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Excitation and ionisation cross-sections in condensed-phase biomaterials by electrons down to very low energy: application to liquid water and genetic building blocks (Electronic Supplementary Information)

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S1. LIST OF ACRONYMS AND ABBREVIATIONS

Due to the length of the article and the large number of acronyms and abbreviations, these are provided here to facilitate the reading:

BEB: binary-encounter Bethe calculations
BO: Born-Ochkur exchange approximation/contribution
corr: Coulomb-field correction to the FBA
DDCS: doubly differential cross-section
DNA: deoxyribonucleic acid
EELS: electron energy-loss spectrum/spectroscopy
ELF: energy-loss function
FBA: first Born approximation
IMFP: inverse mean free path
MELF-GOS: Mermin Energy-Loss Function Generalized Oscillator Strengths
out: outer-shell electrons
RNA: ribonucleic acid
SDCS: singly differential ionisation cross-section
SCS: electronic stopping cross-section
THF: tetrahydrofuran
TCS: total cross-section
TECS: total electronic excitation cross-section
TICS: total ionisation cross-section
xc: exchange correction/contribution/term

S2. COMPILATION OF CROSS SECTIONS FOR THE EXCITATION OF SPECIFIC ELECTRONIC TRANSITIONS OF THE WATER MOLECULE AND THEIR SCALING

Measurements of electronic excitation cross-sections for the water molecule are usually restricted to some particular channels. For example, Thorn *et al.* [1] only report data for the $\tilde{A}^1B_1$ excitation, while Matsui *et al.* [2] also include the $\tilde{a}^3B_1$ transition, and Brunger *et al.* [3] and Ralphs *et al.* [4] present results for the six lowest lying states $^3B_1$, $^1B_1$, $^3A_2$, $^1A_2$, $^3A_1$, and $^1A_1$. These data are presented in Fig. S1(a) by pale open symbols. However, data for 19 more transitions are provided in Ref. [5], which is the most complete information currently available to the best of our knowledge. Since that work contains all the channels reported by the aforementioned authors, it is possible to use the (more complete) latter data to scale the former partial values as if all these channels were comprised, as our calculated TECS for liquid water (line in Fig. S1(a)) includes all possible channels.

Scaling factors have been estimated from Thorn's experiments [5] as the ratio of the data for all 25 measured channels to the data for the specific channels at each particular electron energy, see Table S1. Some of the points from [1] and [4] lie outside the energy range covered by [5] (15-50 eV). For the data from [4], the ratio at 15 eV has been taken below this energy. For [1], whose data lie at energies larger than 50 eV, an average of the ratios for the available energies between 15 and 50 eV has been used. Error bars for the data in Fig. S1(a) correspond to the absolute uncertainties reported by the different authors, when given, or by the relative uncertainties applied to the scaled data.

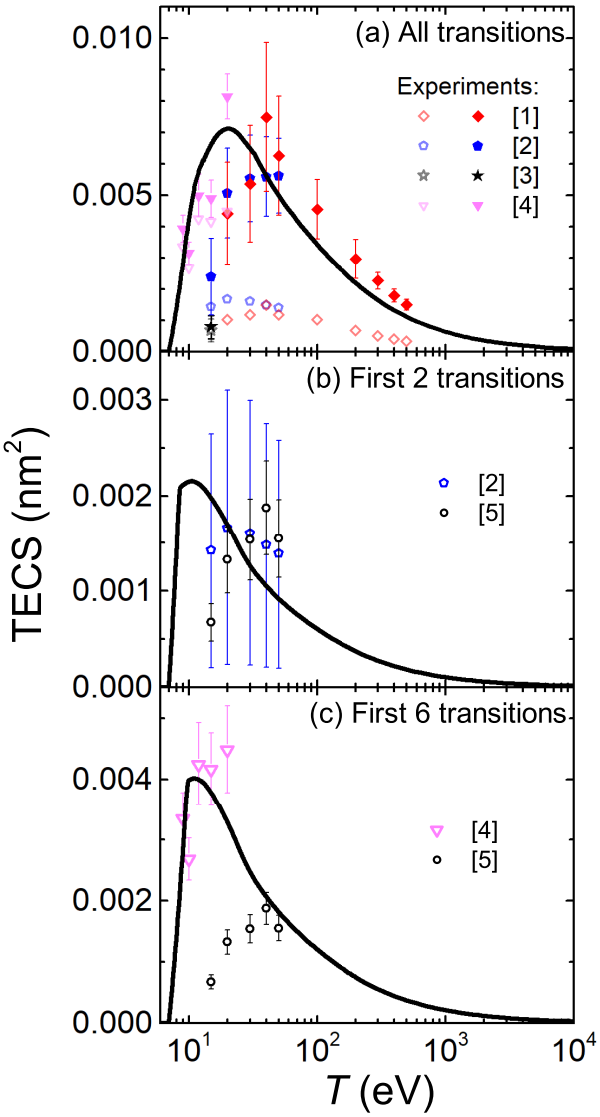

FIG. S1. (a) Total electronic excitation cross section (TECS) for electrons in water. The line represents the full calculation for the liquid, pale symbols depict experimental data from different authors for a limited number of excitation channels of the water molecule [1–4], and full symbols correspond to the latter data scaled as to include all possible channels [5], as explained in the text. (b) Raw data (symbols) from [2, 5] for the two lowest lying transitions and the corresponding calculation (line). (c) Raw data (symbols) from [4, 5] for the six lowest lying transitions and the corresponding calculation (line).

Figures S1(b) and (c) show by symbols, respectively, the raw experimental data for the two [2, 5] and the six [4, 5] lowest lying transitions of the water molecule. In order to further benchmark our model, we calculated TECS for liquid water but, instead of integrating them over the entire allowed energy transfer range, we performed the calculations by artificially establishing an upper limit given by $E_+ = \min[B_{\rm out}, T, E_{\rm max}]$, where $E_{\rm max}$ is an energy above the specific electronic transitions considered in each experimental work. This maximum energy can be estimated from the data available on the energy and width of the different transitions from Refs. [5, 6]. According to this information, we obtained the TECS for the

TABLE S1. Factors used to scale the experimental partial excitation cross sections from [1–4] by using the most complete data from [5]

Transitions:	$^3B_1$, $^1B_1$, $^3A_2$, $^1A_2$, $^3A_1$, $^1A_1$	$^3B_1$, $^1B_1$	$^1B_1$
Electron energy T (eV)	Refs. [3, 4]	Ref. [2]	Ref. [1]
9	1.174		
10	1.174		
12	1.174		
15	1.174	1.685	
20	1.815	3.034	4.332
30		3.439	4.606
40		3.780	5.076
50		4.045	5.298
100			4.472
200			4.472
300			4.472
400			4.472
500			4.472

two lowest lying transitions integrating Eq. (21) of the main text from the threshold energy $E_{\rm th} = 7$ eV to $E_+ = 8.5$ eV, and for the six lowest lying transitions integrating from $E_{\rm th} = 7$ eV to $E_+ = 9.8$ eV. Note that this type of calculation of partial TECS is similar to what is shown in Figs. 6(b), 7(a) and 7(d) of the main text for comparing our calculations with the experimental data for solid cytosine, adenine and thymine.

S3. COMPILATION OF TOTAL ELECTRONIC CROSS SECTIONS FOR THF AND CYTOSINE

In Fig. 6 of the main text, calculated total electronic cross sections for condensed-phase THF and cytosine were compared with a selection of experimental data in the gas and condensed phases. Other available data was omitted there for clarity. In Fig. S2, a compilation of all the experimental and reference data for THF and cytosine known to us is shown for comparison purposes. Apart from the discussion already conducted in the main text, other aspects can be highlighted here.

For THF, Fig. S2(a), the calculated total (ionisation plus excitation) electronic cross-section (dotted line) for the solid agrees very well with the experimental data (for the gas phase) from [7] in the limited range of low energies measured. The experimental TECS data for solid THF from [8] are too low in comparison with our calculations. The dash-dot-dotted line depicts calculated results restricting the excitation process up to 11.5 eV, the range experimentally measured. However, in this case, calculations do not agree with the experimental determination, as it happens for cytosine (Fig. S2(b) or Fig. 6(b) in the main text), adenine or thymine (Fig. 7 in the main text) when using the same limited excitation energy range as analysed in experiments. Apart from the rest of data already discussed in the main text, here we also depict the determination of the TECS in the gas phase from Ref. [9] (pentagons), which agrees nicely with our calculation for the solid above 100 eV. As for the TICS, additional experiments for the gas phase are shown (asterisks and squares)

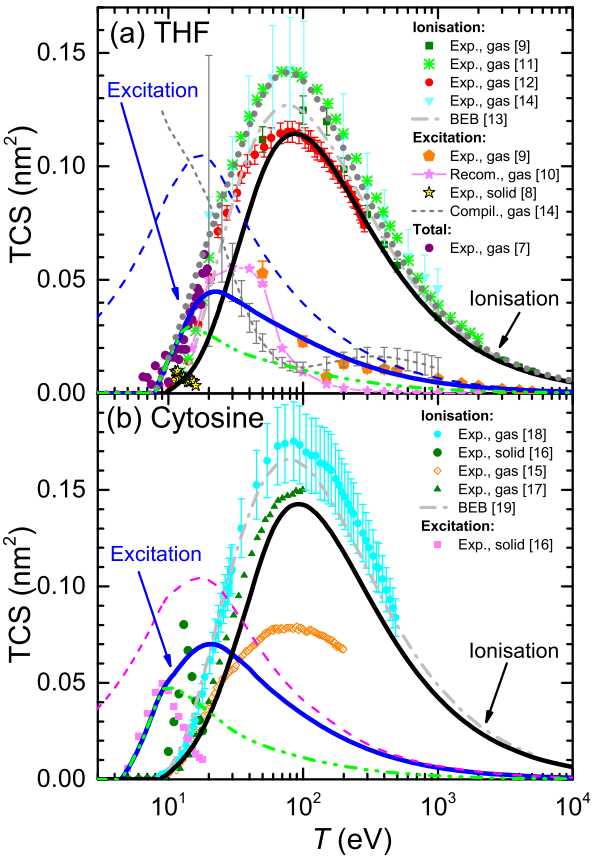

FIG. S2. Total electronic cross-section (TCS) for electrons in (a) THF and (b) cytosine, as a function of the electron incident energy T. Solid lines correspond to our full solid-state calculations for TICS and TECS, while the dotted line in (a) corresponds to the sum of both. Other lines and symbols represent experimental data: for THF, gas-phase TICS [9, 11, 12, 14] and TECS [9, 10, 14], solid-phase TECS (for $T < 11.5$ eV) [8], and gas-phase total electronic cross-section [7]; for cytosine, gas-phase TICS [15–18] and solid phase TECS [16]. BEB calculations for THF [13] and cytosine [19] are depicted by dash-dotted lines. Results from the present model are presented under different assumptions: dashed lines show calculations without using an excitation threshold (i.e., $E_{\rm th} = 0$ eV), while the dash-dot-dotted line in panel (b) depicts results restricting the excitation process up to 9 eV for cytosine.

[10, 11]. The data from [10] (squares) is just slightly higher than [12] and agrees well with BEB calculations [13] and is fairly close to our results. The data from [11] (asterisks) is almost identical to the results from [14], already discussed in the main text.

Regarding cytosine (Fig. S2(b)), apart from the experimental TICS for the gas phase already commented in the main text [15, 17, 18], there are also experimental TICS for the condensed phase from Ref. [16] (green circles). Although these data have their onset at an energy similar to our calculations, the slope and height of the maximum are very different, and also incompatible for the rest of measurements for gas-phase cytosine, which are rather close to our calculations for the condensed phase. The reason for such differences is currently unknown.

Finally, let us check the sensitivity of the calculated TECS on the value of $E_{\rm th}$, both for THF and cytosine, as this quantity is not provided by the parametric model to predict the

optical ELF of biomaterials [20], and thus needs to be obtained from other sources. In Fig. S2 we show by dashed lines the cross-sections obtained when setting $E_{\rm th} = 0$ eV. As can be seen, these values are too large in comparison with the available experimental data, which remarks the importance of counting on with a reliable source for the energy threshold for electronic excitations in order to calculate the TECS (note that the excitation threshold does not affect the TICS).

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