

CROSS-SECTION FOR SINGLE IONIZATION OF H_2O AND D_2O BY ELECTRON IMPACT FROM THRESHOLD UP TO 170 eV

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ABSTRACT

A study was made of electron-impact ionization of the parent-ion in water vapour and in heavy-water vapour as a function of electron energy up to 170 eV in a crossed molecule–electron beam apparatus. Absolute cross-sections were obtained for the processes $\text{H}_2\text{O} + e \rightarrow \text{H}_2\text{O}^+ + 2e$ and $\text{D}_2\text{O} + e \rightarrow \text{D}_2\text{O}^+ + 2e$ by means of a normalization against Ar. The results are compared with previous measurements of $q(\text{H}_2\text{O}^+/\text{H}_2\text{O})$ and are discussed theoretically in terms of the additivity rule. Using the linear-extrapolation method the following ionization potentials were deduced from the low-energy cross-section behaviour: $\text{H}_2\text{O}^+(\text{}^2\text{B}_1) = 12.7 \pm 0.1$ eV, $\text{D}_2\text{O}^+(\text{}^2\text{B}_1) = 12.75 \pm 0.1$ eV, $\text{H}_2\text{O}^+ = 16.2 \pm 0.2$ eV and $\text{D}_2\text{O}^+ = 16.0 \pm 0.2$ eV.

INTRODUCTION

Recently, several experimental studies [1–4] were made on collision processes in discharges produced in pure water or rare-gas–water mixtures. In the course of these studies interest arose about the ionization of water vapour and also heavy-water vapour by electrons. Since amazingly little has been done about this subject, we studied [5] (in extension to an earlier work [6]) electron-impact ionization of the parent-ion in water vapour and heavy-water vapour as a function of the electron energy up to 170 eV.

Apart from a number of papers concerning the ionization potentials, the authors are aware of only one previous study of partial ionization cross-sections for electrons on water vapour. Schutten et al. [7] determined $q(\text{H}_2\text{O}^+/\text{H}_2\text{O})$ for 0.02–2-keV electrons by measuring the relative amounts of fragment ions in a

cycloidal mass spectrometer and by normalizing their sum on the total ionization cross-section. The latter was measured by the same authors using the conventional condenser technique and a temperature bath for the water pressure. However, for electron energies below 100 eV, no total ionization cross-sections were measured, thus leaving some uncertainty as to the partial cross-sections reported.

The material in the present paper will be presented in two sections, the first describing the experimental apparatus and technique, and the second reporting and discussing the results.

EXPERIMENTAL

General

In the usual set-up for the study of electron-impact ionization, the absolute cross-section q is calculated from

$$q = i(\text{ion})/i(\text{electron}) \cdot n \cdot l \quad (1)$$

where $i(\text{ion})$ is the measured ion current, $i(\text{electron})$ is the electron current of the electron beam passing through a collision chamber, n is the target-gas number density, and l is the effective path-length of the electron contributing to ion collection. In order to determine the gas density via the perfect-gas law, the gas pressure p and the gas temperature T are measured with a McLeod gauge and thermocouples, respectively. However, because of possible errors in the McLeod-gauge pressure-readings, owing to entrainment of the gases in the mercury-stream flowing from the McLeod gauge to the cold trap isolating it from the collision chamber [8, 9], Rapp and Englander-Golden [10] incorporated the effusive-flow technique to avoid these difficulties. It was thus possible to measure the pressure with a precisely calibrated Bourdon gauge and to calibrate the relative cross-sections against the absolute cross-section of H_2 determined from McLeod measurements. In this case, eqn. (1) may be rewritten in the form:

$$q(X) = q(\text{H}_2) \cdot \frac{i(X^+)}{i(\text{H}_2^+)} \quad (2)$$

with $i(\text{electron})$, n and l constant.

In the case of condensable vapour, e.g. water, Schutten et al. [7] used a cold-bath pressure determination where the water pressure in the collision chamber depends on the temperature of the bath around the water (ice) supply container. However, a deviation of only 1 °C by a small heat leak would cause in their experiment an error of 13 % in the H_2O gas pressure, making this method somewhat unreliable. This is proved by remeasuring the emission cross-section for Balmer radiation after electron impact [11] and comparing it with the experiment

of Vroom and de Heer [12], who used the same technique to determine the pressure as did Schutten et al. [7]. The new results, where the pressure was measured with MKS Baratron, show that the cross-sections obtained by Vroom and de Heer are about 40 % too high. In an effort to improve the accuracy of the cross-section determination in the present study of electron-impact ionization of water, we incorporated a modified effusive-flow method in connection with an absolute capacitance manometer pressure reading.

Apparatus

Figure 1 shows a block diagram of the apparatus used in the present study. It consists of a Varian MAT double-focussing-type mass spectrometer model CH5, resolving power 30000 (10 % valley definition), with a differentially pumped analyzer head containing an electron-impact ion source with a specially designed

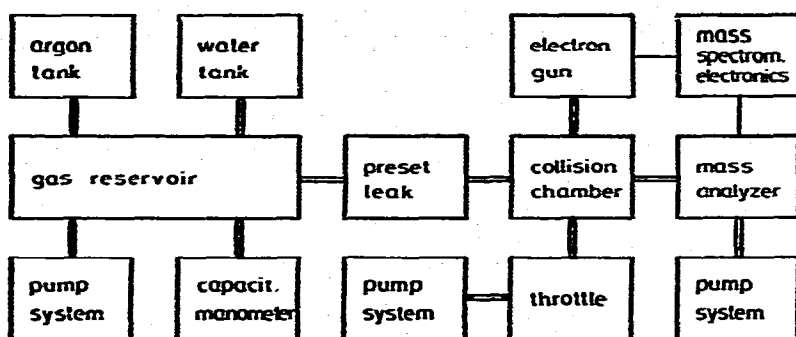


Fig. 1. Schematic view of the experimental apparatus used to measure electron-impact ionization of parent-ions in vapour of H_2O and D_2O , respectively.

ion-source housing for molecular gases, type "Intensitron M". For the present ionization cross-section measurements some changes were made in the connections to and in the electronic supply of the ion source [13]. The pusher electrode, which for measurement of mass spectra is operated positive with respect to the collision chamber proportionally to the ion accelerating voltage, was put at the same potential as the collision chamber. The electron trap collector potential was raised to 24 V to ensure saturation of electron current at all energies. The high electric field at the collector surface also prevented secondary electrons from entering the collision region. The range of the continuously selectable electron-accelerating voltage was expanded up to 170 eV and the voltage of the electron-focussing Wehnelt cylinder was maintained proportionally to the accelerating voltage in order to improve electron-current collimation over the whole energy range. Moreover, stray electron currents to the ion-source housing (usually ca. 5-10 % of the electron trap current) were measured and used to correct

the ionization efficiency curves. The mass-analyzed ion beam was detected by an electron multiplier or on a Faraday collector cup. In that the gain γ (number of secondary electrons per ion) of an electron multiplier is quite different for different ions of different charges and masses which were accelerated through the same potential, the electron multiplier was calibrated by means of the Faraday cup, yielding at 5.25-kV ion accelerating voltage, $\gamma(\text{Ar}^+)/\gamma(\text{H}_2\text{O}^+) \cong \gamma(\text{Ar}^+)/\gamma(\text{D}_2\text{O}^+) = 0.7$. The gas pressure in the collision chamber (characteristically between $5 \cdot 10^{-6}$ and $5 \cdot 10^{-5}$ torr as read on a commercial ion gauge in the vicinity of the ion source) was kept constant by means of a needle valve between the gas supplies and the gas reservoir. The pressure (characteristically between 0.2 and 5 torr) in the gas reservoir was measured with an absolute capacitance manometer, type Barocel from Data-metrics. As the whole apparatus could be heated to 150 °C (the mass spectrometer to 250 °C), the base pressure before gas was introduced was less than 10^{-6} torr. The gases used were Linde spectroscopically pure argon, H_2O -vapour and vapour of deuterium oxide d_2 , 99.8 % D of Stohler Isotope Chemicals.

Consistency checks and technique

Some of the consistency checks that are necessary in electron-beam ionization experiments to obtain accurate cross-sections have been discussed by Kieffer and Dunn [14]. It is important to ensure that the electron current (see above) and the ion current are collected completely, that space charge effects and contact potentials do not cause errors and that electron path-length corrections are negligible.

The latter has been discussed in some detail by Rapp and Englander-Golden [10]. In the present experiment with a high magnetic field [13] one reaches the region of confined flow, and thus l (see eqn. (1)) may be taken as the geometric path-length for all electron energies. The absence of space charge effects was proved in an earlier investigation [15] by the independence of cross-sections on the variation of the electron current and the gas pressure. Complete collection of ion currents is obtained by raising the respective current-collecting potentials until the currents are saturated, 100 % collection then being assumed [10, 16]. Saturation curves for the positive ions under study for different electron energies are shown in ref. 13 in detail.

After the above consistency checks had been carried out positively, relative cross-sections for Ar^+ , H_2O^+ and D_2O^+ were measured under proper collection conditions. This was done by measuring the energy dependence of the parent-ion currents for each sample (Ar , H_2O , D_2O) in a series of runs, where each electron energy was selected manually on a 10-turn helipot. The time for recording a whole cross-section curve in no case exceeded 5 min (sometimes the curve for the reference gas Ar was measured simultaneously), so that any change in filament temperature, emission, conditions in the ion source or in the recording system could be detected

and allowed for. Special care was taken to ensure that the pressure did not drift.

Thus the energy dependence of the cross-sections measured in the present work are believed to give a reliable picture of the true shape. This is further established by the fact that the ionization cross-section curve for singly-charged argon (as shown in detail in ref. 17) is found to have an inflection at about 50-eV electron energy, characteristically reported only when great care was taken to eliminate possible instrumental effects [18–20]. It was postulated that possible causes of such structure in the ionization curves are either due to production of the ion via various channels [20] or to competition between the parent-ion and a new ion [19]. However, Rapp [21] points out that no definite conclusion can be drawn because of wide variation in the shape of the argon ionization-efficiency curve as obtained by numerous workers. In the case of water, the present study suggests that as fragmentation of the molecular ion becomes energetically possible, the increasing probability of production of the fragment ion is matched by a reduction in slope of the curve of the parent-ion (in Fig. 2 at 20 eV). This is in accordance with observations of first-derivative ionization curves from electron impact on the H_2O molecule [19].

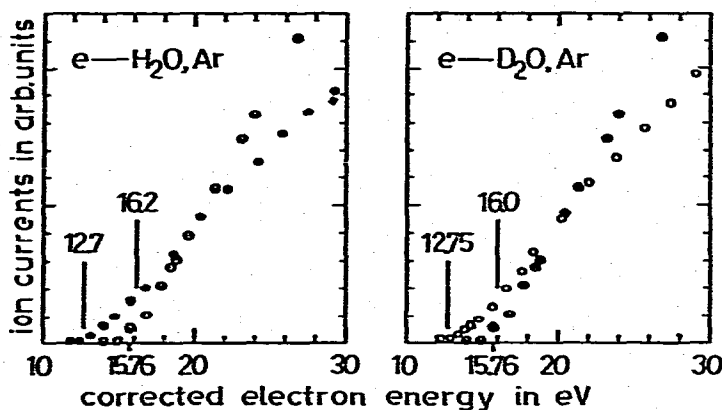


Fig. 2. Low-energy part of the relative ionization cross-section curve of Ar^+ (\circ), H_2O^+ (\bullet) and D_2O^+ (\circ). Electron-energy scale was calibrated against $IP(\text{Ar}) = 15.76\text{ eV}$ [2] using the linear-extrapolation method, thus yielding $IP(\text{H}_2\text{O}) = 12.7\text{ eV}$ and $IP(\text{D}_2\text{O}) = 12.75\text{ eV}$. Distinct breaks correspond to higher ionization potentials $IP(\text{H}_2\text{O}) = 16.2\text{ eV}$ and $IP(\text{D}_2\text{O}) = 16.0\text{ eV}$, respectively.

Energy calibration and absolute normalization

Because of the contact potential difference between the electrode in the electron gun and the collision region in the ion source, the energy scale needs to be calibrated [23]. This was done by measuring the cross-section curve of the simultaneously admitted calibrating gas Ar, where the ionization potential is known spectroscopically, and treating these data with the linear extrapolation method [24]. The difference between the observed ionization potential and the spectroscopic ionization potential for Ar [25] was then added to the energy scale (see Fig. 2).

This method of calibration has been questioned [26], but Morrison [22] has shown that the use of an additive constant from a single calibrating gas is satisfactory.

The absolute normalization of the relative cross-sections $q(\text{H}_2\text{O}^+/\text{H}_2\text{O})$ and $q(\text{D}_2\text{O}^+/\text{D}_2\text{O})$ has been accomplished by a method which compares these relative cross-sections at a particular electron energy with the well known absolute cross-section of Ar using eqn. (2). This means, for all respective measurements, constant path-length, electron current and gas density. Whereas the fulfilment of the two former conditions has been discussed above, the latter condition was established following an argument by Rapp and Englander-Golden [10] on the effusive-flow technique. Whereas Rapp and Englander-Golden used this method because of difficulties arising from their technique of measuring the absolute pressure, in the present experiment the method was used to avoid the necessity of measuring the pressure directly in the ion source. Instead, the pressure was measured absolutely in a finite gas reservoir (see Fig. 1) and is related directly to the pressure in the ion source; the pressure measurement is thus independent of the molecular weight as shown by Rapp and Englander-Golden [10] in Appendix A of their paper. The proportionality in the present experiment is proved in Fig. 3 for various experimental conditions.

Thus a set of self-consistent normalization constants for the relative cross-sections may be derived, allowing for their normalization against the well known absolute cross-section of Ar, usually against the cross-section maximum of argon with a value of $2.72 \cdot 10^{-16} \text{ cm}^2$ at 110-eV electron energy. In obtaining this value the total ionization cross-sections measured by Rapp and Englander-Golden [10] were used. The data from Gaudin and Hagemann [27] were used to adjust Rapp's

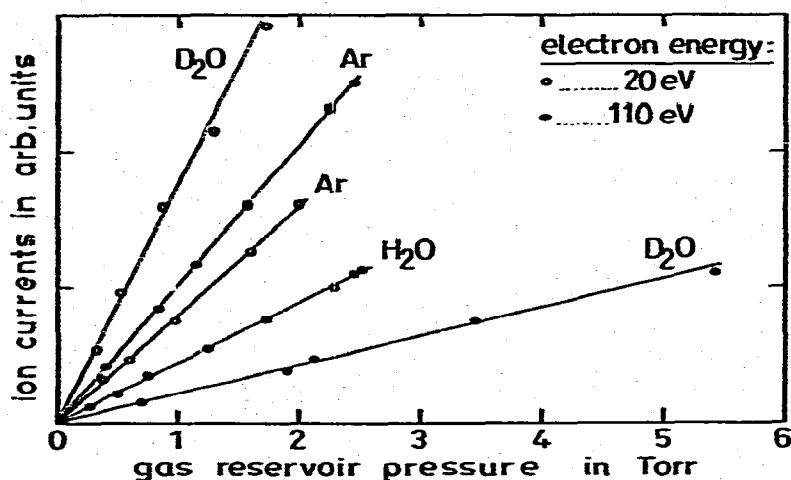


Fig. 3. Ion currents of Ar^+ , H_2O^+ and D_2O^+ as a function of Ar, H_2O and D_2O pressure in the gas reservoir, respectively. Measurements were made at two different electron energies, namely, 20 and 110 eV.

data to single ionization. The absolute ionization cross-sections obtained by this normalization method are, in accordance with Rapp and Englander-Golden [10], believed to be more accurate than those based on direct McLeod-gauge measurements in each gas.

The accuracy of plotting and reading the actual data for the ion current and electron energy was, in general, better than $\pm 1\%$. However, for very low ion currents (e.g. near the threshold) the error could be as large as $\pm 5\%$. The accuracy of pressure measurement for the calibration is estimated to be $\pm 4\%$ [17]. Allowing also for uncertainties of the collection condition in the ion source the estimated maximum possible error, except for the error in the Ar cross-section, is thus about $\pm 10\%$.

RESULTS AND DISCUSSION

Cross-sections for H_2O and D_2O

The absolute cross-section values obtained for the processes $H_2O + e \rightarrow H_2O^+ + 2e$ and $D_2O + e \rightarrow D_2O^+ + 2e$ are shown semi-logarithmically as a

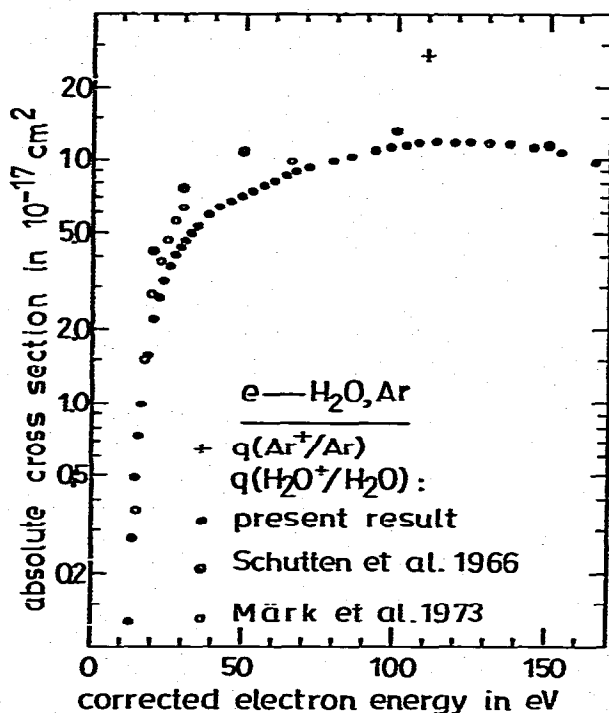


Fig. 4. Absolute ionization cross-section $q(H_2O^+/H_2O)$ as a function of corrected electron energy: (●) present data, (○) results reported by Schutten et al. [7], and (○) results reported by Märk et al. [6] which were recalibrated as described in the text against a maximum $q(Ar^+/Ar)$ of $2.72 \cdot 10^{-16} \text{ cm}^2$ (+).

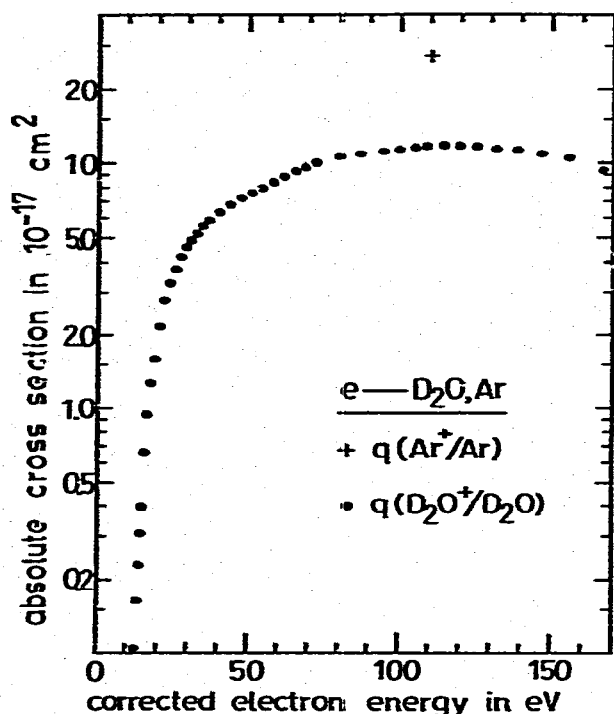


Fig. 5. Absolute ionization cross-section $q(\text{D}_2\text{O}^+/\text{D}_2\text{O})$ as a function of corrected electron energy. Also shown is the maximum $q(\text{Ar}^+/\text{Ar})$ of $2.72 \cdot 10^{-16} \text{ cm}^2$ used to calibrate the present data.

function of electron energy in Figs. 4 and 5 and are given numerically in Table I.

Figure 4 also shows cross-sections $q(\text{H}_2\text{O}^+/\text{H}_2\text{O})$ reported earlier by Schutten et al. [7] and previous results from our laboratory [6], where the pressure determination was probably inaccurate, because a McLeod gauge was used for the calibration. Differences between the present values of $q(\text{H}_2\text{O}^+/\text{H}_2\text{O})$ and the values reported by Schutten et al. may be explained by the following facts.

Schutten et al. reported that they could not obtain saturation for all fragment ions when measuring the relative amounts of all the fragment ions, not even at their maximum field strength of 1000 V cm^{-1} in the cycloidal mass spectrometer. They estimated, for instance, for H^+ from the shape of the curve, that the extracted H^+ current could be as much as 5% from saturation, thus giving a possible total error of 5–20%, which would reduce $q(\text{H}_2\text{O}^+/\text{H}_2\text{O})$ by 2–10%. They also reported that they normalized the sum of all fragment ions on the measured total-ionization cross-section. Judging, however, from Tables I and IV in their paper they have, instead, obtained $q(\text{H}_2\text{O}^+/\text{H}_2\text{O})$ using a theoretically computed cross-section by means of the additivity rule [28, 29], $q(\text{H}_2\text{O}) = q(\text{H}_2) + \frac{1}{2}\{q(\text{O}_2)\}$. Values derived in this way are, in the energy range of interest, 6% higher than values using their experimental cross-section. Moreover, Schutten et al. make no mention of any correction of the energy scale, which might amount to 5–10 eV.

TABLE I

EXPERIMENTAL IONIZATION CROSS SECTIONS VERSUS CORRECTED ELECTRON ENERGY FOR H_2O AND D_2O IN UNITS OF 10^{-16} cm^2 . ABSOLUTE CROSS-SECTIONS ARE NORMALIZED RELATIVE TO ARGON, SEE TEXT

$E \text{ (eV)}$	$q(\text{H}_2\text{O}^+/\text{H}_2\text{O})$	$E \text{ (eV)}$	$q(\text{D}_2\text{O}^+/\text{D}_2\text{O})$
165	0.98	166.5	0.93
154	1.09	155.5	1.05
145	1.13	146.5	1.10
137	1.16	138.5	1.13
130	1.17	131.5	1.15
124	1.18	125.5	1.17
118	1.18	119.5	1.18
113	1.18	114.5	1.18
107	1.17	108.5	1.18
103	1.14	104.5	1.15
98	1.11	99.5	1.14
92	1.08	94	1.12
85	1.02	86.5	1.10
78	0.98	79.5	1.07
71	0.92	68.5	0.96
67	0.89	61.5	0.88
64	0.86	58	0.83
60	0.81	54.5	0.78
53	0.73	51	0.75
46	0.67	47.5	0.72
39	0.59	43.5	0.68
33	0.50	40	0.63
29	0.44	34.5	0.56
26	0.37	29	0.46
22	0.27	22	0.28
17	0.099	17.5	0.127
15	0.049	16	0.066
14	0.028	14	0.023
13	0.012	13	0.0048

Considering all these uncertainties, including the uncertainty of the cold-bath pressure determination, we believe that the present data are to be preferred.

Comparing $q(\text{D}_2\text{O}^+/\text{D}_2\text{O})$, which has not been measured previously, with $q(\text{H}_2\text{O}^+/\text{H}_2\text{O})$, it can be seen that they are identical within the experimental error. This is to be expected, in agreement with theoretical considerations based on the Born approximation (Bethe formula), where a possible difference in cross-section could only be of the order of the difference of the Rydberg energies and the logarithm of the ionization potentials. Moreover, as there is the same agreement between $q(\text{D}_2^+/\text{D}_2)$ and $q(\text{H}_2^+/\text{H}_2)$, as measured by Rapp and Englander-Golden [10], the above mentioned result is to be expected from the concept of a qualitative additivity rule [28, 29].

Ionization potentials of H_2O and D_2O

From the low-energy cross-section behaviour (Fig. 2) it was possible to deduce the minimum ionization potentials by means of the linear-extrapolation method with: $\text{H}_2\text{O}^+(\text{}^2\text{B}_1) = 12.7 \pm 0.1 \text{ eV}$ and $\text{D}_2\text{O}^+(\text{}^2\text{B}_1) = 12.75 \pm 0.1 \text{ eV}$. The former has been measured [30] by various methods and our value is in excellent agreement with these previous measurements. In case of D_2O , the present determination of electron-impact ionization potential can only be compared with a photo ionization-efficiency result of $12.637 \pm 0.005 \text{ eV}$ [31], two photoelectron spectra results of 12.69 eV [32] and $12.624 \pm 0.01 \text{ eV}$ [33], and a series limit result of $12.636 \pm 0.006 \text{ eV}$ [34]. The difference between the ionization potential of H_2O and D_2O , according to Brehm [31], may be related to the difference in the zero-point energies. In both cases the accelerating-potential-positive-ion-current curve (Fig. 2) exhibits in addition a distinct break, corresponding to higher ionizing potentials $IP(\text{H}_2\text{O}^+) = 16.2 \pm 0.2 \text{ eV}$ and $IP(\text{D}_2\text{O}^+) = 16.0 \pm 0.2 \text{ eV}$. Both values are in good agreement with previous studies [30, 32, 33].

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