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Calculation of electron impact ionization cross sections of DNA using the Deutsch–Märk and Binary–Encounter–Bethe formalisms

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Abstract

Electron impact ionization cross sections for fragments of the DNA, the bases adenine, cytosine, guanine and thymine and the sugar-phosphate backbone, have been calculated using the Deutsch–Märk (DM) and the Binary–Encounter–Bethe (BEB) formalism. The necessary molecular structure information was determined by ab initio calculations, which were performed with the Gaussian 98 system using the Hartree–Fock (HF) method with different basis sets. Comparison of the Koopmans ionization potentials of the four bases revealed good agreement with experimental measurements. The two algorithms yield similar total electron impact ionization cross sections but their predictions differ, when cross sections per molecular orbital are compared. (Int J Mass Spectrom 223–224 (2003) 599–611)

Keywords: DNA; DM; BEB; Electron impact; Ionization cross section

1. Introduction

To understand the mechanism of radiation induced DNA damage, Monte Carlo track structure simulations are a useful tool to determine spatial and temporal distributions of new chemical species and specific energy deposition densities. These simulations require a complete set of differential cross sections for the respective primary and secondary particles and target materials. Recently developed methods, like the Deutsch–Märk (DM) formalism [1] or the Binary–Encounter–Bethe (BEB) theory [2] provide possibilities to determine electron impact ionization cross sections for target atoms, molecules, clusters and ions. Here calculations of the electron impact total ionization cross sections of the four DNA bases adenine, cytosine, guanine and thymine and of the sugar-phosphate DNA backbone are presented by applying the two algorithms mentioned above.

2. Methods

The semiclassical DM formalism is fully described in [1,3–9]. Briefly, the total electron impact ionization cross section σ_{tot} of an atom is calculated by

$$\sigma_{\mathrm{tot}} = \sum_j g_j \pi (r_j)^2 \xi_j f\left(\frac{E}{E_j}\right), \tag{1}$$

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where the subscript j refers to the quantum numbers of the corresponding atomic subshell, g_j is the weighting factor as defined in [1], $(r_j)^2$ represents the radius of the maximum radial density and ξ_j stands for the number of electrons in the respective orbital. The function f, also defined in [1], brings in the Gryzinsky-type energy dependence of the ionization cross section, where E is the kinetic energy of the incoming electron and E_j is the binding energy of a target electron. In the case of a molecular target the orbitals must first be expressed in terms of the atomic orbitals of the constituent atoms. This can be done, for example, by a Mullikan population analysis [10].

The Binary–Encounter–Bethe model, developed by Kim and Rudd, is given in [2] and was further developed in [11–13]. The main equation for the calculation of the electron impact ionization cross section is

$$\sigma_{\text{tot}} = \sum_j \frac{4\pi a_0^2 \xi_j (R/E_j)^2}{(E/E_j) + (U_j/E_j) + 1} \times \left[\frac{Q_j \ln(E/E_j)}{2} \left(1 - \frac{1}{(E/E_j)^2}\right) + (2 - Q_j)\left(1 - \frac{1}{E/E_j} - \frac{\ln(E/E_j)}{(E/E_j)+1}\right)\right], \quad (2)$$

where j is the index of the atomic or molecular subshell, a_0 the Bohr radius (0.0529 nm), R the Rydberg energy (13.61 eV), E_j stands for the binding energy, U_j represents the average orbital kinetic energy of the target electron and Q_j, the dipole constant, is defined in terms of the continuum dipole oscillator strength $\mathrm{d}f/\mathrm{d}W$, where W is the kinetic energy of the ejected electron:

$$Q_j = \frac{2}{\xi_j} \int \frac{E_j}{E_j + W} \frac{\mathrm{d}f}{\mathrm{d}W} \mathrm{d}W. \quad (3)$$

Because $\mathrm{d}f/\mathrm{d}W$ is not known in the case of the DNA, $Q_j = 1$ is taken as an approximation, as suggested by Kim and Rudd [2].

Both formalisms require as input quantum mechanically calculated molecular structure information, which was ascertained by ab initio calculations performed with the Gaussian 98 system [14]. The geometry optimizations and the single point calculations have been done by the spin restricted Hartree–Fock (RHF) method [15] with the 3-21G basis set [16] as proposed by Colson et al. [17–20] for the fragments of the DNA. In a recent paper Huo and Kim [12] suggested the use of effective core potential (ECP) basis sets for the application of the BEB method for atoms with principal quantum numbers $n \geq 3$. This is fulfilled for the phosphorus atom in the DNA, hence, ab initio calculations have also been done with the Stuttgart/Dresden ECP basis set [21], which is included in the Gaussian 98 system (SDDALL). The DNA fragments (sugar-phosphate unit, bases adenine, cytosine, guanine and thymine) were treated separately in this work without considering effects of the hydration shells and the results can be summed up linearly to the total DNA cross section. The structure files were downloaded from Klotho database [22]. The atomic dataset for the sugar-phosphate backbone was derived by replacing the base of the 'deoxyadenosine monophosphate' by a hydrogen atom.

3. Results and discussion

3.1. Ab initio calculations for the DNA bases

In Fig. 1 the chemical structure for the four bases adenine, guanine, cytosine and thymine with the numbering used in these calculations can be seen. The geometry has been optimized with RHF/3-21G and the resulting Koopmans ionization potentials are presented in Table 1 for different basis sets. The Koopmans ionization energy is the binding energy of the highest molecular orbital (HOMO) of the neutral molecule and is a good approximation of the vertical ionization energy [23]. Furthermore, Table 1 gives the Koopmans ionization potentials from other calculations and measured ionization energies, which are referenced in the NIST Chemistry WebBook [24]. The calculated RHF/3-21G ionization potentials confirm the values of Colson et al. [17], and are in good agreement with the experiments, except for thymine, for which the calculated ionization potential appears

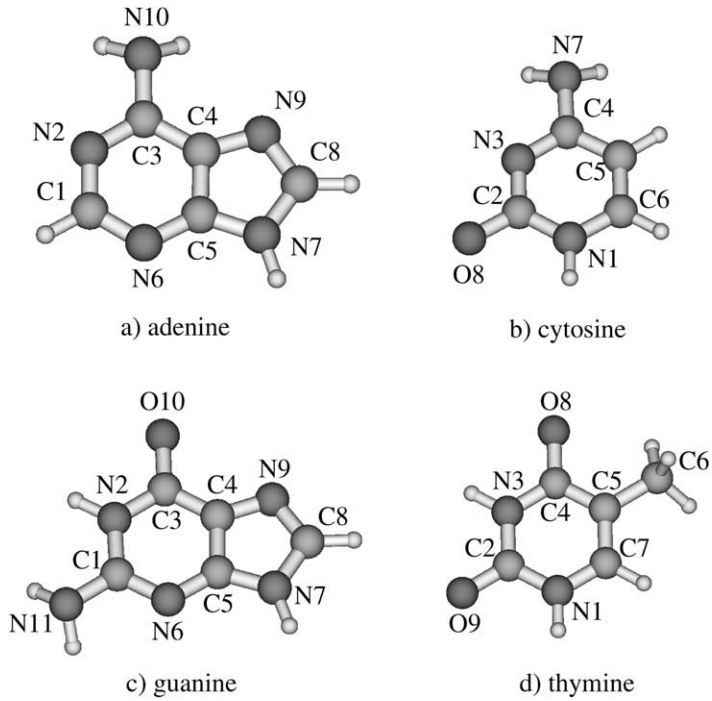

Fig. 1. The chemical structures of the four DNA bases.

Table 1
Calculated Koopmans ionization potentials for the DNA bases (eV), together with experimental values

	Adenine	Cytosine	Guanine	Thymine
This work				
RHF/3-21G//RHF/3-21G	8.48	9.01	8.05	9.48
RHF/6-311+G(2d,p)//RHF/6-31G(d)	8.65	9.24	8.30	9.67
RHF/SDDALL//RHF/3-21G	8.63	9.33	8.32	9.77
Other calculations				
Colson et al. [17], RHF/3-21G	8.48	9.00	8.04	9.45
Colson et al. [17], RHF/6-31+G(d)	8.57	9.42	8.25	9.74
Voitynk et al. [25], NDDO-G	8.53	9.10	8.10	9.15
Experiments				
Verkin et al. [26]	8.3 ± 0.1	9.0 ± 0.1	8.0 ± 0.2	9.0 ± 0.1
Lifschitz et al. [27]	8.9 ± 0.1	8.9 ± 0.2		9.4 ± 0.1
Lin et al. [28]	8.48			
Peng et al. [29]	8.48			
Hush and Cheung [30]	8.44 ± 0.03	8.94 ± 0.03	8.24 ± 0.03	9.14 ± 0.03
Dougherty et al. [31]		8.45	7.85	9.20
Lauer et al. [32]				9.02

to be slightly to high. The mean absolute error in comparison with the results of Hush and Cheung [30] is 0.16 eV. The application of larger basis sets including diffuse and polarization functions for geometric optimization and single point calculation leads to larger overestimations of the ionization potentials for the DNA bases in agreement with the findings of Colson and Sevilla [20] (for example, the calculated IP's at the RHF/6-311+G(2d,p)//RHF/6-31G(d) level shown in Table 1 give a mean absolute error of 0.28 eV). The ECP derived ionization potentials overestimate the values of Hush and Cheung [30] by 0.32 eV on average. In general all measurements and calculations show, that guanine has the lowest ionization potential, whereas cytosine and thymine are most difficult to ionize; this is in agreement with ESR measurements [33–35], which locate the holes of ionized DNA mainly at the guanine sites.

3.2. Ab initio calculations for the DNA sugar-phosphate backbone

Fig. 2 gives the structure of the sugar-phosphate backbone unit of DNA. At the phosphate anion a sodium counter ion has been added in the calculations, as suggested by Colson et al. [19] to compensate its negative charge in solution. The ion was placed between the two anionic oxygen atoms opposite to the phosphorus. Also, the OH group of the deoxyribose was replaced by a single H atom to avoid, that the

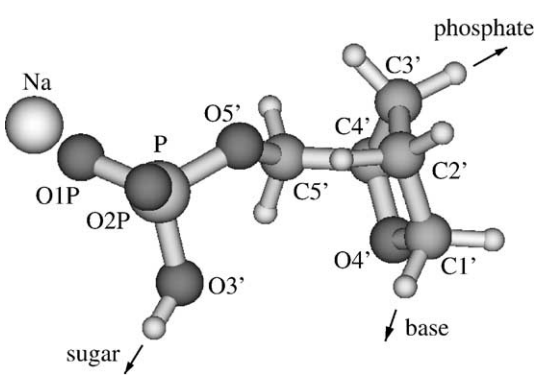

Fig. 2. The chemical structure of the sugar-phosphate backbone unit.

Table 2
Torsion angles that were kept constant during the geometry optimization for the backbone unit (from Colson et al. [19])

	Torsion angle (°)
C3′–O3′–P–O5′	−93.4
O3′–P–O5′–C5′	−58.5
P–O5′–C5′–C4′	177.0
O5′–C5′–C4′–C3′	51.0
C5′–C4′–C3′–O3′	129.0

O3′ atom is considered two times in the backbone unit. To receive a typical B-DNA fiber conformation with a C2′ endo sugar puckering, the backbone and deoxyribose torsion angles were kept fixed during geometric optimization with RHF/3-21G at averaged values given by Colson et al. [19] (Table 2). The resulting Koopmans ionization potentials are 10.58 and 10.94 eV for the RHF/3-21G and RHF/SDDALL level, respectively. The deviation from the value of Colson et al. [19] of 11.13 eV (RHF/3-21G) is due to their additional consideration of three water molecules to model the primary hydration shell.

3.3. Input data for the DM and BEB formalisms

According to Kim and Rudd [2] experimentally determined ionization potentials are in general more reliable than theoretical values. Therefore, the calculated energies were scaled, so that the theoretical first ionization potential agrees with the experimental values of Hush and Cheung [30]. For the backbone unit, for which no experimental data is available, an average scaling factor of 0.9936 for the four DNA bases has been applied to the results of the RHF/3-21G calculation. This leads to a first ionization potential of 10.52 eV. In Table 3, the input data for the DM formalism is shown for the five highest occupied molecular orbitals of the correspondent molecule. Only atomic shells which contribute by more than a certain amount are presented here; this explains, why the sum of the number of electrons in every MO is lower than 2. The weighting factor g_j is calculated according to Deutsch et al. [1], the radius r_j is taken from Desclaux [36]. Input parameters for the

Table 3
Input parameters for the five highest occupied molecular orbitals for the DM formalism for adenine, cytosine, guanine, thymine and the backbone unit

j	E_j (eV)	Atom	n, l	ξ_j	g_j	r_j (10^{-11} m)
Adenine						
5	11.73	N2	2s	0.128	1.706	5.390
		N2	2p	0.640	2.558	5.236
		C4	2p	0.107	2.558	6.443
		N6	2p	0.135	2.558	5.236
		N9	2p	0.544	2.558	5.236
4	11.38	C4	2p	0.200	2.636	6.443
		N7	2p	0.560	2.636	5.236
		N9	2p	0.598	2.636	5.236
		N10	2p	0.445	2.636	5.236
3	10.56	N2	2p	0.609	2.840	5.236
		C4	2p	0.123	2.840	6.443
		N6	2p	0.708	2.840	5.236
		N9	2p	0.175	2.840	5.236
2	10.00	C1	2p	0.108	3.001	6.443
		N2	2p	0.687	3.001	5.236
		C4	2p	0.281	3.001	6.443
		C8	2p	0.275	3.001	6.443
		N6	2p	0.194	3.001	5.236
		N7	2p	0.226	3.001	5.236
		C8	2p	0.138	3.001	6.443
1	8.44	C1	2p	0.151	3.555	6.443
		C3	2p	0.137	3.555	6.443
		C4	2p	0.367	3.555	6.443
		N6	2p	0.327	3.555	5.236
		C8	2p	0.268	3.555	6.443
		N9	2p	0.166	3.555	5.236
		N10	2p	0.379	3.555	5.236
Cytosine						
5	13.16	N1	2p	0.283	2.280	5.236
		C2	2p	0.316	2.280	6.443
		N3	2p	0.130	2.280	5.236
		C5	2p	0.228	2.280	6.443
		C6	2p	0.432	2.280	6.443
		O8	2p	0.610	2.280	4.412
4	11.43	N3	2s	0.177	1.750	5.390
		N3	2p	0.374	2.625	5.236
		O8	2p	1.224	2.625	4.412
3	10.66	N1	2p	0.177	2.814	5.236
		N3	2p	0.988	2.814	5.236
		O8	2p	0.391	2.814	4.412
2	10.06	N1	2p	0.251	2.983	5.236
		N3	2p	0.448	2.983	5.236
		C5	2p	0.284	2.983	6.443
		N7	2p	0.874	2.983	5.236
1	8.94	N1	2p	0.281	3.356	5.236
		N3	2p	0.437	3.356	5.236
		C5	2p	0.545	3.356	6.443
		C6	2p	0.156	3.356	6.443
		O8	2p	0.559	3.356	4.412
Guanine						
5	11.86	N2	2p	0.179	2.530	5.236
		C4	2p	0.130	2.530	6.443
		N6	2p	0.105	2.530	5.236
		O10	2p	1.273	2.530	4.412
4	11.82	N2	2p	0.896	2.538	5.236
		N6	2p	0.151	2.538	5.236
		C8	2p	0.105	2.538	6.443
		O10	2p	0.463	2.538	4.412
		N11	2p	0.163	2.538	5.236
3	11.37	C4	2p	0.130	2.639	6.443
		C5	2p	0.107	2.639	6.443
		N6	2p	0.398	2.639	5.236
		N9	2s	0.118	1.760	5.390
		N9	2p	0.760	2.639	5.236
		O10	2p	0.195	2.639	4.412
2	11.15	C4	2p	0.408	2.690	6.443
		N6	2p	0.126	2.690	5.236
		N7	2p	0.831	2.690	5.236
		N9	2p	0.445	2.690	5.236
1	8.24	C4	2p	0.520	3.641	6.443
		C5	2p	0.201	3.641	6.443
		N6	2p	0.325	3.641	5.236
		C8	2p	0.371	3.641	6.443
		N9	2p	0.113	3.641	5.236
		O10	2p	0.223	3.641	4.412
		N11	2p	0.126	3.641	5.236
Thymine						
5	13.27	N1	2p	0.474	2.261	5.236
		C2	2p	0.146	2.261	6.443
		N3	2p	0.127	2.261	5.236
		C5	2p	0.108	2.261	6.443
		C6	2p	0.133	2.261	6.443
		C7	2p	0.368	2.261	6.443
		O9	2p	0.446	2.261	4.412
4	12.11	N1	2p	0.134	2.477	5.236
		O8	2p	0.271	2.477	4.412
		O9	2p	1.165	2.477	4.412
3	11.32	N3	2p	0.194	2.650	5.236
		C5	2p	0.171	2.650	6.443
		O8	2p	1.100	2.650	4.412
		O9	2p	0.357	2.650	4.412

Table 3 (*Continued*)

j	E_j (eV)	Atom	n, l	ξ_j	g_j	r_j (10^{-11} m)
2	10.92	N3	2p	0.899	2.748	5.236
		O8	2p	0.553	2.748	4.412
		O9	2p	0.511	2.748	4.412
1	9.14	N1	2p	0.452	3.282	5.236
		C5	2p	0.747	3.282	6.443
		C7	2p	0.332	3.282	6.443
		O8	2p	0.167	3.282	4.412
		O9	2p	0.179	3.282	4.412
Backbone						
5	11.70	O5′	2p	0.207	2.565	4.412
		C5′	2p	0.100	2.565	6.443
		C4′	2p	0.169	2.565	6.443
		C3′	2p	0.318	2.565	6.443
		C2′	2p	0.240	2.565	6.443
		O4′	2p	0.464	2.565	4.412
		C1′	2p	0.117	2.565	6.443
4	11.58	O3′	2p	0.151	2.592	4.412
		O5′	2p	0.413	2.592	4.412
		O1P	2p	0.654	2.592	4.412
		O2P	2p	0.391	2.592	4.412
3	10.84	O1P	2p	0.865	2.768	4.412
		O2P	2p	1.057	2.768	4.412
2	10.61	O1P	2p	0.861	2.826	4.412
		O2P	2p	0.910	2.826	4.412
1	10.52	C5′	2p	0.138	2.852	6.443
		O4′	2p	1.081	2.852	4.412

Scaled binding energy E_j of the molecular orbital j; effective number of electrons ξ_j; the weighting factor g_j; radius r_j of the corresponding subshell (c.f. Eq. (1)).

BEB formalism are given in Table 4 for the valence molecular orbitals. Additionally, results from ab initio calculations on the RHF/SDDALL level are included. Whereas the scaled binding energies do not change very much, the average kinetic energy of the target electrons is reduced particularly for more tightly bound orbitals, reflecting the fact that ECP's prevent valence electrons to occupy the core region.

3.4. Electron impact ionization cross section

The resulting electron impact ionization cross section per molecule in dependence on the incoming electron energy can be seen in Fig. 3 for the DM and the BEB formalism, using input data from the RHF/3-21G level. Both theories lead to similar functional shapes for the four DNA bases and the backbone molecule and result in the largest cross sections for the molecules with the largest number of electrons. Only for incident electrons with low energies the influence of the different ionization potentials can be seen, particularly in the case of the backbone cross section, which drops beyond the base cross sections for energies below approximately 15 eV. Small differences between the two formalisms show up in the position of the maximum (77 eV for DM and 82 eV for BEB in the case of adenine) and a smaller decrease of the cross section for higher energies in the case of the BEB theory. The cross sections of the backbone unit also includes the electron interaction with subshells of the sodium counter ion. Their contribution is, indeed, rather small (less than 2.5%) due to the high ionization potential of about 40 eV of the Na^+ ion.

Larger deviations between the two theories can be observed, when electron impact ionization cross sections per subshell are investigated. In Fig. 4 cross sections of five different orbitals of adenine are compared. In the BEB theory the higher molecular orbitals have a stronger influence on the ionization cross sections than in the DM formalism. Whereas in the case of the BEB the cross sections per subshell are separated, there are intersections in the cross sections resulting from the DM formalism. This is mainly caused by the weighting factor g_j, which depends not only on the binding energy of the orbital but also on the type of the corresponding atomic subshell.

In Fig. 5 the ECP derived cross sections are compared with the 3-21G basis set for the BEB formalism for the backbone unit and adenine. Due to the lower average kinetic energy of the target electrons in the case of the effective core potential calculation, the cross sections are slightly larger, about 4% in the maximum region of the cross sections of the backbone unit. The difference between the two basis sets is nevertheless quite small, because the DNA mainly consists of low-Z atoms like carbon, nitrogen and oxygen, where corrections for the core region are not necessary.

Table 4
Input parameters for the valence molecular orbitals for the BEB formalism for adenine, cytosine, guanine, thymine and the backbone unit, showing the scaled binding energy E_j and the average orbital kinetic energy of the target electron U_j for the 3-21G and the SDDALL basis sets

j	E_j (eV) RHF/3-21G	U_j (eV) RHF/3-21G	E_j (eV) RHF/SDDALL	U_j (eV) RHF/SDDALL
Adenine				
25	37.48	48.60	37.33	12.29
24	35.71	50.63	35.60	14.67
23	33.99	53.26	33.92	15.87
22	32.32	57.25	32.20	19.31
21	31.43	58.08	31.31	21.02
20	28.36	49.69	28.47	19.71
19	24.42	45.72	24.40	28.07
18	23.90	46.31	23.87	29.83
17	22.87	44.71	22.79	30.52
16	21.33	41.01	21.17	37.52
15	20.11	42.23	20.00	39.11
14	18.98	39.28	18.86	36.17
13	18.43	47.24	18.33	46.41
12	17.50	29.71	17.28	30.20
11	17.29	43.91	17.19	42.19
10	16.86	44.91	16.77	43.34
9	16.33	42.27	16.24	41.89
8	15.24	34.41	15.06	34.75
7	13.51	35.61	13.39	35.97
6	12.88	52.28	12.87	40.35
5	11.73	51.68	11.73	44.97
4	11.38	42.45	11.31	42.68
3	10.57	52.47	10.58	48.85
2	9.99	39.42	9.97	39.95
1	8.44	39.99	8.44	39.93
Cytosine				
21	37.70	63.86	37.13	17.80
20	35.33	56.94	34.72	17.28
19	34.14	54.88	33.55	16.31
18	31.79	55.93	31.23	20.30
17	28.92	47.78	28.52	17.60
16	24.29	44.27	23.93	26.17
15	23.80	48.32	23.50	32.13
14	20.74	36.62	20.31	33.12
13	20.62	40.04	20.18	40.16
12	19.47	45.88	19.16	40.31
11	18.30	40.42	17.98	38.73
10	17.01	32.56	16.65	33.36
9	16.79	42.93	16.52	38.17
8	16.47	42.14	16.17	40.42
7	15.60	62.01	15.45	53.86
6	14.53	37.96	14.23	38.21
5	13.16	40.83	12.97	41.86
4	11.44	62.35	11.44	59.39
3	10.67	53.93	10.63	49.99
2	10.06	43.61	9.94	44.01
1	8.94	45.75	8.94	44.88

Table 4 (*Continued*)

j	E_j (eV) RHF/3-21G	U_j (eV) RHF/3-21G	E_j (eV) RHF/SDDALL	U_j (eV) RHF/SDDALL
Guanine				
28	39.25	60.66	38.67	16.61
27	38.32	56.72	37.64	16.09
26	37.60	53.85	36.95	15.38
25	34.28	53.36	33.64	18.74
24	34.09	58.34	33.51	19.51
23	32.92	57.68	32.33	20.17
22	29.02	50.65	28.74	20.96
21	25.34	45.53	24.97	29.62
20	24.84	48.84	24.53	32.02
19	23.33	44.88	22.96	30.39
18	22.68	39.51	22.19	38.80
17	20.90	42.62	20.52	39.30
16	20.62	46.93	20.30	41.70
15	19.73	43.62	19.37	38.66
14	18.90	45.64	18.57	43.65
13	18.53	31.29	18.12	31.90
12	17.64	48.24	17.36	48.70
11	16.94	44.69	16.67	44.23
10	16.77	34.48	16.49	55.03
9	16.66	65.04	16.39	34.94
8	15.35	40.59	15.10	41.52
7	13.11	51.53	12.95	42.09
6	12.41	41.10	12.20	41.34
S	11.87	62.90	11.84	62.55
4	11.82	48.41	11.71	48.96
3	11.37	54.71	11.32	47.70
2	11.15	43.27	11.02	43.37
1	8.24	41.60	8.24	41.68
Thymine				
24	37.81	63.89	37.49	17.55
23	37.04	71.53	36.68	22.06
22	34.41	59.46	33.98	19.47
21	32.61	57.82	32.28	19.08
20	29.19	45.78	28.94	15.61
19	25.51	41.90	25.22	19.28
18	24.06	41.39	23.84	26.32
17	23.48	50.09	23.33	33.19
16	20.35	42.61	20.07	41.19
15	20.25	42.31	20.03	35.83
14	18.58	39.21	18.40	36.66
13	17.61	33.92	17.39	34.90
12	17.43	54.74	17.32	45.06
11	16.36	61.26	16.29	52.03
10	15.98	54.50	15.88	49.37
9	15.56	29.76	15.31	31.94
8	14.79	42.67	14.60	40.53
7	14.67	40.01	14.52	39.25
6	14.45	34.08	14.20	32.53
5	13.27	41.16	13.16	41.91
4	12.12	62.22	12.20	60.65
3	11.33	64.19	11.46	63.99

Table 4 (*Continued*)

j	E_j (eV) RHF/3-21G	U_j (eV) RHF/3-21G	E_j (eV) RHF/SDDALL	U_j (eV) RHF/SDDALL
2	10.92	55.19	11.04	55.43
1	9.14	41.53	9.14	41.31
Backbone				
33	37.98	68.72	37.61	16.93
32	36.57	67.45	36.02	18.99
31	36.13	72.19	35.56	19.39
30	34.49	75.67	34.44	20.55
29	32.99	79.00	33.00	21.99
28	28.53	43.54	27.98	13.77
27	27.70	41.24	27.20	15.02
26	24.78	43.24	24.38	19.81
25	21.79	39.66	21.48	32.71
24	21.52	51.76	21.29	23.43
23	20.84	47.11	20.56	27.90
22	18.93	42.24	18.67	38.56
21	18.06	35.65	17.71	32.89
20	17.64	34.36	17.24	34.57
19	17.29	39.94	16.98	36.48
18	16.47	52.38	16.56	41.28
17	15.70	39.99	15.72	43.41
16	15.66	52.97	15.44	35.84
15	15.10	42.63	14.99	46.13
14	15.00	47.81	14.75	37.30
13	14.33	50.16	14.25	48.88
12	13.62	57.74	13.80	51.69
11	13.10	47.45	13.03	49.91
10	13.04	39.86	12.75	40.66
9	12.56	40.18	12.69	51.93
8	12.44	56.82	12.41	45.06
7	12.28	52.58	12.26	50.27
6	11.91	56.04	12.08	51.30
5	11.69	49.48	11.71	52.41
4	11.58	57.93	11.53	46.08
3	10.84	61.52	11.35	60.64
2	10.62	62.47	11.08	62.75
1	10.52	57.61	10.52	56.22

In Monte Carlo track structure calculations for the determination of radiation induced DNA damage in biological environment it is often assumed, that DNA electron cross sections per valence electron do not significantly differ from those of the surrounding liquid water [37–40], because both molecules are built up by covalently bound low-Z atoms. In Fig. 6 the total ionization cross section per valence electron of the DNA and liquid water are compared, the latter was taken from Dingfelder et al. [41]. The DNA cross section per valence electron has been calculated by summing up the calculated cross sections of randomly chosen deoxynucleotide pairs and divided by the number of the valence electrons. For incoming electron energies above 250 eV the cross sections of the DNA of the two formalisms are in good agreement with the cross section of liquid water. However, in the energy range below 250 eV the larger first ionization potential of liquid water of 10.79 eV [41] leads to a smaller ionization cross section than that of DNA. This low energy region is particularly interesting for the investigation of radiation induced effects, because, e.g., 100 keV electrons deposit 50% of their energy only via secondary electrons with energies not larger

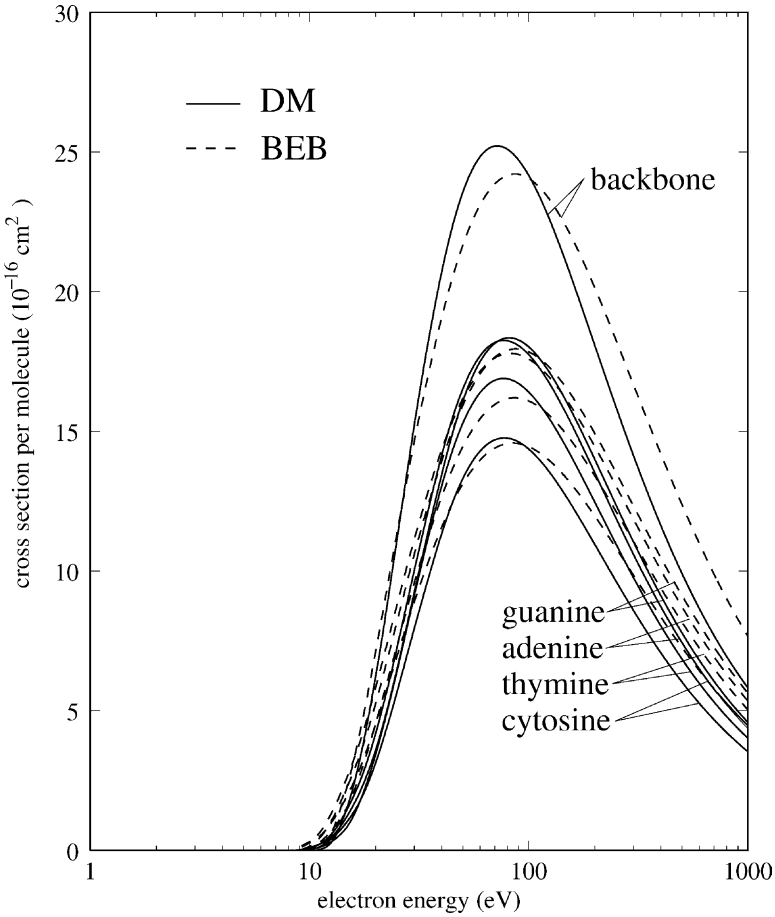

Fig. 3. Electron impact ionization cross sections per molecule for the parts of the DNA calculated by the DM (solid line) and BEB (dashed line) as a function of the energy of the incoming electron. The two upper lines represent the backbone. The lines below them give the cross sections for the four bases in the order written below them.

than 100 eV in liquid water [42]. The difference in the cross sections between DNA and liquid water can improve the understanding of the high effectivity per unit dose with which low energy electrons can damage DNA.

4. Conclusion and further prospects

The Deutsch–Märk formalism and the Binary–Encounter–Bethe theory were applied to calculate total electron impact ionization cross sections for the four DNA bases adenine, cytosine, guanine and thymine, as well as for the sugar-phosphate backbone. These two algorithms lead to quite similar total cross sections, but deviate in the prediction of the partial ionization cross section of single subshells. Further work will be invested to compare these results with upcoming measured ionization cross sections of fragments of the DNA. In addition effects of hydration and the combination of the fragments to a complete DNA molecule on the electron impact ionization cross section should be quantified. The derived ionization cross sections are useful, e.g., for applications in Monte Carlo track structure simulations for the determination of radiation induced DNA damage.

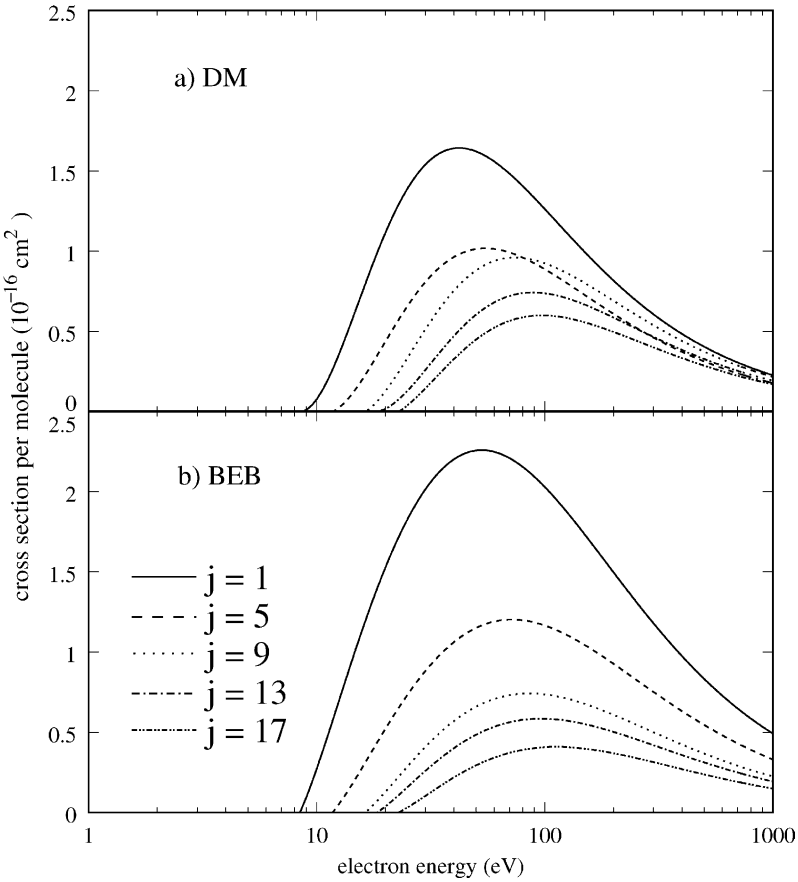

Fig. 4. Electron impact partial ionization cross sections for subshells of adenine calculated by the DM and BEB formalism in dependence on the incoming electron energy.

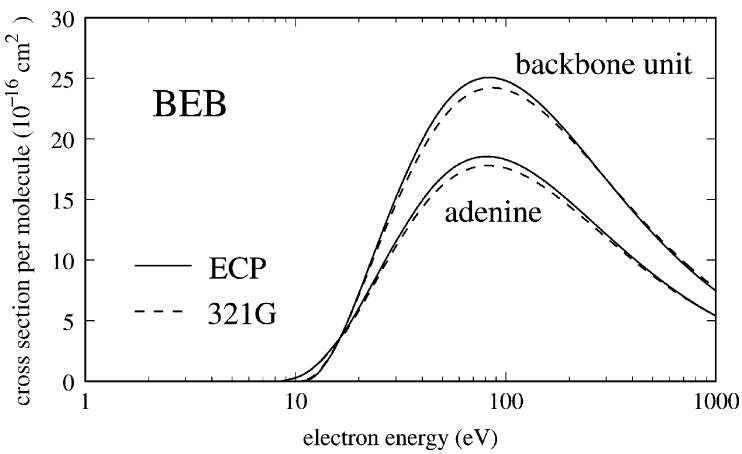

Fig. 5. Comparison between the total electron impact ionization cross sections using the 3-21G and ECP basis set for the BEB theory for adenine.

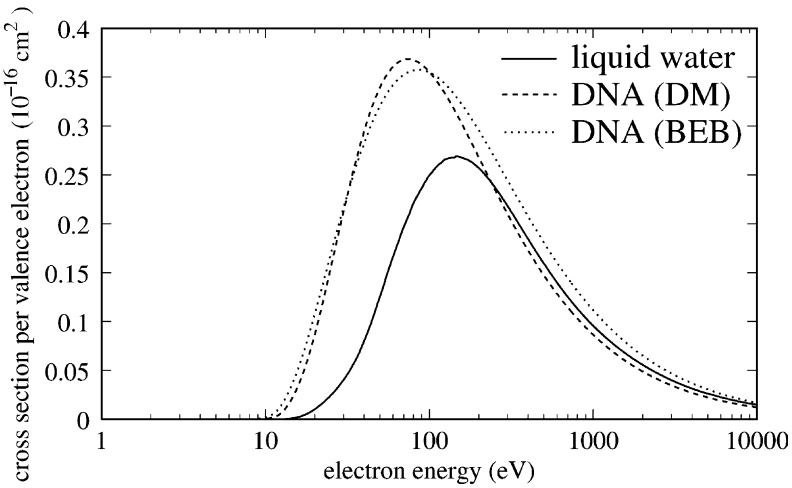

Fig. 6. Comparison between the total electron impact ionization cross sections per valence electron of liquid water (from Dingfelder et al. [41]) and DNA, derived by DM and BEB formalisms.

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