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Dissociative electron attachment to NO molecules and NO clusters

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Dissociative electron attachment (DA) to single NO molecules and NO clusters is studied in two independent crossed electron–molecular-beam experiments with high-energy resolution including a kinetic-energy analysis of the O^- fragment ions. It is shown that the DA cross section exhibits a vertical onset near 7.45 eV that corresponds to the energetic threshold of the DA channel $O^-(^2P)+N^*(^2D)$. No indication of the ground-state channel $O^-(^2P)+N(^4S)$ [O. J. Orient and A. Chutjian, Phys. Rev. Lett. **74**, 501 (1995)] and no indication of long-lived N^- [H. Hiraoka, R. K. Nesbet, and L. W. Welsh, Jr., Phys. Rev. Lett. **29**, 130 (1977)], as recently proposed, could be found. O^- formation from NO clusters shows the same features as from single NO molecules, indicating the same reaction mechanism, thus also excluding coupling to the ground-state DA channel clusters. [S1050-2947(98)50102-3]

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Dissociative attachment (DA) to NO has recently caused serious confusion, which we shall clarify in this Rapid Communication.

The lowest possible DA channels in single NO leading to O^- are

$$e^- + \mathrm{NO} \rightarrow O^-(^2P)+N(^4S) \quad (5.074\ \mathrm{eV}) \qquad (1a)$$

$$\rightarrow O^-(^2P)+N^*(^2D) \quad (7.457\ \mathrm{eV}) \qquad (1b)$$

$$\rightarrow O^-(^2P)+N^*(^2P) \quad (8.650\ \mathrm{eV}), \qquad (1c)$$

with the threshold energies indicated in parentheses. These values are based on the bond dissociation energy $D(\text{N-O})=6.535$ eV [1] and the well established excitation energies for the nitrogen atom, $E(N^*(^2D))=2.383$ eV, $E(N^*(^2P))=3.576$ eV [2], and the electron affinity of the oxygen atom, $A_E(\mathrm{O})=1.461$ eV [3].

DA to NO was studied by Rapp and Briglia [4] and Chantry [5] about three decades ago. The results of these early measurements can be summarized as follows: O^- is formed with a comparatively steep onset at 7.5 ± 0.1 eV with a cross section of 1.15×10^{-18} cm^2 (peak value) [4]. The O^--ion yield curve extends to ≈ 10.5 eV and seems to consists of two overlapping resonances. It was therefore suggested [6] that the low-energy resonance is due to process (1b) and the higher resonance to process (1c). Measurement of the O^- kinetic-energy release by means of a Wien filter [5], however, indicated that the translational energy of O^- continuously increases with the incident electron energy, with the most probable O^- kinetic energy having a slope of 14/30, as expected from momentum conservation in the dissociation of NO^-. It was hence concluded that DA to NO is exclusively restricted to channel (1b) involving an electronically excited negative-ion resonance NO^{*-} [5].

In 1995 a paper was published by Orient and Chutjian [7], where it was claimed that *all* three DA channels (1a)–(1c) are operative in the energy range between ≈ 6.5 eV and ≈ 11 eV with channel (1a) by far the dominant one. The basis of this result was the analysis of the O^- kinetic-energy release in a crossed electric–magnetic-field configuration.

We report on DA to NO and NO clusters using an electron beam with high resolution (≈ 50 meV), including the analysis of O^- translational energies by means of a time-of-flight (TOF) method. It is demonstrated that (a) the major DA channel is Eq. (1b) yielding a vertical onset at the thermodynamic threshold (7.46 eV), (b) above ≈ 9 eV channel (1c) contributes by 15–20 % to the ion yield, and (c) electron impact below 15 eV does not generate long-lived N^-, as previously reported [8,9].

The experiments were performed in a coordinated study at the Innsbruck laboratory and the Berlin laboratory. The Innsbruck dissociative attachment spectrometer has previously been described [10]. It consists of a molecular-beam system, a trochoidal electron monochromator (TEM), and a quadrupole mass filter with a pulse-counting system for analyzing and detecting the ionic DA products.

Details of the Berlin DA spectrometer can be found, e.g., in a recent review [11]. Here, a *homogeneous*, weak electric field is applied to draw out the ions. TOF spectra of ions are recorded by means of a pulsed electron beam. Energetic ions then cause a doublet in their TOF spectrum due to ions emitted parallel and antiparallel to the flight tube axis. The time difference is then a measure of their initial kinetic energy.

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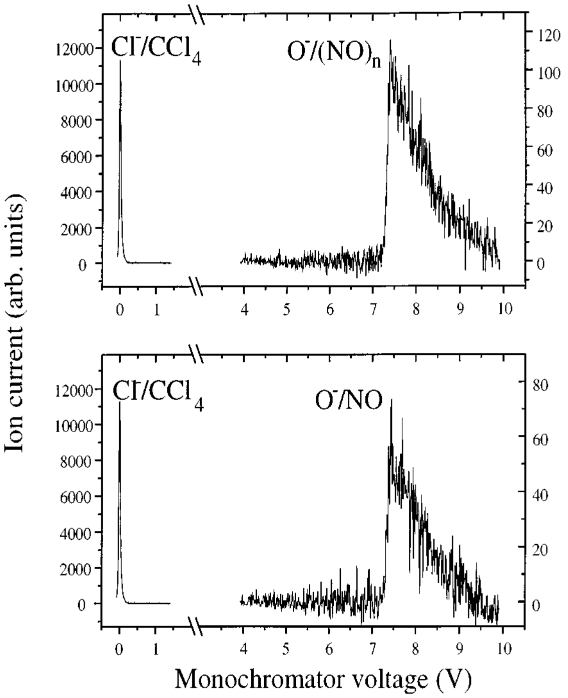

FIG. 1. Relative cross section for DA to NO and NO clusters. The Cl^-/CCl_4 is used for energy calibration control of the electron-energy resolution (Innsbruck laboratory).

In Fig. 1 we present the O^- yield as a function of the incident electron energy in DA to single NO molecules and NO clusters. The figure also contains the DA signal Cl^-/CCl_4, which is used for energy calibration and determination of the energy resolution [10]. For the present experiments the width of the Cl^-/CCl_4 resonance was about 50 meV [full width at half maximum]. The O^- cross-section curve shows a sharp onset at the monochromator voltage of 7.35 V, which we ascribe to the onset of reaction (1b). The vertical onset of this DA reaction can be explained by the particular disposition of the involved potential-energy curves, as illustrated in Fig. 2: Franck-Condon transitions around 8 eV generate an electronically excited anion NO^{*-} in a repulsive state. Since the DA limit $O^-+N^*(^2D)$ is located *within* the resonance region, the DA cross section exhibits a vertical onset at the energetic threshold. The figure also contains the NO^- ground-state potential-energy curve. The (adiabatic) electron affinity of NO is only 26 meV [12,13]. Due to its short autodetachment lifetime, NO^- $(\nu' > 0)$ cannot be detected on the mass spectrometric time scale [14].

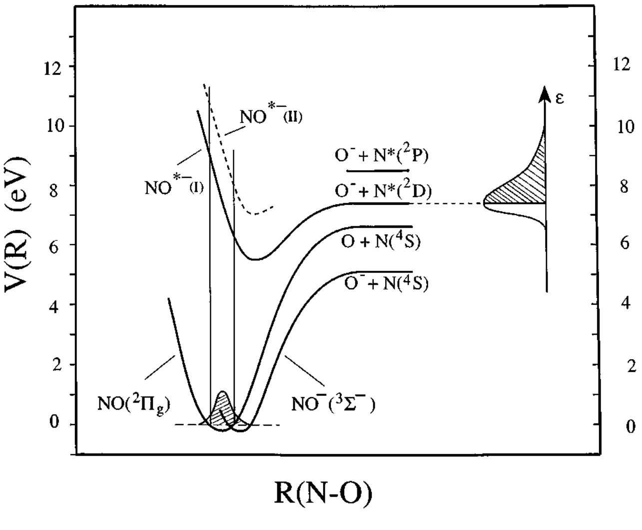

FIG. 2. Schematic potential-energy diagram for ground-state NO and NO^- and two excited negative-ion states NO^{*-}(I) and NO^{*-}(II) involved in DA (see text).

Two observations are noteworthy:

(i) Figure 1 shows that the monochromator voltage at the vertical onset is 7.35 V (with respect to Cl^-/CCl_4 at zero), which is very close to the calculated energetic threshold (7.46 eV). This demonstrates that the electron-energy scale is linear with the monochromator voltage within approximately 1%.

(ii) The width of the differentiated onset at 7.35 V is about 125 meV (FWHM) and thus is larger than the width of the Cl^-/CCl_4 threshold peak. While the width of the threshold peak is directly a measure of the energy resolution near zero eV (the ''s-wave'' capture cross section behaves as $\sigma \sim 1/\varepsilon$), the onset of reaction (1b) is in any case broadened by the thermal energy. However, the comparatively larger width of the onset near 7.45 eV indicates that the energy resolution of the monochromator becomes poorer with increasing electron energy.

Returning to the DA channels operative in NO, there is no indication of channel (1a), i.e., formation of the nitrogen atom in its electronic ground state. In the recent paper by Orient and Chutjian [7] this channel was claimed to be by far the dominant one.

The NO sample used in the Innsbruck laboratory showed some O^- ''background'' signal below the vertical onset and starting near 4 eV. Figure 1 shows the O^- yield after subtraction of this background signal that is mirrored by the increasing noise of the base line towards higher electron energy. Since this signal starts at around 4 eV, it cannot be due to reaction (1a), which has an energetic threshold above 5 eV, and we ascribe this contribution to some O_2 impurity in the sample. A new NO sample used in the Berlin laboratory in fact did not show any background O^- below the vertical onset (see Fig. 3).

As mentioned, Orient and Chutjian [7] concluded that all three channels (1a)–(1c) are operative with channel (1a) (i.e., formation of the fragments in their ground state), by far the dominant one. Their result, however, is *not* based on a direct observation of the O^- yield as a function of the incident electron energy, but rather derived from an analysis of the O^- kinetic-energy release at different electron energies. This experiment was carried out in a very high magnetic field (6 T), which is necessary to deflect *ions* in the crossed E/B configuration. They reported kinetic-energy distributions consisting of three components. The dependence of these components with the electron energy was then used to calculate the energy dependence of the individual cross sections (1a)–(1c). Unfortunately, the authors did not demonstrate or discuss (a) the reliability of their method for kinetic-energy analysis, e.g., by applying this technique to a well-known system like DA to O_2, and (b) the method of

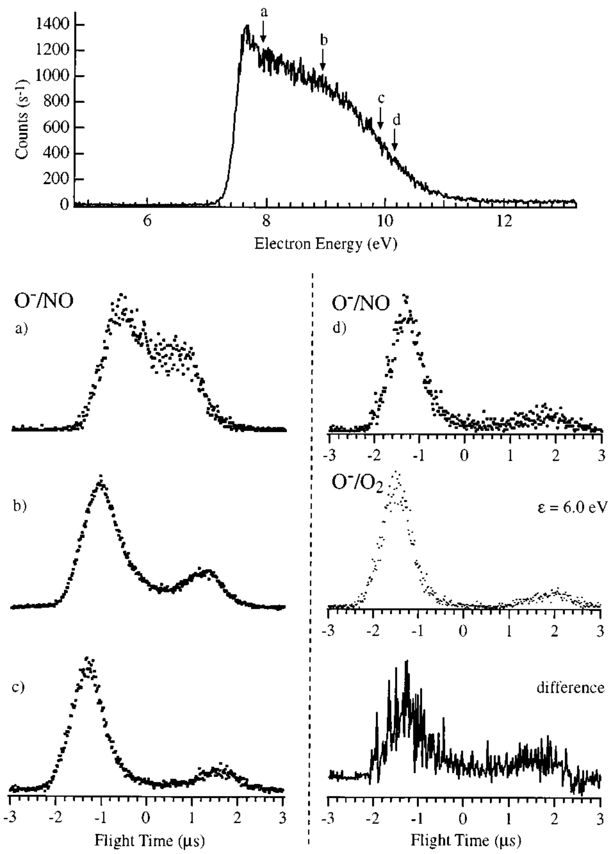

FIG. 3. O^--ion yield curve recorded under TOF conditions (Berlin laboratory, $\varepsilon = 3.5\ \mathrm{V\,cm^{-1}}$). Left-hand side, time-of-flight spectra of O^-/NO recorded at the indicated electron energies. Right-hand side: comparison of the TOF spectra between O^-/NO and O^-/O_2 at comparable ΔT values and difference spectrum. Flight time zero refers to an ion with zero translational energy.

(electron and ion) energy calibration. The rather large energy width was estimated as 0.4 eV simply from the temperature of the hot filament.

As our present results demonstrate, the cross-section curves given by Orient and Chutjian [7] are seriously wrong due to their obviously erroneous O^- kinetic-energy analysis. The conclusion then is that DA to NO does *not* lead to the fragments in their electronic ground state.

We mention here that DA into the ground-state products $O^-(^2P)+N(^4S)$ [channel (1a)] was in fact reported *via DA to laser-excited NO** [15]. Attachment of low-energy electrons (<0.5 eV) during excitation of NO near 226 nm resulted in O^- formation, which was interpreted as electron attachment to the first electronically excited state NO* ($A^2\Sigma^+$) generating an excited resonant state, $\mathrm{NO}^{*-}(^3\Pi)$ [16], which predissociates into the ground-state fragments. The core excited resonance $\mathrm{NO}^{*-}(^3\Pi)$ is considered a bound state (with respect to the nuclei) as is obvious from the vibrational structure seen in electron transmission [17].

The question remains on the origin of the structure near 8.5 eV in the relative cross-section curve. As mentioned above, this was first interpreted as the opening of channel (1c), but from kinetic-energy analysis [5] it was concluded that DA to NO exclusively yields channel (1b).

At this point we mention a further paper published in 1991 by Sambe and Ramaker [8] in which ''previously reported experimental data on dissociative electron attachment (DA) in NO are reinterpreted.'' Since some of these previous experiments were performed without mass analysis (e.g., the classic papers by Rapp and Briglia [4] and Chantry [5]), they concluded that the 8–10-eV contribution in the total ion yield is due to $N^-(^1D)$. Long-lived $N^-(^1D)$ has in fact been predicted (due to slow, spin-forbidden autodetachment) and has been reported [8] as a result of DA to N_2 and NO. We do not want to comment on that particular experiment to any extent (the interested reader may refer to the original paper [8]), but simply state that we *were not able to detect any negative ion with* $m/e=14$ amu *from NO in the energy range* 0–15 eV, neither with the Innsbruck apparatus nor with that at the Berlin laboratory.

This is in accordance with a previous study [18] where the present state of knowledge about N^- was reviewed and calculations of energies and lifetimes of the N^- states belonging to the $2p^4$ configuration were reported. It thus appears that the lowest ionic state, $N^-(^3P)$, is either 70 or 213 meV above the neutral ground state, $N(^4P)$, with an autodetachment lifetime in the 10^{-14}-s region. The decay of the two further configurations, $N^-(^1D)$ and $N^-(^1S)$, is spin forbidden. Their energy is calculated as 1.513 eV (^1D) and 2.903 eV (^1S) above the neutral ground state with lifetimes of 1.3×10^{-10} s (^1D) and 7×10^{-11} s (^1S).

We have performed TOF experiments in order to obtain information on the kinetic-energy release and thus on the possible contribution of further DA channels. Figure 3 shows the TOF spectra recorded at the energies assigned at the O^- yield curve. The time difference (ΔT) and kinetic energy of the ion $[E_T(m_i)]$ are related by

$$E_T(m_i)=(\Delta T q \varepsilon)^2/8m_i,$$

with q the elementary charge and ε the ion draw-out field.

The experimental TOF peaks possess a certain width due to (a) the finite electron-energy resolution, (b) the finite pulse width, (c) inhomogeneities in the ion draw-out field, and (d) a possible small influence of the quadrupole field on the flight time of the ions [19]. It is thus difficult to directly judge whether the TOF spectra in Fig. 3 (left-hand side) contain a second small translational energy component due to dissociation into channel (1c).

We can, however, compare the present TOF spectra from NO with those from O_2, where it is clear that *only one single translational energy component is present*. This is done in Fig. 3 (right-hand side), indicating that TOF spectra recorded from NO at electron energies above ≈ 9 eV are slightly different from those from O_2 recorded for the equivalent time difference ΔT. By subtracting the O^-/O_2 TOF spectrum from that in O^-/NO, we obtain a residual small distribution with a ΔT value like that expected for a dissociation into channel (1c). Since the kinetic energy depends on $(\Delta T)^2$, the ΔT value of the second component is not much different from that of the first component. In Fig. 4 we have plotted the translational energy release as a function of the electron energy for the two components. The first component shows a slope of 14/30, as expected from momentum conservation; for the second component the same slope and an intersection at the energetic threshold fit well into the fairly scattered

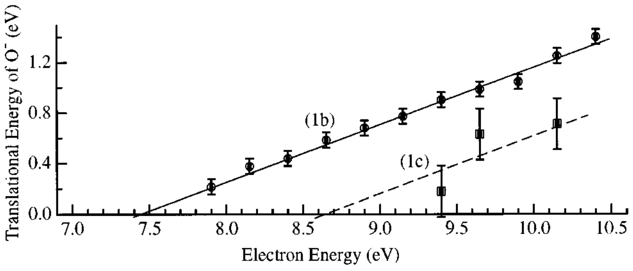

FIG. 4. Translational energy of O^- versus electron energy for the two components corresponding to channels (1b) and (1c).

experimental values. We therefore conclude that DA to NO is dominated by dissociation into channel (1b) with a small (15–20 %) contribution of channel (1c).

So far, we have found a rather controversial discussion in the literature about the *electronic states* involved in DA to NO, which we shall not discuss here (see, e.g., Refs. [8,16,20–22]). A recent molecular-orbital–configuration-interaction calculation [22] predicts two electronic states, a $^3\Pi$ state with a vertical attachment energy of ≈ 7 eV and a $^1\Pi$ state at an energy of ≈ 8.8 eV. Both electronic states are repulsive in the Franck-Condon region and have minima.

In light of the present results, the detailed origin of the structure in the relative cross section still remains unclear. As can be seen by comparing Figs. 1 and 3, the structure as well as the high-energy part of the cross-section curve is more pronounced in the ''Berlin spectrum'' which was recorded at a draw-out field $\varepsilon = 3.5$ V cm^{-1} (TOF conditions), while the collision region in the Innsbruck spectrometer is nearly field free. We note that with low ε the Berlin spectrum becomes virtually identical with the Innsbruck spectrum. At higher ε, energetic ions are less discriminated, which explains the strong suppression of the high-energy part in the Innsbruck spectrum. The structure, however, always appears below 8.5 eV and can thus not (solely) be due to the opening of channel (1c). We therefore suggest that *at least* one additional state (NO^{*-}II) must be involved, which is responsible for the structure and couples to the limit (1b) and probably (1c); see Fig. 2.

The cross-section curve for DA to NO clusters (Fig. 1) does not change to any measurable extent with respect to the isolated molecule. In DA to NO clusters we expect for the Franck-Condon transition some shift to lower energy due to the solvation energy of the negative charge. However, the energetic threshold for the cluster reaction,

$$e^-(\mathrm{NO})_n \rightarrow \mathrm{O}^- + \mathrm{N}\cdot(\mathrm{NO})_{n-1}, \tag{2}$$

differs from the gas phase reaction (1) only within the difference in the interaction energy between $D(\mathrm{NO}-(\mathrm{NO})_{n-1})$ and $D(\mathrm{N}-(\mathrm{NO})_{n-1})$, which is probably less than 50 meV. We thus expect virtually the same DA threshold energy for isolated NO and for NO clusters.

From the present results we can thus finally conclude that (i) DA to NO resulting in the ground-state fragments is not operative, neither in single molecules nor in clusters; (ii) DA to NO does not generate long-lived N^-.

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