Storage of negative carbon ions in an electrostatic ring

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Abstract. Negative carbon atomic ions and cluster ions were stored in an electrostatic ion storage ring. The lifetime of the metastable atomic ion is heavily affected by the blackbody radiation from the surrounding environment. By introducing rare gas target into the ring, collision-induced detachment cross sections of the atomic ion C\textsuperscript{–} were obtained. For cluster ions C\textsubscript{n}\textsuperscript{–} (n = 2\textasciitilde8), decay of metastable ions with sub-millisecond to millisecond lifetime was commonly observed.

1. Introduction

It is generally recognized that negative ions often have no excited bound states, since an excess electron in negative ions is bound in the long range potential. However, C\textsuperscript{–} ions have weakly bound excited states, 2p\textsuperscript{3}2D\textsubscript{3/2} and 2p\textsuperscript{3}2D\textsubscript{5/2}, 50 and 33 meV below the continuum, respectively, together with the ground state 2p\textsuperscript{3}4S\textsubscript{3/2} [1]. For carbon clusters, bound electronic excited states generally exist and the role of these excited states has acquired widespread interest, for example, some of the transitions are considered to be candidates for the carrier of the interstellar diffuse band [2]. So far, many spectroscopic studies on the negative carbon cluster ions have been reported, both in vacuum and in the cold matrices [3].

However, information on the metastable states of the negative carbon ions, which is connected to the ground state by optically forbidden transitions, are very few in spite of its potential importance in astrophysics and chemical reactions involving carbon ions. The difficulty arises from scarcity of the metastable ions and is further enhanced by the fact that some of these species are fragile even in vacuum.

The advent of an ion storage ring allows us to observe the dynamics of the metastable ions with the lifetimes in the time scale from sub-millisecond to second, with high sensitivity [4]. The electrostatic ion storage ring recently developed at Tokyo Metropolitan University (TMU E-ring) has the characteristics that the instruments covering the ion trajectory can be cooled down to the liquid nitrogen (LN\textsubscript{2}) temperature, which is suitable to study the effect of the blackbody radiation on the stored ions [5]. In the present study, negative ions of atomic and clusters were stored in the ring and lifetime measurements were carried out mainly to examine the presence of the metastable states. The collision-induced electron detachment cross section of the ground state of C\textsuperscript{–} will be also discussed.
2. Experiments

The negative carbon ions were generated by using a cesium sputter ion source, and accelerated to 20 keV. The ions were then mass-selected by an E×B Wien filter prior to the injection into the ring. Although the mass resolution was not so high \((M/\Delta M = 37 \text{ at } M/e = 30 \text{ Da/e})\), it was sufficient for size selection of the clusters. The details of the TMU E-ring and the ion injection system are described in our previous publications [5,6].

A typical beam current initially stored in the ring ranged from several hundred pA \((\text{C}^- \text{ or } \text{C}_2^-)\) to a few pA \((\text{C}_7^- \text{ or } \text{C}_8^-)\). The neutral particles produced during the ion storage were detected by a microchannel plate placed at the extension of the straight section of the ring. To examine the effect of blackbody-radiation-induced (BRI) detachment, the inside of the ring was cooled by introducing the LN\(_2\) flow. Under the LN\(_2\) temperature, all electrodes shrunk and the ion beam trajectory slightly deviated from the optimum position, and re-adjustment was carried out when lifetime measurements were performed. The details of the cooling system and the resultant beam profile are also given in the reference [6].

3. Results and discussion

When the excited states of the stored ions considerably contribute to production of the neutral particles during the ion storage, the decay cannot be fitted by a single exponential line nor the signal intensity would not be proportional to the stored ion current. Provided that only a single excited state is effectively populated, the number of the stored ions is given by

\[
N = N_g^0 \exp(-k_{\text{col}}^g t) + N_e^0 \exp(-k_{\text{col}}^e t - k_{\text{rad}}^e t),
\]

where \(N_g^0\) and \(N_e^0\) are the numbers of the initially stored ions in the ground state and the excited state, respectively, and \(k_{\text{col}}^g\), \(k_{\text{col}}^e\) and \(k_{\text{rad}}^e\) are the pseudo first order rate constants of the collision-induced reactions for the ground state, that for the excited states, and the rate constant of the BRI process for the excited state. Both elastic scattering and reactions (detachment and/or dissociation) would contribute to the collision-induced decay, namely, \(k_{\text{col}}^g = k_{\text{col}}^d + k_{\text{col}}^{\text{el}}\) and \(k_{\text{col}}^e = k_{\text{col}}^d + k_{\text{col}}^{\text{el}}\), where the superscripts “d” and “el” stand for “detachment or dissociation” and “elastic scattering”, respectively.

Therefore, the number of detected neutrals is given by

\[
I = \alpha N_g^0 k_g^d \exp(-k_{\text{col}}^g t)
+ \alpha N_e^0 \left( k_e^d + k_e^{\text{rad}} \right) \exp(-k_{\text{rad}}^e t + k_{\text{col}}^e t),
\]

where \(\alpha\) is the proportionality constant related to the collection efficiency.

Since the yield by the collision-induced processes is a function of the gas density in the ring, pressure dependence of the lifetime gives information on the \(k_{\text{col}}^g\) and, in principle, \(k_{\text{col}}^e\). The BRI processes is a function of the environmental temperature, thus, cooling of the ring provides information on the \(k_{\text{rad}}^e\).

3.1. Negative carbon atomic ions

First, \(\text{C}^-\) ions were stored in the ring at room temperature \((293 \text{ K})\), and produced \(\text{C}\) atoms were measured for about 100 ms. The semi-log plot of the relative yields against the storage time is shown in figure 1(a), and that for \(\text{O}^-\) is also shown in 1(b) for comparison. As can be seen in the figure 1(a), a component of the

![Figure 1](image-url)
short lifetime of a few ms was observed, which is attributed to the decay of the $^2D_{3/2, 5/2}$ excited states. The yield is estimated to be about 0.1% of the total ions. It exhibits a sharp contrast to the case of O $^{3/2, 5/2}$ ions shown in figure 1(b), where short lifetime components are not discernible. The result is consistent with the fact that the binding energy of the excited state of O$^-$ ($2p^5 2D_{3/2, 5/2}$) is 1.44 eV, which is too large to be detached by the blackbody radiation at room temperature. As will be shown later, the decay profile of C$^-$ can also be closely fitted by a single exponential line when the storage time is longer. These long-life components originate in the collision-induced reactions with the residual gases.

The lifetime of the fast component is evaluated to be $2.7$ ms, namely $k_{\text{col}} + k_{\text{rad}} = 370$ s$^{-1}$, by subtracting the slow component from the observed decay. The pressure dependence of the lifetime indicates that the BRI reaction is much faster than the collisional processes, therefore, $k_{\text{rad}} \approx 370$ s$^{-1}$. This fact also implies $k_{\text{col}}$ cannot be evaluated precisely from the present experiments, at least at room temperature.

To confirm the effect of the BRI processes, the ring was cooled, and at various temperatures, C$^-$ ions were stored and the decay was observed. The decay plots of the fast component obtained by subtracting the slow component are shown in figure 2. The temperatures indicated in the figure are those of cooled electrodes. As expected, we have observed that the lifetime became longer from 2.7 ms to 5.9 ms by reducing the blackbody radiation at the lower temperature. It should be noted that the pressure did not change considerably since the residual gases were mostly hydrogen molecules under ultra high vacuum conditions. In fact, the rate for collision-induced reactions remains almost constant.

Unfortunately, environmental temperatures of the stored ions were not uniform because of the instrumental limitations. The effect of the LN$_2$ cooling is evaluated according to a crude approximation that the environmental temperature is alternatively $T_h$, the room temperature, or $T_L$, the temperature of the cold electrodes. Then, the BRI detachment rate constant is given by

$$k_e = \phi_L k_{\text{rad}}(T_h) + (1 - \phi_L) k_{\text{rad}}(T_L)$$

$$= \phi_L \int_{0}^{c} \sigma(v)u(v, T_L)dv + (1 - \phi_L) \int_{0}^{c} \sigma(v)u(v, T_H)dv,$$

where

$$u(v, T) = \frac{8\pi v^2}{c^2(e^{hv/kT} - 1)}.$$  

The constants $c$, $h$ and $k$ are the speed of light, Planck’s constant, Boltzmann constant, respectively, and $\sigma(v)$ is the photoelectron detachment cross section of the $^2D$ state, for which we adopted reported experimental data [7]. The fitting parameter $\phi_L$ is the fraction of the cold area with respect to the whole surrounding area of the stored ions and would be the same for all $T_L$ s. The observed and calculated rate constants are shown in figure 3. To fit the

![Figure 2](image-url)  
Figure 2. Decay plots for the fast decay components of C$^-$. The obtained lifetime and the rate constant are also shown.

![Figure 3](image-url)  
Figure 3. Observed and simulated rates for various $T_L$ s.
observed lifetime at various electrode temperatures, the $\phi_L$ is estimated to be 56%. The agreement is quite satisfactory indicating the assumption putted for the BRI processes of the metastable states would be reasonable.

From the lifetime of the ground state $^4S$ of C$^-$ ions, the cross sections of the collision-induced reactions are derivable. The values of $k_{g}^{\text{col}}$ were obtained from the decay plot in the wider time scale as shown in figure 4, where the faster decay component can be seen only at the beginning of the storage. Putting $k_{g}^{\text{col}} = (\sigma_{g}^{\text{el}} + \sigma_{g}^{\text{det}})\rho \nu$, where $\sigma_{g}^{\text{el}}$, $\sigma_{g}^{\text{det}}$, $\rho$ and $\nu$ are the elastic scattering and the detachment cross sections for the ground state ions, the target density, and the ion velocity, respectively, the first term in Eq. (2) may be written as

$$I = aN_0^g\sigma_{g}^{\text{det}}\rho \nu \exp[-(\sigma_{g}^{\text{el}} + \sigma_{g}^{\text{det}})\rho \nu t].$$

(4)

Thus, the values of $\sigma_{g}^{\text{el}} + \sigma_{g}^{\text{det}}$ can be derived from the slope of the decay plot.

The $k_{g}^{\text{col}}$s obtained under various target gas densities are shown in figure 5. The target gases were He, Ne, Ar, Kr and Xe atoms. As shown in the figure, the plots are well fitted by a linear function, indicating that contribution of the background gases and the multiple scattering is negligibly small.

To examine the values of the $\sigma_{g}^{\text{el}} + \sigma_{g}^{\text{det}}$, we calculated the detachment cross section on the basis of a naive model in which an extra electron is treated as a free electron moving at the velocity of the ion, $\nu$, and detachment is a result of elastic scattering by the target. This may be rationalized since the outer electron is very weakly bound in C$. The obtained cross sections for various gas targets are shown in figure 6 as a function of the scattering lengths $L$, which are evaluated to be 1.2, 0.3, -1.7, -3.0 and -6.0 in atomic unit for He, Ne, Ar, Kr, and Xe, respectively.

The theoretical cross sections of the electron-impact elastic scattering are given by the formula $\sigma_{g}^{\text{det}} = 4\pi L^2/(1 + L^2 K^2)$ [8], where $K$ is the wave number vector of s-wave electron, and also plotted in the figure 6. In spite of the crude approximation involved in the calculation, agreement with the experimental values is fairly well. This tendency indicates that the variation in the cross section would be mainly due to the

Figure 4. Decay plot for C$^-$ recorded up to 10 s.

Figure 5. Pressure-dependence of the (pseudo first order) rate constants.

Figure 6. Plot of detachment cross sections obtained from the plots in figure 5 and that of the electron-impact elastic scattering from the theory.
difference in the detachment cross section. In addition, the result indicates the picture that an extra electron in the \(^4S\) state behaves more or less like a free electron in this collision system would be not so far from the realistic model [9], although a quasi-molecular picture, which is often adequate in the low-energy regime, has to be carefully considered for more quantitative treatments [10].

3.2. Carbon cluster ions

Presence of the metastable states of negative carbon cluster ions is reported by J. U. Andersen et al., by using the magnetic ion storage ring, ASTRID [11]. Concerning small clusters up to \(C_5^-\), for which commonly accepted idea is these are chain-form clusters, they stated that fast decay components are observed, namely presence of the metastable state is confirmed, only for odd-numbered clusters except for \(C_2^-\), and fast components were not observed for \(C_4^-, C_6^-\) and \(C_8^-\). That is, if clusters are triplet in the ground state of neutrals, the metastable state of the negative ions with sub-milli ~ milliseconds lifetime cannot be seen in the magnetic storage ring. Presence of the metastable cluster ions is confirmed for \(C_2^-, C_3^-, C_5^-\) by Naaman et al., by using a linear electrostatic ion beam trap [12]. They also reported that fast decay components are observed for all the negative cluster ions up to \(C_6^-\) in terms of the 1064/532 nm laser-induced reaction yields.

The results obtained in the present study are shown in figure 7. In the decay plots for the carbon cluster ions up to \(C_8^-\), fast decay components are clearly observed for all the cases, even for even-numbered clusters. The lifetime of the metastable state of \(C_2^-\) is 3.0 ms, which reasonably agrees with that obtained in ASTRID (2.3 ms, evaluated from the figure 4 of the reference 11). For \(C_3^-, C_5^-, C_7^-\), the plots in figure 7 consist of, at least, two components and those reported by ASTRID also need to invoke multiple components. A general trend in the lifetime of \(C_3^-, C_5^-, C_7^-\) is that larger clusters quench faster, and this is also applicable for the results of ASTRID. On the other hand, the results for \(C_4^-, C_6^-, C_8^-\) are completely different from those reported previously, in which the contrast of even-odd alternation is very sharp.

Adamowicz reported ab initio calculation of the ground and excited states of \(C_5^-\) and \(C_6^-\), including optically forbidden states from the ground state [13, 14]. According to the calculation for \(C_5^-\), vertical excitation energies from the ground state (\(X^2\Pi_u\)) to two spin-forbidden quartet states are 2.50 and 2.61 eV, which are very close to the vertical detachment energy (2.57 eV). A reasonable guess is that these states would contribute to the fast decay. For \(C_6^-\), the calculated vertical excitation energies to the six quartet states are reported to be 2.57, 4.37, 4.42, 4.86, 4.90, 5.10 eV. The first one is much smaller than the vertical detachment energy, 4.08 eV (calc.) or 4.10 eV (exptl. [15]), thus, is not

![Figure 7. Decay plots for the negative carbon ions, from \(C^-\) to \(C_8^-\).](image-url)
likely to contribute to the fast decay component. Some of the others are clearly larger than the
detachment energy and probably cannot survive until the ion storage. Since the adiabatic excitation
energy may be smaller than the vertical ones (for C\textsubscript{6} \textit{adiabatic} and vertical detachment energies are
the same), some of these states may contribute to the fast component, however detailed studies, both
experiments and theoretical calculations, are needed to draw more convincing assignment.

The difference between the works done in the ASTRID and in the TMU E-ring should be
mentioned. The cesium sputter ion sources are employed in both experiments, however difference in
the operation conditions might be a reason of the difference, otherwise the magnetic field used in the
ASTRID might effectively quench the metastable ions. To confirm results on the clusters, lifetime
measurement under cold environment will be conducted in near future.

Finally, the possibility of determining the cross sections for the collision-induced reactions of the
C\textsuperscript{+} ions in the \textit{^2}\textsubscript{D}\textsubscript{3/2,5/2} states should be inferred. To determine the effective radius of such a loosely
bound electron will be quite interesting, however as mentioned previously, the decay of these species
is mainly governed by the BRI processes, which is 1-2 order faster than the collision-induced
processes at room temperature, and will be still faster if our ring is cooled by LN\textsubscript{2} because of the
aforementioned non-uniformity. Now additional cooling devices for the ring are under preparation,
which will allow us to measure the lifetime under the lower average temperature.

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