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Penning ionization electron spectroscopy of water molecules by metastable neon atoms

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ABSTRACT

The Penning ionization electron spectra in metastable $Ne^*(^3P_{0,2})$ colliding with H_2O molecules at 0.040, 0.075, 0.130, 0.200 and 0.300 eV collision energies have been measured and compared with the photo-electron spectrum with $Ne(I)$ photons. The results show the formation of the ground $\tilde{X}(^2B_1)$ and the first excited state $\tilde{A}(^2A_1)$ of the H_2O^+ product ion, with a $\tilde{X}/\tilde{A}$ branching ratio slightly increasing with the collision energy, and with an average value of 0.29 ± 0.03. The spectra have been analyzed in order to obtain some information and some basic features of the potential energy interaction between the two reacting particles.

1. Introduction

Reactions between metastable rare gas atoms and molecules are rather interesting because of their importance in a variety of applications, like electronic energy transfer, molecular dissociation, excimer formation, and Penning ionization. As an example, the reactions between metastable argon, krypton and xenon atoms with halogen-containing molecules have been extensively studied because their applications to the development of rare-gas halide excimer lasers. On the other hand, the role of metastable rare gas atoms in the atmospheric reactions is of interest for several reasons [1].

The content of rare gas atoms in the atmosphere is not negligible: actually argon is the third component of the dry air, after nitrogen and oxygen molecules, and some studies have shown that the exosphere is rich in $He^*(2^1S_0)$ [1]. Moreover, the rate constant for ionization processes induced by metastable rare gas atoms is generally larger than those of common bimolecular chemical reactions of atmospheric interest, involving ground state neutral species.

Furthermore, the metastable rare gas atoms at high interatomic separation behave as alkaline metals because of their weakly bound external electron, whereas at shorter distances becomes prominent the role of their core looking like halogen atoms. Therefore, their phenomenological behaviour, when interacting with hydrogenated molecules (H_2O, NH_3, H_2S), is very interesting for fundamental and applied science, as shown by the many discussions in the literature about the role of hydrogen and halogen bonds [2].

The Penning ionization is a widely studied elementary process, because collisional autoionization of intermediate complexes represents one of the most fundamental processes for chemi-ionization [3,4]. Several experimental techniques are used to study the microscopic dynamics of these collisional autoionization processes. It is well established that the most valuable information about the dynamics of a collisional process is provided by molecular beam scattering experiments [3,4]. In fact, in these cases it is possible to study single collision events and also to define the translational and internal energy of the two colliding partners, thus avoiding statistical averaging. In some systems, molecular orientation or orbital polarization during the collision can also be achieved by using appropriate external fields or laser light as it is discussed, for instance, in Ref. [5]. The most detailed studies on collisional autoionization are those where the molecular beam technique is coupled with an appropriate detection method of product particles such as electrons, ions, neutral atoms or molecules and, in some cases, photons [3,4].

Penning ionization of water molecules is an important subject and has been studied in several previous experimental and theoretical works. Early studies reported by Yee et al. [6] and by Cermák and Yencha [7] have been performed exploiting the electron spectroscopy in collisions with $He^*(2^1S, 2^3S)$ metastable atoms, while Sanders and Muschlitz [8] have reported a mass spectrometric investigation of the final ionization products in this system. Such studies demonstrated that the ionization of H_2O molecules by metastable helium atoms leads to the formation of nascent H_2O^+ ions in the ground, $\tilde{X}(^2B_1)$, and in the first two excited

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states, $\tilde{A}(^2A_1)$ and $\tilde{B}(^2B_2)$. Moreover, a dissociation of the molecular ion takes place with the formation of OH^+ in addition to molecular H_2O^+ ions, beside 4.2% of other ionic products. Later on, Ohno et al. [9], Mitsuke et al. [10] and Haug et al. [11] reported electron energy spectra for the same system, but measured with metastable helium in the pure 2^3S state. More recently, an *ab initio* potential energy surface for $He^*(2^3S)–H_2O$ system was calculated by Ishida [12] and used for a quasi-classical trajectory calculation of the Penning ionization process [13]. These investigations have shown how the formation of each electronic state of the nascent ion is correlated with specific directions of approach of the metastable atom to the molecule and demonstrate that the overall interaction between He^* and H_2O is characterized by a strong attraction, being more intense for the approach direction along the C_{2v} axis of the molecule with respect to the perpendicular case [9–13]. In 1994 Ben Arfa et al. [14] measured the electron energy for the three observed H_2O^+ states, $\tilde{X}(^2B_1)$, $\tilde{A}(^2A_1)$ and $\tilde{B}(^2B_2)$, in a Penning ionization electron spectroscopy (PIES) study of $He^*(2^1S)–H_2O$ collisions, also obtaining evidences for a strong anisotropy of the $He^*–H_2O$ interaction potential energy surface.

The ionization of H_2O by thermal energy collisions with metastable neon atoms involves the formation of only two states of the nascent H_2O^+ ion, $\tilde{X}(^2B_1)$ and $\tilde{A}(^2A_1)$, since the two spin–orbit states ($^3P_2$ and $^3P_0$) of metastable Ne^* atoms have not enough energy to produce upper molecular ionic states. For such a system, only an early low resolution electron spectroscopy experiment [7] and a theoretical study of the potential energy surface [15] have been published so far.

In the present letter we report on an experimental investigation of the ionization of H_2O molecules by collision with $Ne^*(^3P_{2,0})$ atoms, in the 0.040–0.300 eV energy range, by the measurement of the energy distribution of emitted electrons with a resolution higher than in the early experiment [7]. Several PIES spectra have been here recorded at different collision energies and compared with photo-electron spectroscopy (PES) data obtained with Ne(I) photons. Our results are then discussed and compared with experimental and theoretical information previously reported. The analysis of the present PIES and PES spectra provides interesting features about the dynamics of the $Ne^*–H_2O$ collisional autoionization process and makes possible to characterize some aspects of the interaction potential between the two colliding partners. Also the $Ne^*–H_2O$ interaction appears to be strongly anisotropic and attractive with a more attractive approach of the Ne^* atom towards the C_{2v} molecular axis of H_2O when compared with that along the

perpendicular direction, as it has been already found for $He^*–H_2O$ system [9–14].

The present work aims to complete and integrate previous studies on the same system with particular attention to underline possible effects resulting from the collision energy dependence.

2. Experimental

The Perugia crossed molecular beam set up has been already used previously for ionization cross section studies [16–18], and has been recently modified to allow also electron energy analysis of emitted electrons [19,20], which represents a crucial aspect of the present investigation. Basically, it consists of a metastable rare gas atom beam, which crosses at right angles an effusive secondary beam of molecules produced by a microcapillary array source. When an ionization cross section measurement is performed, the ions produced in the collision zone are extracted, focused, mass analyzed by a quadrupole filter and then detected by a channel electron multiplier. The apparatus, schematically shown in Figure 1, consists of three vacuum chambers: the first one contains the rare gas beam source, while in the second chamber the rare gas atoms are electronically excited and pulsed by a slotted disk; in the third chamber the metastable atoms cross the target molecules of a secondary beam (perpendicular to the plane of the figure and therefore not visible). In this chamber the metastable atoms are monitored, while product ions and emitted electrons are detected, after mass analysis, for the ions, and energy selection, for the electrons.

The neon beam can be produced by two sources that can be used alternately. The first one is a standard effusive source at room temperature while the second one is a supersonic device that can be heated to different temperatures. In both cases the metastable atoms are produced by electron bombardment at ~150 eV, that is expected [19] to yield $Ne^*(^3P_2)$ and $Ne^*(^3P_0)$ in a population close to the statistical 5:1 ratio. The metastable atom velocity can be analyzed by a time-of-flight (TOF) technique. In the case of the supersonic expansion, the metastable neon atoms emerge from a nozzle source (60 μm diameter; stagnation pressure between 4 and 5 atm) producing a supersonic atomic beam well-defined in velocity ($\Delta v/v \approx 0.1$). The collision energy dependence of the ionization cross sections and of the PIES spectra is achieved by varying the nozzle temperature (between 300 and 700 K) of the supersonic source and by using, beside pure neon, two different Ne:H_2
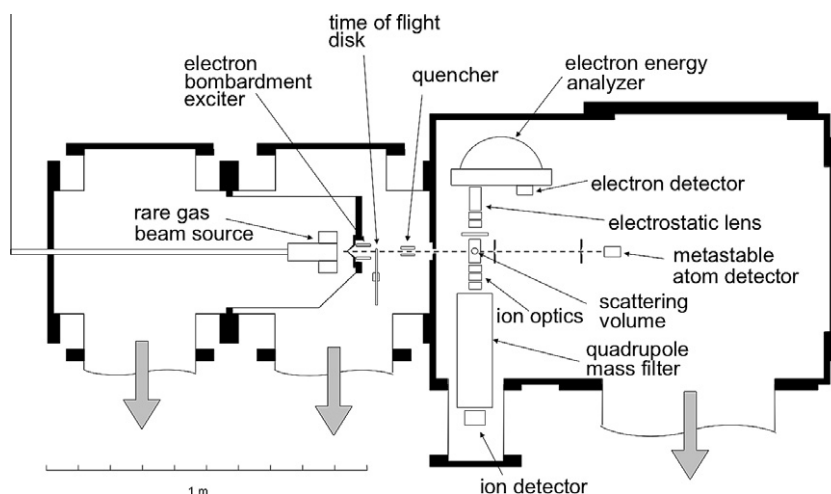

Figure 1. Schematic set up of the apparatus used for the measurement of ionization cross sections and electron energy spectra, in collision of metastable rare gas atoms and target molecules. The target molecule beam, which crosses in the scattering volume the metastable atom beam, is perpendicular to the plane of the figure.

mixtures (50:50 and 20:80 ratios). In this way we have been able to produce neon beams with a velocity distribution centered at 750, 1050, 1260, 1490, 1680 and 2330 m/s (collision energy range from 0.040 to 0.300 eV). In general the two metastable sources are used to carry out both the ionization cross section measurements as well as the PIES spectra. The first method allowed us to obtain the collision energy dependence for the ionization cross sections in a single experiment, while the second, which requires an experiment for each single collision energy, permits to work with higher intensity signals and to record PIES spectra with relatively short accumulation time. For the spectra here reported, typical accumulation times are of the order of few hours.

The secondary molecular beam of H_2O is prepared by effusion of water vapor from a glass microcapillary array kept at room temperature. The metastable atom beam is detected by a channel electron multiplier placed along the beam direction, after the scattering center. A total ionization detector monitors the secondary beam intensity. The collision energy resolution is largely defined by the thermal spread of the target molecules effusing from the microcapillary source.

For the measurement of electron energy spectra, a hemispherical electrostatic selector has been used [19,20]. This is located above the beam crossing volume. During electron spectroscopy experiments, the ion extracting field of the mass spectrometer is maintained off, in order to do not perturb the electron energy. An appropriate electron optics is used to focus the electrons from the scattering volume to the hemispherical analyzer and, after energy selection, the electrons are detected by a channel electron multiplier. To calibrate the electron transmission efficiency and the electron energy scale, some H_2O PES spectra have been measured. In this case, in place of the electron bombardment metastable atom beam source described above, a microwave discharge in pure neon is exploited. Such a source produces a high intensity of $Ne(I_{\alpha,\beta})$ photons, essentially of 73.6 and 74.4 nm wavelenght respectively, in a α:β ratio of about 5.3, checked by photoelectron spectrometric measurements of Kr atoms [19,21]. However, also many metastable neon atoms are produced by such a source. The following procedure has been applied to avoid an interference of the PIES spectrum with that for PES one. The pumping speed in the second chamber has been decreased, resulting in an increased pressure of neon. This produces a strong attenuation by scattering
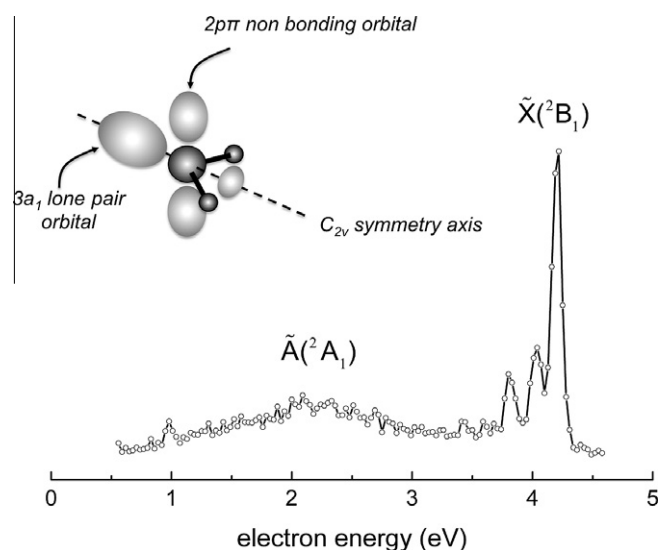

Figure 2. Photoionization spectrum of H_2O by Ne(I) photons. The inset shows schematically the molecular orbitals from where the electron is ejected for the formation of the two observed states of H_2O^+ ion.

of metastable neon atoms in the beam, while the photon intensity does not change sensibly [19]. The photoionization spectrum of H_2O by Ne(I) photons has been then recorded (see Figure 2) and used for calibrating energy scale and transmission of the electron analyzer. In particular, it has been exploited the comparison of our measurements with the expected spectrum as obtained from the He(I) radiation by Kimura et al. [22] to readjust appropriately the ionization energy scale. The resolution of our electron spectrometer is ~45 meV at a transmission energy of 3 eV, as determined by measuring the photoelectron spectra of Ar, O_2, and N_2 by He(I) radiation with the procedure described in a previous paper [20]. Spurious effects due to the geomagnetic field have been reduced to ⩽20 mG by a μ-metal shielding.

3. Results and discussion

The energy spectra of the electrons emitted during the ionization of water molecules by mestastable neon atoms are reported in Figure 3 for five different collision energies: 0.040, 0.075, 0.130, 0.200, and 0.300 eV. For each energy several PIES spectra are recorded and in the Figure 3 we report only a representative set of the experimental data. These data appear to be in good agreement with previous unpublished results from another laboratory [23]. In the PIES studies, it is well known that when the position of the maximum of a certain peak exhibits a sizeable negative shift, here referred as ε_{max}, with respect to the nominal energy, ε_0, defined as the difference between the excitation energy of Ne* and the ionization potential of the relevant molecular state, this is an indication of a phenomenological attractive behavior of the interaction between the neutral and ionic partners [7,8,15,24].

All the measured spectra show the bands for the two energetically accessible states of the H_2O^+ product ion, namely the ground $\tilde{X}(^2B_1)$ and the first $\tilde{A}(^2A_1)$ excited states. Within the experimental uncertainty it appears that the relative intensity of the two bands changes only with a slight increase with the collision energy, at least in the investigated energy range, as can be seen in Figure 4. The measured branching ratio varies between 0.26 and 0.31, with an average value of 0.29 ± 0.03, from 0.040 to 0.300 eV. For the evaluation of the branching ratios we used the peak areas in the PIES spectra, as obtained by a simple Gauss function fitting. Cermák and Yencha [7] in their early PIES studies of He* and $Ne^*(^3P_2)$–H_2O have also observed a larger production of $\tilde{A}(^2A_1)$ excited H_2O^+ ions with respect the ground $\tilde{X}(^2B_1)$ state.

All these experimental findings, together with the energy shift evaluations, are a strong indication that the interaction potential driving the $\tilde{A}$ excited state formation exhibits an effective interaction potential well deeper with respect to that involved in the production of the $\tilde{X}$ ground state [9,10]. However, the slight increase of the $\tilde{X}/\tilde{A}$ branching ratio with the collision energy suggests that the difference between the two potential energy well depth is meaningful, but not very large. These findings cannot be accounted for by assuming an intermolecular interaction arising from van der Waals and dipole-induced dipole attractions, suggesting that Penning ionization takes place over a wide range of intermolecular distances. Note that from our PIES spectra no change on the peak shapes for the $\tilde{X}$ and $\tilde{A}$ states is evident by varying the collision energy (see Figure 3).

How mentioned above, the two bands in the electron energy spectra of Figures 2 and 3 are related to the formation of the two possible $\tilde{X}(^2B_1)$ and $\tilde{A}(^2A_1)$ states of the H_2O^+ ion. The formation of these states corresponds to the removal of one electron from one of the two non bonding orbitals of the neutral molecule [9–11]. The directions of these two orbitals are schematically shown in the inset of Figure 2. The ground state $\tilde{X}(^2B_1)$ H_2O^+ ion is formed by the removal of one electron from the 2pπ lone pair
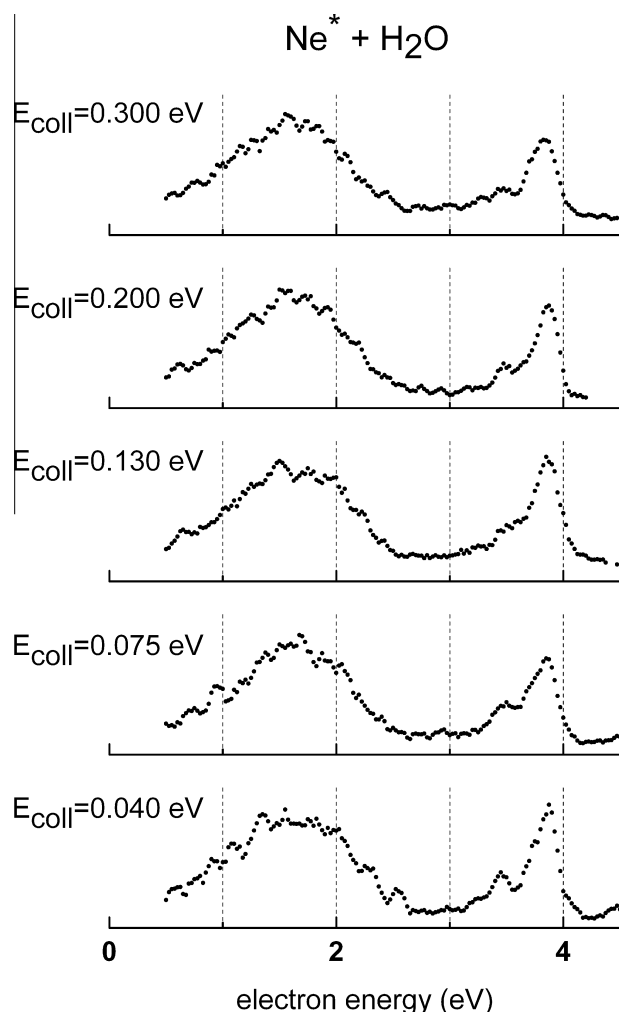
Figure 3. Energy distribution of emitted electrons during the Ne*–H$_2$O ionization, at 0.040, 0.075, 0.130, 0.200 and 0.300 eV collision energies.

orbital, while for the formation of the excited Ã($^2A_1$) H$_2$O$^+$ ion, the electron must be removed from the $3a_1$ lone pair orbital. It is generally assumed that the mechanism for Penning ionization occurs essentially through a passage of the outer shell electron of the molecule to be ionized into the inner shell vacancy of the metastable rare gas atom, leading to the ejection of the excited electron of
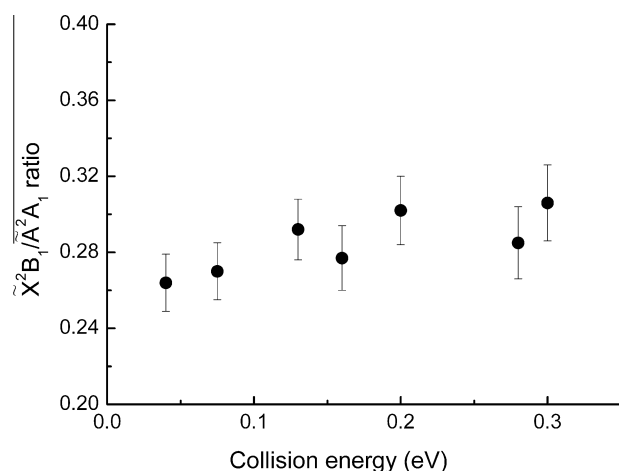

Figure 4. Experimental X̃($^2B_1$)/Ã($^2A_1$) branching ratio for the H$_2$O$^+$ product ion.

the latter [9,24]. This implies that the ionization, leading to a specific state of the product ion, occurs when the metastable atom approaches the molecule closely to the direction of the involved molecular orbital [9,24,25]. Therefore, we can assert that the two bands in the spectra of Figure 3 are related to ionization events occurring with two different geometries of the system: the X̃($^2B_1$) band is originated from a collision complex with the metastable neon atom perpendicular to the plane of the molecule, while for the Ã($^2A_1$) band, at the instant of the ionization, the metastable atom approaches water in the direction of the C_{2v} symmetry axis. According to the potential energy surface calculation of Bentley [15], these interactions between the two colliding partners are found to be different along these two directions, of about 100–200 meV. In particular, the interaction between the metastable atom and the H$_2$O molecule along the C_{2v} direction is much more attractive than along the direction of the $2p\pi$ lone pair orbital. This is in agreement not only with the experimental determination of the X̃/Ã branching ratio obtained in the present work but also with the evaluation of the energy shifts from the measured PIES spectra (see Table 1).

Indeed, the spectra of Figures 2 and 3 clearly show a strong negative shift, ε_{max}, between the maxima of the X̃($^2B_1$) $v = 0$ H$_2$O$^+$ peaks in the PES and in the PIES measurements higher than 0.22 eV, that is the energy difference between Ne(I_α) photons and Ne*($^3P_2$) metastable atoms. A shift value of -140 ± 20 meV was determined assuming that the electron signal in the PIES spectrum is mainly due to Ne*($^3P_2$) atoms (see Section 2), and the Ne(I_α) photons are responsible for the main peak in the PES spectrum at higher electron kinetic energy (4.145 eV). The energy shift so determined, is a good indication of a strong attractive interaction when Ne* atoms approach and ionize H$_2$O perpendicularly to the plane of the molecule. As it can be seen in Table 1, our experimental value shows a considerable difference with the shift value of -70 meV recorded by Cermák and Yencha in 1977 [7]. This discrepancy is probably due to the difference in the electron energy resolution of the electron analysers used. In the case of the Ã($^2A_1$) state of H$_2$O$^+$, we can determine, following the same procedure previously used by Cermák and Yencha [7] and by Haug et al. [11], the energy shift , ε_{max}, referred to the maximum of Ã band measured in the PIES spectra. In that a way we obtained a much higher negative value of the shift, -300 ± 20 meV, respect to the one for the X̃ state. This value is in fairly good agreement with the previous experimental determinations of -350 meV by Cermák and Yencha [7] (see Table 1).

These measured energy shifts are very large, both for the X̃ and Ã H$_2$O$^+$ states, indicating that a chemical interaction takes place during the Ne*–H$_2$O collisions. This strong interaction is probably due to the considerable dipole moment, which characterizes the water molecule being more intense when the neon metastable atoms approach H$_2$O along the C_{2v} direction, encountering the $3a_1$ lone pair orbital of the oxygen atom, and the pronounced electronic cloud deformation of highly polarizable Ne* atom.

Note that just looking at the PIES spectra of Figure 3, in the case of the X̃($^2B_1$) state it is possible to extract not only the negative shift, ε_{max}, for the maximum of peak ($v = 0$) but also the shift between the electron energy value where the peak intensity drop down to the 44% of its maximum at the lower energy side, ε_A, respect to the nominal energy, ε_0 [26], obtaining a value of -320 ± 20 meV, as also reported in Table 1.

These findings allow us to confirm the strong attractive behavior of the Ne*–H$_2$O interaction promoting the Penning process. In fact, as suggested by Haug et al. [11], the energy shift ε_A can be used as a proper indication for the attractive well depth of the interaction between the colliding particles. In our case this estimation can be done only for the Ne* approach interaction perpendicular to the H$_2$O molecular plane. The ε_A value of -320 ± 20 meV is a

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Table 1
Negative energy shifts from the PIES Ne*–H_2O spectra measured in the collision energy range of 0.040–0.300 eV.

Band in PIES	Shifts with respect to nominal energy ε_0 (meV)			
	$\tilde{X}(^2B_1)$ state of the H_2O^+ ion		$\tilde{A}(^2A_1)$ state of the H_2O^+ ion	
	This work	Ref. [7]	This work	Ref. [7]
Maximum of peak ($v=0$) ε_{max}	-140 ± 20	-70	$-300 \pm 20^*$	-350^*
44% of maximum ($v=0$) ε_A	-320 ± 20	–	–	–

* Evaluated from the maximum of band.

proper estimation of the strong attractive interaction for this approach direction in the Ne*–H_2O system and is in good agreement with the calculations performed by Bentley [15] who obtained a dissociation energy of about 250 meV for the formation of a Ne*–O bond when the metastable neon approaches the oxygen atom of the water molecule. An analogous evaluation for the ε_A shift is not possible here for the $\tilde{A}$ state of H_2O^+ ions because in this case a broad band in the PIES spectra do not satisfies the features required by the theory [26–28]. Therefore, concerning the Ne*–H_2O collisions along the C_{2v} molecular axis direction, we can only say that the interaction should be stronger and characterized by an effective potential well depth deeper than 320 meV, since the dipole and deformation effects (see above) play an increased role. Indeed, for this direction of Ne*–H_2O approach, Bentley [15] calculated a well depth for the ground and certain excited states ranging between 400 and 600 meV. Such a behavior for the Ne*–H_2O system is confirmed by the observation of Haug et al. [11] in the He*(2^3S)–H_2O collisions where the binding energy for an approach along the C_{2v} axis is larger than for the approach perpendicular to the molecular plane, the well depths being about 600 and 450 meV respectively.

4. Conclusions

The present experimental results show the evidence of a strong attraction that dominates the potential energy surface describing the interaction and the ionization in metastable neon atoms with H_2O molecule, for those orientations and distances where the ionization mainly occurs. A similar situation for metastable helium and metastable neon atoms interacting with N_2O molecules [29] has been recently explained by the use of a semiempirical method that accounts for the metastable atom orbital deformation because the permanent dipole of the molecule [29]. We have in plan to extend such a model also to the present system, and testing the potential energy surface so obtained by measuring also the collision energy dependence of the total ionization cross section. In such a model, at shorter distances, because of the strong polarization of Ne*, the interaction switches to an electrostatic component due to ion–water charge distribution contribution and size repulsion–induction attraction [29]. In such a way, the present experimental findings could be rationalized, taking into account the critical balancing between molecular orientation effects in the intermolecular interaction field and the ionization probability.

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