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Photodissociation of the free BeC_6^{2-} dianion

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Abstract

We have confirmed the existence of the BeC_6^{2-} dianion produced in a Cs-sputter negative ion source with a cathode of mixed Be metal and graphite powder. Using our laser-accelerator mass spectrometry (AMS) system, we have studied the photoelectric interaction of the dianion and show that it is bound by more than 1.165 eV relative to any photodetachment or dissociation channel. The total cross-section leading to either of the channels for 2.33 eV photons is 6 Mb. © 2000 Elsevier Science B.V. All rights reserved.

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1. Introduction

The possible existence of exotic dianions (doubly charged negative ions) has attracted interest for decades. Kutschera et al. [1] searched for dianion of the elemental atoms of B, C and O using accelerator mass spectrometry (AMS). No evidence for the formation of these ions in an inverted sputter source has been found. Large stable doubly charged negative molecular ions and clusters such as C_{60}^{2-} have been observed [2,3]. However, the existence of small doubly charged negative free molecules (in gas phase) was in question untill recent years. Dianion production is likely to be very meager because their formation requires complicated processes. A doubly charged anion should be stable if the additional binding energy (BE) due to the second electron exceeds the coulomb repulsion between the mononegative ion and the second electron. In the condensed phase, a doubly charged anion can be stabilized by the surrounding medium. Thus, it was thought that if a doubly charged anion exists in a gas phase, it would be mainly produced as a large molecule, which has properties that lie between the gaseous and the condensed phase. Indeed, short-lived and excited small dianion molecules were observed in the past [4,5]. However, recent theoretical calculations show that small stable molecules, which can attach two extra electrons contain at least four atoms of the alkaline-earth and halide elements [6–9] (molecules as LiF_3^{2-} and ClF_3^{2-}). Following the prediction of the existence of small dianion

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molecules, they were first observed by Middleton and Klein [10–12] and very recently by Gnaser [13]. The molecule BeC_6 was found to be a favorite to form dianions [11]. In this work, we have confirmed the existence of the BeC_6^{2-} dianions and studied photon interaction with this molecule.

2. Experimental setup

BeC_6^{2-} dianions are produced in a Cs-sputter negative ion source [14] with a cathode of mixed Be metal and graphite powder. The negative ions, after preacceleration by a voltage of 118.0 kV, are focussed with an electrostatic lens into a 1 m long region (at $\sim 2 \times 10^{-7}$ Torr) between two 3 mm diameter apertures. A laser beam is sent anti-parallel to the negative ion beam, through the same apertures that define the interaction region. Photodissociation and any single or double electron photodetachment of the molecular ion are signatured by the depletion of the doubly negative ion component of the beam after AMS identification (see below). This is because the resulting fragments after the photodissociation in the laser pulse are eliminated from the ion beam after a 90° magnetic analysis. The negative ions surviving the laser interaction are mass-analyzed (see below) and injected into the accelerator. A master oscillator is used to trigger both the laser pulse, and with proper delay, an electrostatic chopper that chops the ion beam to 3.5 μs long pulses, so that only ions which were in the interaction region at the time of laser firing, are transmitted. More details about the laser-accelerator mass spectrometry system were published elsewhere [15,16]. In this work, we have studied the interaction of Nd:YAG first and second harmonic photons, 1.165 and 2.33 eV, respectively, with the dianion.

The injection magnet is first calibrated with carbon clusters and molecules (Fig. 1, top two spectra) using a graphite cathode. Using the mixed cathode, a small peak between mass over charge $m/q = 40$ and 41 is detected by the Faraday cup just after the injection magnet (Fig. 1, bottom). The ions in this peak are identified by AMS [17,18] as the $^{9}Be^{12}C_6^{2-}$ dianion by determining the terminal voltage at which the ^{9}Be or one of the ^{12}C fragments (after stripping) are analyzed and transported to the detector (Fig. 2). The terminal voltage and the detector are calibrated by injecting the negative molecule $^{12}C_3$ and identifying unambiguously the fragment $^{12}C^{4+}$ and by injecting the negative molecule $^{13}C^{12}C_2$ and identifying unambiguously the fragment $^{13}C^{4+}$. The ions are identified by measuring for each ion five parameters in the detector, i.e., three differential energy-loss signals (ΔE_1, ΔE_2 and ΔE_3), total energy loss (E_{cth}) and the residual energy in a silicon detector (E_{res}). In the case of $^{9}Be^{12}C_6^{2-}$, when injecting $m/q = 40.5$, the fragments $^{12}C^{4+}$ and $^{9}Be^{3+}$ are identified unambiguously in the detector (Figs. 3 and 4). Broad-range scan of the terminal voltage shows that only these two isotopes are present in the $m/q = 40.5$ beam. The terminal voltage where the two-ions peak is as they were injected in a molecule of $m/q = 40.5$. The only combination of ^{12}C and ^{9}Be that gives $m/q = 40.5$ is $^{9}Be^{12}C_6^{2-}$.

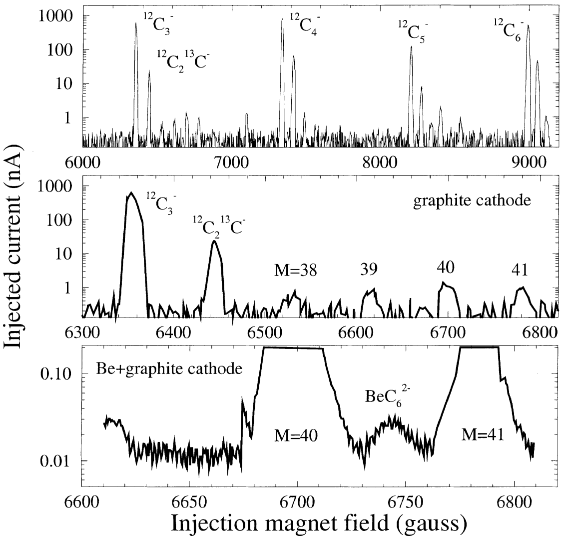

Fig. 1. Mass scan of negative molecular ions produced around 40 amu with a graphite cathode (top and middle) and a Be metal mixed with graphite cathode (bottom). The scans are made with the 90° injection magnet; analyzed currents were measured either with a Faraday cup and Keithley picoammeter (top and middle) or with a high-sensitivity current preamplifier (bottom). The noise of the preamplifier signal is about an order of magnitude lower. The small peak at $m/q = 40.5$ amu is identified as the $Be^{12}C_6^{2-}$ dianion by AMS (see Figs. 2–4).

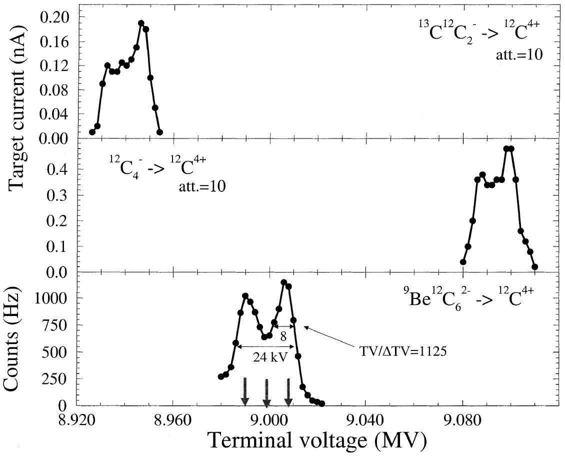

Fig. 2. Terminal voltage scans for negative molecular ions injected at mass 37 ($^{13}C^{12}C_2^-$), 48 ($^{12}C_4^-$) and 40.5 ($^{9}Be^{12}C_6^{2-}$); $^{12}C^{4+}$ fragments dissociated by the stripping process are analyzed by the 90° analyzing magnet and detected by charge current (top and middle, beam attenuated by a factor of 10) or count rate in the AMS detector (bottom). The arrows show the voltages for the energy spectra presented in Fig. 3. The terminal voltage scan presents a mass resolution of $M/\Delta M = \mathrm{TV}/\Delta\mathrm{TV} = 1125$. The larger distribution of terminal voltages is attributed to the Coulomb explosion of the molecule ($M/\Delta M = 375$).

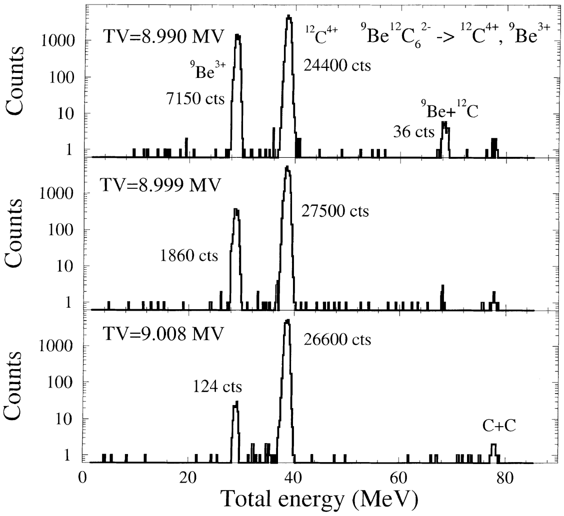

Fig. 3. Energy spectra of analyzed ions after injection of $m/q = 40.5$ measured in the AMS detector at three-terminal voltages, shown by arrows in Fig. 2 (bottom). The spectra demonstrate the presence of ^{9}Be and ^{12}C in the molecular ion injected at $m/q = 40.5$ and the relative abundancies of the two fragments as a function of the terminal voltage. The values of the terminal voltages are also consistent with the identification of the $^{9}Be^{12}C_6^{2-}$ dianion. The calculated difference between the terminal voltage for $^{9}Be^{3+}$ injected as $^{9}Be^{12}C_6^{2-}$ and $^{12}C^{4+}$ injected in the same dianion is 13 kV in agreement with the measured spectra (top and bottom, respectively). The peak around 68 MeV is attributed to the summing of $^{9}B^{3+}$ and $^{12}C^{4+}$. This summing depends very much on details of the molecule Coulomb explosion.

3. Results and discussion

At 2.33 eV, strong absorption of the dianion in the photon beam is observed (Fig. 5). The cross-section (σ) for the dianion photon interaction is measured by the slope of the line $n/n_0 = \exp(-\phi\sigma)$ (Fig. 6), where ϕ is the photon fluence and n, n_0 denote the number of ions accumulated with and without laser, respectively (for details see [15,16]). The line for $h\nu = 2.33$ eV corresponds to a cross-section of 6.0 ± 0.8 Mb. The error bar is combined of a statistical error of ±8% and a systematic error of ±10% that is due to the uncertainty of the effective photon fluence in an interaction of two Gaussian beams (ion and laser beams). The line for $h\nu = 1.165$ eV is consistent with zero interaction ($\sigma < 0.025$ Mb), demonstrating that the BE of the $^{9}Be^{12}C_6^{2-}$ dianion is larger than 1.165 eV relative to any dissociation or photodetachment channel. The existence of a destructive interference effect in the photon–ion interaction (see for example [19]) leading to such a low limit of absorption cross-section is considered unlikely. The time of flight of the $^{9}Be^{12}C_6^{2-}$ dianion from the ion source to the terminal foil stripper is about 35 μs. This time sets a minimum lifetime for the dianion of the same order of magnitude. The relatively longer lifetime and the relatively larger BE suggest that this dianion is stable. The BE of the $^{9}Be^{12}C_6^{2-}$ dianion is of the order of BEs predicted for the small alkine-earth halide dianions, LiF_3^{2-} (BE = 1.7 eV), NaF_3^{2-} (BE = 2.0 eV) and $LiCl_3^{2-}$ (BE = 2.3 eV) in [20]. The system used in this work is suitable for measuring branching ratios of the studied photodissociation process by scaling the AMS system to detect any of the possible fragments BeC_{6-n}^- and C_n^-.

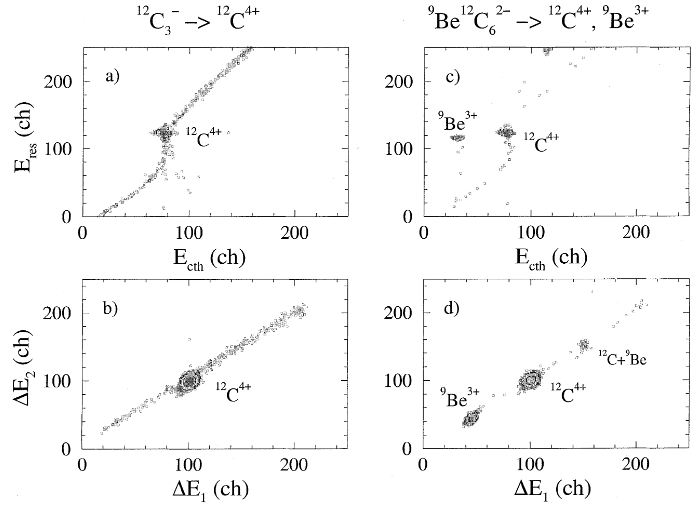

Fig. 4. Energy and energy-loss identification spectra: (a) and (b) the molecule $^{12}C_3^-$ was injected and the accelerator was tuned to detect $^{12}C^{4+}$; (c) and (d) the molecule $^9Be^{12}C_6^{2-}$ was injected and the accelerator was tuned to detect its fragments (TV = 8.990 MV same as in Fig. 3, top).

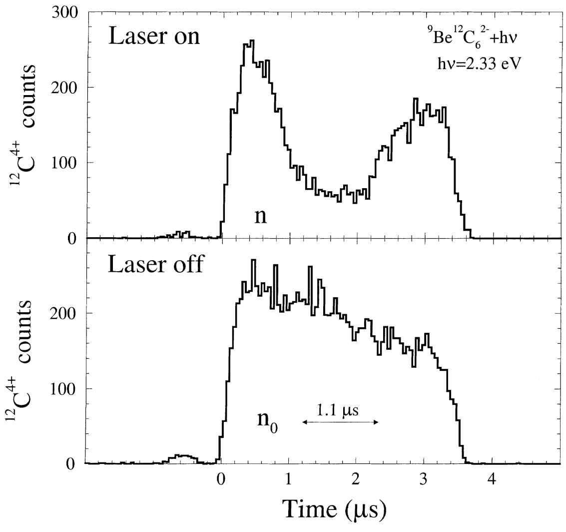

Fig. 5. Time of arrival spectra of $^{12}C^{4+}$ ions from the $^9Be^{12}C_6^{2-}$ dianion with (top) and without (bottom) laser interaction. The two spectra are measured simultaneously. The large dip in the top spectrum results from the photon dissociation of the dianion resulting in any of several channels: electron photodetachment, photodissociation. The ratio n/n_0 of the counts accumulated in the time window indicated by the arrow measures the transmission of the dianion beam through the photon pulse. For details, see [15,16].

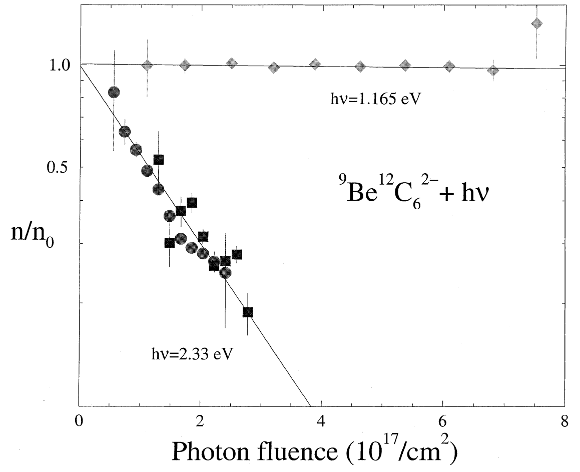

Fig. 6. Dependence of the $^9Be^{12}C_6^{2-}$ negative dianion transmission n/n_0 on the photon fluence of the laser beam for two photon energies. The photodissociation cross-section is extracted from the slope of the line. The different symbols denote independent measurement runs.

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