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ELECTRON-SCATTERING TOTAL CROSS SECTIONS FOR COMPLEX MOLECULES: GROUP ADDITIVITY RULE

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Abstract. Absolute electron-scattering total cross sections (TCSs) for nitrogen containing [$N(CH_3)_3$, NH_2CH_3, NH_3] and for cyclic-ether molecules [$(CH_2)_nO$, n=2–4] have been measured with transmission technique. The TCSs are compared to study how the number of methyl and/or methylene groups within molecule reflects in TCS energy function.

1. INTRODUCTION

Electron-driven low-energy processes play a key role in planetary physics, biology, and nowadays advanced technologies (e.g. Christophorou and Olthoff, 2004), just to cite a few. Recently, it has been also shown that low-energy electrons can initiate amino acid synthesis in the interstellar medium (Lafosse *et al.*, 2006). For understanding and modelling electron-induced reactions comprehensive sets of scattering data are needed. Unfortunately, in spite of great experimental and theoretical effort, data for compounds of current scientific and technological interest, especially those in absolute scale, are rather scarce. Deficiency of results is connected partly with experimental as well as theoretical difficulties. Some help in estimation of required data may come from regularities observed in cross sections which are already known for other molecules. Such trends in electron-scattering total cross section (TCS) energy dependence have already been noticed in our laboratory for hydro- and perfluorocarbon target families: isomer effect (e.g. Szmytkowski and Kwitnewski, 2002) and perfluorination effect (e.g. Szmytkowski and Ptasińska-Denga, 2001). Recently, our studies focused on determining TCS for polyatomic molecules have been extended to nitrogen containing molecules [$N(CH_3)_3$, NH_2CH_3, NH_3] and cyclic ethers series [$(CH_2)_nO$, n=2–5]. These series have been chosen to examine how the number of CH_3 and CH_2 groups, respectively, reflects in the shape and magnitude of TCS energy function.

2. EXPERIMENTAL AND COMPUTATIONAL PROCEDURES

2. 1. EXPERIMENT

The absolute total cross sections for studied molecules have been measured using the electron-transmission method in linear configuration (Bederson and Kieffer, 1971). The electron beam of required energy E and resolution of about 100 meV—prepared by electron gun, followed with 127° cylindrical electrostatic monochromator, and lens systems—is directed into scattering cell filled with target under study. The electrons emerging through the exit slit are energy discriminated by a retarding-field analyzer and eventually collected with a Faraday cup.

To determine the total cross section value, the Bouguer-de Beer-Lambert attenuation formula, in which the thermal transpiration effect was accounted for, is used

$$\mathrm{TCS}(E) = \frac{k\sqrt{T_c T_m}}{pL} \ln \frac{I(E,0)}{I(E,p)},$$

where: $I(E,p)$ and $I(E,0)$ are the transmitted electron currents taken in the presence and absence of the target in the cell, respectively. The other quantities measured directly are: p – the pressure of investigated gas in the scattering cell of the length L; T_m – the temperature of the mks absolute manometer head, and T_c – the temperature of the collision chamber; k is the Boltzmann constant. The energy scale was calibrated by the reference to the well-known resonant oscillatory structure of N_2 appearing near 2.3 eV. The final TCS value at each electron energy is a weighted mean of results from several series carried out at different target pressures and electron-beam controlling conditions.

2. 2. COMPUTATIONS

Elastic cross section (ECS) for electron collisions with complex molecules has been calculated with the independent atom method, while the ionization cross section (ICS) has been obtained within the binary-encounter-Bethe formalism. The theoretical total cross section, as shown in Fig. 2, is the sum (ionization+elastic) of calculated partial cross sections. More details about computational procedures can be found in Możejko *et al.* 2006, and references therein.

3. RESULTS AND DISCUSSION

Figure 1 shows the absolute total cross sections for electron scattering by nitrogen containing molecules: ammonia (NH_3), methylamine (NH_2CH_3) with one hydrogen atom replaced by methyl group, and trimethylamine ($N(CH_3)_3$) – permethylated analogue of ammonia. The variation of TCS magnitude across this series can be associated with the geometrical size of molecules. Regarding the shape, the TCSs are basically similar—they all have maximum located within 7–9 eV range. The only difference is observed below 2 eV, where TCS functions for NH_3 and NH_2CH_3 are rising with energy decrease, while TCS for $N(CH_3)_3$ is nearly constant. The detailed analysis of TCS curves for nitrides family, based on geometrical considerations, shows that TCS of any of three molecules can be estimated as combination of TCSs for molecular fragments: e.g. $\mathrm{TCS}_{\mathrm{NH_2CH_3}} = 1/3{\times}\mathrm{TCS}_{\mathrm{N(CH_3)_3}} + 2/3{\times}\mathrm{TCS}_{\mathrm{NH_3}}$. We have also noticed that the TCS for trimethylamine can be reasonably estimated as a sum of TCSs for

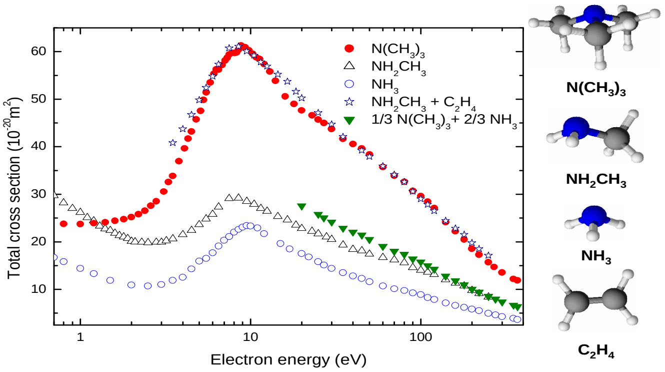

Figure 1: Total cross sections for e$^-$-collision with: NH_3 (Szmytkowski *et al.* 1989, Szmytkowski, *at al.* 2004), NH_2CH_3 (Szmytkowski and Krzysztofowicz 1995) and $N(CH_3)_3$ (Szmytkowski *et al.* 2007). Presented are also examples of TCS estimation for: $N(CH_3)_3$, as the sum of TCSs values for NH_3 and C_2H_4 (Szmytkowski *et al.* 2003), and for NH_2CH_3 - composed as $1/3\times\mathrm{TCS}_{N(CH_3)_3}+2/3\times\mathrm{TCS}_{NH_3}$. The geometries of considered molecules are shown as well.

NH_2CH_3 and C_2H_4. It means that having data for appropriate molecular fragments, it is possible to estimate roughly the cross section before performing measurements or calculations.

That conclusion is also confirmed by our very recent study concerning cyclic ethers $(CH_2)_nO$ (n=2–4) family. The ring of studied molecules is composed of n methylene groups and one oxygen atom (cf. Fig. 2). Measured TCSs curves are compared to find out how the increasing number of CH_2 groups within molecule reflects in the TCS function. The inspection of data reveals that above 20 eV the TCS is in direct proportion to the number of CH_2 groups. Figure 2 shows the estimated TCS values for methylene group and oxygen atom, as well as the estimated TCS for each studied molecules, e.g.: $\mathrm{TCS}_{(CH_2)_3O} = 3\times\mathrm{TCS}_{CH_2} + \mathrm{TCS}_O$. The agreement of estimated and experimental TCS data is excellent. Having in hand the partial contributions we are able to estimate TCS for c-$C_5H_{10}O$ molecule, the next member of the ethers family. As no data can be found in the literature for the electron c-$C_5H_{10}O$ collision, we check the correctness of estimated cross section by comparing it with our theoretical TCS being a sum of ICS and ECS. Above 40 eV, the estimated TCS is consistently lower (3-11%) than computed one, however this difference does not exceed much the typical– experimental TCS uncertainty.

4. CONCLUSION

Based on our intermediate-energy TCS results for nitrides and cyclic ethers we have shown that molecular TCS can be decomposed into cross sections of sub-molecular units. Using these effective partial TCS contributions it is possible to estimate TCS for other complex molecules with reasonable accuracy.

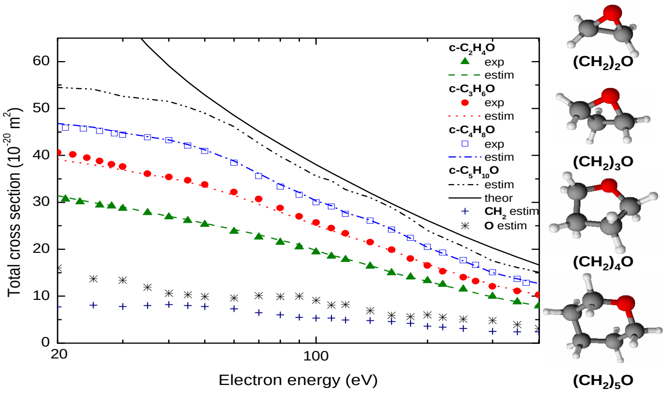

Figure 2: Comparison of the experimental or calculated TCSs with those estimated from group additivity rule for e^--scattering by $(CH_2)_nO$, n=2–5. Experimental data: c-$(CH_2)_2O$ (Szmytkowski *et al.* 2008a), c-$(CH_2)_3O$ (Szmytkowski *et al.* 2008b) and c- $(CH_2)_4O$ (Możejko *et al.* 2006). Theoretical TCS for c- $(CH_2)_5O$ is the sum of elastic and ionization cross sections. Molecule pictographs are included.

Acknowledgements

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