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Electron-scattering total cross sections for triatomic molecules: NO_2 and H_2O

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Absolute total cross sections (TCSs) for electron scattering on nitrogen dioxide (NO_2) molecules and on water-vapour (H_2O) were measured at energies ranging from 3 to 370 eV and 0.5 to 370 eV, respectively. Measurements were carried out using an electron spectrometer with an improved angular and energy resolution. The presented experimental TCS results are at intermediate energies compared with our total cross section estimations based on calculations of elastic and ionization cross sections.

Keywords: electron scattering, elastic cross section, ionization cross section, total cross section, nitrogen dioxide, water.

1. Introduction

The molecules of water vapour and nitrous oxides NO_x molecules are trace – but very important – components of the Earth atmosphere. Due to increasing release of NO_x to atmosphere, the impact of these compounds on environment becomes more and more significant. For understanding and modeling the physico-chemical processes of the planetary atmospheres – among them those involving electrons – it is important to know accurate and comprehensive sets of scattering cross sections and transport data for all particles being constituents of atmosphere. For some atmospheric molecules, *e.g.*, for NO_2, absolute electron-scattering cross sections are rather scarce [1, 2]. For water, which is also natural constituent of living cells, there is urgent requirement of reliable electron-scattering data for modeling the biological processes involving ionizing radiation. Unfortunately, the available experimental low-energy results differ substantially [3, 4].

On the other hand, recent experimental and computational findings [5, 6] revealed that already available intermediate- and high-energy total cross sections (TCSs) for electron-scattering may be strongly affected by insufficient angular and/or energetic discrimination of scattered electrons by detecting systems. Especially striking are the differences (up to 40% at high energies) between TCSs taken in experiments employing magnetic field for selection and guidance of electron beam and those carried out in absence of magnetic fields.

In our early TCS experiments (*e.g.*, [1, 7]) we did not use energy discrimination of scattered electrons and the angular resolution of electron detector system was not better than 1 msr. Therefore, the aforementioned findings [5, 6] prompted us, first, to reinvestigate our early TCS intermediate-energy dependences using linear transmission apparatus with improved angular and energy resolution, and second, to extend experiments to higher energies. Because some high-intermediate results from other laboratories already exist, the present data obtained with linear non-magnetic technique may be also useful for verifying suggestions that data obtained with the use of magnetic field are systematically charged.

2. Experimental

The reported total cross sections have been measured over wide energy range under single-collision conditions employing a linear electron-beam transmission technique. The experimental set-up and procedures applied in the present study have been already used in a long series of recent absolute TCS measurements and were described in detail elsewhere (*e.g.*, [8, 9]). The electron spectrometer is composed of a source of monoenergetic electrons with an electrostatic cylindrical 127° dispersive element, followed by a reaction cell, a retarding field analyzer and a Faraday cup. The target molecules filling the scattering cell are irradiated by an electron beam of a given energy E ($\Delta E = 80$ meV, FWHM). Those electrons which cross the cell and emerge from it through the exit orifice are energy discriminated (to within 0.1 eV) on their route to the detector with the retarding field element which prevents inelastically scattered electrons being collected with a Faraday cup. The solid angle from which the electrons are detected spans to about 0.4 msr in the present experiment, in comparison to 1 msr in older ones [1, 7].

The total cross section $\sigma(E)$ is derived from intensities of the transmitted electron current measured in the presence $I(E,p)$ and absence $I(E,p=0)$, of the target molecules in the reaction cell, and applying the Bouguer–de Beer–Lambert attenuation relationship:

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

in which the thermal transpiration effect [10] is accounted for; k is the Boltzmann constant. Electron intensities $I(E)$, as well as other necessary quantities (the target gas pressure p, the electron path length in the scattering chamber L (equal to 30.5 mm), the temperature of the mks absolute manometer head T_m, and the temperature of the scattering cell T_c), are taken directly in the experiment so the obtained TCSs are in absolute scale. The electron energy scale is established, with an accuracy better than 0.1 eV, in relation to the oscillatory resonant structure visible at around 2.3 eV in N_2.

To keep the conditions in the electron optics region nearly invariable, the target gas/vapour is supplied alternately into the collision cell or its surrounding. Compared to earlier experiments [1, 7], the arrangement of the electron optics elements in the present measurements allows much better evacuation of the scattering cell surrounding from the gas effusing across the cell orifices. The magnetic field in the electron optics volume of the spectrometer is reduced to a value below 0.1 μT.

It was found that the TCS values obtained at the same energy in different series of runs were, within limits of random experimental uncertainties, independent of the applied target pressures (0.5–1.5 Pa) and the electron-beam intensity (less than 0.1 nA). The final TCS value at each energy is a weighted mean of results from series (4–18 and 4–24 for NO_2 and H_2O, respectively) of individual runs (7–10 in series). The reported TCS values are not corrected with respect to the forward scattering effect. The statistical variations of the measured TCS are below 1% over the entire energy range investigated. The systematic uncertainty of measured cross sections was estimated to be 7–9% below 1–2 eV and it decreases gradually to 5–6% in the energy range 10–100 eV, while reaching again about 6–7% at higher applied energies.

Commercially supplied sample of NO_2 (Matheson, 98% purity) and the double distilled water were vacuum distilled before use with repeated freeze–pump–thaw cycles at the liquid-N_2 temperature to remove dissolved air and other volatile impurities.

3. Computational methods

Theoretical approaches and computational procedures employed in the present work are the same as those we have used in previous calculations [11, 12]. Thus only a brief description of the theoretical and numerical issues is provided here.

In the present work, elastic electron collisions with NO_2 and H_2O have been studied with the independent atom method (IAM) [13]. In that approximation the electron–molecule scattering problem is reduced to electron scattering by the atoms constituting molecule. This approach is valid and can provide reasonable results for intermediate- and high-collision energies only (*e.g.*, [11, 12] and references therein). The elastic integral cross section (ICS) within IAM method is given by:

$$\sigma(E) = \frac{4\pi}{k}\sum_{i=1}^{N}\operatorname{Im} f_i(\theta = 0, k) = \sum_{i=1}^{N}\sigma_i^A(E)$$

where E is an energy and $k = \sqrt{2E}$ is the wave number of the incident electron, $f_i(\theta, k)$ is the scattering amplitude due to the i-th atom of the molecule and θ is the scattering angle. To obtain scattering amplitudes and the atomic elastic ICS for the i-th atom of the target molecule $\sigma_i^A(E)$, the radial Schrödinger equation has been solved numerically under the proper boundary conditions. The electron–atom interaction has been represented by the sum of static [14] and polarization [15] model potentials.

The exact phase shifts have been calculated for angular momentum l up to $l_{\mathrm{max}} = 50$ while those remaining have been included using the Born approximation.

Electron-impact ionization cross sections have been obtained using the binary-encounter-Bethe (BEB) approach [16]. Within this formalism the electron-impact ionization cross section per molecular orbital is given by:

$$\sigma_{\mathrm{BEB}} = \frac{S}{t+u+1}\left[\frac{\ln t}{2}\left(1-\frac{1}{t^2}\right)+1-\frac{1}{t}-\frac{\ln t}{t+1}\right]$$

where $S = (4\pi a_0^2 NR^2)/B^2$ ($a_0 = 0.52920$ Å, $R = 13.61$ eV), $u = U/B$, $t = T/B$, and T is the energy of the impinging electron. The electron binding energy B, kinetic energy of the orbital U, and orbital occupation number N, were obtained for the ground states of the molecules with the Hartree–Fock method using the GAUSSIAN code [17] and the Gaussian 6-311G+(d) basis set. Because the valence orbital energies obtained in this way usually differ from experimental ones, we performed also outer valence Green function calculations of correlated electron affinities and ionization potentials [18] with the GAUSSIAN code [17]. To fix the threshold behavior of calculated ionization cross section at the experimental value, the first experimental ionization potentials of 12.6202 eV for H_2O and 9.586 eV for NO_2 were inserted in the calculations instead of those obtained theoretically. Finally, the total cross section for electron-impact ionization was obtained as the sum of σ_{BEB} for all molecular orbitals.

So far as the shape is concerned, the resulting ionization cross sections reproduce satisfactorily the data obtained with the same method by Kim *et al.* [16, 19, 20]. Magnitude of our calculations is slightly higher. However, data from [16, 19, 20] were calculated at RHF level only and that is why the valence orbital energies are higher than the experimental ones and contribute less to cross section. At the ionization cross section maximum the difference between present results and [16, 19, 20] does not exceed 7% for H_2O and 17% for NO_2 molecules.

4. Results and discussion

The variation of absolute electron-scattering TCS for NO_2, measured in this work at energies ranging from 3 to 370 eV, is shown in Fig. 1**a**. Our early low- and intermediate-energy absolute data [1] and intermediate- and high-energy results of Zecca *et al.* [2] obtained with the Ramsauer technique are also included for comparison. As yet, no other experimental e^--NO_2 TCSs are available.

There is a good agreement of all experimental TCS energy functions according to the shape, though some differences in the magnitude are clearly visible. It is worth noting, however, that these differences do not exceed 7% over the whole overlapping energy range, and lie well within limits of combined experimental uncertainties. Above 5 eV the present results are systematically higher than our “old” measurements [1]. This discrepancy may be in part explained due to the difference in angular resolution

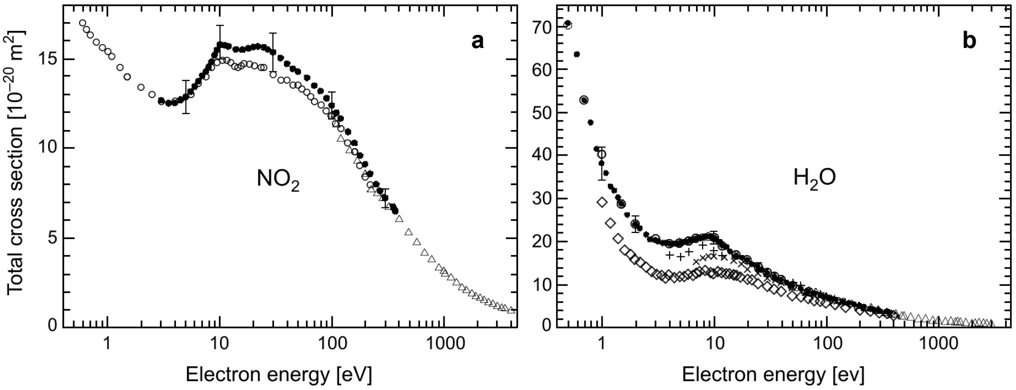

Fig. 1. Energy dependences of experimental total cross sections for the electron scattering from NO_2 (● – present, ○ – old results [1], Δ – [2]) – **a**, and H_2O (● – present, ○ – old results [7], ◊ – [21], Δ – [22], × – [23], + – [24]) – **b**. Error bars at selected points represent overall experimental uncertainties.

of electron detecting systems in the "old" and "new" experiments. Besides, the use of energy discrimination in the present experiment prevents electrons scattered inelastically to be detected what results in an extra increase of the measured TCS values. Between 80 and 350 eV the present data are slightly higher than the results from Trento laboratory [2], while above 350 eV present TCS smoothly approach the ZECCA *et al.* [2] findings. Such good agreement of intermediate data obtained with completely different experimental techniques (in the presence – [2] and absence of magnetic field – [1] and present work) suggests that, at least at intermediate energies, TCS results obtained with devices employing magnetic field are consistent with those taken without that field.

Recent experimental total cross sections for electron scattering from H_2O molecules [7, 21–24] are shown in Fig. 1**b**. According to the shape, there is a good agreement between all experimental TCS energy dependences. Visible are, however, some discrepancies in the magnitude of TCSs indicated in Fig. 1**b**. The present results are distinctly higher (up to 30%) than normalized data of SUEOKA *et al.* [21] obtained with TOF apparatus; this disaccord is mainly related to their normalization procedure. Agreement of the present TCS with other results is much better: to within 4–8% with Trento data [22] taken with the Ramsauer technique, 3–15% with linear measurements of NISHIMURA and YANO [23] and less than 3% with linear experiment of SAGLAM and AKTEKIN [24]. From that comparison it is difficult to conclude if the observed differences are related to application of magnetic field in the experiment. It is also interesting, that the present TCS is generally lower (1–4%) than our "old" TCS data [7] obtained under distinctly different experimental conditions, although – like for NO_2 – one would expect that applied improvements should result in increasing of the measured TCS values. Such behavior is all the more surprising, since the H_2O molecule is highly polar ($\mu \sim 1.8$ D) while NO_2 has a rather low electric dipole moment ($\mu \sim 0.32$ D).

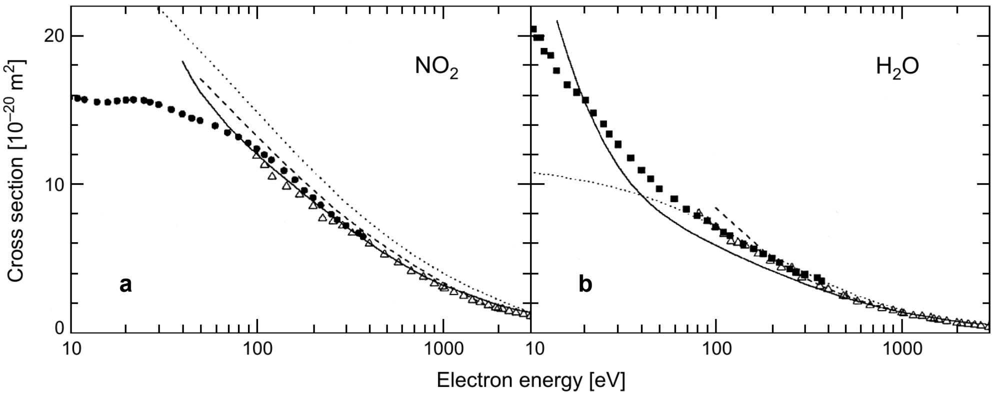

Fig. 2. Comparison of experimental TCSs and calculated total cross sections for NO_2 (experimental: • – present, Δ – [2]; computed: — present; – – – [25]; ···· [26]) – **a**, and H_2O (experimental: • – present, Δ – [22]; computed: — present; ···· [27]; – – – [28]) – **b**.

In Figure 2 we have compared our computed “total” (elastic plus ionization) cross sections with the present experimental TCSs and with high energy measurements of Trento group. Other intermediate- and high-energy calculations are also included for comparison.

The agreement of the measured TCS for NO_2 (Fig. 2**a**) with that calculated is excellent above 70 eV. At lower energies, where principles of independent atom model (IAM) become less realistic, the discrepancy between experiment and computations drastically increases mainly due to overestimation of elastic contribution. The present calculations agree reasonable with those of Joshipura and Patel [25], while their results are systematically lower than those reported in very recent computations of Shi *et al.* [26].

For H_2O (Fig. 2**b**) our high-energy calculations agree well with experiment. At intermediate energies the experiment and the present calculations distinctly diverge: at 200 eV disagreement reaches nearly 20%, increasing towards lower energies up to 25% at 70 eV – the low limit of energy at which IAM reasonably works. Below 1000 eV our computations are systematically lower than those obtained basing on modified additivity model of Liu *et al.* [27] and Joshipura [28].

5. Conclusions

We reported the absolute electron-scattering total cross sections for NO_2 molecules between 3 and 370 eV and for H_2O molecules at 0.5–370 eV, measured using a linear transmission method. Although our absolute TCS results differ from those obtained with set-ups using magnetic field, the differences are – over whole overlapping energy range – still within limits of combined experimental uncertainties. This indicates that the absolute total cross section experiments performed with devices employing magnetic field provide data consistent with the results obtained using systems free of magnetic field, at least at intermediate energies. For solving the problem of consistency of high-energy TCS data obtained with the techniques employing magnetic field and without it, further experiments with different techniques as well as computations are encouraged.

Our calculated intermediate- and high-energy total cross sections (elastic plus ionization) reproduce quite satisfactorily the experimental TCS data what suggests applicability of employed approximations for predictive determination of credible electron-scattering TCSs for simple molecular targets.

Finally, it should also be mentioned that taking the theoretical elastic calculations as the ground for recommended total cross section data [4], seems to be rather weekly justified in the face of the available experimental low-energy TCS as well as elastic results (*cf.* [3]).

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