Dications formation and escape probability of ions from planetary atmospheres



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Robert Richter Sincrotrone Trieste – Area Science Park – Basovizza, Trieste - Italy A very important characteristic for the chemistry of molecules in the interstellar medium and planets ionospheres is that they interact with the electromagnetic waves: γ and X rays, UV light.

For example, the interaction with the ultraviolet light is responsible of the limited growth of the organic molecules.



The UV photochemistry studies can be performed by using an intense and tunable light source as the synchrotron radiation

By using the UV light, molecules can be ionized producing mono-, and di-cations

It has to be noted that molecular CO_2^{2+} and N_2^{2+} dications have been predicted to exist with significant densities in the Mars, Venus and Titan ionospheres.



O. Witasse, et al. Geophys. Res. Lett., 2002, 29, 104.

- O. Witasse, et al. Geophys. Res. Lett., 2003, 30, 12.
- J. Lilensten, et al. Geophys. Res. Lett., 2005, 32, 03203.
- G. Gronoff, et al. Astron. Astrophys., 2007, 465, 641–645.

In the case of CO_2 , by using 34-50 eV photon energy, the molecular fragmentation can be observed:

$$CO_2 + hv \rightarrow CO^+ + O^+ + 2e^-$$

With a total kinetic energy of product ions ranging between 2 and 6 eV

In general, when a molecule is ionized, can change deeply its chemical behavior because:

1 – the removed electron may change sensibly the electronic configuration of the neutral species modifying its chemical reactivity;

2 – the ion-molecule interaction is much more intense than the neutralneutral one, making more probable the collision;

3 – the double ionization producing a molecular dication can induce Coulombic explosion and fragment ions formation with high kinetic energy content.





The CO_2^{2+} dication formation and its dissociation is of importance in the atmosphere of Mars, where CO_2 is the main component

The production of CO^+ and O^+ with a high kinetic energy content could explain the lack in the O^+ expected concentration CO₂ is involved in several atmospheric phenomena of the Earth and of other planets like Mars and Venus



Nicolas, C.; Alcaraz, C.; Thissen, R.; Zabka, J.; Dutuit, O. *Planet. Space Sci.* **2001**, 50, 877. Witasse, O.; Dutuit, O.; Lilensten, J.; Thissen, R.; Zabka, J.; Alcaraz, C.; Blelly, P. L.; Bougher, S. W.; Engel, S.; Andersen, L. H.; Seiersen, K. *Geophys. Res. Lett.* **2002**, 29, 1263. The double photoionization of CO_2 molecules has been studied in the 34-50 eV photon energy range, by the use of synchrotron radiation...



and detecting electron-ion and electron-ion-ion coincidences





Interacting with 34-50 eV photons, the CO_2 molecule gives four different processes:

CO₂ + hv →
$$(CO_2^+)^*$$
 + e⁻ hv ≥ 35.6 eV
Fast dissociation
 $(\tau \le 0.05 \ \mu s)$
(B)
 $(CO_2^{2^+})^*$
 $CO^+ + O^+ + 2e^-$
hv ≥ 39.0 eV

 $CO_2 + hv \rightarrow CO_2^{2+} + 2e^{-}$ $hv \ge 37.3 \text{ eV}$

CO₂ + hv → $(CO_2^{2+})^*$ + 2e⁻ → CO⁺ + O⁺ hv ≥ 38.7 eV Slow dissociation ($\tau \ge 3.1 \ \mu s$)

Franceschi, P.; Thissen, R.; Zabka, J.; Roithová, J.; Herman, Z.; Dutuit, O. Int. J. Mass Spectrom. 2003, 228, 507.

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

Alagia, M.; Candori, P.; Falcinelli, S.; Lavollée, M.; Pirani, F.; Richter, R.; Stranges, S.; Vecchiocattivi, F. *J. Phys. Chem. A* **2009**, *113*, 14755.

Spectra of coincidences for the double photoionization of CO₂ at a photon energy of 44 eV

At each wavelenght the total counts in the peak for each ion pair gives the intensity and the cross section, and the peak dimensions and shapes give plot of the ions delay the Kinetic Energy Released (KER) for product ions

> The intensity of the CO_2^{2+} peak in the mass spectrum, as a function of the photon energy, normalized for the photon flux, gives the relative cross section for the molecular dication formation

> > Counting the true coincidences in area "A"

provides the cross section for the "direct fast

dissociation", while counting the true

coincidences in the areas "B" and "C" provides

the cross section for the formation of the

metastable $(CO_2^2+)^*$ (slow dissociation).

The relative cross sections as a function of the photon energy are so obtained and the density distribution of the coincidences along the areas "A", "B" and "C" is related to the lifetime of the molecular dication

the different areas for the analysis of the lifetime of metastable $(CO_2^{2+})^*$ dication are indicated

times t and t

CO

mass spectrum of the

product ions at 44eV

CO22+

 t_2

CO⁺

 t_2



For the <u>fast molecular dication dissociation</u> we confirm the presence of two different mechanisms as indicated by the analysis of the measured total kinetic energy released for the CO⁺ and O⁺ fragment ions



Atmospheric escape of O⁺ by dissociative double photoionization of CO_2 molecules cO^+

One consequence of the exotic behavior of doubly charged molecular ions in planetary atmospheres is the possibility of creation of dissociative products with a kinetic energy of several eV.

In the case of CO_2 , the production of CO^+ and O^+ fragments with a high kinetic energy content (2.0 and 3.8 eV, respectively) could explain the lack in the O^+ expected concentration of the Mars Atmosphere.

This energy is large enough in the case of Mars and Titan to allow these fragments to reach sufficient velocity to escape into space. Therefore this process can in principle contribute to the continuous erosion of these atmospheres.

Typical escape energy (eV) for the C^+ , N^+ and O^+ ions in the atmosphere of Venus, Earth, Mars and Titan, at the exobase

Ion/planet	Venus	Earth	Mars	Titan
C^+	6.4	7.4	1.5	0.28
N	7.5	8.6	1.8	0.32
<u>O</u> ⁺	8.6	9.8	2.0	0.37



The kinetic energy distributions of product CO^+ and O^+ ions as obtained from the analysis of ion images as a function of the photon energy.

Atmospheric escape of O^+ by dissociative double photoionization of CO_2 molecules



Where the O⁺ concentration become lower, the concentration of CO_2^{2+} increases.

This could be explained by the CO_2^{2+} fragmentation towards the CO^+ and O^+ ions production with a high kinetic energy content (3.5-3.8 eV for O^+ ions).

This energy is large enough to allow the O⁺ escape from the Mars atmosphere.

 $CO_2^{2^+}$ ion density profiles for Viking 1 lander (V1) and Mariner 6 spacecraft (M6) geophysical conditions. Ion density profiles measured by Viking 1 lander are also plotted.

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

towards $C_2H_2...$

Acetylene molecules have been detected in interstellar medium. Astronomers have observed it in the infrared, in both molecular clouds and in the envelopes of evolved stars. It is an important link in the chemistry of heavier carbon chain molecules and related species in these regions.

Acetylene is also found as a minor component in the atmospheres of gas giants like the planet Jupiter, in the atmosphere of Saturn's satellite Titan, and in comets.

Photochemical experiments have demonstrated that acetylene is a likely precursor of C_2 , a widely observed component of comets. It may therefore be itself a ubiquitous constituent of comets.

It has been proposed that polymerization of acetylene in cometary impact on planetary atmospheres may be responsible for the formation of polycyclic aromatic hydrocarbons (PAHs) which may in turn be responsible for the colors of the atmospheres of Jupiter and Titan.

T.Y. Brooke, A.T. Tokunaga, H.A. Weaver, J. Crovisier, D. Bockelee-Morvan, D. Crisp, Nature 1996, *383*, 606.
J. Cernicharo *et al.*, Astrophys. J. 2001, *546*, L123.
P.M. Woods *et al.*, Astrophys. J. 2002, *574*, L167.
R. Kaiser, Chem Rev. 2002, *102(5)*, 1309-1358.
P.O. Momoh, S.A. Abrash, R. Mabrouki, M.S. El-Shall, J. Am. Chem Soc. 2006, *128*, 12408-12409.

Photoionization in the 35-65 eV photon energy range produces ethyne dication with subsequent two-body dissociation reactions:



Thissen, R.; Delwiche, J.; Robbe, J.M.; Duflot, D.; Flament, J.P.; Eland, J.H.D. J. Chem. Phys. 1993, 99, 6590.

Alagia, M.; Callegari, C.; Candori, P.; Falcinelli, S.; Pirani, F.; Richter, R.; Stranges, S., Vecchiocattivi, F. *J. Chem. Phys.* **2012**, *136*, 204302.



In the case of acetylene, the dissociation leading to $C_2H^++H^+$ products occurs through a metastable dication with a lifetime of 108±22 ns, and a KER of



3500

3000

2500

H⁺ + C₂H⁺

This can better be seen looking at the kinetic energy distributions of each fragment ions at 39 eV



The double photoionization of N_2O in the 28-40 eV photon energy range

In the whole investigated energy range, we observed two dissociation channels with a threshold energy of 32.2 eV:

$$N_2O + hv \rightarrow (N_2O^{2+})^* + 2e^- \rightarrow N_2^+ + O^+ + 2e^-$$

N₂O + hv →
$$(N_2O^{2+})^*$$
 + 2e⁻ → N⁺ + NO⁺ + 2e⁻

intermediate "short lived" molecular dication with a lifetime shorter than 10⁻⁶ sec (typical average ion time-of-flight in our detection device)

The analysis of our results can provide, with the same procedure applied to CO_2 and C_2H_2 molecules, the total kinetic energy of ionic fragments as a function of the investigated photon energy:

44 eV

8



Looking at the typical escape energy for various ions we can argue that the measured kinetic energy content, in the range 2.0÷5.5 eV for N⁺ and 0.8÷5.2 eV for O⁺ ion products are compatible with their possible escape from the upper atmosphere of Mars and Titan

Ion	Measured KER distribution range (eV)	Typical escape energy (eV) for various ions in the atmosphere (at the exobase) of some planets of the Solar System				
H ⁺	2.5÷6.0 ^(a)	0.60	0.51	0.11	0.02	
C ⁺	1.7÷3.5 ^(b)	7.2	6.2	1.35	0.28	
CH^+	1.5÷4.0 ^(c)	7.8	6.7	1.5	0.30	
CH ₂ ⁺	1.5÷2.8 ^(b)	8.4	7.2	1.6	0.32	
N ⁺	2.0÷5.5 ^(d)	8.4	7.2	1.6	0.32	
0+	0.8÷5.2 ^(e) 2.0÷3.7 ^(f)	9.6	8.2	1.8	0.37	
C_2H^+	0.1÷0.3 ^(a)	15.0	12.8	2.9	0.58	
CO ⁺	0.5÷2.5 ^(f)	16.8	14.3	3.2	0.65	
N_2^+	0.5÷2.8 ^(e)	16.8	14.3	3.2	0.65	
NO ⁺	1.0÷2.8 ^(d)	18.0	15.3	3.4	0.70	

N₂O has been recently suggested to be present in the upper atmosphere of Titan in a detectable amount by Dobrijevic et al. [Icarus **228**, 324-346 (2014)] who considered for the first time the coupling between nitrogen and oxygen chemistry in that environment



- The UV photochemistry studies useful to understand the atmospheric chemistry of the Earth and of other planets can be performed by using an intense and tunable light source as the synchrotron radiation

– The double photoionization of CO_2 has been studied in the 34-50 eV energy range

- For $h_{V} \ge 35.6 \text{ eV}$ the fragmentation of CO_2^{2+} dication takes place producing CO^+ and O^+ ions with a kinetic energy release (KER) ranging between 2 and 6 eV

- The measured cross sections for the different fragmentation channels togheter with the KER can be useful to understand the chemistry of the Mars and Venus atmospheres

- The production of CO⁺ and O⁺ with a high kinetic energy content could explain the lack in the O⁺ expected concentration on Mars atmosphere

- Analogous studies can be performed with other simple interesting molecules of astrochemical interest as N_2O , C_2H_2 and C_6H_6

 $A + B^{2+}$ $I_2(B) >> I_1(A)$ $A^+ + B^+$

 $I_2(B) << I_1(A)$

B+

B²⁺

B²⁺

B⁺

 $I_2(B) \geq I_1(A)$



In the gas phase, the two charged parts of the dication tend to repel each other, making this specie metastable, in some particular cases, and more often unstable, determining the fragmentation in two positive ions often with high KER.



Experimental Procedure

Monochromator: 400 lines/mm spherical grating in first order diffraction with entrance and exit slits adjusted in order to give a photon energy resolution of ~ 1.5 meV.

Magnesium film filter: was placed in the synchrotron radiation beam in order to avoid spurious effects due to ionization by photons from higher orders of diffraction.

Ion extraction and detection system: is a TOF spectrometer with an ion-position sensitive detector (stack of three micro-channel-plates with a multi-anode array arranged in 32 rows and 32 columns) especially designed to measure the spatial momentum vectors of the ionic dissociation products.

The light beam is linearly polarized and the direction of the polarization vector is aligned parallel to the molecular beam axis.



The incident photon flux and the gas pressure are monitored and the ion yields are then corrected for pressure and photon flux changes while varying the photon energy.

The gas inlet source (effusive) is supplied with a mixture of the molecule under study and He, allowing the normalization of all ion signals at each photon energy to the total ion yield of helium at that energy.

KER and Cross Sections calculation

At each wavelenght the total counts in the peak for each ion pair gives the intensity, and the peak dimensions give the Kinetic Energy Released (KER) for two-body reactions, or the energies of the observed ions for three-body reactions.



Relative cross sections:

arrival time of the first ion (ns) from the intensity of area related to each ion pair on the assumption that ion detection efficiency is indipendent of mass

Absolute cross sections:

with the assumption: 1) the effective collection efficiencies for electrons from double ionization (49%) and single ionization (27%) can be defined and are indipendent of photon energy; 2) the relative radiation flux at each wavelenght was determined by measuring the ionization of He and by comparison with the known ionization cross section; 3) normalization of the relative yield curves to absolute cross sections can be done using well known results at a known photon energy.

Lifetimes calculation

By analyzing the "tail" in the coincidence plot it's possible to derive the lifetime for the dications leading to the dissociation reaction as in the case of

 $\begin{array}{c} \mathrm{CO}_2 + \mathrm{hv} \twoheadrightarrow (\mathrm{CO}_2^{2+})^* + 2\mathrm{e}^{-} \twoheadrightarrow \mathrm{CO}^+ + \mathrm{O}^+ \\ \mathrm{C}_2\mathrm{H}_2 + \mathrm{hv} \twoheadrightarrow (\mathrm{C}_2\mathrm{H}_2^{2+})^* + 2\mathrm{e}^{-} \twoheadrightarrow \mathrm{C}_2\mathrm{H}^+ + \mathrm{H}^+ \end{array}$

The experimental data are compared with the best Monte Carlo fit simulation



We plot the number of coincidence points along the track of the "tail" as a function of the (t_2-t_1) difference, and we fit the data by a Monte Carlo simulation of the ion trajectories in the mass spectrometer.

The main square values, χ^2 , of the difference between the experimental data and the simulation, are plotted as a function of the dication lifetime: the minimum obtained deviation gives the searched value



 $I(t_2 - t_1) = A_1 \exp\left[-\left(\frac{m_1 + m_2}{m_1 - m_2}\right)\frac{t_2 - t_1}{2\tau}\right]$ $I(t_2 - t_1) = A_2 \left\{ \ln\left[\frac{(t_2 - t_1)_{\max}}{(t_2 - t_1)}\right] + \frac{t_0}{\tau} \left[1 - \frac{(t_2 - t_1)}{(t_2 - t_1)_{\max}}\right] + \frac{t_0^2}{2\cdot 2!\tau^2} \left[1 - \frac{(t_2 - t_1)^2}{(t_2 - t_1)_{\max}^2}\right] \right\}$

Density distribution from the "tail" area





Angular Distributions

The ion imaging detector provides the angular distribution of product ions with respect the light polarization vector direction. Such angular distributions can provide valuable information about the dissociation dynamics and are usually represented as follow (R.N. Zare, Mol. Photochem., **1972**, 4, 1):



 $\beta=0 \rightarrow isotropic$ distribution of fragment ions

 $\beta=2 \rightarrow$ emission of product ions along a direction parallel to the polarization vector

When the photon energy increases, the distribution of products became anisotropic, with the two ions preferentially emitted along the direction of the light polarization vector. This implies that the molecule photoionizes when oriented parallel to that direction, and also that the CO_2^{2+} dication just formed dissociates in a time shorter than its typical rotational period.



At low energy the reaction occurs by the indirect mechanism involving the formation of CO^++O^* autoionizing atom with an isotropic final ions distribution

Angular Distributions

 $C_2H_2^{2+} \rightarrow C_2H^+ + H^+$



Almost isotropic distribution probably due to the lightness of H^+ ion The reaction occurs in a time shorter than the typical rotational period of the acetylene molecules (of the order of 10^{-12} s) proton transfer rearrangement reaction via vinylidene dication H_2CC^{2+} formation



Fragment ions produced prevalently in a perpendicular direction respect to the polarization light vector direction

Cross Sections for Ethyne dication dissociation



Cross sections for two-body dissociations of $C_2H_2^{2+}$ dications.

Thissen, R.; Delwiche, J.; Robbe, J.M.; Duflot, D.; Flament, J.P.; Eland, J.H.D. *J. Chem. Phys.* **1993**, *99*, 6590.

Potential Energy Curves for Ethyne dication dissociation



Potential energy curves calculated for the deprotonation reaction of ethyne dications. Note that the ground state of the dications correlates to an excited state of the products. The energies of the separated product states have been calculated independently to the same accuracy for consistency with the rest of the diagram, but all at the optimum geometry found for the ground state of C_2H^+ .

Potential energy curves calculated for dissociation of ethyne dications into two CH^+ ions. The ground state of the dication again correlates to an excited state of the products.

Thissen, R.; Delwiche, J.; Robbe, J.M.; Duflot, D.; Flament, J.P.; Eland, J.H.D. *J. Chem. Phys.* **1993**, *99*, 6590.

Formation of Vinylidene dication H₂CC²⁺ for Ethyne dication dissociation with protron transfer rearrangement reaction

In theoretical modeling of this reaction, we find two transition states, either of which may be critical, as shown in the figure. The first barrier lies between the linear ethyne dication form and the vinylidene dication H_2CC^{2+} ; its peak is at 34.5 eV and corresponds to a position in which one proton lies almost midway between the two carbons and 1.2 Å away from the line joining them. The vinylidene cation itself at its equilibrium geometry is only a little less stable than the ethyne dication in its ground state and lies at 33 eV. Between the vinylidene dication and the products, another barrier must be surmounted in extending the C-C bond, and its peak is at 34.8 eV. There are only small changes in the HCH bond angle and C-H bond distance from the calculated transition state to the products (see figure on the right), so little internal excitation of the CHt product is predicted.

Thissen, R.; Delwiche, J.; Robbe, J.M.; Duflot, D.; Flament, J.P.; Eland, J.H.D. *J. Chem. Phys.* **1993**, *99*, 6590.



Calculated energy profile of the reactions of $C_2H_2^{2+}$ from the normal ethyne form on the left to the rearrangement products C^+ + CH_2^+ .

