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Chemistry in Quiescent and Star-Forming Molecular Clouds

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Abstract. Recent advances in astrochemistry are discussed and illustrated with examples obtained with new submillimeter and infrared facilities. Simple molecules such as H_3^+, H_2D^+, CH^+, CH_3, H_2O and O_2 provide tests of the basic hydrogen-, carbon- and oxygen chemical networks, as well as clues to the physical structure of molecular clouds. Systematic observations of high-mass star-forming regions allow the chemical evolution from collapsing clouds to hot cores and ultracompact H II regions to be traced. Chemical diagnostics at different wavelengths are identified and the prospects for future observations are discussed.

1. Introduction

Since the development of millimeter telescopes in the early 1970's, more than 120 different molecules have been detected in interstellar space. The first discoveries date back to the late 1930's, when interstellar CH, CH^+ and CN were observed through optical absorption lines superposed on the spectra of background stars. More recently, improved facilities at submillimeter and infrared wavelengths using ground-based telescopes and the Infrared Space Observatory (ISO) have led to the detection of a wealth of new features. As a result, the rate of new identifications continues at a steady pace of $\sim$3 species per year. Besides being interesting in their own right, these molecules are key to our understanding of the neutal interstellar medium.

First, molecular observations can be used to trace the physical structure of the clouds. Compared with atoms, molecules have a much richer energy level structure and their excitation can be used to probe densities and temperatures ranging from 10–3000 K and densities from $10^2 - 10^9$ cm^{-3} (see Genzel 1992 for overview). Molecular lines can also be used to trace the cosmic ray ionization rate ζ and magnetic field strengths, and they are the only probes of the velocity structure (collapse, outflow, turbulence, ...) of dense star-forming regions up to hundreds of magnitudes of extinction.

Second, molecules are excellent chemical diagnostics, because their abundances respond to the changes in density, temperature and amount of ultraviolet irradiation that characterize different types of molecular clouds. Thus, different molecules have enhanced abundances in, for example, cold clouds, shocks, photon-dominated regions (PDRs), and hot cores near massive young stars. The chemical transformations of molecules from quiescent clouds to star-forming regions and circumstellar disks is also of basic astrochemical interest, since these disks provide the raw material from which future planetary systems and perhaps life are made.

Finally, interstellar clouds form a unique chemical laboratory with conditions that are difficult to simulate in a laboratory on Earth. Some molecules like HCO^+, N_2H^+ and HC_7N were identified in space before they were ever synthesized in a laboratory. More recently, new solid-state features due to ices and crystalline silicates have been found at infrared wavelengths. This stimulates fresh views on basic chemical processes and molecular spectroscopy.

This brief lecture will focus on three themes in astrochemistry: (i) simple molecules as tests of the basic chemistry networks in quiescent clouds; (ii) chemistry as a probe of the poorly understood physical structure of the interstellar medium; and (iii) chemical diagnostics during star formation. These themes will be illustrated by recent observations of molecules at submillimeter and infrared wavelengths. Other more extensive reviews and lectures on astrochemistry can be found in the recent books 'The Molecular Astrophysics of Stars and Galaxies', eds. T.W. Hartquist & D.A. Williams (1998), 'Astrochemistry: From Molecular Clouds to Planetary Systems', IAU Symposium 197, eds. Y.C. Minh & E.F. van Dishoeck (2000), 'Formation and Evolution of Solids in Space', eds. J.M. Greenberg & A. Li (1999), 'Solid Interstellar Matter: the ISO Revolution', eds. L. d'Hendecourt et al. (1999), and 'Laboratory Astrophysics and Space Research', eds. P. Ehrenfreund et al. (1999), and in the reviews by Langer et al. (2000), Ehrenfreund & Charnley (2000), van Dishoeck & Hogerheijde (1999) and van Dishoeck & Blake (1998). An up-to-date list of detected molecules as well as references to molecular data bases and astrochemistry programs can be found through the home page of the IAU working group on astrochemistry `http://www.strw.leidenuniv.nl/~iau34`.

2. Methods: recent developments

2.1. Observations

Since the previous Tetons meeting on 'Interstellar Processes' in 1986, there have been several important observational developments. Submillimeter telescopes on high and dry sites equipped with sensitive heterodyne receivers and bolometer arrays have been developed, which allow the chemistry to be probed in higher density and temperature regions associated with star-forming clouds. Moreover, typical beams are only $15''$–$30''$, compared with $\sim 1'$ in the earlier lower frequency data. Pioneering millimeter interferometry observations can probe even smaller scales down to $< 1''$, although applications to astrochemistry are still limited (e.g., van Dishoeck & Blake 2000). At the distance of the nearest star-forming regions (Taurus, Ophiuchus), $30''$ corresponds to $\sim$ 5000 AU —the typical size of a collapse envelope around a protostar—, whereas $1''$ corresponds to $\sim$ 140 AU —the typical size of a circumstellar disk around a pre-main sequence star. The first heterodyne submillimeter observations from space obtained with the Submillimeter Wave Astronomical Satellite (SWAS) have just been reported (Melnick et al. 2000a), and provide crucial constraints on H_2O and O_2, two molecules whose large abundances in the Earth's atmosphere prevent ground-based searches.

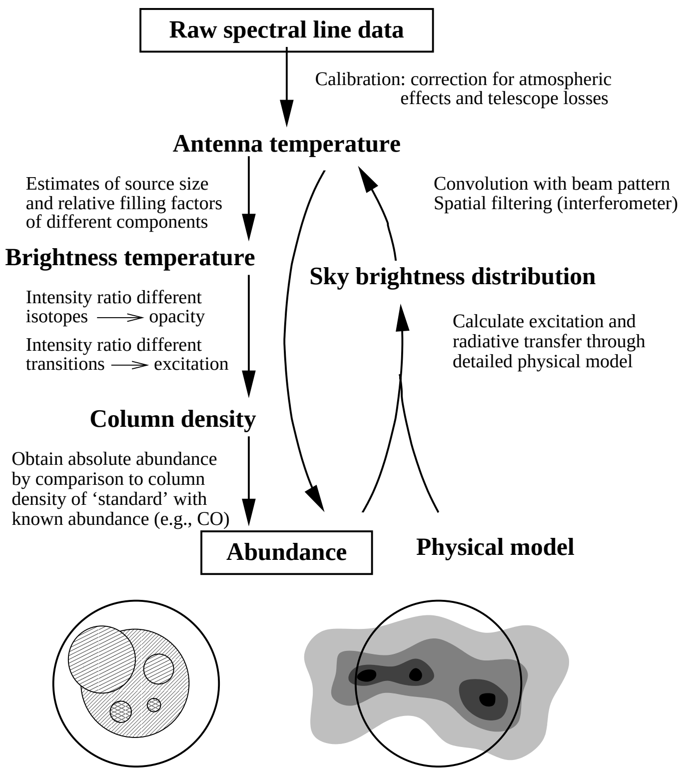

Figure 1. The steps involved in deriving molecular abundances from spectral line data. The left-hand side shows the 'homogeneous' approach as outlined by Irvine et al. (1987); the right-hand side shows the more modern 'detailed' approach from which abundance profiles can be derived (from: van Dishoeck & Hogerheijde 1999).

Improved detectors at infrared wavelengths have opened up the near- and mid-infrared spectrum using ground-based telescopes (e.g., Lacy et al. 1989, Evans et al. 1991, Geballe & Oka 1996) and the Kuiper Airborne Observatory (KAO, Haas et al. 1995), whereas ISO provided the first opportunity to survey the entire infrared spectrum from 2–200 μm unhindered by the Earth's atmosphere (see van Dishoeck & Tielens 2001 for review). Together, the ground and space-based data have allowed the first complete inventory of ices and other solid-state species in interstellar and circumstelllar clouds, as well as detections of gas-phase molecules without dipole moments such as H_3^+, CH_4 and C_2H_2, which cannot be observed at (sub-)millimeter wavelengths.

Finally, new optical and ultraviolet observations from the ground and from space using the Hubble Space Telescope (HST) and the Far Ultraviolet Space Explorer (FUSE) provide crucial constraints on elemental abundances (e.g., Meyer 1997), direct observations of H_2 and HD in diffuse and translucent clouds (e.g., Snow et al. 2000), and an ever increasing number of diffuse interstellar bands, whose carriers still remain unidentified (e.g., Tuairisg et al. 2000). It will be a

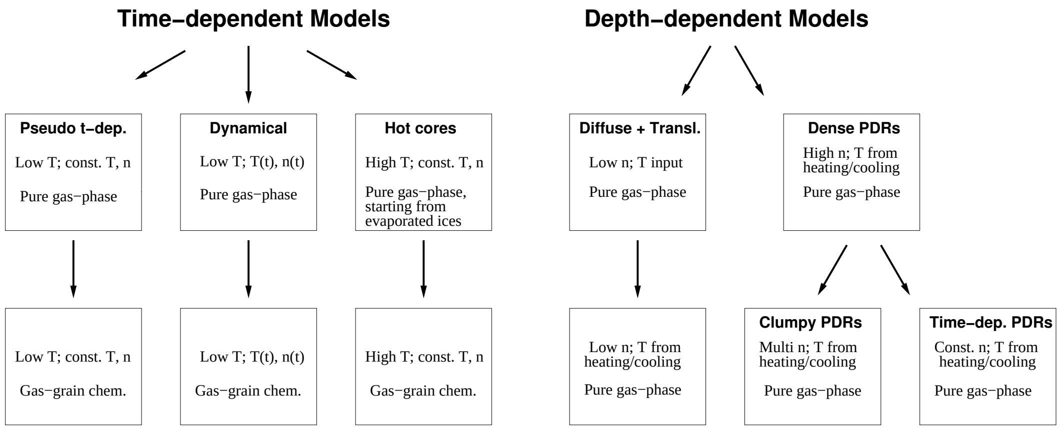

Figure 2. Overview of types of models used in astrochemistry. All models need as input the cosmic ray ionization rate ζ, the elemental abundances and a network of chemical reactions. In the time-dependent models, the initial conditions also need to be specified, whereas in the depth-dependent models the incident radiation field, grain scattering parameters and geometry are required. The external radiation field is usually neglected in time-dependent models of dark clouds.

challenge to integrate the information obtained at different wavelengths into a coherent picture of astrochemistry.

2.2. Analysis

The analysis tools in the last decade have developed from simple 1-dimensional (1-D) radiative transfer models using, for example, the large velocity gradient method, to full 1-D, 2-D and even 3-D (accelerated) Monte Carlo and Lambda Iteration codes (e.g., Juvela 1997, Yates et al. 1997, Hogerheijde & van der Tak 2000). Indeed, the traditional method outlined by Irvine et al. (1987) for determining molecular abundances from spectral line data assuming a single excitation temperature is being replaced by modern methods in which the starting point is a physical model of the region from which abundance *profiles* can be determined (see Figure 1).

2.3. Chemistry

Chemical models have developed from the standard pseudo time-dependent gas-phase models in which temperature and density are kept constant (e.g., Herbst & Leung 1989, Millar et al. 1991) to fully time-dependent models in which the physical parameters change with time (e.g., Rawlings et al. 1992, Bergin & Langer 1997) (see Figure 2). Most chemical models now also include a detailed gas-grain chemistry in which molecules accrete, form and desorb from the grains (e.g., d'Hendecourt et al. 1985, Hasegawa & Herbst 1993), although the precise formulation is still under discussion (Tielens & Charnley 1997, Caselli et al. 1998). The chemistry of evaporated ices leading to complex organic molecules has been developed (e.g., Charnley et al. 1992, Charnley 1997) and is an essential ingredient for explaining the chemistry in 'hot cores' around massive young stars. Finally, models of the chemistry and thermal balance of PDRs have been extended from the 1-D homogeneous steady-state models developed by Tielens & Hollenbach (1985) to 1-D and 2-D inhomogeneous 'clumpy' clouds (e.g., Spaans 1996, Störzer et al. 1996) and 1-D time-dependent PDRs (e.g., Goldshmidt & Sternberg 1995, Störzer & Hollenbach 1998, Bertoldi & Draine 1996). Detailed models have also been applied to the chemistry in shells around evolved stars, but are not discussed here (see Glassgold 1996 for review).

3. Simple species as tests of basic chemistry

The basic gas-phase chemical networks leading to the formation of the simplest molecules within each of the elemental families can be found in van Dishoeck (1998). The extent to which these models are successful in explaining observations will be illustrated with recent examples from each of the H-, C- and O-families. The focus here is on gas-phase molecules; the exciting developments in observations of solid-state features are covered in the chapters by Tielens and Sandford (this volume).

3.1. Hydrogen chemistry: H_3^+ and H_2D^+

Ever since the development of the basic gas-phase chemistry by Herbst & Klemperer (1973), the H_3^+ ion has been recognized to be a cornerstone of the ion–molecule chemical networks. After many unsuccessful attempts, the ion was finally detected by Geballe & Oka (1996) through its infrared absorption lines around 3.7 μm toward two massive young stars, and it has subsequently been observed along a dozen lines of sight (e.g., McCall et al. 1999, Black 2000, see Figure 3). H_3^+ is formed by cosmic ray ionization of H_2, where the resulting H_2^+ reacts rapidly with H_2 to form H_3^+. In dense clouds, H_3^+ is removed principally by reactions with CO, O and N_2. In this simple scheme, the concentration of H_3^+ is constant at about 10^{-4} cm^{-3}, independent of density (Lepp et al. 1987). Thus, its column density is directly proportional to the product of the cosmic ray ionization rate ζ and the length of the cloud L. McCall et al. (1999) have used this property to determine the typical sizes of the observed regions to be 0.4-1.7 pc. Van der Tak & van Dishoeck (2000) took detailed physical models of the envelopes of massive young stars based on other data to infer $\zeta \approx (2.6\pm1.8)\times10^{-17}$ s^{-1} from the H_3^+ and HCO^+ data.

This simple H_3^+ chemistry works well for dense clouds, but fails to explain the large observed H_3^+ column in the diffuse cloud(s) along the line of sight toward Cyg OB2 no. 12 (Geballe et al. 1999, see Figure 3). In these regions, the H_3^+ destruction is dominated by dissociative recombination with electrons — $H_3^+ + e \rightarrow H_2 + H$ or $H + H + H$ —, a process whose rate coefficient has been subject to considerable controversy (see Larsson 2000 for review). The experimental determinations using ion storage rings indicate a relatively rapid rate coefficient of 10^{-7} cm^3 s^{-1} at T=300 K, which would imply an unreasonably long pathlength of ∼1000 pc for typical values of ζ. Possible remedies include use of a slower recombination rate, an enhanced ionization rate near CygOB2 no. 12 (Black 2000), or a 'clumpy' cloud model (Cecchi-Pestellini & Dalgarno 2000). Obser-

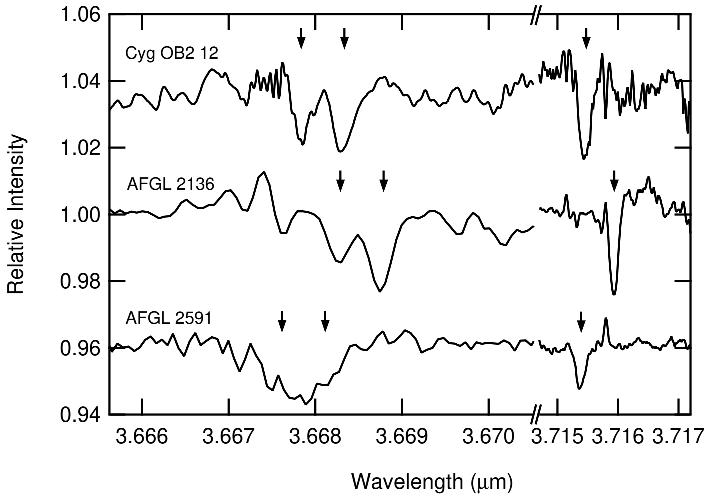

Figure 3. Spectra of H_3^+ obtained with the UKIRT (left) and Kitt Peak (right) telescopes toward the deeply-embedded massive young stars GL 2136 and GL 2591, and of the diffuse cloud(s) along the line of sight toward Cyg OB2 no. 12. The arrows indicate the positions of the H_3^+ lines arising from different lower levels (from: McCall et al. 1999, Geballe et al. 1999).

vations of other lines of sight through diffuse and translucent clouds are needed to determine whether such high H_3^+ abundances are a general phenomenon.

In contrast with H_3^+, H_2D^+ has a small dipole moment and can be searched through its $1_{10}-1_{01}$ submillimeter emission line at 372 GHz. H_2D^+ has recently been detected toward the deeply-embedded low-mass protostar NGC 1333 IRAS 4A (Stark et al. 1999). It is formed through the H_3^+ + HD $\rightarrow$ H_2D^+ + H_2 reaction, which is exoergic by $\sim$230 K due to the difference in zero-point vibrational energy of the molecules involved. Thus, at low temperatures $\lesssim$50 K, the abundance of H_2D^+ is greatly enhanced compared with the overall [D]/[H] abundance ratio, a process called 'fractionation'. In the cold envelope around NGC 1333 IRAS 4A, much of the CO and O —the main destroyers of H_2D^+— is frozen out onto the grains so that the H_2D^+ abundance is even further enhanced. The observed line strength is consistent with this model. H_2D^+ in turn is responsible for the high fractionation found for species such as DCO^+ and DCN (e.g., Wootten 1987, Roberts & Millar 2000), and together these species testify to the importance of ion-molecule chemistry.

3.2. Carbon chemistry: CH^+ and CH_3

The CH^+ mystery. CH^+ was detected in diffuse clouds through its optical absorption lines in 1941, but its large observed abundance is still unexplained (see van Dishoeck 1998 for a recent summary). The problem is caused by the fact that the direct formation route C^+ + H_2 $\rightarrow$ CH^+ + H is endoergic by 4640 K, so that at low temperatures (< 1000 K) only slower, indirect routes are effective. In cold clouds, the formation of carbon-bearing molecules is initiated

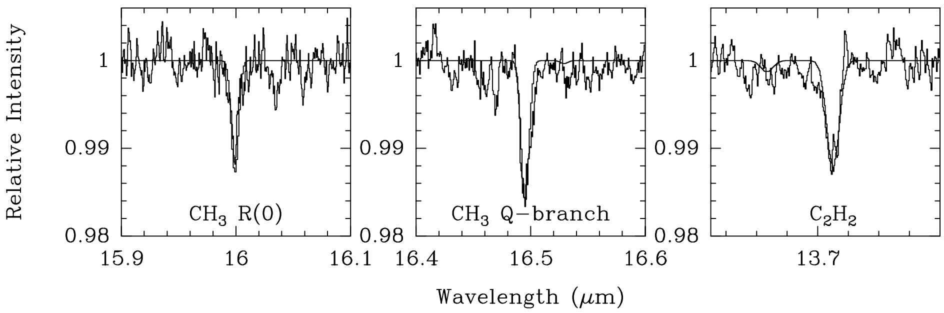

Figure 4. Detection of the $R(0)$ line at 16.0 μm and the Q-branch at 16.5 μm of interstellar gas-phase CH_3 toward SgrA* using the Short Wavelength Spectrometer on ISO. The ratio of the two lines indicates a low excitation temperature of (17 ± 2) K. The detection of gas-phase C_2H_2 is shown as well (from: Feuchtgruber et al. 2000).

by the $C^+ + H_2 \rightarrow CH_2^+ + h\nu$ reaction, followed by reactions with H_2 and dissociative recombination. This chemistry leads to abundant CH and C_2, but not CH^+.

The rates of the reactions involved in the CH^+ chemistry are well known, so in this case the discrepancy points to limitations in the adopted physical models. Interstellar shocks, in particular the hydromagnetic $C-$type shocks, have been proposed as a solution, but appear inconsistent with the observed CH^+ line profiles and the continued increase of CH^+ column density with A_V. More recent explanations favor turbulence as the driving force behind the CH^+ production, either by creating localized hot pockets of gas due to intermittent dissipation of turbulence (e.g., Joulain et al. 1998) or by setting up a non-Maxwellian velocity distribution in which a fraction of C^+ and H_2 move at sufficient relative speed to overcome the reaction barrier (e.g., Spaans 1995).

Whatever its precise formation mechanism, the presence of enhanced CH^+ can affect the abundances of other related molecules such as HCO^+ and HCN through reactions of CH^+ with O and N. HCO^+, HCN and other molecules have been detected in surprisingly high abundances in diffuse clouds through millimeter absorption lines against background quasars (Lucas & Liszt 1997). Together with CH^+, these molecules provide important clues about the structure of, and physical processes in, low density molecular clouds. Future (magneto-)hydrodynamical models of turbulent clouds such as developed by Ostriker et al. (1999) and Klessen et al. (2000) should be tested against these data.

Detection of CH_3. CH_3, like H_3^+, is a symmetric molecule which can only be detected through its vibrational transitions at infrared wavelengths. Its strongest ν_2 bending mode occurs near 16 μm, close to the strong atmospheric CO_2 ν_2 absorption at 15 μm, and can therefore only be observed from space. CH_3 was recently detected by ISO toward SgrA* (Feuchtgruber et al. 2000, see Figure 4). Gaseous CH and C_2H_2 have been observed for the same line of sight, whereas CH_4 is only seen in solid form. The inferred column densities of the gas-phase species are comparable, whereas the limit on gas-phase CH_4 is significantly below that of CH_4-ice. The absorption is thought to arise in several cold diffuse and translucent clouds along the line of sight toward the Galactic center. Gas-phase models of such clouds with central temperatures of $\sim$15 K, densities of a few$\times 10^3$ cm^{-3} and $A_V \approx 3$ mag have successfully reproduced the observed column densities of small carbon-bearing molecules like CH, C_2 and C_2H (e.g., van Dishoeck & Black 1989, Turner 2000). However, these same models fail to reproduce the observed column density ratios CH:CH_3:$C_2H_2$$\approx$1:1:1. At the edge of the model clouds, CH is the most abundant carbon-hydride, but deeper in the cloud CH_3, CH_4 and C_2H_2 become more prominent as the ultraviolet radiation decreases. This example illustrates the importance of depth-dependent models for comparison with observations of translucent clouds: the observed ratio can be reproduced as a local density ratio at a specific location or A_V in the cloud, but not when integrated from edge to center. Possible solutions include a mix of diffuse and dense clouds along the line of sight but such a mix would have to be tailored rather specifically. Alternatives are the inclusion of gas-grain chemistry in translucent clouds or reactions of H with Polycyclic Aromatic Hydrocarbons (PAHs) or Hydrogenated Amorphous Carbon (HAC), whose presence is revealed through absorption at 3.4 μm and 6.2 μm (Chiar et al. 2000, Schutte et al. 1998).

The presence of large amounts of CH_3 and C_2H_2 in translucent gas has implications for building long carbon chains and other large molecules which may be the carriers of the diffuse interstellar bands. It is clear that much remains to be learned about the chemistry of the larger carbon-bearing molecules, and that better knowledge of basic reaction rate coefficients will be crucially important.

3.3. Oxygen chemistry: H_2O and O_2

H_2O and O_2 are predicted to be the dominant oxygen-bearing molecules in dense molecular gas by pure gas-phase chemical models (e.g., Millar et al. 1997, see Figure 6 left), but ground-based data have been limited to high-excitation (masing) H_2O lines and isotopic $^{16}O^{18}O$ searches away from the atmospheric lines. ISO and SWAS provided the first opportunity for sensitive searches of thermal lines of these molecules, improving significantly on pioneering KAO and balloon data (e.g., Zmuidzinas et al. 1995, Olofsson et al. 1998).

H_2O: extremely high and low abundances. ISO has detected a multitude of gas-phase H_2O lines in warm star-forming regions, including the ν_2 vibration-rotation lines around 6 μm in absorption (van Dishoeck & Helmich 1996, Dartois et al. 1998) and emission (González-Alfonso et al. 1998), the pure-rotational lines in absorption at 25–45 μm (Wright et al. 2000), and the pure rotational lines in absorption and emission (e.g., Liseau et al. 1996, Harwit et al. 1998, Nisini et al. 1999, Spinoglio et al. 2000). The inferred abundances range from $\sim 10^{-5}$ to a few $\times 10^{-4}$, locking up a significant fraction —if not all— of the available gas-phase oxygen.

In contrast, the SWAS satellite measures orders of magnitude lower H_2O abundances in molecular clouds (e.g., Snell et al. 2000). SWAS observes the lowest $1_{10}-1_{01}$ H_2O and $H_2^{18}O$ transitions at 557 and 548 GHz at high spectral resolution and is therefore also sensitive to cold H_2O (see Figure 5). The SWAS beam is $3.3' \times 4.5'$, compared with the ISO-LWS beam of $\sim 1.3'$. The inferred abundances in the large SWAS beam are only $10^{-9}-10^{-8}$, even in warm GMCs,

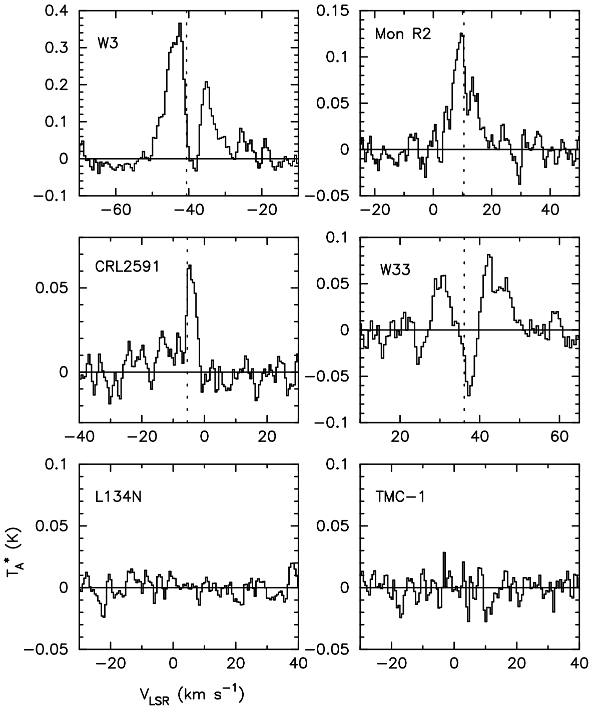

Figure 5. SWAS spectra of the $1_{10} - 1_{01}$ transition of ortho-H_2O for six cloud cores. The line center velocity of the ^{13}CO $5-4$ transition observed simultaneously with SWAS is indicated by the dotted line. Note the complex, self-absorbed line profiles for deeply embedded sources such as W 3 and W 33 and the lack of emission from dark clouds such as L134N and TMC-1 (from: Snell et al. 2000).

whereas the best upper limit for dark clouds is 7×10^{-8}. Only Orion and SgrB2 appear to have higher H_2O abundances on large scales, but the $H_2^{18}O$ data indicate that the majority of the enhanced H_2O is in the outflow in Orion rather than the warm quiescent ridge gas (Melnick et al. 2000b). Because only a single line is observed with SWAS, the analysis is sensitive to the adopted density. Beam-averaged densities have been derived from multi-transition CS and HC_3N data but may not be representative of all of the molecular gas in the SWAS beam.

Missing O_2. Deep SWAS searches for the O_2 $3_3 - 1_2$ line at 487 GHz toward more than a dozen sources have not revealed any detections to date (Goldsmith et al. 2000). The 3σ upper limits are typically 7×10^{-7}, nearly two orders of magnitude below steady-state model predictions. Together with the low gas-phase H_2O abundances, this implies that most of the gas-phase oxygen must be in atomic O. Indications of high atomic O abundances in translucent and dense clouds have been suggested by observations of the [O I] 63 μm line (e.g., Poglitsch et al. 1996, Baluteau et al. 1997, Caux et al. 2000), although the interpretation of these data is hampered by limited spectral resolution.

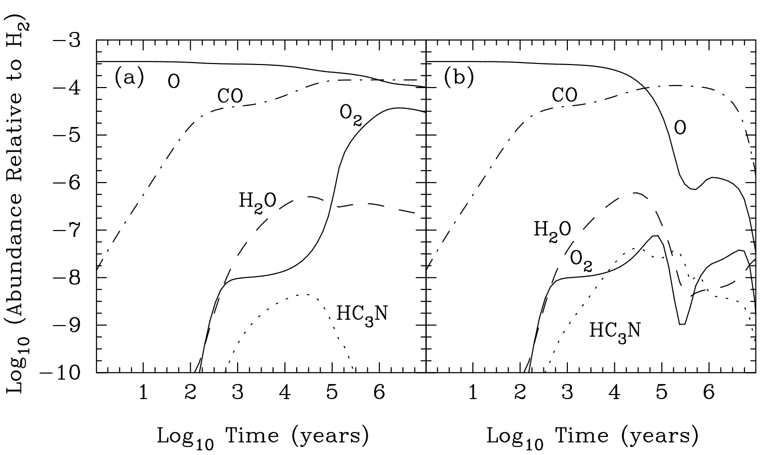

Figure 6. Abundances of CO, O, O_2, H_2O and HC_3N as functions of time for two models of the gas-grain chemistry for $n = 10^5$ cm^{-3} and $T_{\rm gas} = T_{\rm dust} = 30$ K. The HC_3N behavior is typical of that of other carbon-chain molecules. (a) Model including depletion and desorption onto grains, but no surface chemistry. Note the characteristic 'early-time' peak of the carbon-chains around a few $\times 10^4$ yr. (b) Model including depletion and desorption onto grains but with a simple surface chemistry. The latter models are consistent with the observed H_2O abundances of 10^{-9} to a few $\times 10^{-8}$, and with the 3σ upper limits for O_2 of 10^{-6} (from: Bergin et al. 2000).

H_2O and O_2 models. The high H_2O abundances observed by ISO in warm regions can be explained by two processes: (i) ice evaporation in regions with $T_{\rm dust} \gtrsim 90$ K; and (ii) high-temperature gas-phase chemistry at $T_{\rm gas} > 230$ K, where atomic O is driven into H_2O through the reactions $O + H_2 \rightarrow OH + H$ and $OH + H_2 \rightarrow H_2O + H$. The latter process likely dominates in large-scale shocks such as in Orion (Harwit et al. 1998), whereas both processes must operate in the dense warm envelopes around low- and high-mass stars. High spectral and spatial resolution data such as will be provided by the Far Infrared and Submillimeter Telescope (FIRST) are needed to disentangle their contributions.

The low abundances of H_2O and O_2 found by SWAS on large scales in quiescent clouds are inconsistent with standard pure gas-phase chemistry models. Several explanations have been put forward. The most promising model for dark clouds includes gas-grain chemistry and freeze-out onto grains (Bergin et al. 2000, see Figure 6 right). In these models, gas-phase atoms such as O and C collide with the grains on time scales of $\sim 10^5$ yr and are assumed to be transformed into solid H_2O and CH_4, respectively. H_2O-ice is strongly bound to the surface and sticks as an icy mantle, whereas a large fraction of the weakly-bound CH_4 evaporates back into the gas phase. The resulting low gas-phase oxygen abundance naturally produces little O_2. Since this process changes the gas-phase [C]/[O] elemental ratio, consistency with the observed abundances of other molecules needs to be checked.

An alternative model has been proposed by Spaans & van Dishoeck (2001) for warmer GMCs, where the absence of H_2O and O_2 is explained by inhomogeneous 'clumpy' PDR models. The inhomogeneous structure of such clouds is well known from strong [C I] and [C II] fine-structure line emission which persists deeper into the region than predicted by homogeneous PDR models (e.g., Keene et al. 1985, Stutzki et al. 1998). In the large SWAS beam, the emission is likely dominated by lower density quiescent material rather than the dense gas in the immediate vicinity of any young star. The O_2 abundance is particularly reduced in clumpy models because the O_2 removal remains dominated by photodissociation up to large depths. The observed H_2O and O_2 abundances can be reproduced for reasonable clump parameters and extinctions. Variations on this type of model include the cyclic or turbulent models developed e.g., by Boland & de Jong (1982) and Xie et al. (1995) in which parcels of gas circulate from the dense shielded interior to the surface of the cloud where the molecules are photodissociated.

3.4. Successes and problems

The above examples of recent observations of simple molecules in a variety of clouds illustrate well the successes and problems of astrochemistry models. Pure gas-phase models can explain the abundances of many simple molecules in diffuse and translucent clouds and (clumpy) PDRs; the presence of H_3^+ and related high abundances of protonated species such as HCO^+ in dark clouds; the large deuterium fractionations, and the high abundances of unsaturated and metastable molecules such as HC_7N and l-C_3H. Problems include the presence of CH^+ and polyatomic molecules in diffuse and trannslucent clouds, and the fact that the observed abundances of carbon-chain molecules in dark clouds can only be reproduced if reactions of bare carbon-chains with O and/or N are assumed to be slow (Bettens et al. 1995). Another complication is the fact that the non-linear time-dependent equations give more than one solution in certain regions of parameter space, leading to 'bi-stability' and perhaps even chemical 'chaos' (e.g., Le Bourlot et al. 1995).

The presence of H_2 in diffuse clouds and that of ices in dark clouds emphasize the importance of gas-grain interactions, so that inclusion of accretion, surface chemistry and evaporation is important for explaining many aspects dense cloud chemistry. The main problems stem from the fact that the basic grain surface processes are not well understood and ill constrained by laboratory experiments. Even the grain surfaces themselves remain poorly characterized. As discussed in §2.3, the proper formulation of gas-grain chemistry is still under discussion. Finally, it remains difficult to identify efficient desorption mechanisms which prevent most molecules from freezing out on time scales longer than 10^6 yr in cold clouds without star formation.

The previous sections have shown examples of chemistry as a tracer of the physical stucture of the interstellar medium. Observations of extended [C I] and [C II] emission, together with the absence of O_2, point to an inhomogeneous structure. The presence of CH^+ in diffuse clouds is likely related to turbulence or low-velocity (few km s^{-1}) shocks. Detailed tests await a better quantitative description of the physical structure and processes.

4. Chemical evolution of massive star-forming regions

4.1. Observations and scenario

Massive star-forming regions ($L \approx 10^4 - 10^6$ $L_\odot$) have traditionally been prime targets for astrochemistry owing to their strong molecular lines and rich spectra (see Ohishi 1997, van Dishoeck & van der Tak 2000, Millar 2000 for reviews). Most surveys have centered on two sources, Orion-KL and SgrB2, which have led to an extensive inventory of molecules (e.g., Blake et al. 1987, Schilke et al. 1997, Nummelin et al. 1998). In recent years, improved submillimeter facilities have allowed a more systematic study of the envelopes of deeply-embedded massive young stellar objects (YSOs) with smaller beams. These data reveal large variations between sources, not only between different clouds but also within the same parent cloud. Examples are provided by the Orion-KL hot core compared with the Orion South source (Groesbeck 1995), SgrB2 (N) vs. (M) vs. (NW) (Nummelin et al. 2000), W 3 IRS5 vs. W 3 IRS4 vs. W 3(H_2O) (Helmich & van Dishoeck 1997) and G34.3 vs. G45.47 (Hatchell et al. 1998). Interferometer data reveal changes on even smaller scales of $\sim$ 2000 AU, with differentiation between O-rich and N-rich species. Examples are the Orion hot core vs. the compact ridge (e.g., Wright et al. 1996, Blake et al. 1996) and W 3(H_2O) vs. W 3(OH) (Wyrowski et al. 1999). The W 3(H_2O) position —the position of the H_2O masers— is an example of a 'hot core', which, like the Orion hot core, SgrB2(N), G34.3+0.15 and G327.3-0.6, is a dense ($\sim 10^7$ cm^{-3}), warm ($T \approx 200$ K) clump of gas with a rich spectrum containing strong lines of saturated organic molecules like CH_3OCH_3 and $HCOOCH_3$ (see Figure 7). Hot cores are often located close to ultracompact H II regions such as W 3 (OH) —the position of the OH masers–, but usually not coincident with them. Hot cores can be either internally heated by the young star (e.g., W 3(H_2O)) or externally heated (e.g., the Orion compact ridge) (Watt & Mundy 1999). Other massive YSOs like W 3 IRS5 and SgrB2(M) show strong lines of sulfur-bearing species such as SO and SO_2, whereas a third class of sources including W 3 IRS4 and SgrB2(NW) show mostly simple molecules, radicals and ions.

Complementary variations between sources are seen in the 2.4–200 μm infrared spectra obtained with ISO (van den Ancker et al. 2000). For example, the spectra of Cep A and W 3 IRS5 are characteristic of the deeply embedded phase in which the silicates and ices in the cold outer envelope and foreground material are seen in absorption. The spectra of S 106 and W 3(OH) are representative of more evolved massive YSOs with prominent PAH features and strong atomic and ionic fine-structure lines in emission (see Figure 8).

The most successful models for explaining these different chemical characteristics involve accretion of species in an icy mantle during the (pre-)collapse phase, followed by grain-surface chemistry and evaporation of ices once the young star has started to heat its surroundings (e.g., Millar 1997). The evaporated molecules subsequently drive a rapid high-temperature gas-phase chemistry for a period of $\sim 10^4 - 10^5$ yr, resulting in complex saturated organic molecules (e.g., Charnley et al. 1992, 1995). Thus, the abundance ratios of species such as CH_3OCH_3/CH_3OH show strong variations with time and may be used as 'chemical clocks' for a period of 5,000–30,000 yr since evaporation. Differentiation between O-rich and N-rich species can be either due to the different time

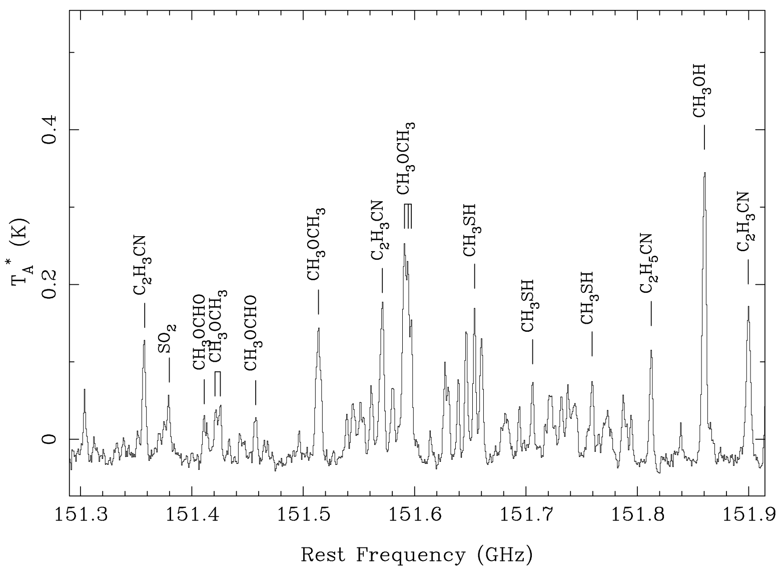

Figure 7. Example of part of the spectrum of a hot core region showing strong lines due to saturated molecules. This hot core, G327.3-0.6, was observed with SEST and is particularly rich in complex organic species (from: Gibb et al. 2000).

scales of the chemistries (the N-chemistry has a longer time scale) or to different initial compositions of the evaporating ices (Caselli et al. 1993). Once most of the envelope has cleared, the ultraviolet radiation can escape and create a PDR at the surrounding cloud material, resulting in photodissociation of molecules (e.g., HCN $\rightarrow$ CN) and excitation of PAHs to produce infrared emission. Finally, once an ultracompact H II region has formed, it gives rise to strong ionic lines.

Table 1 summarizes the chemical characteristics of the various physical components, together with the observational diagnostics at submillimeter and infrared wavelengths. Within the single-dish submillimeter and ISO beams, many of these components are blended together and higher spatial resolution data will be essential to disentangle them.

4.2. Example: a sample of infrared-bright massive YSOs

The availability of complete ISO spectra for a significant sample of massive young stars provides a unique opportunity to study these sources through a combination of infrared and submillimeter spectroscopy. Van der Tak et al. (2000a) selected 9 massive young stars with $L \approx 10^4 - 2 \times 10^5$ L$_\odot$, which are bright at mid-infrared wavelengths (12 μm flux > 100 Jy) and relatively nearby, d ~2 kpc. The sources are all in an early, deeply embedded evolutionary state, comparable to the 'Class 0 or I' stage of low-mass stars (cf. Lada 1999), as indicated by their weak radio continuum emission and absence of ionic lines and PAH features. For comparison, 5 infrared-weak sources with similar luminosities are studied at submillimeter only, including hot cores and ultracompact H II regions.

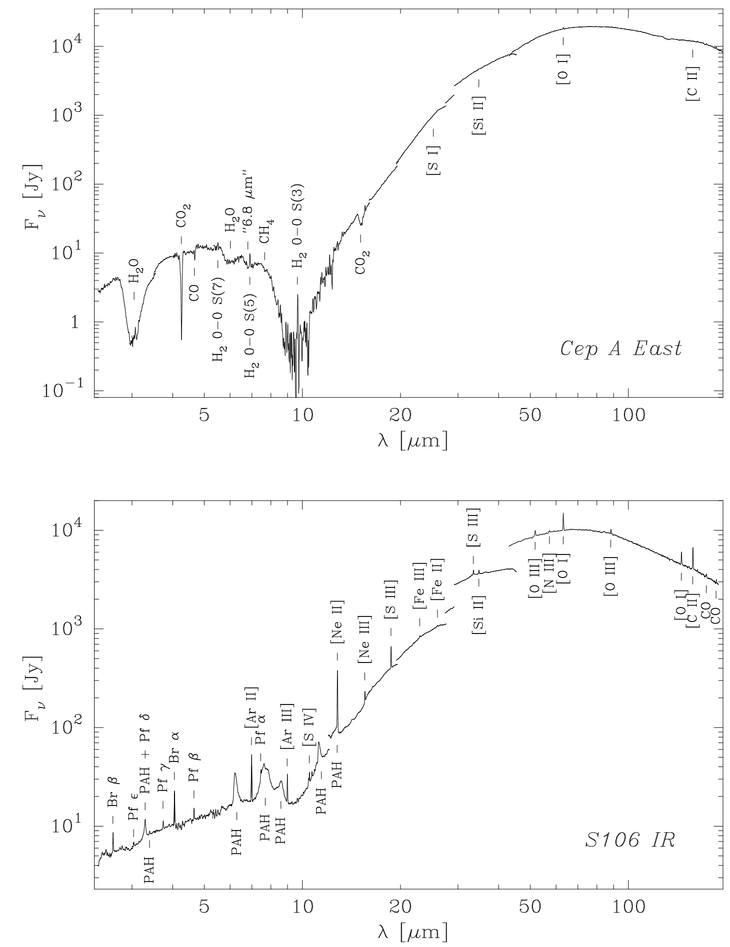

Figure 8. ISO-SWS spectra of two massive YSOs at different evolutionary stages. Cep A ($L \approx 2.4 \times 10^4$ L$_\odot$) is in the embedded stage, whereas S 106 ($L \approx 4.2 \times 10^4$ L$_\odot$) is in a more evolved stage. Note the difference in spectral features between the two sources (from: van den Ancker et al. 2000).

Physical structure. The analysis starts with the derivation of the temperature and density structure of the envelope. The temperature structure of the dust is calculated by solving the continuum radiative transfer given the luminosity of the source and a power-law density structure. The total mass in the beam is constrained from optically-thin submillimeter photometry, whereas the size of the envelope is obtained from submillimeter continuum and line maps. It is then assumed that $T_{\rm gas} = T_{\rm dust}$ over most of the envelope, consistent with explicit calculations of the gas and dust temperatures (e.g., Doty & Neufeld 1997).

The continuum data are sensitive to temperature and total mass, but observations of molecules with a large dipole moment are needed to constrain the density structure. One of the best choices is CS and its isotope C^{34}S, for which lines ranging from J=2–1 to 10–9 can constrain the power-law density profile $n(r) \propto (r/r_o)^{-\alpha}$. The best fit to the data for the infrared-bright sources

Table 1. Chemical characteristics of massive star-forming regions

Component	Chemical characteristics	Submillimeter diagnostics	Infrared diagnostics	Examples
Dense cloud	Low-T chemistry	Ions, long-chains (HC_5N, ...)	Simple ices (H_2O, CO_2)	SgrB2 (NW)
Cold envelope	Low-T chemistry, Heavy depletions	Simple species (CS, H_2CO)	Ices (H_2O, CO_2, CH_3OH)	N7538 IRS9, W 33A
Inner warm envelope	Evaporation High-T chemistry	High T_{ex} (CH_3OH)	High gas/solid, High T_{ex}, Heated ices (C_2H_2, H_2O, CO_2)	GL 2591, GL 2136
Hot core	Hot-core chemistry	Complex organics (CH_3OCH_3, CH_3CN, vib. excited mol.)	Hydrides (OH, H_2O)	Orion hot core, SgrB2(N),G34.3 W 3(H_2O)
Outflow: Direct impact	Shock chemistry, Sputtering	Si- and S-species (SiO, SO_2)	Atomic lines, Hydrides ([S I], H_2O)	W 3 IRS5, SgrB2(M)
PDR, Compact H II regions	Photodissociation, Photoionization	Ions, radicals (CN/HCN, CO^+)	Ionic lines, PAHs ([NeII], [CII])	S 140, W 3 IRS4

gives α=1.0–1.5, whereas the hot core/ultracompact H II region sample requires higher values, $\alpha \approx 2$. Figure 9 shows the derived temperature and density structure for the source GL 2591. The submillimeter data are weighted toward the colder outer envelope, whereas the infrared pencil beam line-of-sight is more sensitive to the inner warm ($\sim$ 1000 K) gas.

Chemical structure: evidence for 'global warming'. The ISO spectra of the infrared-bright sources show strong absorption by ices as well as absorption by various gas-phase molecules including H_2O, CO_2, C_2H_2 and HCN. Their submillimeter spectra have strong lines, but lack the crowdedness of typical 'hot core' spectra. The data for molecules such as CH_3OH —which have many lines throughout the submillimeter range probing a wide range of conditions— cannot be fitted with a constant abundance, but require enhanced abundances at higher temperatures. This has led to so-called 'jump' models, in which the abundance 'jumps' from a typical dark cloud value to a $\sim 100\times$ higher value at the ice evaporation temperature $T_{\rm dust} \approx 90$ K (van der Tak et al. 2000b). Another 'jump' temperature is $\sim$ 230 K, when most of the atomic oxygen is driven into H_2O, affecting the abundance of, for example, HCN (Boonman et al. 2001).

Taken together, the infrared and submillimeter indicate a systematic heating trend of the sources as a function of the 'average' temperature of the envelope, measured either from the 45/100 μm continuum flux ratio or the excitation temperature of CO and other molecules: (i) the shapes of the ice bands ($^{12}CO_2$, $^{13}CO_2$, 6.8 μm) show evidence for restructuring and segregation of the ices at higher temperatures; (ii) the abundances of CO, C_2H_2, HCN and CH_3OH show systematic increases within the infrared-bright sample, whereas the complex organics are enhanced in the hot core sample; and (iii) the gas/solid ratios of H_2O and CO_2 show systematic evaporation of ices.

Since these diagnostics sample both the gas and the ices in the inner and outer envelopes over temperatures from <50 K to 1000 K, the heating must be 'global' throughout the source, rather than localized in small shocked hot spots.

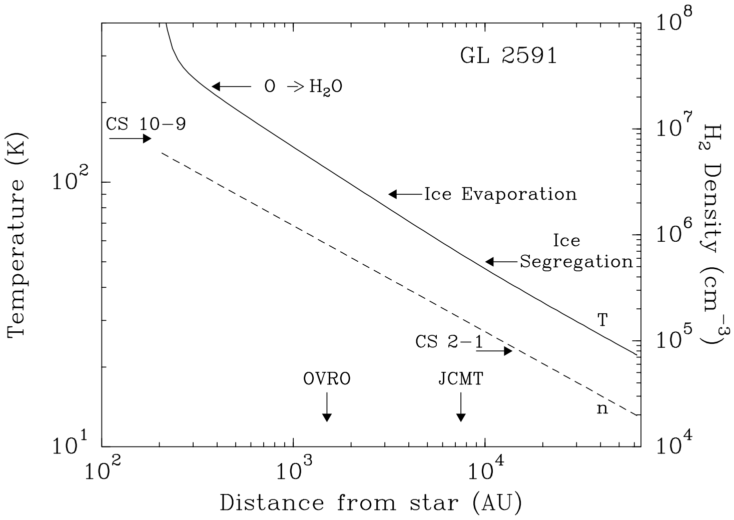

Figure 9. Derived temperature and density structure for the envelope around the massive YSO GL 2591 (L=2×10^4 $L_\odot$, d=1 kpc). The chemically important temperature regimes of ice evaporation ($>$ 90 K) and transformation of O$\rightarrow H_2O$ are indicated, as are the critical densities of the CS 2–1 and 10–9 lines and the typical beam sizes of the JCMT at 345 GHz and OVRO at 100 GHz (Based on: van der Tak et al. 1999).

Also, it cannot be a geometrical effect since the same trend is seen in both the infrared and submillimeter data. The observational trends correlate with $M_{\rm env}/L_*^{1/3.5}$, which is a measure of the ratio of envelope mass to stellar mass. Thus, the data suggest that we may be witnessing the dispersal of the envelope: a lower envelope mass leads to a higher temperature throughout the envelope for the more evolved objects. Combined with the anticorrelation between infrared brightness and strong radio continuum, this suggests the following evolutionary ordering: infrared-bright objects $\rightarrow$ hot cores $\rightarrow$ ultracompact H II regions. This example illustrates that observations of the gas- and solid-state features are essential to trace the evolution within the earliest deeply-embedded phase ($10^4 - 10^5$ yr).

5. Conclusions and future directions

The remarkable progress in astrochemistry over the last decade has been driven by new observational techniques. With the increased sensitivity at submillimeter wavelengths and the opening up of the infrared wavelength region, 'astrochemistry has come of age' and is now an integral part of astrophysics (Dalgarno 2000). Systematic inventories of both the gas and the solid phase have been made —at least for high-mass sources– and scenarios for the evolution of the abundances during star formation have been developed. Clear spectroscopic diagnostics of different physical components have been identified. The detection of new, simple molecules continue to test the basic chemical networks and at the same time provide clues on the physical structure of the regions.

The next steps in astrochemistry will be driven by new facilities with increased sensitivity and orders of magnitude better spatial resolution, in particular SOFIA, SIRTF and eventually NGST at mid-infrared wavelengths and the SMA, ALMA and FIRST at submillimeter and far-infrared wavelengths. This will allow astrochemists to address new questions, in particular the chemical evolution of low-mass star-forming regions in which solar-type stars are born. What are the similarities and differences with high-mass regions? Are shocks relatively more important in clearing the envelopes than radiation in low-mass objects, and how does this affect the chemistry? Do low-mass YSOs develop a 'hot core' chemistry in which complex organic molecules are formed? A particularly exciting prospect is the study of the chemistry of circumstellar disks, for which the first results are just emerging (e.g., Dutrey et al. 1997, van Zadelhoff et al. 2001, Qi et al. 2001).

On the basic chemistry side, much remains to be learned about reactions on the surfaces of grains, reactions with large molecules such as PAHs and desorption of ices. Laboratory data and theoretical studies of basic molecular processes remain essential for analyzing and interpreting the wealth of new observational results. Future modeling efforts are directed at coupling the chemical networks with increasingly sophisticated numerical hydrodynamical models, leading to a new class of 'chemo-hydrodynamical' models. The next generation of accelerated 2-D and 3-D radiative transfer codes will be essential for comparing the results of such numerical models with observations. Altogether, astrochemistry is well positioned to address major questions in interstellar medium research in the coming decade, and to provide significant insight into the processes that occur during the formation of new planetary systems.

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