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Abstracts

Characterization of thin film CO2 ice through the infrared v1+v3 combination mode

J.He, G.Vidali

Carbon dioxide is abundant in ice mantles of dust grains; some is found in the pure crystalline form as inferred from the double peak splitting of the bending profile at about 650 cm-1. To study how CO2 segregates into the pure form from water-rich mixtures of ice mantles and how it then crystallizes, we used Reflection Absorption InfraRed Spectroscopy (RAIRS) to study the structural change of pure CO2 ice as a function of both ice thickness and temperature. We found that the v1+v3 combination mode absorption profile at 3708 cm-1 provides an excellent probe to quantify the degree of crystallinity in CO2 ice. We also found that between 20 and 30 K, there is an ordering transition that we attribute to reorientation of CO2 molecules, while the diffusion of CO2 becomes significant at much higher temperatures. In the formation of pure crystalline CO2 in ISM ices, the rate limiting process is the diffusion/segregation of CO2 molecules in the ice instead of the phase transition from amorphous to crystalline after clusters/islands of CO2 are formed.

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VUV-absorption cross section of carbon dioxide from 150 to 800 K and applications to warm exoplanetary atmospheres

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Most exoplanets detected so far have atmospheric temperatures significantly higher than 300 K. Often close to their star, they receive an intense UV photons flux that triggers important photodissociation processes. Our aim is to quantify the temperature dependency of the VUV absorption cross section of important molecules in planetary atmospheres. We want to provide both 1) high-resolution data at temperatures prevailing in these media and 2) a simple parameterization of the absorption in order to simplify its use in photochemical models. We present a full set of high resolution absorption cross sections of CO2 from 115 to 230 nm for temperatures ranging from 150 to 800 K. The VUV absorption cross section of CO2 increases with the temperature. A parameterization allows to calculate the continuum of absorption in this wavelength range. Extrapolation at higher temperature has not been validated experimentally and therefore has to be used with caution. We used these data in our 1D thermo-photochemical model in order to study their impact on the predicted

atmospheric compositions. It modifies significantly the abundance and the photodissociation rates of many species, in addition to CO2, such as methane and ammonia. These deviations have an impact on synthetic transmission spectra, leading to variations of up to 5 ppm.

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Effects of collision energy and vibrational excitation of CH3+ cations on its reactivity with hydrocarbons: But-2-yne CH3CCCH3 as reagent partner

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The methyl carbocation is ubiquitous in gaseous environments, such as planetary ionospheres, cometary comae, and the interstellar medium, as well as combustion systems and plasma setups for technological applications. Here we report on a joint experimental and theoretical study on the mechanism of the reaction CH3+ + CH3CCCH3 (but-2-yne, also known as dimethylacetylene), by combining guided ion beam mass spectrometry experiments with ab initio calculations of the potential energy hypersurface. Such a reaction is relevant in understanding the chemical evolution of Saturn’s largest satellite, Titan. Two complementary setups have been used: in one case, methyl cations are generated via electron ionization, while in the other case, direct vacuum ultraviolet photoionization with synchrotron radiation of methyl radicals is used to study internal energy effects on the reactivity. Absolute reactive cross sections have been measured as a function of collision energy, and product branching ratios have been derived. The two most abundant products result from electron and hydride transfer, occurring via direct and barrierless mechanisms, while other channels are initiated by the electrophilic addition of the methyl cation to the triple bond of but-2-yne. Among the minor channels, special relevance is placed on the formation of C5H7+, stemming from H2 loss from the addition complex. This is the only observed condensation product with the formation of new C—C bonds, and it might represent a viable pathway for the synthesis of complex organic species in astronomical environments and laboratory plasmas.

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The formation of urea in space I. Ion-molecule, neutral-neutral, and radical gas-phase reactions

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Many organic molecules have been observed in the interstellar medium thanks to advances in radioastronomy, and very recently the presence of urea was also suggested. While those molecules were observed, it is not clear what the mechanisms responsible to their formation are. In fact, if gas-phase reactions are responsible, they should occur through barrierless mechanisms (or with very low barriers). In the past, mechanisms for the formation of different organic molecules were studied, providing only in a few cases energetic conditions favorable to a synthesis at very low temperature. A particularly intriguing class of such molecules are those containing one N--C--O peptide bond, which could be a building block for the formation of biological

molecules. Urea is a particular case because two nitrogen atoms are linked to the C--O moiety. Thus, motivated also by the recent tentative observation of urea, we have considered the synthetic pathways responsible to its formation. We have studied the possibility of forming urea in the gas phase via different kinds of bi-molecular reactions: ion-molecule, neutral, and radical. In particular we have focused on the activation energy of these reactions in order to find possible reactants that could be responsible for to barrierless (or very low energy) pathways. We have used very accurate, highly correlated quantum chemistry calculations to locate and characterize the reaction pathways in terms of minima and transition states connecting reactants to products. Most of the reactions considered have an activation energy that is too high; but the ion-molecule reaction between NH2OH2+ and formamide is not too high. These reactants could be responsible not only for the formation of urea but also of isocyanic acid, which is an organic molecule also observed in the interstellar medium.

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Mechanism of Atomic Hydrogen Addition Reactions on np-ASW

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Hydrogen, being the most abundant element, is the driver of many if not most reactions occurring on interstellar dust grains. In hydrogen atom addition reactions, the rate is usually determined by the surface kinetics of the hydrogen atom instead of the other reaction partner. Three mechanisms exist to explain hydrogen addition reactions on surfaces: Langmuir-Hinshelwood, Eley-Rideal, and hot-atom. In gas-grain models, which mechanism is assumed greatly affects the simulation results. In this work, we quantify the temperature dependence of the rates of atomic hydrogen addition reactions by studying the reaction of H + O3 -> O2 + OH on the surface of a film of non-porous amorphous solid water (np-ASW) in the temperature range from 10 K to 50 K. The reaction rate is found to be temperature independent. This disagrees with the results of simulations with a network of rate equations that assume Langmuir-Hinshelwood mechanism through either thermal diffusion or tunneling diffusion; the reaction rates assuming such mechanism possesses a strong temperature dependence, either explicitly or implicitly, that is not seen experimentally. We suggest that the Eley-Rideal and/or hot-atom mechanism play a key role in hydrogen atom addition reactions, and should be included in gas-grain models. We also suggest that our newly developed time-resolved reactive scattering can be utilized to measure the chemical desorption efficiency in grain surface reactions.

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Consistent dust and gas models for protoplanetary disks. II. Chemical networks and rates

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Aims: We aim to define a small and large chemical network which can be used for the quantitative simultaneous analysis of molecular emission from the near-IR to the submm. We also aim to revise reactions of excited molecular hydrogen, which are not included in UMIST, to provide a homogeneous database for future applications. Methods: We have used the thermo-chemical disk modeling code ProDiMo and a standard T Tauri disk model to evaluate the impact of various chemical networks,

reaction rate databases and sets of adsorption energies on a large sample of chemical species and emerging line fluxes from the near-IR to the submm wavelength range. Results: We find large differences in the masses and radial distribution of ice reservoirs when considering freeze-out on bare or polar ice coated grains. Most strongly the ammonia ice mass and the location of the snow line (water) change. As a consequence molecules associated to the ice lines such as N2H+ change their emitting region; none of the line fluxes in the sample considered here changes by more than 25% except CO isotopologues, CN and N2H+ lines. The three-body reaction N+H2+M plays a key role in the formation of water in the outer disk. Besides that, differences between the UMIST 2006 and 2012 database change line fluxes in the sample considered here by less than a factor of two (a subset of low excitation CO and fine structure lines stays even within 25%); exceptions are OH, CN, HCN, HCO+ and N2H+ lines. However, different networks such as OSU and KIDA 2011 lead to pronounced differences in the chemistry inside 100 au and thus affect emission lines from high excitation CO, OH and CN lines. H2 is easily excited at the disk surface and state-to-state reactions enhance the abundance of CH+ and to a lesser extent HCO+. For sub-mm lines of HCN, N2H+ and HCO+, a more complex larger network is recommended. Conclusions: More work is required to consolidate data on key reactions leading to the formation of water, molecular ions such as HCO+ and N2H+ as well as the nitrogen chemistry. This affects many of the key lines used in the interpretation of disk observations. Differential analysis of various disk models using the same chemical input data will be more robust than the interpretation of absolute fluxes.

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New measurements on water ice photodesorption and product formation under ultraviolet irradiation

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The photodesorption of icy grain mantles has been claimed to be responsible for the abundance of gas-phase molecules toward cold regions. Being water a ubiquitous molecule, it is crucial to understand its role in photochemistry and its behavior under an ultraviolet field. We report new measurements on the UV-photodesorption of water ice and its H2 , OH, and O2 photoproducts using a calibrated quadrupole mass spectrometer. Solid water was deposited under ultra-high-vacuum conditions and then UV-irradiated at various temperatures starting from 8 K with a microwave discharged hydrogen lamp. Deuterated water was used for confirmation of the results. We found a photodesorption yield of 1.3 × 10^−3 molecules per incident photon for water, and 0.7 × 10^ −3 molecules per incident photon for deuterated water at the lowest irradiation temperature, 8 K. The photodesorption yield per absorbed photon is given and comparison with astrophysical scenarios, where water ice photodesorption could account for the presence of gas-phase water toward cold regions in the absence of a thermal desorption process is addressed.

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The ALMA-PILS survey: Formaldehyde deuteration in warm gas on small scales toward IRAS 16293-2422 B

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[abridged] The enhanced degrees of deuterium fractionation observed in envelopes around protostars demonstrate the importance of chemistry at low temperatures, relevant in pre- and protostellar cores. Formaldehyde is an important species in the formation of methanol and more complex molecules. Here, we present the first study of formaldehyde deuteration on small scales around the prototypical low-mass protostar IRAS 16293-2422 using high spatial and spectral resolution Atacama Large Millimeter/submillimeter Array (ALMA) observations. Numerous isotopologues of formaldehyde are detected, among them H2C17O, and D213CO for the first time in the ISM. The large range of upper energy levels covered by the HDCO lines help constrain the excitation temperature to 106+/-13 K. Using the derived column densities, formaldehyde shows a deuterium fractionation of HDCO/H2CO=6.5+/-1%, D2CO/HDCO=12.8+3.3/-4.1%, and D2CO/H2CO=0.6(4)+/-0.1%. The isotopic ratios derived are 16O/18O=805, 18O/17O=3.2 and 12C/13C=56. The HDCO/H2CO ratio is lower than found in previous studies, highlighting the uncertainties involved in interpreting single dish observations of the inner warm regions. The D2CO/HDCO ratio is only slightly larger than the HDCO/H2CO ratio. This is consistent with formaldehyde forming in the ice as soon as CO has frozen onto the grains, with most of the deuteration happening towards the end of the prestellar core phase. A comparison with available time-dependent chemical models indicates that the source is in the early Class 0 stage.

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X-ray radiative transfer in protoplanetary disks - The role of dust and X-ray background fields

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The X-ray luminosities of T Tauri stars are about two to four orders of magnitude higher than the luminosity of the contemporary Sun. As these stars are born in clusters, their disks are not only irradiated by their parent star but also by an X-ray background field produced by the cluster members. We aim to quantify the impact of X-ray background fields produced by young embedded clusters on the chemical structure of disks. Further, we want to investigate the importance of the dust for X-ray radiative transfer in disks. We present a new X-ray radiative transfer module for the radiation thermo-chemical disk code ProDiMo, which includes X-ray scattering and absorption by both the gas and dust component. For the X-ray radiative transfer, we consider irradiation by the star and by X-ray background fields. To study the impact of X-rays on the chemical structure of disks we use the well-established disk ionization tracers N2H+ and HCO+. For evolved dust populations, X-ray opacities are mostly dominated by the gas; only for photon energies E≳5−10keV, dust opacities become relevant. Consequently, the local disk X-ray radiation field is only affected in dense regions close to the disk midplane. X-ray background fields can dominate the local X-ray disk ionization rate for disk radii r≳20au. However, the N2H+ and HCO+ column densities are only significantly affected in case of low cosmic-ray ionization rates, or if the background flux is at least a factor of ten higher than the flux level expected for clusters typical for the solar vicinity. Observable signatures of X-ray background fields in low-mass star-formation regions, like Taurus, are only expected for cluster members

experiencing a strong X-ray background field. For the majority of the cluster members, the X-ray background field has only little impact on the disk chemical structure.

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The Final Integrations of the Caltech Submillimeter Observatory

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We present the final observations of the Caltech Submillimeter Observatory (CSO), taken toward Orion KL, prior to its decommissioning after nearly three decades of operation.

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Is the Gas-phase OH+H2CO Reaction a Source of HCO in Interstellar Cold Dark Clouds? A Kinetic, Dynamic and Modelling Study

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The chemical kinetics of neutral–neutral gas-phase reactions at ultralow temperatures is a fascinating research subject with important implications on the chemistry of complex organic molecules in the interstellar medium (T~10–100 K). Scarce kinetic information is currently available for these kinds of reactions at T<200 K. In this work, we use the Cinétique de Réaction en Ecoulement Supersonique Uniforme (CRESU; Reaction Kinetics in a Uniform Supersonic Flow) technique to measure for the first time the rate coefficients (k) of the gas-phase OH+H2CO reaction between 22 and 107 K. The k values greatly increase from 2.1×10−11 cm3 s−1 at 107 K to 1.2×10−10 cm3 s−1 at 22 K. This is also confirmed by quasi-classical trajectories (QCT) at collision energies down to 0.1 meV performed using a new full dimension and ab initio potential energy surface that generates highly accurate potential and includes long-range dipole–dipole interactions. QCT calculations indicate that at low temperatures HCO is the exclusive product for the OH+H2CO reaction. In order to revisit the chemistry of HCO in cold dense clouds, k is reasonably extrapolated from the experimental results at 10 K (2.6×10−10 cm3 s−1). The modeled abundances of HCO are in agreement with the observations in cold dark clouds for an evolving time of 10^5–10^6 yr. The different sources of production of HCO are presented and the uncertainties in the chemical networks are discussed. The present reaction is shown to account for a few percent of the total HCO production rate. This reaction can be expected to be a competitive process in the chemistry of prestellar cores. Extensions to photodissociation regions and diffuse cloud environments are also addressed.

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Revised Models of Interstellar Nitrogen Isotopic Fractionation

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Nitrogen-bearing molecules in cold molecular clouds exhibit a range of isotopic fractionation ratios and these molecules may be the precursors of 15N enrichments found in comets and meteorites. Chemical model calculations indicate that atom-molecular ion and ion-molecule reactions could account for most of the fractionation patterns observed. However, recent quantum-chemical computations demonstrate that several of the key processes are unlikely to occur in dense clouds. Related model calculations of dense cloud chemistry show that the revised 15N enrichments fail to match observed values. We have investigated the effects of these reaction rate modifications on the chemical model of Wirström et al. (2012) for which there are significant physical and chemical differences with respect to other models. We have included 15N fractionation of CN in neutral-neutral reactions and also updated rate coefficients for key reactions in the nitrogen chemistry. We find that the revised fractionation rates have the effect of suppressing 15N enrichment in ammonia at all times, while the depletion is even more pronounced, reaching 14N/15N ratios of >2000. Taking the updated nitrogen chemistry into account, no significant enrichment occurs in HCN or HNC, contrary to observational evidence in dark clouds and comets, although the 14N/15N ratio can still be below 100 in CN itself. However, such low CN abundances are predicted that the updated model falls short of explaining the bulk 15N enhancements observed in primitive materials. It is clear that alternative fractionating reactions are necessary to reproduce observations, so further laboratory and theoretical studies are urgently needed.

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Deep K-band observations of TMC-1 with the Green Bank Telescope: Detection of HC7O, non-detection of HC11N, and a search for new organic molecules

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The 100 m Robert C. Byrd Green Bank Telescope K-band (KFPA) receiver was used to perform a high- sensitivity search for rotational emission lines from complex organic molecules in the cold interstellar medium towards TMC-1 (cyanopolyyne peak), focussing on the identification of new carbon-chain-bearing species as well as molecules of possible prebiotic relevance. We report a detection of the carbon-chain oxide species HC7O and derive a column density of (7.8 ± 0.9) × 10^11 cm−2 . This species is theorized to form as a result of associative electron detachment reactions between oxygen atoms and C7H−, and/or reaction of C6H2+ with CO (followed by dissociative electron recombination). Upper limits are given for the related HC6O, C6O and C7O molecules. In addition, we obtained the first detections of emission from individual 13C isotopologues of HC7N, and derive abundance ratios HC7N/HCCC13CCCCN = 110±16 and HC7N/HCCCC13CCCN = 96±11, indicative of significant 13C depletion in this species relative to the local interstellar elemental 12C/13C ratio of 60-70. The observed spectral region covered two transitions of HC11N, but emission from this species was not detected, and the corresponding column density upper limit is 7.4 × 10^10 cm−2 (at 95% confidence). This is significantly lower than the value of 2.8 × 10^11 cm−2 previously claimed by Bell et al. (1997) and confirms the recent non-detection of HC11N in TMC-1 by Loomis et al. (2016). Upper limits were also obtained for the column densities of malononitrile and the nitrogen heterocycles quinoline, isoquinoline and pyrimidine.

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Investigating the importance of edge-structure in the loss of H/H2 of PAH cations: The case of dibenzopyrene isomers

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We present a detailed study of the main dehydrogenation processes of two dibenzopyrene cation (C24H14+) isomers, namely dibenzo(a,e)pyrene (AE+) and dibenzo(a,l)pyrene (AL+). First, action spectroscopy under VUV photons was performed using synchrotron radiation in the 8-20 eV range. We observed lower dissociation thresholds for the non-planar molecule (AL+) than for the planar one (AE+) for the main dissociation pathways: H and 2H/H2 loss. In order to rationalize the experimental results, dissociation paths were investigated by means of density functional theory calculations. In the case of H loss, which is the dominant channel at the lowest energies, the observed difference between the two isomers can be explained by the presence in AL+ of two C-H bonds with considerably lower adiabatic dissociation energies. In both isomers the 2H/H2 loss channels are observed only at about 1 eV higher than H loss. We suggest that this is due to the propensity of bay H atoms to easily form H2. In addition, in the case of AL+, we cannot exclude a competition between 2H and H2 channels. In particular, the formation of a stable dissociation product with a five-membered ring could account for the low energy sequential loss of 2 hydrogens. This work shows the potential role of non-compact PAHs containing bay regions in the production of H2 in space.

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SO3 formation from the X-ray photolysis of SO2 astrophysical ice analogue: FTIR spectroscopy and thermodynamic investigations

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In this combined experimental-theoretical work we focus on the physical and chemical changes induced by soft X-rays on sulfur dioxide (SO2) ice at a very low temperature, in an attempt to clarify and quantify its survival and chemical changes in some astrophysical environments. SO2 is an important constituent of some Jupiter moons and has also been observed in ices around protostars. The measurements were performed at the Brazilian Synchrotron Light Source (LNLS/CNPEM), in Campinas, Brazil. The SO2 ice sample (12 K) was exposed to a broadband beam of mainly soft X-rays (6-2000 eV) and in-situ analyses were performed by IR spectroscopy. The X-rays photodesorption yield (upper limit) was around 0.25 molecules per photon. The values determined for the effective destruction (SO2) and formation (SO3) cross sections were 2.5 x 10-18 cm2 and 2.1 x 10-18 cm2, respectively. The chemical equilibrium (88% of SO2 and 12% of SO3) was reached after the fluence of 1.6 x 1018 photons cm-2. The SO3 formation channels were studied at second-order Møller-Plesset perturbation theory (MP2) level, which showed three most favorable reaction routes (ΔH < - 79 kcal/mol) in simulated SO2 ice: i) SO + O2 → SO3, ii) SO2 + O → SO3, and iii) SO2 + O+ → SO3+ + e– → SO3. The amorphous solid environment effect decreases the reactivity of intermediate species towards the SO3 formation, and ionic species are even more affected. The experimentally determined effective cross sections and

theoretical reaction channels identified in this work allow us to better understand the chemical evolution of certain sulfur-rich astrophysical environments.

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