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Calculated absolute cross-sections for the electron-induced detachment of the B_2^-, O_2^-, BO^-, and CN^- anions using the Deutsch-Märk (DM) formalism

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ABSTRACT

We report calculations of the cross-sections for electron impact detachment of the diatomic anions B_2^-, O_2^-, BO^-, and CN^- using the DM formalism. The calculations use 'ionic' weighting factors to adequately represent the ionic character of the target and in each case a Mulliken population analysis of the anion and the neutral molecule was carried out in an effort to localize the 'extra' electron in the anion compared to the neutral molecule. When compared with available experimental data, the calculated DM cross-sections were found to exceed the measured data by factors ranging from 1.6 to 5.5.

1. Introduction

The dynamics of a collision between an incident electron and a molecular anion are much more complicated than the collision between an electron and an atomic anion [1]. Various approximations have been used to describe the long-range Coulomb interaction between the incident electron and the weakly bound extra target electron in an atomic anion (see e.g. Pedersen et al. [2,3]). The extra electron in molecular anions, on the other hand, has often valence character. Diatomic anions are of particular interest because of their comparatively simple structure. Electron-induced detachment of a diatomic anion AB^- is often the dominant break-up channel (reaction (1a)), but dissociation may also occur (reaction (1b)):

$$e^- + AB^- \rightarrow AB + 2e^- \tag{1a}$$

$$e^- + AB^- \rightarrow A + B + 2e^- \tag{1b}$$

A second dissociation pathway, ion pair formation (reaction 1c), is also possible:

$$e^- + AB^- \rightarrow A^- + B^+ + 2e^- \quad (\text{or} \quad A^+ + B^- + 2e^-) \tag{1c}$$

Experimental studies of electron interactions with various diatomic anions such as B_2^-, C_2^-, O_2^-, BN^-, BO^-, and CN^- were carried out by Pedersen et al. [2,3] and Andersen et al. [4]. These authors described their measured cross-section σ as a function of the electron energy E by a formula of the form:

$$\sigma(E) = p\pi R_{\mathrm{th}}^2 \left(\frac{1 - E_{\mathrm{th}}}{E}\right) \quad \text{with } E_{\mathrm{th}} = E_A + \frac{1}{R_{\mathrm{th}}} \tag{2}$$

where p is an empirically determined constant (which is close to one), E_A is the electron affinity, and $1/R_{\mathrm{th}}$ denotes the Coulomb energy lost by the electron at distance R_{th}.

In this paper, we present the results of a calculation of the electron-induced detachment of the four diatomic anions B_2^-, O_2^-, BO^-, and CN^- using a recently published variant of the semi-classical Deutsch-Märk (DM) formalism [5,6], which was derived

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for the ionization of singly positively charged ions. Based on a comparison of the quantum chemically calculated molecular orbital populations of the neutral molecule and the molecular cation the position of the 'missing' electron in the positively charged molecular ion compared to the neutral molecule was localized. Furthermore, 'ionic' weighting factors (see below) rather than the corresponding neutral weighting factors were used to describe the 'ionic' component of the target. Here we extend this concept to the electron-induced detachment of the diatomic anions B_2^-, O_2^-, BO^-, and CN^-. As part of the calculations, population analyses of the diatomic anion and the corresponding neutral diatomic molecule were carried out in each case in an effort to localize the 'extra' electron in the diatomic anion. Furthermore, for reasons of comparison calculations for the ionization cross-sections of the corresponding neutral molecules (B_2, O_2, BO, ands CN) were also carried out. The calculated detachment cross-sections were found to lie significantly above the measured data [2,3] by factors ranging from 1.6 to 5.5.

2. Background

The DM formalism was originally developed for the calculation of atomic ionization cross-sections [7] and has been modified and extended several times (see e.g., Ref. [5]). The DM formula expresses the atomic ionization cross-sections σ as the sum over all partial ionization cross-sections corresponding to the removal of a single electron from a given atomic sub-shell labeled by the quantum numbers n and l as

$$\sigma(u) = \sum_{n,l} g_{nl}\pi r_{nl}^2 \xi_{nl} b_{nl}^{(q)}(u)\left[\frac{\ln(c_{nl}u)}{u}\right] \tag{3}$$

where r_{nl} is the radius of maximum radial electron density in the atomic sub-shell characterized by quantum numbers n and l (as listed in column 1 in the tables of Desclaux [8]) and ξ_{nl} is the number of electrons in that sub-shell. The sum extends over all atomic sub-shells labelled by n and l. The factors g_{nl} are weighting factors which were originally determined from a fitting procedure [7,9,10] using reliable experimental cross-section data (H, He, C, Ne, Mg, Al, Ag). The quantity u refers to the "reduced" energy $u = E/E_{nl}$, where E denotes the incident energy of the electrons and E_{nl} is the ionization energy in the (n, l) sub-shell. The function $b_{nl}^{(q)}(u)$ in Eq. (3) has the form:

$$b_{nl}^{(q)} = \frac{A_1 - A_2}{1 + (u/A_3)^p} + A_2 \tag{4}$$

where the four quantities A_1, A_2, A_3, and p are constants that were determined from reliable measured cross-sections for the various values of n and l [10]. The superscript "q" refers to the number of electrons in the (nl) sub-shell. The constant c_{nl} in Eq. (3) was found to be identical to one for s-, p-, and f-electrons.

The DM formula can be extended for the case of a molecular ionization cross-section calculation provided one carries out a Mulliken (or other) molecular orbital population analysis [11] which expresses the molecular orbitals in terms of the atomic orbitals of the constituent atoms. Various orbital population analyses can be obtained routinely using standard quantum chemistry codes, many of which are available in the public domain. These codes can also be used to obtain the necessary molecular structure information in cases where this information is not available accurately otherwise. The application of the DM formalism to positively charged molecular ions as described in our recent publications [5,6] required several modifications as well as additional assumptions and approximations:

(i) The energy-dependent part in formulas (3) and (4), which was derived for neutral targets, was extended to the positive ions in a straightforward fashion by replacing the neutral ionization energy E_{nl} by the corresponding ionization energy of the ion. This neglects the fact that the Coulomb interaction between the incident electron and the target may affect the impact energy. However, this is not expected to be a serious problem, except perhaps for impact energies very close to the ionization threshold.

(ii) The weighting factors g_{nl} for the ionic component of the molecular ion were derived semi-empirically from a fitting procedure using well-established ionization cross-sections of atomic ions [5].

Therefore, the ionic character of the target was reflected (1) in the population analysis of the molecular orbitals as a 'missing' electron, which resulted in different populations ξ_{nl} and different energies E_{nl} and (2) in the ionization of the ionic constituent.

In an earlier paper, we introduced a remedy to some of the limitations of the approach described above for cations. In the present paper, we extend this approach to case of anions. In a first step, we carry out a Mullikan population analysis for both the negative molecular ion and the neutral molecule in an effort to "localize" the additional electron in the molecular anion. As an example, in the present case of BO^-, this means trying to identify whether the ionic character can be associated with a B^- ion in the target or an O^- ion. If the ionization can be localized in this fashion, the second step involves the determination of the weighting factors for the corresponding atomic ion. This can be done by applying the DM formalism to experimentally determined cross-sections for the ionization of the corresponding singly charged ion. Such a comparison yields a value for the product $(r_{nl}^2 g_{nl})$ for the atomic ion, which, in turn, yields directly a value for the weighting factors g_{nl} for the atomic ion, if the ion radii r_{nl} are known. If these radii are not known, they must be estimated in order to obtain the g_{nl} values. With this information, the DM formalism can now be applied to the ionization of a molecular ion with far fewer assumptions and approximations compared to our previous approach.

3. Application of the DM formalism to the detachment of negative molecular ions

Here we discuss the application of the DM formalisms to the electron-induced detachment of the four negative molecular ions B_2^-, O_2^-, BO^-, and CN^-, for which experimental data are available. The required molecular data are shown only for B_2^- and BO^- to illustrate the methodology; for O_2^- and CN^-, we only present the calculated cross-sections.

The results of the pertinent molecular population analyses for B_2^-/B_2 and BO^-/BO are summarized in Tables 1 and 2, respectively. In the case of B_2^-/B_2 (Table 1), the 'extra' electron in B_2^- is localized in an outermost (2p)-orbital, orbital 4. This has the following consequences for the values of the parameter ξ_{nl} in Eq. (3): for orbital 4, ξ_{nl} is attributed to B^- (100%), whereas for orbitals 1–3, ξ_{nl} is attributed equally to B^- (50%) and B (50%). It is only for the outermost orbital (orbital 4) that we need an additional reduced weighting factor, $g_{nl}E_{nl}$ (see Ref. [1]). The reduced weighting factors for the orbitals 1–3 are the same as those for the neutral B_2. Table 2 shows the same data for BO^- and BO. Here, the extra electron in BO^- is added to the outermost orbital, orbital 7, which is populated by only a single electron in the neutral molecule. If one looks at the population differences between BO^- and BO in orbital 7 (Table 3), it is apparent that the extra electron is localized to 92% near the B atom and only to 8% near the O atom. The values of the reduced weighting

Table 1
Mulliken analysis of the MO populations of B_2 (top) and B_2^- (bottom)

B_2	Orbital 1	Orbital 2	Orbital 3
B(2s)	1.65	1.13	–
B(2p$_x$)	–	–	2.00
B(2p$_y$)	–	–	–
B(2p$_z$)	0.35	0.87	–
Sum	2.00	2.00	2.00

B_2^-	Orbital 1	Orbital 2	Orbital 3	Orbital 4
B(2s)	1.70	0.91	–	–
B(2p$_x$)	–	–	2.00	–
B(2p$_y$)	–	–	–	1.00
B(2p$_z$)	0.30	1.09	–	–
Sum	2.00	2.00	2.00	1.00

See text for details.

Table 2
Mulliken analysis of the MO populations of BO (top) and BO^- (bottom)

BO	Orbital 3	Orbital 4	Orbital 5	Orbital 6	Orbital 7
B(2s)	0.25	0.13	–	–	0.52
B(2p)	0.29	0.09	0.44	0.44	0.41
O(2s)	1.36	0.27	–	–	0.02
O(2p)	0.10	1.51	1.56	1.56	0.05
Sum	2.00	2.00	2.00	2.00	1.00
B(2s)	0.24	0.18	–	–	1.20
B(2p)	0.28	0.09	0.36	0.36	0.65
O(2s)	1.42	0.22	–	–	0.03
O(2p)	0.06	1.51	1.64	1.64	0.12
Sum	2.00	2.00	2.00	2.00	2.00

See text for details.

factors for B^- and O^- in the outermost orbital are taken from Ref. [1], whereas in analogy to B_2^-, the reduced weighting factors for all other orbitals are those for the neutral atoms. For the E_{nl} values of the outermost orbitals, we used the experimentally determined values [2–4].

The results of the calculated detachment cross-sections are presented in Figs. 1–4. For each negative molecular ion, we show the calculated detachment cross-section as well as the calculated ionization cross-section of the corresponding neutral molecule for reasons of comparison and the experimental detachment cross-sections.

In the case of B_2^- (Fig. 1), the experimental B_2^- detachment cross-section is smaller than the calculated cross-section by about a factor 3 at all energies for which experimental data are available (up to 25 eV) and exceeds the maximum value of the B_2 ionization cross-section by about a factor of 2 (notwithstanding the expected difference in the cross-section shape and the threshold value). If the experimental detachment cross-section is multiplied by a factor of 3, the resulting cross-section (shown in Fig. 1 as the open triangles) shows an energy dependence that is reproduced reasonably well by the DM calculation for electron energies, for which experimental data were reported. A slight shift in the experimental data towards higher electron energies is somewhat exaggerated

Table 3
Difference in the BO^- and BO MO populations in the outermost orbital (orbital 7)

Orbital	BO^- – BO
B(2s)	0.681
B(2p)	0.235
O(2s)	0.016
O(2p)	0.068

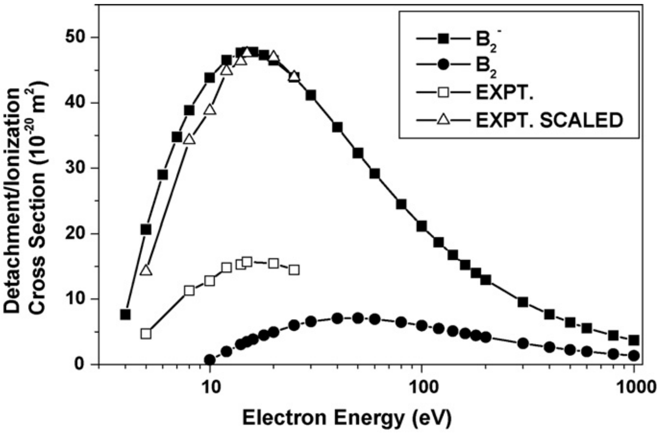

Fig. 1. Detachment cross-section for B_2^- as a function of electron energy. The calculated cross-section (solid squares) is compared with the experimental data from Ref. [3] (open squares) and the scaled experimental cross-section (open triangles; see text for details). Also shown (solid circles) is the calculated B_2 ionization cross-section.

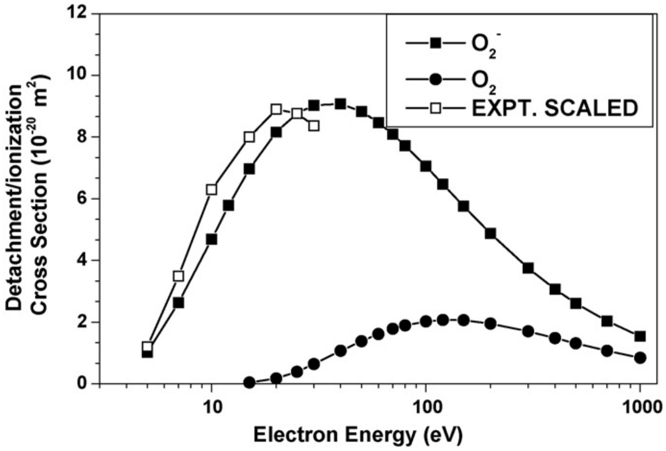

Fig. 2. Detachment cross-section for O_2^- as a function of electron energy. The calculated cross-section (solid squares) is compared with the scaled experimental data from Ref. [3] (open squares; see text for details). Also shown (solid circles) is the calculated O_2 ionization cross-section.

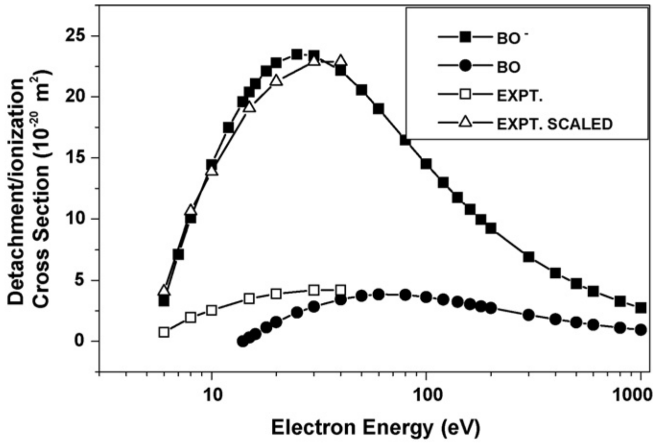

Fig. 3. Detachment cross-section for BO^- as a function of electron energy. The calculated cross-section (solid squares) is compared with the experimental data from Ref. [4] (open squares) and the scaled experimental cross-section (open triangles; see text for details). Also shown (solid circles) is the calculated BO ionization cross-section.

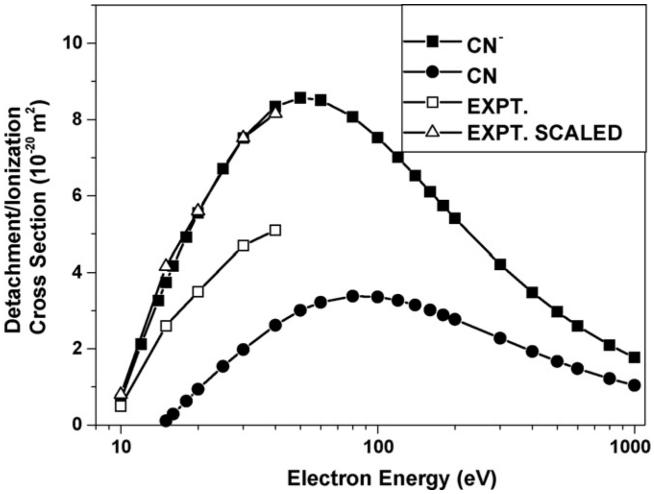

Fig. 4. Detachment cross-section for CN as a function of electron energy. The calculated cross-section (solid squares) is compared with the experimental data from Ref. [4] (open squares) and the scaled experimental cross-section (open triangles; see text for details). Also shown (solid circles) is the calculated CN ionization cross-section.

because of the logarithmic energy scale. We note that this kind of discrepancy between the calculated and measured $B_2{}^-$ detachment cross-section (a factor of 3) is much larger than the discrepancy found for the ionization cross-sections of essentially all neutral molecules and positive ions. Fig. 2 shows the same data for $O_2{}^-$ (and O_2). However, the authors of Ref. [3] do not provide an absolute $O_2{}^-$ detachment cross-section, but give only a relative cross-section curve. If we normalize the reported relative $O_2{}^-$ detachment to our calculated cross-section at 25 eV, we find reasonable agreement in the cross-section shapes for all electron energies, for which experimental data are available (up to 30 eV), notwithstanding a slight shift in the experimental data towards lower electron energies (which again appears somewhat exaggerated because of the logarithmic energy scale).

In the case of BO^- (Fig. 3), the experimental detachment cross-section lies below the calculated cross-section by a factor of about 5.5. If the experimental data are multiplied by this factor (shown again as the open triangles in Fig. 3), there is good agreement between the scaled experimental data and our calculated cross-section up to its maximum at about 40 eV, which is the highest electron energy for which experimental data have been reported. It is noteworthy that the experimental BO^- detachment cross-section has a maximum value that is almost identical to the calculated BO ionization cross-section (see Fig. 3). Lastly, in the case of CN^- (Fig. 4), the DM detachment cross-section lies again above the experimental data, but only by a factor of about 1.6, and both curves show a very similar energy dependence in the energy range covered by the experiment as can be seen from a comparison of the scaled experimental data (shown as the open triangles) with the calculation. We note that the calculation of the CN^- detachment cross-section requires formally a calculation of the detachment from the N^- anion, which is not a stable atomic anion. The procedure for the calculation of a detachment cross-section for N^- is discussed in an Appendix A.

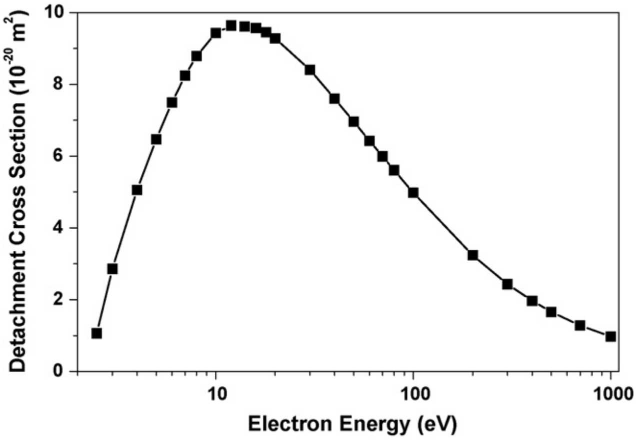

Fig. A1. Calculated detachment cross-section for N^- as a function of electron energy.

4. Conclusions

In this paper, we report calculated cross-sections for the electron-induced detachment of the diatomic anions $B_2{}^-$, $O_2{}^-$, BO^-, and CN^- using the DM formalism. For the three ions $B_2{}^-$, BO^-, and CN^-, for which experimental data are available, we found that the measured data lie significantly below the calculated cross-sections by factors ranging from 1.6 to 5.5. Such a discrepancy is much larger than any discrepancy between measured cross-sections and calculated DM cross-sections for neutral molecules and positive molecular ions, where the level of agreement is typically better than ±30% [5,6,11]. We have no simple explanation for this discrepancy.

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Appendix A. Calculation of a N^- detachment cross-section

We determined a N^- detachment cross-section by extrapolation using the data presented in Ref. [5]. This results in estimated values of the electron affinity $E_a = 1.34$ eV, the orbital binding energy $E_{nl} = 2.3$ eV and a value of the reduced weighting factor of $g_{nl}E_{nl} = 123$, which is the same value that we used for C^-, O^-, and F^-. The result of the calculation of a detachment cross-section from N^- is shown in Fig. A1.

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