

# AstroChemical Newsletter #88

March 2023

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## Abstracts

### First detection of the atomic $^{18}\text{O}$ isotope in the mesosphere and lower thermosphere of Earth

H. Wiesemeyer, R. Güsten, R. Aladro, B. Klein, H.W. Hübers, H. Richter, U.U. Graf, M. Justen, Y. Okada, J. Stutzki

In the lower atmosphere of Earth, oxygen contains a higher fraction of the heavy  $^{18}\text{O}$  isotope than ocean water does (Dole effect). This isotopic enrichment is a signature of biological activity, set by the equilibrium between oxygenic photosynthesis and respiratory metabolisms in terrestrial and oceanic ecosystems. While the mixing between stratospheric and tropospheric oxygen leads to a slow isotopic homogenization, little is known about the isotopic oxygen enrichment in the mesosphere and thermosphere of Earth. In situ measurements from rocket-borne air samplers are limited to altitudes below the mesopause, while higher layers have only been accessible through the analysis of the oxidation of ancient cosmic spherules. Here we report the detection of the far-infrared fine-structure lines ( $3\text{P}_1 \leftarrow 3\text{P}_2$  and  $3\text{P}_0 \leftarrow 3\text{P}_1$ ) of  $^{18}\text{O}$  in absorption against the Moon, and determine the  $^{16}\text{O}/^{18}\text{O}$  ratio in atomic oxygen from the mesosphere and lower thermosphere. After correcting for isotopic exchange between atomic and molecular oxygen, our values for the bulk  $^{16}\text{O}/^{18}\text{O}$  ratio of 468 and 382 in February and November 2021, respectively, fall significantly below that found in solar wind samples ( $530 \pm 2$ ), and encompass, within uncertainties, the corresponding ratios pertaining to the Dole effect in the troposphere (487), and those found in stratospheric ozone (429 to 466). We show that with existing technology, future, more sensitive measurements will allow us to monitor deviations from isotopic homogeneity in the mesosphere and lower thermosphere of Earth by remote sensing. We demonstrate that the collisional excitation of the fine-structure levels of the  $3\text{P}$  ground-state triplet of  $^{18}\text{O}$  may compete with isotopic exchange reactions, implying a deviation from the Boltzmann distribution that would be established under local thermodynamic equilibrium.

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### An accurate set of $\text{H}_3\text{O}^+$ – $\text{H}_2$ collisional rate coefficients for non-LTE modelling of warm interstellar clouds

S. Demes, F. Lique, A. Faure, F.F.S. van der Tak

Hydronium ( $\text{H}_3\text{O}^+$ ) was first detected in 1986 in interstellar molecular clouds. It was reported in many Galactic diffuse and dense regions, as well as in extragalactic sources.  $\text{H}_3\text{O}^+$  plays a major role both in interstellar oxygen and water chemistry. However, despite the large number of  $\text{H}_3\text{O}^+$  observations, its collisional excitation was investigated only partially. In this work, we study the state-to-state rotational (de-)excitation of ortho- and para- $\text{H}_3\text{O}^+$  in collisions both with ortho- and para- $\text{H}_2$ . The cross sections are calculated within the close-coupling formalism using a highly accurate potential energy surface developed for this system. The rate coefficients are computed up to a kinetic temperature of 300 K. Transitions between the lowest 21 rotation-inversion states were studied for para- $\text{H}_3\text{O}^+$ , and the lowest 11 states for ortho- $\text{H}_3\text{O}^+$ , i.e. all levels with rotational energies below 430 K ( $\sim 300 \text{ cm}^{-1}$ ) are considered. In order to estimate the impact of the new rate coefficients on the astrophysical models for  $\text{H}_3\text{O}^+$ , radiative transfer calculations were also carried out. We have examined how the new collisional data affect the line intensities with respect to older data previously used for the interpretation of observations. By analysing all detected transitions we find that our new, accurate rate coefficients have a significant impact (typically within a factor of 2) on radiation temperatures, allowing more accurate estimation of column densities and relative abundances of hydronium, especially in warm molecular clouds, paving the path towards better interpretation of interstellar water and oxygen chemistry.

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### New measurement of the diffusion of carbon dioxide on non-porous amorphous solid water

Jiao He, Paula Caroline Pérez Rickert, Tushar Suhasaria, Oriane Sohier, Tia Bäcker, Dimitra Demertzi, Gianfranco Vidali, Thomas Henning

The diffusion of molecules on interstellar grain surfaces is one of the most important driving forces for the molecular complexity in the interstellar medium. Due to the lack of laboratory measurements, astrochemical modeling of grain surface processes usually assumes a constant ratio between the diffusion energy barrier and the desorption energy. This oversimplification inevitably causes large uncertainty in model predictions. We present a new measurement of the diffusion of  $\text{CO}_2$  molecules on the surface of non-porous amorphous solid water (np-ASW), an analog of the ice mantle that covers

cosmic dust grains. A small coverage of CO<sub>2</sub> was deposited onto an np-ASW surface at 40 K, the subsequent warming of the ice activated the diffusion of CO<sub>2</sub> molecules, and a transition from isolated CO<sub>2</sub> to CO<sub>2</sub> clusters was seen in the infrared spectra. To obtain the diffusion energy barrier and pre-exponential factor simultaneously, a set of isothermal experiments were carried out. The values for the diffusion energy barrier and pre-exponential factor were found to be 1300±110 K and 107.6±0.8 s<sup>-1</sup>. A comparison with prior laboratory measurements on diffusion is discussed.

Molecular Physics

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## Simulation of CH<sub>3</sub>OH ice UV photolysis under laboratory conditions

W. R. M. Rocha, P. Woitke, S. Pilling, W. -F. Thi, J. K. Jørgensen, L. E. Kristensen, G. Perotti, I. Kamp

Methanol is the most complex molecule securely identified in interstellar ices and is a key chemical species for understanding chemical complexity in astrophysical environments. Important aspects of the methanol ice photochemistry are still unclear such as the branching ratios and photo-dissociation cross-sections at different temperatures and irradiation fluxes. This work aims at a quantitative agreement between laboratory experiments and astrochemical modelling of the CH<sub>3</sub>OH ice UV photolysis. This work also allows us to better understand which processes govern the methanol ice photochemistry present in laboratory experiments. We use ProDiMo to simulate the conditions of laboratory measurements. The simulations start with simple chemistry consisting only of methanol ice and helium to mimic the residual gas in the experimental chamber. A surface chemical network enlarged by photo-dissociation reactions is used to study the chemical reactions within the ice. Additionally, different surface chemistry parameters (surface competition, tunnelling, thermal diffusion and reactive desorption) are adopted to check those that reproduce the experimental results. The chemical models with ProDiMo can reproduce the methanol ice destruction via UV photodissociation at temperatures of 20, 30, 50 and 70 K as observed in the experiments. We note that the results are sensitive to different branching ratios after photolysis and to the mechanisms of reactive desorption. In the simulations of a molecular cloud at 20 K, we observed an increase in the methanol gas abundance of one order of magnitude, with a similar decrease in the solid-phase abundance. Comprehensive astrochemical models provide new insights into laboratory experiments as the quantitative understanding of the processes that govern the reactions within the ice. Ultimately, those insights can help to better interpret astronomical observations.

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## Spectral variations among different scenarios of PAH processing or formation

A. Maragkoudakis, E. Peeters, A. Ricca

We examine the variations in the spectral characteristics and intensities of PAHs in two different scenarios of PAH processing (or formation): (1) small PAHs are being destroyed (or equivalently large PAHs are being formed, referred to as SPR i.e. small PAHs removed), and (2) large PAHs are being destroyed (or equivalently small PAHs are being formed referred to as LPR i.e. large PAHs removed). PAH emission was measured considering both the presence or absence of plateau components. The variation in the PAH band intensities as a function of the average number of carbon atoms <NC> has the highest dynamic range in the SPR case suggesting that smaller PAHs have higher impact on the PAH band strengths. The plateaus show overall declining emission with <NC>, and their higher dynamic range in the SPR case also suggests that smaller PAHs are mainly contributing to the plateau emission. The 7.7/(11.0+11.2) μm PAH band ratio presents the least amount of variance with the lowest dynamic range, rendering this ratio as the better choice for tracing PAH charge. The 3.3/(11.2+11.0) μm PAH band ratio is the only ratio that has both a monotonic variance and fully separated values among the SPR and LPR scenarios, highlighting its efficiency as PAH size tracer but also allowing the characterization of the dominant scenario of processing or formation in a given region or source. We present new PAH charge – size diagnostic diagrams, which can provide insights on the average, maximum, or minimum NC within astrophysical sources.

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## Resonant infrared irradiation of CO and CH<sub>3</sub>OH interstellar ices

J. C. Santos, K.-J. Chuang, J. G. M. Schrauwen, A. Traspas Muiña, J. Zhang, H. M. Cuppen, B. Redlich, H. Linnartz, S. Ioppolo

Solid-phase photo-processes involving icy dust grains greatly affect the chemical evolution of the interstellar medium by leading to the formation of complex organic molecules and by inducing photodesorption. So far, the focus of laboratory studies has been mainly on the impact of energetic UV photons on ices, but direct vibrational excitation by infrared photons is expected to influence the morphology and content of interstellar ices as well. However, little is still known about the mechanisms through which this excess vibrational energy is dissipated, and its implications on the structure and ice photochemistry. In this work, we present a systematic investigation of the behavior of interstellar relevant CO and CH<sub>3</sub>OH ice analogues upon resonant excitation of vibrational modes using tunable infrared radiation, leading to both the quantification of infrared-induced photodesorption and insights in the impact of vibrational energy dissipation on ice morphology. We utilize an ultrahigh vacuum setup at cryogenic temperatures to grow pure CO and CH<sub>3</sub>OH ices, as well as

mixtures of the two. We expose the ices to intense, near-monochromatic mid-infrared free electron-laser radiation using the LISA end-station at the FELIX free electron laser facility to selectively excite the species. Changes to the ice are monitored by means of reflection-absorption infrared spectroscopy combined with quadrupole mass-spectrometry. The methods also allow to characterize the photodesorption efficiency. The dissipation of vibrational energy is observed to be highly dependent on the excited mode and the chemical environment of the ice. All amorphous ices undergo some degree of restructuring towards a more organized configuration upon on-resonance irradiation. Moreover, IR-induced photodesorption is observed to occur for both pure CO and CH<sub>3</sub>OH ices, with interstellar photodesorption efficiencies of the order of 10 molecules cm<sup>-2</sup> s<sup>-1</sup>—i.e., comparable to or higher than UV-induced counterparts. Indirect photodesorption of CO upon vibrational excitation of CH<sub>3</sub>OH in ice mixtures is also observed to occur, particularly in environments rich in methanol. The astrochemical implications of these IR-induced phenomena are discussed.

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## Announcements

### First Announcement: SOFIA School 2023, April 18-21

We are pleased to invite you to the second SOFIA School, held on April 18-21, 7:30-11 am Pacific Time. This free virtual event is designed for anyone who considers using astronomical mid- and far-IR data in their scientific research.

Through scientific, analysis and data reduction examples, paired with lectures on fundamental concepts, attendees will be introduced to the range of scientific information leveraged by such data, on a variety of sources. The school will focus on SOFIA data, but the content presented will be relevant to other mid-/far-IR data from balloon facilities or satellites.

Invited lectures will be given by Sarah Nickerson (BAERI/NASA), Ed Montiel (SOFIA/USRA), David Neufeld (JHU), Valentin Le Gouellec (NPP/NASA), David Chuss (Villanova), Martin Houde (Western), Jessica Sutter (USCD), Dario Fadda (SOFIA/USRA), Gary Ferland (Kentucky), Lars Bonne (SOFIA/USRA), Ronan Higgins (Cologne), Mark Wolfire (UMD) and Marc Pound (UMD).

Click here to register: <https://events.r20.constantcontact.com/register/eventReg?oeidk=a07ejmcef3nba4cf227&oseq=&c=&ch=>

SOFIA School Website: <https://sofia-school-2022.constantcontactsites.com/>

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