

# AstroChemical Newsletter #1

November 2015

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## Abstracts

### Searching for Trans Ethyl Methyl Ether in Orion KL

**B. Tercero, J. Cernicharo, A. Lopez, N. Brouillet, L. Kolesnikova, R. A. Motiyenko, L. Margules, J. L. Alonso, J.-C. Guillemin**

We report on the tentative detection of trans Ethyl Methyl Ether (tEME), t-CH<sub>3</sub>CH<sub>2</sub>OCH<sub>3</sub>, through the identification of a large number of rotational lines from each one of the spin states of the molecule towards Orion KL. We also search for gauche-trans-n-propanol, Gt-n-CH<sub>3</sub>CH<sub>2</sub>CH<sub>2</sub>OH, an isomer of tEME in the same source. We have identified lines of both species in the IRAM 30m line survey and in the ALMA Science Verification data. We have obtained ALMA maps to establish the spatial distribution of these species. Whereas tEME mainly arises from the compact ridge component of Orion, Gt-n-propanol appears at the emission peak of ethanol (south hot core). The derived column densities of these species at the location of their emission peaks are  $<4.0 \pm 0.8 \times 10^{15} \text{ cm}^{-2}$  and  $<1.0 \pm 0.2 \times 10^{15} \text{ cm}^{-2}$  for tEME and Gt-n-propanol, respectively. The rotational temperature is  $\sim 100 \text{ K}$  for both molecules. We also provide maps of CH<sub>3</sub>OCOH, CH<sub>3</sub>CH<sub>2</sub>OCOH, CH<sub>3</sub>OCH<sub>3</sub>, CH<sub>3</sub>OH, and CH<sub>3</sub>CH<sub>2</sub>OH to compare the distribution of these organic saturated O-bearing species containing methyl and ethyl groups in this region. Abundance ratios of related species and upper limits to the abundances of non-detected ethers are provided. We derive an abundance ratio  $N(\text{CH}_3\text{OCH}_3)/N(\text{tEME}) > 150$  in the compact ridge of Orion.

A&A, 2015, 582, L1

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### The Distribution and Chemistry of H<sub>2</sub>CO in the DM Tau Protoplanetary Disk

**R. A. Loomis, L. I. Cleaves, Karin I. Oberg, V. V. Guzman, S. M. Andrews**

H<sub>2</sub>CO ice on dust grains is an important precursor of complex organic molecules (COMs). H<sub>2</sub>CO gas can be readily observed in protoplanetary disks and may be used to trace COM chemistry. However, its utility as a COM probe is currently limited by a lack of constraints on the relative contributions of two different formation pathways: on icy grain-surfaces and in the gas-phase. We use archival ALMA observations of the resolved distribution of H<sub>2</sub>CO emission in the disk around the young low-mass star DM Tau to assess the relative importance of these formation routes. The observed H<sub>2</sub>CO emission has a centrally peaked and radially broad brightness profile (extending out to 500 AU). We compare these observations with disk chemistry models with and without grain-surface formation reactions, and find that both gas and grain-surface chemistry are

necessary to explain the spatial distribution of the emission. Gas-phase H<sub>2</sub>CO production is responsible for the observed central peak, while grain-surface chemistry is required to reproduce the emission exterior to the CO snowline (where H<sub>2</sub>CO mainly forms through the hydrogenation of CO ice before being non-thermally desorbed). These observations demonstrate that both gas and grain-surface pathways contribute to the observed H<sub>2</sub>CO in disks, and that their relative contributions depend strongly on distance from the host star.

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Full-text URL: <http://arxiv.org/abs/1508.07004>

## **A proposed chemical scheme for HCCO formation in cold dense clouds**

**V. Wakelam, J.-C. Loison, K. M. Hickson, M. Ruaud**

The ketenyl radical (HCCO) has recently been discovered in two cold dense clouds with a non-negligible abundance of a few 1e-11 (compared to H<sub>2</sub>). Until now, no chemical network has been able to reproduce this observation. We propose here a chemical scheme that can reproduce HCCO abundances together with HCO, H<sub>2</sub>CCO and CH<sub>3</sub>CHO in the dark clouds Lupus-1A and L486. The main formation pathway for HCCO is the OH + CCH → HCCO + H reaction as suggested by Agúndez et al. but with a much larger rate coefficient than used in current models. Since this reaction has never been studied experimentally or theoretically, this larger value is based on a comparison with other similar systems.

MNRAS Letters, 2015, 453, L48

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## **The λ6614 diffuse interstellar absorption band: evidence for internal excitation of the carrier**

**Charlotte C. M. Marshall, Jacek Krelowski and Peter J. Sarre**

An analysis of absorption profiles of the λ6614 diffuse interstellar band recorded along the lines of sight towards HD 179406 (20 Aql) and HD 147889 is described. The difference in band shape is attributed to the degree of internal excitation of the carrier, which is principally due to vibrational hot bands although an electronic component may also be present. The results are discussed with respect to other models of diffuse band spectral line shape.

2015, MNRAS, 453 (4), 3912-3917.

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## **Carbon dioxide influence on the thermal formation of Complex Organic Molecules in interstellar ice analogs**

**V. Vinogradoff, F. Duvernay, N. Fray, M. Bouilloud, T. Chiavassa, and H. Cottin**

Interstellar ices are submitted to energetic processes (thermal, UV, and cosmic-ray radiations) producing complex organic molecules. Laboratory experiments aim to reproduce the evolution of interstellar ices to better understand the chemical changes leading to the reaction, formation, and desorption of molecules. In this context, the thermal evolution of an interstellar ice analogue composed of water, carbon dioxide, ammonia, and formaldehyde is investigated. The ice

evolution during the warming has been monitored by IR spectroscopy. The formation of hexamethylenetetramine (HMT) and polymethylenimine (PMI) are observed in the organic refractory residue left after ice sublimation. A better understanding of this result is realized with the study of another ice mixture containing methylenimine (a precursor of HMT) with carbon dioxide and ammonia. It appears that carbamic acid, a reaction product of carbon dioxide and ammonia, plays the role of catalyst, allowing the reactions toward HMT and PMI formation. This is the first time that such complex organic molecules (HMT, PMI) are produced from the warming (without VUV photolysis or irradiation with energetic particles) of abundant molecules observed in interstellar ices (H<sub>2</sub>O, NH<sub>3</sub>, CO<sub>2</sub>, H<sub>2</sub>CO). This result strengthens the importance of thermal reactions in the ices' evolution. HMT and PMI, likely components of interstellar ices, should be searched for in the pristine objects of our solar system, such as comets and carbonaceous chondrites.

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## Identification of more interstellar C<sub>60</sub><sup>+</sup> bands

**Gordon Walker, David Bohlender, John Maier, Ewen Campbell**

Based on gas-phase laboratory spectra at 6K, Campbell et al. (2015) confirmed that the diffuse interstellar bands (DIBs) at 9632.7 and 9577.5Å are due to absorption by the fullerene ion C<sub>60</sub><sup>+</sup>. They also reported the detection of two other, weaker bands at 9428.5 and 9365.9Å. These lie in spectral regions heavily contaminated by telluric water vapour lines. We acquired CFHT ESPaDOnS spectra of HD183143 close to the zenith and chopped with a nearby standard to correct for the telluric line absorption which enabled us to detect a DIB at 9365.9Å of relative width and strength comparable to the laboratory absorption. There is a DIB of similar strength and FWHM at 9362.5Å. A stellar emission feature at 9429Å prevented detection of the 9428.5Å band. However, a CFHT archival spectrum of HD169454, where emission is absent at 9429Å, clearly shows the 9428.5Å DIB with the expected strength and width. These results further confirm C<sub>60</sub><sup>+</sup> as a DIB carrier.

The Astrophysical Journal Letters, 2015, 812, 1

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## Probing the effects of external irradiation on low-mass protostars through unbiased line surveys

**Johan E. Lindberg, Jes K. Jørgensen, Yoshimasa Watanabe, Suzanne E. Bisschop, Nami Sakai, Satoshi Yamamoto**

(abridged) Method: The envelopes of molecular gas around embedded low-mass protostars show different chemistries, which can be used to trace their formation history and physical conditions. The excitation of some molecular species can also be used to trace these physical conditions, making it possible to constrain e.g. sources of heating and excitation. Aims: To study the range of influence of an intermediate-mass Herbig Be protostar, and to find what chemical and physical impact feedback effects from the environment may have on embedded protostars. Methods: We follow up on an earlier line survey of the Class 0/I source R CrA IRS7B in the 0.8 mm window with an unbiased line survey of the same source in the 1.3 mm window using the APEX telescope. We also study the excitation of the key species H<sub>2</sub>CO, CH<sub>3</sub>OH, and c-C<sub>3</sub>H<sub>2</sub> in

a complete sample of the 18 embedded protostars in the Corona Australis star-forming region. Radiative transfer models are employed to establish abundances of the molecular species. Results: We detect line emission from 20 molecular species (32 including isotopologues) in the two surveys. The most complex species detected are CH<sub>3</sub>OH, CH<sub>3</sub>CCH, CH<sub>3</sub>CHO, and CH<sub>3</sub>CN. CH<sub>3</sub>CN and several other complex organics are significantly under-abundant in comparison with what is found towards "hot corino" protostars. The H<sub>2</sub>CO temperatures of the sources in the region decrease with the distance to the Herbig Be star R CrA, whereas the c-C<sub>3</sub>H<sub>2</sub> temperatures remain constant across the star-forming region. Conclusions: The high H<sub>2</sub>CO temperatures observed towards objects close to R CrA suggest that this star has a sphere of influence of several 10000 AU in which it increases the temperature of the molecular gas to 30-50 K through irradiation. The chemistry in the IRS7B envelope differs significantly from many other embedded protostars, which could be an effect of the external irradiation from R CrA.

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## Inverse internal conversion in C<sub>4</sub>

**Naoko Kono, Takeshi Furukawa, Hajime Tanuma, Jun Matsumoto, Haruo Shiromaru, Toshiyuki Azuma, Kaveh Najafian, Maria Susanne Pettersson, Bertil Dynefors and Klavs Hansen**

Inverse internal conversion followed by recurrent fluorescence was observed as a fast decay (10 ms range) in the time profile of neutral yields from photo-excited C<sub>4</sub><sup>-</sup> molecular ions. We also elucidated the contribution of such electronic radiative cooling to the C<sub>4</sub><sup>-</sup> ions with internal energy far below the detachment threshold by an alternative novel approach, observing the laser wavelength and storage time dependence (ms range) of the total yield of the photo-induced neutrals.

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## The effect of broadband soft X-rays in SO<sub>2</sub>-containing ices: Implication on the photochemistry of ices towards young stellar objects

**S. Pilling, A. Bergantini**

We investigate the effects produced mainly by broadband soft X-rays up to 2 keV (plus fast (~keV) photoelectrons and low-energy (eV) induced secondary electrons) in the ice mixtures containing H<sub>2</sub>O:CO<sub>2</sub>:NH<sub>3</sub>:SO<sub>2</sub> (10:1:1:1) at two different temperatures (50 K and 90 K). The experiments are an attempt to simulate the photochemical processes induced by energetic photons in SO<sub>2</sub>-containing ices present in cold environments in the ices surrounding young stellar objects (YSO) and in molecular clouds in the vicinity of star-forming regions, which are largely illuminated by soft X-rays. The measurements were performed using a high vacuum portable chamber from the Laboratório de Astroquímica e Astrobiologia (LASA/UNIVAP) coupled to the spherical grating monochromator (SGM) beamline at the Brazilian Synchrotron Light Source (LNLS) in Campinas, Brazil. In-situ analyses were performed by a Fourier transform infrared (FTIR) spectrometer. Sample processing revealed the formation of several organic molecules, including nitriles, acids, and other compounds such as H<sub>2</sub>O<sub>2</sub>, H<sub>3</sub>O<sup>+</sup>, SO<sub>3</sub>, CO, and OCN<sup>-</sup>. The dissociation cross section of parental species was in the order of 2-7x10<sup>-18</sup> cm<sup>2</sup>. The

ice temperature seems not to affect the stability for SO<sub>2</sub> in the presence of X-rays. Formation cross sections of produced new species were also determined. Molecular half-lives at ices towards YSOs due to the presence of incoming soft X-rays were estimated. The low obtained values, employing two different models of radiation field of YSOs (TW Hydra and typical T Tauri star), reinforce that soft X-rays are indeed a very efficient source of molecular dissociation in such environments.

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## Detection of extragalactic argonium, ArH<sup>+</sup>, toward PKS 1830-211

H. S. P. Müller, S. Müller, P. Schilke, E. A. Bergin, J. H. Black, M. Gerin, D. C. Lis, D. A. Neufeld S. Suri

Argonium has recently been detected as a ubiquitous molecule in our Galaxy. Model calculations indicate that its abundance peaks at molecular fractions in the range of 1e-4 to 1e-3 and that the observed column densities require high values of the cosmic ray ionization rate. Therefore, this molecular cation may serve as an excellent tracer of the very diffuse interstellar medium (ISM), as well as an indicator of the cosmic ray ionization rate. We attempted to detect ArH<sup>+</sup> in extragalactic sources to evaluate its diagnostic power as a tracer of the almost purely atomic ISM in distant galaxies. We obtained ALMA observations of a foreground galaxy at  $z = 0.89$  in the direction of the lensed blazar PKS 1830-211. Two isotopologs of argonium, <sup>36</sup>ArH<sup>+</sup> and <sup>38</sup>ArH<sup>+</sup>, were detected in absorption along two different lines of sight toward PKS 1830-211, known as the SW and NE images of the background blazar. The argonium absorption is clearly enhanced on the more diffuse line of sight (NE) compared to other molecular species. The isotopic ratio <sup>36</sup>Ar/<sup>38</sup>Ar is  $3.46 \pm 0.16$  toward the SW image, i.e., significantly lower than the solar value of 5.5. Our results demonstrate the suitability of argonium as a tracer of the almost purely atomic, diffuse ISM in high-redshift sources. The evolution of the isotopic ratio with redshift may help to constrain nucleosynthetic scenarios in the early Universe.

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## Interstellar Detection of Methyl Isocyanate CH<sub>3</sub>NCO in Sgr B2(N): A Link from Molecular Clouds to Comets

DeWayne T. Halfen, Vadim V. Ilyushin, and Lucy M. Ziurys

A new interstellar molecule, CH<sub>3</sub>NCO (methyl isocyanate), has been detected using the 12 m telescope of the Arizona Radio Observatory (ARO). CH<sub>3</sub>NCO was identified in spectra covering 48 GHz (68–116 GHz) in the 3 mm segment of a broadband survey of Sgr B2(N). Thirty very favorable rotational lines ( $K_a = 0$  and  $K_a = 1$  only;  $E_u < 60$  K) originating in five consecutive transitions ( $J = 8 \rightarrow 7, 9 \rightarrow 8, 10 \rightarrow 9, 11 \rightarrow 10, \text{ and } 12 \rightarrow 11$ ) in both the A and E internal rotation species are present in this frequency range. Emission was observed at all of the predicted frequencies, with seventeen lines appearing as distinct, uncontaminated spectral features, clearly showing the classic a-type, asymmetric top pattern, with  $TR^* \approx 20\text{--}70$  mK. The CH<sub>3</sub>NCO spectra also appear to exhibit two velocities components near  $V_{LSR} \approx 62$  and  $73$  km s<sup>-1</sup>, both with  $\Delta v_{1/2} \approx 10$  km s<sup>-1</sup> - typical of molecules such as CH<sub>2</sub>CHCN, HNCO, and HCOOCH<sub>3</sub> in Sgr B2(N). The column density of CH<sub>3</sub>NCO in Sgr B2(N) was determined to be  $N_{\text{tot}} \approx 2.3 \times 10^{13}$  cm<sup>-2</sup>.



2 and  $1.5 \times 10^{13} \text{ cm}^{-2}$  for the 62 and 73 km s<sup>-1</sup> components, corresponding to fractional abundances, relative to H<sub>2</sub>, of  $f \approx 7.6 \times 10^{-12}$  and  $5.0 \times 10^{-12}$ , respectively. CH<sub>3</sub>NCO was recently detected in volatized material from comet 67P/Churyumov-Gerasimenko by Rosetta's Philae lander, with an abundance  $\sim 1.3\%$  of water; in Sgr B2(N), CH<sub>3</sub>NCO is roughly  $\sim 0.04\%$  of the H<sub>2</sub>O abundance.

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## Resolving the chemical substructure of Orion-KL

S. Feng ( ), H. Beuther, Th. Henning, D. Semenov, A. Palau and E. A. C. Mills

The Kleinmann-Low nebula in Orion (Orion-KL) is the nearest example of a high-mass star-forming environment. For the first time, we complemented 1.3 mm Submillimeter Array (SMA) interferometric line survey with IRAM 30 m single-dish observations of the Orion-KL region. Covering a 4 GHz bandwidth in total, this survey contains over 160 emission lines from 20 species (25 isotopologues), including 11 complex organic molecules (COMs). At a spatial resolution of 1200 AU, the continuum substructures are resolved. Extracting the spectra from individual substructures and providing the intensity-integrated distribution map for each species, we studied the small-scale chemical variations in this region. Our main results are: (1) We identify lines from the low-abundance COMs CH<sub>3</sub>COCH<sub>3</sub> and CH<sub>3</sub>CH<sub>2</sub>OH, as well as tentatively detect CH<sub>3</sub>CHO and long carbon-chains C<sub>6</sub>H and HC<sub>7</sub>N. (2) We find that while most COMs are segregated by type, peaking either towards the hot core (e.g., N-bearing species) or the compact ridge (e.g., O-bearing species like HCOOCH<sub>3</sub> and CH<sub>3</sub>OCH<sub>3</sub>), while the distributions of others do not follow this segregated structure (e.g., CH<sub>3</sub>CH<sub>2</sub>OH, CH<sub>3</sub>OH, CH<sub>3</sub>COCH<sub>3</sub>). (3) We find a second velocity component of HNCO, SO<sub>2</sub>, <sup>34</sup>SO<sub>2</sub>, and SO lines, which may be associated with a strong shock event in the low-velocity outflow. (4) Temperatures and molecular abundances show large gradients between central condensations and the outflow regions, illustrating a transition between hot molecular core and shock-chemistry dominated regimes. Our observations of spatially resolved chemical variations in Orion-KL provide the nearest reference source for hot molecular core and outflow chemistry, which will be an important example for interpreting the chemistry of more distant HMSFRs.

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## Theoretical study of deuterated PAHs as carriers for IR emission features in the ISM

Mridusmita Buragohain, Amit Pathak, Peter Sarre, Takashi Onaka, Itsuki Sakon

This work proposes deuterated PAH (DPAH<sup>+</sup>) molecules as a potential carrier of the 4.4 and 4.65  $\mu\text{m}$  mid infrared emission bands that have been observationally detected towards the Orion and M17 regions. Density Functional Theory calculations have been carried out on DPAH<sup>+</sup> molecules to see the variations in the spectral behaviour from that of a pure PAH. DPAH<sup>+</sup> molecules show features that arise due to the stretching of the aliphatic C-D bond. Deuterated PAHs have been previously reported as carriers for such features. However, preferred conditions of ionization of PAHs in the interstellar medium (ISM) indicates the possibility of the formation of DPAH<sup>+</sup> molecules. Comparison of band positions of DPAH<sup>+</sup> s shows reasonable agreement

with the observations. We report the effect of size of the DPAH+ molecules on band positions and intensities. This study also reports a D/H ratio ( $[D/H]_{sc}$ ; the ratio of C – D stretch and C – H stretch bands per  $[D/H]_{num}$ ) that is decreasing with the increasing size of DPAH+ s. It is noted that large DPAH+ molecules (no. of C atoms  $\sim 50$ ) match the D/H ratio that has been estimated from observations. This ratio offers prospects to study the deuterium abundance and depletion in the ISM.

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## Chemical Imaging of the CO Snow Line in the HD 163296 Disk

**C. Qi, K. Oberg, S. Andrews, David Wilner, Edwin Bergin, A.M. Hughes, M. Hogherheijde, Paola D'Alessio**

The condensation fronts (snow lines) of H<sub>2</sub>O, CO and other abundant volatiles in the midplane of a protoplanetary disk affect several aspects of planet formation. Locating the CO snow line, where the CO gas column density is expected to drop substantially, based solely on CO emission profiles is challenging. This has prompted an exploration of chemical signatures of CO freeze-out. We present ALMA Cycle 1 observations of the N<sub>2</sub>H<sup>+</sup> J=3-2 and DCO<sup>+</sup> J=4-3 emission lines toward the disk around the Herbig Ae star HD~163296 at  $\sim 0.5''$  (60 AU) resolution, and evaluate their utility as tracers of the CO snow line location. The N<sub>2</sub>H<sup>+</sup> emission is distributed in a ring with an inner radius at 90 AU, corresponding to a midplane temperature of 25 K. This result is consistent with a new analysis of optically thin C<sup>18</sup>O data, which implies a sharp drop in CO abundance at 90 AU. Thus N<sub>2</sub>H<sup>+</sup> appears to be a robust tracer of the midplane CO snow line. The DCO<sup>+</sup> emission also has a ring morphology, but neither the inner nor the outer radius coincides with the CO snow line location of 90 AU, indicative of a complex relationship between DCO<sup>+</sup> emission and CO freeze-out in the disk midplane. Compared to TW Hya, CO freezes out at a higher temperature in the disk around HD 163296 (25 vs. 17 K in the TW Hya disk), perhaps due to different ice compositions. This highlights the importance of actually measuring the CO snow line location, rather than assuming a constant CO freeze-out temperature for all disks.

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## Physical conditions in the central molecular zone inferred by H<sub>3</sub><sup>+</sup>

**F. Le Petit, M. Ruaud, E. Bron, B. Godard, E. Roueff, D. Languignon, J. Le Bourlot**

The H<sub>3</sub><sup>+</sup> molecule has been detected in many lines of sight within the central molecular zone (CMZ) with exceptionally large column densities and unusual excitation properties compared to diffuse local clouds. The detection of the (3,3) metastable level has been suggested to be the signature of warm and diffuse gas in the CMZ. We use the Meudon PDR code to re-examine the relationship between the column density of H<sub>3</sub><sup>+</sup> and the cosmic-ray ionization rate, zeta, up to large values of zeta. We study the impact of the various mechanisms that can excite H<sub>3</sub><sup>+</sup> in its metastable state. We produce grids of PDR models exploring different parameters (zeta, size of clouds, metallicity) and infer the physical conditions that best match the observations toward ten lines of sight in the CMZ. For one of them, Herschel observations of HF, OH<sup>+</sup>, H<sub>2</sub>O<sup>+</sup>, and H<sub>3</sub>O<sup>+</sup> can be used as additional constraints. We check that the results found for H<sub>3</sub><sup>+</sup> also account for the observations of these molecules. We find that the linear relationship between N(H<sub>3</sub><sup>+</sup>) and

zeta only holds up to a certain value of the cosmic-ray ionization rate, which depends on the proton density. A value  $\zeta \sim 1\text{E-}14 - 11\text{E-}14 \text{ s}^{-1}$  explains both the large observed  $\text{H}_3^+$  column density and its excitation in the metastable level (3,3) in the CMZ. It also reproduces  $\text{N}(\text{OH}^+)$ ,  $\text{N}(\text{H}_2\text{O}^+)$  and  $\text{N}(\text{H}_3\text{O}^+)$  detected toward Sgr B2(N). We confirm that the CMZ probed by  $\text{H}_3^+$  is diffuse,  $n_{\text{H}} < 100 \text{ cm}^{-3}$  and warm,  $T \sim 212\text{-}505 \text{ K}$ . This warm medium is due to cosmic-ray heating. We also find that the diffuse component probed by  $\text{H}_3^+$  must fill a large fraction of the CMZ. Finally, we suggest the warm gas in the CMZ enables efficient  $\text{H}_2$  formation via chemisorption sites as in PDRs. This contributes to enhance the abundance of  $\text{H}_3^+$  in this high cosmic-ray flux environment.

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## The molecular composition of the planet-forming regions of protoplanetary disks across the luminosity regime

Catherine Walsh, Hideko Nomura, Ewine van Dishoeck

Context: Near- to mid-infrared observations of molecular emission from protoplanetary disks show that the inner regions are rich in small organic volatiles (e.g.,  $\text{C}_2\text{H}_2$  and  $\text{HCN}$ ). Trends in the data suggest that disks around cooler stars ( $T_{\text{eff}} \sim 3000 \text{ K}$ ) are potentially (i) more carbon-rich; and (ii) more molecule-rich than their hotter counterparts ( $T_{\text{eff}} > 4000 \text{ K}$ ). Aims: We explore the chemical composition of the planet-forming region ( $< 10 \text{ AU}$ ) of protoplanetary disks around stars over a range of spectral types (from M dwarf to Herbig Ae) and compare with the observed trends. Methods: Self-consistent models of the physical structure of a protoplanetary disk around stars of different spectral types are coupled with a comprehensive gas-grain chemical network to map the molecular abundances in the planet-forming zone. The effects of (i)  $\text{N}_2$  self shielding; (ii) X-ray-induced chemistry; and (iii) initial abundances, are investigated. The chemical composition in the "observable" atmosphere is compared with that in the disk midplane where the bulk of the planet-building reservoir resides. Results: M dwarf disk atmospheres are relatively more molecule rich than those for T Tauri or Herbig Ae disks. The weak far-UV flux helps retain this complexity which is enhanced by X-ray-induced ion-molecule chemistry.  $\text{N}_2$  self shielding has only a small effect in the disk molecular layer and does not explain the higher  $\text{C}_2\text{H}_2/\text{HCN}$  ratios observed towards cooler stars. The models underproduce the  $\text{OH}/\text{H}_2\text{O}$  column density ratios constrained in Herbig Ae disks, despite reproducing (within an order of magnitude) the absolute value for OH: the inclusion of self shielding for  $\text{H}_2\text{O}$  photodissociation only increases this discrepancy. One possible explanation is the adopted disk structure. Alternatively, the "hot"  $\text{H}_2\text{O}$  ( $T > 300 \text{ K}$ ) chemistry may be more complex than assumed. The results for the atmosphere are independent of the assumed initial abundances; however, the composition of the disk midplane is sensitive to the initial main elemental reservoirs. The models show that the gas in the inner disk is generally more carbon rich than the midplane ices. This effect is most significant for disks around cooler stars. Furthermore, the atmospheric C/O ratio appears larger than it actually is when calculated using observable tracers only. This is because gas-phase  $\text{O}_2$  is predicted to be a significant reservoir of atmospheric oxygen. Conclusions: The models suggest that the gas in the inner regions of disks around cooler stars is more carbon rich; however, calculations of the molecular emission are necessary to definitively confirm whether the chemical trends reproduce the observed trends.

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## CSO and CARMA Observations of L1157. I. A Deep Search for Hydroxylamine (NH<sub>2</sub>OH)

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A deep search for the potential glycine precursor hydroxylamine (NH<sub>2</sub>OH) using the Caltech Submillimeter Observatory (CSO) at 1.3 mm and the Combined Array for Research in Millimeter-wave Astronomy at 3 mm is presented toward the molecular outflow L1157, targeting the B1 and B2 shocked regions. We report non-detections of NH<sub>2</sub>OH in both sources. We perform a non-LTE analysis of CH<sub>3</sub>OH observed in our CSO spectra to derive the kinetic temperatures and densities in the shocked regions. Using these parameters, we derive upper limit column densities of NH<sub>2</sub>OH  $<1.4 \times 10^{13}$  cm<sup>-2</sup> and  $<1.5 \times 10^{13}$  cm<sup>-2</sup> toward the B1 and B2 shocks, respectively, and upper limit abundances of N(NH<sub>2</sub>OH)/N(H<sub>2</sub>) of  $<1.4 \times 10^{-8}$  and  $<1.5 \times 10^{-8}$ , respectively.

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## Born-Oppenheimer and Renner-Teller coupled-channel quantum reaction dynamics of O(<sup>3</sup>P) + H<sub>2</sub>(<sup>+</sup>X(<sup>2</sup>Σ<sub>g</sub>(<sup>+</sup>)) collisions.

**P. Gamallo, P. Defazio, M. González, M. Paniagua, C. Petrongolo**

We present Born–Oppenheimer (BO) and Renner–Teller (RT) time dependent quantum dynamics studies of the reactions  $O + H_2^+ \rightarrow OH^+ + H$  and  $OH + H^+$ . We consider the OH<sub>2</sub><sup>+</sup> ground (X) and first excited (A) electronic states that correlate with a linear 2P species. The electronic angular momenta operators L and L<sub>2</sub> are considered in nonadiabatic coupled-channel calculations, where the associated RT effects are due to diagonal (V) RT potentials that add up to the PESs and to off-diagonal (C) RT couplings between the potential energy surfaces (PESs). Initial-state-resolved reaction probabilities, integral cross sections, and rate constants are obtained using recent ab initio PESs and couplings and the real wavepacket formalism. Because the PESs are strongly attractive, probabilities have no threshold energy and are large, cross sections decrease with collision energy, and rate constants depend little on the temperature. The ground PES is up to three times more reactive than the excited PES and H<sub>2</sub><sup>+</sup> rotational effects ( $j_0 = 0, 1$ ) are negligible. The diagonal (V) RT potentials are strongly repulsive at the collinearity and nearly halve all low-energy observables with respect to the BO ones. The off-diagonal (C) RT couplings are important at low partial waves, where they mix the ground and excited states up to 20%. However, V RT effects predominate over the C RT ones that change at most by 19% the BO values of cross sections and rate constants. The reaction  $O + H_2^+ \rightarrow OH^+ + H$  is probably one of the most reactive atom + diatom collisions because its RT rate constant at room temperature is equal to  $2.26 \times 10^{-10}$  cm<sup>3</sup> s<sup>-1</sup>. Within the BO approximation, the present results agree rather well with recent quasiclassical and centrifugal-sudden data using the same PESs.

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## Formation of the Hydroxyl Radical by Radiative Association

**S. K.-M. Svensson, M. Gustafsson, G. Nyman**

The reaction rate constant for the radiative association of O(3P) and H(2S) has been calculated by combining a few different methods and taking account of both direct and resonance-mediated pathways. The latter includes both shape resonances and Feshbach type inverse predissociation. The reaction rate constant is expressed as a function of temperature in the interval 10–30000 K. This reaction may be astrochemically relevant and is expected to be of use in astrochemical networks.

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## **Evolution of stratospheric chemistry in the Saturn storm beacon region**

**Julianne I. Moses, Eleanor S. Armstrong, Leigh N. Fletcher, A. James Friedson, Patrick G.J. Irwin, James A. Sinclair, Brigitte E. Hesman**

The giant northern-hemisphere storm that erupted on Saturn in December 2010 triggered significant changes in stratospheric temperatures and species abundances that persisted for more than a year after the original outburst. The stratospheric regions affected by the storm have been nicknamed “beacons” due to their prominent infrared-emission signatures (Fletcher, L.N. et al. [2011]. *Science* 332, 1413). We model the expected photochemical evolution of the stratospheric constituents in the beacons from the initial storm onset through the merger and on out to March 2012. The results are compared with longitudinally resolved Cassini/CIRS spectra from May 2011. If we ignore potential changes due to vertical winds within the beacon, we find that C<sub>2</sub>H<sub>2</sub>, C<sub>2</sub>H<sub>6</sub>, and C<sub>3</sub>H<sub>8</sub> remain unaffected by the increased stratospheric temperatures in the beacon, the abundance of the shorter-lived CH<sub>3</sub>C<sub>2</sub>H decreases, and the abundance of C<sub>2</sub>H<sub>4</sub> increases significantly due to the elevated temperatures, the latter most notably in a secondary mixing-ratio peak located near mbar pressures. The C<sub>4</sub>H<sub>2</sub> abundance in the model decreases by a factor of a few in the 0.01–10 mbar region but has a significant increase in the 10–30 mbar region due to evaporation of the previously condensed phase. The column abundances of C<sub>6</sub>H<sub>6</sub> and H<sub>2</sub>O above ~30 mbar also increase due to aerosol evaporation. Model-data comparisons show that models that consider temperature changes alone underpredict the abundance of C<sub>2</sub>H<sub>x</sub> species by a factor of 2–7 in the beacon core in May 2011, suggesting that other processes not considered by the models, such as downwelling winds in the vortex, are affecting the species profiles. Additional calculations indicate that downwelling winds of order 10 cm s<sup>-1</sup> near ~0.1 mbar need to be included in the photochemical models in order to explain the inferred C<sub>2</sub>H<sub>x</sub> abundances in the beacon core, indicating that both strong subsiding winds and chemistry at elevated temperatures are affecting the vertical profiles of atmospheric constituents in the beacon. We (i) discuss the general chemical behavior of stratospheric species in the beacon region, (ii) demonstrate how the evolving beacon environment affects the species vertical profiles and emission characteristics (both with and without the presence of vertical winds), (iii) make predictions with respect to compositional changes that can be tested against Cassini and Herschel data, and higher-spectral-resolution ground-based observations of the beacon region, and (iv) discuss future measurements and modeling that could further our understanding of the dynamical origin, evolution, and chemical processing within these unexpected stratospheric vortices that were generated after the 2010 convective event.

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## Far-infrared study of tracers of oxygen chemistry in diffuse clouds

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The chemistry of the diffuse interstellar medium rests upon three pillars: exothermic ion-neutral reactions (“cold chemistry”), endothermic neutral-neutral reactions with significant activation barriers (“warm chemistry”), and reactions on the surfaces of dust grains. While warm chemistry becomes important in the shocks associated with turbulent dissipation regions, the main path for the formation of interstellar OH and water is that of cold chemistry. The aim of this study is to observationally confirm the association of atomic oxygen with both atomic and molecular gas phases, and to understand the measured abundances of OH and OH<sup>+</sup> as a function of the available reservoir of molecular hydrogen. We obtained absorption spectra of the ground states of OH, OH<sup>+</sup> and OI with high-velocity resolution, with GREAT onboard SOFIA, and with the THz receiver at the APEX. We analyzed them along with ancillary spectra of HF and CH from HIFI. To deconvolve them from the hyperfine structure and to separate the blend that is due to various velocity components on the sightline, we fit model spectra consisting of an appropriate number of Gaussian profiles using a method combining simulated annealing with downhill simplex minimization. Together with HF and/or CH as a surrogate for molecular hydrogen, and HI  $\lambda$ 21 cm data, the molecular hydrogen fraction can be determined. The column density of OI is correlated at a high significance with the amount of available molecular and atomic hydrogen, with an atomic oxygen abundance of 300 ppm relative to H nuclei. While the velocities of the absorption features of OH and OH<sup>+</sup> are loosely correlated and reflect the spiral arm crossings on the sightline, upon closer inspection they display an anticorrespondence. The arm-to-interarm density contrast is found to be higher in OH than in OH<sup>+</sup>. While both species can coexist, with a higher abundance in OH than in OH<sup>+</sup>, the latter is found less frequently in absence of OH than the other way around, which is a direct consequence of the rapid destruction of OH<sup>+</sup> by dissociative recombination when not enough molecular hydrogen is available. This conjecture has been substantiated by a comparison between the OH/OH<sup>+</sup> ratio with the molecular hydrogen fraction, showing a clear correlation. The hydrogen abstraction reaction chain from OH<sup>+</sup> to H<sub>3</sub>O<sup>+</sup> is confirmed as the pathway for the production of OH and water. Our estimate of the branching ratio of the dissociative recombination of H<sub>3</sub>O<sup>+</sup> to OH and H<sub>2</sub>O is confined within the interval of 82 to 88%, which matches laboratory measurements (74 to 83%). A correlation between the linewidths and column densities of OH<sup>+</sup> features is found to be significant with a false-alarm probability below 5%. Such a correlation is predicted by models of interstellar MHD turbulence. For OH the same correlation is found to be insignificant because there are more narrow absorption features. While it is difficult to assess the contributions of warm neutral-neutral chemistry to the observed abundances, it seems fair to conclude that the predictions of cold ion-neutral chemistry match the abundance patterns we observed.

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## Water deuteration and ortho-to-para nuclear spin ratio of H<sub>2</sub> in molecular clouds formed via accumulation of HI gas

K. Furuya, Y. Aikawa, U. Hincelin, G. E. Hassel, E. A. Bergin, A. I. Vasyunin, Eric Herbst

We investigate the water deuteration ratio and ortho-to-para nuclear spin ratio of H<sub>2</sub> (OPR(H<sub>2</sub>))

during the formation and early evolution of a molecular cloud, following the scenario that accretion flows sweep and accumulate HI gas to form molecular clouds. We follow the physical evolution of post-shock materials using a one-dimensional shock model, with post-processing gas-ice chemistry simulations. This approach allows us to study the evolution of the OPR(H<sub>2</sub>) and water deuteration ratio without an arbitrary assumption concerning the initial molecular abundances, including the initial OPR(H<sub>2</sub>). When the conversion of hydrogen into H<sub>2</sub> is almost complete, the OPR(H<sub>2</sub>) is already much smaller than the statistical value of three due to the spin conversion in the gas phase. As the gas accumulates, the OPR(H<sub>2</sub>) decreases in a non-equilibrium manner. We find that water ice can be deuterium-poor at the end of its main formation stage in the cloud, compared to water vapor observed in the vicinity of low-mass protostars where water ice is sublimated. If this is the case, the enrichment of deuterium in water should mostly occur at somewhat later evolutionary stages of star formation, i.e., cold prestellar/protostellar cores. The main mechanism to suppress water ice deuteration in the cloud is the cycle of photodissociation and reformation of water ice, which efficiently removes deuterium from water ice chemistry. The removal efficiency depends on the main formation pathway of water ice. The OPR(H<sub>2</sub>) plays a minor role in water ice deuteration at the main formation stage of water ice.

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## High-resolution absorption cross sections of C<sub>2</sub>H<sub>6</sub> at elevated temperatures

**R. J. Hargreaves, E. Buzan, M. Dulick, P. F. Bernath**

Infrared absorption cross sections near 3.3 μm have been obtained for ethane, C<sub>2</sub>H<sub>6</sub>. These were acquired at elevated temperatures (up to 773 K) using a Fourier transform infrared spectrometer and tube furnace with a resolution of 0.005 cm<sup>-1</sup>. The integrated absorption was calibrated using composite infrared spectra taken from the Pacific Northwest National Laboratory (PNNL). These new measurements are the first high-resolution infrared C<sub>2</sub>H<sub>6</sub> cross sections at elevated temperatures.

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## Herschel HIFI Observations of the Sgr A +50 km/s Cloud. Deep Searches for O<sub>2</sub> in Emission and Foreground Absorption

**Aa. Sandqvist, B. Larsson, Å. Hjalmarson, P. Encrenaz, M. Gerin, P.F. Goldsmith, D.C. Lis, R. Liseau, L. Paganì, E. Roueff, S. Viti**

To date O<sub>2</sub> has definitely been detected in only two sources, namely rho Oph A and Orion, reflecting the extremely low abundance of O<sub>2</sub> in the interstellar medium. One of the sources in the HOP program is the +50 km/s Cloud in the Sgr A Complex in the centre of the Milky Way. The Herschel HIFI is used to search for the 487 and 774 GHz emission lines of O<sub>2</sub>. No O<sub>2</sub> emission is detected towards the Sgr A +50 km/s Cloud, but a number of strong emission lines of methanol (CH<sub>3</sub>OH) and absorption lines of chloronium (H<sub>2</sub>Cl<sup>+</sup>) are observed. A 3 sigma upper limit for the fractional abundance ratio of (O<sub>2</sub>)/(H<sub>2</sub>) in the Sgr A +50 km/s Cloud is found to be X(O<sub>2</sub>) less than 5 x 10<sup>(-8)</sup>. However, since we can find no other realistic molecular candidate than O<sub>2</sub> itself, we very tentatively suggest that two weak absorption lines at 487.261 and 487.302 GHz may be

caused by the 487 GHz line of O<sub>2</sub> in two foreground spiral arm clouds. By considering that the absorption may only be apparent, the estimated upper limit to the O<sub>2</sub> abundance of less than  $(10-20) \times 10^{-6}$  in these foreground clouds is very high. This abundance limit was determined also using Odin non-detection limits. If the absorption is due to a differential Herschel OFF-ON emission, the O<sub>2</sub> fractional abundance may be of the order of  $(5-10) \times 10^{-6}$ . With the assumption of pure absorption by foreground clouds, the unreasonably high abundance of  $(1.4-2.8) \times 10^{-4}$  was obtained. The rotation temperatures for CH<sub>3</sub>OH-A and CH<sub>3</sub>OH-E lines in the +50 km/s Cloud are found to be 64 and 79 K, respectively, and the fractional abundance of CH<sub>3</sub>OH is approximately  $5 \times 10^{-7}$ .

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## **On the accretion process in a high-mass star forming region - A multitransitional THz Herschel-HIFI study of ammonia toward G34.26+0.15**

**M. Hajigholi, C.M. Persson, E.S. Wirström, J.H. Black, P. Bergman, A.O.H. Olofsson, M. Olberg, F. Wyrowski, A. Coutens, Å. Hjalmarson, and K.M. Menten**

[Abridged] Our aim is to explore the gas dynamics and the accretion process in the early phase of high-mass star formation. The inward motion of molecular gas in the massive star forming region G34.26+0.15 is investigated by using high-resolution profiles of seven transitions of ammonia at THz frequencies observed with Herschel-HIFI. The shapes and intensities of these lines are interpreted in terms of radiative transfer models of a spherical, collapsing molecular envelope. An accelerated Lambda iteration (ALI) method is used to compute the models. The seven ammonia lines show mixed absorption and emission with inverse P-Cygni-type profiles that suggest infall onto the central source. A trend toward absorption at increasingly higher velocities for higher excitation transitions is clearly seen in the line profiles. The  $J = 3-2$  lines show only very weak emission, so these absorption profiles can be used directly to analyze the inward motion of the gas. This is the first time a multitransitional study of spectrally resolved rotational ammonia lines has been used for this purpose. Broad emission is, in addition, mixed with the absorption in the  $1_0-0_0$  ortho-NH<sub>3</sub> line, possibly tracing a molecular outflow from the star forming region. The best-fitting ALI model reproduces the continuum fluxes and line profiles, but slightly underpredicts the emission and absorption depth in the ground-state ortho line  $1_0-0_0$ . The derived ortho-to-para ratio is approximately 0.5 throughout the infalling cloud core similar to recent findings for translucent clouds in sight lines toward W31C and W49N. We find evidence of two gas components moving inwards toward the central region with constant velocities: 2.7 and 5.3 km/s, relative to the source systemic velocity. The inferred mass accretion rates derived are sufficient to overcome the expected radiation pressure from G34.26+0.15.

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## **Impact of supernova and cosmic-ray driving on the surface brightness of the galactic halo in soft X-rays**

**T. Peters, P. Girichidis, A. Gatto, T. Naab, S. Walch, R. Wünsch, S. C. O. Glover, P. C. Clark, R. S. Klessen, C. Baczynski**

The halo of the Milky Way contains a hot plasma with a surface brightness in soft X-rays of the



order  $10\text{-}12 \text{ erg cm}^{-2} \text{ s}^{-1} \text{ deg}^{-2}$ . The origin of this gas is unclear, but so far numerical models of galactic star formation have failed to reproduce such a large surface brightness by several orders of magnitude. In this paper, we analyze simulations of the turbulent, magnetized, multi-phase interstellar medium including thermal feedback by supernova explosions as well as cosmic-ray feedback. We include a time-dependent chemical network, self-shielding by gas and dust, and self-gravity. Pure thermal feedback alone is sufficient to produce the observed surface brightness, although it is very sensitive to the supernova rate. Cosmic rays suppress this sensitivity and reduce the surface brightness because they drive cooler outflows. Self-gravity has by far the largest effect because it accumulates the diffuse gas in the disk in dense clumps and filaments, so that supernovae exploding in voids can eject a large amount of hot gas into the halo. This can boost the surface brightness by several orders of magnitude. Although our simulations do not reach a steady state, all simulations produce surface brightness values of the same order of magnitude as the observations, with the exact value depending sensitively on the simulation parameters. We conclude that star formation feedback alone is sufficient to explain the origin of the hot halo gas, but measurements of the surface brightness alone do not provide useful diagnostics for the study of galactic star formation.

ApJ Letters in press

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## Empirical line lists and absorption cross sections for methane at high temperature

R. J. Hargreaves, P. F. Bernath, J. Bailey, M. Dulick

Hot methane is found in many "cool" sub-stellar astronomical sources including brown dwarfs and exoplanets, as well as in combustion environments on Earth. We report on the first high-resolution laboratory absorption spectra of hot methane at temperatures up to 1200 K. Our observations are compared to the latest theoretical spectral predictions and recent brown dwarf spectra. The expectation that millions of weak absorption lines combine to form a continuum, not seen at room temperature, is confirmed. Our high-resolution transmittance spectra account for both the emission and absorption of methane at elevated temperatures. From these spectra, we obtain an empirical line list and continuum that is able to account for the absorption of methane in high temperature environments at both high and low resolution. Great advances have recently been made in the theoretical prediction of hot methane, and our experimental measurements highlight the progress made and the problems that still remain.

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# Announcements

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