Proton-impact ionization cross sections of adenine measured at 0.5 and 2.0 MeV by electron spectroscopy

Y. Iriki, Y. Kikuchi, M. Imai, and A. Itoh*
Department of Nuclear Engineering, Kyoto University, Kyoto 606-8501, Japan
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Double-differential ionization cross sections (DDCSs) of vapor-phase adenine molecules ($C_5H_5N_5$) by 0.5- and 2.0-MeV proton impact have been measured by the electron spectroscopy method. Electrons ejected from adenine were analyzed by a 45° parallel-plate electrostatic spectrometer over an energy range of 1.0–1000 eV at emission angles from 15° to 165°. Single-differential cross sections (SDCSs) and total ionization cross sections (TICSs) were also deduced. It was found from the Platzman plot, defined as SDCSs divided by the classical Rutherford knock-on cross sections per target electron, that the SDCSs at higher electron energies are proportional to the total number of valence electrons (50) of adenine, while those at low-energy electrons are highly enhanced due to dipole and higher-order interactions. The present results of TICS are in fairly good agreement with recent classical trajectory Monte Carlo calculations, and moreover, a simple analytical formula gives nearly equivalent cross sections in magnitude at the incident proton energies investigated.

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I. INTRODUCTION

Ionization of atoms and molecules by fast charged particles has been studies extensively for decades, and some fundamentals are well understood, as described in several review articles [1–4]. In recent studies [5–8], biological molecules, such as water, amino acids, and nucleic-acid-base molecules, have attracted increasing attention due to a wide range of applications in radiation physics, radiation biology, and radiation therapy. As described in [9], ionizing radiation produces various damages in deoxyribonucleic acid (DNA) and other macromolecules in living cells. Ionization of nucleobases may lead to DNA damage such as single-strand breaks (SSBs) and, in particular, double-strand breaks (DSBs), which are the critical lesions for killing cells. In a Bragg peak region, a large number of secondary electrons with various energies are produced along ion tracks [10]. In general, secondary electrons are produced from a variety of ionization processes, such as soft collisions, binary-encounter collisions, electron capture or loss to the continuum, and Auger processes [4]. Low-energy electrons below 50 eV are produced predominantly via soft collisions and carry away most of the energy deposition from fast projectile particles. Furthermore, low-energy electrons may induce excitation, fragmentation, and ionization of surrounding molecules continuously [11]. Hence, it is undoubtedly important to achieve quantitative understanding of ionization processes in biological matter.

On the other hand, several theoretical studies have been reported recently for ionization of various polyatomic molecules. Abbas *et al.* [12] and Lekadir *et al.* [13,14] obtained total ionization cross sections (TICSs) of various nucleobases by the classical trajectory Monte Carlo (CTMC) calculation combined with the classical overbarrier (COB) model [12–14]. Dal Cappello *et al.* calculated differential and total ionization cross sections for cytosine by *ab initio* quantum methods [15]. Champion *et al.* have presented double-differential ionization cross sections (DDCSs), single-differential cross sections (SDCSs), and TICSs for the ionization of various nucleobases with the first Born approximation with Coulomb wave (FBA-CW) model [16].

In our recent paper we reported double-differential cross sections for ionization of adenine ($C_5H_5N_5$) impacted by 1.0-MeV protons [17], which is referred to as paper I hereinafter. In this work, we extend DDCS measurements of adenine to impact energies of 0.5 and 2.0 MeV. The experimental method is briefly described in Sec. II. Experimental cross sections are presented in Sec. III and are compared with the available theoretical calculations described above. Concluding remarks are given in Sec. IV.

II. EXPERIMENT

The experiment was performed at the Quantum Science and Engineering Centre heavy-ion accelerator facility of Kyoto University. The experimental apparatus and method have already been described in detail in paper I, and only an outline is given below. A beam of protons produced by a Van de Graff accelerator was collimated to about 1×3 mm^2 in size by a magnetic lens, charge purified by a magnetic charge selector, and collected by a Faraday cup. A typical beam current used in the experiment was about 100 nA. A passivated implanted planar silicon (PIPS) type solid-state detector (Canberra PD-25-12-100-AM) was also installed to measure projectile particles scattered into forward angles of 2.5° after collisions with target molecules. The inner wall of the collision chamber was covered by double permalloy magnetic shields to reduce residual or earth's magnetic fields to less than a few milligauss inside the chamber. A molecular beam target of adenine ($C_5H_5N_5$) was produced from crystalline adenine powder of 99% purity contained in a 5.3-cm-long stainless steel (SUS304) oven placed inside a copper container equipped with two cylinder-shaped heaters. Measurements were carried out at an oven temperature of 473 K. An effusive molecular beam of adenine was ejected through an outlet aperture of 1 mm in diameter placed at the top of the oven and was trapped effectively by a water-cooled copper plate placed at

*itoh@nucleng.kyoto-u.ac.jp

100 mm above the proton beam line. The position of the outlet aperture was 3 mm below the beam line, and the spot size of the molecular vapor was about 3 mm in diameter. A base pressure of the collision chamber was kept below 2×10^{-7} Torr during the experiment. Ejected electrons were analyzed by a 45° parallel-plate electrostatic spectrometer mounted on a turntable controlled by a pulse motor. Electrons were detected by a channel electron multiplier. Data were taken for electron energies ϵ from 1 eV to 1 keV and emission angles θ from 15° to 165° at 15° intervals with respect to the incident H^+ beam direction. The energy resolution $\Delta\epsilon/\epsilon$ of the spectrometer was 8% at FWHM. In order to collect efficiently low-energy electrons of a few eV, a positive bias of 40 V was applied as an extraction voltage into the spectrometer.

The target thickness of adenine vapor was determined by a vapor deposition method combined with the Rutherford forward-scattering method; the reader is referred to paper I.

Note DDCS and SDCS are defined as

$$\sigma(\epsilon,\theta) = \frac{d^2\sigma}{d\epsilon d\omega}, \quad \sigma(\epsilon) = \frac{d\sigma}{d\epsilon} = 2\pi \int_0^\pi \sigma(\epsilon,\theta)\sin\theta d\theta,$$

where $d\omega$ is the solid angle.

III. RESULTS AND DISCUSSIONS

A. Differential cross sections

Experimental data for DDCS and SDCS for electron emission from adenine obtained for 0.5- and 2.0-MeV proton impacts are shown in Figs. 1 and 2, respectively. The numerical data are presented in the Supplemental Material [18]. The uncertainties in the absolute value of the measured DDCSs are 9–15%. All the DDCSs spectra exhibit broad humps around 6 eV, similar to those for the 1.0-MeV proton impact shown in paper I. Note that the hump becomes sharper with increasing impact energy. Low-energy electrons ($\leqslant$30 eV) are found to be ejected nearly isotropically. Two peaks located at about 250 and 400 eV are *K-LL* Auger electros ejected from carbon and nitrogen, respectively. The classical binary encounter peaks appear in Fig. 1 at forward emission angles.

The uppermost energy spectra in Figs. 1 and 2 represent SDCSs obtained from DDCSs by integration over the electron emission angle.

B. Platzman plot

As examined in detail by Kim [19,20] and Toburen *et al.* [21], the Platzman plot [2,3] of a SDCS provides information about the characteristics of ionization cross sections. The Platzman plot Y is the ratio of experimental SDCS $\sigma(\epsilon)$ to the classical Rutherford knock-on cross section per target electron. The Rutherford cross section for an electron in the ith subshell with binding energy I_i is written by

$$\sigma_R = \frac{4\pi a_0^2}{T}\left(\frac{R}{Q_i}\right)^2, \tag{1}$$

and Y reads

$$Y = \frac{T}{4\pi a_0^2}\left(\frac{Q_i}{R}\right)^2 \sigma(\epsilon), \tag{2}$$

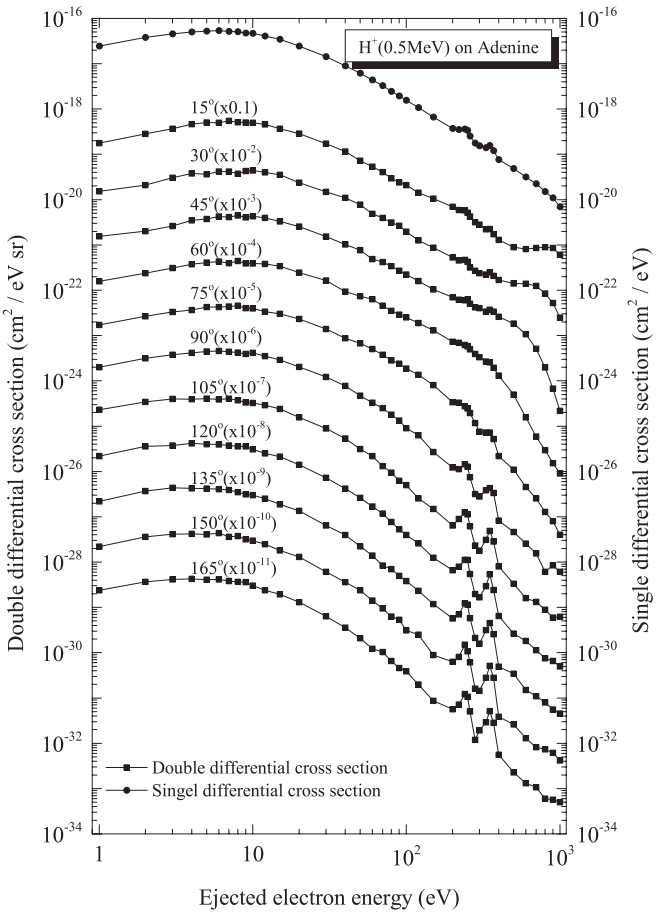

FIG. 1. DDCSs for the ejection of electrons from adenine impacted by 0.5-MeV protons. The uppermost energy distribution is the SDCSs obtained by integrating the DDCSs, which are plotted by multiplying scaling factors as shown in parentheses. Two peaks at approximately 250 and 400 eV are *K-LL* Auger electrons from carbon and nitrogen, respectively.

where $Q_i = \epsilon + I_i$ stands for the energy transfer to the electron, a_0 is the Bohr radius (0.529 Å), R is the Rydberg energy (13.6 eV), and $T = mv^2/2$ is the energy of the electron with the incident proton velocity. Figure 3(a) shows our measured $\sigma(\epsilon)$ and Rutherford cross sections at three incident energies, and Fig. 3(b) depicts the corresponding Platzman plots. Here we used in Eq. (1) the first ionization potential $I_1 = 8.32$ of adenine [14].

As the velocities of incident protons used here are sufficiently high compared to valence electrons [14], the SDCS for electron energy distribution may be described well by the Born approximation as given in [19,21],

$$\sigma_B(\epsilon) \simeq \frac{4\pi a_0^2}{T}\sum_i \left[\frac{R^2}{Q_i}\frac{df_i}{d\epsilon}\ln\frac{4T}{R} + B_i(\epsilon)\right], \tag{3}$$

where $df_i/d\epsilon$ is the optical oscillator strength density in the continuum. It is shown in [21] that for low-energy electrons the first term in the brackets in Eq. (3) becomes predominant and the shape of $\sigma_i(\epsilon)$ should be similar to the dipole oscillator-strength density for ionization. For fast electrons, on the other hand, the first term diminishes quickly, and the second term $B_i(\epsilon)$, corresponding to knock-on collisions, approaches the

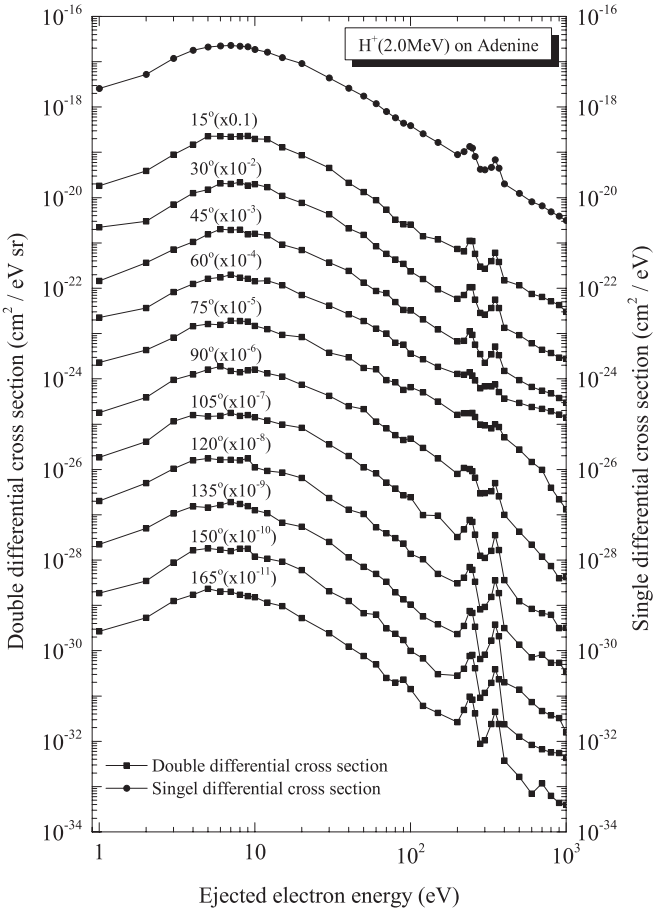

FIG. 2. The same as Fig. 1 but for 2.0-MeV proton impact.

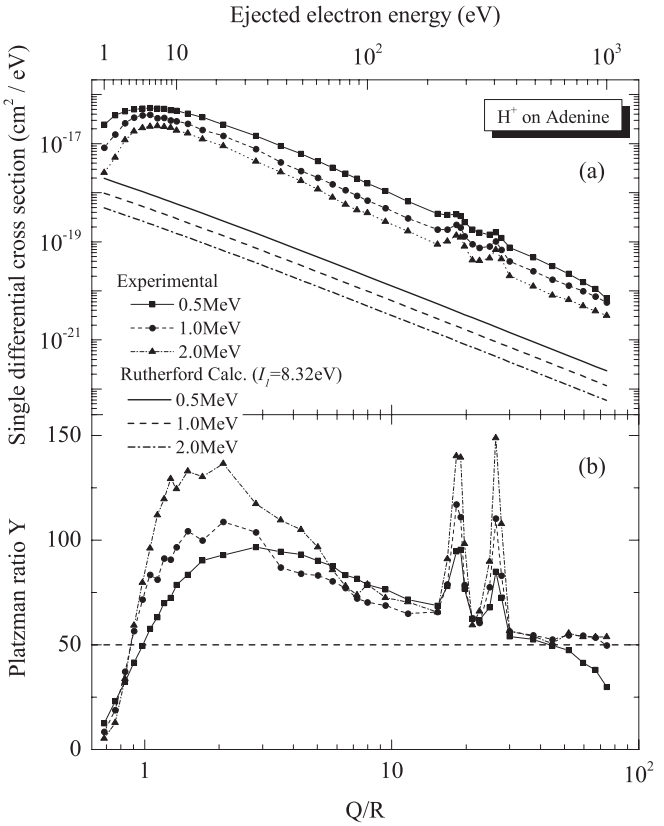

FIG. 3. (a) Comparison of SDCSs obtained with 0.5-, 1.0-, and 2.0-MeV proton impacts with Rutherford cross sections per electron calculated from Eq. (1) with $I_1 = 8.32$ eV being the first ionization potential of adenine. (b) Platzman plot of our SDCSs obtained as the ratio of $\sigma(\epsilon)$ to the Rutherford cross section. The abscissa Q/R is the energy transfer $Q = \epsilon + I_1$ divided by the Rydberg energy R. The horizontal dotted line shows the total number of valence electrons of adenine.

classical Rutherford term $(R/Q_i)^2$. Hence, with increasing Q_i, or ϵ, the ratio Y is expected to approach the effective number of electrons contributing to ionization since the Rutherford cross section, Eq. (1), is defined for one electron. Actually, the present results are very close to 50, the number of valence electrons of adenine, shown by a horizontal dotted line in Fig. 3(b).

As for small values of Q_i, or small ϵ, the energy spectra should show optical properties of valence electrons, where the collision with fast protons is distant and the dipole interaction contributes predominantly. The humps at $Q/R \sim 2$ are then supposed to exhibit the characteristics of photoionization cross sections of adenine. It is pointed out that the height and the peak position of the humps vary as the proton impact energy changes, indicating clearly the predominance of the T-dependent first term in Eq. (3). These features are consistent with the results by Toburen *et al.* [21] for neon and argon targets.

C. Total ionization cross section

Total ionization cross sections were obtained by integrating $\sigma(\epsilon)$ over the electron energy ϵ. Results are compared in Fig. 4 with recent theoretical data of CTMC calculations from Lekadir *et al.* [14] and FBA-CW calculations from Champion *et al.* [16]. Also plotted at 80 keV is an experimental value from Tabet *et al.* [6] obtained from time-of-flight measurements of fragment ions in coincidence with final charge states of projectile particles. We also compare our results with a simple analytical formula proposed by Stolterfoht *et al.* [4], from which the TICS for a molecule is obtained as

$$\sigma_S = \frac{4\pi a_0^2}{T} \sum_i \frac{R^2}{I_i} \sqrt{\ln\left(\frac{2T}{I_i}\right)}. \tag{4}$$

The formula was derived semiempirically from the Rutherford cross section modified by replacing I_i in the denominator of Eq. (1) by $I_i/[\ln(2T/I_i)]^{1/2}$ by taking account of the Bethe-Born-type impact-energy dependence. We calculated TICSs using all the subshell binding energies of adenine listed in [14].

Our results are in good agreement with the CTMC calculations [14] within about 10%, while those of FBA-CW calculations [16] are smaller than our cross sections by more than 30%. It is, on the other hand, interesting to point out that the simple formula of Stolterfoht gives nearly the same results as the CTMC calculations. While the reason for these discrepancies between theories and experimental results is not clear at present, we speculate that these calculations might have underestimated the contribution from the ionization of low-energy electrons, which may be excited not only via the dipole interaction but also via higher-order interactions.

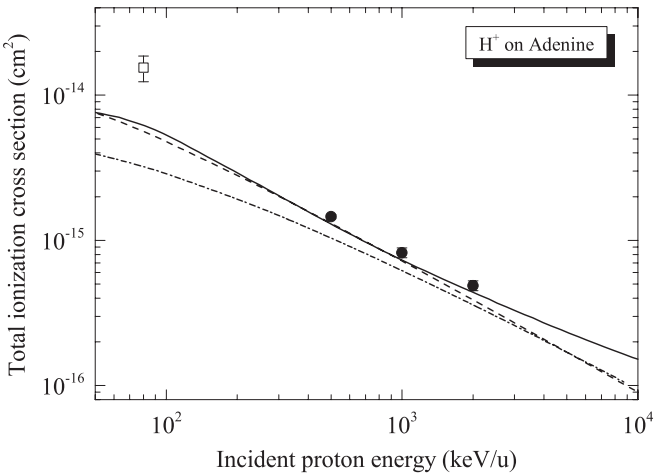

FIG. 4. TICSs of adenine plotted as a function of the incident proton energy. The present results are shown by solid circles. Theoretical calculations are as follows: solid curve is from CTMC [14], dash-dotted curve is from FBA-CW [16], and dashed line is from Eq. (4) [4]. The open square at 80 keV depicts experimental data from Tabet *et al*. [6].

Despite these discrepancies, the impact-energy dependences of these studies are nearly identical above 500 keV, exhibiting the typical Bethe-Born-type dependence of $\ln E_p/E_p$ [2], with E_p being the impact energy of protons.

Experimental values at 80 keV measured by Tabet *et al*. seem obviously too large in comparison with other data.

IV. CONCLUSION

Total and differential ionization cross sections of adenine bombarded by fast protons have been measured at impact energies from 0.5 to 2.0 MeV by means of an electron spectroscopy method. We found that high-energy electrons, which are produced in collisions accompanying large energy transfer Q from protons, are ejected via classical knock-on collisions and that loosely bound valence electrons contribute to ionization independently; namely, the corresponding SDCSs are proportional to the total number of valence electrons. On the other, the ionization of low-energy electrons produced in low-Q collisions is enhanced largely due to dipole and probably higher-multipole interactions. Comparison of our experimental values with recent theoretical calculations shows that the CTMC calculation by Lekadir *et al*. [14] gives more reliable cross sections than FBA-CW calculations [16], which predict more than 30% lower values than ours. It is worth noting that the simple analytical formula of Stolterfoht [4] may serve as a quite useful expression to estimate total ionization cross sections of rather complicated polyatomic molecules. Actually, agreement with experimental results is amazingly good. This fact implies evidently that the TICS of molecules by fast protons is essentially proportional to the number of outer-shell electrons and may not depend strongly on the molecular structure or alignment unless some specific coincidence measurements are involved. Extension of measurements to other polyatomic molecules is desirable to check this possibility and to develop more rigorous theoretical models.

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