AstroChemical Newsletter #47

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You can access the full abstracts by clicking the paper titles. Submit your abstracts before the 25th of each month for inclusion in the following newsletter.

Abstracts

Developing a self-consistent AGB wind model: II. Non-classical, non-equilibrium polymer nucleation in a chemical mixture

J. Boulangier, D. Gobrecht, L. Decin, A. de Koter, J. Yates

Unravelling the composition and characteristics of gas and dust lost by asymptotic giant branch (AGB) stars is important as these stars play a vital role in the chemical life cycle of galaxies. The general hypothesis of their mass loss mechanism is a combination of stellar pulsations and radiative pressure on dust grains. However, current models simplify dust formation, which starts as a microscopic phase transition called nucleation. Various nucleation theories exist, yet all assume chemical equilibrium, growth restricted by monomers, and commonly use macroscopic properties for a microscopic process. Such simplifications for initial dust formation can have large repercussions on the type, amount, and formation time of dust. By abandoning equilibrium assumptions, discarding growth restrictions, and using quantum mechanical properties, we have constructed and investigated an improved nucleation theory in AGB wind conditions for four dust candidates, TiO2, MgO, SiO, Al2O3. This paper reports the viability of these candidates as first dust precursors and reveals implications of simplified nucleation theories. Monomer restricted growth underpredicts large clusters at low temperatures and overpredicts formation times. Assuming the candidates are present, Al2O3 is the favoured precursor due to its rapid growth at the highest considered temperatures. However, when considering an initially atomic chemical mixture, only TiO2-clusters form. Still, we believe Al2O3 to be the prime candidate due to substantial physical evidence in presolar grains, observations of dust around AGB stars at high temperatures, and its ability to form at high temperatures and expect the missing link to be insufficient quantitative data of Al-reactions.

MNRAS, Volume 489, Issue 4, November 2019, Pages 4890–4911
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Investigation of 13C Isotopic Fractionation of CCH in Two Starless Cores: L1521B and L134N

Kotomi Taniguchi, Eric Herbst, Hiroyuki Ozeki, and Masao Saito

We have carried out observations of CCH and its two 13C isotopologues, 13CCH and C13CH, in the 84 – 88 GHz band toward two starless cores, L1521B and L134N (L183), using the Nobeyama 45 m radio telescope. We have detected C13CH with a signal-to-noise (S/N) ratio of 4, whereas no line of 13CCH was detected in either the dark clouds. The column densities of the normal species were derived to be (1.66±0.18)×10^(14)

cm−2 and (7.3±0.9)×10^(13) cm−2 (1σ) in L1521B and L134N, respectively. The column density ratios of N(C13CH)/N(13CCH) were calculated to be > 1.1 and > 1.4 in L1521B and L134N, respectively. The characteristic that 13CCH is less abundant than C13CH is likely common for dark clouds. Moreover, we find that the 12C/13C ratios of CCH are much higher than those of HC3N in L1521B by more than a factor of 2, as well as in Taurus Molecular Cloud-1 (TMC-1). In L134N, the differences in the 12C/13C ratios between CCH and HC3N seem to be smaller than those in L1521B and TMC-1. We discuss the origins of the 13C isotopic fractionation of CCH and investigate possible routes that cause the significantly high 12C/13C ratio of CCH especially in young dark clouds, with the help of chemical simulations. The high 12C/13C ratios of CCH seem to be caused by reactions between hydrocarbons (e.g., CCH, C2H2, l,c-C3H) and C+.

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Origin of the PN molecule in star-forming regions: the enlarged sample

F. Fontani, V.M. Rivilla, F.F.S. van der Tak, C. Mininni, M.T. Beltràn, P. Caselli

Phosphorus nitride (PN) is the P-bearing species with the highest number of detections in star-forming regions. We detected PN lines with the IRAM-30m and APEX telescopes in 13 new massive star-forming regions which, together with 11 similar targets previously detected in PN, allowed us to analyse the largest sample of star-forming regions to date (24 sources in total). Our analysis indicates that the PN lines are sub-thermally excited, but well described by a single excitation temperature. We have compared line profiles and fractional abundances of PN and SiO, a typical shock tracer, and found that almost all objects detected in PN have high-velocity SiO wings. Moreover, the SiO and PN abundances with respect to H2 are correlated over several orders of magnitude, and uncorrelated with gas temperature. This clearly shows that the production of PN is strongly linked to the presence of shocked gas, and rules out alternative scenarios based on thermal evaporation from iced grain mantles.

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Rotational spectroscopy of methyl mercaptan CH3(32)SH at millimeter and submillimeter wavelengths

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We present a new global study of the millimeter (mm) wave, submillimeter (sub-mm) wave, and terahertz (THz) spectra of the lowest three torsional states of methyl mercaptan (CH3SH). New measurements have been carried out between 50 and 510 GHz using the Kharkiv mm wave and the Cologne sub-mm wave spectrometers whereas THz spectra records were used from our previous study. The new data, involving torsion–rotation transitions with J up to 61 and Ka up to 18, were combined with previously published measurements and fit using the rho-axis-method torsion–rotation Hamiltonian. The final fit used 124 parameters to give an overall weighted root-mean-square deviation of 0.72 for the dataset consisting of 6965 microwave (MW) and 16 345 far-infrared line frequencies sampling transitions within and between the ground, first, and second excited torsional states. This investigation presents a two-

fold expansion in the J quantum numbers and a significant improvement in the fit quality, especially for the MW part of the data, thus allowing us to provide more reliable predictions to support astronomical observations.

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Chronology of Episodic Accretion in Protostars - an ALMA survey of the CO and H2O snowlines

Tien-Hao Hsieh, Nadia M. Murillo, Arnaud Belloche, Naomi Hirano, Catherine Walsh, Ewine F. van Dishoeck, Jes K., Jørgensen, Shih-Ping Lai

Episodic accretion has been used to explain the wide range of protostellar luminosities, but its origin and influence on the star forming process are not yet fully understood. We present an ALMA survey of N2H+ (1−0) and HCO+ (3−2) toward 39 Class 0 and Class I sources in the Perseus molecular cloud. N2H+ and HCO+ are destroyed via gas-phase reactions with CO and H2O, respectively, thus tracing the CO and H2O snowline locations. A snowline location at a much larger radius than that expected from the current luminosity suggests that an accretion burst has occurred in the past which has shifted the snowline outward. We identified 18/18 Class 0 and 9/10 Class I post-burst sources from N2H+, and 7/17 Class 0 and 1/8 Class I post-burst sources from HCO+. The accretion luminosities during the past bursts are found to be ∼10 − 100 Lsun. This result can be interpreted as either evolution of burst frequency or disk evolution. In the former case, assuming that refreeze-out timescales are 1000 yr for H2O and 10,000 yr for CO, we found that the intervals between bursts increases from 2400 yr in the Class 0 to 8000 yr in the Class I stage. This decrease in the burst frequency may reflect that fragmentation is more likely to occur at an earlier evolutionary stage when the young stellar object is more prone to instability.

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Simulations of ice chemistry in cometary nuclei

Robin T. Garrod

The first computational model of solid-phase chemistry in cometary nuclear ices is presented. An astrochemical kinetics model, MAGICKAL, is adapted to trace the chemical evolution in multiple layers of cometary ice, over a representative period of 5 Gyr. Physical conditions are chosen appropriate for ``cold storage'' of the cometary nucleus in the outer Solar System, prior to any active phase. The chemistry is simulated at a selection of static temperatures in the range 5 - 60 K, while the ice is exposed to the interstellar radiation field, inducing a photochemistry in the outer ice layers that produces significant formation of complex organic molecules. A treatment for the chemistry resulting from cosmic-ray bombardment of the ices is also introduced into the model, along with a new formulation for low-temperature photochemistry. Production of simple and complex molecules to depth on the order of 10m or more is achieved, with local fractional abundances comparable to observed values in many cases. The production of substantial amounts of O2 (and H2O2) is found, suggesting that long-term processing by high-energy cosmic rays of cometary ices in situ, over a period on the order of 1 Gyr, may be sufficient to explain the large observed abundances of O2, if the overall loss of material from the comet is limited to a depth on the order of 10 m. Entry into the inner solar system could produce a further

enhancement in the molecular content of the nuclear ices that may be quantifiable using this modeling approach.

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Experimental Studies of Gas-Phase Reactivity in Relation to Complex Organic Molecules in Star-Forming Regions

I. R. Cooke and I. R. Sims

The field of astrochemistry concerns the formation and abundance of molecules in the interstellar medium, star-forming regions, exoplanets, and solar system bodies. These astrophysical objects contain the chemical material from which new planets and solar systems are formed. Around 200 molecules have thus far been observed in the interstellar medium; almost half containing six or more atoms and considered “complex” by astronomical standards. All of these complex molecules consist of at least one carbon atom and thus the term complex organic molecules (COMs) has been coined by the astrochemical community. In order to understand the formation and destruction of these COMs under the extreme conditions of star-forming regions, three kinds of activity are involved: (1) the astronomical identification of complex molecules present in the interstellar medium; (2) the construction of astrochemical models that attempt to explain the formation routes of the observed molecules; and (3) laboratory measurements and theoretical calculations of critical kinetic parameters that are included in the models. In the following review, we present recent laboratory efforts to produce quantitative kinetic data for gas-phase reactions at low temperatures. We discuss the use of the CRESU technique, a French acronym standing for Cinétique de Réaction en Ecoulement Supersonique Uniforme, which means reaction kinetics in uniform supersonic flow, to measure reactions of astrochemical importance. In particular, we highlight recent and future advances in the measurement of product-specific reaction kinetics at low temperatures.

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The full infrared spectrum of molecular hydrogen

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Context. The high spectral resolution R~45000 provided by IGRINS (Immersion Grating INfrared Spectrometer) at MacDonald Observatory and R~100000 achieved by CRIRES (CRyogenic high-resolution InfraRed Echelle Spectrograph) at VLT (Very Large Telescope) challenges the present knowledge of infrared spectra. Aims. We aim to predict the full infrared spectrum of molecular hydrogen at a comparable accuracy. Methods.We take advantage of the recent theoretical ab initio studies on molecular hydrogen to compute both the electric quadrupole and magnetic dipole transitions taking place within the ground electronic molecular state of hydrogen. Results. We computed the full infrared spectrum of molecular hydrogen at an unprecedented accuracy and derive for the first time the emission probabilities including both electric quadrupole (DeltaJ = 0, ±2) and magnetic dipole transitions (DeltaJ = 0) as well as the total radiative lifetime of each rovibrational state. Inclusion of magnetic dipole transitions increases the emission probabilities by factors of a few for highly excited rotational levels, which occur in the 3–20 micron range.

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Gas-Phase Vibrational Spectroscopy of the Hydrocarbon Cations l-C3H+, HC3H+, and c-C3H2+: Structures, Isomers, and the Influence of Ne-Tagging

S. Brünken, F. Lipparini, A. Stoffels, P. Jusko, B. Redlich, J. Gauss, S. Schlemmer

We report the first gas-phase vibrational spectra of the hydrocarbon ions C3H+ and C3H2+. The ions were produced by electron impact ionization of allene. Vibrational spectra of the mass-selected ions tagged with Ne were recorded using infrared predissociation spectroscopy in a cryogenic ion trap instrument using the intense and widely tunable radiation of a free electron laser. Comparison of high-level quantum chemical calculations and resonant depletion measurements revealed that the C3H+ ion is exclusively formed in its most stable linear isomeric form, whereas two isomers were observed for C3H2+. Bands of the energetically favored cyclic c-C3H2+ are in excellent agreement with calculated anharmonic frequencies, whereas for the linear open-shell HCCCH+ (2Πg) a detailed theoretical description of the spectrum remains challenging because of Renner–Teller and spin–orbit interactions. Good agreement between theory and experiment, however, is observed for the frequencies of the stretching modes for which an anharmonic treatment was possible. In the case of linear l-C3H+, small but non-negligible effects of the attached Ne on the ion fundamental band positions and the overall spectrum were found.

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Interstellar formamide (NH2CHO): A key prebiotic precursor

A. López-Sepulcre, N. Balucani, C. Ceccarelli, C. Codella, F. Dulieu, P. Theulé

Formamide (NH2CHO) has been identified as a potential precursor of a wide variety of organic compounds essential to life, and many biochemical studies propose it likely played a crucial role in the context of the origin of life on our planet. The detection of formamide in comets, which are believed to have --at least partially-- inherited their current chemical composition during the birth of the Solar System, raises the question whether a non-negligible amount of formamide may have been exogenously delivered onto a very young Earth about four billion years ago. A crucial part of the effort to answer this question involves searching for formamide in regions where stars and planets are forming today in our Galaxy, as this can shed light on its formation, survival, and chemical re-processing along the different evolutionary phases leading to a star and planetary system like our own. The present review primarily addresses the chemistry of formamide in the interstellar medium, from the point of view of (i) astronomical observations, (ii) experiments, and (iii) theoretical calculations. While focusing on just one molecule, this review also more generally reflects the importance of joining efforts across multiple scientific disciplines in order to make progress in the highly interdisciplinary science of astrochemistry.

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Photochemistry and desorption induced by X-rays in water rich astrophysical ice analogs: implications for the moon Enceladus and other frozen space environments

S. Pilling, W. R. M. Rocha, F. M. Freitas, P. A. da Silva

Soft X-rays are an important agent for chemical processing in the Solar System and in the interstellar medium. The photolysis and photodesorption processes of H2O-rich ices triggered by soft X-rays was, experimentally, addressed in this paper. The experiments were performed at the Brazilian synchrotron facility LNLS/CNPEN employing broadband radiation (from 6 to 2000 eV; mainly soft X-rays and a small fraction of VUV) in solid samples at temperatures of 20 and 80 K. The icy samples were monitored by infrared spectroscopy. We determined the effective destruction cross section (in the order 10^18 cm^2) as well as the formation cross section for the new species produced after the irradiation. Among them, we list OCN-, CO, CO3, CH3OH, H2O2, HCOO-, NH4+, HCONH2 and CH3HCO, mostly formed in the experiment at 80 K. The chemical equilibrium stage was characterized and molecular abundances were quantified. In addition, we discuss a methodology to estimate the amount of unknown species in the ice produced by photolysis. The samples reach chemical equilibrium at fluences around 2–3 10^18 cm^2. Timescales for reaching chemical equilibrium in space environments illuminated by X-rays were given, as well as the desorption yields induced by X-rays. The astrophysical implication on the surface chemistry and desorption processes at the moon Enceladus are provided.

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Radiative association of atomic and ionic carbon

James F. Babb, R. T. Smyth, and B. M. McLaughlin

We present calculated cross sections and rate coefficients for the formation of the dicarbon cation (C2+) by the radiative association process in collisions of a C(3P) atom and a C(+2Po) ion. Molecular structure calculations for a number of low-lying doublet and quartet states of C2+ are used to obtain the potential energy surfaces and transition dipole moments coupling the states of interest, substantially increasing the available molecular data for C2+. Using a quantum-mechanical method, we explore a number of allowed transitions and determine those contributing to the radiative association process. The calculations extend the available data for this process down to the temperature of 100 K, where the rate coefficient is found to be about 2 x 1e-18 cm3/s. We provide analytical fits suitable for incorporation into astrochemical reaction databases.

ApJ accepted
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Experimental and theoretical investigation on the OH + CH3C(O)CH3 reaction at interstellar temperatures (T=11.7-64.4 K)

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R. Mereau, A. Canosa, B. Ballesteros, J. Albaladejo, and E. Jiménez.

The rate coefficient, k(T), for the gas-phase reaction between OH radicals and acetone CH3C(O)CH3, has been measured using the pulsed CRESU (French acronym for Reaction Kinetics in a Uniform Supersonic Flow) technique (T = 11.7−64.4 K). The temperature dependence of k(T =10−300 K) has also been computed using a RRKM-Master equation analysis after partial revision of the potential energy surface. In agreement with previous studies we found that the reaction proceeds via initial formation of two prereactive complexes both leading to H2O + CH3C(O)CH2 by H-abstraction tunneling. The experimental k(T) was found to increase as temperature was lowered. The measured values have been found to be several orders of magnitude higher than k(300 K). This trend is reproduced by calculations, with an especially good agreement with experiments below 25 K. The effect of total gas density on k(T) has been explored. Experimentally, no pressure dependence of k(20 K) and k(64 K) was observed, while k(50 K) at the largest gas density 4.47 × 1e17 cm−3 is twice higher than the average values found at lower densities. The computed k(T) is also reported for 1e3 cm−3 of He (representative of the interstellar medium). The predicted rate coefficients at 10 K surround the experimental value which appears to be very close to that of the low pressure regime prevailing in the interstellar medium. For gas-phase model chemistry of interstellar molecular clouds, we suggest using the calculated value of 1.8 × 1e−10 cm3 molecule−1 s−1 at 10 K, and the reaction products are water and CH3C(O)CH2 radicals

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What Can Infrared Spectra Tell Us about the Crystallinity of Nanosized Interstellar Silicate Dust Grains?

L. Zamirri, A. Macià Escatllar, J. Mariñoso Guiu, P. Ugliengo, S. T. Bromley

Infrared (IR) spectroscopy is the main technique used to identify and characterize silicate dust grains in astronomical environments. From IR spectra, the fraction of crystalline dust particles can be estimated and used to help understand the processing of dust occurring in different astronomical environments such as the interstellar medium (ISM) and circumstellar shells. Narrow spectral lines are assigned to crystalline grains, while broad signals are usually assumed to originate from amorphous material. Herein, we accurately calculate the IR spectra and energetic stabilities of several amorphous and crystalline silicate nanograins with an astronomically common Mg-rich olivinic (Mg2SiO4) stoichiometry and with sizes ranging from hundreds to thousands of atoms. First, unlike at larger length scales, crystalline forsterite-like grains at the nanoscale are found to be energetically metastable with respect to amorphous grains. However, from our careful analysis, we further show that the IR spectra of such nanosilicate grains cannot be unambiguously used to identify their structural nature. In particular, our work indicates that amorphous and crystalline silicate nanograins both exhibit broad IR spectra typical of noncrystalline grains, raising potential issues for estimates of the fraction of crystalline silicate dust in the ISM.

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Dust-gas chemistry in AGB outflows: Chemical modelling of

dust-gas chemistry within AGB outflows I. Effect on the gas-phase chemistry

M. Van de Sande, C. Walsh, T. P. Mangan, L. Decin

Chemical modelling of AGB outflows is typically focused on either non-thermodynamic equilibrium chemistry in the inner region or photon-driven chemistry in the outer region. We include, for the first time, a comprehensive dust-gas chemistry in our AGB outflow chemical kinetics model, including both dust-gas interactions and grain-surface chemistry. The dust is assumed to have formed in the inner region, and follows an interstellar-like dust-size distribution. Using radiative transfer modelling, we obtain dust temperature profiles for different dust types in an O-rich and a C-rich outflow. We calculate a grid of models, sampling different outflow densities, drift velocities between the dust and gas, and dust types. Dust-gas chemistry can significantly affect the gas-phase composition, depleting parent and daughter species and increasing the abundance of certain daughter species via grain-surface formation followed by desorption/sputtering. Its influence depends on four factors: outflow density, dust temperature, initial composition, and drift velocity. The largest effects are for higher density outflows with cold dust and O-rich parent species, as these species generally have a larger binding energy. At drift velocities larger than ~10 km s-1, ice mantles undergo sputtering; however, they are not fully destroyed. Models with dust-gas chemistry can better reproduce the observed depletion of species in O-rich outflows. When including colder dust in the C-rich outflows and adjusting the binding energy of CS, the depletion in C-rich outflows is also better reproduced. To best interpret high-resolution molecular line observations from AGB outflows, dust-gas interactions are needed in chemical kinetics models.

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ALMA observations of water deuteration: A physical diagnostic of the formation of protostars

S. S. Jensen, J. K. Jørgensen, L. E. Kristensen, K. Furuya, A. Coutens, E. F. van Dishoeck, D. Harsono, M. V. Persson

How water is delivered to planetary systems is a central question in astrochemistry. The deuterium fractionation of water can serve as a tracer for the chemical and physical evolution of water during star formation and can constrain the origin of water in Solar System bodies. The aim is to determine the HDO/H2O ratio in the inner warm gas toward three low-mass Class 0 protostars selected to be in isolated cores, i.e., not associated with any cloud complexes. Previous sources for which the HDO/H2O ratio have been established were all part of larger star-forming complexes. Determining the HDO/H2O ratio toward three isolated protostars allows comparison of the water chemistry in isolated and clustered regions to determine the influence of local cloud environment. We present ALMA observations of the HDO 3,1,2–2,2,1 and 2,1,1–2,1,2 transitions at 225.897 GHz and 241.562 GHz along with the H-2-18-O 3,1,3–2,2,0 transition at 203.407 GHz. The high angular resolution observations (0".3-1".3) allow the study of the inner warm envelope gas. Model-independent estimates for the HDO/H2O ratios are obtained and compared with previous determinations of the HDO/H2O ratio in the warm gas toward low-mass protostars. We determine the HDO/H2O ratio toward L483, B335 and BHR71–IRS1 to be (2.2 ± 0.4)×10−3, (1.7 ± 0.3)×10−3, and (1.8 ± 0.4)×10−3, respectively, assuming Tex = 124 K. The degree of water deuteration of these isolated protostars are a factor of 2–4 higher relative to Class 0 protostars that are members of known nearby clustered star-forming regions.

The results indicate that the water deuterium fractionation is influenced by the local cloud environment. This effect can be explained by variations in either collapse timescales or temperatures, which depends on local cloud dynamics and could provide a new method to decipher the history of young stars.

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Announcements

Symposium Announcement: Astrochemical Complexity in Planetary Systems

This symposium will be held the 259th ACS National Meeting, Philadelphia, PA, 22-26 March 2020.
The aim is to bring together laboratory, theoretical and observational astrochemists with planetary scientists to generate insights into the origins of chemical complexity in planetary systems.
Session Topics:
1. Chemical Complexity from the ISM to Disks: Observations and Models.
2. Experimental and Theoretical Techniques for Interstellar/Planetary Chemistry.
3. The Outer Solar System, Comets, Icy Rings, and Satellites.
4. Inner Solar System, Asteroids and Giant Planets.
5. Organics in Meteorites.
6. Organics on the Primordial Earth.
7. Emerging Techniques for Sample Analysis.
Confirmed Invited Speakers:
Brett McGuire, Jennifer Bergner, Susanna Widicus Weaver, Hervé Cottin, Chao He, Kathrin Altwegg, Hunter Waite, Yoko Kebukawa, Jay Forsythe, Mehmet Yesiltas, Amanda Hendrix, Jamie Elsila, Ryan Fortenberry, Reggie Hudson, Mike McCarthy, Steven Charnley, Scott Sandford.
Visit https://callforpapers.acs.org/philadelphia2020/PHYS to submit a talk or poster abstract (deadline is 2019 October 14th).

Postdoctoral Research Fellowship

A Post Doctoral Research Fellowship position is available at the Smithsonian Astrophysical Observatory in Cambridge, MA.
Interested candidates with experience in theoretical and computational methods for atomic and molecular collisions are invited to apply.
The successful candidate will work under the supervision of Dr. James Babb (jbabb@cfa.harvard.edu) and will join the Atomic and Molecular Physics Division at the Center for Astrophysics | Harvard & Smithsonian.
Applications must be submitted before October 31, 2019 through the usajobs.gov portal; search for opportunity 54615610 or access the link https://www.usajobs.gov/GetJob/ViewDetails/546156100