

AstroChemical Newsletter #14

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Abstracts

An observational study of dust nucleation in Mira (omicron Ceti): II. Titanium oxides are negligible for nucleation at high temperatures

T. Kamiński, H.S.P. Müller, M.R. Schmidt, I. Cherchneff, K.T. Wong, S. Brünken, K.M. Menten, J.M. Winters, C.A. Gottlieb, N.A. Patel

The formation of silicate dust in oxygen-rich envelopes of evolved stars is thought to be initiated by formation of seed particles that can withstand the high temperatures close to the stellar photosphere and act as condensation cores farther away from the star. Candidate species considered as first condensates are TiO and TiO₂. We aim to identify and characterize the circumstellar gas-phase chemistry of titanium that leads to the formation of solid titanium compounds in the envelope of o Ceti, the prototypical Mira, and seek an observational verification of whether titanium oxides play a major role in the onset of dust formation in M-type AGB stars. We present high angular-resolution ALMA observations at submillimeter (submm) wavelengths supplemented by APEX and Herschel spectra of the rotational features of TiO and TiO₂. In addition, circumstellar features of TiO and TiI are identified in optical spectra which cover multiple pulsation cycles of o Ceti. The submm ALMA data reveal TiO and TiO₂ bearing gas within the extended atmosphere of Mira. While TiO is traceable up to a radius (FWHM/2) of 4.0 R_{star}, TiO₂ extends as far as 5.5 R_{star} and unlike TiO appears to be anisotropically distributed. Optical spectra display variable emission of TiI and TiO from inner parts of the extended atmosphere (<3 R_{star}). Chemical models which include shocks are in general agreement with the observations of gas-phase titanium-bearing molecules. It is unlikely that substantial amounts of titanium is locked up in solids because the abundance of the gaseous titanium species is very high. Formation of hot titanium-rich condensates is very improbable because we find no traces of their hot precursor species in the gas phase. It therefore appears unlikely that the formation of dust in Mira, and possibly other M-type AGB stars, is initiated by titanium oxides.

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Submillimeter H₂O and H₂O⁺ emission in lensed ultra- and hyper-luminous infrared galaxies at z~2-4

C. Yang, A. Omont, A. Beelen, E. González-Alfonso, R. Neri, Y. Gao, P. van der Werf, A. Weiss, R. Gavazzi, N. Falstad, A. J. Baker, R. S. Bussmann, A. Cooray, P. Cox, H. Dannerbauer, S. Dye, M. Guélin, R. Ivison, M. Krips, M. Lehnert, M.J. Michałowski, D.A. Riechers, M. Spaans, and E. Valiante

(abridged) We report rest-frame submillimeter H₂O emission line observations of 11

HyLIRGs/ULIRGs at $z \sim 2-4$ selected among the brightest lensed galaxies discovered in the Herschel-ATLAS. Using the IRAM NOEMA, we have detected 14 new H₂O emission lines. The apparent luminosities of the H₂O emission lines are $\mu\text{LH}_{2\text{O}} \sim 6-21 e8 L_{\odot}$, with velocity-integrated line fluxes ranging from 4-15 Jy km s⁻¹. We have also observed CO emission lines using EMIR on the IRAM 30m telescope in seven sources. The velocity widths for CO and H₂O lines are found to be similar. With almost comparable integrated flux densities to those of the high-J CO line, H₂O is found to be among the strongest molecular emitters in high- z Hy/ULIRGs. We also confirm our previously found correlation between luminosity of H₂O (LH₂O) and infrared (LIR) that $\text{LH}_{2\text{O}} \sim \text{L}_{1.1-1.2\text{IR}}$, with our new detections. This correlation could be explained by a dominant role of far-infrared (FIR) pumping in the H₂O excitation. Modelling reveals the FIR radiation fields have warm dust temperature $T_{\text{warm}} \sim 45-75$ K, H₂O column density per unit velocity interval $\text{NH}_{2\text{O}}/\Delta V \geq 0.3 e15 \text{ cm}^{-2} \text{ km}^{-1} \text{ s}$ and 100 μm continuum opacity $\tau_{100} > 1$ (optically thick), indicating that H₂O is likely to trace highly obscured warm dense gas. However, further observations of $J \geq 4$ H₂O lines are needed to better constrain the continuum optical depth and other physical conditions of the molecular gas and dust. We have also detected H₂O⁺ emission in three sources. A tight correlation between LH₂O and LH₂O⁺ has been found in galaxies from low to high redshift. The velocity-integrated flux density ratio between H₂O⁺ and H₂O suggests that cosmic rays generated by strong star formation are possibly driving the H₂O⁺ formation.

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On the chemical ladder of esters. Detection and formation of ethyl formate in the W51 e2 hot molecular core

V. M. Rivilla, M. T. Beltrán, J. Martín-Pintado, F. Fontani, P. Caselli, R. Cesaroni

The detection of organic molecules with increasing complexity and potential biological relevance is opening the possibility to understand the formation of the building blocks of life in the interstellar medium. One of the families of molecules with astrobiological interest are the esters, whose simplest member, methyl formate, is rather abundant in star-forming regions. The next step in the chemical complexity of esters is ethyl formate, C₂H₅OCHO. Only two detections of this species have been reported so far, which strongly limits our understanding of how complex molecules are formed in the interstellar medium. We have searched for ethyl formate towards the W51 e2 hot molecular core, one of the most chemically rich sources in the Galaxy and one of the most promising regions to study prebiotic chemistry, especially after the recent discovery of the P–O bond, key in the formation of DNA. We have analyzed a spectral line survey towards the W51 e2 hot molecular core, which covers 44 GHz in the 1, 2 and 3 mm bands, carried out with the IRAM 30m telescope. We report the detection of the trans and gauche conformers of ethyl formate. A Local Thermodynamic Equilibrium analysis indicates that the excitation temperature is 78 ± 10 K and that the two conformers have similar source-averaged column densities of $(2.0 \pm 0.3) \times 1e16 \text{ cm}^{-2}$ and an abundance of $\sim 1e-8$. We compare the observed molecular abundances of ethyl formate with different competing chemical models based on grain surface and gas-phase chemistry. We propose that grain-surface chemistry may have a dominant role in the formation of ethyl formate (and other complex organic molecules) in hot molecular cores, rather than reactions in the gas phase.

Robustness of N₂H⁺ as tracer of the CO snowline

Merel L.R. van 't Hoff, Catherine Walsh, Mihkel Kama, Stefano Facchini, Ewine F. van Dishoeck

Snowlines in protoplanetary disks play an important role in planet formation and composition. Since the CO snowline is difficult to observe directly with CO emission, its location has been inferred in several disks from spatially resolved ALMA observations of DCO⁺ and N₂H⁺. N₂H⁺ is considered to be a good tracer of the CO snowline based on astrochemical considerations predicting an anti-correlation between N₂H⁺ and gas-phase CO. In this work, the robustness of N₂H⁺ as a tracer of the CO snowline is investigated. A simple chemical network is used in combination with the radiative transfer code LIME to model the N₂H⁺ distribution and corresponding emission in the disk around TW Hya. The assumed CO and N₂ abundances, corresponding binding energies, cosmic ray ionization rate, and degree of large-grain settling are varied to determine the effects on the N₂H⁺ emission and its relation to the CO snowline. For the adopted physical structure of the TW Hya disk and molecular binding energies for pure ices, the balance between freeze-out and thermal desorption predicts a CO snowline at 19 AU, corresponding to a CO midplane freeze-out temperature of 20 K. A model with a total, i.e. gas plus ice, CO abundance of 3e-6 with respect to H₂ fits the position of the emission peak observed by Qi et al. 2013 for the TW Hya disk. However, the relationship between N₂H⁺ and the CO snowline is more complicated than generally assumed: for the investigated parameters, the N₂H⁺ column density peaks at least 5 AU outside the CO snowline. Moreover, the N₂H⁺ emission can peak much further out, as far as ~50 AU beyond the snowline. Hence, chemical modeling, as done here, is necessary to derive a CO snowline location from N₂H⁺ observations.

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Missing Fe: hydrogenated iron nanoparticles

G. Bilalbegovic, A. Maksimovic, V. Mohacek-Grosev

Although it was found that the FeH lines exist in the spectra of some stars, none of the spectral features in the ISM have been assigned to this molecule. We suggest that iron atoms interact with hydrogen and produce Fe-H nanoparticles which sometimes contain many H atoms. We calculate infrared spectra of hydrogenated iron nanoparticles using density functional theory methods and find broad, overlapping bands. Desorption of H₂ could induce spinning of these small Fe-H dust grains. Some of hydrogenated iron nanoparticles possess magnetic and electric moments and should interact with electromagnetic fields in the ISM. Fe_nH_m nanoparticles could contribute to the polarization of the ISM and the anomalous microwave emission. We discuss the conditions required to form FeH and Fe_nH_m in the ISM.

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Trans-cis molecular photoswitching in interstellar Space

S. Cuadrado, J. R. Goicoechea, O. Roncero, A. Aguado, B. Tercero, and J. Cernicharo

As many organic molecules, formic acid (HCOOH) has two conformers (trans and cis). The energy barrier to internal conversion from trans to cis is much higher than the thermal energy available in molecular clouds. Thus, only the most stable conformer (trans) is expected to exist in detectable amounts. We report the first interstellar detection of cis-HCOOH. Its presence in ultraviolet (UV) irradiated gas exclusively (the Orion Bar photodissociation region), with a low trans-to-cis abundance ratio of 2.8 ± 1.0 , supports a photoswitching mechanism: a given conformer absorbs a stellar photon that radiatively excites the molecule to electronic states above the interconversion barrier. Subsequent fluorescent decay leaves the molecule in a different conformer form. This mechanism, which we specifically study with ab initio quantum calculations, was not considered in Space before but likely induces structural changes of a variety of interstellar molecules submitted to UV radiation.

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Chemistry in a forming protoplanetary disk: main accretion phase

Haruaki Yoneda, Yusuke Tsukamoto, Kenji Furuya, Yuri Aikawa

We investigate the chemistry in a radiation-hydrodynamics model of star-forming core which evolves from a cold (~ 10 K) prestellar core to the main accretion phase in $\sim 10^5$ yr. A rotationally-supported gravitationally unstable disk is formed around a protostar. We extract the temporal variation of physical parameters in ~ 1500 SPH particles which end up in the disk, and perform post-processing calculations of the gas-grain chemistry adopting a three-phase model. Inside the disk, the SPH particles migrate both inward and outward. Since a significant fraction of volatiles such as CO can be trapped in the water-dominant ice in the three-phase model, the ice mantle composition depends not only on the current position in the disk but also on whether the dust grain has ever experienced higher temperatures than the water sublimation temperature. Stable molecules such as H₂O, CH₄, NH₃ and CH₃OH are already abundant at the onset of gravitational collapse and simply sublimated as the fluid parcels migrate inside the water snow line. On the other hand, various molecules such as carbon chains and complex organic molecules (COMs) are formed in the disk. COMs abundance sensitively depends on the outcomes of photodissociation and diffusion rates of photofragments in bulk ice mantle. As for S-bearing species, H₂S ice is abundant in the collapse phase. In the warm regions in the disk, H₂S is sublimated to be destroyed, while SO, H₂CS, OCS and SO₂ become abundant.

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The Pure Rotational Spectrum of the ScO (X 2Σ⁺) Radical

D. T. Halfen, J. Min, and L. M. Ziurys

The rotational spectrum of ScO (X 2Σ⁺) has been measured in the gas phase in the frequency range 30 – 493 GHz using a combination of Fourier transform microwave/millimeter-wave (FTM/mmW) and submillimeter direct absorption methods. This work is the first pure rotational study of this radical. Both the ground vibrational

and $v = 1$ states were observed. ScO was created from the reaction of metal vapor, produced either by a laser ablation source or a Broida-type oven, and N₂O, in the former case heavily diluted in argon. Extensive hyperfine structure was observed in the FTM/mmW data, although the spin-rotation splitting was found to be small (~3 MHz). In the mm-wave spectra, however, the fine and hyperfine structure was blended together, resulting in broad, single lines for a given transition $N + 1 \leftarrow N$. The data were analyzed in a combined fit using the very accurate hyperfine measurements of Childs and Steimle (1988), employing a Hund's case b Hamiltonian, and an improved set of rotational and centrifugal distortion constants were determined. These measurements improve the accuracy of predicted frequencies for astronomical searches by 14 - 18 MHz, or 16 - 20 km/s, in the 1 mm region - a difference of half to a full linewidth for certain interstellar sources. This work also demonstrates the capabilities of the FTM/mmW spectrometer at 61 GHz.

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The Charge State of Polycyclic Aromatic Hydrocarbons Across Reflection Nebulae: PAH Charge Balance and Calibration

C. Boersma, J. Bregman, L.J. Allamandola

Low-resolution Spitzer spectral map data (>1700 spectra) of ten reflection nebulae (RNe) fields are analyzed using the data and tools available through the NASA Ames PAH IR Spectroscopic Database. The PAH emission is broken down into PAH charge state using a database fitting approach. Here, the physics of the PAH emission process is taken into account and uses target appropriate parameters, e.g., a stellar radiation model for the exciting star. The breakdown results are combined with results derived using the traditional PAH band strength approach, which interprets particular PAH band strength ratios as proxies for the PAH charge state, e.g., the 6.2/11.2 μm PAH band strength ratio. These are successfully calibrated against their database equivalent; the PAH ionized fraction (f_i). The PAH ionized fraction is converted into the PAH ionization parameter, which relates the PAH ionized fraction to the strength of the radiation field, gas temperature and electron density. The behavior of the 12.7 μm PAH band is evaluated as a tracer for PAH ionization and erosion. The plot of the 8.6 versus 11.2 μm PAH band strength for the northwest photo-dominated region (PDR) in NGC 7023 is shown to be a robust diagnostic template for the PAH ionized fraction. Remarkably, most of the other RNe fall within the limits set by NGC 7023. Finally, PAH spectroscopic templates are constructed and verified as principal components. Template spectra derived from NGC 7023 and NGC 2023 compare extremely well with each other, with those derived for NGC 7023 successfully reproducing the PAH emission observed from NGC 2023.

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A search for AlO in the winds of oxygen-rich AGB stars

E. De Beck, L. Decin, S. Ramstedt, H. Olofsson, K. M. Menten, N. A. Patel, W. H. T. Vlemmings

Aluminium monoxide, AlO, is likely efficiently depleted from the gas around oxygen-rich evolved stars to form alumina clusters and dust seeds. Its presence in the extended

atmospheres of evolved stars has been derived from optical spectroscopy. More recently, AIO gas was also detected at long wavelengths around the supergiant VY CMa and the oxygen-rich asymptotic giant branch (AGB) star o Cet (Mira A). In search of AIO, we mined data obtained with APEX, the IRAM 30m telescope, Herschel/HIFI, SMA, and ALMA, which were primarily aimed at studying other molecular species. We report here on observations of AIO towards a sample of eight oxygen-rich AGB stars in different rotational transitions, up to seven for some stars. We present definite detections of one rotational transition of AIO for o Cet and R Aqr, and tentative detections of one transition for R Dor and o Cet, and two for IK Tau and W Hya. The presented spectra of WX Psc, R Cas, and TX Cam show no signature of AIO. For o Cet, R Aqr, and IK Tau, we find that the AIO(N=9-8) emission likely traces the inner parts of the wind, out to only a few tens of AU, where the gas has not yet reached its terminal velocity. The conclusive detections of AIO emission in the case of o Cet and R Aqr confirm the presence of AIO gas in outflows of AGB stars. The tentative detections further support this. Since most of the observations presented in this study were obtained with stronger emission from other species than AIO in mind, observations with higher sensitivity in combination with high angular resolution will improve our understanding of the presence and behaviour of AIO. From the current data sets we cannot firmly conclude whether there is a direct correlation between the wind properties and the detection rate of AIO emission. We hope that this study can serve as a stimulus to perform sample studies in search of AIO in oxygen-rich outflows.

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The ALMA-PILS survey: First detections of ethylene oxide, acetone and propanal toward the low-mass protostar IRAS 16293-2422

J. M. Lykke, A. Coutens, J. K. Jørgensen, M. H. D. van der Wiel, R. T. Garrod, H. S. P. Müller, P. Bjerkeili, T. L. Bourke, H. Calcutt, M. N. Drozdovskaya, C. Favre, E. C. Fayolle, S. K. Jacobsen, K. I. Öberg, M. V. Persson, E. F. van Dishoeck, and S. F. Wampfler

Context. One of the open questions in astrochemistry is how complex organic and prebiotic molecules are formed. The unsurpassed sensitivity of the Atacama Large Millimeter/submillimeter Array (ALMA) takes the quest for discovering molecules in the warm and dense gas surrounding young stars to the next level. **Aims.** Our aim is to start the process of compiling an inventory of oxygen-bearing complex organic molecules toward the solar-type Class 0 protostellar binary IRAS 16293-2422 from an unbiased spectral survey with ALMA, Protostellar Interferometric Line Survey (PILS). Here we focus on the new detections of ethylene oxide (c-C₂H₄O), acetone (CH₃COCH₃), and propanal (C₂H₅CHO). **Methods.** With ALMA, we surveyed the spectral range from 329 to 363 GHz at 0.5" (60 AU diameter) resolution. Using a simple model for the molecular emission in local thermodynamical equilibrium, the excitation temperatures and column densities of each species were constrained. **Results.** We successfully detect propanal (44 lines), ethylene oxide (20 lines) and acetone (186 lines) toward one component of the protostellar binary, IRAS16293B. The high resolution maps demonstrate that the emission for all investigated species originates from the compact central region close to the protostar. This, along with a derived common excitation temperature of $T_{\text{ex}} \sim 125$ K, is consistent with a coexistence of these molecules in the same gas. **Conclusions.** The observations mark the first detections of acetone, propanal and ethylene oxide toward a low-mass protostar. The relative

abundance ratios of the two sets of isomers, a $\text{CH}_3\text{COCH}_3/\text{C}_2\text{H}_5\text{CHO}$ ratio of 8 and a $\text{CH}_3\text{CHO}/\text{c-C}_2\text{H}_4\text{O}$ ratio of 12, are comparable to previous observations toward high-mass protostars. The majority of observed abundance ratios from these results as well as those measured toward high-mass protostars are up to an order of magnitude above the predictions from chemical models. This may reflect either missing reactions or uncertain rates in the chemical networks. The physical conditions, such as temperatures or densities, used in the models, may not be applicable to solar-type protostars either.

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On the origin of C₄H and CH₃OH in protostellar envelopes

Johan E. Lindberg, Steven B. Charnley, Martin A. Cordiner

The formation pathways of different types of organic molecules in protostellar envelopes and other regions of star formation are subjects of intense current interest. We here present observations of C₄H and CH₃OH, tracing two distinct groups of interstellar organic molecules, toward 16 protostars in the Ophiuchus and Corona Australis molecular clouds. Together with observations in the literature, we present C₄H and CH₃OH data from single-dish observations of 40 embedded protostars. We find no correlation between the C₄H and CH₃OH column densities in this large sample. Based on this lack of correlation, a difference in line profiles between C₄H and CH₃OH, and previous interferometric observations of similar sources, we propose that the emission from these two molecules is spatially separated, with the CH₃OH tracing gas that has been transiently heated to high (~70-100 K) temperatures, and the C₄H tracing the cooler large-scale envelope where CH₄ molecules have been liberated from ices. These results provide insight in the differentiation between hot corino and warm carbon-chain chemistry in embedded protostars.

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Externally heated protostellar cores in the Ophiuchus star-forming region

Johan E. Lindberg, Steven B. Charnley, Jes K. Jørgensen, Martin A. Cordiner, Per Bjerkeli

We present APEX 218 GHz observations of molecular emission in a complete sample of embedded protostars in the Ophiuchus star-forming region. To study the physical properties of the cores, we calculate H₂CO and c-C₃H₂ rotational temperatures, both of which are good tracers of the kinetic temperature of the molecular gas. We find that the H₂CO temperatures range between 16 K and 124 K, with the highest H₂CO temperatures toward the hot corino source IRAS 16293-2422 (69-124 K) and the sources in the rho Oph A cloud (23-49 K) located close to the luminous Herbig Be star S 1, which externally irradiates the rho Oph A cores. On the other hand, the c-C₃H₂ rotational temperature is consistently low (7-17 K) in all sources. Our results indicate that the c-C₃H₂ emission is primarily tracing more shielded parts of the envelope whereas the H₂CO emission (at the angular scale of the APEX beam; 3600 au in Ophiuchus) mainly traces the outer irradiated envelopes, apart from in IRAS 16293-2422, where the hot corino emission dominates. In some sources, a secondary velocity component is also seen, possibly tracing the molecular outflow.

Announcements

ALMA Postdoctoral Fellow

ALMA provides the world-wide astronomical community with transformational capabilities to study the origin of galaxies, stars, and planets. ALMA started its first Early Science observations in late 2011 and has led to the publication of more than 500 papers to date, many of them in influential journals. At the Cycle 4 Call for Proposals, ALMA received more submissions than any other telescope in history. The JAO is offering postdoctoral fellowship positions to join the ALMA science operations group in Santiago, Chile. ALMA Postdoctoral Fellows will be appointed for a period of three years and will spend 50% of their time dedicated to their personal scientific research. The remaining time will be spent in support of ALMA operations, including observing at the ALMA Operations Support Facility (OSF) near San Pedro de Atacama for hands-on interaction with the telescope. The goal of these fellowships is to offer early career scientists the opportunity to enhance their research programs through involvement in science activities and interactions with experienced staff at the world's foremost observatory for sub-mm astronomy. At present, there are over 40 scientists with a wide range of research interests working at ALMA in Santiago. The JAO also hosts regular visits from scientists from the ALMA Regional Centers (ARCs) in Europe, North America and East Asia. The ALMA office is located adjacent to ESO's Santiago office, and the offices of AUI/NRAO and NAOJ are located nearby. Fellows have the opportunity to collaborate with the rapidly growing Chilean astronomical community as well as with astronomers from other international observatories located in Chile. The ALMA Postdoctoral Fellows will be provided with resources for science trips and will be encouraged to visit one or more of the ARCs for science collaborations. The JAO runs a visitor program through which science collaborators can be invited to work in Santiago. ALMA Postdoctoral Fellows are expected to lead a vigorous research program in any area related to the use of ALMA. Fellows will also actively participate in and contribute to the science activities of the JAO. The ALMA Postdoctoral fellows are expected to support ALMA science operations and will work in the JAO Department of Science Operations (DSO). They will perform their duties as part of the large team of international scientists working at the JAO and in the ARCs. Successful candidates will act as Astronomers on Duty at the OSF. A fraction of the technical duties can be spent on data processing, participation in the ALMA review process as technical experts, software testing, and development and testing of new capabilities of the array, among other technical activities necessary for the successful operations of the facility. Candidates should provide three reference letters. Please send letters of recommendation to resumes@nrao.edu as a PDF file with ALMA3821 in the subject line. Applicants submitting their application to NRAO are invited to apply online at <https://careers.nrao.edu> refer to job number 3821. At the bottom of the job requisition please click "Apply". Additional details at <https://careers.nrao.edu> Deadline for receipt of applications to be considered is December 30, 2016. 1

PCMI contribution to building an European network of researchers interested by ISM studies

Information given by Jean-Hugues Fillion, Jerome Pety, Karine Demyk on behalf of the the PCMI community. PCMI is a French infrastructure emanating from CNRS to animate inter-disciplinary studies around the Inter-Stellar Medium. However, cutting-edge

astronomical observatories are international, almost worldwide infrastructures. In this context, the PCMI community thought how it could contribute to build a European network of researchers interested into ISM studies. The resulting document is available here : http://pcmi.cnrs.fr/IMG/pdf/pcmi_astrolaboecu-2016-11-19_.pdf

Postdoctoral position in astrochemistry

Applications are invited for a postdoctoral position in astrochemistry working with Valentine Wakelam at the Laboratoire d'astrophysique de Bordeaux, Bordeaux University, France. The successful applicant will be working on the chemical modeling of star forming regions and protoplanetary disks. The applicant should have a PhD in astronomy/astrophysics or a closely related field. Candidates with experience in chemical modeling are encouraged to apply. The position is available for a period of two years and is funded by the ERC Starting Grant 3DICE. The start date will be March/April 2017. Salary (including benefits) will depend on skills and experience. For further information on our project please visit our website: <http://www.obs.u-bordeaux1.fr/amor/VWakelam/3DICE> To apply, please send a cover letter with a curriculum vitae, publication list and brief statements of research accomplishments and interests (not exceeding 2 pages each) via email at valentine.wakelam@u-bordeaux.fr. Applicants should arrange for two letters of reference to be sent to the same email address. Closing date for receipt of applications is January 15th, 2017. Late applications may be considered until the position is filled.