

See discussions, stats, and author profiles for this publication at: <https://www.researchgate.net/publication/262071165>

Penning Ionization Electron Spectroscopy of Hydrogen Sulfide by Metastable Helium and Neon Atoms

ARTICLE *in* THE JOURNAL OF PHYSICAL CHEMISTRY A · MAY 2014

Impact Factor: 2.69 · DOI: 10.1021/jp5030312 · Source: PubMed

CITATIONS

4

READS

35

5 AUTHORS, INCLUDING:



Stefano Falcinelli

Università degli Studi di Perugia

83 PUBLICATIONS 757 CITATIONS

[SEE PROFILE](#)



Pietro Candori

Università degli Studi di Perugia

54 PUBLICATIONS 580 CITATIONS

[SEE PROFILE](#)



Bettoni Marta

Università degli Studi di Perugia

15 PUBLICATIONS 89 CITATIONS

[SEE PROFILE](#)



Franco Vecchiocattivi

Università degli Studi di Perugia

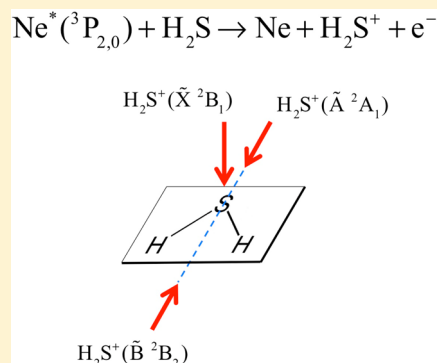
120 PUBLICATIONS 1,773 CITATIONS

[SEE PROFILE](#)

Penning Ionization Electron Spectroscopy of Hydrogen Sulfide by Metastable Helium and Neon Atoms

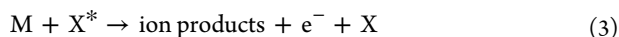
Stefano Falcinelli,[†] Pietro Candori,[†] Marta Bettoni,[†] Fernando Pirani,[‡] and Franco Vecchiocattivi^{*,†}[†]Dipartimento di Ingegneria Civile ed Ambientale, Università di Perugia, 06125 Perugia, Italy[‡]Dipartimento di Chimica, Biologia e Biotecnologie, Università di Perugia, 06123 Perugia, Italy

ABSTRACT: The dynamics of the Penning ionization of hydrogen sulfide molecules by collision with helium and metastable neon atoms, occurring in the thermal energy range, has been studied by analyzing the energy spectra of the emitted electrons obtained in our laboratory in a crossed beam experiment. These spectra are compared with the photoelectron spectra measured by using He(I) and Ne(I) photons under the same experimental conditions. In this way we obtained the negative energy shifts for the formation of H₂S⁺ ions in the first three accessible electronic states by He*(2^{3,1}S_{1,0}) and Ne*(³P_{2,0}) Penning ionization collisions: the 2b₁ (\tilde{X}^2B_1) fundamental one, the first 5a₁ (\tilde{A}^2A_1), and the second 2b₂ (\tilde{B}^2B_2) excited states, respectively. The recorded energy shifts indicate that in the case of He* and Ne*–H₂S the autoionization dynamics depends on the features of the collision complex and is mainly driven by an effective global attraction that comes from a balance among several non covalent intermolecular interaction components. This suggests that the Penning ionization should take place, in a specific range of intermolecular distances, as we have already observed in the case of Penning ionization of water molecules [Brunetti, B. G.; Candori, P.; Falcinelli, S.; Pirani, F.; Vecchiocattivi, F. *J. Chem. Phys.* **2013**, 139, 164305-1–164305-8].



1. INTRODUCTION

In general, an atomic or molecular species (M) can be ionized by using photons of enough energy: in this case, we can perform photoionization studies (reaction 1). Alternatively, it is possible to induce ionization via collision events involving energetic and excited particles, like energetic electrons (reaction 2) and metastable atoms or molecules (reaction 3).



In the latter case, we have the so-called Penning ionization or chemionization processes after the early observation in 1927 by Penning.¹ In such a reaction, X* indicates an excited atom or molecule with an energy content large enough to ionize the collisional partner M, and the products can be the parent M⁺ ion (Penning ionization), the aggregate MX⁺ (associative ionization), or possible fragment product ions coming by dissociative ionization.^{2,3}

Energetic particles able to induce Penning ionization are the rare gas atoms excited to their first electronic level (of ns¹ external configuration). These atoms are metastable because of their long lifetime. They are also able to ionize almost all atomic and molecular collisional partners. (Their high-energy content ranges from 8.315 eV in the case of Xe*(³P₂) up to 20.616 eV for He*(¹S₀).)

The rate constants for Penning ionization processes are on the same order of magnitude of gas-phase bimolecular reactions

of O(¹D), Cl, or Br, which are known to be relevant in atmospheric chemistry, whereas other reactions exhibit rate constants that are at least one order of magnitude smaller.^{4,5} This means that Penning ionization is a fast reaction that can play an important role in the characterization of thermal plasmas, electrical discharges, and the production of laser systems.^{2,3} Moreover, these reactions are also important in the atmospheric chemistry studies not only of our planet.^{6,7} Considering the planetary atmospheric compositions, we have already proposed that rare gas atoms can be involved in several phenomena not only on Earth but also on other planets of the Solar System, like Mars and Mercury.⁸

Looking more carefully at the microscopic dynamics of the reaction 3, it can be seen that during the collision between a metastable rare gas atom, Rg*, and an atomic or molecular target, M, an excited collisional complex [M⋯Rg]* can be produced. This transient species will lose its energy content by electron emission forming different product ions. Such a collisional autoionization process can be schematically written as follows



[M⋯Rg]* is a collision complex in an autoionizing state that ejects one electron in an average time on the order of 10^{−15} s,

Special Issue: Franco Gianturco Festschrift

Received: March 27, 2014

Revised: May 2, 2014

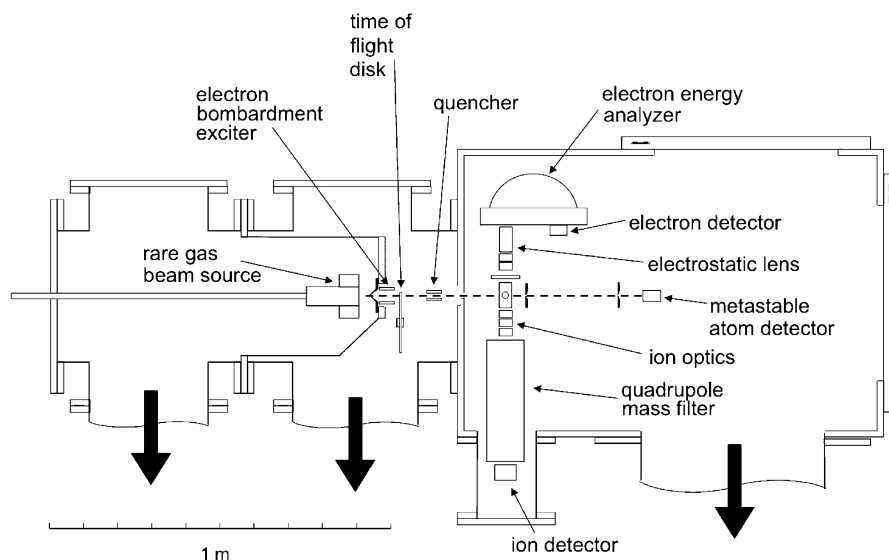
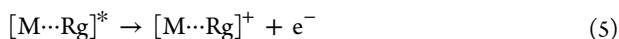


Figure 1. Schematic representation of the experimental setup used for Penning ionization experiments. The apparatus is used for the measurement of ionization cross sections and electron energy spectra in collision of metastable rare gas atoms and target molecules. The target molecule beam, which crosses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

making the electron spectrum a sort of instantaneous picture of the energy content of the collision complex, which mirrors the interaction potential at the instant of the ionization event



In that sense, reactions 4 and 5 represent the collisional microscopic dynamics formation of the transition state for Penning ionization reactions. The $[M \cdots Rg]^+$ ionic complex then evolves toward the final ionic products (reaction 6). For this reason, Penning ionization processes are also called collisional autoionization reactions³



Therefore, the experimental investigation of these phenomena is important to discover details of the stereo dynamics, arising from the combined effects of intermolecular forces, which control the entrance and exit channels of the ionizing processes. In addition, the obtainable information is crucial to formulate reliable models to be used for the description of complex systems interesting for applications.

In general, to experimentally investigate the microscopic dynamics of these processes it is usual to detect the ionic products by a mass spectrometry technique or it is possible to measure the kinetic energy of emitted electrons, performing a real spectroscopy of the transition state for such a reaction. In that way, information can be obtained concerning structure and energetics of the intermediate collision complex.

Moreover, it has to be noted that the chemical behavior of the rare gas excited atoms shows a double chemical behavior: at large separation from atomic or molecular partners, they behave as alkali metals because of their weakly bound and highly polarizable external electron, whereas at shorter distances the interaction predominantly involves their internal ionic core, exhibiting the electronic configuration of an halogen atom. For this reason, their behavior, when interacting with hydrogenated molecules (H_2O , NH_3 , H_2S), becomes even more intriguing, as witnessed by the several discussions in the literature about the possible differences and similarities of hydrogen and halogen bonds.^{9,10}

We have recently studied the ionization of water molecules by penning ionization electron spectroscopy (PIES) technique. The analysis of the obtained results shows the evidence of a strong anisotropic attraction that controls the stereo dynamics in the entrance channels of Ne^*-H_2O ionization processes.^{11,13} In this paper, we report new experimental results, obtained in our laboratory about $He^*(2^1S_0, 2^3S_1)$ and $Ne^*(3P_{0,2})-H_2S$ systems. Previous PIES experiments on H_2S were made in early works by Čermák and Yench¹⁴ and by Brion and Yee.¹⁵ Later on, Ohno and coworkers measured the total and angular distributions of emitted electrons by $He^*(2^3S_1)-H_2S$ collisional ionization,^{16,17} and the kinetic energy dependence of partial cross section in $He^*(2^3S_1)-H_2S$ producing H_2S^+ in the three energetically allowed electronic states \tilde{X}^2B_1 , \tilde{A}^2A_1 , and \tilde{B}^2B_2 .¹⁸ More recently, Tokue et al. studying the $He^*(2^3S_1)-H_2S$ Penning ionization has calculated the Franck–Condon factors for the $H_2S(\tilde{X}^2A_1, v' = 0) \rightarrow H_2S^+(\tilde{X}^2B_1, \tilde{A}^2A_1)$ ionization and $H_2S^+(\tilde{A}-\tilde{X})$ transition.^{19,20}

In the following sections, we present a comparative analysis of the measured PIES and PES (photo electron spectra) results for $He^*(2^1S_0, 2^3S_1)$ and $Ne^*(3P_{2,0})-H_2S$ autoionizing collisions. Moreover, the comparison of present results with those recently measured for Ne^*-H_2O , obtained under the same experimental conditions, also allows us to perform an internally consistent comparison of the observed behaviors and permits us to identify relevant differences in the Penning ionization stereo dynamics of the two hydrogenated molecules.

2. EXPERIMENTAL SETUP

In general, bimolecular reactions relevant in the atmospheric chemistry can be studied in a crossed molecular beams apparatus, like the one in operation in our laboratory for a long time and sketched in Figure 1. The used setup is a crossed beam apparatus already described in detail elsewhere.^{21–24} It consists of three vacuum chambers that are differentially pumped at a pressure of $\sim 10^{-7}$ mbar. In the first and second chambers, on the left side of the Figure, we produce a metastable rare gas atomic beam by electron bombardment or by microwave discharge. In the third chamber, which contains

the scattering zone on the right side of the Figure, the atomic beam of metastable atoms crosses at right angle a molecular beam of the target particles, inducing the collisional auto-ionization events under study. When we are interested in mass spectrometric study (this is not the case of the present work), the product ions are extracted from the crossing beam region by an electrostatic lens system toward the quadrupole mass spectrometer located just below the scattering center. After their mass selection, the ions are detected by a channel electron multiplier. When interested in the kinetic energy of emitted electrons, we use an hemispheric electrostatic analyzer that is located above the crossing beam volume. In such a way, we can perform, under the same experimental conditions, both PES and PIES measurements. This can be easily achieved because the microwave discharge produces not only metastable atoms but also many He(I) and Ne(I) photons having an energy comparable to that of metastable atoms.¹¹ The differences that we have observed between the spectra for photo and for Penning ionization are crucial to better isolate the main characteristics of the collision dynamics for these processes, such as the effect of the intermolecular potentials, the preferential geometries for the approach of the collisional partners, and the molecular orbitals involved in the ionization mechanism. To calibrate the electron transmission efficiency and the electron energy scale, some He*–H₂S PIES and Ne(I)–H₂S PES spectra have been measured by the microwave discharge: in the first case, we use for the energy calibration the weak electron signal by He(I) photons of 21.22 eV (see Figure 2), whereas in the latter case we record a PES spectrum (see

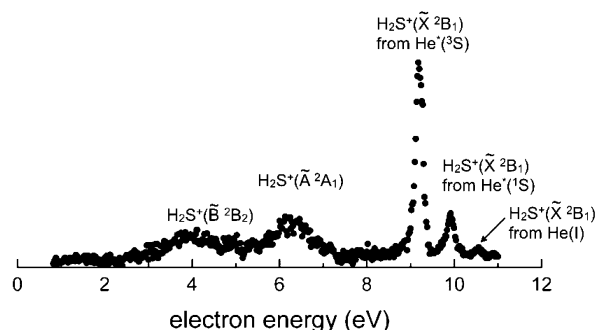
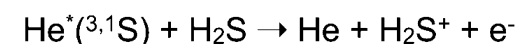


Figure 2. PIES spectrum obtained in He*(2¹S₀, 2³S₁)–H₂S collisions with a resolution of ~45 meV. The spectrum contributions of the two He*(2³S₁) and He*(2¹S₀) states for the production of H₂S⁺ in the ground 2b₁ (\tilde{X}^2B_1) state are well separated. The small signal recorded at an electron energy of 10.74 eV is due to He(I) photons and was used to calibrate the energy scale.

Figure 3) using the discharge source in pure neon producing a high intensity of Ne(I _{α,β}) photons, essentially of 16.84 and 16.66 eV, respectively, in a α/β ratio of ~5.3, checked by photoelectron spectrometric measurements of Kr atoms.^{24,25} However, also many metastable neon atoms are produced by such a source, as previously mentioned. The following procedure has been applied to avoid an interference of the PIES spectrum with that for the PES one. The pumping speed in the second chamber has been decreased, resulting in an increased pressure of rare gas. This produces a strong attenuation by scattering of metastable helium and neon atoms with the background gas, while the photon intensity does

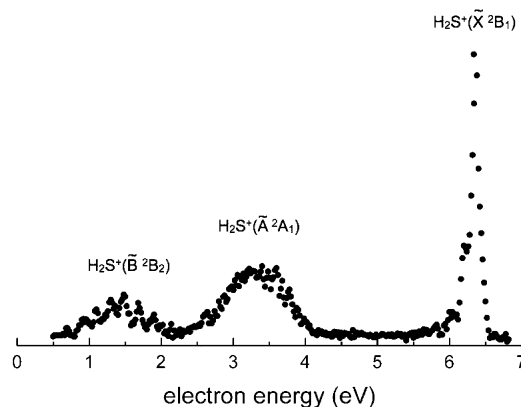
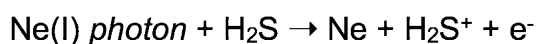


Figure 3. Photoionization spectrum of H₂S by Ne(I) photons. The spectrum contributions of the two α and β components of Ne(I) photons are partially resolved.

not change sensibly.²⁴ Applying such a procedure, the comparison of our measurements has been exploited with the expected spectrum, as obtained from the He(I) radiation by Kimura et al.²⁶ to appropriately calibrate 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, O₂, and N₂ by He(I) radiation with the procedure described in a previous paper.⁶ Spurious effects due to the geomagnetic field have been reduced to ≤ 20 mG by a μ -metal shielding. Finally, the metastable atom velocity can be analyzed by a time-of-flight technique: the beam is pulsed by a rotating slotted disk and the metastable atoms are counted, using a multiscaler, as a function of the delay time from the beam opening. The secondary molecular beam is prepared by effusion of H₂S from a glass microcapillary array kept at room temperature. The collision energy resolution is largely defined by the thermal spread of target molecules effusing from the microcapillary source, and in our experiment the average collision energy is ~55 meV.

3. RESULTS AND DISCUSSION

3.1. He*(2^{3,1}S_{1,0})–H₂S Autoionizing Collisions. First of all, to check the experimental setup, we have measured the product electron energy distribution in the ionization of H₂S molecules by He metastable atoms. By using the microwave discharge source, metastable He*(2³S₁) and He*(2¹S₀) are produced together with a small amount of He(I) photons, and the recorded electron spectrum is reported in Figure 2. The structure of such a spectrum suggests the formation of the three accessible (see previous) electronic states of the H₂S⁺ final ion, the 2b₁ (\tilde{X}^2B_1) fundamental one, the first 5a₁ (\tilde{A}^2A_1), and the second 2b₂ (\tilde{B}^2B_2) excited states, with an ionization energy of 10.48, 13.25, and 15.35 eV, respectively, and shows a good agreement with that obtained by Ohno and coworkers.¹⁶ The small signal recorded at an electron energy of 10.74 eV and related to photoionization by He(I) photons was used to calibrate the energy scale, as mentioned in Section 2.²⁶ Moreover, our PIES spectrum of Figure 2, showing the well-separated contributions of the two He*(2³S₁) and He*(2¹S₀) states for the production of H₂S⁺ in the ground 2b₁ (\tilde{X}^2B_1) state, contains additional information with respect to the previous spectrum by Ohno and coworkers, related to

Table 1. Negative Energy Shifts from the PIES He* and Ne*–H₂S Spectra As Measured at an Average Collision Energy of 55 meV, with Respect to Nominal Energy ϵ_0 (meV)

band in PIES		H ₂ S ⁺ (\tilde{X}^2B_1)–2b ₁			H ₂ S ⁺ (\tilde{A}^2A_1)–5a ₁	
maximum of peak ($\nu = 0$)	–150 ± 20	–130 ^a	–80 ^b	–85 ^c	–190 ± 40 ^b	–170 ^{a,d}
ϵ_{max} for He*(³ S ₁) collisions						
44% of maximum ($\nu = 0$)	–265 ± 20					
ϵ_A for He*(³ S ₁) collisions						
maximum of peak ($\nu = 0$)	–220 ± 20				–230 ± 40 ^b	
ϵ_{max} for He*(¹ S ₀) collisions						
44% of maximum ($\nu = 0$)	–405 ± 20					
ϵ_A for He*(¹ S ₀) collisions						
maximum of peak ($\nu = 0$)	–90 ± 20		0 ^b		–120 ± 30 ^b	
ϵ_{max} for Ne* collisions						
44% of maximum ($\nu = 0$)	–195 ± 20					
ϵ_A for Ne* collisions						

^aFrom ref 16. ^bFrom ref 14. ^cFrom ref 15. ^dEvaluated from the maximum of band.

He*(²3S₁)–H₂S ionizing collisions.¹⁶ In fact, by analyzing our spectrum, we are able to obtain important findings (see later) such as the energy shifts for both He*(²3S₁) and He*(²1S₀)–H₂S collisions. (See Table 1.) It is well known that these energy shifts depend on the strength, range, and anisotropy of the effective intermolecular interaction controlling the stereo dynamics in the entrance (neutral) and the exit (ionic) channels of ionizing collisional events.^{11,13} In particular, when the position of the maximum of a certain peak in the PIES spectrum exhibits a sizable negative shift, here referred to as ϵ_{max} with respect to the nominal energy, ϵ_0 , defined as the difference between the excitation energy of the metastable He* or Ne* atoms and the ionization potential of the relevant molecular state, this is an indication that a phenomenological global attractive interaction affects the collision dynamics of the partners on a multidimensional potential energy surface, including entrance and exit channels.^{11,14,27} Unfortunately, the energy resolution of our electron analyzer is not good enough to allow the separation of the two He*(²3S₁) and He*(²1S₀) states in the formation band of the H₂S⁺ 2b₂ (\tilde{B}^2B_2) excited state because of the low intensity signal for such an ionic band. Looking at the negative shifts of Table 1, the good agreement of present results with the values extracted from the He*(²3S₁)–H₂S spectrum measured by Ohno and coworkers can be noted.¹⁶ On the other hand, the comparison with the previous He*–H₂S spectra by Čermák and Yenchá,¹⁴ and by Brion and Yee¹⁵ is not very good. These authors measured negative energy shifts for the formation of the ground 2b₁ (\tilde{X}^2B_1) state of H₂S⁺ product ion by He*(²3S₁), which are sensibly smaller than our value (–80 and –85 meV, respectively, see Table 1), whereas in our spectrum we obtain a value of –150 ± 20 meV that is in fairly good agreement with the data of –130 meV extracted from the PIES spectrum by Ohno and coworkers.¹⁶ This discrepancy is probably due to the difference in the electron energy resolution of the electron analyzers used in the different laboratories. Our resolution, that is almost the same of the Ohno device,¹⁶ is higher than that of the early experiments performed by Čermák and Yenchá¹⁴ and by Brion and Yee.¹⁵ In fact, in the present work we are able to evaluate for the first time the negative energy shifts ϵ_{max} also for the production of the first 5a₁ (\tilde{A}^2A_1) electronic excited state of the H₂S⁺ product ions by both He*(²1S₀) and He*(²3S₁) autoionizing collisions: –230 ± 40 and –190 ± 40 meV, respectively. (See Table 1.) It has to be noted that just looking at the PIES spectra of Figure 2, in the case of the 2b₁ ground

state it is possible to extract not only the negative shift, ϵ_{max} for the maximum of peak but also the shift between the electron energy value where the peak intensity drops to 44% of its maximum at the lower energy side, ϵ_A , with respect to the nominal energy, ϵ_0 ,²⁸ obtaining a value of –265 ± 20 meV for He*(³S₁) collisions and –405 ± 20 meV for He*(¹S₀) collisions, as also reported in Table 1. These findings allow us to recognize a relatively strong attractive behavior of the He*–H₂S interaction promoting the Penning process. In fact, as suggested by Haug et al.,²⁹ 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 the entrance channel. This suggestion is reasonable considering the weaker attraction in the exit channel due to the very low polarizability of neon atom (0.40 Å³) in the ground electronic state with respect to that in the excited ones (27.8 Å³, see later). In our case, this estimate can be done only for the interaction of He* approaching the H₂S, producing H₂S⁺ final ions in the 2b₁ ground electronic state. An analogous evaluation for the ϵ_A shift is not possible for the two excited states of H₂S⁺ ions because in these cases the recorded broad bands in the PIES spectrum do not satisfy the features required by the theory.^{28–31}

These experimental results are an indication that the interaction potential driving the \tilde{A} excited-state formation exhibits an effective interaction potential well deeper (of about 25–30%) with respect to that involved in the production of the \tilde{X} ground state. Moreover, these attractive interactions are stronger (up to ~50%) in the case of He*(²1S₀) with respect to those related to He*(²3S₁) autoionizing collisions. This feature can be justified by tacking into account the higher polarizability of the singlet state of helium metastable atoms with respect to the triplet one (119 and 46.9 Å³, respectively).² The more “floppy” external electron in the singlet state reduces its shielding on the ionic core, therefore favoring an increase in the induction and electrostatic attraction when the intermolecular distance decreases.

3.2. Ne(I) and Ne*(³P_{2,0})–H₂S Electron Energy Spectra.

The measured PES and PIES spectra for Ne(I) and Ne*(³P_{2,0}) ionizing collisions are reported in Figures 3 and 4, respectively, and the latter refers to an average collision energy of 55 meV. In both spectra, the peak signals related to the formation of the same three 2b₁ (\tilde{X}^2B_1), 5a₁ (\tilde{A}^2A_1), and 2b₂ (\tilde{B}^2B_2) electronic states of H₂S⁺ product ions are evident, as already discussed in the case of the PIES spectrum obtained by He* collisions. Looking at the photoionization spectrum (Figure 3),

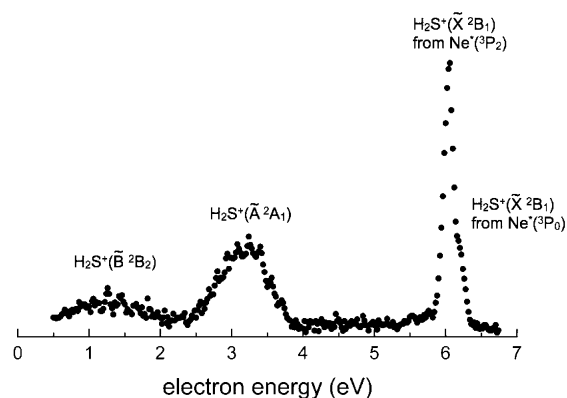
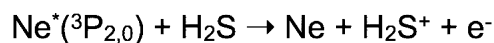


Figure 4. PIES spectrum obtained in $\text{Ne}^*(^3\text{P}_{2,0})\text{--H}_2\text{S}$ collisions with a resolution of ~ 45 meV. In the spectrum contributions of the two spin–orbit states of neon metastable atoms are partially resolved.

contributions of the two α and β components of $\text{Ne}(\text{I})$ photons are partially resolved in the $2b_1$ peak signal. (See Section 2.) In the PIES spectrum of Figure 4, the good resolution of our electron spectrometer has been crucial to evidence the contributions to the same peak signal of the two spin–orbit states, $^3\text{P}_2$ and $^3\text{P}_0$, of metastable neon atoms. It has to be noted that the resolution of these spectra allows us to successfully characterize the formation of the three possible and energetically accessible electronic states of the H_2S^+ final ions. In fact, the fairly poor resolution of the previous spectrum, recorded by Čermák and Yenchá in $\text{Ne}^*(^3\text{P}_2)\text{--H}_2\text{S}$ collisions,¹⁵ did not allow these authors to record any excited electronic state of H_2S^+ over the $2b_1$ ($\tilde{X}^2\text{B}_1$) fundamental one. Moreover, for such a state these authors were not able to obtain any negative energy shift, whereas in our PIES spectrum we record a negative shift ε_{max} of -90 ± 20 meV for the ground $2b_1$ ($\tilde{X}^2\text{B}_1$) state and of -120 ± 30 in the case of the $5a_1$ ($\tilde{A}^2\text{A}_1$) first excited state. (See Table 1.) The poor signal recorded at low electron energies, below 2.5 eV in the PIES spectrum of Figure 4, did not allow any evaluation for the energy shift related to the second excited state $2b_2$ ($\tilde{B}^2\text{B}_2$) of H_2S^+ ion products. As we have already done for He^* (see Section 3.1), also in the case of $\text{Ne}^*\text{--H}_2\text{S}$ autoionizing collisions, we can extract, by analyzing the PIES spectrum of Figure 4, the energy shift ε_A that provides useful information on the order of magnitude of the attractive well depth of the interaction affecting the approach of the colliding partners. Considering only the electron signal peak related to the formation of H_2S^+ in the $2b_1$ ground electronic state (see the discussion in Section 3.1), for ε_A , a value of -195 ± 20 meV is obtained. (See Table 1.)

The recorded negative energy shifts of Table 1 indicate that because of the dominance of the attraction in the collision complexes, both He^* and $\text{Ne}^*\text{--H}_2\text{S}$ Penning ionizations should take place, at intermolecular distances in the neighborhood of the potential well in the entrance channel, as we already observed in the case of Penning ionization of water molecules.^{11–13} This indication exploits the feature that while the interaction in the entrance channel provides a pronounced well depth, in the exit channel it is much less effective, being controlled by the low electronic polarizability value of the neon atom in the ground state.

Moreover, the comparison of so derived ε_{max} and ε_A energy shifts for H_2S with those more pronounced previously obtained

with the same methodology for $\text{Ne}^*\text{--H}_2\text{O}$ system (see table 1 of ref 11) suggests the occurrence of a more attractive intermolecular potential in the case of water, which drives the $\text{Ne}^*\text{--H}_2\text{O}$ system to the formation of a more stable intermediate complex with respect to the $\text{Ne}^*\text{--H}_2\text{S}$. The different behavior can be ascribed to the higher anisotropy charge distribution of water (responsible of the higher permanent dipole moment) that promotes a more pronounced polarization of the Ne^* atom in the entrance channel of the process.

Finally, for a more detailed PIES spectra analysis, a novel semiclassical method, recently developed in our laboratory,¹³ could be used in the next future for a deeper understanding of the stereo dynamics of the systems here presented. By using such a procedure, already successfully applied in the study of the Penning ionization of water molecules,¹³ we could be able to calculate the PIES spectra assuming ionization events as mostly occurring in the vicinities of the collision turning points. The goal of such an analysis will be to put clearly in evidence how different approaches of the metastable atom to the H_2S molecule can lead to ions in different electronic states. In particular, applying the same procedure used for $\text{Ne}^*\text{--H}_2\text{O}$ autoionizing collisions,¹³ we could provide the angular acceptance cones where the selectivity of the process leads to the specific formation of each one of the three energetically possible ionic product states of H_2S^+ . This work is actually in progress in our laboratory.

4. CONCLUSIONS

The electron energy spectra recorded in the case of $\text{He}^*(2^3\text{S}_{1,0})$, $\text{Ne}^*(^3\text{P}_{2,0})$, and $\text{Ne}(\text{I})\text{--H}_2\text{S}$ and here discussed show the evidence of a relatively strong attraction that dominates the potential energy surface describing the interaction and the ionization in metastable helium and neon atoms with hydrogen sulfide molecules. The recorded energy shifts indicate that in the case of He^* and $\text{Ne}^*\text{--H}_2\text{S}$ autoionizing collisions the effective intermolecular interaction is weaker when qualitatively compared with systems involving H_2O . This could be related to the larger electronegativity of oxygen with respect to sulfur atom, which causes a more pronounced anisotropic charge distribution on the molecular frame.

A qualitative discussion about the spectral features indicates that a semiempirical model like the one recently applied to $\text{Ne}^*\text{--H}_2\text{O}$ system¹³ could be successful also for this system in describing the Penning ionization stereo dynamics. Such an analysis is in progress in our laboratory, with the hope of arriving to a comparison between calculated spectra and experimental results. In such a way, we are confident that it will be possible to perform a general discussion on the stereo dynamics of the He^* and $\text{Ne}^*\text{--H}_2\text{S}$ collisional autoionization, as we have recently made in the case of water molecules.¹³

AUTHOR INFORMATION

Notes

The authors declare no competing financial interest.

ACKNOWLEDGMENTS

Financial contributions from the MIUR (Ministero dell'Istruzione, dell'Università e della Ricerca) are gratefully acknowledged.

REFERENCES

- (1) Penning, F. M. Über Ionisation durch metastabile Atome. *Naturwissenschaften* **1927**, *15*, 818–818.
- (2) Siska, P. E. Molecular-beam studies of Penning ionization. *Rev. Mod. Phys.* **1993**, *65*, 337–412.
- (3) Brunetti, B. G.; Vecchiocattivi, F. Autoionization dynamics of collisional complexes. In *Ion Clusters*; Ng, C., Baer, T., Powis, I., Eds.; Springer: New York, 1993; pp 359–445.
- (4) Atkinson, R.; Baulch, D. L.; Cox, R. A.; Hampson, R. F.; Kerr, J. A., Jr.; Troe, J. Evaluated kinetic and photochemical data for atmospheric chemistry: Supplement IV. IUPAC Subcommittee on kinetic data evaluation for atmospheric chemistry. *J. Phys. Chem. Ref. Data* **1989**, *21*, 1125–1499.
- (5) Biondini, F.; Brunetti, B. G.; Candori, P.; De Angelis, F.; Falcinelli, S.; Tarantelli, F.; Pirani, F.; Vecchiocattivi, F. Penning ionization of N_2O molecules by $\text{He}^*(2^3\text{S})$ and $\text{Ne}^*(^3\text{P}_{2,0})$ metastable atoms: Theoretical considerations about the intermolecular interactions. *J. Chem. Phys.* **2005**, *122*, 164308-1–164308-11.
- (6) Biondini, F.; Brunetti, B. G.; Candori, P.; De Angelis, F.; Falcinelli, S.; Tarantelli, F.; Teixidor, M. M.; Pirani, F.; Vecchiocattivi, F. Penning ionization of N_2O molecules by $\text{He}^*(2^3\text{S})$ and $\text{Ne}^*(^3\text{P}_{2,0})$ metastable atoms: A crossed beam study. *J. Chem. Phys.* **2005**, *122*, 164307-1–164307-10.
- (7) Kelley, M. C. *The Earth's Ionosphere*; Academic: San Diego, 1989.
- (8) Alagia, M.; Balucani, N.; Candori, P.; Falcinelli, S.; Pirani, F.; Richter, R.; Rosi, M.; Stranges, S.; Vecchiocattivi, F. Production of ions at high energy and its role in extraterrestrial environments. *Rend. Fis. Acc. Lincei* **2013**, *24*, 53–65.
- (9) Legon, A. C. The halogen bond: an interim perspective. *Phys. Chem. Chem. Phys.* **2010**, *12*, 7736–7747.
- (10) Cappelletti, D.; Ronca, E.; Belpassi, L.; Tarantelli, F.; Pirani, F. Revealing charge-transfer effects in gas-phase water chemistry. *Acc. Chem. Res.* **2012**, *45*, 1571–1580.
- (11) Brunetti, B. G.; Candori, P.; Cappelletti, D.; Falcinelli, S.; Pirani, F.; Stranges, D.; Vecchiocattivi, F. Penning Ionization Electron Spectroscopy of water molecules by metastable neon atoms. *Chem. Phys. Lett.* **2012**, *539–540*, 19–23.
- (12) Balucani, N.; Bartocci, A.; Brunetti, B. G.; Candori, P.; Falcinelli, S.; Palazzetti, F.; Pirani, F.; Vecchiocattivi, F. Collisional autoionization dynamics of $\text{Ne}^*(^3\text{P}_{2,0})\text{--H}_2\text{O}$. *Chem. Phys. Lett.* **2012**, *546*, 34–39.
- (13) Brunetti, B. G.; Candori, P.; Falcinelli, S.; Pirani, F.; Vecchiocattivi, F. The stereodynamics of the Penning ionization of water by metastable neon atoms. *J. Chem. Phys.* **2013**, *139*, 164305-1–164305-8.
- (14) Čermák, V.; Yench, A. J. Penning Ionization Electron Spectroscopy of H_2O , D_2O , H_2S and SO_2 . *J. Electron Spectrosc. Relat. Phenom.* **1977**, *11*, 67–73.
- (15) Brion, C. E.; Yee, D. S. C. Electron spectroscopy using excited atoms and photons IX. Penning ionization of CO_2 , CS_2 , COS , N_2O , H_2S , SO_2 , and NO_2 . *J. Electron Spectrosc. Relat. Phenom.* **1977**, *12*, 77–93.
- (16) Ohno, K.; Mutoh, H.; Harada, Y. Study of electron distributions of molecular orbitals by Penning ionization electron spectroscopy. *J. Am. Chem. Soc.* **1983**, *105*, 4555–4561.
- (17) Mitsuke, K.; Kusafuka, K.; Ohno, K. Angular distributions of electrons emitted by collisional ionization of hydrogen sulfide and argon with helium metastable atom. *J. Phys. Chem.* **1989**, *93*, 3062–3068.
- (18) Mitsuke, K.; Takami, T.; Ohno, K. Kinetic energy dependence of partial cross sections for the collisional ionization of H_2O , H_2S , O_2 , and Ar with $\text{He}(2^3\text{S})$ metastable atoms. *J. Chem. Phys.* **1989**, *91*, 1618–1625.
- (19) Tokue, I.; Yamasaki, K.; Nanbu, S. $\text{He}^*(2^3\text{S})$ Penning ionization of H_2S . I. Theoretical Franck–Condon factors for the $\text{H}_2\text{S}(\tilde{X}^1A_1, v' = 0) \rightarrow \text{H}_2\text{S}^+(\tilde{X}^2B_1, \tilde{A}^2A_1)$ ionization and $\text{H}_2\text{S}^+(\tilde{A}-\tilde{X})$ transition. *J. Chem. Phys.* **2003**, *119*, 5874–5881.
- (20) Tokue, I.; Yamasaki, K.; Nanbu, S. $\text{He}^*(2^3\text{S})$ Penning ionization of H_2S . II. Formation of the $\text{SH}^+(\tilde{A}^3\Pi)$ and $\text{H}_2\text{S}^+(\tilde{A}^2A_1)$ ions. *J. Chem. Phys.* **2003**, *119*, 5882–5888.
- (21) Ben Arfa, M.; Lescop, B.; Cherid, M.; Brunetti, B.; Candori, P.; Malfatti, D.; Falcinelli, S.; Vecchiocattivi, F. Ionization of ammonia molecules by collision with metastable neon atoms. *Chem. Phys. Lett.* **1999**, *308*, 71–77.
- (22) Brunetti, B.; Candori, P.; Falcinelli, S.; Vecchiocattivi, F.; Sassara, A.; Chergui, M. Dynamics of the Penning Ionization of Fullerene Molecules by Metastable Neon Atoms. *J. Phys. Chem. A* **2000**, *104*, 5942–5945.
- (23) Brunetti, B.; Candori, P.; Falcinelli, S.; Kasai, T.; Ohoyama, H.; Vecchiocattivi, F. Velocity dependence of the ionization cross section of methyl chloride molecules ionized by metastable argon atoms. *Phys. Chem. Chem. Phys.* **2001**, *3*, 807–810.
- (24) Brunetti, B.; Candori, P.; Falcinelli, S.; Lescop, B.; Liuti, G.; Pirani, F.; Vecchiocattivi, F. Energy dependence of the Penning ionization electron spectrum of $\text{Ne}^*(^3\text{P}_{2,0}) + \text{Kr}$. *Eur. Phys. J. D* **2006**, *38*, 21–27.
- (25) Kraft, T.; Bregel, T.; Ganz, J.; Harth, K.; Ruf, M.-W.; Hotop, H. Accurate comparison of HeI, NeI photoionization and $\text{He}(2^3\text{S})$, $\text{Ne}(3s^3P, ^3P_0)$ Penning ionization of argon atoms and dimers. *Z. Phys. D* **1988**, *10*, 473–481.
- (26) Kimura, K.; Katsumata, S.; Achiba, Y.; Yamazaki, T.; Iwata, S. *Handbook of HeI Photoelectron Spectra of Fundamental Organic Molecules*; Japan Scientific Societies Press: Tokyo, 1981.
- (27) Hotop, H.; Niehaus, A. Reactions of excited atoms molecules with atoms and molecules. II. Energy analysis of penning electrons. *Z. Phys. D* **1969**, *228*, 68–88.
- (28) Miller, W. H. Theory of Penning Ionization. I. Atoms. *J. Chem. Phys.* **1970**, *52*, 3563–3571.
- (29) Haug, B.; Morgner, H.; Staemmler, V. Experimental and Theoretical Study of Penning Ionisation of H_2O by Metastable Helium $\text{He}(2^3\text{S})$. *J. Phys. B: At. Mol. Phys.* **1985**, *18*, 259–274.
- (30) Niehaus, A. Penning ionization. *Ber. Bunsenges. Phys. Chem.* **1973**, *77*, 632–640.
- (31) Hotop, H. Analysis of Ions and Electrons Resulting from Penning Ionization. *Radiat. Res.* **1974**, *59*, 379–404.