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The Escape of O^+ and CO^+ Ions from Mars and Titan Atmospheres by Coulomb Explosion of CO_2^{2+} Molecular Dications

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Main properties of multiply charged molecular ions (energetics, structure, stability, lifetime and fragmentation dynamics) are relevant to know and to model the behavior of gaseous plasmas, planetary ionospheres, and astrophysical environments. Experimental measurements of the kinetic energy released of fragment ions produced by the Coulomb explosion of molecular dications (doubly charged molecular species) originating by double photoionization of CO_2 molecules, are reported and discussed. The kinetic energy released, as a function of the UV photon energy in the range of 34–50 eV, is extracted from the electron–ion–ion coincidence spectra recorded by using tunable synchrotron radiation coupled with ion imaging techniques at the GasPhase beam line of ELETTRA Synchrotron Light Laboratory Trieste, Italy. This kind of experiment allows assessing the probability of escape for simple ionic species in the ionosphere of Mars and Titan. The kinetic energy released, measured in the case of O^+ and CO^+ fragment ions, are ranging between 1.0–5.0 and 0.4–3.0 eV, respectively. These values are large enough to allow such ionic species in participating in the atmospheric escape from Mars (only O^+ ions) and Titan (both O^+ and CO^+ ions) into space. In the case of Mars, we suggest a possible rationalization for the observed behavior of the O^+ and CO_2^{2+} ion density profiles by Viking 1 lander and Mariner 6 spacecraft.

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1. Introduction

Ionization processes occurring in gas phase and induced by photons, electrons or excited metastable neutral species (also called the Penning ionization, chemi-ionization, or collisional autoionization reactions [1–3]) play an important role in several phenomena taking place in low energy ionized plasmas and electric discharges [4, 5]. Moreover, ions are extremely important in the upper atmosphere of planets, where they control the chemistry of ionospheres [6, 7]. For example, the chemistry of the upper atmosphere of Titan has been detected to be extremely active by the instruments on board Cassini [8, 9]. Finally, various simple ionic species, as for example H_2O^+, CO^+, CN^+, CO^+, have also been detected in comet tails [10].

In space, ions can be formed in different ways, whose importance depends on specific conditions of the extraterrestrial environment considered [11–13]. The interaction of neutral molecules with cosmic rays, UV photons, X-rays and other phenomena such as shock waves are all important processes for their production. On that sense, it has to be noted that the absorption of UV photons, with an energy content higher than the ionization potential of the absorbing species, can induce ionization with the formation of both singly and doubly charged ions. In the latter case there are produced the so-called molecular dications. These ionic species can be formed by using different techniques, as mass spectrometry [14], ion–molecule reactions [15], and double photoionization processes [16–19]. Molecular dications can be formed in stable or metastable states [13, 19, 20] and may be used, in principle, as energy storage at a molecular level [14, 15, 21]. Such species, and more in general multiply charged ions, can be produced also by cosmic rays, which are meaningful since they are ubiquitous and carry a large energy content (up to 100 GeV). It is well known that cosmic rays consist mainly of protons, alpha particles, electrons, γ-rays, and also a small amount of heavier nuclei, such as C^{6+} [7]. They are very penetrating and may induce ionization processes in astronomical environments that are completely opaque to UV photons. X-rays are relatively abundant in several regions, such as active galactic nuclei, young stellar objects, and planetary nebulae with hot central stars. Finally, single or double ionization can occurs also by absorption of X-rays. In this case the ejection of a core electron followed by the Auger emission of another electron, produces molecular dications, which have been suggested to play a role in the envelope of young stellar objects [22] and upper planetary atmospheres [23–26].

In general, when we ionize a molecule we can modify deeply its chemical behavior. In fact, first of all, the removed electron may change sensibly the electronic configuration of the neutral species, modifying its chemical reactivity. In addition, the ion–molecule interaction is much more intense than the neutral–neutral one, making more probable any collision event. Finally, double ionization processes forming molecular dications can induce

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Coulomb explosion and fragment ions production with a kinetic energy released considerably high, that in the most cases is of several eV. For such a reason molecular dications are considered as exotic species, and when they are formed in planetary ionospheres the possibility to generate dissociative products with a high kinetic energy content, allows these ionic fragments to reach sufficient velocity to escape into space. Therefore, double ionization processes can, in principle, contribute to the continuous erosion of the atmosphere of some planets of the Solar System, like Mars and Titan (the largest satellite of Saturn), as discussed in the following sections. As reported and discussed in the following sections, the use of a tunable and high intensity UV light source, as the synchrotron radiation ones, coupled with a molecular beam apparatus working in high vacuum conditions (the operative working pressure is of about 10^{-7} mbar), allows the possibility to simulate the environmental conditions of planetary ionospheres. Our experimental technique appears to be particularly suitable in order to measure with high accuracy the spatial momentum components of the fragment ions coming out from double photoionization events of neutral molecular precursors, allowing the determination of the kinetic energy content of each final product ion. In our knowledge, such a kind of experimental determinations, applied to the case of the double photoionization of carbon dioxide molecules, allowed an original rationalization of the O^+ and CO_2^{2+} observed ion density profiles by Viking 1 lander and Mariner 6 spacecraft in the Mars ionosphere.

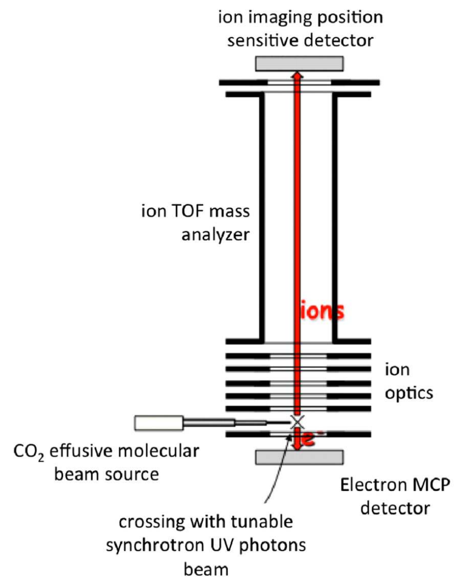

Fig. 1. The scheme of the electron–ion extraction and detection system used for the photoelectron–photoion–photoion coincidence measurements.

2. Experimental

The kinetic energy released (KER) data, concerning the double photoionization of carbon dioxide molecules in the photon energy range between 34 and 50 eV, are presented and discussed in the next section. They have been recorded by double photoionization experiments performed at the ELETTRA Synchrotron Light Laboratory (Trieste, Italy) using the angle-resolved photoemission spectroscopy (ARPES) end station of the gas phase beamline. Details about the beamline and the end station have been already reported elsewhere [27, 28], and the apparatus used for the experiment discussed here has also been described previously [29–31]. Therefore, only some features relevant for the present investigation are outlined here.

As it can be seen in Fig. 1, the monochromatic energy from the selected UV synchrotron light beam crosses at right angles with an effusive molecular beam of CO_2 neutral precursors, and the product ions are then detected in coincidence with photoelectrons.

The coincidence electron–ion–ion extraction and detection system, schematized in Fig. 1, consists in a time of flight (TOF) mass spectrometer equipped with an ion position sensitive detector (stack of three micro-channel-plates with a multi-anode array arranged in 32 rows and 32 columns). It has been especially designed in order to properly measure the spatial momentum components of the dissociation ionic products [32]. Finally, by the analysis of density distribution of coincidences in the recorded coincidence spectra for each investigated photon energy (see, for example, the coincidence plot reported in the part of Fig. 2a), the kinetic energy of the two products, released into the two ionic fragments, can be extracted. Such kinetic energy is obtained by a simple analysis of the ion intensity maps based on the method suggested by Lundqvist et al. [33]. In particular, this target can be reached by looking at the dimensions and shapes of the peak for each ion pair in the coincidence spectra (see the dashed circle in Fig. 2a) measured at all investigated photon energies. By the analysis of coincidences distribution as a function of the arrival time differences ($t_2 - t_1$) of fragment ions (to the ion position sensitive detector, being a multi-channel-plate (MCP)), generated by the Coulomb explosion of the molecular dication under study, we are able to calculate the lifetime of such metastable species by using the procedure proposed by Field and Eland [34]. All experimental components were controlled by a computer used to record experimental data. The incident photon flux and the gas pressure have been monitored and stored in separate acquisition channels [31, 35].

Carbon dioxide from a commercial cylinder at room temperature with a 99.99% nominal purity, was supplied to a needle effusive beam source. An adjustable leak valve along the input gas pipe line was used in order to control the gas flow, which was monitored by checking the pressure in the main vacuum chamber.

3. Results and discussion

Carbon dioxide is a simple molecule of interest for interstellar medium (ISM) and planetary atmospheres of the Earth and of other planets of the Solar System like

Mars, Venus and Titan, the largest moon of Saturn. Its presence in the ISM has been demonstrated by microwave spectroscopy, as reported in a recent review paper by Witasse et al. [36].

Carbon dioxide is a well known green house gas having a growing annual concentration in the Earth atmosphere. Furthermore, CO_2 is the main component in the Mars (95.3%) and Venus (96.5%) atmospheres and, together with acetylene molecules, has been detected as a minor component in Titan atmosphere (2–4 ppm and about 10 ppb, respectively) [37]. It has to be noted that the presence of VUV light's photons in such environments makes highly probable the double photoionization of this molecular species with its subsequent dissociation into ionic fragments having a high kinetic energy content that can reach 5–6 eV. As we point out below, this translational energy content is large enough in order to allow these ionic species to realize an escape process from the upper atmosphere of Mars and Titan into space.

Our double photoionization experiment of CO_2 by VUV synchrotron light (in the 34–50 eV energy range) is in good agreement with previous experiments [31, 38, 39], and indicates that four processes are possible with the measured threshold energies reported below:

$$CO_2 + h\nu \to (CO_2^+)^* + e^- \to CO^+ + O^* \to CO^+ + O^+ + e^-, \ h\nu \geq 35.6 \text{ eV}, \quad (1)$$

$$CO_2 + h\nu \to CO_2^{2+} + 2e^-, \ h\nu \geq 37.3 \text{ eV}, \quad (2)$$

$$CO_2 + h\nu \to (CO_2^{2+})^*_{\text{long lived}} + 2e^- \to CO^+ + O^+, \ h\nu \geq 38.7 \text{ eV}, \quad (3)$$

$$CO_2 + h\nu \to (CO_2^{2+})^*_{\text{short lived}} + 2e^- \to CO^+ + O^+, \ h\nu \geq 39.0 \text{ eV}. \quad (4)$$

The reactions (3) and (4) involve various electronic states of the intermediate molecular (CO_2^{2+}) dication having different lifetimes τ. Reaction (3) takes place through two possible microscopic mechanisms: (i) via formation of a long lived dication with $\tau \geq 3.1\ \mu$s, corresponding to the production of CO_2^{2+} ions in the ground $X^3\Sigma_g^+$ electronic state with an internal energy below the threshold towards the Coulomb explosion; (ii) or via formation of CO_2^{2+} dications in excited singlet states undergoing slow spin forbidden intersystem crossing to the triplet ground state, followed by fast dissociation over the ground state potential energy surface [31–39]. The reaction (4), involving a short lived dication ($\tau \leq 50$ ns), occurs through the formation of the ground $X^3\Sigma_g^+$ electronic state of CO_2^{2+} with an internal energy above the threshold for dissociation. It is to be noted that reactions (1), (3) and (4) are producing the same CO^+ and O^+ product ions. In particular, the reaction (1) is an indirect process occurring below the double photoionization threshold of 37.34 eV, via the formation an excited state of the $(CO_2^+)^*$ monocation, followed by the production of an intermediate autoionizing oxygen atom O^*.

The analysis of coincidence spectra obtained at each investigated photon energy (as the one shown in Fig. 2a), allows us the determination of the KER for the CO^+ and O^+ production in the "fast" fragmentation process by looking at the dimensions and shapes of the dot intensity for each ion pair peak. By applying such a procedure, already described in the previous section (for more details, see Ref. [33]), and applied to the CO^+/O^+ coincidences signal related to the (1) and (4) fragmentation processes, we have measured kinetic energy distributions of each product ions for different values of the investigated photon energy (36.0, 39.0, 41.0, 44.0, and 49.0 eV) as shown in Fig. 2b.

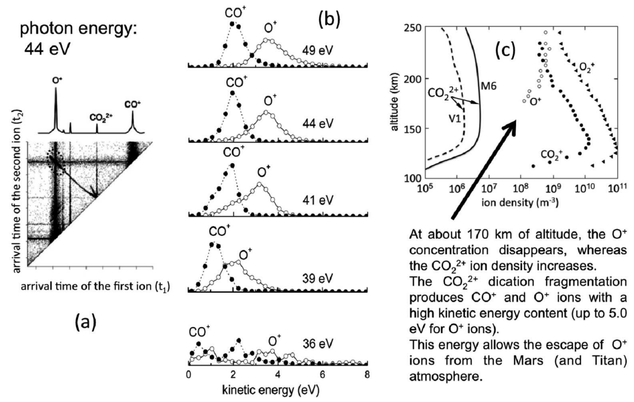

Fig. 2. (a) A typical coincidence spectrum recorded by the double photoionization of CO_2 at a photon energy of 44 eV, where it is pointed out with a dashed circle the dots region used for the evaluation of the CO^+ and O^+ KER distributions (see text). (b) Kinetic energy distributions for CO^+ and O^+ fragment ions originating by the Coulomb explosion of CO_2^{2+} dication produced in the same photoionization experiment, as a function of the photon energy. (c) Calculation of CO_2^{2+} ion density profiles for Viking 1 lander (V1) and Mariner 6 spacecraft (M6) conditions by Witasse et al. [36]. The O^+, CO_2^+, and O_2^+ densities profiles (on the right part of the panel) measured by Viking 1 lander are also plotted.

Looking at the kinetic energy distributions reported in Fig. 2b it appears clearly evident that the KER value for the O^+ ions ranges between 1.0 and 5.0 eV changing its maximum value with the investigated photon energies. This is a consequence of the general behavior of doubly charged molecular ions coming from their instability towards the Coulomb explosion, with the subsequent formation of dissociative ionic fragments with a kinetic energy of several eV, as already mentioned above. In the case of O^+ formation by VUV double photoionization of carbon dioxide molecules, this energy is large enough for the atmosphere of Mars and Titan to allow these fragments to reach enough velocity to escape into space contributing to the continuous erosion of these atmospheres. In Table I there is reported the range of measured KER values for fragments ions produced by VUV dissociative double photoionization of CO_2 in comparison with the typical escape energy for various ions at the exobase in the atmosphere of Earth, Venus, Mars, and Titan [23]. In particular, considering the ionosphere of Mars, the possibility to form in this environment carbon dioxide CO_2^{2+} dication (by UV light double photoionization of CO_2) followed by its Coulomb explosion and subsequent production of O^+ fragments having a high translational energy (ranging between 1.0 and 5.0 eV — see Fig. 2b and Table I), could explain the lack in the O^+ expected concentration on Mars atmosphere. In fact, by looking at O^+, we can argue that the observed behavior of its density profile measured by Viking 1 lander in the upper atmosphere of Mars, compared with the CO_2^{2+} density profile as calculated by Witasse et al. for Viking 1 lander and Mariner 6 spacecraft geophysical conditions (see Fig. 2c) [36], could be explained by invoking the dissociative double photoionization of CO_2 induced by VUV photons. These authors found a maximum in the CO_2^{2+} density of about 5×10^6 ions m^{-3} at a 160 km of altitude where the O^+ concentration (measured by Viking 1 with an ion density decreasing from 6×10^8 ions m^{-3} at 250 km to 1×10^8 ions m^{-3} at 175 km of altitude) disappears, becoming undetectable [22, 23, 36]. This surprising behavior could be explained by our experimental observations here discussed: by double VUV photoionization of CO_2 molecules, when the photon energy is higher than 48 eV, the stable molecular dication formation (reaction (2)) and the "fast" fragmentation process (reactions (1) and (4)) achieve the same importance and their cross-sections gain the maximum value [31, 38, 39], so the O^+ formation with a KER sufficient to escape from the Mars atmosphere becomes highly probable, and its experimental detectability very hard. An analogous situation could characterize the Titan ionosphere where the low typical escape energy values for ions (see Table I) allow with high probability the escape process into space, not only for O^+, but also for CO^+ ions, having typical escape energy smaller than 1.0 eV.

TABLE I

The range of measured values of KER distributions for O^+ and CO^+ fragments ions produced by VUV dissociative double photoionization of CO_2 in the range of 34–50 eV compared with the typical escape energy for such ions in the atmosphere (at the exobase) of some planets of the Solar System [23].

Ion	KER [eV]	Typical escape energy [eV]			
		Earth	Venus	Mars	Titan
O^+	$1.0 \div 5.0$	9.8	8.6	2.0	0.37
CO^+	$0.4 \div 3.0$	17.3	14.9	3.5	0.65

4. Conclusion

Double photoionization processes induced by VUV light's photons and producing ionic fragments with a high kinetic energy content, are in general an important microscopic route through which ionic species can escape from the upper atmosphere of some planets of the Solar System, like Venus, Mars, and Titan. In fact, these processes occur via formation of intermediate molecular dications that could dissociate by Coulomb explosion towards the formation of two ionic fragment species having a kinetic energy released of several eV, and therefore much larger than the limiting thermal escape velocity characterizing some planetary atmospheres. In the case of the double VUV photoionization of CO_2 molecules (studied in the photon energy range of 34–50 eV), the fragment product ions O^+ and CO^+ are characterized by a translational energy ranging between 1.0–5.0 and 0.4–3.0 eV, respectively, that is large enough to allow their escape process from the upper atmospheres of Mars (in the case of O^+ ions) and Titan (for both O^+ and CO^+ ions). Moreover, these studies could be helpful in understanding important details about the chemistry of planetary ionospheres [40–42], as in the case of Mars where we were able to propose a possible rationalization of the observed behavior of the O^+ and CO_2^{2+} ion density profiles as they were measured by Viking 1 lander and Mariner 6 spacecraft in the ionosphere of such a planet.

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References

[1] B. Brunetti, P. Candori, R. Ferramosche, S. Falcinelli, F. Vecchiocattivi, A. Sassara, M. Chergui, *Chem. Phys. Lett.* **294**, 584 (1998).

[2] F. Biondini, B.G. Brunetti, P. Candori, F. De Angelis, S. Falcinelli, F. Tarantelli, F. Pirani, F. Vecchiocattivi, *J. Chem. Phys.* **122**, 164308 (2005).

[3] B. Brunetti, P. Candori, D. Cappelletti, S. Falcinelli, F. Pirani, D. Stranges, F. Vecchiocattivi, *Chem. Phys. Lett.* **539-540**, 19 (2012).

[4] S. Falcinelli, A. Bartocci, S. Cavalli, F. Pirani, F. Vecchiocattivi, *J. Chem. Phys.* **143**, 164306 (2015).

[5] S. Falcinelli, A. Bartocci, S. Cavalli, F. Pirani, F. Vecchiocattivi, *Chem. Eur. J.* **22**, 764 (2016).

[6] S. Falcinelli, F. Pirani, F. Vecchiocattivi, Atmosphere **6**, 299 (2015).

[7] M. Alagia, N. Balucani, P. Candori, S. Falcinelli, F. Pirani, R. Richter, M. Rosi, S. Stranges, F. Vecchiocattivi, *Rendic. Lincei Sci. Fis. Natur.* **24**, 53 (2013).

[8] V. Vuitton, O. Dutuit, M.A. Smith, N. Balucani, in: *Titan: Surface, Atmosphere and Magnetosphere*, Eds. I. Müller-Wodarg, C.A. Griffith, E. Lellouch, T.E. Cravens, Cambridge University Press, 2013, Ch. 7.

[9] S. Falcinelli, M. Rosi, P. Candori, F. Vecchiocattivi, J.M. Farrar, F. Pirani, N. Balucani, M. Alagia, R. Richter, S. Stranges, *Lect. Notes Comput. Sci. LNCS* **8579**, 554 (2014).

[10] M. Larsson, W.D. Geppert, G. Nyman, *Rep. Prog. Phys.* **75**, 066901 (2012).

[11] S. Falcinelli, in: *Recent Advances in Energy, Environment and Financial Planning — Mathematics and Computers in Science and Engineering Series*, Eds. F. Batzias, N.E. Mastorakis, C. Guarnaccia, Vol. 35, WSEAS Press, Athens 2014, p. 84.

[12] L. Pei, E. Carrascosa, N. Yang, S. Falcinelli, J.M. Farrar, *J. Phys. Chem. Lett.* **6**, 1684 (2015).

[13] P. Candori, S. Falcinelli, F. Pirani, F. Tarantelli, F. Vecchiocattivi, *Chem. Phys. Lett.* **436**, 322 (2007).

[14] S. Falcinelli, F. Fernandez-Alonso, K. Kalogerakis, R.N. Zare, *Mol. Phys.* **88**, 663 (1996).

[15] P. Tosi, R. Correale, W. Lu, S. Falcinelli, D. Bassi, *Phys. Rev. Lett.* **82**, 450 (1999).

[16] M.M. Teixidor, F. Pirani, P. Candori, S. Falcinelli, F. Vecchiocattivi, *Chem. Phys. Lett.* **379**, 139 (2003).

[17] M. Alagia, B.G. Brunetti, P. Candori, S. Falcinelli, M.M. Teixidor, F. Pirani, R. Richter, S. Stranges, F. Vecchiocattivi, *J. Chem. Phys.* **120**, 6985 (2004).

[18] M. Alagia, F. Biondini, B.G. Brunetti, P. Candori, S. Falcinelli, M. Moix Teixidor, F. Pirani, R. Richter, S. Stranges, F. Vecchiocattivi, *J. Chem. Phys.* **121**, 10508 (2004).

[19] M. Alagia, P. Candori, S. Falcinelli, F. Pirani, M.S. Pedrosa Mundim, R. Richter, M. Rosi, S. Stranges, F. Vecchiocattivi, *Phys. Chem. Chem. Phys.* **13**, 8245 (2011).

[20] L. Pauling, *J. Chem. Phys.* **1**, 56 (1933).

[21] C.A. Nicolaides, *Chem. Phys. Lett.* **161**, 547 (1989).

[22] P. Stauber, S.D. Doty, E.F. van Dishoeck, A.O. Benz, *Astron. Astrophys.* **440**, 949 (2005).

[23] R. Thissen, O. Witasse, O. Dutuit, C.S. Wedlund, G. Gronoff, J. Lilensten, *Phys. Chem. Chem. Phys.* **13**, 18264 (2011).

[24] L. Schio, C. Li, S. Monti, P. Salén, V. Yatsyna, R. Feifel, M. Alagia, R. Richter, S. Falcinelli, S. Stranges, V. Zhaunerchyk, V. Carravetta, *Phys. Chem. Chem. Phys.* **17**, 9040 (2015).

[25] M. Alagia, E. Bodo, P. Decleva, S. Falcinelli, A. Ponzi, R. Richter, S. Stranges, *Phys. Chem. Chem. Phys.* **15**, 1310 (2013).

[26] S. Falcinelli, M. Rosi, P. Candori, J.M. Farrar, F. Vecchiocattivi, F. Pirani, N. Balucani, M. Alagia, R. Richter, S. Stranges, *Planet. Space Sci.* **99**, 149 (2014).

[27] R.R. Blyth, R. Delaunay, M. Zitnik, J. Krempasky, R. Krempaska, J. Slezak, K.C. Prince, R. Richter, M. Vondracek, R. Camilloni, L. Avaldi, M. Coreno, G. Stefani, C. Furlani, M. de Simone, S. Stranges, M.-Y. Adam, *J. Electron Spectrosc. Relat. Phenom.* **101-103**, 959 (1999).

[28] M. Alagia, P. Candori, S. Falcinelli, M. Lavollée, F. Pirani, R. Richter, S. Stranges, F. Vecchiocattivi, *Chem. Phys. Lett.* **432**, 398 (2006).

[29] M. Alagia, P. Candori, S. Falcinelli, M. Lavollée, F. Pirani, R. Richter, S. Stranges, F. Vecchiocattivi, *Phys. Chem. Chem. Phys.* **12**, 5389 (2010).

[30] M. Alagia, P. Candori, S. Falcinelli, M. Lavollée, F. Pirani, R. Richter, S. Stranges, F. Vecchiocattivi, *J. Chem. Phys.* **126**, 201101 (2007).

[31] M. Alagia, P. Candori, S. Falcinelli, M. Lavollée, F. Pirani, R. Richter, S. Stranges, F. Vecchiocattivi, *J. Phys. Chem. A* **113**, 14755 (2009).

[32] M. Lavollée, *Rev. Sci. Instrum.* **70**, 2968 (1990).

[33] M. Lundqvist, P. Baltzer, D. Edvardsson, L. Karlsson, B. Wannberg, *Phys. Rev. Lett.* **75**, 1058 (1995).

[34] T.A. Field, J.H.D. Eland, *Chem. Phys. Lett.* **211**, 436 (1993).

[35] M. Alagia, C. Callegari, P. Candori, S. Falcinelli, F. Pirani, R. Richter, S. Stranges, F. Vecchiocattivi, *J. Chem. Phys.* **136**, 204302 (2012).

[36] O. Witasse, O. Dutuit, J. Lilensten, R. Thissen, J. Zabka, C. Alcaraz, P.-L. Blelly, S.W. Bougher, S. Engel, L.H. Andersen, K. Seiersen, *Geophys. Res. Lett.* **29**, 1263 (2002).

[37] T.E. Cravens, I.P. Robertson, J.H. Jr. Waite, R.V. Yelle, W.T. Kasprzak, C.N. Keller, S.A. Ledvina, H.B. Niemann, J.G. Luhmann, R.L. McNutt, W.-H. Ip, V. De La Haye, I. Mueller-Wodarg, J.-E. Wahlund, V.G. Anicich, V. Vuitton, *Geophys. Res. Lett.* **33**, L07105 (2006).

[38] P. Franceschi, R. Thissen, J. Zabka, J. Roithová, Z. Herman, O. Dutuit, *Int. J. Mass Spectrom.* **228**, 507 (2003).

[39] A.E. Slattery, T.A. Field, M. Ahmad, R.I. Hall, J. Lambourne, F. Penent, P. Lablanquie, J.H.D. Eland, *J. Chem. Phys.* **122**, 084317 (2005).

[40] S. Falcinelli, F. Pirani, M. Alagia, L. Schio, R. Richter, S. Stranges, N. Balucani, F. Vecchiocattivi, *Atmosphere* **7**, 112 (2016).

[41] S. Falcinelli, F. Pirani, M. Alagia, L. Schio, R. Richter, S. Stranges, F. Vecchiocattivi, *Chem. Phys. Lett.* **666C**, 1 (2016).

[42] S. Falcinelli, M. Rosi, S. Cavalli, F. Pirani, F. Vecchiocattivi, *Chem. Eur. J.* **22**, 12518 (2016).