AstroChemical Newsletter #100

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Abstracts

The CO-to-H2 conversion factor of molecular outflows

Miguel Pereira-Santaella, Eduardo González-Alfonso, Ismael García-Bernete, Santiago García-Burillo, Dimitra Rigopoulou

We analyze JWST/NIRSpec observations of the CO rovibrational v=1-0 band at 4.67um around the dust-embedded southern active galactic nucleus (AGN) of NGC3256 (d=40Mpc; L(IR)=10^11.6 Lsun). We classify the CO v=1-0 spectra into three categories based on the behavior of P- and R-branches of the band: (a) both branches in absorption toward the nucleus; (b) P-R asymmetry (P-branch in emission and R-branch in absorption) along the disk of the galaxy; and (c) both branches in emission in the outflow region above and below the disk. In this paper, we focus on the outflow. The CO v=1-0 emission can be explained by the vibrational excitation of CO in the molecular outflow by the bright mid-IR ~4.7um continuum from the AGN up to r~250pc. We model the ratios between the P(J+2) and R(J) transitions of the band to derive the physical properties (column density, kinetic temperature, and CO-to-H2 conversion factor, alpha_CO) of the outflowing gas. We find that the 12CO v=1-0 emission is optically thick for J<4, while the 13CO v=1-0 emission remains optically thin. From the P(2)/R(0) ratio, we identify a temperature gradient in the outflow from >40K in the central 100pc to <15K at 250pc sampling the cooling of the molecular gas in the outflow. We used three methods to derive alpha_CO in eight 100pc (0.5") apertures in the outflow by fitting the P(J+2)/R(J) ratios with non-LTE models. We obtain low median alpha_CO factors (0.40-0.61) x 3.2e-4/[CO/H2] Msun (K km/s/pc2)^-1 in the outflow regions. This implies that outflow rates and energetics might be overestimated if a ULIRG-like alpha_CO, which is 1.3-2 times larger, is assumed. The reduced alpha_CO can be explained if the outflowing molecular clouds are not virialized. We also report the first extragalactic detection of a broad (sigma=0.0091um) spectral feature at 4.645um associated with aliphatic deuterium on polycyclic aromatic hydrocarbons (D_n-PAH).

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Hydrocarbon chemistry in the inner regions of planet-forming disks

Jayatee Kanwar, Inga Kamp, Peter Woitke, Christian Rab, Wing Fai-Thi

Context. The analysis of the mid-infrared spectra helps understanding the composition of the gas in the inner, dense and warm terrestrial planet forming region of disks around young stars. ALMA has detected hydrocarbons in the outer regions of the planet forming disk and Spitzer detected C2H2 in the inner regions. JWST-MIRI provides high spectral resolution observations of C2H2 and a suite of more complex hydrocarbons are now reported. Interpreting the fluxes observed in the spectra is challenging and radiation thermo-chemical codes are needed to properly take into account the disk structure, radiative transfer, chemistry and thermal balance. Various disk physical parameters like the gas-to-dust ratio, dust evolution including radial drift, dust growth and settling can affect the fluxes observed in the mid-IR. Still, thermo-chemical disk models were not always successful in matching all observed molecular emission bands simultaneously. Aims. The goal of this project is two-fold. Firstly, we analyse the warm carbon chemistry in the inner regions of the disk, namely within 10 au, to find pathways forming C2H2 potentially missing from the existing chemical networks. Secondly, we analyse the effect of the new chemistry on the line fluxes of acetylene. Methods. We used the radiative thermo-chemical disk code called PRODIMO to expand the hydrocarbon chemistry that occurs in a typical standard T Tauri disks. We used the UMIST and the KIDA rate databases for collecting reactions for the species. We included a number of three-body and thermal decomposition reactions from the STAND2020 network. We also included isotopomers for the species that were present in the databases. The chemistry was then analysed in the regions that produce observable features in the mid-infrared spectra. We studied the effect of expanding the hydrocarbon chemistry on the mid-infrared spectra. Methods. We used the radiative thermo-chemical disk code called PRODIMO to expand the hydrocarbon chemistry that occurs in a typical standard T Tauri disks. We used the UMIST and the KIDA rate databases for collecting reactions for the species. We included a number of three-body and thermal decomposition reactions from the STAND2020 network. We also included isotopomers for the species that were present in the databases. The chemistry was then analysed in the regions that produce observable features in the mid-infrared spectra. We studied the effect of expanding the hydrocarbon chemistry on the mid-infrared spectra. Methods. We used the radiative thermo-chemical disk code called PRODIMO to expand the hydrocarbon chemistry that occurs in a typical standard T Tauri disks. We used the UMIST and the KIDA rate databases for collecting reactions for the species. We included a number of three-body and thermal decomposition reactions from the STAND2020 network. We also included isotopomers for the species that were present in the databases. The chemistry was then analysed in the regions that produce observable features in the mid-infrared spectra. We studied the effect of expanding the hydrocarbon chemistry on the mid-infrared spectra.

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Spatially resolving the volatile sulfur abundance in the HD 100546 protoplanetary disc

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Volatile elements play a crucial role in the formation of planetary systems. Their abundance and distribution in protoplanetary discs provide vital insights into the connection between formation processes and the atmospheric composition of individual planets. Sulfur, being one of the most abundant elements in planet-forming environments, is of great significance, and now observable in exoplanets with JWST. However, planetary formation models currently lack vital knowledge regarding sulfur chemistry in protoplanetary discs. Developing a deeper understanding of the major volatile sulfur carriers in discs is essential to building models that can meaningfully predict planetary atmospheric composition, and reconstruct planetary formation pathways. In this work, we combine archival observations with new data from the Atacama Large sub-Millimeter Array (ALMA) and the Atacama Pathfinder EXperiment (APEX), covering a range of sulfur-bearing species/isotopologs. We interpret this data using the DALI thermo-chemical code, for which our model is highly refined and disc-specific. We find that volatile sulfur is heavily depleted from the cosmic value by a factor of ∼1000, with a disc-averaged abundance of S/H ∼ 10−8. We show that the gas-phase sulfur abundance varies radially by ≳3 orders of magnitude, with the highest abundances inside the inner dust ring and coincident with the outer dust ring at r ∼ 150–230 au. Extracting chemical abundances from our models, we find OCS, H2CS, and CS to be the dominant molecular carriers in the gas phase. We also infer the presence of a substantial OCS ice reservoir. We relate our results to the potential atmospheric composition of planets in HD 100546, and the wider exoplanet population.

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Deuterium fractionation in cold dense cores in the low-mass star-forming region L1688

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In this work, we study deuterium fractionation in four starless cores in the low-mass star-forming region L1688 in the Ophiuchus molecular cloud. We study how the deuterium fraction (RD) changes with environment, compare deuteration of ions and neutrals, core centre and its envelope, and attempt to reproduce the observed results with a gas-grain chemical model. We chose high and low gas density tracers to study both core centre and the envelope. With the IRAM 30m antenna, we mapped N2H+(1-0), N2D+(1-0), H13CO+ (1-0) and (2-1), DCO+(2-1), and p-NH2D(111-101) towards the chosen cores. The missing p-NH3 and N2H+(1-0) data were taken from the literature. To measure the molecular hydrogen column density, dust and gas temperature within the cores, we used the Herschel/SPIRE dust continuum emission data, the GAS survey data (ammonia), and the COMPLETE survey data to estimate the upper limit on CO depletion. We present the deuterium fraction maps for three species towards four starless cores. Deuterium fraction of the core envelopes traced by DCO+/H13CO+ is one order of magnitude lower (∼0.08) than that of the core central parts traced by the nitrogen-bearing species (∼0.5). Deuterium fraction increases with the gas density as indicated by high deuterium fraction of high gas density tracers and low deuterium fraction of lower gas density tracers and by the decrease of RD with core radii, consistent with the predictions of the chemical model. Our model results show a good agreement with observations for RD(N2D+/N2H+) and RD(DCO+/HCO+) and underestimate the RD(NH2D/NH3).

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A HITRAN-formatted UV line list of S2-containing transitions involving X3 Σg-, B3 Σu-, and B″ 3 Πu electronic states

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The sulfur dimer (S2) is an important molecular constituent in cometary atmospheres and volcanic plumes on Jupiter's moon Io. It is also expected to play an important role in the photochemistry of exoplanets. The UV spectrum of S2 contains transitions between vibronic levels above and below the dissociation limit, giving rise to a distinctive spectral signature. By using spectroscopic information from the literature, and the spectral simulation program PGOPHER, a UV line list of S2 is provided. This line list includes the primary B3Σ−u−X3Σ−g (v′=0-27, v″=0-10) electronic transition, where vibrational bands with v′≥10 are predissociated. Intensities have been calculated from existing experimental and theoretical oscillator strengths, and semi-empirical strengths for the predissociated bands of S2 have been derived from comparisons with experimental cross-sections. The S2 line list also includes the B″3Πu−X3Σ−g (v′=0-19, v″=0-10) vibronic bands due to the strong interaction with the B state. In summary, we present the new HITRAN-formatted S2 line list and its validation against existing laboratory spectra. The extensive line list covers the spectral range 21700−41300~cm−1 (∼242−461~nm) and can be used for modeling both absorption and emission.

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The Astrochemistry Low-energy Electron Cross-Section (ALeCS) database I. Semi-empirical electron-impact ionization cross-section calculations and ionization rates

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(Abridged) Electron-molecule interaction is a fundamental process in radiation-driven chemistry in space, from the interstellar medium to comets. Therefore, knowledge of interaction cross-sections is key. While there has been a plethora of studies of total ionization cross-sections, data is often spread over many sources, or not public or readily available. We introduce the Astrochemistry Low-energy Electron Cross-Section (ALeCS) database, a public database for electron interaction cross-sections and ionization rates for molecules of astrochemical interest. In this work, we present the first data release comprising total ionization cross-sections and ionization rates for over 200 neutral molecules. We include optimized geometries and molecular orbital energies at various levels of theory, and for a subset of the molecules, the ionization potentials. We compute total ionization cross-sections using the binary-encounter Bethe model and screening-corrected additivity rule, and ionization rates and reaction network coefficients for molecular cloud environments for >200 neutral molecules ranging from diatomics to complex organics. We demonstrate that our binary-encounter Bethe cross-sections agree well with experimental data. We show that the ionization rates scale roughly linearly with the number of constituent atoms in the molecule. We introduce and describe the public ALeCS database. For the initial release, we include total ionization cross-sections for >200 neutral molecules and several cations and anions calculated with different levels of quantum chemistry theory, the chemical reaction rates for the ionization, and network files in the formats of the two most popular astrochemical networks, the KIDA and UMIST. The database will be continuously updated for more molecules and interactions.

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Reactivity of the Ethenium Cation ($C_2H_5^+$) with Ethyne (C_2H_2): A Combined Experimental and Theoretical Study

Vincent Richardson, Miroslav Polášek, Claire Romanzin, Paolo Tosi, Roland Thissen, Christian Alcaraz, Ján Žabka and Daniela Ascenzi

The gas-phase reaction between the ethyl cation and ethyne is re-investigated by measuring absolute reactive cross sections (CSs) and branching ratios (BRs) as a function of collision energy, in the thermal and hyperthermal energy range, via tandem-guided ion beam mass spectrometry under single collision conditions. Dissociative photoionization of C_2H_5Br using tuneable VUV radiation in the range 10.5–14.0 eV is employed to generate $C_2H_5^+$, which has also allowed us to explore the impact of increasing (vibrational) excitation on the reactivity. Reactivity experiments are complemented by theoretical calculations, at the G4 level of theory, of the relative energies and structures of the most relevant stationary points on the reactive potential energy hypersurface (PES) and by mass-analyzed ion kinetic energy (MIKE) spectrometry experiments to probe the metastable decomposition from the $[C_4H_7]^+$ PES and elucidate the underlying reaction mechanisms. Two main product channels have been identified at a centre-of-mass collision energy of ∼ 0.1 eV: (a) $C_3H_3^+ + CH_4$, with BR = 0.76±0.05 and (b) $C_4H_5^+ + H_2$, with BR = 0.22±0.02. A third channel giving $C_2H_3^+$ in association with C_2H_4 is shown to emerge at both high internal excitation of $C_2H_5^+$ and high collision energies. From CS measurements, energy-dependent total rate constants in the range $4.3\times10^{-11} - 5.2\times10^{-10}$ $cm^3\cdot molecule^{-1}\cdot s^{-1}$ have been obtained. Theoretical calculations indicate that both channels stem from a common covalently bound intermediate, $CH_3CH_2CHCH^+$, from which barrierless and exothermic pathways exist for the production of both cyclic c-$C_3H_3^+$ and linear H_2CCCH^+ isomers of the main product channel. For the minor $C_4H_5^+$ product, two isomers are energetically accessible: the three-member cyclic isomer c-$C_3H_2(CH_3)^+$ and the higher energy linear structure $CH_2CHCCH_2^+$, but their formation requires multiple isomerization steps and passages via transition states lying only 0.11 eV below the reagents' energy, thus explaining the smaller BR. Results have implications for the modeling of hydrocarbon chemistry in the interstellar medium and the atmospheres of planets and satellites as well as in laboratory plasmas (e.g. plasma-enhanced chemical vapor deposition of carbon nanotubes and diamond like carbon films).

Molecules 2024, 29, 810
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Machine learning prediction of state-to-state rate constants for astrochemistry

D. Bossion, G. Nyman & Y. Scribano

In this work, we investigate the possibility to use an artificial neural network to predict a large number of accurate state-to-state rate constants for atom-diatom collisions, from available rates obtained at two different accuracy levels, using a few accurate rates and many low-accuracy rates. The $H + H_2 \rightarrow H_2 + H$ chemical reaction is used to benchmark our neural network, as both low and high accuracy state-to-state rates are available in the literature. Our artificial neural network is a multilayer perceptron, using 8 input neurons including the low-accuracy rate constants, with the high accuracy rate constants as the output neuron. The use of machine learning to predict rate constants is very encouraged, as the rates obtained are accurate, even using as low as 1% of the full dataset to train the neural network, and improve greatly the low accuracy rates previously available. This approach can be used to generate full rate constant datasets with a consistent accuracy, from sparse rates obtained with various methods of different accuracies.

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FAUST XII. Accretion streamers and jets in the VLA 1623--2417 protocluster

C. Codella, L. Podio, M. De Simone, and the FAUST team

The ALMA interferometer has played a key role in revealing a new component of the Sun-like star forming process: the molecular streamers, i.e. structures up to thousands of au long funneling material non-axisymmetrically to disks. In the context of the FAUST ALMA LP, the archetypical VLA1623-2417 protostellar cluster has been imaged at 1.3 mm in the SO(56–45), SO(66–55), and SiO(5–4) line emission at the spatial resolution of 50 au. We detect extended SO emission, peaking towards the A and B protostars. Emission blue-shifted down to 6.6 km/s reveals for the first time a long (2000 au) accelerating streamer plausibly feeding the VLA1623 B protostar. Using SO, we derive for the first time an estimate of the excitation temperature of an accreting streamer: 33(9) K. The SO column density is 1e14 cm−2, and the SO/H2 abundance ratio is ∼ 1e-8. The total mass of the streamer is 3e-3 Msun, while its accretion rate is 3–5 e-7 Msun/yr. This is close to the mass accretion rate of VLA1623 B, in the 0.6–3e-7 Msun/yr range, showing the importance of the streamer in contributing to the mass of protostellar disks. The highest blue- and red-shifted SO velocities behave as the SiO(5–4) emission, the latter species detected for the first time in VLA1623-2417: the emission is compact (100-200 au), and associated only with the B protostar. The SO excitation temperature is 100 K, supporting the occurrence of shocks associated with the jet, traced by SiO.

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Testing analytical methods to derive the cosmic-ray ionisation rate in cold regions via synthetic observations

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Context. Cosmic rays (CRs) heavily impact the chemistry and physics of cold and dense star-forming regions. However, characterising their ionisation rate is still challenging from an observational point of view. Aims. In the past, a few analytical formulas have been proposed to infer the cosmic-ray ionization rate CRIR from molecular line observations. These have been derived from the chemical kinetics of the involved species, but they have not been validated using synthetic data processed with a standard observative pipeline. We aim to bridge this gap. Methods. We perform the radiative transfer on a set of three-dimensional magneto-hydrodynamical simulations of prestellar cores, exploring different initial CRIR, evolutionary stages, types of radiative transfer (e.g. assuming local-thermodynamic-equilibrium conditions), and telescope responses. We then compute the column densities of the involved tracers to determine CRIR, using, in particular, the equation proposed by Bovino et al. (2020) and by Caselli et al. (1998), both used nowadays. Results. Our results confirm that the method of Bovino et al. (2020) accurately retrieves the actual CRIR within a factor of 2 − 3, in the physical conditions explored in our tests. Since we also explore a non-local thermodynamic equilibrium radiative transfer, this work indirectly offers insights into the excitation temperatures of common transitions at moderate volume densities (n~10^5 cm−3). We have also performed a few tests using the formula proposed by Caselli et al. (1998), which overestimates the actual CRIR by at least two orders of magnitudes. We also consider a new derivation of this method, which, however, still leads to large overestimates. Conclusions. The method proposed by Bovino et al. (2020), further validated in this work, represents a reliable method to estimate CRIR in cold and dense gas. We also confirm that the former method by Caselli et al. (1998), as already pointed out by its authors, has no global domain of application, and should be employed with caution.

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Effect of temperature on the gas-phase reaction of CH3CN with OH radicals: experimental (T = 11.7–177.5 K) and computational (T = 10–400 K) kinetic study

Daniel González, André Canosa, Emilio Martínez-Núñez, Antonio Fernández-Ramos, Bernabé Ballesteros, Marcelino Agúndez, José Cernicharo and Elena Jiménez

Acetonitrile (CH3CN) is present in the interstellar medium (ISM) in a variety of environments. However, at the ultracold temperatures of the ISM, radical-molecule reactions are not widely investigated because of the experimental handicap of getting organic molecules in the gas phase by conventional techniques. The CRESU (French acronym for Reaction Kinetics in a Uniform Supersonic Flow) technique solves this problem. For this reason, we present in this work the kinetic study of the gas-phase reaction of CH3CN with one of the most ubiquitous radicals, the hydroxyl (OH) radical, as a function of temperature (11.7–177.5 K). The kinetic technique employed to investigate the CH3CN + OH reaction was the pulsed laser photolysis-laser induced fluorescence. The rate coefficient for this reaction k(T) has been observed to drastically increase from 177.5 K to 107.0 K (about 2 orders of magnitude), while the increase in k(T) from 107.0 K to 11.7 K was milder (around 4 times). The temperature dependent expressions for k(T) are provided in the two distinct T-ranges, excluding the upper limit obtained for k(177.5 K): kð11:7135:0 KÞ ¼ ð1:50 0:12Þ 1011 T 300 K ð0:530:03Þ cm3 s1 kð135:0149:9 KÞ ¼ ð1:50 1:48Þ 1020 T 300 K ð26:41:5Þ cm3 s1: In addition, the rate coefficients estimated by the canonical competitive unified statistical (CCUS) theory show a similar behaviour to the experimental results, when evaluated within the high-pressure limit. This is consistent with the experimentally observed independence of k(T) with total gas density at selected temperatures. Astrochemical networks, such as the KIDA database or UMIST, do not include the CH3CN + OH reaction as a potential depletion process for acetonitrile in the ISM because the current studies predict very low rate coefficients at IS temperatures. According to the model (T = 10 K), the impact of the titled reaction on the abundances of CH3CN appears to be negligible in dark molecular clouds of the ISM (B1% of the total depletion reactions included in UMIST network). With respect to the potential formation of the CH2CN radical in those environments, even in the most favourable scenario, where this radical could be formed in a 100% yield from the CH3CN + OH reaction, this route would only contribute around 2% to the current assumed formation routes by the UMIST network.

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Can astronomical observations be used to constrain crucial chemical reactions? The methoxy case. SOLIS XVII

Nadia Balucani, Cecilia Ceccarelli, Fanny Vazart, Francois Dulieu, Dimitrios Skouteris, Marzio Rosi, Fernando Pirani, Eleonora Bianchi, Paola Caselli, Claudio Codella

To understand the origin of interstellar molecules we rely on astrochemical models, the gas-phase networks of which contain ≥7000 reactions. However, just a tiny fraction of them have parameters derived in laboratory experiments. Theoretical quantum mechanical (QM) calculations can also provide this information. Unfortunately, sometimes theoretical predictions and experimental values disagree, as is the case for the paradigmatic reaction CH3OH + OH → CH3O + H2O. Both laboratory experiments and QM calculations found an unexpected increase in the rate coefficients with decreasing temperature. However, experimental and theoretical estimates of the rate coefficients diverge by up to two orders of magnitude at the low temperatures of interest in interstellar chemistry. This work aims to test whether astronomical observations can help untangle this confusing situation. To this end, we first carried out new QM calculations to derive the rate coefficients of the major destruction reaction of the methoxy radical, CH3O + H, and then we compared astronomical observations from the IRAM/NOEMA Large Programme SOLIS with astrochemical model predictions. Our new rate coefficient for the CH3O + H reaction is 5–10 times larger than that in the astrochemical data base KIDA in the 10–100 K range. When including the new methoxy destruction rate coefficients, the comparison between observations and model predictions favours the rate coefficients of the CH3OH + OH reaction from QM calculations. We conclude that QM calculations are an important alternative to laboratory experiments when it comes to the harsh conditions of interstellar objects and that astronomical observations can be used to constraint the rate coefficients of relevant reactions.

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PRODIGE - Planet-forming disks in Taurus with NOEMA. I. Overview and first results for 12CO, 13CO, and C18O

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We are performing a line survey of 8 planet-forming Class II disks in Taurus with NOEMA, as a part of the large program PRODIGE (PROtostars and DIsks: Global Evolution; PIs: P. Caselli and Th. Henning). Compact and extended disks around T Tauri stars CI, CY, DG, DL, DM, DN, IQ Tau, and UZ Tau E are observed in multiple lines from > 20 key C-, O,- N-, and S-bearing species. The observations in four spectral settings at 210-280 GHz with 1 sigma rms of ∼ 8 − 12 mJy/beam at 0.9″ and 0.3 km/s resolution will be completed in 2024. The uv-visibilities are fitted with the DiskFit model to obtain key stellar and disk properties. In this first paper, the combined 12CO, 13CO and C18O J = 2 − 1 data are presented. We find that the CO fluxes and disk masses inferred from dust continuum tentatively correlate with the CO emission sizes. We constrain dynamical stellar masses, geometries, temperatures, the CO column densities and gas masses for each disk. The best-fit temperatures at 100 au are ∼ 17 − 37 K, and decrease radially with the power-law exponent q ∼ 0.05 − 0.76. The inferred CO column densities decrease radially with the power-law exponent p ∼ 0.2 − 3.1. The gas masses estimated from 13CO (2-1) are ∼ 0.001 − 0.2 M_sun. The best-fit CO column densities point to severe CO freeze-out in these disks. The DL Tau disk is an outlier, and has stronger CO depletion than the rest of the sample. The CO isotopologue ratios are roughly consistent with the observed values in disks and the low-mass star-forming regions.

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