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The Role of Molecular Dications in Planetary Atmospheric Escape

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Abstract: Fundamental properties of multiply charged molecular ions, such as energetics, structure, stability, lifetime and fragmentation dynamics, are relevant to understand and to model the behavior of gaseous plasmas as well as ionosphere and astrophysical environments. Experimental determinations of the Kinetic Energy Released (KER) for ions originating from dissociations reactions, induced by Coulomb explosion of doubly charged molecular ions (molecular dications) produced by double photoionization of CO_2, N_2O and C_2H_2 molecules of interest in planetary atmospheres, are reported. The KER measurement as a function of the ultraviolet (UV) photon energy in the range of 28-65 eV are extracted from the electron-ion-ion coincidence spectra obtained by using tunable synchrotron radiation coupled with ion imaging techniques at the ELETTRA Synchrotron Light Laboratory Trieste, Italy. These experiments allow assessing the probability of escape for simple ionic species in the upper atmosphere of Mars, Venus and Titan. The measured KER in the case of H^+, C^+, CH^+, CH_2^+, N^+, O^+, CO^+, N_2^+ and NO^+ fragment ions are ranging between 1.0 and 5.5 eV, being large enough to allow these ionic species in participating in the atmospheric escape from such planets into space.

Keywords: molecular dications; astrochemistry; planetary atmospheres; ionospheres; synchrotron radiation; ions escape; mass spectrometry; coincidence technique; ion imaging

1. Introduction

Gas phase ionization processes induced by energetic photons, electrons or by excited metastable neutral species (also called collisional autoionization reactions [1,2]) play an important role in several phenomena occurring in low energy ionized plasmas, electric discharges [3,4]. Furthermore, ionic species are extremely important in the upper atmosphere of planets, where they govern the chemistry of ionospheres [5,6]. In particular, the ionosphere chemistry of Titan has recently been revealed to be extremely active by the instruments on board Cassini [7,8]. Finally, molecular ions have also been detected in comet tails [9].

In space, ions are formed in various ways, the importance of which depends on the specific conditions of the extraterrestrial environment considered [10–12]. 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. In particular, 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 we have the so called molecular dications. These ionic species can be produced by different techniques, as mass spectrometry [13], ion-molecule reactions [14], and double photoionization processes [15–18]. They can be stable or metastable [13,19] and can be used, in principle, as energy storage at a molecular level [13,14,20]. Multiply charged ionic species can be produced also by cosmic rays, which are significant since they are ubiquitous and carry a large energy content (up to 100 GeV). They consist of protons, alpha particles, electrons, γ-rays and (to a small extent) also heavier nuclei (such as C^{6+}). Furthermore, 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 [21] and upper planetary atmospheres [22–25].

In general, the double ionization producing a molecular dication can induce Coulomb explosion and fragment ions formation with a high kinetic energy content. 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 kinetic energy of several eV, 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.

2. Experiments

The data here presented and discussed have been recorded by double photoionization experiments performed at the ELETTRA Synchrotron Light Laboratory (Trieste, Italy) using the ARPES (Angle-Resolved Photoemission Spectroscopy) end station of the Gas Phase Beamline. Details about the beamline and the end station have been already reported elsewhere [26], and the apparatus used for the experiment discussed here has also been described previously [27,28]. Therefore, only some features relevant for the present investigation are outlined here.

As it can be seen in Figure 1, the monochromatic energy from the selected synchrotron light beam crosses an effusive molecular beam of CO_2, N_2O and C_2H_2 neutral precursors, and the product ions are then detected in coincidence with photoelectrons. The molecular beam of CO_2, N_2O and C_2H_2 crosses at right angles the VUV light beam, having the light polarization vector parallel to the synchrotron ring plane and perpendicular to the time-of-flight direction of detected ions. Incident photon fluxes and the gas pressure are monitored, and the ion yield has been corrected for flux changes of pressure and photon, when the photon energy was scanned. In order to record photoions in coincidence with photoelectrons, we used the electron-ion-ion coincidence technique. The coincidence electron-ion-ion extraction and detection system has been built following the model described in detail in Ref. 17 and its scheme can be seen in Figure 1. This device consists in a time of flight (TOF) spectrometer equipped with an ion position sensitive detector, being especially designed in order to properly measure the spatial momentum components of the dissociation ionic products [29]. The analysis of the recorded coincidences distribution (at each investigated photon energy) as a function of the arrival time differences (t_2–t_1) of fragment ions to the ion position sensitive detector (shown in Figure 1), can provide, by using the procedure already applyied in several works [30–32], the following observables: (i) the kinetic energy distributions for each product ion; (ii) the life time of the intermediate molecular dications; and (iii) the angular distributions of final ions coming out from its Coulomb explosion.

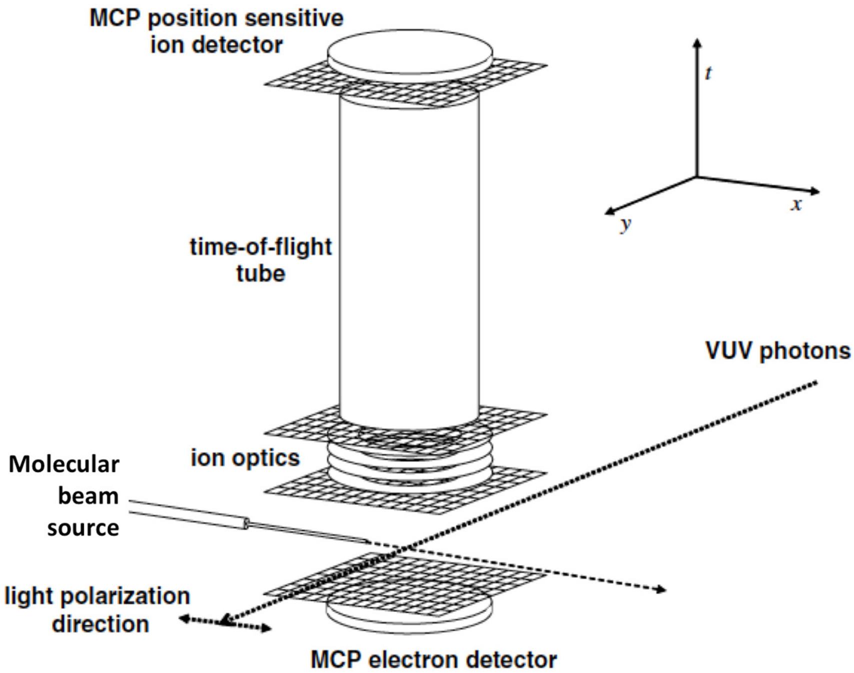

Figure 1. The scheme of the used electron-ion extraction and detection system used for the photoelectron-photoion-photoion coincidence measurements.

Carbon dioxide, nitrous oxide and acetylene, from a commercial cylinder at room temperature, were supplied to a needle effusive beam source. The used CO_2, N_2O and C_2H_2 gases had a 99.99% and ~99.0% (in the case of acetylene) nominal purity, respectively.

3. Results and Discussion

Carbon dioxide, nitrous oxide and acetylene are simple molecules of interest for interstellar medium ISM and planetary atmospheres (not only for the Earth but also for other planets of the Solar System like Mars, Venus and also Titan). The presence of CO_2, N_2O in the ISM has been demonstrated by microwave spectroscopy, whereas C_2H_2 was detected by IR spectroscopic measurements [33]. Furthermore, in the Earth atmosphere carbon dioxide and nitrous oxide are important green house gases, and N_2O can participate to the ozone depletion [37,38]. Acetylene was found as a minor component in the atmosphere of gas giants like the planet Jupiter, in the atmosphere of Saturn's satellite Titan [39], and in comets, where photochemical experiments have demonstrated that this simple hydrocarbon is a likely precursor of C_2, a widely observed component in such environments [34–36].

3.1. Carbon Dioxide

The double photoionization of CO_2 was performed by using VUV synchrotron light in a photon energy range of 34-50 eV. The obtained data are in fairly good agreement with previous experiments *[40–42*]. By analysing recorded coincidence spectra obtained at each investigated photon energy, we were able to exctract the KER for CO^+ and O^+ fragment ions produced by the Coulomb explosion of CO_2^{2+} intermediate molecular dication, formed with a threshold energy of 36.6 eV. This was possible by analyzing dimensions and shapes of the dot intensity for each recorded ion pair peak, according to the simple method suggested by Lundqvist et al. [30]. With such a procedure, we have obtained the KER 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 Figure 2.

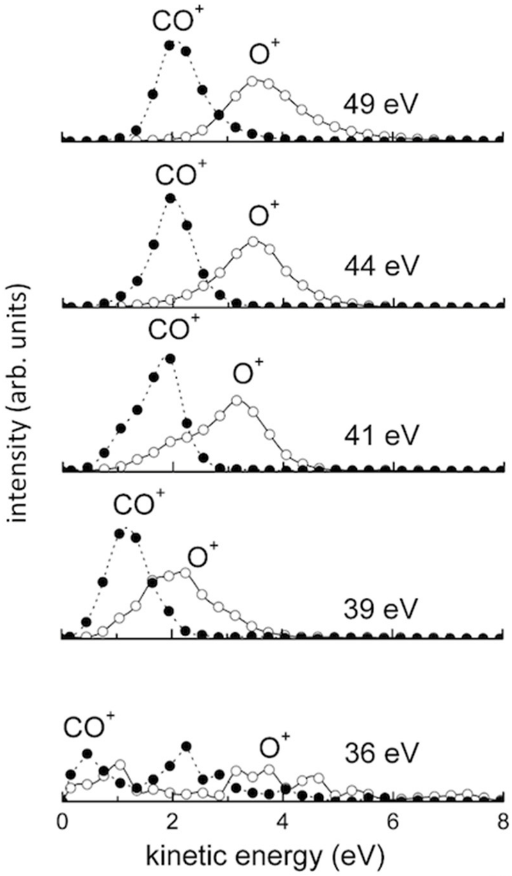

Figure 2. Kinetic energy distributions for CO^+ and O^+ fragment ions originating by Coulomb explosion of CO_2^{2+} dication produced in the double VUV photoionization experiment of CO_2 (see text) as a function of the photon energy.

From the kinetic energy distributions reported in Figure 2 it is 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 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, as it can be appreciated by looking at the comparison with the typical escape energy of O^+ ions at the exobase in the atmosphere of Mars and Titan (2.0 and 0.37 eV, respectively [23]).

3.2. Nitrous Oxide

When nitrous oxide molecules are photoionized by using VUV synchrotron radiation in the 28–40 eV energy range the production of N_2O^{2+} molecular dications in a metatstable state is possible with a measured threshold energy of 32.2 eV, accordingly to a previous experiment [37], to which we refer for an overview of the experimental and theoretical works already performed by other laboratories. The analysis of recorded coincidence spectra at each invetigated photon energy, by using the same procedure already mentioned in the case of CO_2, allow us to obtain the KER distributions of ionic fragments as a function of the investigated photon energy. They are reported in Figure 3 for the two couples of product ions N^++NO^+ and O^++N_2^+ coming out from the Coulomb explosion of the intermediate N_2O^{2+} dication (the two possible two-body fragmentation processes are reported in the Figure), as a function of the analyzed photon energy: 35, 38, 41, 44 eV.

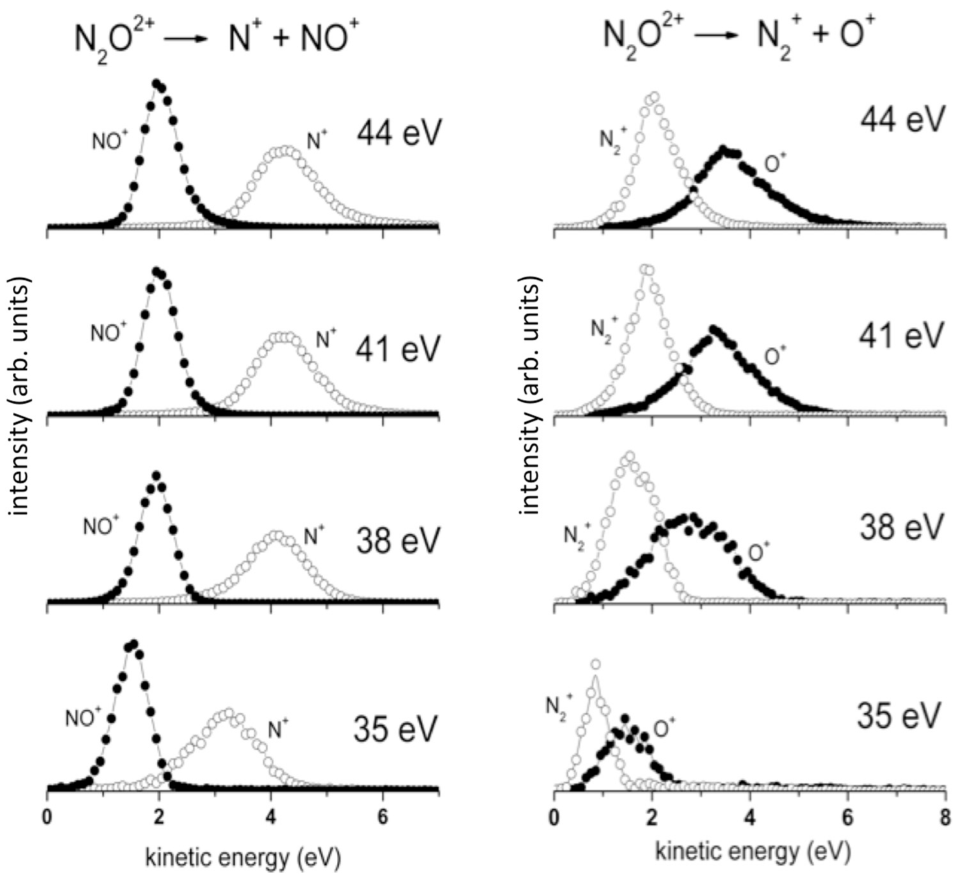

Figure 3. Kinetic energy distributions for each fragment ion N^+ and NO^+ coming from the Coulomb explosion of N_2O^{2+} dication (following the two possible two-body fragmentation processes indicated on the top of the respective panel), produced in the double VUV photoionization experiment of nitrous oxide (see text), as a function of the investigated photon energy.

From Figure 3 it is possible to see that N^+ and O^+ ions $+N_2^+$, are formed with a KER ranging between 2.0–5.2 eV and 1.0–5.5 eV, respectively. By looking at the typical escape energy for such ions from the upper atmosphere of Mars and Titan (1.8 and 0.32 eV (in the case of N^+), 2.0 and 0.37 eV (in the case of O^+), respectively [23]), we can argue that their measured kinetic energy content is, in principle, compatible with their possible escape from the upper atmosphere of such planets.

3.3. Ethyne

The double photoionization of ethyne molecules by using VUV synchrotron radiation in the 32-65 eV photon energy range produces $C_2H_2^{2+}$ dication with a measured threshold energy of 31.7 eV. Such e dication can dissociate by Coulomb explosion via three different two-body fragmentation channels producing the following ion pairs: H^++C_2H^+, CH^++CH^+, and C^++CH_2^+. The determination of the threshold energy for such fragmentation reactions (33.8, 34.0, and 34.0 eV, respectively) was the aim of a previous work from our laboratory [32], in agreement with experimental determinations by Eland and coworkers [43]. In the present work we have focused our attention on the KER distributions for such ions measured by using the synchrotron radiation at a photon energy of 39.0 eV. By analyzing the density distribution of the recorded coincidence plot at such an energy, we are able to extract the translational energy distributions of each product ion (see Figure 4) by using the same procedure already applied to carbon dioxide and nitrous oxide double photoionization.

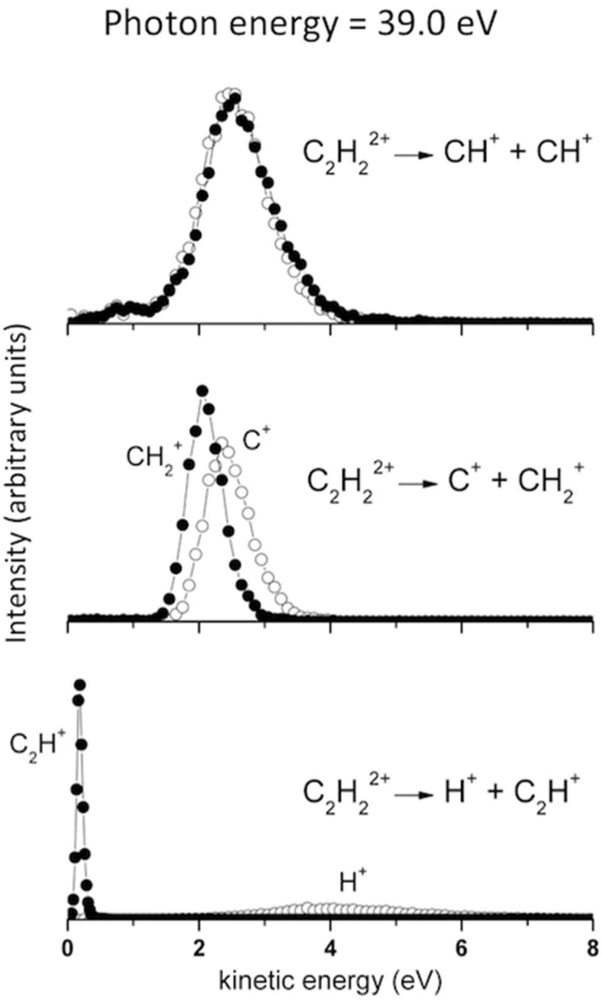

Figure 4. Kinetic energy distributions for each two-body fragment ion coming out from the Coulomb explosion of the $C_2H_2^{2+}$ molecular dication (see reactions text), as measured at a photon energy of 39 eV.

It has to be noted that the translational energy content of each H^+, C^+, CH^+ and CH_2^+ product ion is quite big, having an average value ranging between 4.0, 2.5, 2.0 and 2.5 eV, respectively. This kinetic energy is sufficient to allow this species participating in the atmospheric escape from Mars and Titan where they are characterized by a typical escape energy of 0.13 and 0.02 eV (in the case of H^+), 1.5 and 0.28 eV (in the case of C^+), 1.6 and 0.30 eV (for CH^+), 1.8 and 0,32 eV (for CH_2^+), respectively [23].

4. Conclusions

The dissociative double photoionization processes, induced by VUV light's photons and producing fragment ions with a high kinetic energy content, could be in general an important way for ionic species to escape from the atmosphere of some planets of the Solar System, like 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 photoionizazion of CO_2, N_2O and C_2H_2 molecules (in the photon energy range of 28–65 eV), the fragment product ions O^+, CO^+, N^+, CH_2^+, CH^+, C^+, H^+ are characterized by a translational energy ranging between 1.0 and 6.0 eV that is large enough to allow their escape process from the upper atmospheres of Mars and Titan. The studies here presented could be helpful in understanding important details about the chemistry of planetary ionospheres.

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Abbreviations

The following abbreviations are used in this manuscript:

KER: Kinetic Energy Released
VUV: Vacuum Ultraviolet
UV: Ultraviolet
ARPES: Angle-Resolved Photoemission Spectroscopy

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References must be numbered in order of appearance in the text (including citations in tables and legends) and listed individually at the end of the manuscript. We recommend preparing the references with a bibliography software package, such as EndNote, ReferenceManager or Zotero to avoid typing mistakes and duplicated references.

Citations and References in Supplementary files are permitted provided that they also appear in the main text and in the reference list.

In the text, reference numbers should be placed in square brackets [], and placed before the punctuation; for example [1], [1–3] or [1,3]. For embedded citations in the text with pagination, use both parentheses and brackets to indicate the reference number and page numbers; for example [5] (p. 10), or [6] (pp. 101–105).

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