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## Abstracts

### Adsorption of HCN on cosmic silicates: a periodic quantum mechanical study

N. Bancone, S. Pantaleone, P. Ugliengo, A. Rimola, M. Corno

Hydrogen cyanide (HCN) represents a small but widely distributed fraction of the interstellar molecules, and it has been observed in all the environments characterizing the formation of a new planetary system. HCN can polymerize to form biomolecules, including adenine (H<sub>5</sub>C<sub>5</sub>N<sub>5</sub>), and it has drawn attention as a possible precursor of several building blocks of life due to the presence of its polymerization products in meteorites, comets and other asteroidal bodies. To elucidate the potential catalytic role that cosmic silicates have played in these processes, we have investigated, at DFT-PBE level inclusive of a posteriori dispersion correction, the energetic and spectroscopic features of the adsorption of HCN molecules on the most relevant crystalline surfaces of the mineral forsterite (Mg<sub>2</sub>SiO<sub>4</sub>), a common silicate constituent of the interstellar core grains and planetary rocky bodies. The results reveal that HCN adsorbs both in molecular and dissociative ways, within a wide range of adsorption energies (-29.4 to -466.4 kJ/mol). For the dissociative adsorption, thermodynamic and kinetic results show these systems to be dominant already at low temperatures, a fact particularly relevant at the protoplanetary conditions (i.e., the latest stages in the star system formation process). The simulated spectroscopic features of the studied adducts show a wide range of different degrees of perturbation of C-H and C≡N bonds. This agrees with previous experimental works, and our results confirm that a complex chemistry is observed when this astrochemically-relevant molecule interacts with Mg<sub>2</sub>SiO<sub>4</sub>, which may be associated with a considerable potential reactivity towards the formation of relevant prebiotic compounds.

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### Quantum Chemical Exploration of the Binding Motifs and Binding Energies of Neutral Molecules, Radicals and Ions With Small Water Clusters: Characterization and Astrochemical Implications.

Josie Hendrix, Partha P. Bera, Timothy J. Lee, and Martin Head-Gordon

Accurate binding energies of molecules to water clusters are relevant to understanding intermolecular interactions and various chemical applications. They enter models of interstellar chemical processes, as binding to icy grains influences surface reactions, and thus affects calculated gas-phase abundances. Unfortunately, many astrochemical molecules (especially radicals and ions) are incompletely characterized in these models. To address this, we report computational searches for optimal structures and benchmark binding and condensation energies for sets of neutral, radical, cationic, and 1 anionic molecules of astrochemical relevance with clusters of N = 1–4 water molecules. These calculations utilized reliable density functionals for geometry optimization, and coupled cluster (CCSD(T)) single point calculations with large basis sets. Four energetic binding motifs (weak, intermediate, strong or covalently bonded) were observed depending on the chemical nature of the guest molecule. Neutral closed and openshell molecules with strong dipoles and a greater potential for hydrogen bonding are more tightly bound to water clusters compared to non-polar ones. For closed-shell cationic and anionic species, barrier-less reactions with water clusters occur, which reveals radical-free routes to molecular processing on amorphous ice surfaces.

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### Rotational spectroscopy of the thioformaldehyde isotopologues H<sub>2</sub>CS and H<sub>2</sub>C<sup>34</sup>S in four interacting excited vibrational states and an account on the rotational spectrum of thioketene, H<sub>2</sub>CCS

Holger S. P. Müller, Atsuko Maeda, Frank Lewen, Stephan Schlemmer, Ivan R. Medvedev, Eric Herbst

An investigation of the rotational spectrum of the interstellar molecule thioformaldehyde between 110 and 377 GHz through a pyrolysis reaction revealed a multitude of absorption lines assignable to H<sub>2</sub>CS and H<sub>2</sub>C<sup>34</sup>S in their lowest four excited vibrational states besides lines of numerous thioformaldehyde isotopologues in their ground vibrational states reported earlier as well as lines pertaining to several by-products. Additional transitions of H<sub>2</sub>CS in its lowest four excited vibrational states were recorded in selected regions between 571 and 1386 GHz. Slight to strong Coriolis interactions occur between all four vibrational states with the exception of the two highest lying states because both are totally symmetric vibrations. We present combined analyses of the ground and the four interacting states for our rotational data of H<sub>2</sub>CS and H<sub>2</sub>C<sup>34</sup>S. The

H<sub>2</sub>CS data were supplemented with two sets of high-resolution IR data in two separate analyses. The  $v_2=1$  state has been included in analyses of Coriolis interactions of low-lying fundamental states of H<sub>2</sub>CS for the first time and this improved the quality of the fits substantially. We extended furthermore assignments in J of transition frequencies of thioketene in its ground vibrational state.

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## **SUNRISE: The rich molecular inventory of high-redshift dusty galaxies revealed by broadband spectral line surveys**

**Chentao Yang (□□□), Alain Omont, Sergio Martín, Thomas G. Bisbas, Pierre Cox, Alexandre Beelen, Eduardo González-Alfonso, Raphaël Gavazzi, Susanne Aalto, Paola Andreani, Cecilia Ceccarelli, Yu Gao (□□), Mark Gorski, Michel Guélin, Hai Fu (□□), R. J. Ivison, Kirsten K. Knudsen, Matthew Lehnert, Hugo Messias, Sebastien Muller, Roberto Neri, Dominik Riechers, Paul van der Werf, and Zhi-Yu Zhang (□□□)**

Understanding the nature of high-redshift dusty galaxies requires a comprehensive view of their interstellar medium (ISM) and molecular complexity. However, the molecular ISM at high redshifts is commonly studied using only a few species beyond 12C16O, limiting our understanding. In this paper, we present the results of deep 3 mm spectral line surveys using the NOthern Extended Millimeter Array (NOEMA) targeting two strongly lensed dusty galaxies observed when the Universe was less than 1.8 Gyr old: APM 08279+5255, a quasar at redshift  $z = 3.911$ , and NCV1.143 (H-ATLAS J125632.7+233625), a  $z=3.565$  starburst galaxy. The spectral line surveys cover rest-frame frequencies from about 330 to 550 GHz for both galaxies. We report the detection of 38 and 25 emission lines in APM 08279+5255 and NCV1.143, respectively. These lines originate from 17 species, namely CO, 13CO, C18O, CN, CCH, HCN, HCO<sup>+</sup>, HNC, CS, C34S, H<sub>2</sub>O, H<sub>3</sub>O<sup>+</sup>, NO, N<sub>2</sub>H<sup>+</sup>, CH, c-C<sub>3</sub>H<sub>2</sub>, as well as the vibrationally excited HCN and neutral carbon. The spectra reveal the chemical richness and the complexity of the physical properties of the ISM. By comparing the spectra of the two sources and combining the analysis of the molecular gas excitation, we find that the physical properties and the chemical imprints of the ISM are different between them: the molecular gas is more excited in APM 08279+5255, exhibiting higher molecular gas temperatures and densities compared to NCV1.143; the molecular abundances in APM 08279+5255 are akin to the values of local active galactic nuclei (AGN), showing boosted relative abundances of the dense gas tracers that might be related to high-temperature chemistry and/or the X-ray-dominated regions, while NCV1.143 more closely resembles local starburst galaxies. The most significant differences between the two sources are found in H<sub>2</sub>O, where the 448GHz ortho-H<sub>2</sub>O(423–330) line is significantly brighter in APM08279+5255, likely linked to the intense far-infrared radiation from the dust powered by AGN. Our astrochemical model suggests that, at such high column densities, FUV radiation is less important in regulating the ISM, while cosmic rays (and/or X-rays and shocks) are the key players in shaping the molecular abundances and the initial conditions of star formation. Both our observed CO isotopologues line ratios and the derived extreme ISM conditions (high gas temperature and density, high cosmic-ray ionization rate) suggest the presence of a top-heavy initial mass function. From the ~330–550GHz continuum, we also find evidence of non-thermal millimeter flux excess in APM 08279+5255 that might be related to the central supermassive black hole. Such deep spectral line surveys open a new window to study the physics and chemistry of the ISM and the radiation field of galaxies in the early Universe.

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## **Anharmonicity and deuteration in the IR absorption and emission spectrum of phenylacetylene**

**Vincent J. Esposito, Piero Ferrari, Wybren Jan Buma, Christiaan Boersma, Cameron J. Mackie, Alessandra Candian, Ryan C. Fortenberry, Alexander G. G. M. Tielens**

Anharmonic cascade emission simulations, herein evinced by full reproduction and deep insights into recent emission spectroscopy experiments of phenylacetylene, are integral to the future successful analysis of JWST observational spectra. Experimental infrared absorption experiments conducted in this study reveal a complex spectrum dominated by quantum effects that are uncovered by anharmonic computational analysis. From this work, it becomes clear that phenylacetylene exhibits strong resonance coupling between fundamental and two-quanta combination modes as well as giving indication for coupling with higher-order, three-quanta combination bands. This study benchmarks the development of advanced computational methods that will be extended to larger systems of astronomical relevance and those including isotopic substitution and side group functionalization with groups such as acetylene. The astrophysical implications of these results, including the potential for detection of acetylenic C–H stretches in space, are discussed in the vein of the impact polycyclic aromatic hydrocarbons have on astronomical infrared emission bands.

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## **Anharmonic IR absorption spectra of the prototypical interstellar PAHs phenanthrene, pyrene, and pentacene in their neutral and cation states**

**Vincent J. Esposito, Louis J. Allamandola, Christiaan Boersma, Jesse D. Bregman, Ryan C. Fortenberry, Alexandros Maragkoudakis, Pasquale Temi**

The combination band and overtone transitions of cationic polycyclic aromatic hydrocarbons (PAHs) in the 2000 – 2900 cm<sup>-1</sup> (5-3.5 μm) region are implicated as carriers of the 'quasi-continuum' observed in the near-infrared (IR) emission spectra of astronomical objects showing the PAH features. In neutral PAHs, the largest intensity absorption features are concentrated in the 700 – 900 cm<sup>-1</sup> (14 – 11 μm) range, corresponding to the CH out-of-plane bending motions. Following ionization, this intensity shifts to the 1000 – 1600 cm<sup>-1</sup> (10 – 6 μm) range, C=C stretches and CH in-plane bends, due to delocalization of the positive charge across the entire aromatic system. Anharmonicity is required in order to accurately characterize/compute the IR absorption spectrum of PAHs, indicated herein by the ability to directly assign high-resolution experimental absorption spectra of neutral and cationic phenanthrene, pyrene, and pentacene. The differences in the neutral and cation spectra support that neutral PAHs are the source of the strong 3.3 and 11.2 μm astronomical PAH features, while the very strong, broad features in the 6 – 10 μm region as well as the 'quasi-continuum' from 3.5 – 5 μm are dominated by PAH cations. This study reinforces the requirement for the continued inclusion of anharmonicity in the IR absorption and emission spectra of PAHs as advancements in methodology make larger and more complex systems computationally accessible. This is particularly pertinent to the interpretation of the high-fidelity data returned by the James Webb Space Telescope (JWST).

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## Millimetre and submillimetre spectroscopy of isobutene and its detection in the molecular cloud G+0.693

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Isobutene ((CH<sub>3</sub>)<sub>2</sub>C=CH<sub>2</sub>) is one of the four isomers of butene (C<sub>4</sub>H<sub>8</sub>). Given the detection of propene (CH<sub>3</sub>CH=CH<sub>2</sub>) toward TMC-1, and also in the warmer environment of the solar-type protostellar system IRAS 16293–2422, one of the next alkenes, isobutene, is a promising candidate to be searched for in space. We aim to extend the limited line lists of the main isotopologue of isobutene from the microwave to the millimetre region in order to obtain a highly precise set of rest frequencies and to facilitate its detection in the interstellar medium. We investigated the rotational spectrum of isobutene in the 35–370 GHz range using absorption spectroscopy at room temperature. Quantum-chemical calculations were carried out to evaluate vibrational frequencies. We determined new or improved spectroscopic parameters for isobutene up to a sixth-order distortion constant. These new results enabled its detection in the G+0.693 molecular cloud for the first time, where propene was also recently found. The propene to isobutene column density ratio was determined to be about 3:1. The observed spectroscopic parameters for isobutene are sufficiently accurate that calculated transition frequencies should be reliable up to 700 GHz. This will further help in observing this alkene in other, warmer regions of the ISM.

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## Formation and Destruction of Si<sub>6</sub>O<sub>12</sub> Nanostructures in the Gas Phase: Applications to Grain Nucleation and Water Generation

Athena R. Flint and Ryan C. Fortenberry

Silica grains are ubiquitous in both circumstellar media and rocky bodies and are vital to cosmic chemical processes, such as surface-catalyzed reactions and lunar water generation. Despite their pervasiveness, the chemical processes behind their formation and destruction, both of which are key to understanding their broader chemistry, are not fully established as of yet. Using chemically accurate CCSD(T)-F12/cc-pVTZ-F12 quantum chemical calculations, a reaction pathway including the possible bulk silica precursors Si<sub>3</sub>O<sub>6</sub> and Si<sub>6</sub>O<sub>12</sub> is mapped out herein. Through the reaction of SiO and H<sub>2</sub>O, the formation of such precursors is possible under circumstellar conditions. Expansion of this pathway may contribute to a complete understanding of silica and silicate chemistry throughout the universe. The constructed reaction pathway also shows that in the reverse reaction, processing of lunar silicates under the available photon flux of the sun can result in H<sub>2</sub>O production, following previous observations. The acceleration of H<sub>2</sub>O generation may be made possible through exposure of lunar silica to applied H<sub>2</sub> in future aerospace ventures.

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## Interstellar Carbonaceous Dust Erosion Induced by X-Ray Irradiation of Water Ice in Star-forming Regions

K.-J. Chuang, C. Jäger, N.-E. Sie, C.-H. Huang, C.-Y. Lee, Y.-Y. Hsu, Th. Henning, and Y.-J. Chen

The chemical inventory of protoplanetary midplanes is the basis for forming planetesimals. Among them, solid-state reactions based on CO/CO<sub>2</sub> toward molecular complexity on interstellar dust grains have been studied in theoretical and laboratory work. The physicochemical interactions between ice, constituted mainly of H<sub>2</sub>O, and dust surfaces are limited to a few experimental studies focusing on vacuum ultraviolet and cosmic-ray processing. In this work, the erosion of C dust grains induced by X-ray irradiation of H<sub>2</sub>O ice was systematically investigated for the first time. The work aims to provide a

better understanding of the reaction mechanism using selectively isotope-labeled oxygen/carbon species in kinetic analysis. Ultrahigh vacuum experiments were performed to study the interstellar ice analog on submicron, thick C dust at  $\sim 13$  K. H<sub>2</sub>O or O<sub>2</sub> ice was deposited on the presynthesized amorphous C dust and exposed to soft X-ray photons (250–1250 eV). Fourier-transform infrared spectroscopy was used to monitor in situ the newly formed species as a function of the incident photon fluence. Field emission scanning electron microscopy was used to monitor the morphological changes of (non-)eroded carbon samples. The X-ray processing of the ice/dust interface leads to the formation of CO<sub>2</sub>, which further dissociates and forms CO. Carbonyl groups are formed by oxygen addition to grain surfaces and are confirmed as intermediate species in the formation process. The yields of CO and CO<sub>2</sub> were found to be dependent on the thickness of the carbon layer. The astronomical relevance of the experimental findings is discussed.

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## Bottom-up dust nucleation theory in oxygen-rich evolved stars II. Magnesium and calcium aluminate clusters

David Gobrecht, S. Rasoul Hashemi, John M. C. Plane, Stefan T. Bromley, Gunnar Nyman, Leen Decin

Spinel (MgAl<sub>2</sub>O<sub>4</sub>) and krotite (CaAl<sub>2</sub>O<sub>4</sub>) are alternative candidates to alumina (Al<sub>2</sub>O<sub>3</sub>) as primary dust condensates in the atmospheres of oxygen-rich evolved stars. Moreover, spinel was proposed as a potential carrier of the circumstellar 13  $\mu$ m feature. However, the formation of nucleating spinel clusters is challenging; in particular, the inclusion of Mg constitutes a kinetic bottleneck. We aim to understand the initial steps of cosmic dust formation (i.e. nucleation) in oxygen-rich environments using a quantum-chemical bottom-up approach. Starting with an elemental gas-phase composition, we constructed a detailed chemical-kinetic network that describes the formation and destruction of magnesium-, calcium-, and aluminium-bearing molecules as well as the smallest dust-forming (MgAl<sub>2</sub>O<sub>4</sub>)<sub>1</sub> and (CaAl<sub>2</sub>O<sub>4</sub>)<sub>1</sub> monomer clusters. Different formation scenarios with exothermic pathways were explored, including the alumina (Al<sub>2</sub>O<sub>3</sub>) cluster chemistry studied in Paper I of this series. The resulting extensive network was applied to two model stars, a semi-regular variable and a Mira-type star, and to different circumstellar gas trajectories, including a non-pulsating outflow and a pulsating model. We employed global optimisation techniques to find the most favourable (MgAl<sub>2</sub>O<sub>4</sub>)<sub>n</sub>, (CaAl<sub>2</sub>O<sub>4</sub>)<sub>n</sub>, and mixed (Mg<sub>x</sub>Ca<sub>(1-x)</sub>Al<sub>2</sub>O<sub>4</sub>)<sub>n</sub> isomers, with  $n=1-7$  and  $x \in [0..1]$ , and we used high level quantum-chemical methods to determine their potential energies. The growth of larger clusters with  $n=2-7$  is described by the temperature-dependent Gibbs free energies. In the considered stellar outflow models, spinel clusters do not form in significant amounts. However, we find that in the Mira-type non-pulsating model CaAl<sub>2</sub>O<sub>3</sub>(OH)<sub>2</sub>, a hydroxylated form of the calcium aluminate krotite monomer forms ...

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## Potential energy surfaces for singlet and triplet states of the LiH<sub>2</sub><sup>+</sup> system and quasi-classical trajectory cross sections for H + LiH<sup>+</sup> and H<sup>+</sup> + LiH

J. Hernández-Rodríguez, C. Sanz-Sanz, P. A. Enríquez, M. González, M. Paniagua

A new set of six accurate ab initio potential energy surfaces (PESs) is presented for the first three singlet and triplet states of LiH<sub>2</sub><sup>+</sup> (1,2 1A', 1 1A'', 1,2 3A', 1 3A'' states, where four of them are investigated for the first time), which have allowed new detailed studies gaining a global view on this interesting system. These states are relevant for the study of the most important reactions of the lithium chemistry in the early universe. More than 45000 energy points were calculated using the multi-reference configuration interaction level of theory using explicitly correlated methods (ic-MRCI-F12), and the results obtained for each individual electronic state were fitted to an analytical function. Using quasiclassical trajectories and considering the initial diatomic fragment in the ground rovibrational state, we have determined the integral cross sections for the H + LiH<sup>+</sup>(X, C) and H<sup>+</sup> + LiH(X, B) reactions. In these calculations all available reaction channels were considered: the chemically most important H or H<sup>+</sup> transfer/abstraction as well as atom exchange and collision induced dissociation for up to 1.0 eV of collision energy.

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## A Theoretical Approach to the Complex Chemical Evolution of Phosphorus in the Interstellar Medium

M. Fernández-Ruz, I. Jiménez-Serra, and J. Aguirre

The study of phosphorus chemistry in the interstellar medium has become a topic of growing interest in astrobiology because it is plausible that a wide range of P-bearing molecules were introduced in the early Earth by the impact of asteroids and comets on its surface, enriching prebiotic chemistry. Thanks to extensive searches in recent years, it has become clear that P mainly appears in the form of PO and PN in molecular clouds and star-forming regions. Interestingly, PO is systematically more abundant than PN by factors typically of  $\sim 1.4-3$ , independently of the physical properties of the observed source. In order to unveil the formation routes of PO and PN, in this work we introduce a mathematical model for

the time evolution of the chemistry of P in an interstellar molecular cloud and analyze its associated chemical network as a complex dynamical system. By making reasonable assumptions, we reduce the network to obtain explicit mathematical expressions that describe the abundance evolution of P-bearing species and study the dependences of the abundance of PO and PN on the system's kinetic parameters with much faster computation times than available numerical methods. As a result, our model reveals that the formation of PO and PN is governed by just a few critical reactions, and fully explains the relationship between PO and PN abundances throughout the evolution of molecular clouds. Finally, the application of Bayesian methods constrains the real values of the most influential reaction rate coefficients making use of available observational data.

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## Thermal Decomposition of 2- and 4-Iodobenzyl Iodide Yields Fulvenallene and Ethynylcyclopentadienes: A Joint Threshold Photoelectron and Matrix Isolation Spectroscopic Study

M. Saraswat, A. Portela-Gonzalez, G. Karir, E. Mendez-Vega, W. Sander\*, and P. Hemberger\*

The thermal decomposition of 2- and 4-iodobenzyl iodide at high temperatures was investigated by mass-selective threshold photoelectron spectroscopy (ms-TPES) in the gas phase, as well as by matrix isolation infrared spectroscopy in cryogenic matrices. Scission of the benzylic C–I bond in the precursors at 850 K affords 2- and 4-iodobenzyl radicals (ortho- and para-IC<sub>6</sub>H<sub>4</sub>CH<sub>2</sub>•), respectively, in high yields. The adiabatic ionization energies of ortho-IC<sub>6</sub>H<sub>4</sub>CH<sub>2</sub>• to the  $\tilde{X}^+(1A')$  and  $\tilde{a}^+(3A')$  cation states were determined to be  $7.31 \pm 0.01$  and  $8.78 \pm 0.01$  eV, whereas those of para-IC<sub>6</sub>H<sub>4</sub>CH<sub>2</sub>• were measured to be  $7.17 \pm 0.01$  eV for  $\tilde{X}^+(1A')$  and  $8.98 \pm 0.01$  eV for  $\tilde{a}^+(3A')$ . Vibrational frequencies of the ring breathing mode were measured to be  $560 \pm 80$  and  $240 \pm 80$  cm<sup>–1</sup> for the  $\tilde{X}^+(1A')$  and  $\tilde{a}^+(3A')$  cation states of ortho-IC<sub>6</sub>H<sub>4</sub>CH<sub>2</sub>•, respectively. At higher temperatures, subsequent aryl C–I cleavage takes place to form  $\alpha$ ,2- and  $\alpha$ ,4-didehydrotoluene diradicals, which rapidly undergo ring contraction to a stable product, fulvenallene. In addition, high-energy and astrochemically relevant C<sub>7</sub>H<sub>6</sub> isomers 1-, 2-, and 5-ethynylcyclopentadiene are observed at even higher pyrolysis temperatures along with fulvenallene. Complementary quantum chemical computations on the C<sub>7</sub>H<sub>6</sub> potential energy surface predict a feasible reaction cascade at high temperatures from the diradicals to fulvenallene, supporting the experimental observations in both the gas phase and cryogenic matrices.

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## State-to-state rovibrational transition rates for CO<sub>2</sub> in the bend mode in collisions with He atoms

Taha Selim, Ad van der Avoird, Gerrit C. Groenenboom

Modeling environments that are not in local thermal equilibrium, such as protoplanetary disks or planetary atmospheres, with molecular spectroscopic data from space telescopes requires knowledge of the rate coefficients of rovibrationally inelastic molecular collisions. Here, we present such rate coefficients in a temperature range from 10 to 500 K for collisions of CO<sub>2</sub> with He atoms in which CO<sub>2</sub> is (de)excited in the bend mode. They are obtained from numerically exact coupled-channel (CC) calculations as well as from calculations with the less demanding coupled-states approximation (CSA) and the vibrational close-coupling rotational infinite-order sudden (VCC-IOS) method. All of the calculations are based on a newly calculated accurate ab initio four-dimensional CO<sub>2</sub>-He potential surface including the CO<sub>2</sub> bend ( $\nu_2$ ) mode. We find that the rovibrationally inelastic collision cross sections and rate coefficients from the CSA and VCC-IOS calculations agree to within 50% with the CC results at the rotational state-to-state level, except for the smaller ones and in the low energy resonance region, and to within 20% for the overall vibrational quenching rates except for temperatures below 50 K where resonances provide a substantial contribution. Our CC quenching rates agree with the most recent experimental data within the error bars. We also compared our results with data from Clary et al. calculated in the 1980's with the CSA and VCC-IOS methods and a simple atom-atom model potential based on ab initio Hartree-Fock calculations and found that their cross sections agree fairly well with ours for collision energies above 500 cm<sup>–1</sup>, but that the inclusion of long range attractive dispersion interactions is crucial to obtain reliable cross sections at lower energies and rate coefficients at lower temperatures.

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## Sakurai's Object revisited: new laboratory data for carbonates and melilites suggest the carrier of 6.9- $\mu$ m excess absorption is a carbonate

Bowey, J. E. and Hofmeister, A. M.

We present new room-temperature 1100–1800-cm<sup>–1</sup> spectra of melilite silicates and 600–2000-cm<sup>–1</sup> spectra of three randomly orientated fine-grained carbonates to determine the possible carrier(s) of a 6.9- $\mu$ m absorption feature observed in a variety of dense astronomical environments, including young stellar objects and molecular clouds. We focus on the low-mass post-asymptotic giant branch star Sakurai's Object, which has been forming substantial quantities of carbonaceous

dust since an eruptive event in the 1990s. Large melilite grains cannot be responsible for the 6.9- $\mu\text{m}$  absorption feature because the similarly shaped feature in the laboratory spectrum was produced by very low (0.1 per cent by mass) carbonate contamination, which was not detected at other wavelengths. Due to the high band strength of the 6.9- $\mu\text{m}$  feature in carbonates, we conclude that carbonates carry the astronomical 6.9- $\mu\text{m}$  feature. Replacement of melilite with carbonates in models of Sakurai's Object improves fits to the 6–7- $\mu\text{m}$  Spitzer spectra without significantly altering other conclusions of Bowey's previous models except that there is no link between the feature and the abundance of melilite in meteorites. With magnesite ( $\text{MgCO}_3$ ), the abundance of 25- $\mu\text{m}$ -sized SiC grains is increased by 10–50 per cent and better constrained. The mass of carbonate dust is similar to the mass of polycyclic aromatic hydrocarbon dust. Existing experiments suggest that carbonates are stable below 700 K; however, it is difficult to ascertain the applicability of these experiments to astronomical environments, and more studies are required.

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## Shaping the CO snowline in protoplanetary disks

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Characterizing the dust thermal structure in protoplanetary disks is a fundamental task as the dust surface temperature can affect both the planetary formation and the chemical evolution. Since the temperature is dependent on many parameters, including the grain size, properly modeling the grain temperature structure can be challenging. Many chemistry disk models usually employ a sophisticated single dust structure designed to reproduce the effect of a realistic population presumably composed of a large diversity of sizes. This generally represents a good approximation in most cases. Nonetheless, this dilutes the effects of the complex radiative interactions between the different grain populations on the resulting dust temperature, and thus the chemistry. We seek to show that the radiative interactions between dust grains of different sizes can induce a non-trivial dust temperature structure that cannot be reproduced by a single dust population and that can significantly affect the chemical outcome. The disk thermal structures are computed using the Monte-Carlo radiative transfer code RADMC-3D. The thermal structures are post-processed using the gas-grain code NAUTILUS to calculate the evolution of the chemical abundance. We find that simultaneously using at least two independent dust grain populations in disk models produces a complex temperature structure due to the starlight intercepted by the upper layers of the disk. In particular, we find that micron-sized dust grains are warmer than larger grains and can even show a radial temperature bump in some conditions. This dust temperature spread between the grains populations results in the segregation of the CO snowline and the presence of an unexpected CO gas hole along the midplane. We compare the results with observed close to edge-on class I/II disks.

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## Modelling deuterated isotopologues of methanol towards the pre-stellar core L1544

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In the extremely cold and dark environments of pre-stellar cores, methanol is formed on the surface of interstellar dust grains and released into the gas phase via non-thermal desorption mechanisms. Gaseous methanol constitutes the starting point for the formation of many massive complex organic molecules and is therefore of utmost importance for the build-up of chemical complexity. We aim to improve upon a previous model for the prediction of column densities and deuterium fractions of non-deuterated and singly deuterated methanol. Thereby, we try to identify crucial chemical and physical parameters for which the study of deuteration could provide valuable additional constraints. We employed a gas-grain chemical code to devise a model that is in agreement with the observed column density and deuterium fraction profiles of the innermost region of the pre-stellar core L1544. For that purpose, we developed a new treatment of reactive desorption, deriving an individual reactive desorption efficiency for every product species in a chemical reaction that depends on the reaction enthalpy and type of the underlying surface. Furthermore, we explored several options to promote the diffusion of hydrogen and deuterium atoms over the surface of interstellar dust grains in order to increase methanol formation. Our fiducial model employs diffusion via the quantum tunnelling of hydrogen and deuterium atoms, resulting in  $\text{CH}_3\text{OH}$  and  $\text{CH}_2\text{DOH}$  column densities that are approximately an order of magnitude lower than the observed values, which is an improvement over the results of the previous model by a factor of 10. The  $\text{N}(\text{CH}_2\text{DOH})/\text{N}(\text{CH}_3\text{OH})$  ratio is reproduced within a factor of 1.2 for the centre and 1.8 for the position of the methanol peak. Given the large uncertainties that chemical models typically have, we consider our predictions to be in agreement with the observations. In general, we conclude that a diffusion process with a high diffusion rate needs to be employed to obtain methanol column densities that are in accordance with the observed values. Also, we find that the introduction of abstraction reactions into the methanol formation scheme suppresses deuteration when used in combination with a high diffusion rate.

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## Shocking Sgr B2(N1) with its own outflow: A new perspective on segregation between O- and N-bearing molecules

Laura A. Busch, Arnaud Belloche, Robin T. Garrod, Holger S. P. Müller, and Karl M. Menten

We want to investigate the influence of the powerful outflow driven by the hot core Sgr B2(N1) on the gas molecular inventory of the surrounding medium. We used the data taken as part of the 3mm imaging spectral-line survey ReMoCA (Re-exploring Molecular Complexity with ALMA). Integrated intensity maps of SO and SiO emission reveal a bipolar structure with blue-shifted emission dominantly extending to the SE from the centre of the hot core and red-shifted emission to the NW. This is also prominently observed in emission of other S-bearing molecules and species that only contain N as a heavy element, including COMs, but also CH<sub>3</sub>OH, CH<sub>3</sub>CHO, HNCO, and NH<sub>2</sub>CHO. For a selection of COMs and simpler species, spectra were modelled under the assumption of LTE and population diagrams were derived at two positions, one in each outflow lobe. From this analysis, we obtained rotational temperatures, which are in a range of ~100-200K, and column densities. Abundances were subsequently compared to predictions of astrochemical models and to observations of L1157-B1, a position located in the well-studied outflow of the low-mass protostar L1157, and the source G+0.693-0.027, located in the Sgr B2 molecular cloud complex. Given the short distance of the analysed outflow positions to the centre of Sgr B2(N1), we propose a scenario in which a phase of hot-core chemistry (i.e. thermal desorption of ice species and high-temperature gas-phase chemistry) preceded a shock wave. The subsequent compression and further heating of the material resulted in the accelerated destruction of (mainly O-bearing) molecules. Gas-phase formation of cyanides seems to be able to compete with their destruction in the post-shock gas. Abundances of HCnN (n=3,5) are enhanced in the outflow component pointing to (additional) gas-phase formation. To confirm such a scenario, appropriate chemical shock models need to be run.

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## Spectroscopy and Photochemistry of Aluminum-Bearing Species in the Universe

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Metal-bearing molecules impact the chemical and physical environment of many astronomical sources such as the circumstellar envelopes of large asymptotic giant branch and red supergiant stars, the interstellar medium, and planetary atmospheres (e.g., ablation of ~20 tons per day into the Earth's upper atmosphere). In recent decades, the number of successfully detected metal-containing molecules has increased via rotational spectroscopic observations, which are driven by theoretical and experimental investigations. Following formation, the ultimate fate of each species (stabilization, dissociation, etc.) is determined by its electronic structure and electronic spectroscopic properties as it encounters the pervasive radiation fields in the vacuum of space. Studying these properties can evince the possibility of detection and predict the impact each molecule has on its surrounding environment. Aluminum, one of the most abundant elements and metals, is distributed throughout the universe as a constituent of gas-phase molecules (e.g., AlO, AlOH, AlCl, etc.) as well as condensed onto solid dust grains such as Al<sub>2</sub>O<sub>3</sub>. Free gas-phase aluminum-bearing molecules are synthesized by nonthermal equilibrium processes such as shocks and pulsations near the stellar photosphere or via the reaction of molecules on the surface of dust grains. Recent investigations in our research group utilizing quantum chemical methods, such as coupled cluster (CCSD(T) and CCSD(T)-F12) and multireference configuration interaction (MRCI) with large basis sets, have explored a wide breadth of spectroscopy and photochemistry of small (triatomic and tetratomic) aluminum-bearing molecules, including Al-H, Al-C, Al-N, Al-O, Al-Si, Al-P, and Al-S bonds, among others. The ground-state spectroscopy (rotational and vibrational) of various aluminum-bearing molecules is discussed in the context of experimental and observational detection potentials. These detection potentials depend on various factors, such as the magnitude of the permanent dipole moment (PDM) and the population of states yielding transition frequencies in detectable ranges. Many aluminum-bearing molecules possess large PDMs and may be prime candidates for astronomical and laboratory detection. Within this discussion, interesting aspects of the ground-state molecular orbital configuration of OAlNO are shown to lead to an uncommon triplet ground state. Additionally, the electronic absorption spectrum of the quasi-isoenergetic ground-state isomers of AlOSO is discussed as a sensitive method for detecting this species and differentiating between the two isomers. Finally, photochemical mechanisms key to the production of AlO and AlOH in low-density regions and the destruction of AlCO and AlOC are also discussed in order to understand the radiation-induced formation and destruction of these molecules.

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## Space weathering record and pristine state of Ryugu samples from MicrOmega spectral analysis

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The samples returned from asteroid Ryugu were collected both at its surface and at its subsurface by Hayabusa2 and can, thus, provide information on the space weathering of C-type asteroids at different depths without terrestrial contamination. The near-infrared hyperspectral microscope MicrOmega gathered data on the -OH feature at ~2.7 μm for 177 individual grains from the two collection sites. Here, through a spectral analysis of these data, we show that the position of the band peak can be used as an indicator of the degree of space weathering. Most subsurficial grains do not present space weathering features, indicating that Ryugu's subsurface layers have never been exposed to the interplanetary medium. Moreover, the ~2.7 μm feature for the Ryugu samples is narrower than that observed for CI chondrites, which are the closest meteorite analogues to Ryugu, suggesting that these contain more absorbed molecular water than Ryugu due to

terrestrial aqueous contamination. We conclude that Ryugu samples should be considered as a reference for the primordial water abundance within primitive bodies.

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## Announcements

### **QuantumGrain Workshop: Emerging Horizons in the Chemistry of the Universe**

Barcelona, June 9th – 12th 2024

How does the chemical complexity transform throughout the intricate process that culminates in the creation of a Sun and its accompanying planetary system? Does the chemical diversity observed in Solar-like planetary systems have its roots in the earliest stages of their formation, or does a complete chemical reset occur at some point? A potent approach for addressing these inquiries involves a comparative analysis of the chemical compositions found in interstellar clouds, young protostars and primitive celestial bodies within the Solar System, utilizing astrochemistry as a pivotal tool. However, to undertake such investigations effectively, a comprehensive comprehension of the mechanisms governing the chemical evolution from a molecular cloud to a nascent planetary system is essential.

By joining the efforts from observational measurements in combination with astrochemical modeling and laboratory experiments great advances have been done to improve our know-how on the chemical composition and evolution and space. More recently, computational chemistry based on quantum mechanical simulations and molecular modeling has recently been integrated into this fascinating interdisciplinary field by providing unprecedented and invaluable atomic-scale information to chemistry occurring in the Universe, which is fundamental to fully understand Astrochemistry, this way becoming at the new frontier and an indispensable hinge between the different astrochemical disciplines.

The overarching objective of this conference is to convene the key players in this inherently interdisciplinary pursuit, including observational astrochemists, computational chemists, experimentalists and astrochemical modelers. Recent substantial advancements in these domains have created an opportune moment for these communities to come together and collectively ride the crest of this scientific wave.

<https://workshop.quantumgrain.eu>

### **Global Astrochemistry Lecture Series (GALS)**

Astrochemistry: From the Big Bang to Life

Our universe is full of molecules, from the simplest – molecular hydrogen – all the way up to the complex molecular structures essential to the chemistry of life on Earth. A large and diverse array of chemical species has been detected not only on planets but in interstellar clouds, in regions of star formation, in protoplanetary disks, and in comets and meteorites within the solar system. But how and when was all this material formed, and how does it evolve over time? How much molecular content is inherited from one stage of star and planet formation to the next? What role does the chemistry of the universe through cosmic time play in the origins of life? A major unanswered question remains whether the molecules essential to life were produced on the early Earth (endogenous origin), or whether they were produced in the parent interstellar medium or planet-forming disk and delivered to Earth via asteroids, comets and their meteoritic remains (exogenous origin).

This lecture course will be devoted to astrochemistry and the exploration of topics related to the chemical origins of life. In 18 lectures from the world-leading experts, we will discuss the history of the early molecular universe starting from the Big Bang; environmental conditions and key physico-chemical processes in space; astronomical observations (from ground to space) of objects of astrochemical interest; chemical models describing astrophysical environments and their reaction networks; key laboratory techniques and approaches for studying astrochemical processes; chemistry in specific environments, such as the interstellar medium, protoplanetary disks, and atmospheres of (exo)planets; exogenous synthesis and delivery of biomolecule precursors; and, finally, evolution of these precursors on the early Earth.

GALS is aimed at providing a broad overview of scientific issues, problems, achievements, and open questions in astrochemistry; and at helping senior undergraduate and postgraduate students as well as early career scientists to expand their interests and develop a firm understanding of this area, sufficient to choose an appropriate direction for their future career. The course is open to students and scientists from all over the world.

GALS is an annual event. The first round took place in summer semester 2023 and was organized by Robin Garrod, Wolf Geppert, Martin McCoustra, and Alexey Potapov. GALS in summer semester 2024 is organized by Robin Garrod, Wolf Geppert, Serge Krasnokutski, Martin McCoustra, and Alexey Potapov, is supported by the COST Action "Nanospace" (CA21126), and is accredited by the Faculty of Sciences, University of La Laguna (ULL, Spain). The course carries a credit weighting of 3 ECTS.

Registration: December 01 2023 - January 21 2024 Webpage: <https://www.astrochemistry.de/online-course/>