Absolute cross sections for electronic excitation of condensed tetrahydrofuran (THF) by 11–16 eV electrons

V. Lemelin, A. D. Bass, P. Cloutier, and L. Sanche

Groupe en Sciences des Radiations, Département de Médecine Nucléaire et Radiobiologie,
Faculté de Médecine et Sciences des Radiations, Université de Sherbrooke, Sherbrooke, Québec
J1H 5N4, Canada

Abstract

Absolute cross section (CS) data on the interaction of low energy electrons with DNA and its molecular constituents are required as input parameters in Monte-Carlo type simulations, for several radiobiological applications. Previously [V. Lemelin *et al.*, *J. Chem. Phys.* **144**, 074701 (2016)], we measured absolute vibrational CSs for low-energy electron scattering from condensed tetrahydrofuran, a convenient surrogate for the deoxyribose. Here we report absolute electronic CSs for energy losses of between 6 and 11.5 eV, by electrons with energies between 11 and 16 eV. The variation of these CSs with incident electron energy shows no evidence of transient anion states, consistent with theoretical and other experimental results, indicating that initial electron capture leading to DNA strand breaks occurs primarily on DNA bases or the phosphate group.

I. INTRODUCTION

It is now well-known that the energy deposited by ionizing radiation is transferred into biological matter largely by the secondary electrons it produces.^{1–5} Most of these latter have energies between 0 and 30 eV⁴ and interact with the biological medium by multiple inelastic processes that can ionize biomolecules, excite their vibrational modes, and produce electronically excited states. Dissociative excited states lead to the production of reactive species. Thus, these low-energy electrons (LEEs) can break DNA strands^{5–7} and perturb the biochemistry of the cell. DNA damage may lead to cellular mutation or necrosis.⁸ Furthermore, the development of new radiotherapy modalities such as concomitant chemoradiotherapy^{1,9,10} and targeted radionuclide therapy (TRT)¹¹ requires dose calculations at the subcellular and nanoscopic level via Monte Carlo simulations to improve treatment.^{7,12} Input parameters for such calculations should include absolute cross sections (CSs) for LEE interactions with DNA or its subunits (i.e., bases, sugar, and phosphate group).^{13,14}

Recently, we reported absolute vibrational CSs for LEE scattering from condensed tetrahydrofuran (THF-C₄H₈O),¹⁵ a convenient model for the deoxyribose sugar,^{2,16–24} that links phosphate groups in the DNA backbone. Multiple studies report on the interactions of electron with THF,^{2,8,15,16,18,24–30} but *absolute* electronic CSs are unavailable for the condensed phase. Here, we report absolute electron impact CSs for electronic excitation of condensed THF, corresponding to energy losses between ~6 and 11.5 eV, so as to provide a more complete set of CS data. Due to the maximum value of energy loss recorded, the

weakness of the THF signal, and energy losses in the substrate, the incident electron energy range had to be limited to the window 11–16 eV.

II. EXPERIMENT

Measurements were performed with a previously described high-resolution electron energy loss spectrometer (HREELS),³¹ working at a resolution of about 20 meV. Experimental conditions were similar to those in our study of vibrational CSs for THF,¹⁵ with the exception of an incident current of 0.39 nA. In the present experiments, one monolayer (ML) of THF (Sigma Aldrich, 99%) is condensed onto a 10 ML argon spacer film, itself condensed onto a Pt foil substrate held at 20 K. The Ar spacer reduces image-charge polarization and limits the interaction of THF with metal.³² Argon is chosen for this purpose due to its inert nature, and the absence of vibrational and electronic excitations below the first exciton at 11.75 eV (i.e., a very large bandgap).^{33–35}

An Ar thickness of 10 ML was chosen instead of 3 or 6 ML, as in the previous experiments,^{15,33–35} to suppress extraneous signal arising from the interaction with the Ar overlayer of electrons backscattered from the Pt substrate. Owing to the low absolute cross sections for electronic excitation of THF, HREELS spectra recorded with 3 or 6 ML Ar contained structures derived from elastic and quasi-elastic scattering in the Ar spacer; these features could be related to electronic band structure and density of electronic states of Ar.³⁶ Despite the thicker Ar spacer in the present experiment, due to this latter effect and due to the weakness of the THF signal below incident electron energies (E_0) of ~11 eV, we had to limit the measured electron energy loss (EEL) spectra to the range $E_0 = 11\text{--}16$ eV.

III. SCATTERING MODEL

The scattering model used to calculate the electronic CSs of THF is the same as that described in our previous work¹⁵ on THF vibrational CSs. Within the single collision model,^{15,33,37} we have

$$I(\theta_d, E_0, E - E_0) \cong \frac{I_0(\theta_d, E_0)}{\cos\theta_0} \sigma_r(E_0, E - E_0) n_s. \quad (1)$$

In this equation, I is a current of electrons, measured by the analyzer in the backscattered direction θ_d , that have transferred an energy of $E - E_0$ into the film. $I_0(\theta_d, E_0)$ is defined as an effective incident electron current. The latter can be seen as that fraction of the incident electron current I_0 that would be backscattered into the analyzer positioned at an angle θ_d with respect to the surface normal, in the plane of I_0 and that of the detected inelastic current $I(\theta_d, E_0, E - E_0)$; here, the diffuse elastic reflectivity is one, from the assumption that all incident electrons are scattered out of the film.³³ The quantity $\sigma_r(E_0, E - E_0)$ represents the CS for an electron to deposit an energy of $E - E_0$ in the film and be backscattered into the vacuum. The value n_s is the surface number density of molecules on the substrate.

In this experiment, a value of 8024 counts $\text{s}^{-1} \text{eV}$ ($\pm 4\%$) was obtained for $I_0(\theta_d, E_0)$ at $\theta_d = 45^\circ$. The determination of this parameter has been described by Lévesque *et al.*³³ To determine the absolute CSs values, multiple EEL spectra $I(\theta_d, E_0, E - E_0)$ are recorded at different E_0 in the direction $\theta_d = 45^\circ$ on the THF target. Under the present experimental conditions (i.e., near normal incidence and an azimuthally disordered film), it has been shown^{31,38–40} that the backscattered intensity varies only slightly as a function of angle and can be considered isotropic. The model used³³ demonstrates that the measurement of $I(\theta_d, E_0, E - E_0)$ along a single direction (here 45°), once normalized to the incident current $I_0(\theta_d, E_0)$, can lead to the CSs value corresponding to the electrons backscattered over the whole half-angular space (see Eq. (1)).³³ Hence, the CSs presented in this paper represent absolute and integral values. For more details on this particular model, see Ref. 33.

Since at every impact energy studied, the EEL spectra do not exhibit any distinct structure, each spectrum is arbitrarily divided in five sub-regions of 1 eV width (for EEL between 6 and 11 eV), with one further region between 11 and 11.5 eV EEL. From $I_0(\theta_d, E_0)$ together with n_s , $\sigma_r(\theta_d, E_0, E - E_0)$, the absolute CS value for each region of EEL is obtained from the area of the corresponding region using Eq. (1).

IV. RESULTS AND DISCUSSION

A. Electronic spectra

The electronic spectrum of condensed THF is complex, containing multiple overlapping bands that collectively produce the broad featureless structure apparent in the representative EEL spectrum of Fig. 1. Bouchiha *et al.*² have summarized the experimentally observed electronic bands of THF. Briefly, near threshold EEL spectra⁴¹ and the gas-phase vacuum ultraviolet (VUV) photoabsorption studies^{41–43} report three bands at 6.6, 7.2, and 7.8 eV that are assigned to excitation of Rydberg states $1n_0 \rightarrow 3s$, $1n_0 \rightarrow 3p$, and $1n_0 \rightarrow 3d$, respectively. At higher energy loss, three further Rydberg states have been observed at 8.1 eV ($1n_0 - 1 \rightarrow 3s$), 8.57 eV ($1n_0 \rightarrow 4p$), and 8.89 eV ($1n_0 \rightarrow 5p$). The most complete information is contained in the high resolution photoabsorption measurements and calculations of Giuliani *et al.*³⁰ for gas-phase THF, which additionally underline the resolution limitations of HREELS. Nevertheless, despite their lack of spectroscopic identity, HREELS spectra are needed to generate the CSs values for specific incident electron energies and energy losses.

The HREEL spectra recorded at incident energies in the 11–16 eV range, such as that depicted in Fig. 1, can be compared to the results of Antic *et al.*²⁶ for 16 ML THF on Pt, and of Breton *et al.*¹⁶ for 4 ML of THF condensed onto Kr. In both cases, the earlier data closely resemble the present results. In all cases, Rydberg states observed previously in EEL and VUV spectra in gas phase are not readily apparent, probably because Rydberg states are expected to be weaker or absent in condensed phase.^{16,26,44} The sharp rise observed at an energy loss of about 11.5 eV is due to the first exciton of Ar (i.e., the onset of electronic excitation within the Ar layer). It is evident that at energy loss greater than 11.5 eV, spectra also reflect processes occurring in the Ar layer. For this reason, we do not present cross sections for processes having an energy loss greater than 11.5 eV.

B. Electronic scattering cross sections

The energy dependence of the CSs for each region and their numerical values are presented in Fig. 2 and Table I, respectively. For each electron incident energy E_0 , CSs were calculated from the area under the corresponding region ($I(\theta_d, E_0, E - E_0)$), using Eq. (1), along with the experimental parameters: I_0 , n_s , $\cos\theta_0$. The error bars on the data points of Fig. 2 only indicate the reproducibility of each measurement and are $\pm 23\%$ (I), $\pm 15\%$ (II), $\pm 17\%$ (III), $\pm 26\%$ (IV), $\pm 31\%$ (V), $\pm 35\%$ (R), and $\pm 20\%$ (Total). Uncertainties were evaluated by obtaining sets of three energy loss spectra at four incident energies (i.e., at $E_0 = 11.25$, 11.75, 13.75, and 14.5 eV). The spectra were analyzed to obtain three independent CS estimates for each energy loss region, at each E_0 . Uncertainties were first estimated by dividing the difference between the maximum and minimum values of each CS, by 2. Four estimates were thus obtained for each energy loss region, one at each of the four E_0 values, the largest of which was applied (as a percentage) to all CS measurements of the same region.

We see then that experimental uncertainty increases as electron loss approaches that of the first Ar exciton near 11.75 eV. Errors bars do not include uncertainties associated with the stability of the current over time ($\pm 5\%$), systematic errors in the effective incident current $I_0(\theta_d, E_0)$ ($\pm 4\%$), or those in the determination of the molecular coverage n_s ($\pm 10\%$). These three latter uncertainties affect systematically the CSs values (magnitude of the vertical scale of Fig. 2).

Fig. 2 shows that CSs values for all regions lie within the 10^{-17} cm^2 range. Their variation with incident energy shares certain similarities; the highest CSs values are found between 11 and 12 eV of incident energy for each EEL region and decrease slowly towards higher incident energies. No structure that might be clearly assigned to formation of a transient negative ion can be discerned in these CSs. While the incident energy range (11–16 eV) employed here is probably too high to permit formation of such resonances, we note that the magnitude of the absolute electronic CSs of THF measured here are smaller than the ones measured previously for the DNA bases or base derivatives (i.e., cytosine, thymine, pyrimidine, and adenine^{33,35,45–47}). This is consistent with the work of Aflatooni *et al.*⁴⁸ who showed that the CSs for DEA to THF were smaller than the ones of DNA bases. These results and the absence of electron resonance-related structure in these CSs support the idea that DNA strand breaks proceed via attachment of an electron to a base or to a phosphate group, rather than to the sugar.^{49,50}

V. SUMMARY

We reported absolute electronic excitation CSs for LEE impact on condensed THF molecules. THF is a convenient proxy for deoxyribose, an important constituent of DNA. Multiple EEL spectra were measured from scattering of 11 to 16 eV electrons from 1 ML of THF condensed on an Ar substrate deposited on a Pt surface. The EEL spectra compared favorably to those reported in other condensed phase studies. Each of these spectra was divided in 6 regions corresponding to a precise EEL range. These CSs are found to lie within the 10^{-17} cm^2 range. Considering the difficulties in measuring *absolute* CSs, the

uncertainties of the values appear acceptable and represent the best available data in the investigated ranges of energy loss and incident electron energy.

More generally, the availability of absolute CS for LEE energy losses to crucial cellular molecules should help improving radiobiological models and dose calculations at sub-cellular level. Such advances are expected to contribute to the development of new and more effective radiotherapy modalities, like targeted radionuclide therapy and concomitant chemoradiotherapy. In future experiments, we will determine *absolute* LEE CSs for vibrational and electronic excitation of other *condensed* analogues of deoxyribose and larger DNA sub-units, particularly nucleosides containing a sugar and a base.

Acknowledgments

This research is supported by CIHR Grant No. MOP 86676.

References

1. Duque HV, Do TPT, Lopes MCA, Konovalov DA, White RD, Brunger MJ, Jones DB. J Chem Phys. 2015; 142:124307. [PubMed: 25833579]
2. Bouchiha D, Gorfinkiel JD, Caron LG, Sanche L. J Phys B: At, Mol Opt Phys. 2006; 39:975.
3. Inokuti, M. Applied Atomic Collision Physics. Vol. 4. Academic Press; New York: 1983. p. 179-236.
4. Pimblott SM, Laverne JA, Mozumder A. J Phys Chem. 1996; 100:8595.
5. Boudaïffa B, Cloutier P, Hunting D, Huels MA, Sanche L. Science. 2000; 287:1658. [PubMed: 10698742]
6. Muñoz A, Blanco F, Garcia G, Thorn PA, Brunger MJ, Sullivan JP, Buckman SJ. Int J Mass Spectrom. 2008; 277:175.
7. Sanz AG, Fuss MC, Muñoz A, Blanco F, Limão-Vieira P, Brunger MJ, Buckman SJ, Garcia G. Int J Radiat Biol. 2012; 88:71. [PubMed: 21923304]
8. Chiari L, Duque HV, Jones DB, Thorn PA, Pettifer Z, Da Silva GB, Limão-Vieira P, Duflot D, Hubin-Franskin MJ, Delwiche J, Blanco F, García G, Lopes MCA, Ratnavelu K, White RD, Brunger MJ. J Chem Phys. 2014; 141:024301. [PubMed: 25028013]
9. Eifel PJ. Nat Clin Pract Oncol. 2006; 3:248. [PubMed: 16683003]
10. Zheng Y, Hunting DJ, Ayotte P, Sanche L. Phys Rev Lett. 2008; 100:198101. [PubMed: 18518490]
11. Zalutsky, MR. Handbook of Nuclear Chemistry. Vertes, A.Nagy, S.Klencsar, Z.Lovas, RG., Rosch, F., editors. Springer; Heidelberg: 2013. p. 2179-2203.
12. Rogers DWO. Med Phys. 1995; 22:503. [PubMed: 7643786]
13. Michaud M, Bazin M, Sanche L. Phys Rev E. 2013; 87:032701.
14. Nikjoo H, Terrissol M, Hamm RN, Turner JE, Uehara S, Paretzke HG, Goodhead DT. Radiat Prot Dosim. 1994; 52:165. available at <http://rpd.oxfordjournals.org/content/52/1-4/165.abstract>.
15. Lemelin V, Bass AD, Cloutier P, Sanche L. J Chem Phys. 2016; 144:074701. [PubMed: 26896993]
16. Breton SP, Michaud M, Jäggle C, Swiderek P, Sanche L. J Chem Phys. 2004; 121:11240. [PubMed: 15634080]
17. Dampc M, Milosavljević AR, Linert I, Marinković BP, Zubek M. Phys Rev A. 2007; 75:042710.
18. Lepage M, Letarte S, Michaud M, Motte-Tollet F, Hubin-Franskin MJ, Roy D, Sanche L. J Chem Phys. 1998; 109:5980.
19. Garland NA, Brunger MJ, Garcia G, De Urquijo J, White RD. Phys Rev A. 2013; 88:062712.
20. Gauf A, Hargreaves L, Jo A, Tanner J, Khakoo M, Walls T, Winstead C, McKoy V. Phys Rev A. 2012; 85:052717.
21. Janežová R, May O, Milosavljević AR, Fedor J. Int J Mass Spectrom. 2014; 365–366:163.
22. Khakoo MA, Orton D, Hargreaves LR, Meyer N. Phys Rev A. 2013; 88:012705.

23. Mozejko P, Ptasińska-Dęga E, Domaracka A, Szmytkowski C. *Phys Rev A*. 2006; 74:012708.
24. Park YS, Cho H, Parenteau L, Bass AD, Sanche L. *J Chem Phys*. 2006; 125:074714. [PubMed: 16942371]
25. Sulzer P, Ptasińska S, Zappa F, Mielewska B, Milosavljević AR, Scheier P, Märk TD, Bald I, Gohlke S, Huels MA, Illenberger E. *J Chem Phys*. 2006; 125:044304.
26. Antic D, Parenteau L, Lepage M, Sanche L. *J Phys Chem B*. 1999; 103:6611.
27. Antic D, Parenteau L, Sanche L. *J Phys Chem B*. 2000; 104:4711.
28. Jäggle C, Swiderek P, Breton SP, Michaud M, Sanche L. *J Phys Chem B*. 2006; 110:12512. [PubMed: 16800580]
29. Do TPT, Leung M, Fuss M, Garcia G, Blanco F, Ratnavelu K, Brunger MJ. *J Chem Phys*. 2011; 134:144302. [PubMed: 21495750]
30. Giuliani A, Limão-Vieira P, Duflot D, Milosavljević AR, Marinković BP, Hoffmann SV, Mason N, Delwiche J, Hubin-Franskin MJ. *Eur Phys J D*. 2009; 51:97.
31. Michaud M, Sanche L. *Phys Rev B*. 1984; 30:6078.
32. Michaud M, Sanche L. *Phys Rev B*. 1994; 50:4725.
33. Levesque PL, Michaud M, Sanche L. *J Chem Phys*. 2005; 122:094701. [PubMed: 15836156]
34. Michaud M, Bazin M, Sanche L. *J Chem Phys*. 2012; 137:115103. [PubMed: 22998289]
35. Levesque PL, Michaud M, Cho W, Sanche L. *J Chem Phys*. 2005; 122:224704. [PubMed: 15974700]
36. Michaud M, Sanche L, Goulet T, Jay-Gerin JP. *Phys Rev Lett*. 1991; 66:1930. [PubMed: 10043346]
37. Michaud M, Sanche L. *Phys Rev B*. 1984; 30:6067.
38. Lepage M, Michaud M, Sanche L. *J Chem Phys*. 2000; 112:6707.
39. Michaud M, Sanche L. *Phys Rev A*. 1987; 36:4684.
40. Michaud M, Cloutier P, Sanche L. *Phys Rev B*. 1991; 44:10485.
41. Bremner LJ, Curtis MG, Walker IC. *J Chem Soc, Faraday Trans*. 1991; 87:1049.
42. Doucet J, Sauvageau P, Sandorfy C. *Chem Phys Lett*. 1972; 17:316.
43. Tam WC, Brion CE. *J Electron Spectrosc Relat Phenom*. 1974; 3:263.
44. Robin, MB. *Higher Excited States of Polyatomic Molecules*. Vol. 1. Academic Press; New York: 1974.
45. Michaud M, Bazin M, Sanche L. *Int J Radiat Biol*. 2012; 88:15. [PubMed: 21615242]
46. Bazin M, Michaud M, Sanche L. *J Chem Phys*. 2010; 133:155104. [PubMed: 20969430]
47. Panajotović R, Michaud M, Sanche L. *Phys Chem Chem Phys*. 2007; 9:138. [PubMed: 17164896]
48. Aflatooni K, Scheer AM, Burrow PD. *J Chem Phys*. 2006; 125:054301. [PubMed: 16942207]
49. Sanche, L. *Radical and Radical Ion Reactivity in Nucleic Acid Chemistry*. Greenberg, MM., editor. John Wiley & Sons, Inc; 2010. p. 239-294.
50. Caron, LG., Sanche, L. *Low-Energy Electron Scattering from Molecules, Biomolecules and Surfaces*. Carsky, P., Curik, R., editors. CRC Press; 2011. p. 161-230.

FIG. 1.

Representative EEL spectrum obtained with electrons impinging with an energy E_0 of 14 eV on one monolayer (ML) of THF deposited on 10 ML of Ar. The blue vertical lines delimit the six regions used for CSs calculations. Regions I to V are 1 eV wide and the remaining region (R) has a width of 0.5 eV.

FIG. 2.

Variation with electron collisional energy of the electronic excitation cross sections of THF for the six regions defined in Fig. 1. The last curve represents the total cross sections in the range 6–11.5 eV. The numerical values of these cross sections that result from the integration of each of the regions of energy-loss spectra are given in Table I. The interpolated lines serve only for better visualisation. The vertical errors bars result only from the reproducibility of the measurements of about $\pm 23\%$ (I), $\pm 15\%$ (II), $\pm 17\%$ (III), $\pm 26\%$ (IV), $\pm 31\%$ (V), $\pm 35\%$ (R), and $\pm 20\%$ (Total). Accounting for the uncertainties of the other parameters, the total absolute error on the presents CSs amounts to $\pm 42\%$ (RI), $\pm 34\%$ (RII), $\pm 36\%$ (III), $\pm 45\%$ (IV), $\pm 50\%$ (V), $\pm 54\%$ (R), and $\pm 39\%$ (Total).

Cross sections σ (10^{-17} cm²) for 11–16 eV (E_0) electrons incident on 1 ML THF condensed on an inert Ar spacer. The CS values are given for the six energy loss regions defined in Fig. 1.

TABLE I

E_0	Regions (EEL)					
	σ					
	I (6–7 eV)	II (7–8 eV)	III (8–9 eV)	IV (9–10 eV)	V (10–11 eV)	R (11–11.5 eV)
Total (6–11.5 eV)						
11	0.58	0.89	1.3	1.5	1.4	0.15
11.25	0.56	1.0	1.5	2.4	2.7	0.74
11.5	0.56	0.91	1.3	2.0	2.2	2.1
11.75	0.55	1.0	1.6	2.3	3.0	1.5
12	0.52	0.80	1.1	1.6	1.7	0.74
12.5	0.50	0.79	1.1	1.6	2.0	1.0
13	0.42	0.72	1.1	1.6	2.1	1.3
13.5	0.42	0.64	0.74	1.5	2.0	1.3
13.75	0.36	0.59	0.93	1.5	1.8	1.1
14	0.38	0.52	0.77	1.1	1.4	0.84
14.5	0.34	0.46	0.60	1.1	1.6	0.92
15	0.27	0.49	0.82	1.3	1.8	1.1
15.5	0.25	0.44	0.74	1.2	1.6	1.0
16	0.25	0.35	0.51	0.72	0.97	0.6
						3.4