas temperature. Recently we have drastically improved the energy resolution (down to below 10 meV at electron currents in the order of nA) to be achieved in a crossed beams experiment consisting of a molecular beam and using a trochoidal monochromator (TEM) as the primary electron beam source [8,9,31]. The working principle of the trochoidal monochromator is shown in Fig.1 Electrons emitted from a tungsten filament are collimated by electrodes and aligned in the x-direction by a homogeneous magnetic field produced with a pair of Helmholtz coils situated outside of the vacuum chamber. In the dispersion region consisting of a crossed magnetic (x-direction) and electric (y-direction) field the electrons move in trochoidal trajectories. This leads to a dispersion of the electrons in z-direction according to their velocities in x-direction thus allowing to select a small part of this distribution with an exit orifice. Only this selected part of the original (thermal) electron distribution is then accelerated to the final collision energy and interacts with the neutral target beam in the ion source. In combination with either a temperature controlled effusive molecular beam source or a supersonic nozzle expansion molecular beam source and a quadrupole mass spectrometer for analysis of the anions produced, electron attachment spectra can be measured as a function of electron energy and beam properties such as gas temperature and target composition (for more details see Ref. [8,9,16]). The necessary absolute calibration of the energy scale, the characterization of the achieved electron energy distribution in terms of its FWHM, and the demonstration of the correct gas density dependence on the gas temperature in the molecular beam has been carried out using  $\text{CCl}_4$  and

$\text{SF}_6$  as test cases [8,9,16]. From the electron attachment spectra thus obtained information on the energetics (activation barriers from Arrhenius plots, solvation effects in clusters), on the kinetics (shape and magnitude of cross section functions) and on the underlying capture mechanisms (e.g., s-wave scattering, p-wave scattering, vibrational excitation) can be obtained.

Moreover, the ozone necessary in the present study has been generated by passing oxygen through a negative corona discharge ozonizer. The gaseous ozone-oxygen mixture thus produced was flowing through a stainless steel pipe to the expansion chamber, where the gas mixture was expanded through the conical shaped orifice. The flow rate  $Q$  of the ozone-oxygen mixture between the ozonizer and expansion orifice was extremely low ( $0.05 \text{ cm}^3\text{s}^{-1}$ ). The concentration of the ozone produced by the ozonizer depends exponentially on the ratio  $P/Q$ , where  $P$  is the applied discharge power. For high values of this ratio (as used in the present experiments) the ozone concentration in the ozonizer reaches a saturation value of about 10 % , depending on the geometry and materials of electrodes as well as on the temperature of the gas. A certain part of the ozone molecules is destroyed during their flow from the ozonizer to the expansion orifice. As it was not possible due to details in the construction of the expansion chamber to measure the ozone concentration directly at the moment of expansion we have prepared an identical experimental set-up (including the ozonizer and expansion source) to determine this concentration in a separate experiment. In this calibration the absorption of UV light of the Hartley band of the ozone spectrum was used for the determination of the ozone concentration by comparing the light intensity after passing the light through two identical cells one filled with the gas mixture to be determined and the other filled only with oxygen, respectively. Typical concentrations obtained for the gas mixture in the molecular beam were 0.65 to 0.85 % ozone in oxygen.

## Results and Discussion

### 1. Electron attachment to oxygen clusters.

As in previous studies two homologous anion series are observed by electron attachment to the neutral oxygen cluster beam. Fig.2 (full line) shows the measured relative attachment cross section function for the production of  $O_2^-$  in the low energy regime produced via reaction



Measured cross sections for larger homologous ions  $(O_2)_m^-$  exhibit the same characteristic behaviour, i.e., the cross section is largest at about zero energy and then strongly decreases with increasing energy. Moreover, the decreasing cross section is structured by additional peaks whose maxima appear to lie (within the experimental error bar of  $\pm 10$  meV) in all cases at the same energy, i.e. for the  $O_2^-$  ion shown in Fig.2 the distance between the zero energy and the first additional peak is 82 meV, to the next peak 193 meV and to the final peak still discernible 299 respectively. In the following we will first discuss the nature of the first peak and then proceed to the interpretation of the structures.

The inset in Fig.2 gives a log-log plot of the measured  $O_2^-$  ion current versus electron energy. It can be seen that the anion current decreases strongly with increasing energy before the appearance of the additional structures at approximately 30 meV. This strong decrease is compatible with the energy dependence predicted by quantum theory [32] for s-wave scattering (i.e., an  $E^{-1}$  dependence) and such a strong decrease has been observed for several molecules in this low energy region [8,9,21]. Thus we conclude that the present



observation indicates that s-wave electron capture is also a likely mechanism in the electron attachment to oxygen clusters. After the initial s-wave capture of the electron by the entire  $(\text{O}_2)_n$  cluster subsequent inelastic scattering processes (energy losses to phonons) reduces the electron energy below the vacuum level and leads via monomer evaporation to the final reaction product observed, i.e.,  $\text{O}_2^-$  (and higher homologues).

Peaks at higher electron energies are attributed to the attachment of an incoming electron to a single oxygen molecule within the target cluster via a direct Franck-Condon transition from the ground vibrational state  $v = 0$  to a vibrational excited state  $v'$  of the ensuing anions. Subsequent collisional stabilisation [33] of this anion within the cluster environment to a vibrational state below  $v' = 4$  gives a stable  $\text{O}_2^-$ . The energy thus released leads to the evaporation of neutral oxygen molecules (the heat of condensation of  $\text{O}_2$  with 1.63 kcal/mole [34] being the order of magnitude in energy which can be disposed in a single evaporation step). Depending on the amount of energy released (which depends on the  $v'$  state reached) and on the size of the neutral precursor this may lead to the production of naked  $\text{O}_2^-$  ions or to higher homologues.

Identification of the vibrational states populated in the anion can be done by comparing the presently observed vibrational spacings with the known spacings of the monomer given in Ref. [35]. The peak present at 80 meV thus has to be either  $v' = 7$  or a higher state assuming similar spacings in the monomer and solvated anion. A similar result is obtained from the calculation of the downward shift of the anion potential in the cluster environment due to polarization forces (for details of this calculations see [13]). Moreover, a further confirmation of this identification comes from a calculation where we have

modelled the energy dependence of the attachment cross section (see broken line in Fig.2) adding to the s-wave scattering component calculated contributions resulting from the respective Franck-Condon overlap integrals. The excellent agreement between the experimental shape and the theoretical prediction (up to the fourth peak, see Fig.2; the higher order transitions are possibly contaminated in the experiment by additional reaction channels above 0.4 eV, e.g., p-wave capture) confirms the assumed vertical attachment of the incoming electron.

## 2. *Electron attachment to ozone and ozone/oxygen clusters.*

### 2.1. Ozone

Fig.3 shows the measured  $O^-$  current as a function of electron energy obtained by attaching electrons to a molecular beam consisting of pure oxygen (designated as a dashed line) and a gas mixture of  $O_2$  and 0.85 %  $O_3$  (designated as a full line), respectively. The cross section shape for the pure oxygen case exhibits the typical behaviour for dissociative attachment of  $O_2$ , i.e., a single peak starting at around 4 eV and peaking at about 6.5 eV. In contrast, in the case of the mixed beam an additional peak appears in the low energy regime which is due to reaction (2). As both measurements were made under the same total expansion pressure and the 6.5 eV peak shows about the same shape and the same magnitude in both data sets, it can be concluded that contributions from ozone- if at all- are negligible for this resonance. The small difference at around 5.5 eV, i.e., the additional signal in the case of the mixed beam, is interpreted as  $O^-$  production via dissociative electron attachment to the singlet  $\Delta_g$  oxygen state [36]. In the case of  $O_2^-$  (not shown in Fig.3) there appears only a signal in the presence of ozone (i.e., a single small peak produced via reaction

(3) starting at about 0.2 eV and centered at around 1 eV with no signal above 2 eV). Also shown for comparison in Fig.3 is the attachment cross section function for the parent  $\text{SF}_6$  anion measured under identical monochromator conditions allowing us to determine a measure for the electron energy spread in this experiment. The electron energy spread here is about 160 meV FWHM. This is much larger than the possible resolution of about 5 meV, however, still better than the 200 meV FWHM resolution used previously by Curran [26]. This constitutes a compromise between a desired high energy resolution and a desired high electron current (the latter necessary to compensate for the low ozone concentration in the beam), both of which vary inversely to each other in the TEM. Moreover, the  $\text{SF}_6^-$  peak can also be used for the calibration of the energy scale. Appearance energies can then be estimated from the threshold energy behaviour of the cross sections yielding in the case of  $\text{O}^-$  a value of 0 eV and in the case of  $\text{O}_2^-$  a value of about 0.5 eV in agreement with the previous crossed beams results of Curran [26] and thermochemical data.

From the known ozone concentration and the measured peak heights in Fig.3 for the  $\text{O}^-$  peaks (the one at low energies being due to ozone, the one at high energies due to oxygen) it is possible to calibrate absolutely the cross section scale using the known cross section for  $\text{O}^-$  production from oxygen ( $1.3 \times 10^{-18} \text{ cm}^2$  at 6.5 eV electron energy [37]). Fig.4 shows the obtained absolute cross section data for both reactions taking also into account in the calibration procedure the different extraction efficiencies from the collision chamber (in analogy to the procedure outlined in Ref. [39]) being due to the different kinetic energies obtained by the fragment ions in the dissociative ionization process, i.e.,  $\text{O}^-$  from ozone having a maximum kinetic energy of 0.3 eV [8],  $\text{O}_2^-$  from ozone being essential thermal [26] and  $\text{O}^-$  from oxygen having in the peak maximum a kinetic energy of 1.5 eV [1]. It is interesting to note that both

dissociative attachment channels have absolute cross sections in the same order of magnitude. This is of relevance for understanding the appearance of anion concentrations in corona discharges in oxygen or in air at low gas pressures and relatively high  $E/N$  values (above 10 Td), where the  $O_2^-$  observed is produced in appreciable amounts via reaction (3) and not via three body attachment to  $O_2$ [40]. The ratio of the cross section maxima for reaction (2) and (3), i.e.,  $2.8 \times 10^{-17} / 1.83 \times 10^{-17} = 1.53$  is very close to the ratio for  $O^-$  to  $O_2^-$  formation at their peak value  $11/7 = 1.57$  as reported by Curran [26]. A final point worth mentioning here is the fact that the crude estimate of the absolute cross sections for reaction (1) and (2) given by Curran [26] with a value of  $10^{-17}$  to  $10^{-18}$   $cm^2$  is below the present results, whereas the electron attachment cross sections for ozone reported by [28] (for the actual data see Fig.9 in Ref. [38]) ,e.g., a value of about  $1 \times 10^{-17}$   $cm^2$  at an electron energy of about 0.5 eV, is in excellent agreement with the present data. It is noteworthy, that the cross section data of [28] appear to deviate ,however, with lower electron energies (below 0.3 eV) from the present data set, whereas the cross sections shown in Fig.9 in Ref.[38] derived from drift tube measurements agree much better with the present data in this lower electron energy regime (see Fig.4) than the cross sections of [28].

## 2.2. Ozone/oxygen clusters

In the energy range from about 0 up to about 4 eV electron attachment to oxygen/ozone clusters (produced by expanding the gaseous ozone-oxygen mixture produced in the ozonizer) leads to  $O_p^-$  ions in all stoichiometric composition  $p \geq 2$ . Some of the ion yield curves are shown in Figs. 5a and 5b. In order to designate the nature/structure of these anions we have to consider anion formation from the oxygen molecule, pure oxygen clusters and also from the ozone molecule (see above). Although  $O_3^-$  is by 1.74 eV more stable than  $O^-$

+ O<sub>2</sub> [41] one expects some activation barrier in the potential energy surface separating the chemically different species (O<sub>2</sub>)<sup>-</sup> and O<sub>3</sub><sup>-</sup>. In any case, from the previous experiments on pure oxygen and from thermochemical data [41] one can definitely conclude that species of the stoichiometric composition O<sub>3</sub><sup>-</sup> are not formed in the energy range below 4 eV. Electron impact on single O<sub>3</sub> molecules, on the other hand, yields only the fragment ions O<sup>-</sup> and O<sub>2</sub><sup>-</sup> at the electron energy around 1 eV. Returning to the present experiments it can be seen by comparing Figs. 5a and 5b that the intensity of O<sub>p</sub><sup>-</sup> ions with p = 3,6 is distinctly enhanced which suggests formation of undissociated ozone clusters ions (O<sub>3</sub>)<sub>m</sub><sup>-</sup> with m = 1,2. In the case of p = 3 the only and unambiguous possibility is the ozone anion O<sub>3</sub><sup>-</sup>. For p = 6 on the other hand we cannot exclude contributions having the chemical nature (O<sub>2</sub>)<sub>3</sub><sup>-</sup>. However, as can be seen from Fig. 5b the signal due to undissociated molecular oxygen anions from the mixed neutral clusters is in any case relatively weak. Nevertheless O<sub>3</sub> is by far the dominant product in these attachment studies (approximately by more than one order of magnitude more abundant than O<sub>2</sub><sup>-</sup>) which seems a surprising result with respect to the low ozone concentration in the initial gas mixture. This behavior must be due to (i) a considerable enrichment of ozone in the process of cluster formation by the adiabatic expansion of the gas mixture and/or (ii) a preferential formation of the O<sub>3</sub><sup>-</sup> component from mixed clusters in the course of the attachment reaction. For instance due to the much higher condensation temperature of ozone (161 K for O<sub>3</sub> as opposed to 55 K for O<sub>2</sub> [41]) a preferential clustering of ozone in a mixture is expected. Moreover, due to the large electron affinity of ozone, one expects a preferential formation of O<sub>3</sub><sup>-</sup> over O<sub>2</sub><sup>-</sup>.

From Fig. 5 one can see the pronounced formation of O<sub>3</sub><sup>-</sup> in the very low energy region and a continuous increase of the signal above about 2 eV. In

single ozone molecules, on the other hand, only near 1 eV the formation of the product ions  $O^-$  and  $O_2^-$  is observed. According to a recent *ab initio* calculations of [42] there exists no crossing of the  $O_3^-$  ground state potential energy surface with that of the ground state neutral molecule. We therefore conclude, that  $(O_3)_m^-$  formation at very low energies is dominated by *s wave capture* of the initial cluster with subsequent collisional stabilization leading to the evaporation of neutral monomers due to this stabilization and the release of the electron affinity. The  $O_3^-$  cross section follows reasonably well the  $E^{-1}$  behavior with a pronounced deviation between  $\approx 0.3$  eV and  $\approx 1.3$  eV. We ascribe this contribution to electron capture by an individual  $O_3$  molecule in the mixed cluster through a Feshbach resonance mechanism. Under single collision conditions this process is purely dissociative leading to the fragmentation products  $O^-$  and  $O_2^-$  with  $O^-$  the dominant ion. From the fact that in the present experiment virtually no  $O^-$  signal is observed at that energy we conclude the dissociative processes is strongly quenched in favour of processes leading to the undissociated species  $(O_3)_m^-$ . Similar intramolecular quenching processes have already been observed in electron attachment to clusters of  $SO_2$  [43]. Finally in view of the low known excitation energies of neutral ozone we interpret the continuous increase of the  $(O_3)_m^-$  signal above 1.5 eV as *self scavenging*, i.e. inelastic scattering of the primary electron at one ozone molecule creating an electronically excited neutral  $O_3$  molecule and subsequent capture of the slowed down electron via *s wave capture* and/or formation of a *Feshbach resonance* as described above within the same cluster (see earlier observation of self scavenging in clusters composed of molecules with the ability to capture low energy electrons [33]).

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### Figure headings.

Fig.1 Schematic view of the crossed beams apparatus. Electrons emitted from filament F are deflected in the dispersion region (SC) consisting of a crossed  $E_y$  and  $B_x$  field. In the collision region (CS) the electrons react with the neutral target beam (NB) producing ions which are extracted (IB) and mass analyzed in a quadrupole mass spectrometer (QM). Electrons passing the collision region without reaction are collected with a Faraday cup (FC).

Fig.2 Measured  $O_2^-$  anion signal (full line) produced by electron attachment to a  $(O_2)_n$  cluster beam as a function of corrected electron energy (Electron current: 30 nA, energy resolution: 30 meV FWHM; guiding magnetic field: 50 G, ion extraction field: 100 meV/cm, stagnation pressure: 4.7 bar; stagnation temperature: -138 C). Also shown (broken line) calculated cross section behaviour (see text).

Inset: Measured  $O_2^-$  ion current versus corrected electron energy on a log-log scale. Dashed line indicates the  $E^{-1}$  dependence predicted by s-wave scattering theory.

Fig.3 Fig.2  $O^-$  ion current as a function of corrected (see text) electron energy produced by electron attachment to a pure oxygen beam (designated dashed line) and to a oxygen beam containing an 0.85 % ozone admixture (designated full line). Also shown for comparison the  $SF_6^-$  ion current (designated dotted line) produced by electrons attaching to  $SF_6$  being present in the beam in a  $5 \times 10^{-3}$  concentration. In the insert we show the difference signal for the  $O^-$  production for the pure and mixed beam; this contribution is due to dissociative attachment to the  $^1\Delta_g$  state which is also present in the mixed beam in small amounts (see text).

Fig.4 Absolute electron attachment cross sections as a function of corrected electron energy for the production of  $O^-$  (designated full line) and  $O_2^-$  (designated dashed line) obtained in the present crossed beams attachment study to ozone. The present data have been corrected by deconvoluting with the measured electron energy distribution. Also shown for comparison (designated filled squares) cross sections calculated from the drift tube rate coefficients reported by Phelps and coworkers [38].

Fig.5a Formation of  $O_2^-$  and  $O_4^-$  from mixed oxygen/ozone clusters.

Fig.5b Formation of  $(O_3)_m$  with  $m = 1$  and 2 from mixed oxygen/ozone clusters.

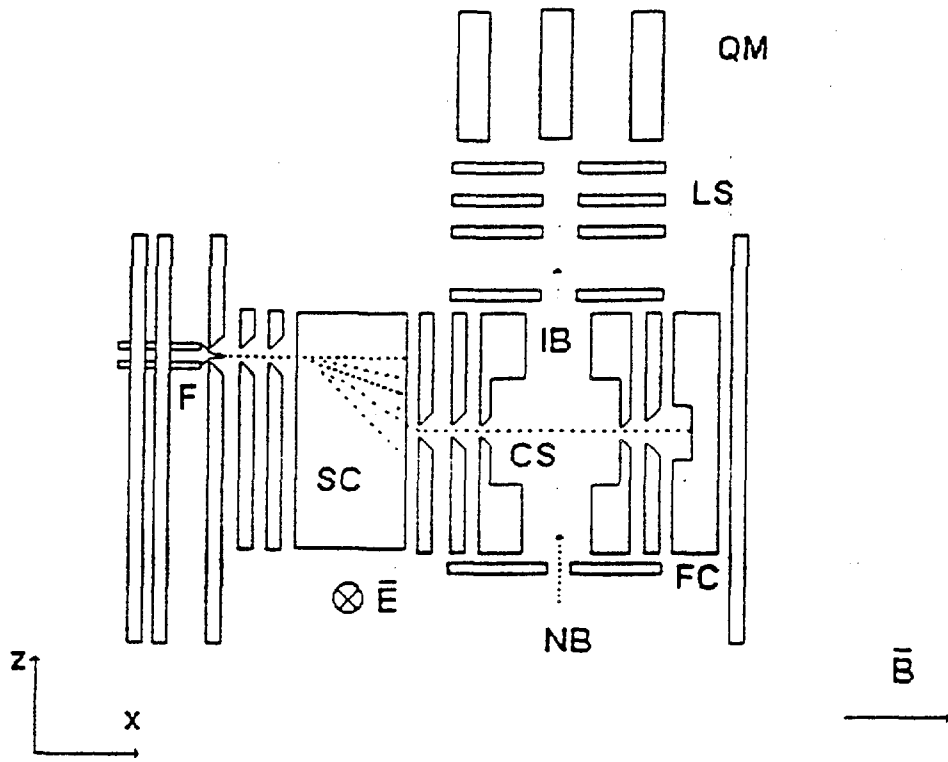


Fig. 1

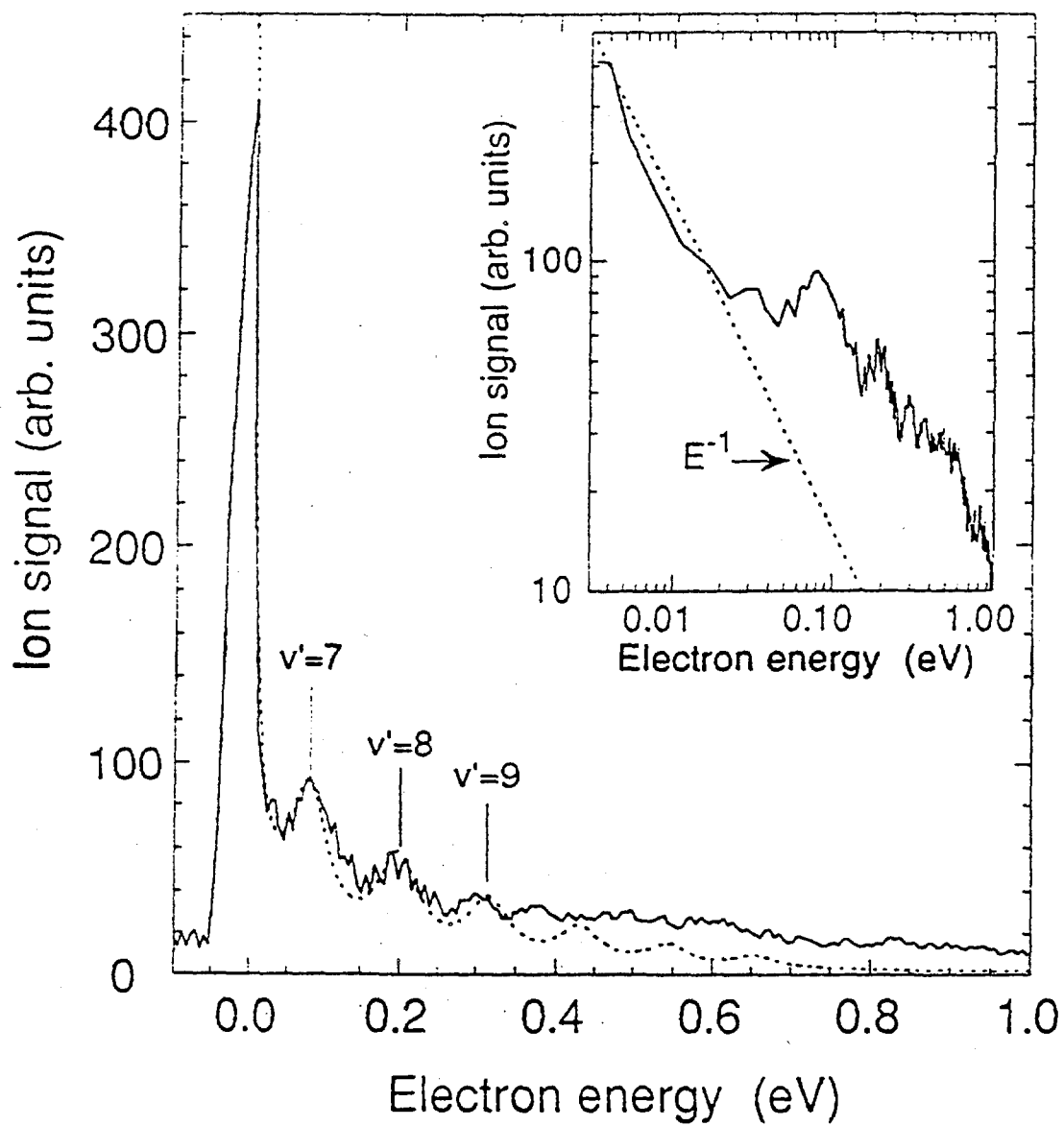


Fig. 2

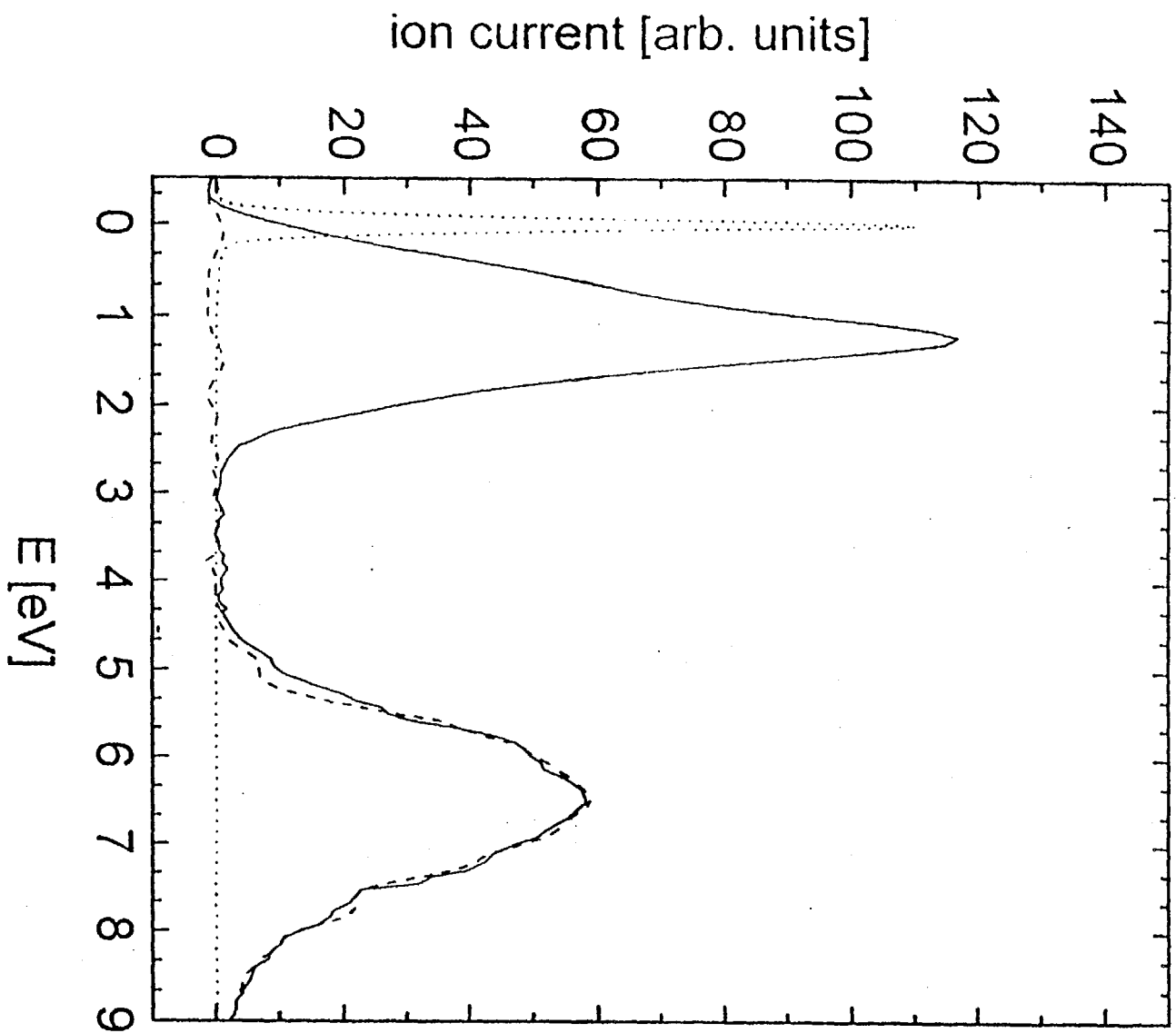


Fig. 2

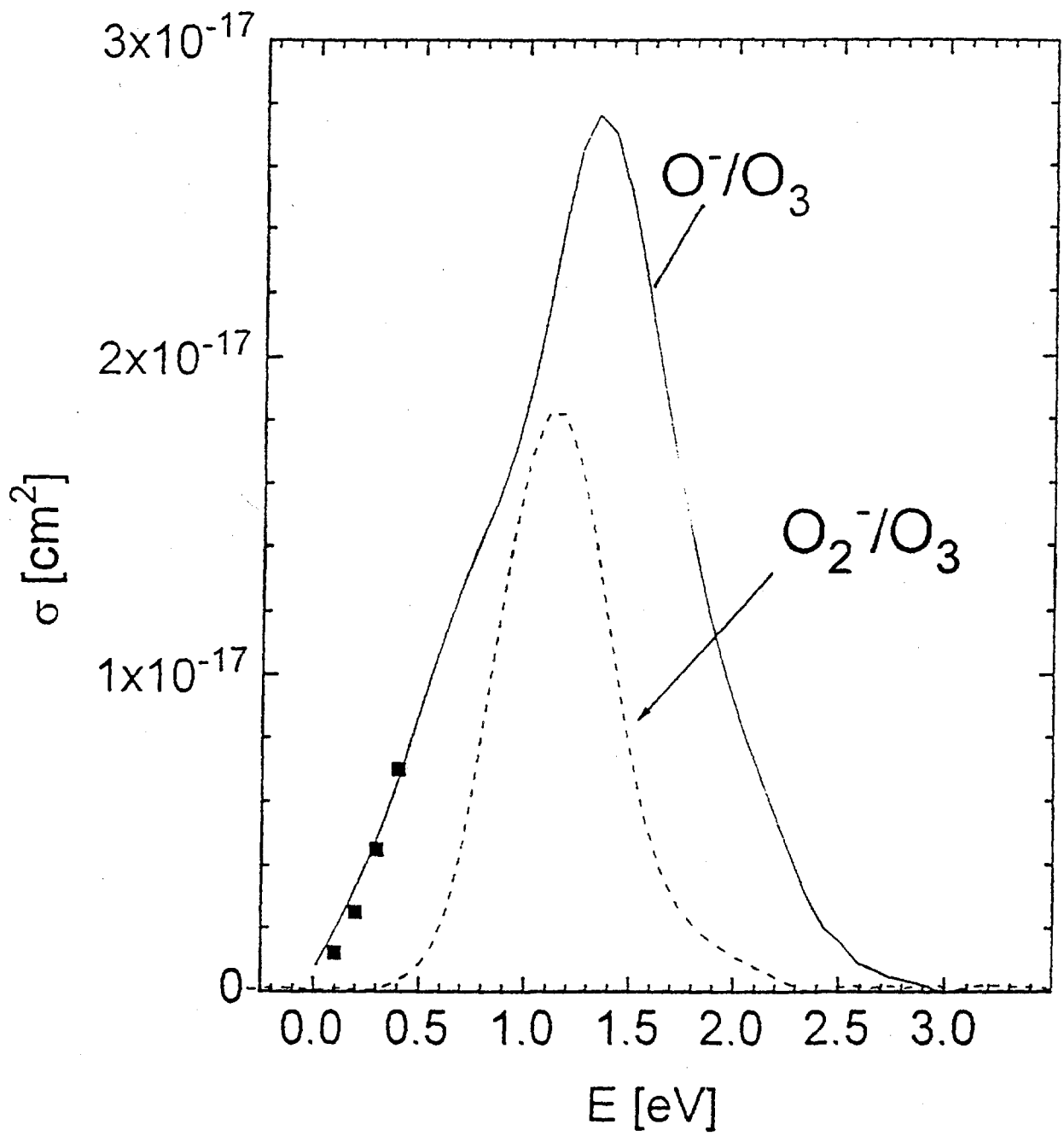


Fig. 4

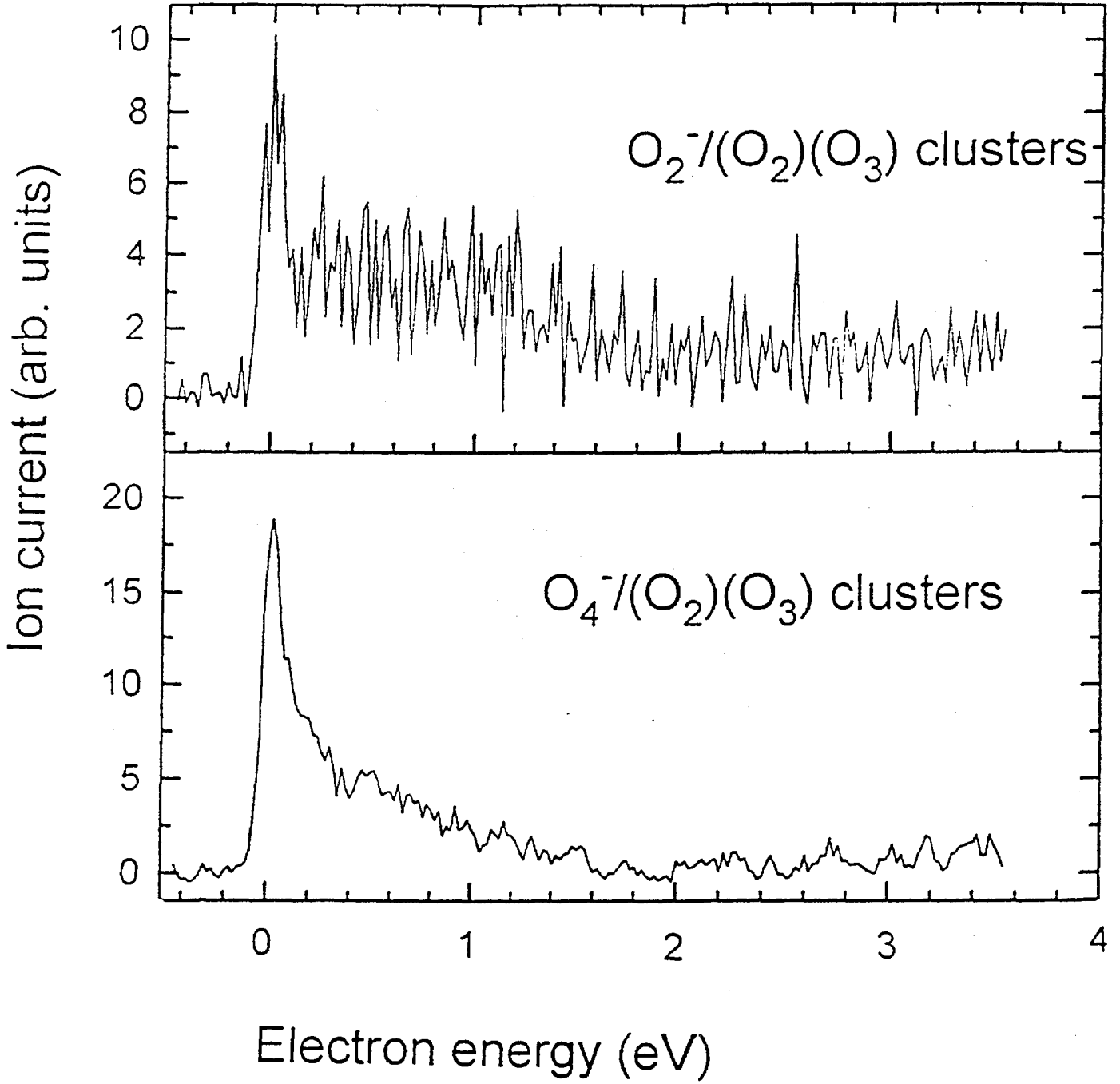


Fig. 5a



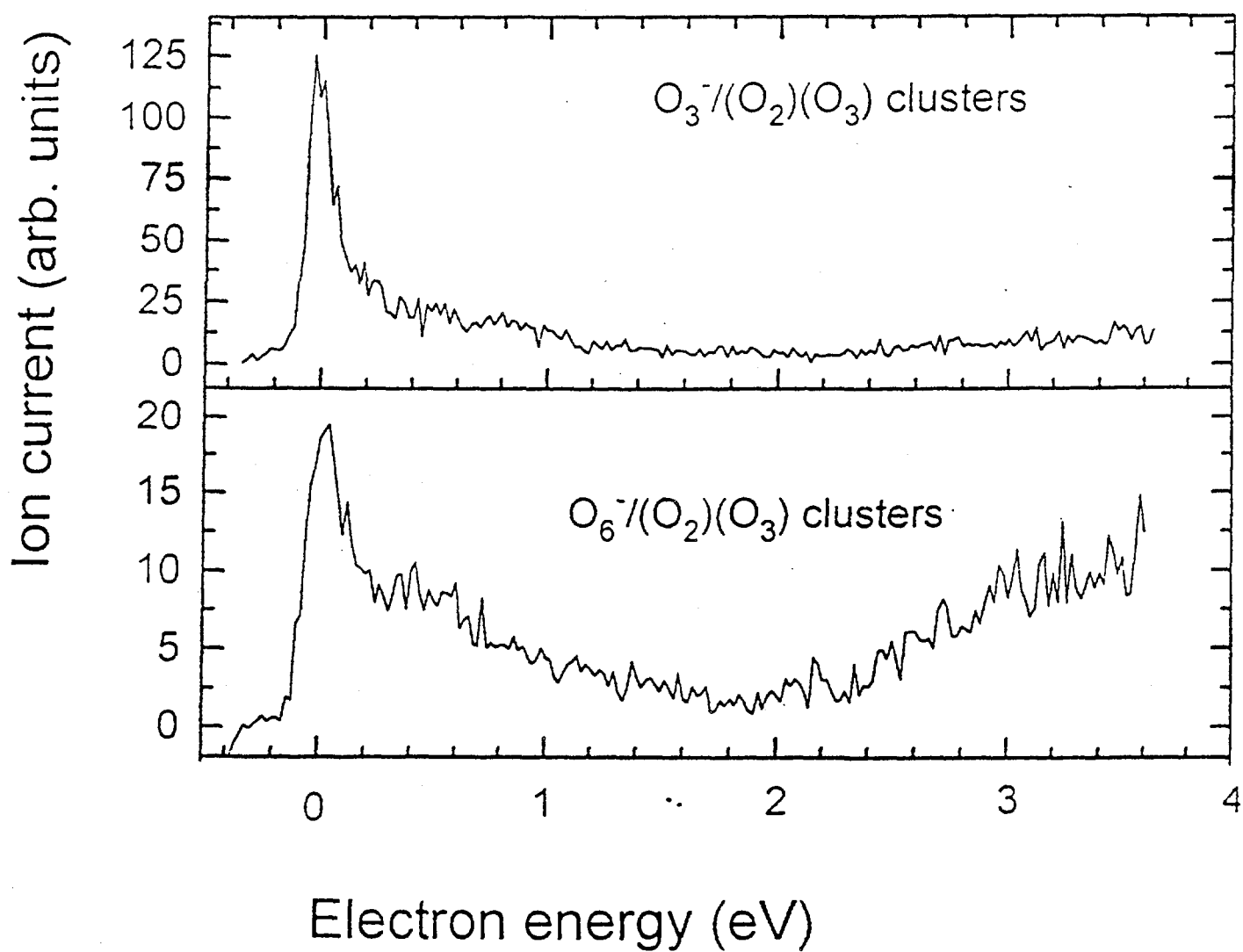


Fig. 5b