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Cosmic-ray ionization and chemistry: theory

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Abstract. The interstellar medium is rich in chemistry, and much of the chemistry is initiated by cosmic rays, which ionize material as they traverse both diffuse and dense interstellar clouds. The ionization leads to sequences of ion-neutral reactions, which produce polyatomic positive ions, which in turn recombine with electrons to form polyatomic neutral fragments. The chemistry depends on the ionization rate induced by cosmic rays and their secondary electrons; to be most productive chemically, the rate must lie in some intermediate range. At overly large and overly small ionization rates, few molecules can be formed. The value of the ionization rate ζ in specific interstellar clouds depends on a variety of factors such as the initial flux-spectrum, the depth into a cloud, and the inhomogeneity of the overall spectral flux of cosmic rays in space.

Key words. ISM: molecules – Physical processes

1. Introduction

Cosmic rays play a principal role in the chemistry of the interstellar medium, which is not homogeneous but instead is composed of clouds of gas and dust (Herbst & Millar 2008). The elemental composition of the clouds is similar to stellar averages, known as cosmic abundances, in which hydrogen and helium are dominant, with carbon, oxygen and nitrogen lower by three-to-four orders of magnitude. The elements are divided between the gas and the dust particles, which comprise typically 1% of the mass of a cloud. The result is that the gas is somewhat depleted in elements heavier than helium, with elements such as silicon almost totally in the solid phase, and oxygen, carbon, and nitrogen depleted far less strongly. Interstellar clouds, which can range in size from 0.1 pc to more than 100 pc, can be crudely divided into diffuse and dense categories. Diffuse clouds have gas densities in the range $10 - 10^3$ cm^{-3}, with the element hydrogen in atomic and molecular form, and a kinetic temperature of 50 – 100 K (Black & Dalgarno 1977). In the nearby interstellar medium, these objects can be studied by the absorption and scattering of visible light from background stars. The scattering yields information about the size distribution of dust particles, which range in size from 1 – 1000 nm (Weingartner & Draine 2001). Spectral lines show the heavy elements in the gas to be mainly in atomic form. Dense clouds extinguish visible and ultraviolet light from background stars heavily, and are mainly studied at longer wavelengths, namely the infrared and millimeter-wave, with which the dust particles interact less extensively (Herbst & van Dishoeck 2009). Infrared spectroscopy, however, cannot easily be undertaken from

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the ground due to atmospheric water vapor, and the major technique for the study of molecules in the gas-phase of dense clouds has been discrete millimeter-wave astronomy, in which frequency range molecules possess rotational spectral lines. Infrared astronomy has also been utilized, although the best information comes from satellites such as *Spitzer* and *Herschel*. Typical densities in dense clouds range from 10^{3-6} cm^{-3}, with many cold condensations ("cold cores") at a temperature of 10 K and a density of 10^4 cm^{-3}. These condensations are the first stage in the evolution of low-mass stars (Herbst & van Dishoeck 2009).

As star formation takes place, temperatures far in excess of 10 K can be reached, especially in the vicinity of the newly forming star. In the dense cloud gas, cold or hot, virtually all hydrogen is in molecular form, with the second-most abundant molecule CO, a factor of 10^4 lower in abundance. Regarding more complex molecular species, the composition of the low-temperature gas is quite different from that in star-forming regions. In the former, the larger molecules tend to consist of long chains of carbon atoms with few hydrogen atoms, whereas in the warmer regions (100 K - 300 K) the chemistry is much more terrestrial in nature, with standard hydrogen-rich organic molecules. The composition of dust particles, unlike the case in the gas, has been characterized by infra-red absorption spectroscopy of broader features, which indicate dust particles mainly in the form of silicates with, in cold regions, mantles of ices composed primarily of water, CO, CO_2, and methanol CH_3OH) (Whittet 2003).

The current total number of gas-phase molecules detected in all of the different types of interstellar sources currently stands at approximately 166 if we exclude all isotopomers (see http://www.astrochymist.org/). Most of the molecules are neutral, but 21 molecular ions have been detected, including six negatively-charged species. The molecules are mainly organic in nature, which means that they are composed of the elements carbon, hydrogen, and possibly nitrogen and oxygen as well. The largest species detected at high spectral resolution has 13 atoms, and is a linear "nitrile" consisting of 11 carbon atoms with a nitrogen atom at one end and a hydrogen atom at the other end. Much larger species are inferred from broad spectra in the infrared; these include a class of molecules known as polycyclic aromatic hydrocarbons, which consist of six-membered rings of carbon atoms and are planar, and the fullerenes C_{60} and C_{70}, which consist of combinations of five-membered and six-membered rings and have the shapes of (non-American) footballs.

Molecular spectroscopy and chemistry are important tools in our understanding of the physical conditions and life histories of interstellar sources. From the spectral lines that characterize a given region, one can learn about the heterogeneity of a source, the types of molecules present, their relative abundances, their rotational temperatures, and whether the source is collapsing or rotating. But if one wishes to understand as well the age of a source, one can turn to chemical simulations since the chemistry is a function of time until steady-state conditions are reached, if ever. In a chemical simulation, one solves for the chemical concentrations (or more complex parameters such as spectral line shapes) as a function of time, most commonly via the use of rate equations, in which the time dependence of the concentration of any molecule is set equal to the sum of source and sink terms, comprising both chemical reactions, in the gas and on granular surfaces, and physical processes such as accretion, desorption, photodissociation, and ionization. The rationale for a chemical simulation is to compare calculated results as a function of time with observational results and to optimize the agreement between them including the uncertainties in both. Approximate uncertainties in calculated concentrations are obtained in a Monte Carlo approach by variation of the rate coefficients for gas-phase chemical reactions over their measured or estimated uncertainties (Wakelam et al. 2010). Our knowledge of the surface chemistry on granular surfaces is too minimal to extend uncertainty analyses to such processes. Indeed, it is common though hardly correct to ignore surface chemistry except for the production of the most abundant molecule in the gas

- H_2 - which cannot be formed efficiently in the gas under low-density conditions (Herbst & Millar 2008).

The best studied mechanism for surface chemistry is the diffusive one, also known as the Langmuir-Hinshelwood mechanism, in which two species diffuse randomly over a surface until they find one another and possibly react. This and other mechanisms can be modeled by rate equations similar to those used for gas-phase systems of reactions, but the small size of dust particles in the interstellar medium renders this approach inaccurate because of the small number of reactive species on any given granular particle. More accurate but computer intensive techniques are based on stochastic principles, which take into account both discrete numbers of species and their fluctuations. There is also the problem of coupling a stochastic approach to surface chemistry with a deterministic (rate-equation) approach to the gas-phase chemistry. This problem has been partially solved by using stochastic techniques for the gas-phase chemistry even if they are not really needed (Vasyunin et al. 2009).

The complexity of a kinetic analysis also depends upon the heterogeneity and time dependence of the physical conditions of the source being modeled. The simplest case is one in which the physical conditions are both constant and homogeneous. Even for cold cores not involved in star formation, this so-called pseudo-time-dependent calculation is an approximation, which, moreover, gives us little knowledge as to what the initial chemical concentrations are. Nevertheless, it is often used for cold cores in dense clouds, with starting conditions in which all elements are atomic except for hydrogen, or with slightly more complex initial abundances that resemble those measured for diffuse clouds, where the chemistry is far less complex. The agreement between observation and model results is often best at a time of 10^{4-6} yr, before steady-state conditions are reached in a gas-phase analysis. At later times, the abundances of complex molecules decline precipitously as most of the carbon in them is converted into carbon monoxide. A more complex physical situation is a one-dimensional "photon-dominated region" (PDR) in which a nearby star illuminates and heats up portions of a diffuse or dense cloud depending upon the distance of each portion of the cloud from the exciting star. A more complex temporal situation involves a so-called "hot core" , which is a cold core that is heated up to a temperature of 100-300 K depending upon the mass of the star being formed inside it. A protoplanetary disk, which is in the act of collapsing into an extra-solar planetary system, is a PDR in two dimensions, the distance along the midplane of the disk from the newly formed star, and the height of material above and below the midplane. The most complex situation requires the use of hydrodynamics along with the chemical simulation (Aikawa et al. 2008).

Table 1. Major Classes of Reactions

Studied	Class
Well	Cosmic Ray Ionization
Well	Photodissociation
Well	Ion-neutral reactions
Well	Radical-neutral reactions
Well	Dissociative recombination
Poorly	Radiative association
Poorly	Radiative attachment
Poorly	Ion-ion recombination

2. Gas-phase chemical networks and cosmic rays

Chemical gas-phase networks used in simulations started in the era when cold clouds were the primary objects of study, and so the chemistry is mostly a low-temperature chemistry, in which reactions that are significantly endothermic or have intermediate barriers, known as activation energy barriers, play a negligible role. Table 1 lists some of the major classes of reactions found in the standard low-temperature gas-phase networks. The reaction types are divided into two classes - those studied relatively well in the laboratory or theoretically and those studied relatively sparsely or not at all. For a detailed discussion of these types of reactions, as well as surface processes, used in interstellar models, see Wakelam et al. (2010) and the URL http://kida.obs.u-bordeaux1.fr/ . The ma-

jor networks have been augmented by reactions that operate at temperatures as high as 800 K in order to simulate warmer regions near stars, such as the inner portions of protoplanetary disks (Harada et al. 2010).

The key initiating process for most sources is ionization by cosmic rays, unless a stronger alternative source of ionization exists locally. Examples of strong local sources include black holes, which emit copious amounts of X-rays, and bright stars, which emit significant amounts of VUV radiation. The rate of ionization of atomic hydrogen by cosmic rays is labeled ζ and has units of s^{-1}. Since in most sources studied observationally, the atomic hydrogen has been mainly converted to its molecular form, one often sees the rate of ionization for H_2, ζ_{H_2} used; this ionization rate is roughly double that of H (Rimmer et al. 2011). For cosmic rays to initiate the growth of complex molecules from a mainly atomic inventory of gases a medium range of ζ is required; too large a value just destroys molecular complexity while too small a value is inefficient in achieving anything chemical. The range of values of chemical interest is $10^{-17} - 10^{-14}$ s^{-1}, and not surprisingly values throughout this range have been utilized in chemical models over the last 40 years (Rimmer et al. 2011). The lowest value of ζ in the range leads to a fractional ionization of $\approx 10^{-7}$ for a cold core at a density of 10^4 cm^{-3}, where "fractional" typically refers to concentration with respect to the total density of hydrogen nuclei. Diffuse clouds have a higher fractional ionization of 10^{-4} due mainly to photoionization of neutral atomic carbon. Since most of the ionization in dense sources is accomplished by low-energy cosmic rays, and the flux of these rays is highly uncertain, values of ζ are difficult to determine theoretically, and ζ is often treated as a parameter. A more-or-less standard value for cold and warm dense clouds is $(1 - 5) \times 10^{-17}$ s^{-1}.

More recently, a number of calculations of the column-dependence of the flux of cosmic rays as a function of energy have been undertaken and show, with a large amount of uncertainty, that the cosmic ray ionization rate decreases sharply ($\approx 1 - 2$ orders of magnitude) as cosmic rays are extinguished in their path towards the center of dense cold cores. Thus, an ionization rate of 10^{-15} s^{-1} at the edge of a dense cloud can be reduced to less than 10^{-16} s^{-1} by the center of a dense cloud, while it would hardly be reduced at all towards the center of a diffuse cloud. In a recent calculation, Rimmer et al. (2011) have shown that a column-dependent ionization rate used in a one-dimensional PDR model of the so-called Horsehead Nebula in Orion leads to somewhat better agreement with observation for small carbon-chain species than do fixed rates. The result is still controversial however. It should also be mentioned that it is quite likely that the spectral flux of cosmic rays throughout our galaxy and others is not constant, so that it is quite likely that even in diffuse clouds, different sources can have very different ionization rates.

Once H_2 is formed on granular surfaces and desorbed into the gas phase, its partial ionization by cosmic rays leads to the ion H_2^+, which almost "immediately" reacts with H_2 via an ion-neutral reaction to form H_3^+:

$$H_2^+ + H_2 \longrightarrow H_3^+ + H. \quad (1)$$

A glimpse of how unusual molecules are produced by ion-neutral reactions can be seen by consideration of a sequence of reactions leading to water and the OH (hydroxyl) radical especially important in dense clouds:

$$O + H_3^+ \longrightarrow OH^+ + H_2, \quad (2)$$

$$OH^+ + H_2 \longrightarrow H_2O^+ + H, \quad (3)$$

$$H_2O^+ + H_2 \longrightarrow H_3O^+ + H, \quad (4)$$

$$H_3O^+ + e^- \longrightarrow OH + 2H; H_2O + H. \quad (5)$$

Here the ion-neutral reactions lead to the formation of the rather inert ion H_3O^+, which is depleted by reaction with electrons in a so-called dissociative recombination reaction. Such reactions favor three-body to two-body channels, so that the "unsaturated" (hydrogen-poor) radical OH is favored over water. The term "radical" refers to a reactive neutral species with an odd number of electrons. The

neutral products of a number of dissociative recombination reactions have been studied in storage rings in three European countries (Sweden, Denmark, Germany). Had we started with atomic carbon, many carbon-chain species would have been formed by similar but longer synthetic reaction sequences involving positive ions. But, most of these species would also be hydrogen-poor despite the high abundance of molecular hydrogen.

Recent work on low-temperature reactions involving two neutral species, one a reactive radical, shows that such reactions can be rapid at low temperature. One important example is the reaction (Sims et al. 1993)

$$CN + C_2H_2 \longrightarrow HCCCN + H, \quad (6)$$

which can be more efficient in the production of HCCCN than the ion-molecule synthesis through the precursor ion $H_2C_3N^+$.

The formation of negative ions in dense sources starts from thermal electrons produced originally by cosmic ray bombardment. In a low-density plasma, negative molecular ions are produced initially by radiative attachment to neutral species; i.e.,

$$A + e^- \longrightarrow A^- + h\nu, \quad (7)$$

a poorly understood process, which involves the temporary attachment of an electron to a neutral species to form a negative ion which is then stabilized by emission of a photon. Simple statistical calculations of the rate of radiative attachment show that the process can be efficient for neutral species of 5 or more atoms as long as the electron binding energy (electron affinity) is as large as 3.5 − 4.0 eV (Osamura & Herbst 2008). For abundant radicals such as C_6H, which possess high electron affinities, observable abundances of anions are predicted, in agreement with observation. Unfortunately, radiative attachment has not been studied seriously, and is listed in Table 1 among the classes of poorly studied reactions. A similar process, radiative association, which involves the association of two heavy species via emission of a photon is also poorly studied, and yet is estimated to be efficient in the synthesis of larger species, especially if one of the reactants is an ion (Herbst et al. 2009). The third class of poorly studied reactions in Table 1 consists of neutralization reactions between positive and negative ions; construction of several pieces of apparatus to study the rates and products of such reactions is in progress.

2.1. Other roles of ζ

In addition to the direct ionization of atomic and molecular hydrogen, cosmic rays play other roles in chemical simulations. First, they produce secondary electrons, which both ionize and excite other species. The secondary ionization is typically included in the parameter ζ but the excitation of atomic and molecular hydrogen, upon fluorescence, leads to a far ultra-violet spectrum that can photodissociate other molecules at rates $A\zeta$, where $A \gg 1$. The rates of this dissociation compete with dissociation by chemical processes. Finally, cosmic rays can interact with molecules on and in dust particles in a variety of manners. Cosmic rays can desorb molecules from the mantles of cold dust particles both by sputtering and by heating of the particles to allow evaporation. In addition they can fragment dust particles if enough energy is deposited.

3. An unusual source

The *Herschel Space Observatory* is currently studying the heavens in the far infra-red region of the spectrum, which produces spectra involving high-frequency rotational transitions and low-frequency vibrational transitions of molecules. The rotational transitions arise from light hydrides and from transitions between excited levels of heavier species. Among the many interesting types of sources seen are those lying in front of other sources that emit continua in the far-infrared and so can be used as lamps for absorption studies. The continua normally arise from so-called HII (proton) regions associated with high-mass star formation. Absorption of these continua occurs from somewhat cooler regions surrounding the sources and from regions between them and us. In the latter category are myriads of diffuse clouds in the spiral arms of our Galaxy. Studies

of these diffuse clouds by *Herschel* have revealed a surprisingly complex chemistry containing a number of polyatomic molecules as well as the ionic species OH^+ and H_2O^+. The latter has been somewhat of a surprise, since these ions are destroyed on every collision with molecular hydrogen, and so are expected to be very difficult to detect. Nevertheless, revised models have been proposed, in which the diffuse clouds with these ions have their hydrogen mainly in atomic rather than molecular form and possess a value of ζ somewhat in excess of 10^{-16} s^{-1} (Neufeld et al. 2010).

A more exotic source lies in front of the HII region known as Orion KL (Gupta et al. 2010). The source appears to be a dense outflow, and is rich in OH^+ and H_2O^+, although the more likely ion to be present, H_3O^+, is not detected. There is also much neutral water and ultra-violet radiation from the HII region at an intensity roughly 10^4 times the average interstellar radiation field. To account for these unusual observations, Rimmer & Herbst (in preparation) have considered models based on a one-dimensional PDR, in which the inner edge of the outflow reaches temperatures as high as 500 K. Nevertheless, the large UV radiation field by itself cannot account for the observations, so Rimmer & Herbst have had to include large values of ζ as well in three different models:

1. A model with $\zeta = 2 \times 10^{-14}$ s^{-1}. Here the ionic abundances can be reproduced, but the calculated abundance of water is low by at least several orders of magnitude!
2. A model with an inflow of water from other regions of the cloud and a somewhat lower value of ζ depending upon the chosen density. This model does a reasonable but imperfect job of reproducing all of the observed abundances, with neutral water and H_2O^+ low by an order of magnitude or so.
3. A model, currently under study, starting with icy mantles from a cooler era.

In all of the models, the unusual ions are produced near the inner edge of the outflow source in a region of high temperature and large amounts of atomic hydrogen, while the water column is produced under more typical dense cloud conditions. Nevertheless, it is clear that the complexity of the source is far greater than the models used to try to understand it. Complexity will soon become even more of a salient feature of interstellar sources when the *Atamaca Large Millimeter Array (ALMA)* starts observing the heavens with unparalleled spatial resolution.

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