

# AstroChemical Newsletter #55

June 2020

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## Abstracts

### Anharmonic Frequencies of (MO)<sub>2</sub> & Related Hydrides for M = Mg, Al, Si, P, S, Ca, & Ti and Heuristics for Predicting Anharmonic Corrections of Inorganic Oxides

B. R. Westbrook and R. C. Fortenberry

The low-frequency vibrational fundamentals of D<sub>2h</sub> inorganic oxides are readily modeled by heuristic scaling factors at fractions of the computational cost compared to explicit anharmonic frequency computations. Oxygen and the other elements in the present study are abundant in geochemical environments and have the potential to aggregate into minerals in planet-forming regions or in the remnants of supernovae. Explicit quartic force field computations at the CCSD(T)-F12b/cc-pVTZ-F12 level of theory generate scaling factors that accurately predict the anharmonic frequencies with an average error of less than 1.0 cm<sup>-1</sup> for both the metal–oxygen stretching frequencies and the torsion and antisymmetric stretching frequencies. Inclusion of hydrogen motions is less absolutely accurate but is similarly relatively predictive. The fundamental vibrational frequencies for the seven tetra-atomic inorganic oxides examined presently fall below 876 cm<sup>-1</sup> and most of the hydrogenated species do as well. Additionally, ν<sub>6</sub> for the SiO dimer is shown to have an intensity of 562 km mol<sup>-1</sup>, with each of the other molecules having one or more frequencies with intensities greater than 80 km mol<sup>-1</sup>, again with most in the low-frequency infrared range. These intensities and the frequencies computed in the present study should assist in laboratory characterization and potential interstellar or circumstellar observation.

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### The Leiden Atomic and Molecular Database (LAMDA): Current status, recent updates, and future plans

Floris van der Tak, François Lique, Alex Faure, John Black, Ewine van Dishoeck

The Leiden Atomic and Molecular Database (LAMDA) collects spectroscopic information and collisional rate coefficients for molecules, atoms, and ions of astrophysical and astrochemical interest. We describe the developments of the database since its inception in 2005, and outline our plans for the near future. Such a database is constrained both by the nature of its uses and by the availability of accurate data: we suggest ways to improve the synergies among users and suppliers of data. We summarize some recent developments in computation of collisional cross sections and rate coefficients. We consider atomic and molecular data that are needed to support astrophysics and astrochemistry with upcoming instruments that operate in the mid- and far-infrared parts of the spectrum.

Accepted by Atoms (special issue about Atomic and Molecular Databases)

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Full-text URL: <https://arxiv.org/abs/2004.11230>

### Chemical modelling of dust-gas chemistry within AGB outflows -- II. Effect of the dust-grain size distribution

M. Van de Sande, C. Walsh, T. Danilovich

AGB stars are, together with supernovae, the main contributors of stellar dust to the interstellar medium (ISM). Dust grains formed by AGB stars are thought to be large. However, as dust nucleation and growth within their outflows are still not understood, the dust-grain size distribution (GSD) is unknown. This is an important uncertainty regarding our knowledge of the chemical and physical history of interstellar dust, as AGB dust forms ~ 70% of the starting point of its evolution. We expand on our chemical kinetics model, which uniquely includes a comprehensive dust-gas chemistry. The GSD is now allowed to deviate from the commonly assumed canonical Mathis et al. (1977) distribution. We find that the specific GSD can significantly influence the dust-gas chemistry within the outflow. Our results show that the level of depletion of gas-phase species depends on the average grain surface area of the GSD. Gas-phase abundance profiles and their possible depletions can be retrieved from observations of molecular emission lines when using a range of transitions. Due to degeneracies within the prescription of GSD, specific parameters cannot be retrieved, only (a lower limit to) the average grain surface area. Nonetheless, this can discriminate between dust composed of predominantly large or small grains. We show that when combined with other observables such as the spectral energy distribution and polarised light, depletion levels from molecular gas-phase abundance profiles can constrain the elusive GSD of the dust delivered to the ISM by AGB outflows.

17 pages, 10 figures, 6 tables. Accepted for publication in MNRAS

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## A Molecular Candle Where Few Molecules Shine: HeHHe+

Ryan C. Fortenberry and Laurent Wiesenfeld

HeHHe<sup>+</sup> is the only potential molecule comprised of atoms present in the early universe that is also easily observable in the infrared. This molecule has been known to exist in mass spectrometry experiments for nearly half-a-century and is likely present, but as-of-yet unconfirmed, in cold plasmas. There can exist only a handful of plausible primordial molecules in the epochs before metals (elements with nuclei heavier than 4 He as astronomers call them) were synthesized in the universe, and most of these are both rotationally and vibrationally dark. The current work brings HeHHe<sup>+</sup> into the discussion as a possible (and potentially only) molecular candle for probing high-*z* and any metal-deprived regions due to its exceptionally bright infrared feature previously predicted to lie at 7.43 μm. Furthermore, the present study provides new insights into its possible formation mechanisms as well as marked stability, along with the decisive role of anharmonic zero-point energies. A new entrance pathway is proposed through the triplet state (<sup>3</sup>B<sub>1</sub>) of the He<sub>2</sub>H<sup>+</sup> molecule complexed with a hydrogen atom and a subsequent 10.90 eV charge transfer/photon emission into the linear and vibrationally-bright 1Σ<sup>+</sup>g HeHHe<sup>+</sup> form.

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## Novel approach to distinguish between vacuum UV-induced ice photodesorption and photoconversion. Investigation of CH<sub>4</sub>, CH<sub>3</sub>OH, and CH<sub>3</sub>CN.

M. Bulak, D. M. Paardekooper, G. Fedoseev, H. Linnartz

Context. In cold regions of the interstellar medium with intense ultraviolet radiation fields, photodesorption has been suggested as a nonthermal desorption mechanism promoting the transition of molecules from the solid state to the gas phase. Laboratory experiments measuring photodesorption rates are crucial in attempting to explain high molecular gas phase abundances of species that are expected to form in the solid state, such as methane, methanol, and acetonitrile, and to aid astrochemical modeling. Due to the convoluted competition between photodesorption and photoconversion, it is far from trivial to derive accurate photodesorption rates. Aims. The aim of this study is to apply a new methodology to discriminate between the two processes. The method has been validated using the well-studied case of CO and extended to CH<sub>4</sub>, CH<sub>3</sub>OH, and CH<sub>3</sub>CN. Methods. Vacuum ultraviolet (VUV; photon energy of 7–10.2 eV) irradiated ices at 20 K are studied, first as a pure CH<sub>4</sub>, CH<sub>3</sub>OH, or CH<sub>3</sub>CN ice and subsequently with an Ar coating on top. The latter is transparent to the VUV photons (wavelength below 200 nm), but it quenches the photodesorption process. Comparing the laser desorption post ionization time-of-flight mass spectrometry of the ices with and without the Ar coating provides information on the different interactions of the VUV photons with the ice. Results. The newly developed experimental technique allowed for a derivation of photodesorption rates for ices at 20 K of: CO ( $3.1 \pm 0.3 \times 10^{-3}$  mol. photon<sup>-1</sup>), CH<sub>4</sub> ( $3.1 \pm 0.5 \times 10^{-2}$  mol. photon<sup>-1</sup>), and upper limits for CH<sub>3</sub>OH ( $< 6 \times 10^{-5}$  mol. photon<sup>-1</sup>) and CH<sub>3</sub>CN ( $< 7.4 \times 10^{-4}$  mol. photon<sup>-1</sup>); in the latter case, no literature values have been reported yet. The newly introduced approach provides more insight into the photodesorption process, in particular, for commonly observed complex organic molecules (COMs). Photoconversion cross sections are presented in the 7–10.2 eV range. The possible role of photodesorption and photoconversion in the formation of interstellar COMs is discussed.

Bulak et al. A&A 636, A32 (2020)

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## How does successive hydrogen addition to PAH ions impact their unimolecular chemistry?

Malick Diedhiou, Brandi J. West, Paul M Mayer

Hydrogenated polycyclic aromatic hydrocarbons (PAHs) have been proposed to contribute to the formation of interstellar H<sub>2</sub> by acting as a surface catalyst for the adsorption of hydrogen atoms and desorption of H<sub>2</sub> molecules. In the present study, imaging photoelectron photoion coincidence (iPEPICO) spectroscopy and tandem mass spectrometry were employed to examine the unimolecular chemistry of four hydrogenated polycyclic aromatic hydrocarbon ions: 9,10-dihydroanthracene (DHA<sup>+</sup>) and 1,2,3,4,5,6,7,8-octahydroanthracene (OHA<sup>+</sup>), having opposite patterns of hydrogenation, and 1,2,3,4-tetrahydrophenanthrene (THP<sup>+</sup>) and 1,2,3,4,9,10-hexahydrophenanthrene (HHP<sup>+</sup>). DHA<sup>+</sup> exhibits the same reactions previously observed for 1,2-dihydronaphthalene and 9,10-dihydrophenanthrene, namely competing loss of H<sup>•</sup> and CH<sub>3</sub><sup>•</sup>. However, the energy required for H<sup>•</sup>-loss, as predicted by RRKM modeling of the iPEPICO results, was lower than the latter ions, presumably due to charge delocalization across the central ring upon dehydrogenation. OHA<sup>+</sup> behaves similarly to ionized tetralin, displaying losses of H<sup>•</sup>, CH<sub>3</sub><sup>•</sup>, C<sub>2</sub>H<sub>4</sub> and C<sub>3</sub>H<sub>5</sub><sup>•</sup> in its collision induced dissociation (CID) mass spectra, but under iPEPICO conditions CH<sub>3</sub><sup>•</sup>-loss is not observed. THP<sup>+</sup> and HHP<sup>+</sup> have aspects of both DHA<sup>+</sup> and OHA<sup>+</sup> chemistries, displaying losses of H<sup>•</sup>, CH<sub>3</sub><sup>•</sup>, C<sub>2</sub>H<sub>4</sub> and C<sub>3</sub>H<sub>5</sub><sup>•</sup>. RRKM modeling produced minimum energies for all observed reaction channels, which were also computationally explored at the B3LYP/6–31+G(d,p) level of theory. The results indicate that small PAH ions may not be effective surfaces for the catalytic formation of H<sub>2</sub> in the ISM, but rather sources of small hydrocarbons.

## Isomers in Interstellar Environments (I): The Case of Z- and E-Cyanomethanimine

Christopher N. Shingledecker, Germán Molpeceres, Víctor Rivilla, Liton Majumdar, Johannes Kästner

In this work, we present the results of our investigation into the chemistry of Z- and E-cyanomethanimine (HNCHCN), both of which are possible precursors to the nucleobase adenine. Ab initio quantum chemical calculations for a number of reactions with atomic hydrogen were carried out. We find that the reaction  $H + Z/E\text{-HNCHCN}$  leading both to H-addition as well as  $H_2$ -abstraction proceed via similar short-range barriers with bimolecular rate coefficients on the order of  $\sim 1e-17 \text{ cm}^3 \text{ s}^{-1}$ . These results were then incorporated into astrochemical models and used in simulations of the giant molecular cloud G+0.693. The calculated abundances obtained from these models were compared with previous observational data and found to be in good agreement, with a predicted [Z/E] ratio of  $\sim 3$  - somewhat smaller than the previously derived value of  $6.1 \pm 2.4$ . We find that the [Z/E] ratio in our simulations is due mostly to ion-molecule destruction rates driven by the different permanent dipoles of the two conformers. Based on these results, we propose a general rule-of-thumb for estimating the abundances of isomers in interstellar environments.

ApJ, accepted

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## C18O, 13CO, and 12CO abundances and excitation temperatures in the Orion B molecular cloud: An analysis of the precision achievable when modeling spectral line within the Local Thermodynamic Equilibrium approximation

Roueff, Antoine ; Gerin, Maryvonne ; Gratier, Pierre ; Levrier, Francois ; Pety, Jerome ; Gaudel, Mathilde ; Goicoechea, Javier R. ; Orkisz, Jan H. ; Souza de Magalhaes, Victor ; Vono, Maxime ; Bardeau, Sebastien ; Bron, Emeric ; Chanussot, Jocelyn ; Chainais, Pierre ; Guzman, Viviana V. ; Hughes, Annie ; Kainulainen, Jouni ; Languignon, David ; Le Bourlot, Jacques ; Le Petit, Franck ; Liszt, Harvey S. ; Marchal, Antoine ; Miville-Deschenes, Marc-Antoine ; Peretto, Nicolas ; Roueff, Evelyn ; Sievers, Albrecht

CO isotopologue transitions are routinely observed in molecular clouds to probe the column density of the gas, the elemental ratios of carbon and oxygen, and to trace the kinematics of the environment. We aim at estimating the abundances, excitation temperatures, velocity field and velocity dispersions of the three main CO isotopologues towards a subset of the Orion B molecular cloud. We use the Cramer Rao Bound (CRB) technique to analyze and estimate the precision of the physical parameters in the framework of local-thermodynamic-equilibrium excitation and radiative transfer with an additive white Gaussian noise. We propose a maximum likelihood estimator to infer the physical conditions from the 1-0 and 2-1 transitions of CO isotopologues. Simulations show that this estimator is unbiased and efficient for a common range of excitation temperatures and column densities ( $T_{\text{ex}} > 6 \text{ K}$ ,  $N > 1e14 - 1e15 \text{ cm}^{-2}$ ). Contrary to the general assumptions, the different CO isotopologues have distinct excitation temperatures, and the line intensity ratios between different isotopologues do not accurately reflect the column density ratios. We find mean fractional abundances that are consistent with previous determinations towards other molecular clouds. However, significant local deviations are inferred, not only in regions exposed to UV radiation field but also in shielded regions. These deviations result from the competition between selective photodissociation, chemical fractionation, and depletion on grain surfaces. We observe that the velocity dispersion of the C18O emission is 10% smaller than that of 13CO. The substantial gain resulting from the simultaneous analysis of two different rotational transitions of the same species is rigorously quantified. The CRB technique is a promising avenue for analyzing the estimation of physical parameters from the fit of spectral lines.

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## Molecular globules in the Veil bubble of Orion. IRAM 30m 12CO, 13CO, and C18O(2-1) expanded maps of Orion A

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Strong winds and ultraviolet (UV) radiation from O-type stars disrupt and ionize their molecular core birthplaces, sweeping up material into parsec-size shells. Owing to dissociation by starlight, the thinnest shells are expected to host low molecular abundances and therefore little star formation. Here, we expand previous maps taken with the IRAM 30m telescope and present square-degree 12CO and 13CO ( $J=2-1$ ) maps of the wind-driven "Veil bubble" that surrounds the Trapezium cluster and its natal Orion molecular core (OMC). Although widespread and extended CO emission is largely absent from the Veil, we show that several CO "globules" exist and are embedded in the [CII]158 $\mu\text{m}$ -bright shell that confines the bubble. This includes the first detection of quiescent CO at negative LSR velocities in Orion. Given the harsh UV irradiation conditions in this translucent material, the detection of CO globules is surprising. These globules are small ( $R=7,100 \text{ AU}$ ), not massive ( $M=0.3M_{\text{Sun}}$ ), and are moderately dense:  $n_{\text{H}}=4 \times 10^4 \text{ cm}^{-3}$  (median values). They are confined by the external pressure of the shell,  $P_{\text{ext}}/k=10^7 \text{ cm}^{-3} \text{ K}$ , and are likely magnetically supported. They are either transient objects formed

by instabilities or have detached from pre-existing molecular structures, sculpted by the passing shock associated with the expanding shell and by UV radiation from the Trapezium. Some represent the first stages in the formation of small pillars, others of isolated small globules. Although their masses do not suggest they will form stars, one globule matches the position of a known YSO. The lack of extended CO in the "Veil shell" demonstrates that feedback from massive stars expels, agitates, and reprocesses most of the disrupted molecular cloud gas, thereby limiting the star-formation rate in the region. The presence of globules is a result of this feedback.

Astronomy & Astrophysics. Accepted.

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Full-text URL: <https://arxiv.org/abs/2004.12938>

## Near-infrared Methanol Bands Probe Energetic Processing of Icy Outer Solar System Objects

R. G. Urso, D. Baklouti, Z. Djouadi, N. P. Alonso, R. Brunetto

Frozen methanol was detected in the outer solar system on the surfaces of the Centaur 5145 Pholus, the Trans-Neptunian Object (55638) 2002 VE95, and more recently on (486958) Arrokoth. The icy surfaces of these objects are subjected to solar and cosmic ions that modify the physico-chemical properties of their surface. To study the effects of ion bombardment on methanol-rich surfaces, we performed experiments of ion irradiation of H<sub>2</sub>O:CH<sub>3</sub>OH mixtures and we monitored the evolution of the methanol near-infrared bands. We observed significant variations of the 2.34/2.27  $\mu\text{m}$  methanol band ratios as a function of the irradiation dose. We then used the Arrokoth and Pholus spectra to test the 2.34/2.27  $\mu\text{m}$  band ratio as a probe of irradiation of methanol-rich surfaces, and we estimated the timescales of processing by solar and cosmic ions. Our results indicate that solar energetic particles are the main drivers of changes in the near-infrared spectra of frozen surfaces in the outer solar system.

The Astrophysical Journal Letters, 894:L3 (11pp), 2020 May 1

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Full-text URL: <https://iopscience.iop.org/article/10.3847/2041-8213/ab8ad9>

## VUV Photoionization Dynamics of the C60 Buckminsterfullerene: 2D-Matrix Photoelectron Spectroscopy in an Astrophysical Context

Helgi Rafn Hrodmarsson, Gustavo Adolfo Garcia, Harold Linnartz and Laurent Nahon

We present the photoionization dynamics of the C<sub>60</sub> Buckminsterfullerene from threshold up to 14.0 eV recorded with VUV synchrotron radiation at the DESIRS beamline at the SOLEIL synchrotron. The recorded data is obtained using a double-imaging photoelectron photoion coincidence spectrometer and is presented as a two-dimensional photoelectron matrix which contains a wealth of spectroscopic data. We present these data in an astrophysical context which relates to (i) the threshold photoelectron spectrum which is compared to data relevant to the diffuse interstellar bands (DIBs), (ii) the kinetic photoelectron distribution at the Lyman- $\alpha$  line which is relevant to the dominant heating source in the ISM, and (iii) the absolute photoionization cross section of C<sub>60</sub> up to approx. 10.5 eV. The photoelectron spectrum implies that the symmetry of the ground state is different than previous theoretical models have predicted, and this result is discussed in context of recent experimental and theoretical findings. Also presented are partial photoionization cross sections of the first two photoelectron bands and their anisotropy parameters. These data are compared with previous theoretical values and discussed where appropriate.

Phys. Chem. Chem. Phys., 2020, Accepted Manuscript.

DOI: [10.1039/D0CP01210F](https://doi.org/10.1039/D0CP01210F)

Full-text URL: <https://pubs.rsc.org/en/content/articlelanding/2020/cp/d0cp01210f#!divAbstract>

## Announcements

### EPSC2020 conference -- EXO3 session "From Protoplanetary Disks to Small Bodies, Planets, and their Atmospheres"

We would like to bring to your attention the following session that will take place during the Europlanet Science Congress 2020 (EPSC2020, [www.epsc2020.eu](http://www.epsc2020.eu)), as part of the Exoplanets and Origins of Planetary Systems group:

EXO3

From Protoplanetary Disks to Small Bodies, Planets, and their Atmospheres

Since the discovery of the first exoplanet in 1995 more than 4000 exoplanets have been detected to date. This indicates that planet formation is a robust mechanism and nearly every star in our Galaxy should host a system of planets.

However, many crucial questions about the origin of planets are still unanswered: How and when planets formed in the Solar System and in extra-solar systems? Are protoplanetary disks massive enough to form the planets cores? And what chemical composition do planets and primitive Solar System bodies inherit from their natal environment? Is the chemical composition passed unaltered from the earliest stages of the formation of a star to its disk and then to the bodies which assemble in the disk? Or does it reflect chemical processes occurring in the disk and/or during the planet formation process?

A viable way to answer these questions is to study the planets formation site, i.e. protoplanetary disks. In the recent years, the advent of ALMA and near-infrared/optical imagers aided by extreme adaptive optics revolutionised our comprehension of planet formation by providing unprecedented insights on the protoplanetary disks structure, both in its gaseous and solid components.

The aim of this session is to review the latest results on protoplanetary disks; to foster a comparison with the recent outcomes of small bodies space missions (e.g. Rosetta, Dawn, Hayabusa 2, OSIRIS-REX) and ground-based observations; and to discuss how these will affect the current models of planet formation and can guide us to investigate the origin of planets and small bodies and of their chemical composition.

<https://meetingorganizer.copernicus.org/EPSC2020/session/38481>

Please note that due to the pandemic, EPSC2020 will be held as a virtual meeting on 21 September – 9 October 2020.

The deadline for abstract submission is \*\*\* 24 June 2020, 13:00 CEST \*\*\*.

Information on how to submit an abstract can be found at the following link:

[https://www.epsc2020.eu/abstract\\_management/how\\_to\\_submit\\_an\\_abstract.html](https://www.epsc2020.eu/abstract_management/how_to_submit_an_abstract.html)

We would like to encourage all people interested in this topic to submit an abstract, in particular early career scientists.

Linda Podio, Mauro Ciarniello, Cecile Favre, Carlo Felice Manara. and Francesco Marzari