Doubly Charged Negative Ions of B₂ and C₂

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The formation of short-lived doubly charged negative diatomic molecular ions has been studied at a heavy-ion storage ring by bombarding singly charged negative ions of B_2^- and C_2^- by free electrons of well-defined energy. Structures are observed in the cross sections for detachment and fragmentation which are argued to be due to short-lived dianion resonances. The resonance energy of B_2^- (~ 5 eV) is close to a calculated dianion ground-state energy and to the energy of some low-lying excited states of B_2^{2-}. The C_2^- resonance energy (~ 10 eV) is close to predicted excited states of C_2^{2-} and significantly above the calculated dianion ground-state energy. From the width of the resonances a lifetime of about 10^{-16} s is obtained for these fragile gas-phase dianions. [S0031-9007(98)07892-2]

Over the past few years there has been an ongoing experimental and theoretical search for the rarely occurring doubly charged negative ions (dianions) [1,2]. It seems evident that atomic dianions are not stable (see, e.g., Refs. [3–5]), which was, in fact, already predicted by Bohr in the case of hydrogen [6]. It is still an open question under what conditions *metastable* atomic and molecular dianions exist. Such systems are challenging from both theoretical and experimental points of view. Large molecular systems can hold many extra electrons because the electron cloud can spread out over an extensive volume or the excess electrons can stay well separated. The question that we address here is whether dianions can be formed when small diatomic negative molecular ions are bombarded by electrons of well-defined energy. The physics of dianions of small molecules is to a large extent determined by the extreme amount of electron correlation, and the stability is determined by the destructive decay modes of autodetachment and dissociation. In the present work we have found evidence for the existence of two gas-phase diatomic dianions. We determined their energy, estimated their lifetimes, and studied some of their decay modes.

Laser ablation combined with a coincidence technique has recently provided evidence for the existence of carbon cluster dianions [7], which has also been seen by mass spectroscopy [8,9]. The interpretation of mass spectrometer measurements is difficult due to the presence of small impurity beams that erroneously may be assumed to be dianions [10]. Moreover, when dianions are formed directly in an ion source via electron-anion collisions, the electron energy in the formation process is not very well known [9], which limits the obtainable information.

We have previously reported on a significant structure in the electron-impact detachment cross section of C_2^- at about 10 eV [11]. At first, the structure was tentatively suggested to be due to the formation of ground state C_2^{2-}. Later, elaborate calculations [7,12] showed that the metastable ground state of C_2^{2-} lies at about 3 eV above

the negative ion ground state and hence could not be the origin of the resonance at 10 eV.

We consider here the following detachment reactions (with and without dissociation):

$$X_2^- + e^- \rightarrow \begin{cases} X_2^0 + 2e^-, \\ X^0 + X^0 + 2e^-, \end{cases} \quad (1)$$
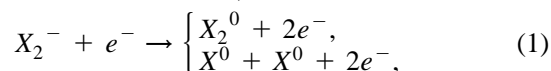
and two reactions involving dissociation (with and without ionization):

$$X_2^- + e^- \rightarrow \begin{cases} X^- + X^0 + e^-, \\ X^- + X^+ + 2e^-, \end{cases} \quad (2)$$
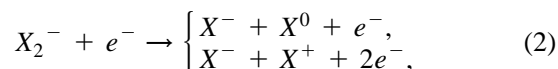
where e^- is a free electron and X is either the boron atom (B) or the carbon atom (C). The negative ion B_2^- is known from *ab initio* calculations [13] and C_2^- is known from several previous works (see, e.g., Ref. [11] and its references). Of interest here are the electron affinities $EA(B^-) = 0.28$ eV [14], $EA(C^-) = 1.26$ eV [14], $EA(B_2^-) = \sim 2$ eV [13], $EA(C_2^-) = 3.27$ eV [15], and the dissociation energies $D_e(B_2^-) = \sim 4.8$ eV [13] and $D_e(C_2^-) = 8.45$ eV [16]. Both molecular negative ions have excited states below the neutral molecular ground state.

The experiment was carried out at the ASTRID storage ring. The ring is 40 m in circumference and has a square geometry with two 45° bending magnets in each of the four corners. We used a sputter-ion source for the production of B_2^- and C_2^-. The beams of approximately 200 nA–1 μA were preaccelerated to 150 keV, injected into the ring, and accelerated to approximately 5 MeV. At this energy, the lifetime of the beams was about 1.5 s, determined by collisions with the residual gas (2×10^{-11} torr). In the ring the ions were merged with the electron beam of the electron cooler [4,17]. The electron energy resolution (FWHM) was about 0.12 eV at $E = 5$ eV and 0.16 at 10 eV, i.e., small enough to detect resonances with sub eV widths.

Neutral particles produced by detachment [Eq. (1)] and dissociation [Eq. (2)] were detected with a 60×40 mm² surface barrier detector located behind the dipole magnet

following the electron cooler (see Fig. 1). Another surface barrier detector was placed inside the dipole magnet chamber to detect negative fragment ions (B^- and C^-). This detector had a diameter of only 20 mm and detected about 80% of the negative fragments.

The detection of a single atom X (B or C) gives an output pulse which is half of that obtained from a hit by two atoms $2X$ (2B or 2C) or a molecule X_2 (B_2 or C_2) (see Fig. 1). Because the ion-beam diameter was smaller than the electron-beam diameter (~ 2.5 cm), and the electron density (ρ_e) was constant to a good approximation [17], the cross sections were obtained from

$$\sigma(Y) = \frac{R(Y) - R_0(Y)}{R(X_2^-)} \frac{v_i}{l \epsilon \rho_e v}, \qquad (3)$$

where Y represents either the X or the $2X$ peak from the detector, and $R(Y)$ is the rate of detected neutrals (Y) when the electron beam is turned on. $R_0(Y)$ is the background rate primarily due to interactions with the residual gas in the ring, $R(X_2^-)$ is the number of stored ions (B_2^- or C_2^-) entering the interaction region per unit time, and $l(= 95$ cm) is the effective length of the interaction section. ϵ is the detector efficiency, v_i is the ion velocity, and v is the electron velocity in the ion frame. The true signal $R(Y) - R_0(Y)$ was obtained by chopping the electron beam on and off.

To distinguish between a pair of atoms and a molecule, we inserted a grid with known transmission probability T in front of the neutral detector and measured the rate (R) of the half ($1X$) and full ($2X$) energy peaks [18]. These yields are related to the cross sections for X_2^0, $X^0 + X^0$, and $X^0 + X^-$ production in the following way:

$$R_{1X}(T) = \frac{1}{N(T)} [T \sigma_{X^0+X^-} + 2T(1-T) \sigma_{X^0+X^0}], \quad (4)$$

$$R_{2X}(T) = \frac{1}{N(T)} (T \sigma_{X_2^0} + T^2 \sigma_{X^0+X^0}), \qquad (5)$$

where $N(T)$ is a normalization constant. These equations were solved to yield the individual cross sections. We detected only signals related to single negative atomic ions (B^- and C^-) with the detector placed inside the magnet chamber; no signal related to negative ions with the full energy ($2X$) was observed. Thus, the two final channels $X^- + X^-$ and X_2^{2-} were completely absent at all electron energies (see Fig. 1).

Absolute cross sections were obtained at fixed energies. At 15 eV the cross section for B_2^0 formation was $1.2 \pm 0.8 \times 10^{-15}$ cm^2 and at 13 eV the cross section for C_2^0 formation was $2.5 \pm 0.5 \times 10^{-16}$ cm^2. The somewhat large error bar stems from the uncertainty of the ion-current measurement. Relative cross sections are associated with much smaller error bars.

In Fig. 2 we show the results obtained with B_2^-. The upper part of the figure shows the detachment cross sections without dissociation (final B_2^0) and with dissociation (final $B^0 + B^0$). Evidently pure detachment is the dominating process with a cross section maximum of about 10^{-15} cm^2. The lower part of the figure shows the cross section that leads to detection of B^-. Background collisions contribute little to this channel and although it is 2 orders of magnitude smaller than the detachment channel, it is readily detectable. The energy threshold for dissociation is almost 5 eV and the low-energy onset of the cross section is attributed to vibronic excitation of the B_2^- ions [13] (the vibrational excitation does not relax by infrared emission since the dipole moment is zero for homonuclear molecular ions). The $B^- + B^+$ channel opens at about 13 eV, but is apparently not very important at these low energies. At about 5 eV there is a significant peak in the dissociation cross section; its origin will be discussed later. No structures were detected in the detachment channels.
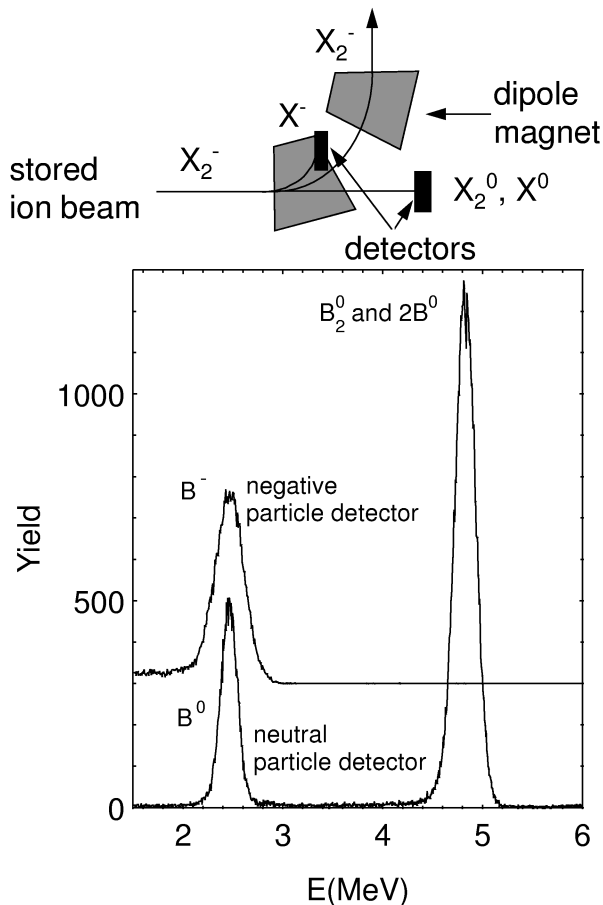

FIG. 1. A schematic drawing of the corner of the ASTRID storage ring after the electron target showing the dipole magnets and the positions of the particle detectors. The pulse-height distributions from the detectors are shown for storage of B_2^-. In the detector for neutrals, two peaks were recorded corresponding to singles (B^0) and doubles ($B^0 + B^0$ and B_2^0). In the detector for negative fragments only singles (B^-) were detected with no sign of doubles ($B^- + B^-$) at the beam energy of ~ 5 MeV.
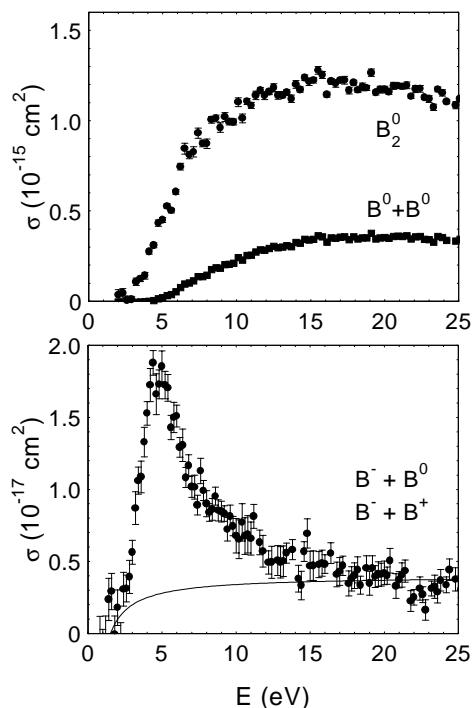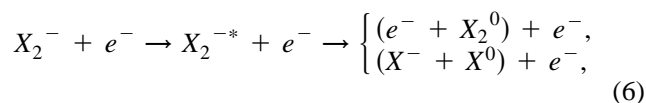
FIG. 2. The cross sections obtained with B_2^- for detachment (B_2^0), detachment + dissociation ($B^0 + B^0$) and dissociation without and with ionization ($B^- + B^0$ and $B^- + B^+$) as a function of electron energy (note the difference in the ordinate). The error bars show the relative uncertainty. Absolute error bars are larger; see text. The solid line is the nonresonant background the shape of which is estimated from a classical calculation [4].
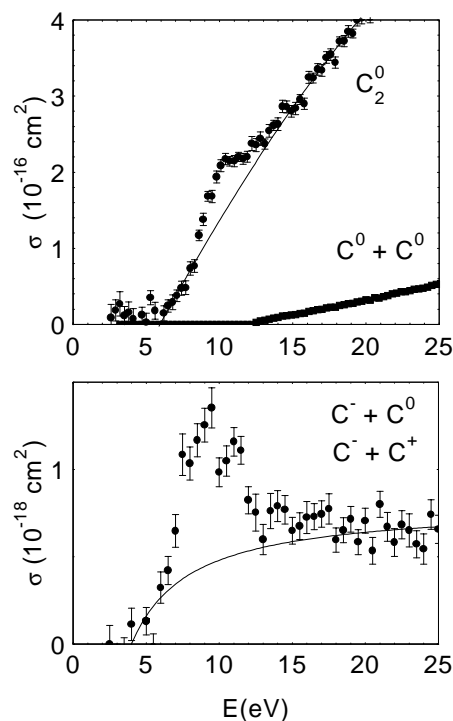

FIG. 3. As Fig. 2 with C_2^-. A straight line is used to visualize the nonresonant cross section under the peak in the detachment channel.

In Fig. 3 we show the results obtained with C_2^-. The measurement reproduced the earlier observed structure [11] in the detachment cross section (final C_2^0) at about 10 eV. As with B_2^-, pure detachment is the dominating process. The dissociation channels from detection of C^- are shown on the lower part of the figure. The energy threshold for dissociation (D_0) is 8.33 eV, so the earlier onset of the cross section is evidence of vibrational excitation in the C_2^- beam. Of importance is the appearance of a significant peak in the dissociation cross section at about the *same* energy where the structure appears in the detachment channel.

Because of the relatively low electronic binding energy, the dominating process is nonresonant electron detachment [see Eq. (1)]. Electron detachment may also proceed via an excited state of the singly charged negative ion that may be in the electronic and the dissociative continuum,

$$X_2^- + e^- \rightarrow X_2^{-*} + e^- \rightarrow \begin{cases} (e^- + X_2^0) + e^-, \\ (X^- + X^0) + e^-, \end{cases} \quad (6)$$

where the asterisk indicates an excited ion. These processes are not expected to yield resonance structures in

the cross section since the first step of the reaction may happen at any incident electron energy above the excitation energy. In another type of process, the incoming electron is resonantly *captured* into a state of the dianion, which then subsequently decays either by simultaneous or sequential emission of two electrons into a molecular bound state or by autodetachment to a repulsive negative molecular ion state,

$$X_2^- + e^- \rightarrow X_2^{2-} \rightarrow \begin{cases} X_2^0 + 2e^-, \\ X^- + X^0 + e^-. \end{cases} \quad (7)$$
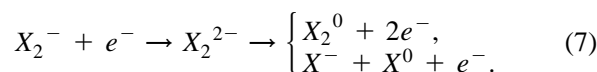
These processes are truly *resonant* in the sense that the incoming electron energy has to match the energy of the dianion resonance (~ 5 eV for B_2^{2-} and ~ 10 eV for C_2^{2-}). The second channel corresponds to resonant dissociative excitation that appears as broad resonances in the dissociative excitation cross section [19] of molecular cations.

We have performed *ab initio* calculations on the CCSD(T)/6-311 + G(d) level with the Gaussian94 program [20] which show that excited states of C_2^{2-} of $^1\Pi_g$ and $^3\Pi_g$ symmetry lie about 8 eV above the $^2\Sigma_g^+$ ground state of C_2^-, and excited states of B_2^{2-} of $^1\Sigma_u^+$ and $^3\Sigma_u^+$ symmetry lie about 5.5 eV above the $^4\Sigma_g^-$ ground state of B_2^-. The calculated excited states have energies of the right order of magnitude to explain the observed resonances for both ions. There is a significant difference between the two ions, however. In the case of C_2^- the

resonance is several eV above the dianion ground state, whereas the resonance of B_2^- is close to the dianion ground state, which is calculated to be 4.5 eV above the B_2^- ground state.

The dianions X_2^{2-} can decay by several channels to repulsive curves and bound states of both the negative ion and the neutral molecule. If we ignore a possible broadening due to vibrational excitation of the initial molecular ion, we obtain lifetimes of about $(1-3) \times 10^{-16}$ s from the widths of the observed resonances that are of the order of $3-5$ eV. We find that the C_2^{2-} resonance state primarily decays to C_2^0 and a small fraction to $C^- + C^0$, whereas for boron a resonance was found only in the $B^- + B^0$ channel (see Fig. 2). The decay to B_2^0 may be too small to be detected in the presence of a dominating direct detachment channel (also final B_2^0). The decay into the $X^- + X^-$ continuum is completely absent for both ions, probably because of a small tunneling probability through the barrier of the X_2^{2-} state. The "elastic" channel, with emission of a single electron (final X_2^-), is not observable in the present experiment.

To summarize, a merged beams technique has been used to study collisions between free electrons and molecular negative ions. We find large structures in the electron-impact detachment and dissociation cross sections for diatomic B_2^- and C_2^-. The resonance character and the energy of the structures suggest that dianions have been formed. From the experiment we get the energy of the resonances, the approximate lifetime as well as information about the decay path. New calculations, which will be published separately, show that there exist dianion states at the appropriate energy.

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