[redacted]

AD637661

AF 61(052)-762 10 May 1966

AFCRL-66-593

SCIENTIFIC REPORT
NUMBER 7

THE IONIZATION OF WATER, METHYLAMINE, AND METHYL ALCOHOL, USING ELECTRON AND ION IMPACT

Distribution of this document is unlimited.

H. SJÖGREN

PHYSICS DEPARTMENT
THE ROYAL INSTITUTE OF TECHNOLOGY
STOCKHOLM 70
SWEDEN

The research reported in this document has been sponsored by, or in part by, the AIR FORCE CAMBRIDGE RESEARCH LABORATORIES, OAR through the European Office, Aerospace Research, United States Air Force.

CLEARINGHOUSE
FOR FEDERAL SCIENTIFIC AND
TECHNICAL INFORMATION

Hardcopy	Microfiche		
$2.00	$0.50	34 pp	kl

ARCHIVE COPY

The ionization of water, methylamine, and methyl alcohol, using electron and ion impact.

By H. Sjögren

Abstract

The ionization of H_2O was investigated, using charge exchange in a double mass spectrometer. The breakdown graph was constructed. A break in the electron impact ionization efficiency curve is explained as being due to preionization, as its explanation as being due to an ion-molecule reaction between H^+ ions and H_2O seems to be less probable. The appearance potential of OH^+ was found to be considerably higher with charge exchange than when electron impact was used, which agrees with AN ~~our~~ earlier finding that intercombination transitions seem to be more strictly forbidden in charge exchange than in electron impact.

CH_3NH_2 and CH_3OH were investigated, using charge exchange at elevated pressures. The breaks in the ionization efficiency curves for these molecules are discussed and ascribed to preionization or secondary processes.

Introduction

Our knowledge of the higher ionization potentials (IP) of small and large molecules has been rather limited hitherto. The IP's are calculated quantum-mechanically for a number of small molecules. Few comparisons with experimental results have been possible and have in some cases shown a discouraging lack of agreement. The high IP of methane was thus calculated to be about 25 eV, while the generally accepted experimental value was 19.4 eV. The third IP of water has been calculated to be 18.6 eV while experiments have given the value 16.2 eV. This lack of agreement has generally been interpreted as being due to considerable unreliability inherent in the quantum-mechanical calculations. In consequence the theoretical calculations on other molecules have also been considered less reliable.

This situation has now been changed. It has been possible to explain the discrepancies in the case of methane as due to ion-molecule reactions in the ion source of the mass spectrometers used [1, 2]. Experiments indicating a value of 24 eV have also been performed [2]. The good agreement between theory and experiment thus obtained shows that the theoretical calculations have reached a higher degree of reliability than previously was believed to exist, at least by experimentalists.

Ion-molecule reactions in the ion source have also been shown to give breaks in the electron impact ionization efficiency (IE) curves for O_2 [3] and CO_2 [4]. In this paper we will show that the earlier experimental value of the third IP of H_2O is not related to direct ionization, and that the correct experimental value is close to the theoretical value. The difference between ion and electron impact processes will also be discussed.

We have also performed investigations on CH_3NH_2 and CH_3OH in order to see whether some discrepancies between the mass spectrometrically determined IP's and the ones determined by other methods can be explained in a similar way.

The structure of H_2O

The structure of water according to Mulliken [5] and Ellison and Shull [6], is given below, together with the IP's of the different electrons in eV.

	$1a_1^2$	$2a_1^2$	$1b_2^2$	$3a_1^2$	$1b_1^2$
Probable ionic state			$^2B_2$	$^2A_1$	$^2B_1$
IP's [6]	557	36	18.6	13.2	11.8
IP's [7]	560	36	18.5	15.1	13.4
IP's [8]			18.02	14.23	12.61

The IP's were obtained by LCAO-MO-SCF calculation [6, 7] and by photoelectron spectroscopy [8].

No potential energy curves for H_2O seem to have been computed, although qualitative curves have been given by Schulz [9], Laidler [10], and Fiquet-Fayard [11, 12]. We have, therefore, tried to estimate the Franck-Condon factors for ionization of H_2O from theoretical considerations and photoelectron spectroscopic measurements [13].

According to theoretical discussions [6, 14 - 16], the $1b_1$ orbital is approximately nonbonding, the $1b_2$ orbital is strongly bonding while the $3a_1$ orbital is important for the angle between the OH bonds. Turner found evidence of at least three vibrational levels at 12.61 eV with a mean spacing of 0.4 eV. At 14.23 eV he found evidence that a strongly bonding electron is ionized, giving vibrations up to 17 eV. Finally, at 18.02 another strongly bonding electron is ionized, giving vibrations up to 20 eV. Since the $3a_1$ orbital tends to diminish the angle between the OH bonds, ionization of this electron must lead to strong bending vibrations. Therefore Turner's observations are in good agreement with theory.

By using this information we have approximately plotted the Franck-Condon curves in Fig. 1a. These curves give a picture of the probabilities for ionization when using electron and ion impact. No transitions to repulsive states are included in Fig. 1a, since these are not known, although they must also be taken into consideration. It was shown earlier (CO_2 [4]) that the probabilities of these transitions are sometimes appreciable.

Molecular states of H_2O

Our knowledge of the excited states of the neutral water molecule has improved considerably during recent years. Walsh [15] has discussed the absorption of H_2O at 1655 Å and 1290 Å and has given reasons that both transitions go to a Rydberg state $3sa_1$, that is broadened owing to interaction with a repulsive a_1 state. In the first case, the transition is due to a non-bonding $1b_1$ electron, and in the second case a $3a_1$ electron makes the transition. Therefore, in the last case bending vibrations are observed in the upper state. Owing to these vibrations, the energy of the 3s state is best determined from the long wavelength absorption with maximum at 1655 Å, and can therefore be given as 5.1 eV below the ionization limit. The higher Rydberg levels 4s and 5s were observed by Price [17], and have recently been discussed by Johns [18]. They have energies 1.5 and 0.9 eV respectively, below the ionization limit. (The transitions measured by Johns are of minor interest owing to low intensity.)

Recently, Skerbele and Lassettre were able to observe all these transitions by means of electron impact spectra [19]. Their results are given in Fig. 2. The high broad peak at 7.5 eV shows the transition $1b_1 \rightarrow 3s$. The transition $3a_1 \rightarrow 3s$ starts at 9.1 eV, and the bending vibrations in the upper state make this peak very broad up to 10.4 eV. At 11.1 eV a very intense and narrow peak corresponds to the transition $1b_1 \rightarrow 4s$, and at 11.7 eV a small peak corresponds to $1b_1 \rightarrow 5s$.

Above the ionization limit in Skerbele and Lassettre's paper a very intense and broad peak can be observed. Since the excitation of an inner electron $3a_1$ to 3s gives a very intense peak in Lassettre's measurements, it is natural to suggest that the intense peak at 13 eV may be due to transitions of the inner electron $1b_2$. As Turner's new measurements have given the energy 18.0 eV for the $1b_2$ electron, the energy of the transition $1b_2 \rightarrow 3s$ can immediately be calculated as 12.9 eV. But it is further necessary to take into consideration that the $1b_2$ electron is the main bonding electron in water according to Ellison and Shull [6], and that, therefore, very strong vibrations will be introduced on excitation of such an electron. It is, therefore, natural that the peak will extend from 12.9 eV up to 14 or 15 eV, which is in complete agreement with the results obtained by Skerbele and Lassettre.

As the transition at 11.1 eV ($1b_1 \rightarrow 4s$) is nearly as intense as the transition at 7.5 eV ($1b_1 \rightarrow 3s$), we expect that also the transition $1b_2 \rightarrow 4s$ will be intense, and, owing to the vibrations, we will expect a broad peak between 16 and 17 eV. Such a peak is present in Fig. 2.

It is clear that a molecule in the state at about 16 eV will preionize, if a $3a_1$ electron fills the hole in the $1b_2$ orbital (which is an allowed transition), and at the same time the 4s electron is ionized. In the state at 12.9 eV the molecule must have a small probability for preionization, for transition of a $3a_1$ electron into the $1b_2$ orbital does not give enough energy for preionization, and the transition $1b_1 \rightarrow 1b_2$ must be weak. The state $1b_2^2\ 3a_1\ 1b_1^2\ 4sa_1$ also at about 12.9 eV (not discussed earlier) can of course preionize as the transition $1b_1 \rightarrow 3a_1$ is allowed and the energy is slightly higher than the ionization energy.

If there exists an excited neutral state of H_2O at 16 eV, this would be expected to appear by photoionization and photoabsorption measurements. Such investigations have been made by a number of authors. Astoin [20], Rathenau [21], and Henning [22] have found strong photoabsorption close to 16 eV. Metzger and Cook [23], on the other hand have found a minimum in their photoabsorption curve at this energy. The situation is therefore not clear.

Earlier electron impact investigations of H_2O

Using photoelectrons, Price and Sugden [24] studied the total ionization of H_2O and found breaks in the IE curve at 12.6, 14.5, 16.2, and 18.0 eV. Schulz [9] and Sjögren [25, 26], using the RPD technique according to Fox et al. [27] and ionization chambers, found breaks at 12.6 and 14.5, and at 12.6, 14.2, and 16.2 eV, respectively. In addition, some of Sjögren's curves showed breaks at about 18 eV (unpublished). Using a mass spectrometer, Frost and McDowell [28] and Cottin [29] found breaks at 12.61, 14.35, and 16.34, and at 12.61, 14.5, and 16.1 eV, respectively.

It is evident that the first and second breaks in all these determinations correspond to ionization of the $1b_1$ and $3a_1$ electrons in good agreement with the previous values. Further, the break at 18 eV, obtained in some of the total ionization experiments, agrees well with Turner's value 18.02 eV for the ionization of the $1b_2$ electron and also with the calculations by Ellison and Shull and by Moccia. In an earlier paper [2] Sjögren showed that especially Moccia's calculations of the high IP of methane [30] agree well with the new experimental determination of this IP. Since Moccia has performed the same type of calculations on water, a high degree of reliability must be ascribed to his values.

It therefore seems necessary to assume that the value at about 16.2 eV obtained in most of the electron impact experiments is not due to direct ionization but to a different process. This process must differ from the charge exchange described in the case of methane [1, 2] and CO_2 [4], since the break is observed not only by mass spectrometry but also in the total ionization experiments.

The electron impact mass spectrum of H_2O is given in Table 1 together with the appearance potentials (AP) [29, 31], possible dissociation limits, and the corresponding minimum energies. The minimum energies were calculated using known dissociation [32] and excitation [33] energies and the electron affinity of OH determined by Branscomb et al. [34]. Since the two OH^+ states $^1\Delta$ and $^1\Sigma^+$ do not seem to have been detected spectroscopically, we have estimated their excitation energies in analogy to the similar states in the isoelectronic NH molecule [33] at 2 and 3 eV respectively. It may be remarked that the earlier value, 18.8 eV for the AP (O^+), has been shown by Cottin [29] to be due to pressure induced metastable OH^+ ions at mass 16.05. In addition, Cottin [29] found AP's of both H^+ and OH^- at 16.0 eV indicating that these ions are formed in an ion-pair process at this energy.

However, these appearance potentials are not in agreement with the values calculated in Table 1. It is of course possible, that Cottin has an uncertain calibration of his energy scale and that the correct appearance potentials are 16.9 eV. Measurements by De Souza and Green [35], indicating that the AP (OH^-) is 17.5 eV also support this point of view. In such a case, however, it is impossible to explain the formation of H_2O^+ at 16.2 eV by means of the ion-molecule reaction involving H^+ discussed below. On the other hand, it is possible that the theoretical calculation is inaccurate. The electron affinity of OH is still a matter for discussion, and also the dissociation energy of H_2O is somewhat uncertain.

In this situation there are evidently two possible ways of explaining the break at 16.2 eV in the electron impact experiments

Ion-pair formation and preionization. Both processes must at least in principle, give rise to breaks in the total ionization curves.

In order to explain the break at 16.2 eV by ion-pair formation, it is further necessary to assume that the H^+ ions by subsequent charge exchange form new molecule ions according to

$$H^+ + H_2O \rightarrow H + H_2O^+ \qquad (1)$$

in analogy to what was found in the case of O_2 [3]. That this is the case will be evident from our ion-impact investigations of H_2O. Although the recorded intensities of the H^+ ions have been found to be low (Table 1) it must be remembered that these light H^+ ions are discriminated in the mass spectrometer.

The possibility of preionization has been discussed above, and it was pointed out that the break would be situated near 16.2 eV. The energy of the break will thus be in better agreement with the observations than if ion-molecule reactions are considered.

Ion impact investigations on H_2O

In order to investigate the ionization processes, we bombarded H_2O with slow positive ions in a double mass spectrometer described earlier [36, 37], and recorded the mass spectra. The results are shown in Table 2. The last column in the Table gives the relative cross sections (Q) in arbitrary units. The pressure of the target gas was determined by use of a Knudsen gauge. Unfortunately, the apparatus did not permit observation of H^+. Therefore the Q-values at high RE's are only lower limits.

In Fig. 1b the Q-values at high velocities are plotted. Evidently they are in good agreement with the estimated Franck-Condon factors in Fig. 1a. Bombardment with CO_2^+, recombination energy (RE) 13.8 eV [4, 36], thus gives approximately the same Q-values as with Kr^+, RE's 14.00 and 14.67 eV. This demonstrates the partly bonding character of the $1b_1$ electron. It also shows that the charge exchange reaction (1) is allowed, since the lower RE of H^+, 13.6 eV, ought to give increased transition probability in comparison with CO_2^+. Also Ar^+, RE 15.8 eV, gives similar Q-values. The probability for ionization of the $3a_1$ electron is therefore still large, 1.5 eV above the IP.

F^+ ions exist in three states, $2s^2\ 2p^4\ {}^3P$, ${}^1D$, and ${}^1S$ with RE's 17.42 (${}^3P$, 60%), 20.01 (${}^1D$, 30%), and 22.98 (${}^1S$, 10%) eV [3]. At low velocities, RE 17.42 eV gives no contribution to the mass spectrum according to Fig. 1a, while RE 20.01 eV gives H_2O^+ predominantly in the stable ${}^2B_2$ state. RE 22.98 eV is only of minor importance due to the low abundance of the ${}^1S$ state and probably gives only OH^+ ions from repulsive state. At high velocities translational energy enables the F^+ (${}^1D$) ions to transfer more energy to the H_2O molecule. This explains the important velocity dependence in Table 2 since the H_2O^+ ions will then be able to reach the dissociation limit of the $^2B_2$ state and give OH^+ ions according to Table 1. It is also possible that H_2O^+ ions begin to form in repulsive states belonging to the same dissociation limit in Table 1. At the same time, the F^+ (^3P) ions will be able to ionize the $^2B_2$ state, giving increasing absolute amounts of H_2O^+ ions and increasing Q-values. Using F^+ ions with 500 eV kinetic energy, Lindholm [38] obtained equal amounts of H_2O^+ and OH^+ ions.

Xe^{++} ions have RE's about 12.5 and 18-20 eV, but formation of Xe^+ through collisions above the collision chamber must also be considered at higher pressures [2]. Xe^{++} gives similar velocity dependence as F^+ ions, but extrapolation down to zero pressure and zero velocity shows that no OH^+ ions form below 20 eV.

Using Ne^+ ions, RE 21.6 eV, small Q-values are obtained in agreement with Fig. 1a. However, since the repulsive states leading to formation of H^+ cannot be studied in the present experiment, these Q-values are only lower limits. Evidently the OH^+ ions are predominating at low pressures.

When the pressure is increased, the relative abundances of H_2O^+ increase, when bombarding with Ne^+, F^+, and Xe^{++}, probably according to reaction (1) or to

$$OH^+ + H_2O \rightarrow OH + H_2O^+ \qquad (2)$$

which also is energetically possible. Extrapolation down to zero pressure must therefore be performed and shows in the case of Ne^+ that the H_2O^+ ions are unstable at 21.6 eV. This is very interesting because together with the F^+ and Xe^{++} results above it shows that the AP of OH^+ seems to be much higher when using charg exchange than when electron impact is used.

In Fig. 1c a tentative breakdown graph of H_2O^+ is plotted, using the results from Table 2 and the AP's discussed above. This graph gives but little information about the dissociation above 19.5 eV because of the unknown amounts of H^+ ions. Since H^+ must be formed from repulsive states, it seems likely that the abundances of H^+ at 20 eV are still low. This is consistent with the fact that no further breaks seem to have been reported above 18 eV in the mass spectrometrically determined IE curve of H_2O.

A theoretical discussion of the dissociation of H_2O^+

The dissociation of H_2O has been the subject of many theoretical and experimental investigations [11, 12, 39 - 43]. On the other hand, the dissociation of H_2O^+ has been the subject of only few theoretical investigations [10 - 12] performed by means of a generalization of the Wigner-Witmer correlation rules. In this way it was possible for Fiquet-Fayard to draw the potential energy curves for H_2O^+ approximately (ref. 12, p. 459). We will accept the main features of her diagram with a few minor exceptions. Firstly, it must be corrected for the new experimental IP of the $^2B_2$ state, and, secondly, we think it is necessary to include OH^+ ($^1\Delta$) and OH^+ ($^1\Sigma$) amongst the dissociation products, although these states have not yet been observed by the spectroscopists (Table 1) (cf. [33]).

In view of the results and discussions above it is evident that formation of the $^2B_1$ state by means of ionization of a $1b_1$ electron will not be followed by dissociation; this electron is essentially nonbonding. The $^2B_1$ state is, therefore, stable.

Nor will formation of the $^2A_1$ state by means of ionization of a $3a_1$ electron cause any dissociation. The HOH angle will increase considerably and the $^2A_1$ state is probably linear (cf. the corresponding state of NH_2, which has been proven to be linear [44]). The $^2A_1$ state will therefore be formed with vibrational excitation, but will also be stable.

When the $^2B_2$ state is obtained after ionization of the bonding $1b_2$ electron it is necessary to distinguish between high and low vibrational energy of the state. As the $1b_2$ electron is bonding [6] both cases are possible. In the first case the $^2B_2$ ion is formed with low vibrational energy. It is then perfectly stable, although it is energetically higher than the dissociation limit at 17.9 eV, since predissociation is forbidden for reasons of symmetry. However, this rule no longer holds in a collision with a gas molecule, and pressure induced metastable OH^+ ions, probably formed in this manner, were observed by Cottin [29]. In the second case dissociation takes place as soon as the energy exceeds the dissociation limit $OH^+ (^1\Delta \text{ or } ^1\Sigma) + H$. The AP of OH^+ is therefore expected to be about 21 eV, in perfect agreement with our results that for ions with [illegible] lower than 20.0 eV no OH^+ ions are obtained.

Using electron impact, the lowest AP of OH^+ has been found to be 18.1 eV [29] in disagreement with theory and with our ion impact results. The explanation must probably involve the repulsive state $^4B_1$ or $^4A_2$, correlating with the dissociation limit $OH^+ (^3\Sigma^-) + H$ at 17.9 eV. The quartet state can be formed either directly in the electron impact or via a preionizaing neutral triplet state. Evidently these results imply that intercombination transitions, which seem to be forbidden in charge exchange, can be of importance in electron impact. The results on H_2O are similar in this respect to our results with CO_2 [4].

The next repulsive state ($^2B_1$ or $^2A_2$) correlates with the dissociation limit $H^+ + OH\ (^2\Pi_i)$ at 18.7 eV, but all other repulsive states go to limits higher than about 20 eV and are therefore without interest in connection with our discussion of the formation of OH^+ below 20 eV.

The fragmentation of H_2O^+ giving O^+ and H_2^+ has also been treated theoretically by Fiquet-Fayard [11, 12] and experimentally by Cottin [29]. It will not be discussed further in this paper since no H_2^+ ions can be observed in our apparatus and the AP of O^+ is higher than 29 eV [29].

The structures of CH_3NH_2 and CH_3OH

The structures of CH_3NH_2 and CH_3OH have been given by Mulliken [45] and were further discussed in earlier papers from this laboratory [37, 46]. They are given below for reference together with earlier and new estimations of the IP's in eV. The changes that have been made are discussed below.

CH_3NH_2	$1s^2$	$1s^2$	$2s^2$	$2s^2$	z^2	x^2	y^2	z^2	x^2
Location	N	C	NH_2	CH_3	NH_2	CH_3	CN	CH_3	N
IP, earlier [37]				19.89	16.57	15.07	13.94	12.16	9.18
IP	421	304	30	24	16.57	15.07	13.94	12.16	9.18
Mulliken [45]			(27)	(22)	16	14.5	13.5	14.5	11
CH_3OH	$1s^2$	$1s^2$	$2s^2$	$2s^2$	z^2	x^2	y^2	z^2	x^2
Location	O	C	OH	CH_3	OH	CH_3	CO	CH_3	O
IP, earlier [46]				19	15.3	15.0	13.1	13.0	10.9
IP	557	304	36	24	17.23	14.64	14.64	12.33	10.83
Mulliken [45]			32	22	17.5	14.5	16	14.5	12.5

As the two isoelectronic molecules are very similar and have nearly identical breakdown graphs [37, 46], similar coordinate systems have been chosen for their representation. From the designation of the orbitals the interaction between different orbitals is immediately clear.

In CH_3NH_2, the IP of the CH_3 bonding 2s electron has been changed to 24 eV in accordance with the value obtained by Sjögren for the corresponding IP in methane [2]. In agreement with the discussion in [37] the lower IP's have been taken from photoelectron spectroscopy measurements by Turner [8] and the higher values are taken from Moccia's quantum-mechanical calculations for CH_4 [30] and NH_3 [47]. In this way, one of the values given by Turner (19.89 eV) has not been used. Since it was put in parentheses by Turner it is probably dubious.

In CH_3OH, the IP of the CH_3 bonding 2s electron has been changed to 24 eV for the same reason as in CH_3NH_2. The values for the IP's of the O (1s) and the C (1s) orbitals are taken from Moccia's calculations for H_2O [7] and CH_4 [30]. The earlier IP of the OH [z] orbital was estimated as the mean of the second and third IP of H_2O. This third IP has now been shown to be 18 eV, which gives the mean value 16.1 eV. Interaction with the CH_3 [z] orbital of the same symmetry is probably strong enough to elevate the IP further to reach Turner's value at 17.2 eV, at the same time as the CH_3 [z] orbital is depressed by about the same amount to around 12 eV. The assignment to the lower IP's is complicated by the fact that Turner has found one IP too few in CH_3OH. In lack of further data the same value has therefore been assigned to the CO [y] orbital and the CH_3 [x] orbital at 14.6 eV. It is of course possible to assume that the IP of the CO [y] orbital would be 12.3 eV. However, with such an assignment, the IP of the CO orbital would be much lower than the IP of the CN orbital. In consequence, it would therefore seem necessary to assume that in CH_3NH_2 the IP's of the CO [y] and the CH_3 [z] orbitals have the same value 12.16 eV, and that also the value 13.94 eV must be disregarded, which is less probable.

It is possible that photoelectron spectroscopical measurements with increased resolution will solve some of these problems. It is remarkable how well the IP's obtained in this way agree with the old estimations by Mulliken in Journal of Chemical Physics 3, 506 (1935), except that Mulliken did not take the interaction of the CH_3 orbitals with the other orbitals into consideration.

Earlier measurements

Using electron impact and an ionization chamber, Sjögren [26] has studied the IE curve for CH_3OH. Breaks in the IE curve for CH_3OH were found at 10.8, 11.7, 12.6, and 14.3 eV in reasonable agreement with the IP's above, except for the value 11.7 eV. Similar measurements on CH_3NH_2 will be described below.

Using electron impact and mass spectrometric analysis Collin [48] measured the IE curves for CH_3OH and CH_3NH_2. In the CH_3OH^+ curve breaks appeared at 10.85, 12.82, 14.5, 16.06, and 18.85 eV, and in the $CH_3NH_2^+$ curve the breaks appeared at 9.45, 12.35, 13.90, 17.70, 21.75, and 23.75 eV. CH_3OH has also been investigated with a similar technique by Tsuda and Hamill [49] who found breaks at 10.85, 11.1, 12.1, 13.2, and 13.7 eV.

Using photoabsorption, Samson et al. [50] obtained the IP's 14.3 and 17.6 eV for CH_3OH in good agreement with Turner's values.

The ion impact mass spectra of CH_3OH and CH_3NH_2 have been studied by Wilmenius and Lindholm [46] and Sjögren [37]. It was found that the CH_3OH^+ ion rapidly dissociates having received energies above 12 eV, and that the $CH_3NH_2^+$ ion is stable only up to 10 eV. In view of these results it is difficult to understand how the breaks in the mass spectroscopically determined IE curves are obtained.

Experimental results

In order to investigate whether the mass spectroscopically determined breaks may be due to preionization or to a charge exchange mechanism of the same type as was observed in CH_4 [2] and CO_2 [4], the following experiments were performed.

CH_3NH_2 was bombarded with quasi-monochromatic electrons in an ionization chamber and the total ionization curve was measured at an estimated pressure of 10^{-4} torr. The apparatus has been described earlier [2, 26]. The energy scale was calibrated using the resonance capture peak of CH_3NH_2 which was measured simultaneously with the positive ion curve. This peak was found to have a narrow maximum at 5.4 eV. The position was determined using different mixtures of CH_3NH_2 and H_2O. The latter molecule has a resonance capture peak at 6.6 eV determined earlier [51] in agreement with results by Bucholnikova [52] 6.4 eV and Schultz [9] 6.5 eV. The difference between the two peaks was found to be 1.2 eV.

Breaks in the positive ion curve of pure CH_3NH_2 were observed at 9.0 ± 0.1, 9.5 ± 0.1, and 9.9 ± 0.1 eV (mean of 8 runs). The AP is therefore 9.0 eV in good agreement with the spectroscopic value 8.97 eV of Watanabe [53]. Additional breaks were observed at 10.3 ± 0.1 eV (6 runs) and 10.8 ± 0.3 eV (5 runs). No reproducible breaks at higher energies were obtained. The breaks must be ascribed to preionization or to excitation of vibrational states.

CH_3OH and CH_3NH_2 were further investigated by means of charge exchange at elevated pressures in a double mass spectrometer. A Knudsen gauge was used to determine the pressures.

The relative abundances of the molecule ions after charge exchange with slow positive ions are shown in Table 3. The spectra were resolved into mono-isotopic peaks and the sums of the peak heights were normalized to 100.

The molecule ions in Table 3 are no doubt formed in secondary processes, but evidently the small increase is insufficient to explain the breaks in the IE curves as being due to charge exchange between fragment ions formed after the primary charge exchange and the parent gas. The behaviour of the ions "parent-plus-one" shows, however, that ion-molecule reactions do occur in the collision chamber.

A further possibility, that cannot be investigated using this method, is that the fragment ions that might be responsible for the electron impact results are obtained through ion-pair formation. Since $CH_3^+ + OH$ appears at 13.7 eV [49] and since the electron affinity of OH is 1.8 eV [34, 49] one may assume that $CH_3^+ + OH^-$ appears at 11.9 eV. This is also verified by experiments [49], and may explain the break at 11.7 eV in Sjögren's IE curve for CH_3OH [26]. No corresponding break would be obtained in a mass spectrometrically determined IE curve, since the RE of CH_3^+ is too low, 9.8 eV [37], but, in spite of this, Tsuda and Hamill obtained a number of breaks in their curve for CH_3OH at energies below 13.7 eV. It is therefore impossible to decide whether the break is due to ion-pair formation, preionization, or, perhaps, vibrational excitation.

To explain the break found by Collin at 12.35 eV in CH_3NH_2 a similar discussion can be carried through. Since $CH_3^+ + NH_2$ appears at about 13.9 eV and since the electron affinity of NH_2 is about 1.2 eV [54] the appearance potential of $CH_3^+ + NH_2^-$ can be calculated to be 12.7 eV. In this case charge exchange is allowed because of the low AP of the $CH_3NH_2^+$ ion, and it is therefore natural that the pressure dependence is more pronounced for this ion than for the CH_3OH^+ ion (Table 3). However, since the electron impact measurements have shown a number of breaks below 12 eV and since the abundance of CH_3^+ ions is low in the mass spectrum of CH_3NH_2, it must be concluded that also in the case of CH_3NH_2 this process is a less likely reason for the low energy breaks.

The breaks at higher energies for both molecules may, in addition, be explained by charge exchange reactions between parent gas and fragment ions with higher RE's formed from molecular or ionic states that are not possible to reach by ion bombardment (cf. the discussion of H_2O). In this case it is, of course, not possible to investigate the reactions by ion bombardment.

Regardless of whether the breaks in the electron impact IE curves for CH_3OH and CH_3NH_2 thus are caused by charge exchange, or by preionization, it is evident that they cannot be used to determine the higher ionization potentials of the molecules without further analysis. The agreement with independently measured IP's seem, therefore, to be accidental.

Acknowledgements

The author is greatly indebted to Professor Einar Lindholm for stimulating guidance and advice. He is also indebted to Professor Einar Stenhagen and Professor Stina Stenhagen, who supplied the pure methylamine. This project was supported by the Swedish Natural Science Research Council and by Air Force Cambridge Research Laboratories under Contract AF 61(052)-762 through the European Office of Aerospace Research (OAR), United States Air Force. A grant from Knut och Alice Wallenbergs Stiftelse made possible the construction of the apparatus. The author would also lika to thank Gunnar Sahlström for valuable assistance.

Department of Physics, The Royal Institute of Technology,
Stockholm 70, Sweden.

References

1. Sjögren, H., Phys. Letters 19, 210 (1965).
2. Sjögren, H., Arkiv Fysik 31, 159 (1966).
3. Sjögren, H., and Lindholm, E., Arkiv Fysik, in press.
4. Sjögren, H., Arkiv Fysik, in press.
5. Mulliken, R.S., J. Am. Chem. Soc. 77, 887 (1955).
6. Ellison, F.O., and Shull, H., J. Chem. Phys. 23, 2348 (1955).
7. Moccia, R., J. Chem. Phys. 40, 2186 (1964).
8. Al-Joboury, M.I., and Turner, D.W., J. Chem. Soc. 4434 (1964).
9. Schulz, G.J., J. Chem. Phys. 33, 1661 (1960).
10. Laidler, K.J., J. Chem. Phys. 22, 1740 (1954).
11. Fiquet-Fayard, F., J. Chim. Phys. 54, 274 (1957).
12. Fiquet-Fayard, F., J. Chim. Phys. 57, 453 (1960).
13. Turner, D.W., private communication.
14. Walsh, A.D., J. Chem. Soc. 2260 (1953).
15. Walsh, A.D., Advances in Molecular Spectroscopy, Pergamon Press, London, 1961, p. 148.
16. Coulson, C.A., and Neilsen, A.H., Disc. Faraday Soc. 35, 71 (1963).
17. Price, W.C., J. Chem. Phys. 4, 147 (1936).
18. Johns, J.W.C., Can. J. Phys. 41, 209 (1963).
19. Skerbele, A., and Lassettre, E.N., J. Chem. Phys. 42, 395 (1965).
20. Astoin, N., C.R. Acad. Sci. Paris 242, 2327 (1956).
21. Rathenau, G., Z. Phys. 87, 32 (1934).
22. Henning, H.J., Ann. Phys. 13, 599 (1932).
23. Metzger, P.H., and Cook, G.R., J. Chem. Phys. 41, 642 (1964).

24. Price, W.C., and Sugden, T.M., Trans. Faraday Soc. 44, 108 (1948).

25. Sjögren, H., and Lindholm, E., Phys. Letters 4, 85 (1963).

26. Sjögren, H., Proc. 3rd Intern. Conf. on Physics of Electronic and Atomic Collisions, London, 1963, North-Holland Publishing Company, Amsterdam, 1964, p. 474.

27. Fox, R.E., Hickam, W.M., Grave, D.J., and Kjeldaas, T., Rev. Sci. Instr. 26, 1101 (1955).

28. Frost, D.C., and McDowell, C.A., Can. J. Chem. 36, 39 (1958).

29. Cottin, M., J. Chim. Phys. 56, 1024 (1960).

30. Moccia, R., J. Chem. Phys. 40, 2164 (1964).

31. Mann, M.M., Hustrulid, A., and Tate, J.T., Phys. Rev. 58, 340 (1940).

32. Cottrell, T.L., The Strengths of Chemical Bonds, Butterworths Publications Limited, London, 1958.

33. Herzberg, G., Spectra of Diatomic Molecules, Van Nostrand Company, Inc., New York, 1959.

34. Branscomb, L.M., Smith, S.J., and Tisone, G., Proc. IVth Intern. Conf. on Physics of Electronic and Atomic Collisions, Québec, 1965, Science Bookcrafters, Inc., New York, 1965, p. 106.

35. De Souza, B.C., and Green, J.H., Nature 203, 1165 (1964).

36. von Koch, H., and Lindholm, E., Arkiv Fysik 19, 123 (1961).

37. Sjögren, H., Arkiv Fysik 29, 565 (1965).

38. Lindholm, E., Z. Naturforsch. 9a, 535 (1954).

39. Niira, K., J. Phys. Soc. Japan 4, 230 (1949).

40. Niira, K., J. Phys. Soc. Japan 7, 193 (1952).

41. Horie, T., Nagura, T., and Otsuka, M., J. Phys. Soc. Japan 11, 1157 (1956).

42. Shuler, K.E., J. Chem. Phys. 21, 624 (1953).

43. Carrington, T., J. Chem. Phys. 41, 2012 (1964).

44. Ramsay, D.A., Advances in Spectroscopy 1, 1 (1959).

45. Mulliken, R.S., J. Chem. Phys. 3, 506 (1935).

46. Wilmenius, P., and Lindholm, E., Arkiv Fysik 21, 97 (1962).

47. Moccia, R., J. Chem. Phys. 40, 2176 (1964).

48. Collin, J., Colloq. Spectros. Intern. 9th Lyon, 1961, 3, 596 (1962).

49. Tsuda, S., and Hamill, W.H., Institute of Petroleum/ASTM Mass Spectrometry Symposium, Paris, 1964.

50. Samson, L., and Damany-Astoin, N., C.R. Acad. Sci. Paris 250, 4138 (1960).

51. Sjögren, H., Proc. 6th Intern. Conf. Ionization Phenomena in Gases, Paris, 1963, SERMA, Paris, 1963.

52. Buchelnikova, N.S., Soviet Phys. JETP 35, 783 (1959).

53. Watanabe, K., J. Chem. Phys. 26, 542 (1957).

54. Pritchard, H.O., Chem. Revs. 52, 529 (1953).

Table 1. Electron impact mass spectra of H_2O, AP's in eV, dissociation limits and minimum energies in eV.

Ion	Electron impact mass spectrum				Possible processes	Minimum energy
	Mann et al. [24]		Cottin [22]			
	MS^a	AP's	MS^b	AP's		
H_2O^+	100	13.0	100	12.6	$H_2O(^1A_1) \rightarrow H_2O^+(^2B_1)$	-
OH^+	23.2	18.7	23.0	18.1	$H_2O^+(^4A_2) \rightarrow OH^+(^3\Sigma^-)+H$	17.9
		-		21.0	$H_2O^+(^2B_2) \rightarrow OH^+(^1\Delta)+H$	~20
					or $\rightarrow OH^+(^1\Sigma^+)+H$	~21
O^+	2.0	18.8	1.25		$H_2O(^2B_2) \rightarrow OH^+(^3\Sigma^-)+H$	17.9
					Pressure induced metastable peak.	
		28.1		29.1		
H^+	5.0	-	5.05	16.0	$H_2O^* \rightarrow H^+(^1S)+OH^-(^1\Sigma)$	16.9
		19.5		19.6	$H_2O^+(^2A_2) \rightarrow H^+(^1S)+OH(^2\Pi_i)$	18.7

[a] electron energy 100 eV

[b] electron energy 50 eV

Table 2. Mass spectra of H_2O obtained in charge exchange with incident positive ions of low kinetic energy (KE) as a function of the pressure in the collision chamber.

Incident ion	KE eV	Pressure microns		Ions			
			H_3O^+	H_2O^+	OH^+	m/e=16	Q
Ne^+	25	2.0	(73.3)	66.7	33.3	-	0.2
	25	0.8	(21.2)	39.5	60.5	-	0.1
	25	0.1	(2.3)	14.3	85.7	-	0.2
	100	0.1	(2.8)	19.4	80.6	-	0.1
	900	0.1	(1.9)	15.3	84.7	-	0.2
F^+	10	0.6	(14.4)	79.7	20.3	-	3
	10	0.3	(5.9)	81.0	19.0	-	3
	10	0.1	(3.0)	79.7	20.3	-	4
	23	0.4	(6.0)	82.1	17.7	0.2	5
	23	0.2	(3.1)	82.3	17.7	-	2
	23	0.1	(1.5)	81.3	18.7	-	3
	300	0.8	(9.5)	60.6	39.1	0.3	9
	300	0.3	(3.3)	60.0	40.0	-	9
	300	0.1	(1.7)	59.7	40.3	-	10
	900	0.8	(10.9)	50.8	48.8	0.4	8
	900	0.3	(2.8)	47.2	52.2	0.6	9
	900	0.1	(1.5)	46.2	53.4	0.4	12

Table 2. (Continued)

Incident	KE	Pressure		Ions			
ion	eV	microns	H_3O^+	H_2O^+	OH^+	m/e=16	Q
Xe^{++}	17	1.1	(54.8)	92.1	7.9	-	0.9
	17	0.6	(19.2)	88.4	11.6	-	0.8
	17	0.1	-	85.7	14.3	-	0.7
	35	1.2	(55.1)	84.2	15.8	-	1
	35	0.5	(16.0)	76.4	23.6	-	1
	35	0.1	(3.7)	74.1	25.9	-	1
	100	1.2	(28.8)	65.9	33.8	0.3	4
	100	0.6	(8.5)	58.2	41.4	0.4	3
	100	0.1	(1.9)	54.8	45.2	-	4
	900	1.2	(28.7)	61.3	38.3	0.4	5
	900	0.6	(7.5)	53.9	45.7	0.4	5
	900	0.1	(1.5)	50.2	49.3	0.5	5
Ar^+	12	0.1	(2.9)	100.0	0.0	0.0	8
	100	0.1	(1.3)	98.7	1.3	0.0	11
	900	0.1	(1.6)	97.8	2.2	0.0	6
Kr^+	11	0.1	(2.9)	100.0	0.0	0.0	23
	100	0.1	(1.4)	99.8	0.2	0.0	11
	900	0.1	(1.4)	99.4	0.6	0.0	10
CO_2^+	22	0.1	(1.9)	100.0	0.0	0.0	11
	100	0.1	(1.8)	99.7	0.3	0.0	11
	900	0.1	(1.4)	99.3	0.7	0.0	8

Table 3. Relative abundance in % of molecule ions, p, and "parent-plus-one", p + 1, from CH_3OH and CH_3NH_2 after charge exchange with incident positive ions of low kinetic energy (KE) as a function of the pressure in the collision chamber. The p + 1 ions are not included in the normalization.

Incident ion	KE eV	Pressure μ	CH_3OH p	CH_3OH p + 1
Ne^+	18	1.8	3.2	54.2
	18	0.9	2.1	15.5
	18	0.3	1.0	4.8
	18	0.1	0.7	3.3
F^+	30	1.3	1.2	48.0
	30	0.9	1.0	18.7
	30	0.3	1.6	7.0
	30	0.1	1.5	2.2
Ar^+	15	1.8	0.6	110.0
	15	0.9	0.4	25.7
	15	0.3	0.1	4.8
	15	0.1	0.0	2.0
Kr^+	20	1.8	0.3	108.0
	20	0.9	0.3	27.5
	20	0.3	0.4	5.5
	20	0.1	0.3	2.7
N_2O^+	20	1.8	1.1	87.0
	20	0.9	1.0	23.0
	20	0.3	1.1	6.5
	20	0.1	1.2	3.5

Incident ion	KE eV	Pressure μ	CH_3NH_2 p	CH_3NH_2 p + 1
He^+				
	25	0.7	4.0	8.6
	25	0.3	1.5	2.5
	25	0.1	1.0	1.0
Ne^+				
	18	0.7	3.6	15.3
	18	0.3	1.4	4.0
	18	0.1	1.4	2.0
F^+				
	36	0.7	3.3	13.1
	36	0.3	1.8	4.3
	36	0.1	1.0	3.0
Ar^+				
	20	0.7	2.6	13.6
	20	0.3	1.1	4.4
	20	0.1	0.4	2.3
Kr^+				
	25	0.7	0.7	8.9
	25	0.3	0.3	3.4
	25	0.1	0.5	1.9
Xe^+				
	35	0.7	0.8	9.8
	35	0.3	0.3	3.4
	35	0.1	0.2	1.7

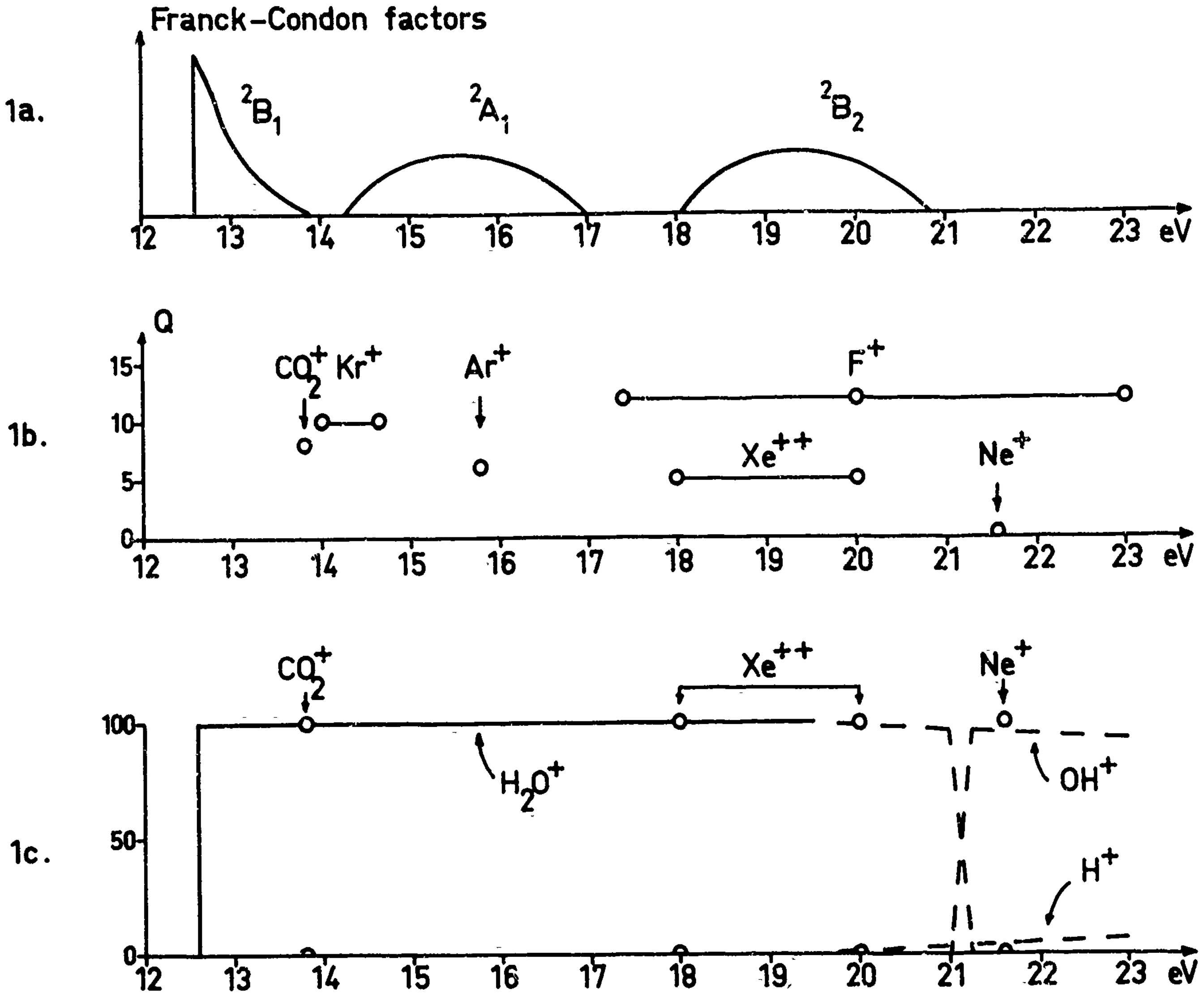

Fig. 1. a) Estimated Franck-Condon factors for ionization of H_2O.

b) Relative cross sections for charge transfer between different positive ions and H_2O.

c) Mass spectrum of H_2O as a function of energy (eV).

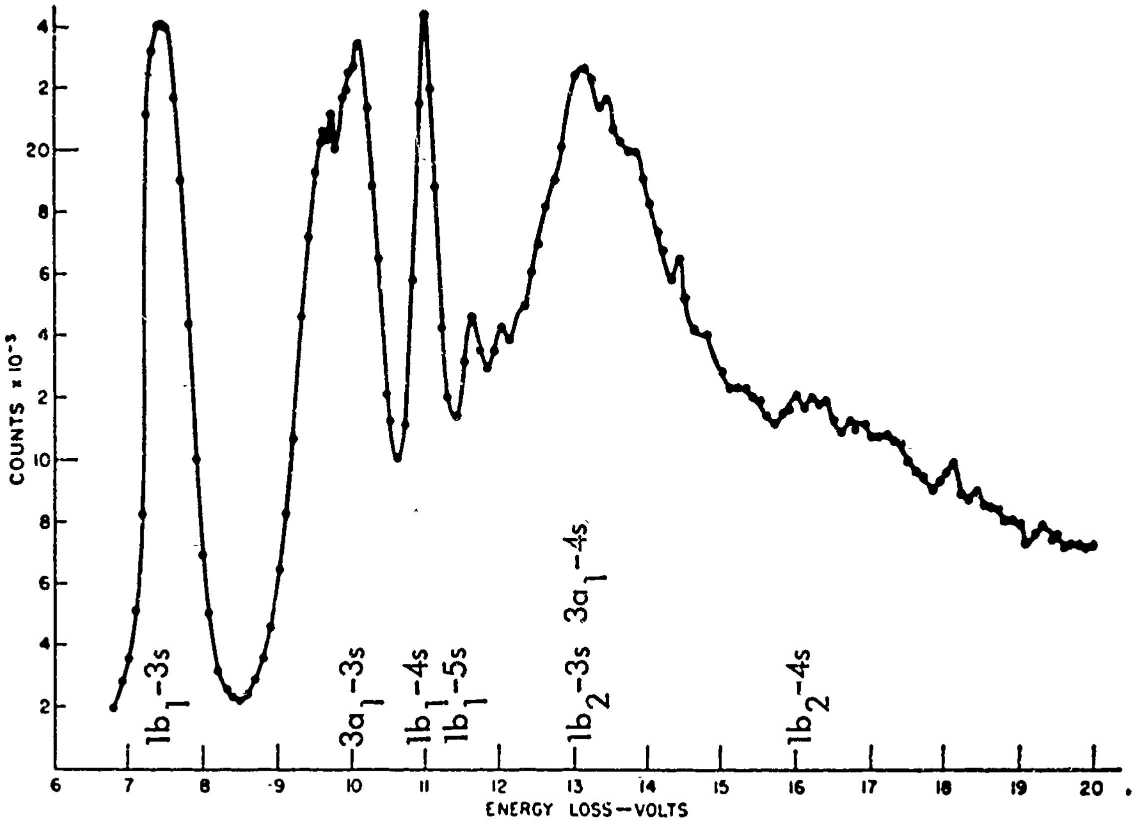

Fig. 2. Energy loss spectrum of H_2O obtained by Skerbele and Lassettre [19]. The transitions discussed in the present paper are included in the figure.

Unclassified

Security Classification

DOCUMENT CONTROL DATA - R&D

(Security classification of title, body of abstract and indexing annotation must be entered when the overall report is classified)

1. ORIGINATING ACTIVITY (Corporate author) Physics Department The Royal Institute of Technology Stockholm 70, Sweden	2a REPORT SECURITY CLASSIFICATION Unclassified 2b GROUP

3. REPORT TITLE

The ionization of water, methylamine, and methyl alcohol, using electron and ion impact.

4. DESCRIPTIVE NOTES (Type of report and inclusive dates)

Scientific report no. 7

5. AUTHOR(S) (Last name, first name, initial)

Sjögren, H.

6. REPORT DATE	7a TOTAL NO OF PAGES	7b NO OF REFS
10 May 1966	33	54

8a CONTRACT OR GRANT NO. Contract AF 61(052)-762 b. PROJECT NO. and Task No. 7635-04 c DOD Element 62405424 d DOD Subelement	9a ORIGINATOR'S REPORT NUMBER(S) 9b OTHER REPORT NO(S) (Any other numbers that may be assigned this report)

10 AVAILABILITY/LIMITATION NOTICES

11. SUPPLEMENTARY NOTES	12. SPONSORING MILITARY ACTIVITY Air Force Cambridge Research Labora- tories (CRUB) L.G. Hanscom Field Bedford, Massachusetts

13. ABSTRACT

The ionization of H_2O was investigated, using charge exchange in a double mass spectrometer. The breakdown graph was constructed. A break in the electron impact ionization efficiency curve is explained as being due to preionization, as its explanation as being due to an ion-molecule reaction between H^+ ions and H_2O seems to be less probable. The appearance potential of OH^+ was found to be considerably higher with charge exchange than when electron impact was used, which agrees with our earlier finding that intercombination transitions seem to be more strictly forbidden in charge exchange than in electron impact.

CH_3NH_2 and CH_3OH were investigated, using charge exchange at elevated pressures. The breaks in the ionization efficiency curves for these molecules are discussed and ascribed to preionization or secondary processes.

DD FORM 1 JAN 64 1473

Unclassified

Security Classification

Unclassified
Security Classification

14. KEY WORDS	LINK A		LINK B		LINK C	
	ROLE	WT	ROLE	WT	ROLE	WT
Mass spectra						
Charge exchange						
Electron impact						
H_2O						
CH_3NH_2						
CH_3OH						
Structure of H_2O						
Dissociation of H_2O^+						
Ionization						
Preionization						

INSTRUCTIONS

1. ORIGINATING ACTIVITY: Enter the name and address of the contractor, subcontractor, grantee, Department of Defense activity or other organization *(corporate author)* issuing the report.

2a. REPORT SECURITY CLASSIFICATION: Enter the overall security classification of the report. Indicate whether "Restricted Data" is included. Marking is to be in accordance with appropriate security regulations.

2b. GROUP: Automatic downgrading is specified in DoD Directive 5200.10 and Armed Forces Industrial Manual. Enter the group number. Also, when applicable, show that optional markings have been used for Group 3 and Group 4 as authorized.

3. REPORT TITLE: Enter the complete report title in all capital letters. Titles in all cases should be unclassified. If a meaningful title cannot be selected without classification, show title classification in all capitals in parenthesis immediately following the title.

4. DESCRIPTIVE NOTES: If appropriate, enter the type of report, e.g., interim, progress, summary, annual, or final. Give the inclusive dates when a specific reporting period is covered.

5. AUTHOR(S): Enter the name(s) of author(s) as shown on or in the report. Enter last name, first name, middle initial. If military, show rank and branch of service. The name of the principal author is an absolute minimum requirement.

6. REPORT DATE: Enter the date of the report as day, month, year; or month, year. If more than one date appears on the report, use date of publication.

7a. TOTAL NUMBER OF PAGES: The total page count should follow normal pagination procedures, i.e., enter the number of pages containing information.

7b. NUMBER OF REFERENCES: Enter the total number of references cited in the report.

8a. CONTRACT OR GRANT NUMBER: If appropriate, enter the applicable number of the contract or grant under which the report was written.

8b, 8c, & 8d. PROJECT NUMBER: Enter the appropriate military department identification, such as project number, subproject number, system numbers, task number, etc.

9a. ORIGINATOR'S REPORT NUMBER(S): Enter the official report number by which the document will be identified and controlled by the originating activity. This number must be unique to this report.

9b. OTHER REPORT NUMBER(S): If the report has been assigned any other report numbers *(either by the originator or by the sponsor)*, also enter this number(s).

10. AVAILABILITY/LIMITATION NOTICES: Enter any limitations on further dissemination of the report, other than those imposed by security classification, using standard statements such as:

(1) "Qualified requesters may obtain copies of this report from DDC."

(2) "Foreign announcement and dissemination of this report by DDC is not authorized."

(3) "U. S. Government agencies may obtain copies of this report directly from DDC. Other qualified DDC users shall request through
____ ."

(4) "U. S. military agencies may obtain copies of this report directly from DDC Other qualified users shall request through
____ ."

(5) "All distribution of this report is controlled. Qualified DDC users shall request through
____ ."

If the report has been furnished to the Office of Technical Services, Department of Commerce, for sale to the public, indicate this fact and enter the price, if known.

11. SUPPLEMENTARY NOTES: Use for additional explanatory notes.

12. SPONSORING MILITARY ACTIVITY: Enter the name of the departmental project office or laboratory sponsoring *(paying for)* the research and development. Include address.

13 ABSTRACT: Enter an abstract giving a brief and factual summary of the document indicative of the report, even though it may also appear elsewhere in the body of the technical report. If additional space is required, a continuation sheet shall be attached.

It is highly desirable that the abstract of classified reports be unclassified. Each paragraph of the abstract shall end with an indication of the military security classification of the information in the paragraph, represented as *(TS)*, *(S)*, *(C)*, or *(U)*.

There is no limitation on the length of the abstract. However, the suggested length is from 150 to 225 words.

14. KEY WORDS: Key words are technically meaningful terms or short phrases that characterize a report and may be used as index entries for cataloging the report. Key words must be selected so that no security classification is required. Identifiers, such as equipment model designation, trade name, military project code name, geographic location, may be used as key words but will be followed by an indication of technical context. The assignment of links, rules, and weights is optional.

Unclassified
Security Classification