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THE NATURE OF ASTROCHEMISTRY

The earliest successful model of interstellar chemistry was based on ion-molecule reactions, a theory which over the years has provided a satisfactory picture of many of the smaller known interstellar molecules, and some of the larger ones. This chemistry is based on the cosmic ray ionization of H_2, and He, producing H_2^+, H_3^+, and He^+ ions which interact with many neutral atoms and molecules to produce a wide variety of molecular ions. Neutral species are formed from these ions by recombination with electrons. The major successes of this chemistry have been the semi-quantitative as well as qualitative predictions of HCO^+, HCS^+, $HCNH^+$, as well as neutral species such as HCN, HNC, OH, C_2H, CN, and others. The chemical fractionation with respect to deuterium of several species (DCO^+, N_2D^+, DCN, DNC, HDCO) and also with respect to ^{13}C in other species is also well explained.

However ion molecule chemistry is beset by major uncertainties (unknown reaction rates, input atomic abundances, the question of whether steady state has been reached, the role of interstellar grains). These presumably explain the severe difficulties in predicting abundances of species such as N_2H^+, NH_3, CH, the CH/CH^+ ratio, and most sulfur-containing compounds. In addition there is evidence that clouds are far more heterogeneous chemically than is expected by standard ion-molecule chemistry. The limits of applicability of this most important interstellar chemistry have not been delineated, because of limitations in both basic laboratory data and in observations, especially those involving spatial resolution and sensitivity.

Many recent observational results also point to the operation of additional types of interstellar chemistry. In particular, high temperature ("shock") chemistry seems indicated in many instances. The abundance of CH^+ in diffuse clouds can only be explained by high temperatures (> 1000 K). Recent observations of rotationally excited CH and of vibrationally excited HCN point to regions of extremely high temperatures and densities Ziurys, L. M. and Turner, B. E. 1985, Ap. J. (Letters) 292, L25, Ziurys, L. M. and Turner, B. E. 1986, Ap. J. (Letters) 300, L19, (> 2000 K and/or $> 10^{10}$ cm^{-3}). High temperature chemistry also applies to refractory compounds such as SiO, which are seen only in regions containing shocks. These regions can only be adequately studied with the high spatial resolution of the proposed array.

Another type of chemistry recently observed is collisional dissociative processes, in particular the breakup of H_2O to form excessive amounts of OH in the interface regions between energetic bipolar particle flows from protostars, and the ambient molecular cloud. Grain chemistry, either as catalytic surface reactions or as the sputtering of grains is another type of chemistry that seems to explain certain phenomena such as the recent observations of enhanced NH_3 in certain regions of high temperature in Orion. Again, small regions are involved.

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The chemistry of circumstellar shells differs from interstellar chemistry in that it is believed to originate largely in the high temperature and high density regions close to the photosphere, where chemical equilibrium obtains. The equilibrium abundances that result may or may not persist throughout the envelope, owing to the possible absorption of some species onto grains, and photochemical processes in the outer envelope.

Finally, an example of a chemistry that may not fit any of the above mentioned pictures is that of the recently speculated polycyclic aromatic hydrocarbons (PAHs) which may contain a significant fraction of the interstellar carbon.

1. High Mass Star Forming Regions

Studies of star-forming regions have been aided greatly by interferometric observations. For example, the tendency for maps of a given region made in different molecular lines to differ from one another was already evident in single dish maps. It is even more pronounced in the higher resolution interferometer pictures. This is evident in Figure 1 which compares maps of Orion/KL in different molecular transitions. The Hat Creek maps of HCN(1-0), SiO (v = 0), J = 2-1), SO[2(2)-1(1)], and HCO+(1-0) are all at a velocity of 19 km/sec with a resolution of 4 km/sec (Plambeck et al. 1982; Wright et al. 1983; Vogel et al. 1984). The NH_3 map from the VLA is the integral over the whole (4,4) line (Pauls et al.; Genzel et al.). The 3 mm continuum has been mapped at both the Owens Valley (Masson et al. 1985) and at Hat Creek (Vogel and Wright, 1985). The Hat Creek map is shown. The HCN and SO are very similar to each other and both are very different from the compact thermal SiO and the extended HCO+. All are "plateau" sources. The NH_3 "hot core" map is different from the others and rather like the thermal continuum. It is difficult to attribute all the differences to excitation effects. All the molecules require comparable collision rates for excitation, and one would be fooled if one mapped just one of these molecules and thought that one had picture of the region where the H_2 density was of the order of 10^5 or 10^5/cc. The study of this sort of region clearly requires the observation of many different molecular species. The interesting picture of the Orion infrared source IRc2, which is emerging from these observations is that IRc2 is surrounded by a dense disk of gas which has a high-velocity bipolar outflow. The disk is composed of molecules such as SO, HCN, SiO, and NH_3. The NH_3 seems to be central to the clumps or condensations in the disk, the OH masers are scattered around inside the dense gas disk, and the inner edges seem to support the SiO masers, within 35 AU of the infrared source IRc2. The outflow is traced in HCO+ and appears to originate either from the surface of the disk or from the central star itself. The diameter of activity is less than one arcmin and, with this region, IRc2 is believed to drive the flow.

In apparent contrast to the Orion picture, W3 is an example of high velocity flow with no constraining disk (Wright, Dickel, and Ho 1984); it has HCN emission as well as OH and H_2O masers. In general, OH, H_2O, and CH_3OH maser observations show that active star forming regions typically have dense clumps of gas. The clumping of molecular material is another aspect of interstellar chemistry (and structure) best studied using aperture synthesis techniques. These clumps of dense material would allow different types of chemistry to occur virtually side by side and be indicators of structure and activity in interstellar sources. One current example is the discovery of small rotating ammonia clouds by Harris et al. (1983). These cloudlets are of a size and mass to be possible sites of future star formation, in effect pre-proto-stellar objects. Another example is the formyl radical, HCO. Recent higher spatial resolution observations of HCO in DR 21 by Schenewerk, Snyder, and Hjalmarson (1985) have revealed all four strong hyperfine lines for the first time in any source (Fig. 1). Comparison of line strengths with previous lower spatial resolution observations indicate that HCO may exist in clumps throughout this source, and serves to highlight the importances of beam size for the detection of such clumps and the molecules specific to them.

2. Cores of Cold Dark Clouds

Relative to the giant molecular clouds, the dark clouds are relatively nearby, less massive, colder, and lack formation sites for massive stars. They are excellent laboratories for astrochemistry, since high spatial resolution allows accurate determination of local physical conditions and the absence of high temperature processes leads to a simplification of the chemical models that need be considered. Although there are some basic similarities in the observed abundances in dark clouds with the more quiescent portions of large, warm molecular clouds, there are also fascinating differences, both among clouds and, apparently, with in a given cloud (e.g., Irvine et al. 1985). The reasons for such variations are not well understood, but are a subject of active study. Determination of isotope ratios can also provide critical tests of ion-molecule chemistry (e.g., Watson and Walmsley 1982).

Two well studied examples are TMC-1, in which Schloerb and Snell Ap. J. 283, 129 (1985) find condensations ("clumps") with dimensions close to their beam size (-1', corresponding to linear sizes approximately equal to the Oort cloud and masses approximately equal to a few solar masses), and L134N, in which maps in species such as $C^{18}O$, SO, $H^{13}CO^+$, and C_3H_2 have quite different appearances (Swade 1985). To adequately evaluate chemical models, it is clear that multitransition, multispecies maps are required in order to compare such physical conditions as kinetic temperature, density, and UV radiation field, with derived abundances.

Since structure is seen in these clouds down to the scale of currrent single dish beams, higher angular resolution is clearly desirable. It is known that dark clouds are formation sites for low mass stars, and TMC-1 has been referred to as a "proto-solar nebula." A search for chemical effects in truly solar system-sized nebulae in such regions would be very exciting. At the distances of nearby dark clouds (~150 pc), the radius of Pluto's orbit would intercept an angle of about 1", so that study of a flattened solar nebula would require resolutions of 0.2" or better.

Dark clouds have been fertile sites for recent searches for new molecules, including both heavy organic species such as CH_3C_4H (Walmsley et al. 1984; Loren et al.; MacLeod et al. 1984) and "non-terrestrial" species such as C_3H and C_3H_2 (Thaddeus et al. 1984, 1985). Many of these have not been mapped, so their spatial scale is not known. It seems likely, however, from comparisons with better known molecules, that the prime criterion in searches for additional complex species witll be sensitivity, rather than angular resolution--the antenna temperatures for the detections of C_3O and

CH_3C_4H were on the order of 30 mK. The 30-50 GHz region is crucial to searches for heavier molecules, as is discussed below. Also, observed line widths in dark clouds may be as small as 0.2 km/s; high spectral resolution studies will therefore require ~20 kHz at 7 mm.

3. Evolved Stars

High spatial resolution will provide an essential check on chemical models which predict abundance variations as a function of radius with the circumstellar molecular shells of evolved stars. The model traditionally used is the "freeze-out" chemical model, in which chemical species are formed under conditions of thermochemical equilibrium in the high temperature, high-density inner shell/photospheric region. These molecular species are then propelled outward by the stellar wind which produces the shell; as they move out in the shell, the density rapidly falls to a value where chemical reaction rates no longer compete with dynamical time scales and the relative abundances are then "frozen," and become independent of distance R from the central star.

Much indirect evidence suggests that this model fails to predict the chemistry accurately. Recent detections of vibrationally excited HCN and CS in the carbon-rich shell IRC10216 (Ziurys and Turner, Ap. J. (Letters) 1986, January 1 issue; Turner and Ziurys, in preparation) show that these species peak sharply in abundance toward the inner regions, and fall off rapidly with increasing R, in contrast to predictions. The failure to detect vibrationally excited CO indicates that CO has a much flattter distribution with R. SiC_2, a three-membered ring, is another species that show intriguing spatial distributions quite at odds with the freeze-out model. A combination of millimeter-wave (Thaddeus et al. 1984) and centimeter-wave data (Snyder et al. 1985b) give a highly reliable rotational temperature of 150 K, which suggests that its abundance peaks at a fairly well-defined radius within the envelope, in contrast to freeze-out models. Its mechanism of formation must be highly specific.

The angular size of IRC 10216, overwhelmingly the most-studied evolved shell, is a maximum of 40" in HCN, 30" in several other species such as SiC_2, and much smaller in centrally condensed species such as the vibrationally excited ones. All require interferometers for direct study. Further, all other evolved stars are considerably more distant, and thus angularly much smaller, than IRC 10216. Only the first rudimentary studies of even IRC10216, at 10" resolution by the Hat Creek interferometer have nevertheless given important initial results, although only in the optically saturated lines of species such as HCN. To probe less abundant, optically thin species which may be more centrally condensed, will require much greater angular resolution and much greater sensitivity. Such measurements, in many species and modes of excitation, will be needed to elucidate the many physical and chemical processes which appear actually to occur throughout the envelope, and to invalidate the simple freeze-out model. Among these proceses are catalytic formation on grain surfaces, adsorption onto grains (particularly in the cooler, outer envelope), shock chemistry, and photodissociation in the outer envelope.

Much of the discussion so far has focused on carbon-rich stars, because the single well studied example, IRC10216, is such a star. Oxygen-rich stars also have circumstellar shells and their own unique chemistry, which besides CO, stresses H_2O, OH, and SiO among species accessible to radio observations. These species all exhibit powerful maser activity and VLBI studies have already revealed important knowledge, such as that the OH masers lie outside the H_2O masers, and the SiO masers inside the H_2O masers. Such studies, while highly suggestive, are subject to interpretive uncertainties involved in the excitation of the masers. Studies of other molecules will add much complementary information, but as their signals will be much weaker, a large and sensitive interferometer will be needed. Highly refractory, and hitherto undetected species such as metal oxides and hydroxides (MgO, MgOH, CaOH) may be detectable according to predictions of thermochemical equilibrium. Intriguing details about the changing relative distributions of the masering OH, H_2O, and SiO species as a function of IR light cycle phase will also be possible, and will shed light on the pumping mechanisms.

The chemistry of evolved stars is singularly important, as these objects undergo copious mass loss to the interstellar medium, thus enriching the gas which is to form subsequent generations of stars. The entire nucleosynthetic history of ours and other galaxies depends on an accurate assessment of the composition of the molecular circumstellar gas. By their very nature, such shells are amenable to direct study only through use of large and sensitive interferometers.

4. The Sun

Spatial resolution of 8" should allow confirmation of the refractory species claimed to exist in sunspots (e.g., SiO) and permit examination of its spatial surface.

5. Extragalactic

Only a few simple molecules have so far been detected in other galaxies but they provide essential tools for detrmining whether, and perhaps why, the chemistry in other galaxies differs from that of the Milky Way. Even so fundamental a species as CO is already known to be relatively lacking in several nearby and well known galaxies such as M31. It is not known whether molecular chemistry, as exemplified by CO, always is enhanced in spiral arms within a galaxy; the study of such arms in even the oldest galaxies requires spatial resolutions beyond those available with single dishes.

HCO^+ is a tracer of cosmic rays, and gradients in HCO^+ abundance with galactocentric radius in those galaxies will answer questions like whether cosmic ray densities correlate with supernovae X-ray sources.

Isotope ratios are fundamental to nuclear processing in stars, so that they depend on the stellar mass distribution, the rate of star formation, and the rate of return of stellar material to the ISM. Models of the Milky Way predict gradients in certain key isotope ratios ($^{12}C/^{13}C$, $^{14}N/^{15}N$, $^{16}O/^{18}O$) with galactocentric radius, and it is difficult because of distance ambiguities to establish whether such gradients exist in our galaxy. Other galaxies will provide this information more easily, and also indicate differences between galaxies. Such differences in turn would reveal fundamental differences in the nature of star formation in galaxies. The high spatial resolution of an array is needed to obtain the ncecessary observational information. Optical studies do not provide such information because the isotopic lines are severely blended.

6. The Solar System

The chemical composition of planetary and satellite atmospheres provides fundamental data for planetary science. The atmospheric composition is dependent (among other factors) on the overall composition of such a body, which reflects basic cosmogonical conditions. Moreover, the abundances of trace constituents probe both the evolutionry history and important on-going physical and chemical processes. For example, day-night gradients in the abundance of CO in the Venus stratosphere provide information on both photochemistry and atmospheric circulation, and the $^{12}CO/^{13}CO$ ratio may be different from the terrestrial value, this apparently reflects poorly understood fractionation processes during the lifetime of the planet or conceivably in the solar nebula (e.g., Schloerb 1985; Clancy and Muhleman 1985). Likewise the apparent detection of CO on Titan and the anomalous abundance of H_2O on Jupiter are examples of non-equilibrium abundances that must relate to important atmospheric processes such a deep circulation patterns or possible infall of material. Gradients across a planetary disk (e.g., the Jovian Great Red Spot) may be reflected in chemical anomalies of species such a phosphine (PH_3), or, in the case of Venus, of sulfur compounds producing the ultraviolet markings abundance measurements in these cases could test models of atmospheric/aerosol chemistry. Molecular lines should be observable in the atmospheres of both Io and Titan. Inversion of line profiles in all these cases provide mixing ratios vs altitude, which cannot be obtained from infrared spectroscopy.

To determine required instrumental parameters, we note that the angular diameter of Titan is ~1", while features such as the Great Red Spot are a few arcseconds across. Mapping of Venus (e.g., in CO) requires resolutions of approximately a few arcseconds. Planetary lines also place important requirements on spectrometers. Pressure broadening is typically ~2-3 GHz/bar, so bandwidths of this magnitude are extremely desirable.

There is suggestive evidence for the survival of interstellar molecular material in primitive solar system objects. The large values of the D/H ratio found in certain fractions of carbonaceous chondrites are particularly interesting, but models of cometary coma chemistry also point in this direction (Kerridge and Cheung 1985). The most pristine material surviving today from the original solar nebula is believed to be in comets, so that determining cometary chemical compositions is a critical problem. Not only may this provide boundary conditions on the solar nebula, but it may conceivably lead to a means for relating the chemistry of comets to that in molecular clouds and hence for determining the type of cloud in which the solar system formed. Rotational transitions appear to hold the best promise for providing this type of information (Snyder 1982). Because different molecules have different lifetimes in the solar radiation field, and because chemical reactions are expected in the inner coma, gradients in the chemical composition and excitation will provide important information on physical conditions and processes. For a moderately bright comet at a distance of 1 AU, the molecular coma may vary in size from ~1000 km (for species such as S_2 and NH_3) to ~10,000 km (HCN), corresponding to angular scales of ~0.1" to ~100".

FREQUENCY COVERAGE

Unlike most other scientific areas which utilize well-chosen but specific molecular lines as probes of the physical conditions in dense clouds, the study of chemistry requires maximum frequency coverage because the most important transitions of different types of molecules under different physical conditions occur from the centimeter to the sub-millimeter in wavelength. This dependency of spectral features on molecular structure and physical conditions is most easily illustrated for linear molecules, and we choose these species for the following discussion. Non-linear molecules do not behave very differently, but are more difficult to treat.

The integrated brightness temperature for a given molecular line is proportional to the square of the frequency of the line multiplied by the population of the initial energy level involved in the transition. For a linear molecule in thermal equilibrium among its rotational energy levels, these two factors result in a transition frequency ν_{max} of optimum intensity, where

$$\nu_{max} \propto \sqrt{BT} \qquad (1)$$

In expression (1), B is the rotation constant, and is roughly proportional to the inverse cube of the number of heavy (non-hydrogen) atoms in the linear molecule. The frequency of the most intense spectral feature of a linear molecule is proportional to $B^{1/2}$ or $n^{-3/2}$ where n is the number of heavy atoms. Larger molecules will have their strong spectral features at lower frequencies, viz., towards the centimeter range, whereas smaller molecules will have their stronger features towards the millimeter and even submillimeter range. Light hydrides such as NaH, MgH will have their lowest frequency (fundamental) transitions in the submillimeter; observation of these particular species would be of extreme importance in determining metallic abundances in dense interstellar and circumstellar clouds.

A glance at equation (1) reveals that as temperature increases, so does ν_{max}. The result is that the study of the emission of a given molecule at higher temperatures is a manner of specifically probing regions of higher temperature. In particular, a change in temperature from say 10 K, which pertains throughout a typical cold interstellar cloud, to 300 K will result in an increase of ν_{max} by a factor of $\sqrt{30}$. Thus, the study of one molecule in a heterogeneous source requires significant "frequency agility."

Perhaps more striking is the tremendous increase in sensitivity which these various factors indicate for particular species which may only form in small, high-temperature regions such as produced by shocks, or in the immediate vicinity of massive protostars. Highly refractory species such as metal compounds (MgO, CaO, FeO, PO, PN, NaO, NaOH) containing elements not yet detectable in dense clouds, may be examples of such species. If the highly excited regions are not angularly larger than the snythesized interferometer beam, as expected, then the signal is dependent on the ratio of source solid angle to beam solid angle and thus varies as ν^2, where ν is the frequency. Further, the intrinsic brightness temperature of a transition of a linear molecule varies as ν^1 or ν^2 as one goes up the rotational ladder, depending on whether the transition is optically thick or thin. At the high temperatures involved in these cases we can observe transitions much more highly excited than if the species occurred in low-temperature regions. Thus the sensitivity for detection and study of refractory compounds which may occur only in small, highly excited regions will vary as ν^3 or ν^4 when studied with an interferometer at high frequencies, yielding many detections which otherwise would be impossible.

The above discussion has focused on why different frequency ranges are necessary for studying different molecules and/or different physical conditions. Frequency agility is often needed for individual molecules in the same physical environment for the purpose of identification. It is difficult to establish the presence of a new interstellar molecule based on a one-line identification. Consider the ion HOC^+, which has been tentatively identified in Sgr B2 via a transition at 90 GHz. Confirmation will require observations of another transition at 270 GHz. In addition to the desirability of frequency agility for the purpose of identification, such a capability would be most useful for simultaneous mapping of two or more transition frequencies of a particular molecule to determine excitation conditions and hence abundances.

Based on the above needs, the following general requirements are suggested:

1. The basic IF pass-band preceding the correlator should be as wide as practical (1-2 GHz or more).

2. Both sidebands of the first local oscillator should be observed, and they may be separated by oscillator phase switching.

3. It should be possible to divide the correlator into a large number of separate bands [10-20] each of which can be tuned to a separate line.

4. It should be possible to observed with more than one resolution in these different bands at the same time.

5. Each band should have up to 64 channels.

6. A bandwidth of 20-40 MHz for each band is desirable for velocity coverage.

7. The resolution in each band should be variable over half a dozen steps of a factor of 2, so that very high velocity resolution may be obtained.

8. Special attention to spectral passband calibration must be paid.

Chemistry Summary

1.	Frequency Range	→	33 GHz Compact heavy molecules	→	345 GHz Small tightly bound refractory molecules
2.	Frequency Agility	→	e.g., Upper and lower sidebands		
3.	Bandwidth Flexibility	→	Smallest resolution 10 kHz Largest bandwidth ~ 3 GHz (planetary atmospheres)		
4.	Angular Resolution	→	1 arcsec for the projects discussed, but summarized in a BET table of 18 chemically interesting objects.		
5.	Collecting Area	→	We can live with a minimum collecting area equivalent to a 46-m dish but we prefer more. We need best receivers available.		
6.	Site	→	The 345 GHz boundary in (1) dictates a high site.		