Technical Physics Letters, 2022, Vol. 48, No. 9

02.4

Anomalous Dissociative Capture Cross Section at the Interaction of Singly Charged Ions with Molecules of Nucleic Acid Bases

© *A.A. Basalaev, V.V. Kuz'michev, M.N. Panov, O.V. Smirnov*

Ioffe Institute, St. Petersburg, Russia
E-mail: a.basalaev@mail.ioffe.ru

Received April 28, 2022
Revised June 20, 2022
Accepted July 14, 2022

The single electron capture process from adenine molecules by H^+, $^3He^+$, N^+, O^+, and Ne^+ ions with an energy of 6.3 keV has been studied. It was found that when one electron is captured by He^+ and Ne^+ ions, the dissociative capture process is dominant, which is fundamentally different from the processes of capture by singly charged ions of atoms with a lower ionization potential and multiply charged ions, as well as from the process of electron impact ionization. This effect is qualitatively explained within the framework of a quasimolecular model.

Keywords: dissociative capture, nucleic acid bases, fragmentation, Landau-Zener model.

DOI: 10.21883/TPL.2022.09.55073.19238

Nitrogenous bases (adenine, cytosine, guanine, thymine, and uracil) are found in DNA and RNA and act as letters of the genetic code. Their biological significance motivated a considerable number of studies into the radiation damage of these molecules induced by charged particles [1–7]. It was demonstrated that the undissociated molecule peak has the highest intensity in mass spectra recorded in the case of ionization of nucleic acid bases by electrons [1–4].

The pattern observed in the interaction of these molecules with ions is ambiguous, since their ionization is the result of a series of elementary processes

$$Ion^{z+} + M \to Ion^{(z-s)+} + \{M\}^{n+} + (n-s)e^-, \qquad (1)$$

the cross sections of which depend strongly on the velocity of incident ions. Here, Ion^{z+} is a projectile with charge z; M is a target molecule and $\{M\}^{n+}$ is an intermediate molecular ion with charge n; s is the number of electrons captured by the projectile; and $(n-s)$ is the number of free electrons produced as a result of a collision.

The processes of interaction between protons with an energy of 80 keV (velocity $V_p = 1.8$ a.u.) and molecules of nucleic acid bases (adenine, cytosine, and thymine) were examined in [8]. It was demonstrated that the ionization process ($s = 0$ in reaction (1)) and the process of capture of a single electron ($s = 1$) produce the same groups of molecular ions, albeit with different relative intensities. The authors of [8] concluded that the „observed product ions were generally consistent with previous measurements, notably for singly-charged ion impact ionization [and] electron impact ionization.“It should be noted that the spectra measured in [8] and in the studies examined in this paper integrated all the possible processes with different numbers of free electrons produced ($(n-s)$ in reaction (1)).

It is common knowledge that the process of capture of a single electron ($s = 1$, $n = 1$ in reaction (1)) in slow ion–atom and ion–molecule collisions (the incident ion velocity is lower than the captured electron velocity) is dominant in terms of the cross section; specifically, its cross section is much higher than the one of the ionization process ($s = 0$). As was demonstrated in [9], the most intense peaks in the mass spectrum recorded in the interaction between a multiply charged Ar^{6+} ion with an energy of 36 keV ($V_p = 0.19$ a.u.) and adenine (Ade) and uracil (Ura) molecules are the peaks of undissociated Ade^+ and Ura^+ ions, which agree well in their intensity with the results for electron impact.

The interaction of C^{z+} ($z = 1-6$, $V_p = 0.1-0.7$ a.u.) ions with uracil molecules was examined in [10], and it was found that the processes of fragmentation are main in interaction with C^{2+} ions. Since the authors of [10] recorded time-of-flight spectra of ion fragments produced in all feasible elementary processes, it was assumed that the observed effect is attributable to the process of double-electron capture ($s = 2$). Our measurements [11] of mass spectra of ion fragments produced in the process of single-electron capture ($s = 1$, $n = 1$) in interaction of C^{2+} ($V_p = 0.15-0.32$ a.u.) ions with uracil molecules proved that assumption to be erroneous and revealed that the single-electron capture process is dominant. In the capture of a single electron by C^{2+} ions, it produces uracil ions in excited states due to the capture of valence electrons located at inner molecular orbitals. This conclusion was drawn based on the analysis of single-electron terms of the quasi-molecular system produced in a collision.

In [12], we made an assumption that the process of capture of a single electron by singly charged He^+ and Ne^+ ions should result in fragmentation of the majority of singly charged molecular ions produced in this process. The aim of the present study is to verify this hypothesis for an adenine molecule ($C_5H_5N_5$). A technique involving „multi-stop“ time-of-flight analysis of masses of produced

Relative cross sections of production of fragments of a singly charged adenine ion (expressed as percentage of the total cross section of single-electron capture ($s = 1$, $n = 1$ in reaction (1))

Ion fragment	m, a.m.u.	At electron impact (average of [1] and [2]), %	H^+, %	N^+, %	O^+, %	He^+, %	Ne^+, %
H^+	1		0.1	0.3	0.1	0.6	0.2
HCN^+	27	0.9	1.9	4.3	1.7	6.1	1.9
CH_2N^+	28	8.6	10.8	15.4	11.7	29.4	30.2
CH_3N^+	29	1.9	2.3	4.1	3.0	4.3	4.9
C_2N^+	38	1.0	1.1	2.2	1.3	4.3	1.7
C_2HN^+	39	1.0	1.1	2.0	1.2	4.3	3.1
CN_2^+, $C_2H_2N^+$	40	0.7	0.9	1.3	1.4	3.0	3.7
$CH_3N_2^+$	43	2.1	1.6	1.4	2.4	2.2	4.5
$C_2HN_2^+$	53	3.2	3.8	5.8	3.2	12.8	11.6
$C_2H_2N_2^+$	54	5.3	4.9	5.6	6.3	6.8	9.6
$C_2H_3N_2^+$	55	1.0	1.3	1.6	1.9	1.8	3.8
$C_2H_4N_2^+$	56	0.8	0.5	0.4	0.5	0.6	0.7
$C_3HN_2^+$	65	0.8	0.8	1.1	1.3	2.5	4.5
$C_3H_2N_2^+$, $C_2N_3^+$	66	2.9	2.8	2.7	3.9	2.7	4.9
$C_3H_3N_2^+$, $C_2HN_3^+$	67	0.9	1.1	1.5	1.8	1.3	3.4
Ade^{2+}	67.5		1.0	0.3	0.2	2.0	1.8
$C_2H_4N_3^+$	70	1.6	1.5	1.9	2.8	0.5	0.3
$C_3H_2N_3^+$	80	1.5	1.4	1.0	1.3	2.6	4.6
$C_3H_3N_3^+$	81	4.7	3.0	2.9	4.6	1.2	2.1
$C_4H_4N_4^+$	108	12.6	10.3	8.3	15.6	0.8	0.5
$C_4H_5N_4^+$	109	0.8	3.1	3.1	4.9	0.4	0.2
$C_5H_4N_5^+$	134	1.2	3.4	5.0	3.3	0.7	0.4
Ade^+	135 + 136	46.3	41.0	27.7	25.7	8.9	1.5

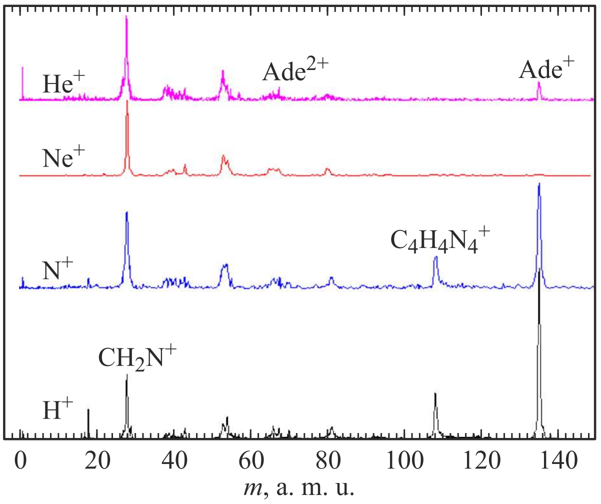

Figure 1. Mass spectra of ion fragments produced in the process of capture of a single electron by H^+, $^3He^+$, N^+, and Ne^+ ions with an energy of 6.3 keV. The spectrum of fragments produced in the capture of an electron by O^+ ions differs little from the spectrum for N^+.

fragments, which was detailed in [9,11,12], was used in the experiment.

The obtained results for the process of capture of a single electron ($s = 1$, $n = 1$) of adenine molecules by H^+, $^3He^+$, N^+, O^+, and Ne^+ ions with an energy of 6.3 keV are presented in Fig. 1 and the table. Ion fragments were identified based on the results of a thorough analysis of the feasible fragmentation channels of singly charged adenine ions that was performed in [4,9]. The presented data reveal a strong dependence of the cross section of production of an Ade^+ ion on the projectile type. The relative intensity of an Ade^+ ion in the capture of a single electron by a proton or a multiply charged Ar^{6+} ion [9] is close to the data for electron impact. The cross section of production of an Ade^+ ion in the capture of a single electron by N^+, O^+ ions is somewhat lower, but this process remains dominant. The process of production of a CH_2N^+ fragment with mass $m = 28$ a.m.u. is dominant in the capture of a single electron by He^+ and Ne^+ ions; the cross section of this process is much higher than the cross section of production of an Ade^+ ion. Thus, the capture of a single electron by He^+ and Ne^+ ions is accompanied primarily by the production of light fragments, which is attributable to the high probability of production of an intermediate molecular Ade^{+*} ion in an excited state.

Apparently, an Ade^{2+} ion is observed in mass spectra due to the fact that the electron emission effectively results in de-excitation.

A qualitative concept of the process of single-electron capture may be formulated by examining single-electron terms of a quasi-molecule produced in a collision at distances of approach of an ion to a molecule that exceed the molecule size. It is assumed within this model that only a single electron, which may be localized initially at one of the valence molecular orbitals of an adenine molecule, is involved in the process. The binding energies for these electrons were calculated in a number of different studies (see [13,14] and references therein), and the obtained results agree closely with each other. The possible input terms of the $\{At\mathrm{Ade}(\mathrm{MO}\#k)\}^+ (At = \mathrm{H, He, N, O, Ne})$ single-electron system are given by

$$U_k = E_b(\mathrm{MO}\#k) - \frac{\mu}{R^2} - \frac{\alpha}{2R^4} \tag{2}$$

$\big(E_b(\mathrm{MO}\#k)$ is the energy of an electron localized at molecular orbital MO#k; μ is the dipole molecule moment (μ=4.55 D = 1.79 a.u. [15] for adenine), α is the isotropic polarizability component ($\alpha = 95$ a. u. [15] for adenine), and R is the distance of approach of an ion to a molecule$\big)$ and are represented by dashed curves in Fig. 2.

The output terms of the single-electron system, which are also presented in Fig. 2, are defined by the electron states of atoms [16] produced in electron capture and are characterized by the following expression:

$$U_{At} = E_b\big(At(nl^{2s+1}L)\big), \tag{3}$$

where $E_b\big(At(nl^{2s+1}L)\big)$ is the energy of captured electron nl in an atom in state ${}^{2s+1}L$.

All the studied systems feature exothermic channels of single-electron capture. In the case of H^+, this channel is the production of a hydrogen atom in the ground state $\mathrm{H}(1s^2S)$. The following three end states of atoms with an electron captured into state $2p$ are feasible for N^+ and O^+: $\mathrm{N}(2s^22p^3\ {}^4S,\ {}^2D,\ {}^2P)$, and O $(2s^22p^4\ {}^3P,\ {}^1D,\ {}^1S)$. In the case of He^+ and Ne^+, these channels are again associated with the production of an atom in the ground state: $\mathrm{He}(1s^2\ {}^1S)$ and Ne $(2s^22p^6\ {}^1S)$. All processes resulting in the production of atoms in excited states are endothermic (Fig. 2). The data for He, which are not shown in Fig. 2, are close to those for Ne, while the omitted results for O are similar to the data for N. The input and output diabatic terms of the considered quasi-molecular systems intersect due to the fact that an adenine molecule features an electric dipole moment and considerable polarizability. Landau–Zener transitions occur [17] in the regions of these intersections. The formation of vacancies at any one of molecular orbitals MO#1–4 leads to the production of Ade^+ ions in states with an excitation energy of 0–3.1 eV [13,14]. Comparing these data with the appearance energies of fragments measured in [3,4], we find that such excitation energies are not sufficient for most channels of the process of Ade^+ ion fragmentation. This explains the large cross section of production of an undissociated molecular Ade^+ ion in the process of capture of a single electron by H^+, N^+, and O^+ ions (and, presumably, other atomic ions with close ionization potentials). At he same time, the formation of vacancies at orbitals MO#10–17 results in the production of Ade^+ ions in states with an excitation energy of 8.2–14.7 eV [13,14]. This enables all the observed channels of fragmentation in the process of capture of a single electron by He^+ and Ne^+ ions.

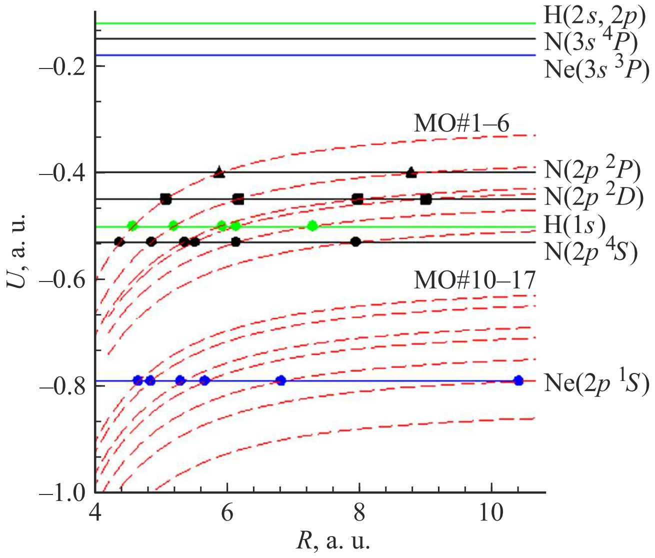

Figure 2. Single-electron diabatic terms of a $\{At\mathrm{Ade}(\mathrm{MO}\#k)\}^+$ quasi-molecule. The input term (dashed curves) is characterized by expression (2). MO#k are molecular orbitals of adenine at which an active electron captured by an incident ion may be localized. The output terms are characterized by expression (3). The possible end states $At(nl^{2s+1}L)$ for H, N, and Ne atoms produced after the capture of an electron by the corresponding singly charged ions are indicated [16]. Symbols denote the intersections of output terms and series of possible input terms at which Landau–Zener transitions occur [17].

Thus, the cross section of dissociative capture depends strongly on the ionization potential of atoms produced in this process. The Landau–Zener mechanism plays a prominent part in the capture process in the case of molecular targets with a high polarizability.

Funding

This study was performed under the state assignment (project No. 0040-2019-0023).

Conflict of interest

The authors declare that they have no conflict of interest.

References

[1] *NIST Standard Reference Database* [Electronic source]. http://www.webbook.nist.gov

[2] *Spectral Database for Organic Compounds SDBS* [Electronic source]. https://sdbs.db.aist.go.jp

[3] M.M. Dawley, K. Tanze, W.A. Cantrell, P. Plattner, N.R. Brinkmann, P. Scheier, S. Denifl, S. Ptasińska, Phys. Chem. Chem. Phys., **16**, 25039 (2014). DOI: 10.1039/C4CP03452J

[4] P.J.M. van der Burgt, S. Finnegan, S. Eden, Eur. Phys. J. D, **69**, 173 (2015). DOI: 10.1140/epjd/e2015-60200-y

[5] M.A. Rahman, E. Krishnakumar, J. Chem. Phys., **144**, 161102 (2016). DOI: 10.1063/1.4948412

[6] J.A. Trocchi, J. Dech, W. Kedzierski, J.W. McConkey, J. Phys. B, **52**, 055204 (2019). DOI: 10.1088/1361-6455/ab0222

[7] M.I. Shafranyosh, M. Zapotokova, M.I. Sukhoviya, V.I. Petrulyak, I.I. Shafranyosh, Surf. Eng. Appl. Electrochem., **58**, 82 (2022). DOI: 10.3103/S1068375522010100

[8] J. Tabet, S. Eden, S. Feil, H. Abdoul-Carime, B. Farizon, M. Farizon, S. Ouaskit, T.D. Márk, Int. J. Mass Spectr., **292**, 53 (2010). DOI: 10.1016/j.ijms.2010.03.002

[9] V.V. Afrosimov, A.A. Basalaev, Yu.G. Morozov, M.N. Panov, O.V. Smirnov, E.A. Tropp, Tech. Phys., **57** (5), 594 (2012). DOI: 10.1134/S1063784212050027.

[10] J. de Vries, R. Hoekstra, R. Morgenstern, T. Schlathölter, J. Phys. B, **35**, 4373 (2002). DOI: 10.1088/0953-4075/35/21/304

[11] V.V. Afrosimov, A.A. Basalaev, O.S. Vasyutinskii, M.N. Panov, O.V. Smirnov, Eur. Phys. J. D, **69**, 3 (2015). DOI: 10.1140/epjd/e2014-50435-5

[12] A.A. Basalaev, V.V. Kuz’michev, M.N. Panov, O.V. Smirnov, Tech. Phys., **64** (8), 1096 (2019). DOI: 10.1134/S1063784219080024.

[13] C. Champion, H. Lekadir, M.E. Galassi, O. Fojón, R.D. Rivarola, J. Hanssen, Phys. Med. Biol., **55**, 6053 (2010). DOI: 10.1088/0031-9155/55/20/002

[14] H. Lekadir, I. Abbas, C. Champion, O. Fojón, R.D. Rivarola, J. Hanssen, Phys. Rev. A, **79**, 062710 (2009). DOI: 10.1103/PhysRevA.79.062710

[15] J. Franz, F.A. Gianturco, Eur. Phys. J. D, **68**, 279 (2014). DOI: 10.1140/epjd/e2014-50072-0

[16] A. Kramida, Yu. Ralchenko, J. Reader, and NIST ASD Team, *NIST Atomic Spectra Database (ver. 5.9)* (2021). DOI: 10.18434/T4W30F

[17] R.K. Janev, L.P. Presnyakov, Phys. Rep., **70**, 1 (1981). DOI: 10.1016/0370-1573(81)90161-7