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Scientific rapport from COST-STSM-CM0601-2805 stay at Institute of Physics, University Nicolaus Copernicus, Toruń (5.07-4.08.2008)

The subject of the stay were studies of kinetics in electronic excitation of atoms and molecules.

Motivation

My studies for PhD thesis (and previous work for Master thesis) regard processes of fragmentation of molecules due to electron impact. Different fragments appear in different energy regions, see fig. 1.

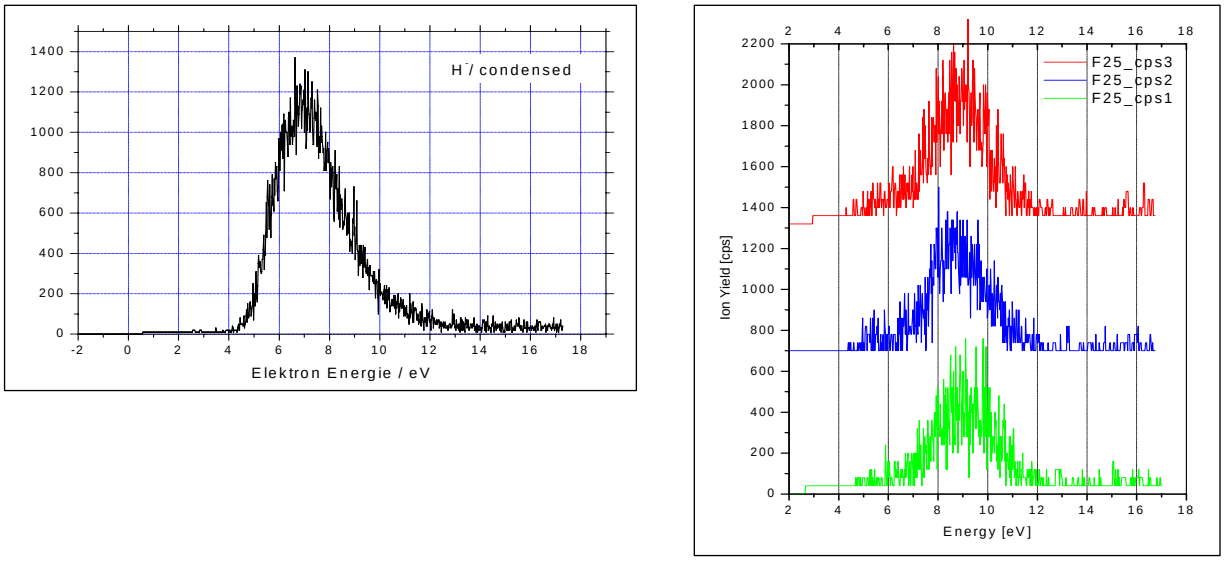


Fig. 1. The H- and F- ion signal from electron stimulated desorption from CF3COOH films during electron irradiation (from M. Orzol Master thesis)

The best known channel for appearing negative ions from electronic impact is the dissociative attachment process [1]. However, this is not the only channel which can lead to molecular fragmentation. Apart from ionization, the electronic excitation is the alternative process.

Experiment

I participated in the set up and preliminary runs of the experiment on electronic excitation in helium, at intermediate (80-100 eV) impact energies. Helium is particularly interesting target, as the optically allowed (singlet-singlet) and optically forbidden (triplet- singlet) transitions are well separated into two distinct groups. The energy scheme is given in figure 2.

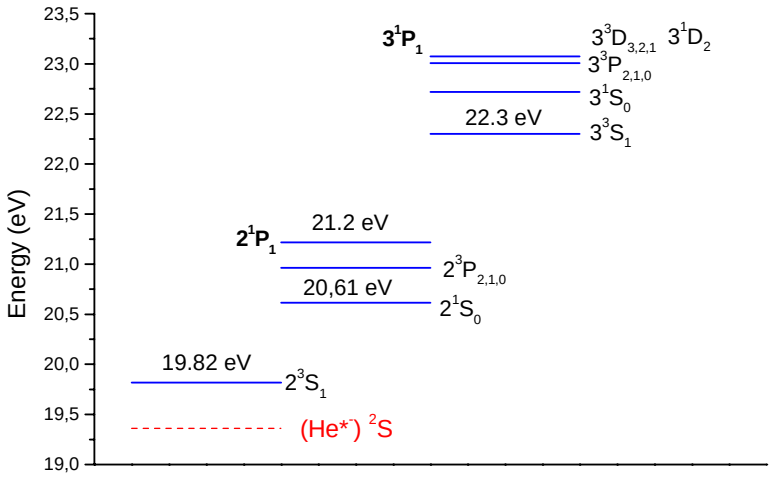


Fig.2 Energy levels of electronically excited state in helium (in bold letters optically allowed excitations, in red – the Feshbach resonance).

Theory finds some problems in exact determining the amplitudes if the electronic excitation cross sections. A stringing test on the theory are predictions of the correlation between the direction of the scattered electron emitted de-excitation photon (these are almost instant with the scattering).

Experiment was performed on an apparatus using “magnetic angle changer”, see fig. 3.

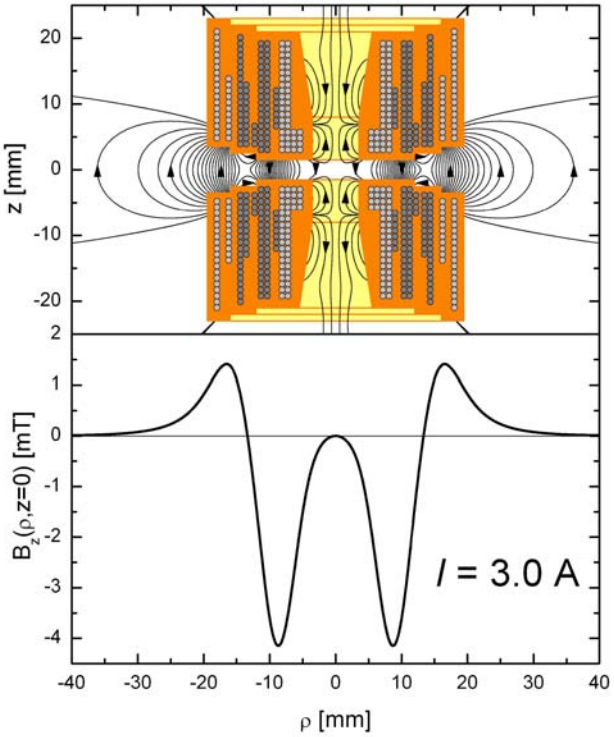


Fig.3 Experimental Arrangement

The innovative part is the special configuration of the magnetic field before and after the collision place (and is zero in the collision region). This configuration allows to study differential cross sections in the whole 0-180° angular range and to check different theories in the high-angle range, where they usually diverge.

I participated in the mounting of a new electron gun and setting of the beam (geometry and energy resolution). The chosen energy resolution, as seen from the energy-loss spectra, is modest, about 1 eV, but sufficient for the present experiment.

Optically allowed and forbidden states

For heavier atoms and molecules the distinction between the states allowed for dipole (optical transitions) is not so evident as for helium. They are some indications coming from experiment. The first one is the differential (in angle) cross section, which is forward-centered for optically-allowed transitions (singlet states) and more uniform in angle for the forbidden transitions (triplet states), see fig. 4.

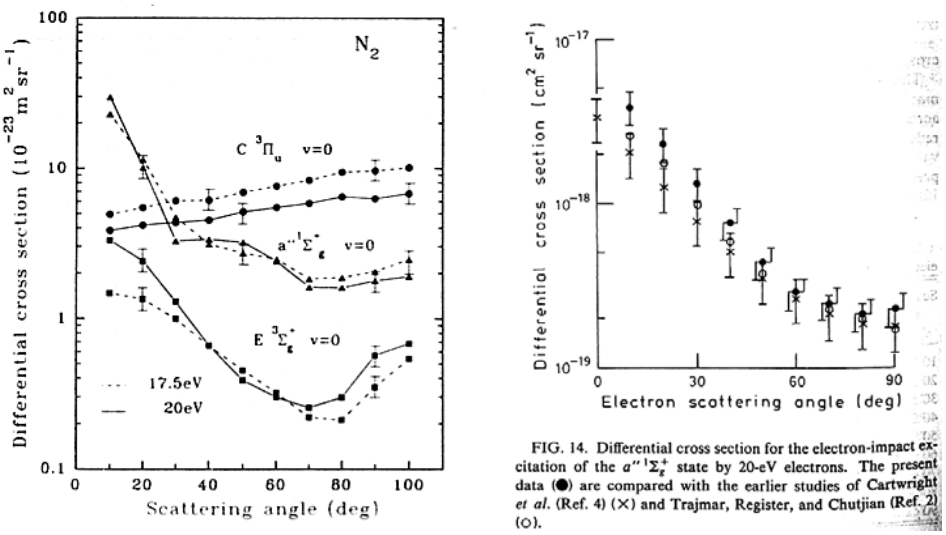


FIG. 14. Differential cross section for the electron-impact excitation of the $a''\,^1\Sigma_g^+$ state by 20-eV electrons. The present data (●) are compared with the earlier studies of Cartwright *et al.* (Ref. 4) (×) and Trajmar, Register, and Chutjian (Ref. 2) (○).

Fig. 4 Differential cross sections for electron- impact electronic excitations in N_2 (from Zubek et al. 1994 and Brunger et al. 1990).

The energy scheme, which is known for N_2 shows that the first optically forbidden states lay much lower than the lowest optically allowed states, see fig. 5.

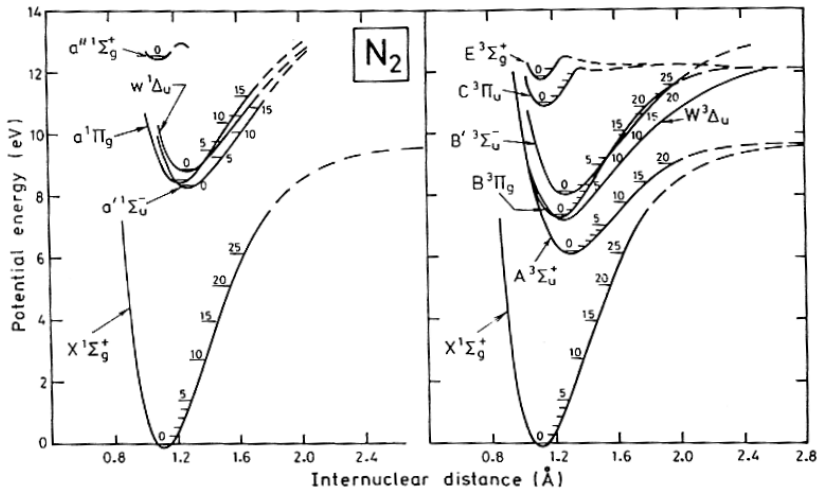


Fig. 5. Energy levels for the N_2 molecule.

Another characteristics to distinguish between allowed forbidden states is the energy dependence of the *integral* electronic-excitation cross section. This is shown as an example for H_2 electronic excitations: the cross sections for allowed state, after the maximum, fall slowly with energy while the cross sections for forbidden states fall quickly, see fig. 6.

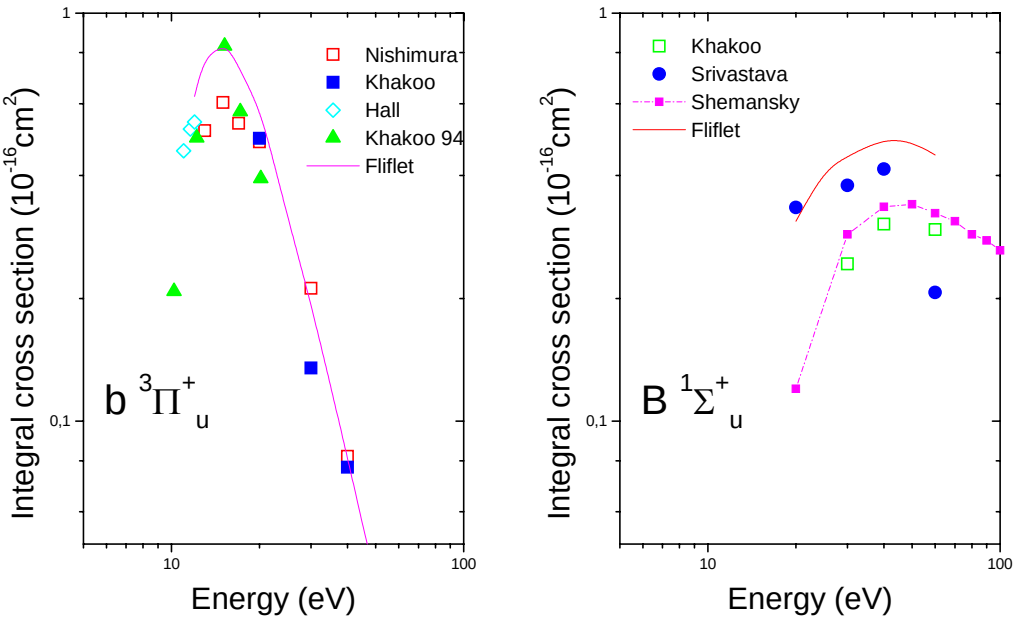


Fig. 6. Comparison between optically forbidden and allowed and states: electronic excitation integral cross sections (from Karwasz et al.)

Resonances

My studies of resonances at FU consist on observing directly negative ions formed by electron bombardment. The alternative techniques for observing resonances are measurements of total cross sections (this is performed in the laboratory of Prof. Czesław Szmytkowski at Technical University of Gdańsk, whom I also visited during my stay) or studies of differential cross sections for elastic scattering and the vibrational excitation (preformed in the laboratory of Prof. Mariusz Zubek, from the same University). Targets recently studies by these laboratories are tretrahydrofuran (Prof. Zubek) , PH_3, hydrocarbons and others (Prof. Szmytkowski). To see interdependencies between these measurements, however, I use the data from other, similar experiments (Kennerly and Bonham for total cross sections and for electron attachment from Prof. Illenberger in SF6 and Kaiserslautern laboratory for chlorofluorocarbons, see fig. 7 and 8).

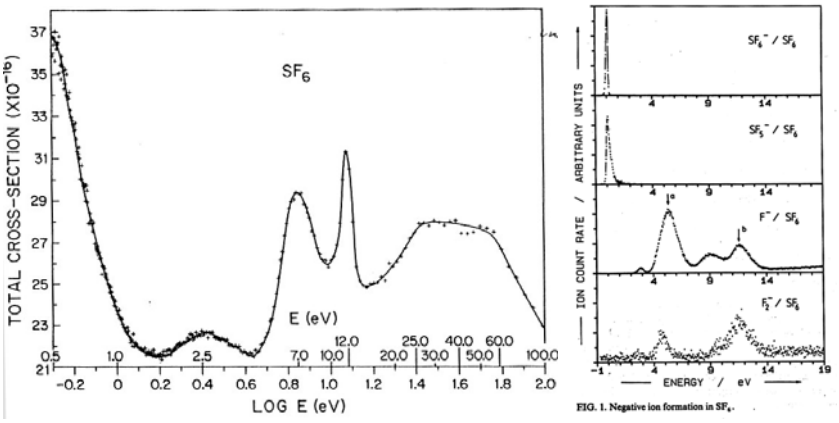
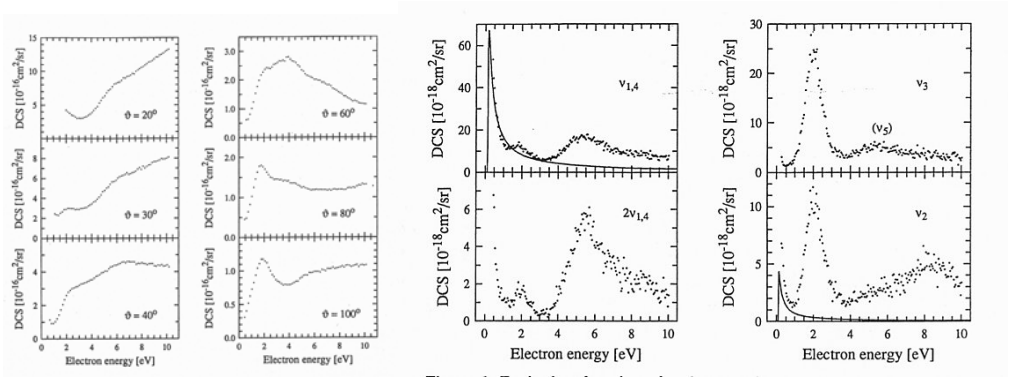


Fig. 7. Comparison between different measurements showing presence of resonances in electron scattering on SF_6 (total cross sections from Kennerly and Bonham and electron attachment from Illenberger).



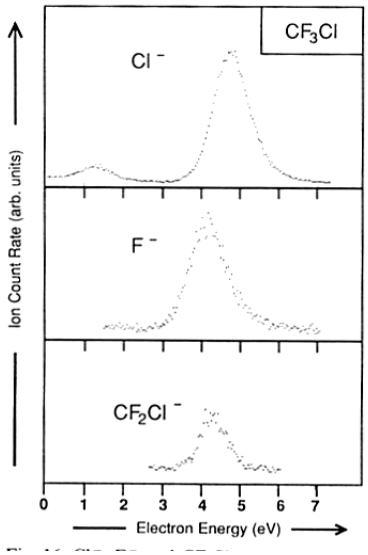


Fig. 8. Comparison between different measurements showing presence of resonances in electron scattering on CF_3Cl (differential elastic cross sections and vibrational excitation cross sections at a given angle from Mann and Linder and electron attachment from prof. Illenberger).

Recently Prof. Zubek studies also the optical emission from the molecules (or radicals) which undergo the electronic collision. For example, in the electron collisions on tetrahyrdofuran he observed the Balmer emission lines from H fragment and the emission in UV from OH radicals. These fragments appear above the collision energy of about 18 eV.

Finally, as shown in Prof. Karwasz reviews on electron scattering cross sections, also electronic excitation can show resonant character, see fig. 9 for the excitation of a metastable state in O_2.

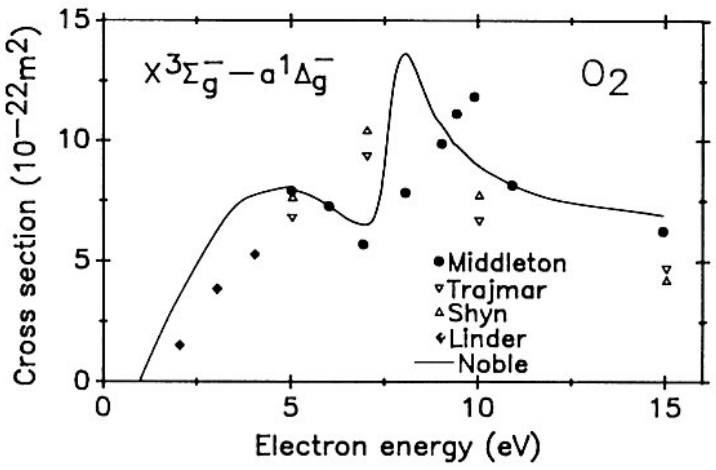


Fig. 9. Integral cross section for the electronic excitation of O_2 (from Karwasz et al.)

Theories of resonances

Different approaches give complementary information on resonances. This is for example the case of CF_4, in which calculations of Prof. Gianturco indicate a shape resonance at about 8 eV, with electronic excitation while Prof. Illenberger suggests the capture of an electron to an antibonding C-F orbital directly. In particular, for chlorofluoromethanes the work of Underwood-Lemons try to fit resonances in electron- transmission spectra to certain molecular orbitals. These work are extremely complex for bigger molecules.

The acquired skills

I learned several new techniques in electron scattering, from the simplest one as the total cross sections measurements via attenuation technique (Prof. Szmytkowski and Prof. Karwasz), differential cross sections measurements for elastic and vibrational-excitation scattering (Prof. Zubek), to electronic excitation measurements via differential cross sections and optical emission (Prof. Zubek), to the coincidence technique in electron- atom scattering (Prof. Chwirot and Dr. M. Piwiński). The general guide into all these techniques and explanations of the elementary processes was done by Prof. G. Karwasz.