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Clustering and condensation effects in the electron scattering cross sections from water molecules

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ABSTRACT

Clustering effects in the differential and integral electron scattering cross sections have been investigated by calculating their magnitudes for different water cluster configurations: specifically for the dimer, trimer and tetramer. By assuming that condensation effects can be described in terms of modifications to the single molecule electron scattering cross sections, induced by the surrounding molecules, effective data for liquid water is also provided. Comparison with previous calculations in liquid water has been carried out through the inelastic mean free path, i.e. the mean length between successive inelastic collisions. Although a satisfactory agreement for high energies, above 100 eV, has been found, for lower energies some discrepancies remain and so will be the subject of further investigation. As an example of modelling electron interactions in soft matter, the present set of data has been employed to simulate single electron tracks in liquid water. This was achieved using our Low Energy Particle Track Simulation (LEPTS) code.

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1. Introduction

An interest in electron scattering from water molecules has increased considerably in recent years [1–3], mainly due to its relevance to the study of biological effects of radiation. Water is the main constituent of the biological environment, being a reference species for dose planning in biomedical uses of radiation. Electrons are abundantly formed as secondary particles when irradiating these media, either from direct molecular ionization or through successive ionizing processes undergone by the secondary species. It has been shown that low energy secondary electrons, such as those formed by charged-particle collisions, can efficiently induce damage at the molecular level, i.e. producing effective bond breaking and molecular dissociations [4]. However since the secondary electrons generated by photon interactions (photoelectrons) have energies typically close to those of the incident photons, modelling radiation interactions at the molecular level requires the study

of the electron scattering processes over a broad energy range. Namely from the MeV down to the meV domains. For electron collisions with molecules the high energy regime begins where the first Born approximation becomes valid, i.e. at around 10 keV in the case of water [1], and therefore, for modelling purposes, we will focus our interest on generating and compiling scattering data below this limit [5]. A comprehensive compilation of electron scattering cross section data from water molecules was published by Itikawa and Mason [6]. Updating those data, by incorporating the latest publications and validating recommended values, is currently in progress and will hopefully be published soon. Nevertheless, most published electron scattering data for water molecules corresponds to that for single molecules, in the gas phase, while in the aforementioned applications the electron interactions occur in liquid water. For this reason, important efforts have been recently made to describe dynamical processes in condensed water. The first approaches were based on the study of the response of the dielectric function of the medium [7–9]. Monte Carlo (MC) simulations in liquid water based on this model can be found in different publications, see e.g. Ref. [10] and references therein. Lately, Wiklund et al. [11] proposed a MC program to analyse “low-energy” electron tracks in liquid water. More recently, Champion et al. [12] extrapolated their differential and total electron scattering cross section calculations in

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the gas phase to the condensed phase. This was undertaken by assuming that single molecules were surrounded by a continuum dielectric medium, which modifies their cross section values by polarizing the molecules. Additionally, White and Robson [13,14] presented a different model for particle transport in soft matter by combining single-molecule gas phase cross sections [15] with a structure function of the medium which accounts for the condensation effects.

In order to incorporate a new point of view to the problem of electron scattering in condensed media, we first discuss here the evolution of the differential and integral electron scattering cross section values for molecular water clusters as a function of the number of their constituent molecules. The properties of the liquid phase might then be inferred from those of the increasing size clusters. However, for modelling purposes, the whole liquid bulk would be unmanageable and it would require some discretization into scattering units. We could initially assume that the size of these liquid units might be defined by the effective wavelength of the projectile during the collision. This of course means that the size of the scattering unit increases as the electron energy decreases. Although this approximation has a clear physical meaning and could be useful for some electron transport models, it is still not practical for an event by event MC simulation procedure, as we propose to perform here. Changing the input cross section data right after a few numbers of collisions, will increase significantly the computing time for single tracks and thus tender impractical a real simulation. Given these conditions we here present an alternative approach to describe electron scattering in liquids, which is based on the modification of the single-molecule cross sections by allowing for the overlap with those of the surrounding molecules. These quantities are calculated by applying our Screening Corrected Additivity Rule (SCAR) procedure to a liquid geometry, as defined by a homogeneous intermolecular configuration [16].

In the following section, we describe our calculation procedure from the single atom scattering potential method to the SCAR technique. Note that it is the latter which is used to derive electron collision cross section data for molecules, clusters and finally condensed molecules. The results of these calculations are presented in Section 3, for all the species studied here, and compared, where possible, with previously available cross section data. For the liquid case, inelastic mean free paths (IMFP) derived from our calculated cross sections are also compared with values given by other approximations. To end this section, we then use the present electron scattering data for condensed water to simulate single tracks of 3 keV electrons entering a liquid water volume. Information about electron penetration and the number and type of interactions taking place in that volume, during the thermalisation process is also given. Finally, in Section 4, some conclusions from this study are drawn.

2. Calculation procedures

2.1. Electron-atom and electron-molecule scattering cross sections

The entire method we use to calculate electron elastic differential and integral as well as integral inelastic scattering cross sections, with atoms and molecules, has been recently summarized (see Ref. [16] and references therein). Basically, atoms constituting the water molecule, i.e. oxygen and hydrogen atoms, are represented by an optical potential which includes all the improvements we introduced in our previous studies [17–20]. In order to obtain molecular cross sections, the independent atom model (IAM) has been followed by applying a coherent addition procedure, commonly known as the additivity rule (AR). In this approach, the

molecular scattering amplitude ($F(\theta)$) is derived from the sum of the above optical potential determined atomic amplitudes, which leads to the differential elastic cross section for the molecule ($d\sigma^{\text{molec}}/d\Omega$), according to:

$$F(\theta) = \sum_{\text{atoms}} f_i(\theta) e^{i\mathbf{q} \times \mathbf{r}_i}; \quad \frac{d\sigma_{el}^{\text{molecule}}}{d\Omega} = \sum_{i,j} f_i(\theta) f_j^*(\theta) \frac{\sin q r_{ij}}{q r_{ij}}, \quad (1)$$

where q is the momentum transferred in the scattering process and r_{ij} is the distance between the i th and j th atoms.

Integral elastic cross sections for the molecule can then be determined by integrating the elastic differential cross sections (see Eq. (1)) in its usual manner. Alternatively, elastic cross sections can be derived from the atomic scattering amplitudes in conjunction with the optical theorem [30] giving:

$$d\sigma_{el}^{\text{molecule}} = \sum_{\text{atoms}} \sigma_{el}^{\text{molecule}} \quad (2)$$

Unfortunately, in its original form, we found an inherent contradiction between the integral cross section derived from those two approaches, which suggested that the optical theorem was being violated [21]. This, however, was solved using a normalisation technique so that integral cross sections determined from the two methods are now entirely consistent [21].

The main limitation of the AR is that no molecular structure is considered, thus it is really only applicable when the incident electrons are fast enough to effectively “see” the target molecule as a sum of the individual atoms (typically above ~ 100 eV). To reduce this limitation we developed the SCAR method [20,22], which considers the geometry of the corresponding molecule (atomic positions and bond lengths) by introducing some screening coefficients which modify both the differential and integral cross sections, especially for lower energies,

$$\sigma^{\text{elast}} = \sum_i s_i \sigma_i^{\text{elast}}, \quad (3)$$

where s_i are the screening coefficients which account for the geometrical overlapping of the atoms. Their values are within the range $0 \leq s_i \leq 1$, so that they reduce the contribution from each atom to the total cross section. To generate these coefficients we only require data for the position and the total cross section σ_i of each atom in the molecule,

$$S_i = 1 - \frac{\varepsilon_i^{(2)}}{2!} + \frac{\varepsilon_i^{(3)}}{3!} - \frac{\varepsilon_i^{(4)}}{4!} + \dots \pm \frac{\varepsilon_i^{(N)}}{N!}, \quad (4)$$

with

$$\varepsilon_i^{(k)} \cong \frac{N-k+1}{N-1} \sum_{j(\neq i)} \frac{\sigma_j \varepsilon_j^{(k-1)}}{\alpha_{ij}} \quad (k = 2, \dots, N) \quad (5)$$

where N accounts for the number of atoms in the target molecule. The j index runs over all the N atoms, except the atom i , and $\alpha_{ij} = \max(4\pi r_{ij}^2, \sigma_i, \sigma_j)$ with r_{ij} being the distance between the atoms i and j (a detailed discussion is given in Refs. [20,22]). The procedure to derive the $\varepsilon_i^{(k)}$ parameters is summarized in the Appendix A of Ref. [20]. With this correction the range of validity of the IAM-SCAR method might be extended down to about 30 eV. For intermediate and high energies (30–5000 eV) our approach has proven to be a powerful tool to calculate electron scattering cross sections, from a wide variety of molecules of very different sizes such as from diatomics to complex biomolecules [22,23].

From the above description of the IAM-SCAR procedure, it is obvious that vibrational and rotational excitations are not considered in this calculation. However, for polar molecules additional

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