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Short communication

On the absolute value for the cross-section of dissociative electron attachment (DEA) to the DNA base thymine

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ABSTRACT

The absolute value for the cross-section of dissociative electron attachment (DEA) to thymine obtained from independent crossed beam experiments differ by more than three orders (!) of magnitude with respect to the value derived in an electron transmission spectrometer. We revisit this problem by means of a modified beam experiment showing that in using solid samples, condensation of the evaporated molecules outside the oven is the dominant source of systematic error.

Here we consider the large discrepancy recently observed in obtaining absolute cross-sections for dissociative electron attachment (DEA) to the DNA bases from different experiments. For thymine (T) two independent beam experiments reported values in the range of 10^{-15} cm^2 [1,2] for the prominent low energy DEA peak at 1.0 eV, while from electron transmission spectroscopy (ETS) a value of 4.7×10^{-19} cm^2 was derived [3]. We present new results for thymine (T) in a modified beam setup, which will shed light on the physical origin behind this large discrepancy (more than three orders of magnitude) and provide an approach towards the true value.

The interaction of low energy electrons with biomolecular systems is considered to play a pivotal role in the description of radiation damage to living cells on a molecular level [4]. This stems from the fact that high-energy radiation generates secondary electrons with energy distributions extending to some tens of eV [4,5]. These secondary electrons are slowed down within picoseconds and within that time window they may induce reactions prior being solvated. Among the low energy electron–molecule processes, DEA plays a crucial role as this reaction can induce the break of chemical bonds by electrons at very low energy, sometimes at virtually no extra energy (near 0 eV) [6]. In fact, the resonant behaviour in the effectiveness of single and double strand breaks in low energy electron impact to plasmid DNA [7] directly suggested, that DEA may be the initial molecular step.

Consequently, strong activities emerged in the last few years to unravel the molecular processes, by which low energy electrons damage DNA. These included DEA to the building blocks of DNA, namely the DNA bases [8], the sugar [9] and the phosphate moiety [10]. It became apparent that most building blocks are sensitive towards sub-excitation electrons, i.e., electrons at energies below the level of electronic excitation. All DNA bases, e.g., show pronounced resonances in the region between about 0.5 and 2.5 eV leading to the loss of a neutral hydrogen atom. For thymine (T) this reaction can be expressed as

$$e^- + T \rightarrow T^{\#-} \rightarrow (T\text{–}H)^- + H \quad (1)$$

where $T^{\#-}$ represents the transient negative ion formed upon electron attachment and $(T\text{–}H)^-$ the closed shell thymine anion which was subjected to the loss of a neutral hydrogen atom. The reaction is operative at low energies due to the appreciable electron affinity of the corresponding radical, T–H, with the ion yield showing a pronounced peak at 1.0 eV. It is the subject of many investigations and discussions whether these low energy capture processes at the DNA bases may trigger strand breaks. It is proposed that electron transfer from the base to the phosphate group can induce cleavage of a C–O bond which would represent a single strand break [11].

An essential quantity in that context is the *absolute* value for the DEA cross-section. A beam experiment at the Innsbruck laboratory arrived at a value of 1.2×10^{-15} cm^2 [1] while a second beam experiment at the Berlin laboratory gives an estimate in the order

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of 10^{-15} cm^2 [2]. In striking contrast, from an electron transmission experiment at the Lincoln laboratory a value of 4.7×10^{-19} cm^2 was derived [3] which differs from the beam values by more than three orders of magnitude.

In the beam experiment, the DEA cross-section is derived by using a calibration gas (C) with a well established cross-section and comparing the count rates of the DEA product ion with that of the calibrant. The latter either refers to the DEA cross-section for CCl_4 yielding a second Cl^- peak at 0.8 eV (Innsbruck) or associative electron attachment SF_6 at energies close to 0 eV (Berlin). The DEA cross-section for a particular anion $\sigma(X^-)$ is then determined according to

$$\sigma(X^-) = \sigma(C) \cdot \frac{N(X^-)}{N(C)} \cdot \frac{p(C)}{p(M)} \quad (2)$$

where $\sigma(C)$ is the well established cross-section of the calibrant, $N(X^-)$ the DEA signal from the target of interest (M), $N(C)$ is the ion count rate of the calibrant (Cl^- and $SF_6{}^-$, respectively) and $p(C)/p(M)$ is the ratio of the partial pressure between calibrant (C) and the target molecule (M) from which the fragment X^- is generated. This ratio is determined by measuring the respective partial pressure at an ionization gauge at one of the flanges of the vacuum system. It is thereby assumed that the pressure ratio remains constant within the vacuum system, i.e., that the ratio obtained at the ionization gauge reflects the ratio in the reaction volume. The evaluation further assumes a constant draw out probability from the reaction zone and a constant transmission and detection probability for the different ions at the quadrupole mass spectrometer. While such a procedure is straightforward for gaseous targets (within the above assumptions) it may have serious limitations when using solid targets which have to be vaporized (like the DNA bases). In the previous beam experiments, the solid sample was deposited in an oven connected with the reaction chamber, and evaporation was performed by *locally* heating the oven. In this case, a fraction of the sublimated molecules may condense on any surface outside the oven having a lower temperature. As a consequence, the pressure ratio at the ionization gauge may be smaller than that in the reaction zone.

In the ETS approach by the Lincoln laboratory [3], the total ion yield of negative and positive ions is compared thereby avoiding the critical quantity of the pressure ratio. In the case of T, hydrogen loss is the only DEA reaction at low energies and thus the total anion yield is a measure of the DEA cross-section generating $(T–H)^-$. The total ion currents of anions and cations are collected at the walls of a static collision cell of the ETS setup. Taking the well-established electron impact ionization cross-section of T at higher energies, the DEA cross-section at 1.0 eV was derived as 4.7×10^{-19} cm^2. In the evaluation it is assumed that the ion conversion factor at the walls of the collision cell is the same for anions and cations.

As already proposed [1,3], condensation of sublimated material may be a main source of error in the beam experiments. We therefore modified our arrangement in the way that no longer the oven (containing the solid material) is locally heated. Instead the overall vacuum system is now heated by a series of penlight bulbs *in vacuo* placed around the electron spectrometer thus preventing condensation directly at the spectrometer.

As described in detail elsewhere [6] the electron attachment spectrometer consists of a trochoidal electron monochromator [12] and a quadrupole mass spectrometer. After passing the quadrupole mass spectrometer the ions are detected by 17-stage electron multiplier. The characteristic of this type of detector is stable over a large range of temperature. The incident electron beam of well-defined energy (FWHM ≈0.2 eV, electron current ≈10 nA) orthogonally intersects with an effusive molecular beam containing the thymine molecules. The beam emanates from a vessel directly connected to the collision chamber. The overall system is heated by *in vacuo* halogen bulbs which provides sufficient vapor pressure to form a molecular beam of thymine. The operating temperature was in the range of 445–448 K (measured by a platinum resistance directly at the oven) resulting in a vapor pressure in the 10^{-6} mbar.

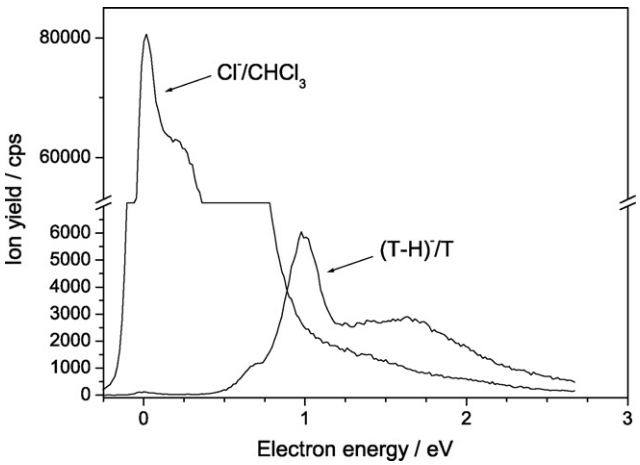

Fig. 1. Ion yield curve of $(T–H)^-$ from thymine and Cl^- from the calibration gas chloroform. Count rates in absolute numbers, $p(CHCl_3) = 2.5 \times 10^{-6}$ mbar, $p(T) = 1.9 \times 10^{-6}$ mbar (reading at the ionisation gauge, see the text).

In the present series of experiments we used the second DEA peak of Cl^- from chloroform ($CHCl_3$) (Fig. 1) to avoid calibration with SF_6 in the critical energy region near 0 eV. Fig. 1 also shows the yields of $(T–H)^-$ from thymine and Cl^- from chloroform. We then use the absolute DEA cross-section value in chloroform recently obtained from an extended experimental and theoretical treatment at 0.3 eV (5.68×10^{-16} cm^2 [13]), the readings at the ion gauge ($p(C) = 2.5 \times 10^{-6}$ mbar, $p(T) = 1.9 \times 10^{-6}$ mbar), and take the absolute count rates from Fig. 1 to calculate the total DEA cross-section for thymine at 1.0 eV. The pressure ratio $p(C)/p(T) = 1.32$ obtained from the reading at the pressure gauge has to be corrected for the different electron impact ionization cross-sections between chloroform and thymine. In ionization gauges, the ion currents are usually measured at electron impact energies of about 70 eV (representing the maximum of the cross-section for most molecules). While the cross-section is well established for T (16.18×10^{-16} cm^2 from the binary encounter Bethe (BEB) approach [3]), to our knowledge the explicit value for chloroform is not available so far. By considering the cross-section for similar molecules [14] like $CFCl_3$ (13×10^{-16} cm^2) or $CHCl_2F$ (11×10^{-16} cm^2), however, we can assume that 12×10^{-16} cm^2 is a reasonable value for the electron impact ionization cross-section in chloroform. With that we arrive at a corrected pressure ratio $p(C)/p(T) = 1.78$ finally yielding $\sigma(T–H)^- = 10.7 \times 10^{-17}$ cm^2 at 1.0 eV electron energy. From a series of five independent experiments values between 4.0×10^{-17} and 10.7×10^{-17} cm^2 were obtained with an average value of 7.9×10^{-17} cm^2. Taking the statistical variation and other uncertainties (ion draw out, transmission and detection) we arrive at $\sigma(T–H)^- = (7.9 \pm 4) \times 10^{-17}$ cm^2.

The remaining discrepancy of more than two orders of magnitude is probably due to systematic errors in both the beam and the ETS experiment. Despite of the more global heating in the modified arrangement, the beam experiment may still be subjected to partial condensation of the sublimated biomolecules, e.g., at the walls of the vacuum vessel (at somewhat lower temperatures than the spectrometer) which results in a lower pressure ratio in the ionization gauge compared to the reaction zone. The other point concerns the assumption in the ETS experiment of the same conversion factor for low kinetic energy cations and anions at a metallic surface.

From a simple mechanistic point of view, conversion of a cation into a neutral at the surface of a metal is driven by the potential drop between the relevant MO in the cation and Fermi level of the metal which will neutralize the cation by electron transfer from the metal. The situation changes for anions, in this case, the usually loosely bound extra electron is transferred into the metal due to the potential drop between the relevant MO of the anion and the Fermi level. For anions with appreciable electron binding energy, like the closed shell thymine $(T–H)^-$ (having a binding energy in the range between 3 and 4 eV) the HOMO of the anion is at about the same level as the Fermi energy thus reducing the driving force for electron transfer. In this case $(T–H)^-$ ions may be physisorbed at the metal surface (bound by image forces) with a low probability for neutralisation. The resulting charging of the metallic surface may then further reduce the probability for anions striking the surface. This effect results in a DEA cross-section which will be too low.

We conclude that the previous very large discrepancy in the DEA cross-sections (a factor of ≈2500) is mainly due to condensation of evaporated molecules in the beam experiment. The remaining discrepancy (a factor of ≈170) may still arise from condensation in the beam experiment, but also from a reduced probability for neutralisation of the $(T–H)^-$ anions (as opposed to cations) in the ETS experiment. From that, we consider the presently obtained DEA cross-section ($(7.9 \pm 4) \times 10^{-17}$ cm^2) as an upper limit, and that recently obtained from ETS (4.7×10^{-19} cm^2) as a lower limit.

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References

[1] S. Denifl, S. Ptasinska, M. Probst, J. Hrusak, P. Scheier, T.D. Märk, J. Phys. Chem. 108 (2004) 6562.
[2] H. Abdoul-Carime, S. Gohlke, E. Illenberger, Phys. Rev. Lett. 92 (2004) 168103.
[3] K. Aflatooni, A.M. Scheer, P.D. Burrow, J. Chem. Phys. 125 (2006) 054301.
[4] L. Sanche, Eur. Phys. J. D 35 (2005) 367.
[5] L. Sanche, Mass Spectrom. Rev. 21 (2002) 349.
[6] R. Balog, J. Langer, S. Gohlke, M. Stano, H. Abdoul-Carime, E. Illenberger, Int. J. Mass Spectrom. 233 (2004) 267 (Review).
[7] B. Boudaiffa, P. Cloutier, D. Hunting, M.A. Huels, L. Sanche, Science 287 (2000) 1658.
[8] S. Ptasinska, S. Denifl, E. Illenberger, P. Scheier, T.D. Märk, Phys. Rev. Lett. 95 (2005) 093201.
[9] I. Bald, J. Kopyra, E. Illenberger, Angew. Chem. Int. Ed. 45 (2006) 4851.
[10] C. König, J. Kopyra, I. Bald, E. Illenberger, Phys. Rev. Lett. 97 (2006) 018105.
[11] J. Simons, Acc. Chem. Res. 39 (2006) 772.
[12] A. Stamatovic, G.J. Schulz, Rev. Sci. Instrum. 41 (1970) 423.
[13] J. Kopyra, I. Szamrej, K. Graupner, L.M. Graham, T.A. Field, P. Sulzer, S. Denifl, T.D. Märk, P. Scheier, I.I. Fabrikant, M. Braun, M.-W. Ruf, H. Hotop, Int. J. Mass Spectrom. 277 (2008) 130.
[14] NIST electron impact ionization cross-section data base: http://physics.nist.gov/PhysRefData/Ionization/Xsection.html.