DISSOCIATIVE EXCITATION, IONIZATION, AND FRAGMENTATION PROCESSES FOR NITROGEN, OXYGEN, METHANE, AND WATER MOLECULES BY ELECTRON BOMBARDMENT

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Abstract

Electron–impact ionization and fragmentation of molecules are investigated by the chromatography mass-spectrometry device. While the excitation processes are investigated by an optical spectroscopy method. The spectral analysis is performed in the vacuum ultraviolet 50-130 nm spectral regions. The absolute value of the fragmentation cross-section in the dissociative ionization and excitation processes is determined. Measurements are performed in the electron energy range 25-120eV for ionization and 200-500eV for excitation processes respectively.

Keywords: *Ionization, fragmentation, excitation*

Electron–impact ionization of N_2, O_2, CH_4 and H_2O molecules is of fundamental importance in atmospheric sciences, man-made plasma processes, and mass spectrometry [1-4].

Earth, Venus, and Mars all have oxidizing atmospheres, but the major constituents of the atmospheres are N_2 and O_2 for Earth[4]. N_2 and O_2 molecules are the main constituents of the atmospheres and are also important in other gaseous media. The importance of obtaining an understanding of their response to electron impact, which occur in the aurora and discharges. due to the interaction with electron component of the solar wind, has prompted a large number of experimental and theoretical investigations of these species. Total electron scattering cross-sections are well-known as are those for ionization, elastic scattering, rotational and vibrational excitation, dissociation, and for the excitation to several of the electronic states in these species. Such comprehensive coverage is required by our expanding need to observe and predict the complex solar-terrestrial interactions that comprise space weather.

Recently, much attention has been given to the investigation of the formation of highly excited molecular states, particularly, to the appearance of inner-shell vacancies. The interest is stimulated by the fact that such highly excited molecules catalyze the creation of complex molecules in the atmosphere and in the plasmas of different origins as well.

Electron impact ionization of atoms or dissociative ionization processes of molecules will be performed by the chromatography mass-spectrometry device (Fig.1). The target gas ions are generated in the ionization region by electron impact. The current of electrons is of order 0.2 mA with the energy inhomogeneity (full with half maximum) E =50meV. Ions produced are extracted and focused by appropriate ion optics and potentials applied to the ionization chamber. The whole spectrum (from mass 2 to mass 1000) can be explored in one second. The detector of the ions, produced by electron impact, is an electron multiplier. The overall gain is of the order of 10^6. The output signal of the electron multiplier is fed either into an analogy measurement signal or into a digital data acquisition system for further treatment by computer.
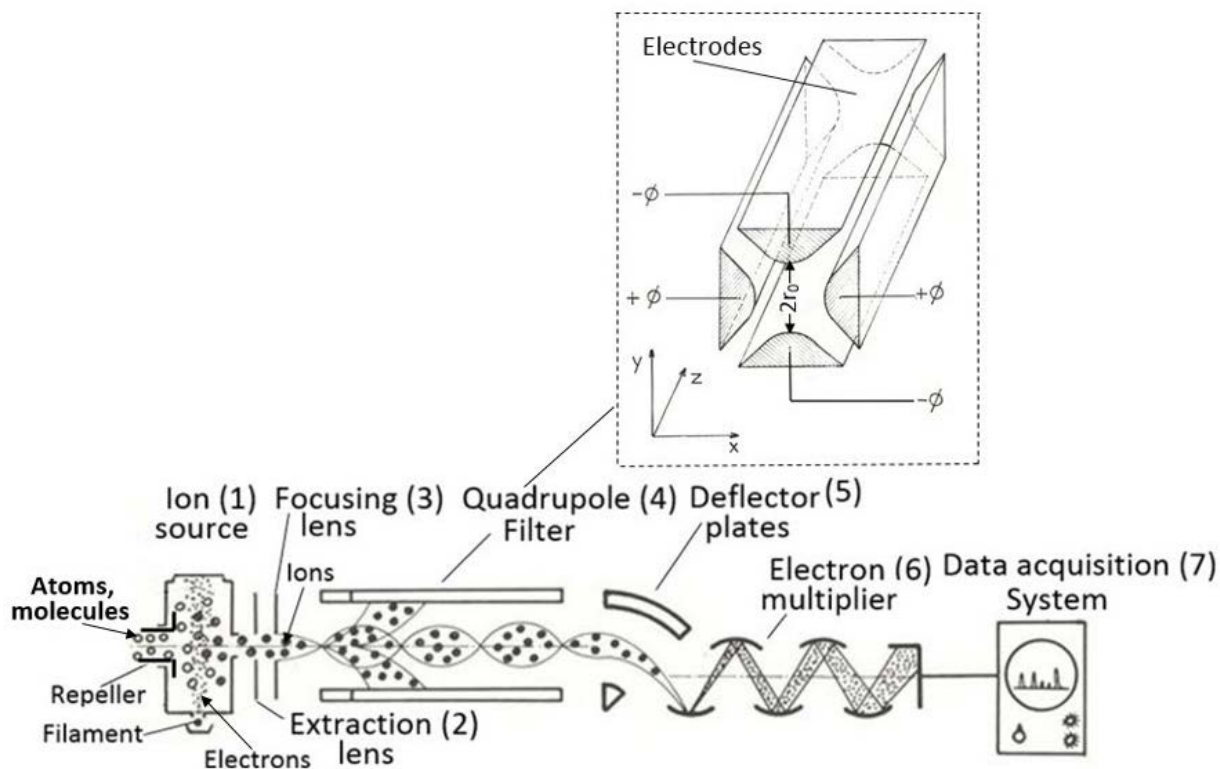
Fig.1. Schematic diagram of the experimental setup: 1-ion source, 2-extracting lens, 3-focusing lens, 4-quadruple filter, 5-deflector, 6-electron multiplier, 7-acquisition system. The insert at the upper right panel shows the device for the quadruple filter.

Significant efforts are put into the determination of the appearance energies of ionic fragments. For this reason, the electron energy was calibrated against the known AE of Ar^+ (15.7 eV) to within $\pm$ 0:25 eV. As a result, the ionic fragment cross-section - curves obtained in the 50-120 eV range are used to confirm the correctness of this approach. We check this approach by performing measurements of the ionization cross-sections for the processes:
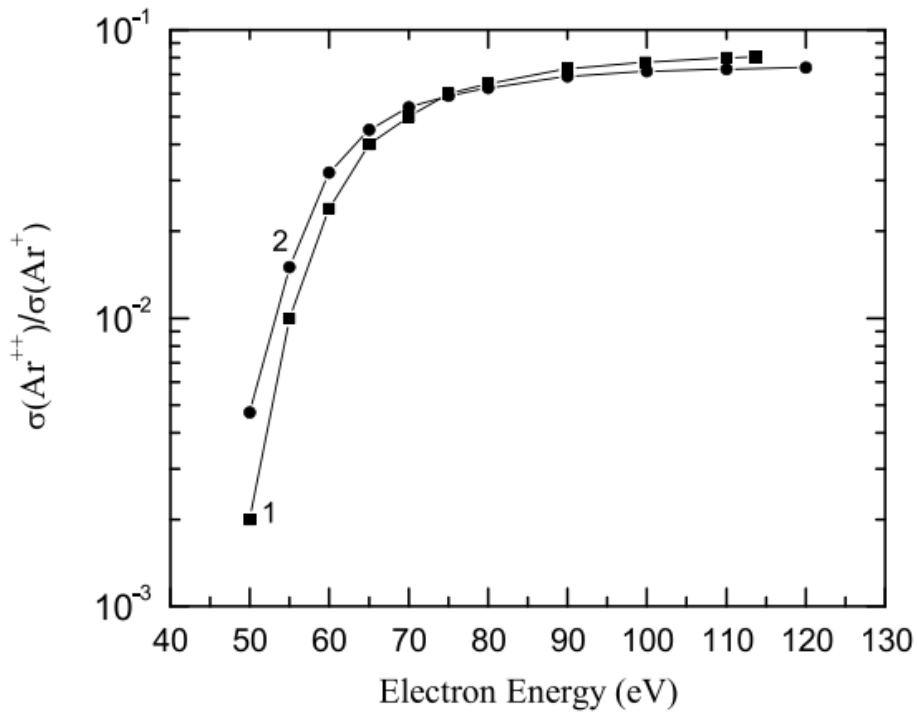
$$e + Ar \rightarrow Ar^+ + 2e,$$
$$\rightarrow Ar^{++} + 3e \qquad (1)$$
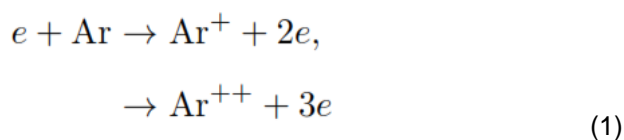
Fig. 2. Dependence of the ratio $\sigma(Ar^{++})/\sigma(Ar^{+})$ of double to single ionization cross-sections of Ar atom in the e-Ar collision on electron energy. Curves:1- present data; 2- the result of our calculations for the ratio $\sigma(Ar^{++})/\sigma(Ar^{+})$ using the measurements from [5].

As can be seen from fig. 2, our cross-sections data show a general agreement with the calculations of
$(Ar^{++})/ (Ar^{+})$ using the experimental data from Ref. [5] within 7%. The close agreement between these data sets demonstrates the expected efficient collection of ion fragments in our apparatus. Results of measurements of N_2^+, O_2^+, N^+ and $, O^+$ ions formation cross section in dissociative ionization processes of Oxigen molecules are presented in fig.3.
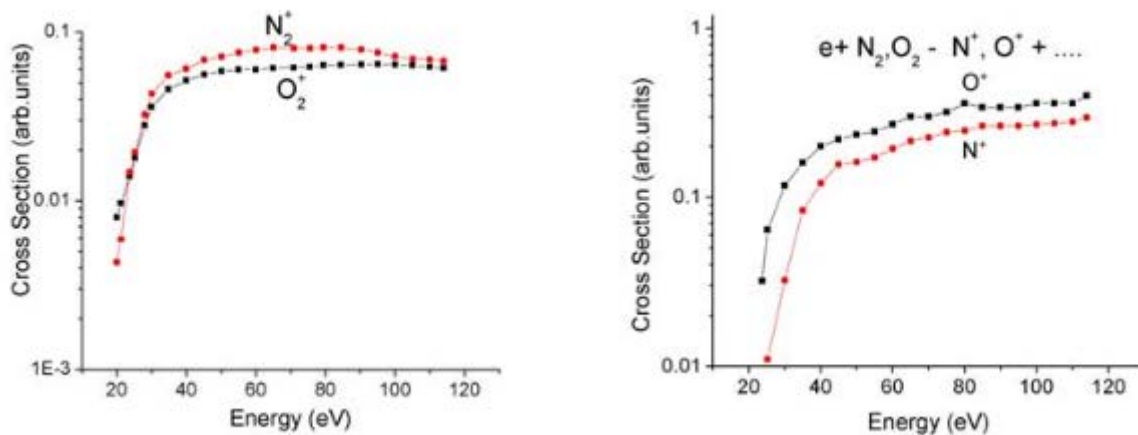

Fig.3. Dependence of the formation cross section of N_2^+, O_2^+, N^+ and $, O^+$ ions from electron energy.

On this fugure the comparison results for e-N_2 and e-O_2 collision system are considered. It seems, that energy dependence of cross section in all energy range are the same , while value of cross section for ionic fragments for tne e-O_2 pair is relatively higher. On fig.4 the experimental results are compared with high acuracy measured results of [6]. For determination of the absolute cross section of ionization and fragmentation processes we have used the experimental results from.[6]
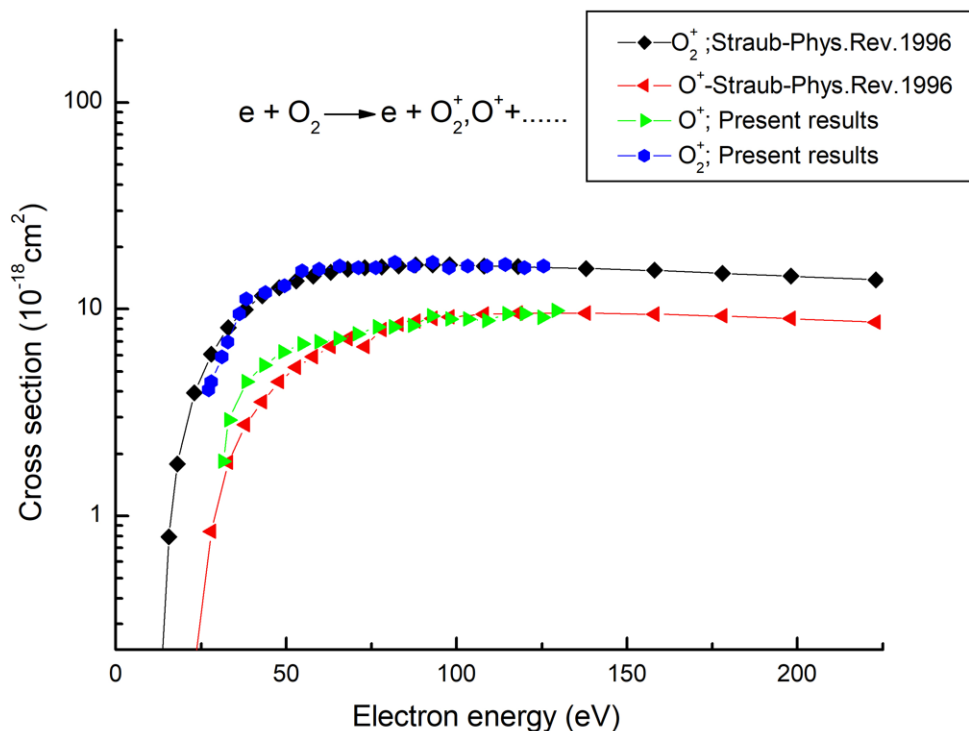

Fig.4 Ionization and fragmentation cross section energy dependence

Our results, in arbitrary units, was calibrated to the results of [6] for electron energy 100eV.
Mass spectrum of dissociative Ionization processes for Methane and Water molecules by electron bombardment are presented on fig.5 and fig.6 respectiveli.
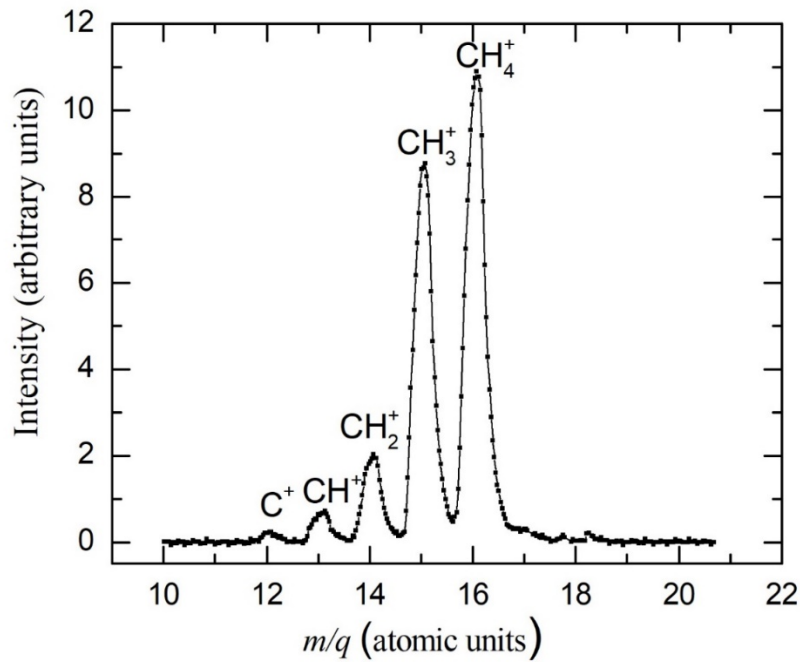
Fig.5. Methane mass spectrum in dissociative ionization processe
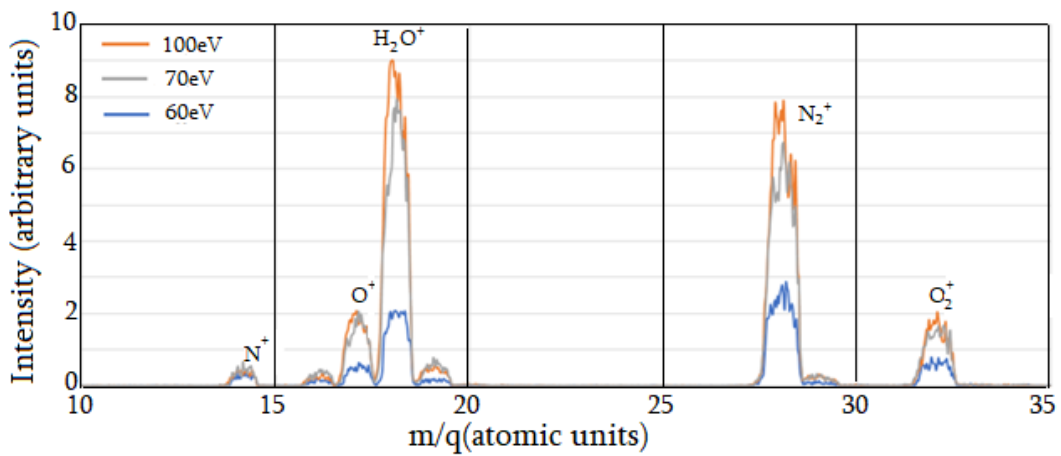

Fig.6. Water mass spectrum, for the different energy of an electron, in dissociative ionization processe.

In Fig.7. The results of the investigation of the energy dependence of the fragmentation cross section in the dissociative ionization processes are presented. Results are compared to the recommended values of the partial ionization cross section (solid line) [7] of H_2O for production of H_2O^+, OH^+, O^+.
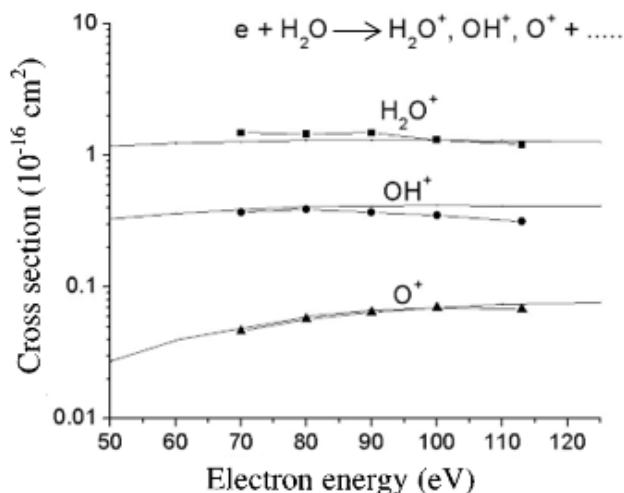
Fig.7

Excitation processes are investigated by an optical spectroscopy method. The spectral analysis are performed in the vacuum ultraviolet 50-130 nm   spectral regions. Measurement method end calibration procedures are ascribed in [8].

For collisions of electrons with oxygen molecules, the emission cross sections of atomic OI and ionic OII lines of oxygen have been measured in the vacuum ultraviolet spectral region (50nm-130nm).

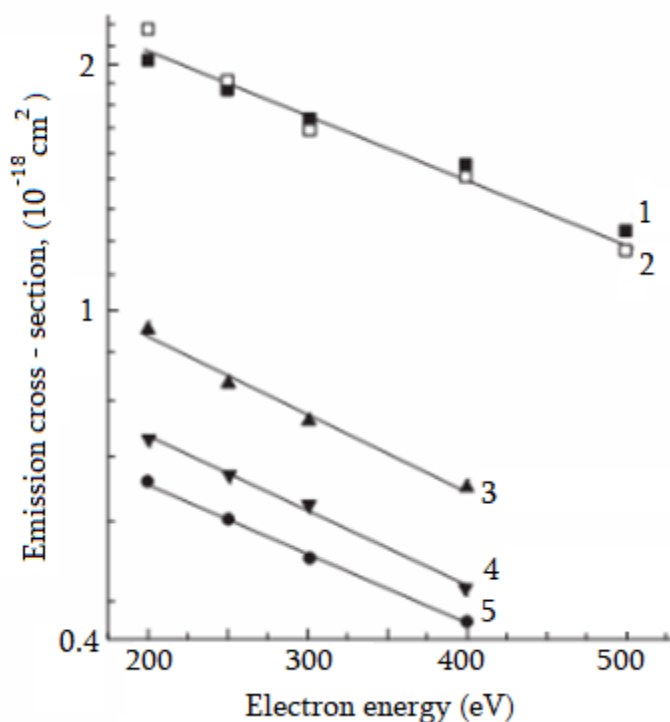Results of measurements of emission cross sections are presented in fig8.

Fig.8. Energy dependence of the excitation cross section. Curves: 1- OI(130.5nm), 2-OII(83.4nm), 3-OI(99.0nm), 4-OI(102.6nm).

During the experiment the most intense lines 130.4nm ($2p^4\ ^3P$ -3s $^3S^0$) of atom O^* and 83.4 nm ($2p^3\ ^4S^0$-$2p^4\ ^4P$) of O^{+*} were observed. Values of the cross-section and energy dependence in both

cases are identical. It is posible, that the formation of excited atomic and ionic lines of dissociatiation is caused by the decay of highly excited molecular states during dissociative ionization of O_2 molecule. In particulmoleculesdecay of the one-hole $2\sigma_g^{-1}$ highly excited states $^2\Sigma_g^-$ or of Oxigen molecules provide excitation of the intense ionic line OII(83.4nm) of Oxygen ion [8,9].

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