Molecular Magic:
Astrochemistry in star-forming regions

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1   Introduction

Molecular line emission is an extremely powerful tool in allowing us to probe conditions in gas throughout the galaxy. In order to make full use of this magician's box of tricks it is important to try and understand the chemical processes at work in the gas. This is in general not easy, and inextricably linked to the local UV field strength and to ice formation on grains etc., but through detailed modelling of the chemical network and of line emission, followed by comparison with observations, it should be possible to constrain the gas properties in different astronomical scenarios.

In this talk I present a (very) brief overview of some of the ideas one must consider when trying to take advantage of the benefits offered by chemical and thermal modelling, particularly with reference to conditions in star-forming regions. I start by recapping the mechanisms behind atomic and molecular spectroscopy at a quantum mechanical level, before moving on to look at the chemical processes present in the interstellar medium, and in circumstellar environments. I will finish with a brief look at two recent case studies where chemical and/or spectroscopic modelling have been utilised with (I hope!) interesting results.

In preparing this talk I have made extensive use of the book *Astrochemistry* by Andrew M. Shaw, as well as my work with my supervisor Peter Woitke (e.g. Woitke et al. 2009a,b, Kamp et al. 2009). Other references as applicable.

2   Spectroscopy

Observations of atomic spectra in the early 20th century led to the idea of the quantum nature of matter and radiation. Atoms and molecules can occupy certain discrete energy levels, and any change in energy must be in the form of a quantum leap between two energy states. Also, radiation transfers energy in the form of discrete particles, or photons. The interaction between matter and radiation, with atoms absorbing or emitting photons of certain energies in order to change between states, is what we refer to as spectroscopy.

The interaction between matter and radiation can take various forms:

- Elastic scattering - scattering of photons by matter with no change in photon energy

- Non-elastic scattering - a photon is absorbed by an atom and re-emitted at a different wavelength, resulting in a change in energy of the atom

- Stimulated absorption - the photon is absorbed and annihilated, and its energy and momentum given to the atom

- Stimulated emission - a photon passes near to an excited atom, stimulating the emission of a photon of equal wavelength

- Spontaneous emission - an excited atom spontaneously creates a photon, dropping down to a lower energy state

Using the example of stimulated absorption for the time being, by studying the absorption spectrum towards a bright source we can learn about the conditions along the line of sight.

Measuring the strength of atomic (and molecular - coming up later!) absorption lines can allow us to determine column densities for the various species. In order to do this we need to know how much light is removed by each atom of a species i.e. how readily the corresponding transition between atomic energy states occurs. The values of these transition strengths are given by the Einstein coefficients.

Einstein's A coefficient describes the likelihood of an atom undergoing spontaneous emission, with a transition from (for example) state 2 to state 1:

$$\left(\frac{\mathrm{d}n_1}{\mathrm{d}t}\right)_{A_{21}} = A_{21}n_2 \tag{1}$$

where n_2 and n_1 refer to the population numbers of the upper and lower states respectively. The Einstein B coefficient describes stimulated emission, and the reverse process of absorption:

$$\left(\frac{\mathrm{d}n_1}{\mathrm{d}t}\right)_{B_{21}} = B_{21}n_2\rho(\nu) \tag{2}$$

$$\left(\frac{\mathrm{d}n_1}{\mathrm{d}t}\right)_{B_{12}} = -B_{12}n_1\rho(\nu) \tag{3}$$

where the local radiation density $\rho(\nu)$ is given by Planck's law:

$$\rho(\nu) = \frac{2h\nu^3}{c^2(e^{h\nu/kT})} \tag{4}$$

The Einstein coefficients are fixed for a given atom, and do not depend on the local conditions in the gas. It follows that if we can find a relationship between the coefficients in the simplifying case of thermal equilibrium, this relationship must be valid in all cases. Using this method it is possible to show that

$$A_{21} = \left(\frac{8\pi h\nu^3}{c^3}\right)B_{21}. \tag{5}$$

The dependence on ν^3 here means that spontaneous decay is fast at high frequencies, for instance $\sim$ns in the visible region of the spectrum. It is much slower at lower frequencies, for instance in rotational molecular transitions and hyperfine level transitions in atoms.

In local thermal equilibrium (LTE) the level populations (i.e. the number of atoms in a given energy state) are given by the Boltzmann distribution. In non-LTE conditions, however, they are a little bit trickier to determine. This could be the case, for instance, at lower densities applicable to interstellar environments. One way of tackling the problem is to use an escape probability treatment, where the likelihood of a photon reaching a given point in a medium is compared to the likelihood of one escaping from this point, and the Einstein coefficients are used to give the rates of the up and down transitions.

2.1   Line profiles

When we observe atomic spectra the lines are not infinitessimally thin, as might be expected from the discussion so far, with atoms absorbing and emitting photons at single
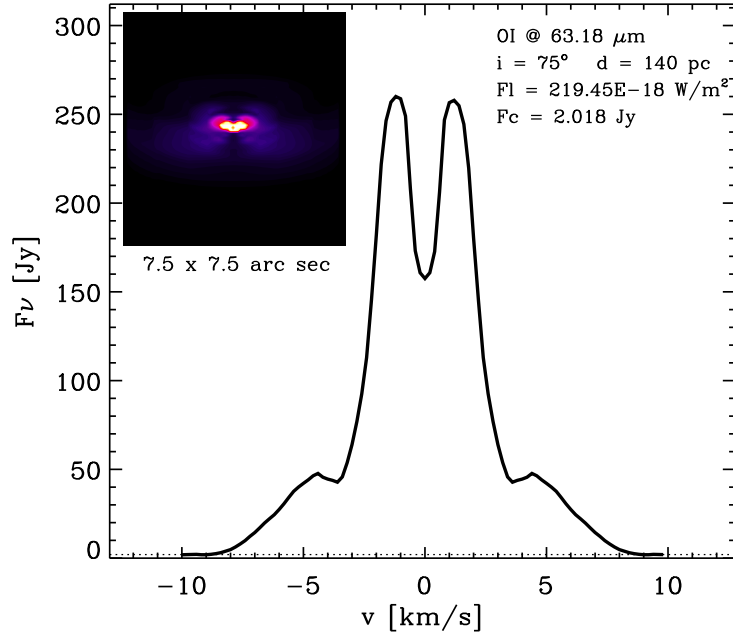
Figure 1: Line profile for for [OI] 63 micron line in a circumstellar disk model

discrete frequencies. The lines have finite width which varies for gas under different conditions, and indeed the shape of these line profiles can prove invaluable when attempting to probe the emission (or absorption) volume.

Line broadening can be classified into three broad (sorry!) categories:

1. Natural broadening - also known as lifetime broadening, this refers to the innate uncertainty in the energy of a quantum state resulting from uncertainty in the lifetime of the state. Heisenberg's uncertainty principle states that $\Delta E \Delta \tau \geq \hbar$ where E is the state's energy, τ its lifetime and $\hbar$ is Planck's constant. The lifetime of the upper state of a spontaneous transition is given by $\tau = A^{-1}$.

2. Pressure broadening - this refers to perturbations of the energy levels due to the presence of nearby atoms, and while irrelevant in the interstellar medium (with low particle densities), this can be more important in disks, planetary atmospheres etc.

3. Doppler broadening - the observed wavelength of transitions can be redshifted or blueshifted if the transitioning atoms have a velocity component along the line of sight, in accordance with the Doppler effect, $\Delta \lambda / \lambda = v/c$. This velocity component may be due to thermal motion (giving a Gaussian line profile), turbulent motion, or due to bulk flow of material.

An example of the use of emission line profiles is in circumstellar disks (see Fig. 1), where differential rotation in the disk coupled with the shape of a line profile can tell us the disk regions responsible for the emission, albeit with various simplifying assumptions. Wide peak separations suggest that the emission originates in the warm inner regions of the disk, whereas narrow separations indicate the outer disk is responsible. This analysis is of course not possible in cases where the disk is viewed face-on.

3   Molecular astronomy

The previous discussion of atomic line transitions is largely applicable also to molecules, however now with added complications arising from their more complex geometry. Molecules, like atoms, have discrete electronic energy levels, but these now correspond to different bond structures within the molecule. Transitions down through these states produce light with wavelength ~ 500nm.

In addition to these electronic levels, molecules have discrete vibrational energy levels. A molecule made up of N atoms has $3N - 6$ normal modes of vibration, corresponding to the stretching and bending of chemical bonds in various combinations. Transitions between vibrational energy states emit light at $\sim 10\mu m$.

Thirdly, molecules have discrete energy levels associated with their rotation. The energy gap between these states is smaller still, and rotational transitions emit in the microwave and mm region of the spectrum. This is the most important type of molecular transition in terms of its usefulness in detecting and identifying molecules in space, and so it would seem appropriate to continue with a brief overview of microwave and mm astronomy.

3.1   Microwave & mm astronomy (rotational transitions)

The smallest energy gaps in isolated molecules are those between the modes of rotational motion. Molecules can only rotate at certain allowed frequencies, of order once every ns. This energy spacing leads to interactions with $\sim$GHz photons. Microwave ovens emit 2.45 GHz radiation which excites the rotational spectrum of liquid water. These molecules then collide with other molecules, transferring their energy and inducing translational and vibrational motion which heats up your ready-meal. The rotational, vibrational and translational energies are equal at equilibrium, in accordance with equipartition theorem.

The rotational energy levels are described by the angular momentum quantum number, J. For a diatomic molecule, the energy levels of allowed end-over-end rotations are given by:

$$E_J = \frac{h}{8\pi^2 I} J(J+1) - DJ^2(J+1)^2 \tag{6}$$

where D is the centrifugal distortion constant and I is the moment of inertia, given by $I = \mu < r^2 >$, where r is the bond length and μ is the reduced mass. The rigid-rotor approximation assumes $D = 0$, which works well for diatomics with low J. This gives a progression of line transitions, each equally-spaced with energy spacing $2B$, where the rotational constant $B = h/(8\pi^2 I)$. This corresponds to a frequency spacing of 115 GHz for CO. The line progression increases to a peak in intensity before decreasing again, with the peak corresponding to the rotational temperature (e.g. of CO). This can then be used to probe the gas temperature in the emission volume, assuming local thermal equilibrium (LTE).

The rotational constant B gets smaller for more complex molecules, and so the lines in the rotational progression become more closely spaced, and harder to resolve (but still easier than for infrared and visible spectroscopy). Also it becomes harder to calculate the moment of inertia I; in general for a 3D molecule we need three moments of inertia about three rotation axes.

A general requirement for a molecule to undergo rotational line transitions (also known

as a gross selection rule) is that is has a permanent electric dipole. This is because the molecule interacts with a photon's electric field, and so some asymmetry in the distribution of charge over the molecule is required. In the case of a molecule absorbing a photon and moving up to the next rotational level, this can be visualised as the photon 'grabbing' the molecule's dipole and increasing its rate of rotation. This is possible, for instance, in the case of CO, where the differing electronegativities of carbon and oxygen result in a permanent dipole moment, which can interact with a photon. In the case of vibrational transitions (observable in the infrared), it is necessary that the molecule's dipole changes as it vibrates.

4   Interstellar medium chemistry

The interstellar medium (ISM) encompasses a range of environments with vastly differing conditions for chemical reactions to take place in. In general it is rich in heavy elements, due to stellar winds depositing the remains of late-stage hydrogen burning, as well as heavier elements from supernovae. The first species to be detected in the ISM was Ca^+ in the visible spectrum, and to date over 100 molecules and moleclar ions have been seen. However, these are all composed of the same 12 elements (H,C,N,O,S,Si,P,F,Cl,Al,Na,Mg). The most abundant elements are C, H, O and N.

The low densities in the ISM compared with laboratory conditions means that a lot of accepted rules of lab-based chemistry are redundant. For instance, carbon doesn't always have four bonds, and in general there are many subvalent species and radicals present. This is due to the unreactive environment at such low densities; molecules which would normally collide and react with other species are able to remain stable. Many organic molecules have been observed, and these are generally less saturated than on Earth, with more double and triple bonds. It is however difficult to detect hydrocarbons, since these are mostly non-polar. They therefore don't exhibit a rotation spectrum, although some vibrational transitions are present.

Processing of such molecules in the ISM may be required in order to seed life, with organic molecules reacting to form the building blocks needed by living organisms. It is unlikely that all organic molecules have gas-phase formation routes, and more probable that reactions take place on the surface of dust grains, or on the grains' ice mantles, possibly requiring UV irradiation from a nearby star.

The most important molecule in terms of probing the ISM is CO. This diatomic is the simplest molecule to have a permanent electric dipole, and scans of the sky at 2.6mm, the wavelength of its $J = 1 - 0$ transition, can reveal a lot about our surroundings in the Galaxy. CO maps of giant molecular clouds indicate the presence of star formation, while they can also uncover diffuse regions of the ISM. Maps of the Taurus molecular cloud at the $J = 1 - 0$ transition of 'normal' ^{12}CO and the isotope ^{13}CO are different, suggesting that mixing processes are important. It is likely that ISM chemistry invovles turbulence, shockwaves, and other physical transport processes.

5 Reaction rates

For a simple chemical reaction between species A and B to form C and D

$$a\mathrm{A} + b\mathrm{B} \longrightarrow c\mathrm{C} + d\mathrm{D} \tag{7}$$

the reaction rate can be written as

$$\nu = k[\mathrm{A}]^a[\mathrm{B}]^b \tag{8}$$

where k is the rate constant, [A] and [B] are the concentrations of the reactants, and the power indices a and b come from the stoichiometry of the reaction (i.e. how many molecules of each reactant take part in the reaction). For gas-phase reactions the rate constant k is given empirically by the Arrhenius equation:

$$k(T) = A \exp\left[-\frac{E_a(T)}{RT}\right] \tag{9}$$

where E_a is the activation energy for the reaction (i.e. the energy required to break the chemical bonds in the reactants), T the temperature, and R the gas constant.

Reactions require a collision, which in the diffuse ISM can be hard to come by. At a particle number density $n \sim 10^2 \mathrm{cm}^{-3}$ the collision frequency is 5×10^{-8}, or once every 1.5 years. The reactant molecules also need the correct orientation to react. An extended version of Eq. 9 includes contributions from these two factors:

$$k(T) = P\ \sigma_{AB}\left(\frac{8kT}{\pi\mu}\right)^{1/2} n_A n_B \exp\left[-\frac{E_a(T)}{RT}\right] \tag{10}$$

Here the pre-exponential factor consists of a steric factor P, which accounts for molecular orientation, multiplied by the collision rate. σ_{AB} is the collisional cross-section for reactants A and B, μ is the reduced mass, n_A and n_B their number densities and k is Boltzmann's constant. The exponential Arrhenius factor accounts for the reactants needing to collide with sufficient energy to react.

Parameterised versions of Eq. 10 are published in collections of astrochemical rate equations. For example, the UMIST 2006 compilation contains data for 420 species, including 4573 chemical reactions. The gas-phase reactions are parameterised as follows:

$$k(T) = \alpha\left(\frac{T}{300}\right)^\beta \exp\left[-\frac{\gamma}{T}\right] \tag{11}$$

where α, β and γ are quoted for a particular reaction in a given temperature range. The parameter values are mostly determined experimentally, although some are purely theoretical. Also they are given with ISM chemistry in mind, and so care should be taken when applying the reaction rates to environments other than the ISM (e.g. outflows, circumstellar disks), or outside the given temperature range.

In reality most astronomical situations will involve many reactions between a large number of chemical species, not just two-body gas-phase reactions but also UV photoreactions, cosmic ray-induced reactions, three body reactions, ice formation on grains and dust grain surface reactions, and more besides... There is a complex interlinked system

of chemical species, with the various reactions competing against or occuring alongside one another, all with interdependent rates. Solving the chemical network is daunting, but can be made (slightly) easier by using the steady-state approximation. Consider the rate of change in concentration of a species A:

$$\frac{\mathrm{d}[A]}{\mathrm{d}t} = -k_1[A][B] + k_2[C][D] + ... \tag{12}$$

where the first term on the r.h.s. comes from a reaction with rate k_1, with species A as a reactant, and the second term is due to a reaction producing species A from species C and D, with rate k_2. There can be many such terms for each species. The steady-state approximation sets the l.h.s. equal to zero in Eq. 12. This assumes the system has evolved to a dynamic equilibrium, with all the reactions cancelling each other so that the species abundances remain constant, constraining the system of coupled differentials. In practice this is a fairly safe assumption at higher densities where the chemical timescale is short (e.g. in circumstellar disks). However, equilibrium may never be reached during (for example) the collapse of a molecular cloud, and so care should be taken when attempting to model the chemistry in such cases.

Once two (or more) species have reacted and formed a new chemical bond, this isn't necessarily enough to guarantee the formation of a new stable species. The two colliding atoms still have the energy of the new bond, which needs to be removed to prevent the atoms dissociating. This is generally achieved through radiation, either of a visible photon, or a cascade of infrared and microwave photons passing down through the vibrational and rotational levels, leaving behind a radiatively-stabilised molecule. This of course requires the molecule to exhibit a vibrational or rotational spectrum, due to having an electric dipole (e.g. CO). This is not the case for H_2, and so it is unable to form in the gas phase. H_2 in fact forms on the surface of dust grains, with the grain absorbing the energy of bond formation, leaving a stable molecule which desorbs from the grain surface. Another way of stabilising a newly-formed molecule is by collision with a third body, although this can be difficult at low particle densities, for instance in the diffuse ISM.

6   Photochemistry

There is a subset of astrochemical reactions which rely on the interaction of the reactant species with the local radiation field, generally in the UV. The most important of these are photodissociation and photoionisation reactions. For example, the photodissocation of CO:

$$CO + h\nu \longrightarrow C + O \tag{13}$$
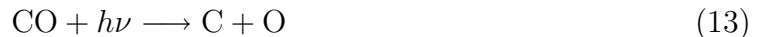
where photons with wavelength ≤ 105nm are required to dissociate the molecule. The general form for a photoionisation reaction is as follows:
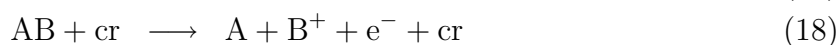
$$A + h\nu \longrightarrow A^+ + e^- \tag{14}$$

Hydrogen is ionised by photons with wavelength ≤ 90nm. The rates of photoreactions are given by the UMIST 2006 database in the form:

$$k(T) = \alpha \exp[-\gamma A_v] \mathrm{s}^{-1} \tag{15}$$

where A_v is the visual extinction into a cloud. The form of this empirical law illustrates that photoreactions are entirely dependent on the strength of the far-UV field (and hence on the extinction).

7   Charged particle chemistry

Molecules can also interact with cosmic rays (cr) emitted by nearby stars. These are composed of 84% protons, 14% He nuclei, and 2% electrons, heavier nuclei and more exotic particles. Cosmic rays have very high kinetic energy and are capable of breaking chemical bonds and ionising species by direct impact:

$$AB + cr \; \longrightarrow \; AB^+ + e^- + cr \tag{16}$$
$$AB + cr \; \longrightarrow \; A + B + cr \tag{17}$$
$$AB + cr \; \longrightarrow \; A + B^+ + e^- + cr \tag{18}$$
$$AB + cr \; \longrightarrow \; AB^* + cr \tag{19}$$

In all of these cases the cosmic rays are less energetic following the reaction. The fourth case is an example of non-elastic scattering, which cools the cosmic rays.

8   Dust grains

Dust is believed to comprise roughly 1% of the mass in interstellar and circumstellar environments. It is formed in the outflows from dying stars. Asymptotic giant branch (AGB) stars develop strong stellar winds once hydrogen burning has been exhausted, and it is in such winds that this crystalline silicate 'soot' coagulates. The reduced luminosity around AGB stars protects molecules such as SiC and TiO from dissociating, and these form aggregation nuclei which produce crystalline structures. They collect oxygen atoms from the ISM to become silicates, and also the condensation of volatile molecules on to the grain surfaces can form ice mantles. It is thought that these icy grain surfaces are home to a rich chemistry, especially when bathed in UV radiation from young stars. However, the mechanisms of dust surface chemistry are not well understood at present, and so models and rate constants are poorly-constrained.

9   Polycyclic aromatic hydrocarbons (PAHs)

PAHs are large carbon-rich molecules consisting of many interlinked benzene rings. The large aromatic ring structures are attributed to broad features in the IR spectra (at around 10μm) of strongly reddened stars (thought to have disks). They play an important role in the chemistry and gas-heating in the ISM and circumstellar environments. It has been postulated that PAHs could be products of biological degradation, similar to remnants in oil deposits on Earth. It is however more likely that they form via carbon insertion reactions, where a carbon chain becomes progressively longer by reacting with C^+ ions. These reactions should have low activation energy. They are followed by a ring closure reaction, then further chain propagation an ring closure reactions to form

the extended PAH structure. Observationally there are a number of vibrational spectral features explained by the presence of PAHs. These include lines from C-H stretch, C-H bend, C=C stretch etc.

One obvious question arising from the presence of PAHs in space is whether it is possible to form graphite. This also has a carbon ring structure, albeit massively extended into a crystalline lattice, and without the presence of hydrogen. There is no IR evidence for the presence of graphite, although its symmetry means that its dipole moment doesn't change when it vibrates, which would imply a weak vibrational spectrum.

PAHs act largely as very small dust grains in terms of their role in the chemical network. They heat the gas via the photoelectric effect. The PAH molecules absorb UV photons and emit high energy electrons which thermalise with the gas, providing an efficient heating source. Indeed, current models of cirumstellar disk chemistry suggest that PAHs play a very important role in heating the gas in these environments, causing it to produce brighter emission lines.

10   PDR chemistry

Photon dominated regions or photodissociation regions (PDRs) are responsible for many emission characteristics of the ISM. PDRs are traditionally defined as regions where H_2-non-ionising far-ultraviolet photons (FUV, $6 < h\nu < 13.6$ eV) from stellar sources control the gas heating and chemistry. Ionising radiation is assumed to be absorbed in a narrow ionisation front between a H II region (in the vicinity of of a UV-luminous star) and a PDR. PDRs are cooled via atomic and molecular line emission from the gas component, and by continuum emission from dust. There are a number of specific mechanisms by which the gas is heated. These include photoelectric emission from grains, triggered by absorption of FUV photons. Photoelectric heating is also provided by PAHs, which at present are treated simply as microscopic dust grains, although their precise role is far from understood . Other sources of gas heating are turbulence, cosmic ray heating and chemical heating.

The chemical structure of the gas in a PDR is determined largely by the FUV intensity. At low visual extinction A_V into the cloud, the high FUV intensity induces ionisation and photodissociation reactions. At larger optical depth where the FUV intensity drops off, more complex species can be formed without being destroyed immediately by FUV photons. This produces the classic layered structure of PDRs, with transitions $H \rightarrow H_2$ and $C^+ \rightarrow C \rightarrow CO$ with increasing A_V (see Figures 2&3) . This in turn affects the cooling. At low extinctions, the gas is cooled by emission of atomic fine-structure lines, mainly [O I]63μm and [C II]158μm. At larger depths molecular rotational line cooling in the millimetre, sub-millimetre and far infrared becomes important (CO, OH, H_2,H_2O etc).

In order to model a PDR it is necessary to compute all relevant local properties of the cloud such as the gas and dust temperature, gas pressure, relative abundance of each chemical species and their level populations, dust composition, as well as the local radiation field. The local wavelength-dependent radiation intensity affects the gas and dust heating, photochemical reaction rates, and molecular excitation levels. It is coupled in general to remote parts of the cloud, and depends on the integrated absorption (again
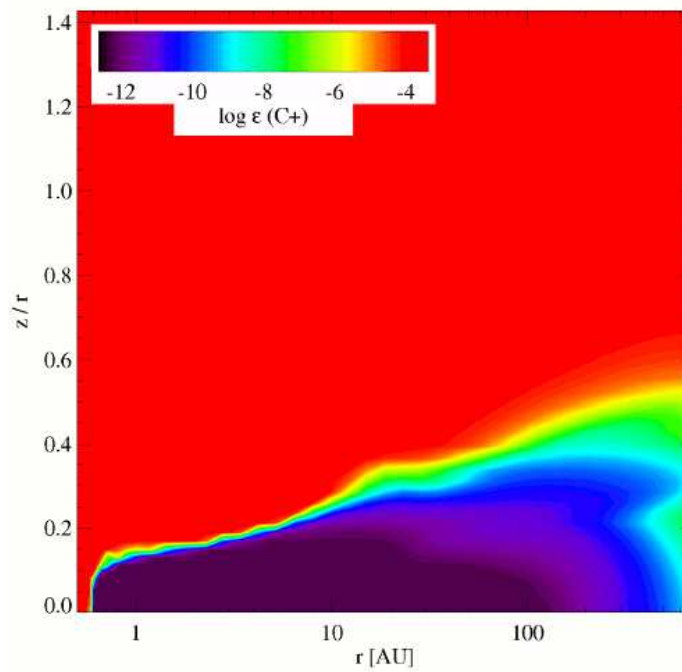
Figure 2: CII abundance contour plot for a vertical section through a circumstellar disk model
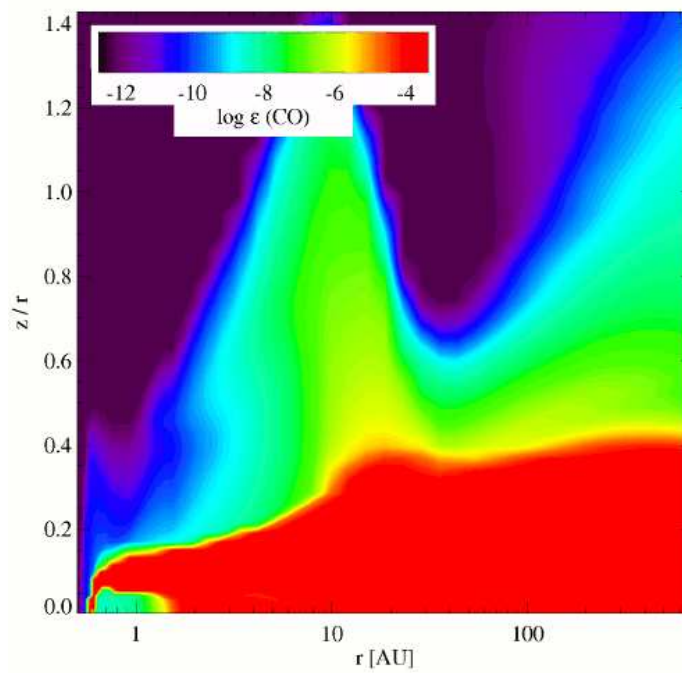

Figure 3: CO abundance contour plot for a vertical section through a circumstellar disk model

wavelength-dependent) along different lines of sight to the local position. This non-local coupling makes numerical PDR calculations computationally expensive.

The majority of PDR models feature plane-parallel geometry, illuminated either from one side or both sides, and either isotropically or with directed light perpendicular to the slab. The latter case simplifies the problem by considering a single line of sight. Another common geometry employed is the spherical case, and there are also a number of specialist PDR models employing disk geometry.

11   Case studies

Case Study 1: Cold CO in circumstellar disks

In circumstellar disks, because of the high densities, CO is expected to 'freeze-out' on dust grains at temperatures below about 17K. However, millimetre interferometry has revealed large amounts of gas-phase CO in disks at temperatures as low as 10K. Hersant et al. (2008) computed circumstellar disk models to investigate the potential of two contrasting mechanisms to explain this overabundance of cold CO. The first mechanism is turbulent mixing of the gas, to explain the presence of gas-phase CO in low temperature disk regions. Hersant et al. (2008), however, found this vertical mixing to have a very small influence on the vertical CO column density.

The second mechanism investigated is photodesorption of CO molecules from dust grain surfaces. This would seem a good candidate since it is a non-thermal process, and so could replenish the gas-phase CO reserves at temperatures below the freeze-out temperature, if the UV intensity is high enough. Hersant et al. (2008) found this to have a large effect on the CO column density, being efficient enough to preserve a significant abundance of CO for visual excitions below about 5 magnitudes.

This seems to be a convincing explanation for the observed CO overabundances, although the modelling gave CO column densities with a flatter radial profile than is observed. Also the results were sensitive in general to the assumed model transition height between the model's cold and warm regions. A more sophisticated model should be able to constrain such sensitivities.

Case Study 2: Detecting vegetation on extrasolar planets

In this *International Journal of Astrobiology* paper, Arnold et al. (2009) explore the possibility of observing spectral signatures of green vegetation on extrasolar planets. They make use of the so called vegetation red-edge (VRE), a property of chlorophyll in green plants whereby it absorbs most of the light in the visible part of the spectrum but is strongly reflective at wavelengths greater than 700 nm. The change can be from 5% to 50% reflectance between 680 nm and 730 nm. This prevents plants from overheating during photosynthesis, and produces a strong spectral feature.

Arnold et al. (2009) considered the Earth as an unresolved extrasolar planet, modelling the integrated observed reflectance spectrum to determine the VRE strength, and hence the detectabilty of vegetation spectra. In addition, they considered the Earth at the last two climatic extrema, the Last Glacial Maximum (with a large ice cap over the Northern

Hemisphere) and the Holocene optimum (with a greener Sahara). The VRE detactability varied between these extremes as might be expected, but in all cases the vegetation spectra should be detectable. Of course, this assumes that extrasolar vegetation has a similar make-up to our terrestrial plants.

References

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