

ELECTRON-IMPACT IONIZATION OF D₂O MOLECULE: SINGLE-IONIZATION CROSS SECTION

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New data on the absolute single-ionization cross section for the D₂O molecule are presented. The experiment was performed by using a quadrupole mass-spectrometric technique. The results are compared with known data showing a fairly good agreement both in the energy dependence of “parent” ion yield and absolute cross section values obtained by normalizing to the reference data.

1. Introduction

The “heavy-water” molecule due to its wide technological application as the working medium of the alternative energy supplies, vacuum pumps, etc. had allowed one to consider it as an important substance being even of a strategic interest. The relative simplicity of the D₂O molecule electronic structure, which stipulates its comparatively poor spectrum of possible fragmentation products, enables it to be treated as a promising subject of both the experimental and theoretical studies. On the other hand, this molecule is an interesting “sister” of the conventional H₂O molecule, and the fact that despite the apparent similarity of these two species their physical and chemical properties differ essentially has been emphasized in a series of recent papers (see, for example, [1]). While for the H₂O molecule the number of data on ionization probabilities are available (see, e.g., review [2]), the relevant information on the partial and total ionization cross sections for the D₂O molecule is quite scarce. In the essence, only few papers, which appeared during last decade [3–5], present some data of that kind.

Just such a pattern of the lack of very important data has stimulated the systematic studies on the production of ionized products in slow (≤ 120 eV) electron collisions with both water-like molecules. The possible spectrum of such products is, as mentioned above, relatively poor. We have measured the

single- and dissociative- ionization cross sections for the yield of all possible ionic fragments, i.e. H⁺, H₂⁺, O⁺, OH⁺/H₂O and D⁺, D₂⁺, O⁺, OD⁺/D₂O. Here we will restrict ourselves to the discussion of the production of only “parent” D₂O⁺ ions with a special emphasis being drawn to the determination of the absolute ionization cross section.

2. Experimental procedure

The experiments were carried out by using the mass-spectrometric apparatus described in detail in our recent paper [6]. Here we would like to present the principal methodological aspects of investigation. The beam of molecules under study was produced by means of the multichannel effusion source providing the target density in the collision region about 10^{11} cm⁻³. The molecular beam source allowed the working gas pressure to be controlled as well as the buffer argon gas to be admixed for the energy scale calibration purposes (see below). The electron beam was formed by a five-electrode electron gun providing the production of a beam of controlled energy (5–120 eV) at the 0.01–0.5 mA current.

The incident electron energy was scanned in an automatic mode by means of a stepwise voltage supply and a voltage amplifier allowing the production of a discrete energy increment within the 0.26–1.3 eV range. This process was synchronized with the pulse analyzer (MCA) switching in a multichannel counting mode. Thus, at each fixed moment

of time the valid signal was accumulated in the MCA memory channel corresponding to the current electron energy value in a real-time mode. The ions produced in the collision region were analyzed by a quadrupole mass spectrometer (QMS) MX-7303 and detected by a channeltron. The channeltron output pulse yield, proportional to the number of ions of mass-selected type, was preamplified, TTL-shaped and then entered the current MCA memory channel. Thus, after the expiration of the preselected number of measurement cycles, we obtained a curve corresponding to the energy dependence of cross section for the process under study. The resulted curve was digitally processed by an IBM PC and stored. The experimental data processing lied in the energy scale calibration with the allowance made for the apparatus factors, curve averaging and smoothing. In general, the problem of absolute energy scale calibration in mass-spectrometric studies is one of the most essential and crucial, since the precise knowledge of true collision energy defines the validity of further analysis of experimental results [4]. An effect of the contact voltage difference at the ion source electrodes and the imposition of complex configurations of electrostatic field in QMS may result in uncertainty of determination of real ionizing electron energy. Therefore we have used a technique of energy calibration against well-known and true reference data. We have chosen argon atom to serve the bench-mark since its first ionization potential is known with high accuracy ($E_i=15.76\pm 0.01$ eV [7]), while the proximity of the atomic mass of the Ar atom ($M=40$) to that of the molecules under study allowed us to work at the constant transmission capacity of the QMS analyzer. The measured near-threshold area of ionization function for the Ar atom was compared with the known reference data [8] (see fig. 1), whereas the use of the double-differentiation technique described in our earlier paper [9] allowed the ion appearance thresholds to be determined.

A good coincidence of both curves both served as a criterion of reliability of the

present experimental technique and enabled the true electron energy values to be determined directly in the experimental conditions. The calibration procedure was repeated few times (4–5 times) during the whole experimental cycle in order to eliminate the effect of possible drift of apparatus factors and determine the ionizing electron energy scale with the accuracy comparable with the electron beam energy spread value (i.e. ± 0.5 eV). It should also be noted that the relative uncertainty of determining the ionization cross section in our experiment was mainly defined by the statistical factors and did not exceed $\pm 10\%$.

3. Experimental results

Figure 2 shows the measured energy dependence of single-ionization cross section for the D_2O molecule within the incident electron energy range from the threshold up to 120 eV with the 1.3 eV energy step. The upper boundary electron energy value was defined by the design peculiarities of the QMS ion optics, since the special experiments have shown that at higher electron energies the ionization cross section anomalies occurred due to the refocusing of ions entering the QMS analyzer. The similar pattern was noticed by us when studying the other targets, including both atomic and polyatomic (see, e.g. [6,9]). Our ionization curve is compared in fig. 2 with that of Straub et al [5]. As is seen, the relative behaviour of both curves is quite similar, testifying to the reliability of our experimental technique and results. In order to compare the absolute ionization cross section values we have normalized our data at 50 eV to that of K.Becker et al [3]. As is seen, the agreement in the absolute cross section values is surprisingly good, except for the fact that the data [5] are rather flat in the energy range from 50 to 120 eV. At the same time Straub et al have reported their data only starting from 13 eV, while our technique has enabled us to go below this point close to the ionization threshold, thus, providing for the first time the very near-threshold cross section data.

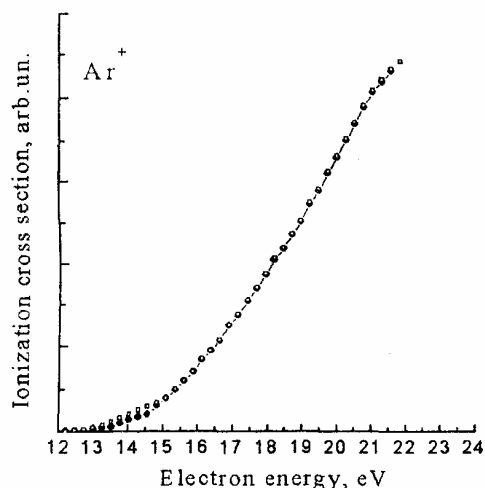


Fig. 1. Near-threshold areas of ionization curve for the Ar atom used in the electron-energy calibration procedure.

Open circles – present results
Solid circles – data of R.S.Freund et al [8].

The most interesting fact, in our opinion, is a distinct shift of the above ionization threshold at the transition from the protonated (p-H₂O) to the deuterated (d-D₂O) target. Figure 3 shows a comparison of the near-threshold areas of ionization cross sections for both water molecules measured by us with the reduced (0.26 eV) energy step. As is seen, in the case of the D₂O molecule, the energy threshold of the process E_{th} appears to be shifted towards the lower energies by 0.7 ± 0.5 eV ($E_{th}^p = 12.6 \pm 0.5$ eV, $E_{th}^d = 11.9 \pm 0.5$ eV). It is interesting to note that the similar pattern was observed in our previous experiments for the organic molecules (see, for instance, [7]). The origin of this phenomenon lies, most probably, in the manifestation of the so-called isotopic effect, stipulated by the presence of heavier atoms in the initial target molecule. U.Fano [10] was among the first who pointed out that the influence of the isotope effect, being quite weak in atoms, is much more clearly pronounced in the excitation spectra for molecules, whose reduced mass depends strongly on the nucleus mass (rotational constant of, say, deuterium molecule is, according to [10], twice less than that in the hydrogen molecule). Our experiments have

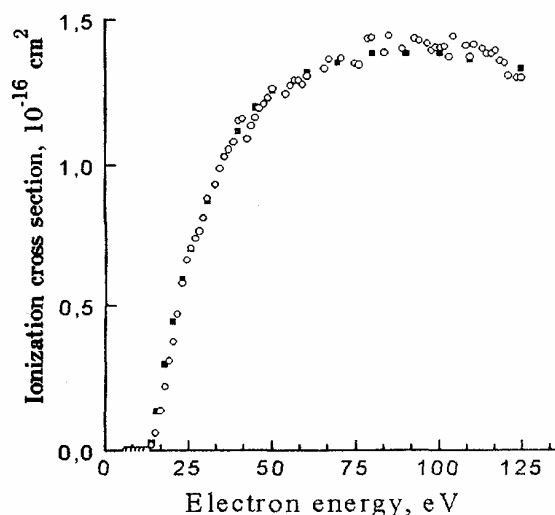


Fig. 2. Energy dependence of the absolute (normalized) ionization cross section for the D₂O molecule.

Open circles – present results
Solid circles – data of H.C.Straub et al [5].

confirmed the isotope effect on the threshold behaviour of the parent molecular ion yield. In [11], it has also been pointed out that the isotope substitution introduces a strong perturbation into the dynamics of population and decay of doubly-excited states in the H₂ and D₂ molecules being closely related to the repulsive potential curves. In addition, in accordance with [11], this effect should be revealed more effectively just in the production of ionized, not neutral, products. We believe that the present results of our investigations give an additional confirmation of that assumption.

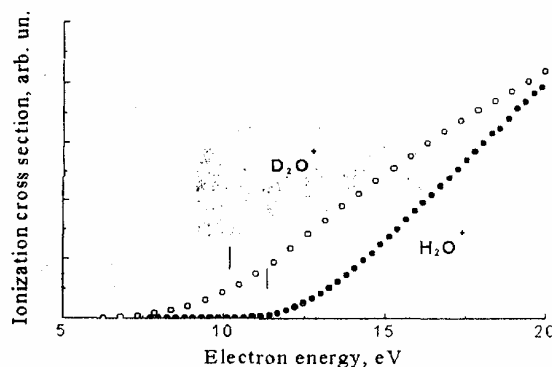


Fig.3. A comparison of the near-threshold areas of ionization cross sections for the H₂O (solid circles) and D₂O (open circles) molecules

Vertical bars indicate the ionization thresholds for both targets.

Thus, we have determined the absolute partial ionization cross section for the D_2O molecule in the incident electron energy range from the threshold up to 120 eV indicating the shift of the threshold of the process towards the lower energies against that for the “conventional” H_2O molecule.

Acknowledgement

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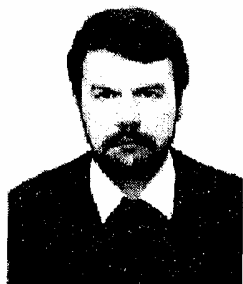
ІОНІЗАЦІЯ МОЛЕКУЛИ D_2O ЕЛЕКТРОННИМ УДАРОМ: ПЕРЕРІЗ ОДНОКРАТНОЇ ІОНІЗАЦІЇ

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Наведено нові дані з перерізу однократної іонізації молекули D_2O електронним ударом. Експеримент виконувався з застосуванням квадрупольного мас-спектрометра. Результати досліджень порівнюються з відомими даними, ілюструючи хороше узгодження як у енергетичній залежності виходу “материнських” іонів, так і у абсолютних величинах перерізу, отриманих шляхом нормування на літературні дані.



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