CONFERENCE SUMMARY: MOLECULES IN ASTROPHYSICS

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Abstract. A summary of the conference is presented along with some outstanding problems and challenges for future work.

1. Introduction

During the last 5 days, thanks in part to the expert organization of the conference, we have heard and seen ample evidence concerning the vibrant and dynamic nature of molecular astronomy. From its effective beginning more than 25 years ago, the field has grown enormously. Because of the large number of invited and review speakers, and the much larger number of posters presented, it is impossible to discuss individual contributions by name. In this summary, therefore, I will discuss within an historical context the many current aspects of astrochemistry brought up at this conference and show how they are related to one another. I will also discuss some outstanding problems remaining to be fully solved.

2. Observations

The field of molecular astronomy has come a long way since its inception in the late 1960's and early 1970's, or, after hearing Professor van de Hulst, in the 1930's and 1940's. It goes without saying that much of the advance in the field derives from observations. Some observers are interested in the molecules themselves, and the development of molecular complexity throughout the universe. Others, indeed most, are interested in molecules as probes and diagnostics of interstellar and circumstellar environments. Information has been learned from both single telescope work and from

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interferometry, from both studies of single molecules and from surveys. Of course, molecules are only accurate probes if we understand both their spectroscopy and dynamics, so that observational molecular astronomy is closely coupled with laboratory investigations and theory.

Although historically a large amount of the observational effort has been devoted to one molecule (CO), it should be obvious from the talks and posters presented here that this molecule is hardly the only molecular probe of gas-phase physical conditions (although much interesting work is still being done with CO). My current list of gas-phase interstellar and circumstellar molecules seen with high resolution techniques (mainly radioastronomical in origin) totals 110, after the recent removal of $HC_{11}N$ and the inclusion of H_2COH^+, C_8H, and CH_3COOH, and many of these play important roles as probes. The largest molecule on this list contains only 11 atoms, although far larger molecules are indeed present. The existence of PAHs as a class of large molecules has been derived from the so-called UIR (unidentified infrared) bands, although the identity of individual PAH species is probably not obtainable from these bands. This week we learned about mass spectrometric measurements that show individual PAHs to be present in IDPs and meteor occlusions. In addition to PAHs, large carbon chains and fullerenes may be present in significant quantities in the diffuse interstellar medium.

Molecules are also probes of condensed phase environments. Infrared and ultra-violet observations have elucidated the core-mantle nature of interstellar grains and the molecular composition of the two phases. Although the broad nature of the molecular spectra occasionally makes for ambiguity in interpretation, there is no doubt that silicate and carbonaceous grains are covered by icy mantles and that the positions and widths of selected spectral lines are sensitive indicators of environment.

Fine structure transitions of atoms are also key probes of the interstellar environment, especially of its heterogeneity. These transitions can be detected in the submillimeter (as in the case of CI) or in the far infrared (as in the case of OI).

Although astrochemical observations started in the visible, and were dominated for many years by the radio, millimeter, and submillimeter, infrared observations are becoming increasingly important for small gas-phase molecules, in addition to their roles in the observation of PAHs and grains. Clearly, molecular observations are now being performed over a variety of frequency ranges and techniques, with satellite and airborne observations playing an increasingly important role because of atmospheric opacity. In the past we had IRAS, Copernicus, IUE, and the KAO, now we have HST and ISO, and soon we will have SWAS, ODIN, FIRST, and SOFIA.

This week, we learned much about preliminary results from ISO in the

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near- and far-infrared regions taken with the SWS and the LWS. The ISO results give us vastly improved spectra of interstellar icy grain mantles. In particular, the strong CO_2 feature at $4.27\mu m$ nicely confirms an earlier identification at lower frequency and shows carbon dioxide to be a major and ubiquitous ice component, presumably produced on grain surfaces via photochemistry or the spin-forbidden association between CO and O. Three gaseous molecules of extreme interest detected by ISO are H_2, H_2O, and possibly CO_2. Although previous observations of H_2 exist, the $S(J)$ rotational lines detected by ISO are excellent probes of excitation conditions. The detection of vapor-phase water in high abundance in winds and shocks is also quite exciting. Finally, we learned that preliminary ISO results show the C-H stretching PAH feature to be widespread.

If one looks at the large number of observational papers presented this week, one is struck by the diversity of physical environments explored, so let me now discuss these environments.

3. Diversity of environments

Given the number of environments we have learned about this week, it is difficult to believe that the role of molecules was once much more restricted. But for a number of years in the early 1970's, interstellar investigators wrote about two types of regions – "diffuse" clouds, in which densities are rather low and a significant amount of light penetrates, and "dense" clouds, in which no light penetrates and the densities are significantly higher. Two different gas-phase chemistries pertained, leading only to diatomic species in diffuse clouds and to larger molecules in dense clouds. Goethe once wrote that "we know accurately only when we know little.." and this neat classification system is now known to be hopelessly simplistic, because of the spatial heterogeneity of the environments and because they cannot be so easily distinguished.

Current observational work on diffuse clouds, both in the optical and UV, and in the millimeter, has been reviewed for us this week (with a particularly interesting analysis of elemental abundances). In the chemistry of diffuse clouds, the role of the poorly understood molecule CH^+ has been crucial historically, first in leading to the now well-developed hypothesis of shock waves with an attendant high-temperature shock chemistry, and more recently, when the shock idea seemed not to explain the data, to the exploration of intermittent turbulence. Further, the demarcation between diffuse and dense clouds has been erased by studies of translucent and high latitude clouds by our hosts and others.

The study of dense clouds has undergone even greater development. It soon became apparent that dense clouds are very inhomogeneous, and that

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simple homogeneous gas-phase chemical models – be they steady-state or pseudo-time-dependent – could not pertain to entire clouds. Such simple models were adapted to relatively homogeneous dense cloud cores, or "dark nebulae", such as TMC-1, although even these rich molecular sources are now known to be rather dynamic and heterogeneous, as we have heard and seen here. Some degree of heterogeneity in dark sources arising from density variations and radiative penetration has been taken account of by modellers using one-dimensional slab treatments, while other treatments have focused on the interplay between dynamics and chemistry. We now refer not to "dense" clouds but to molecular cloud complexes, in which heterogeneity, star formation, and young stars play key roles.

Certainly the most salient aspect of the heterogeneity of molecular clouds is star formation. The astrochemistry of high mass star formation has been studied for perhaps a decade or more, with much observational and theoretical attention paid to so-called Hot Cores. These objects actually appear to be quiescent dense regions in the vicinity of star formation where the current gas-phase material, which is far more saturated (hydrogen-rich) than in other regions, includes material processed and hydrogenated on dust particles in a previous, colder era. Hot Cores can therefore tell us much about grain chemistry as well as warm gas-phase chemistry, and these objects are being actively explored. Besides leading to Hot Cores, high mass star formation is also associated with outflows, shock waves, and maser activity. Shock environments are strongly influenced by the size of the local magnetic field, with both J-shocks and C-shocks discussed here. Sulphur-bearing molecules and SiO appear to be excellent probes of shocks, with the latter molecule produced from silicon and other species coming off dust grains via grain-grain collisions and sputtering.

Once O stars are formed, brilliant emission nebulae, or HII regions, result. Although these sources are not rich in molecules, the photons from them travel far enough to produce "bright" photon-dominated regions (or PDRs) which, from the emphasis here on both observations and modelling, are currently of great interest. PDRs (bright and not-so-bright) embedded in dense interstellar gas may explain much of the fine structure observations of CI, CII, and OI discussed here, although in the case of CI, an alternative explanation in terms of a "high ionization phase" solution under ordinary conditions has been proposed. There now appears to be a transitory transition zone between HII regions and PDRs in which highly energetic photons can produce unusual molecules such as CO^+. Analogous to PDRs, one can think about regions such as disks exposed not to excess ordinary light, but to X-rays, and the infrared response of H_2 to X-rays has been treated.

Of course, most new stars are not high mass O stars. New stars not quite hot enough to maintain HII regions (e.g. B stars) can lead to reflec-

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tion nebulae, and something has been learned about these objects. The formation of low and medium mass stars is an area of current intense interest, and we have learned here about recent research activity in this field. The use of molecules as probes of protostellar evolution, including both the infall and outflow of material, was discussed. Without the high temperatures associated with high mass star formation, one expects the depletion of many gas-phase molecules onto grains at higher densities surrounding sites of star formation, and we have heard about such depletions. The adsorbed species, along with molecules produced on dust grains, may be preserved and incorporated in solar-type nebulae.

Eventually, protostars become young stellar objects (YSOs), and observations and analyses of gas-phase molecules in YSOs were reviewed. Pre-main sequence stars are associated with bipolar flows, winds, and accretion disks; studies and analyses of all of these phenomena were discussed. Once accretion disks are formed, planets, comets, meteors, and IDPs may not be far behind. We have learned this week about cometary volatiles, the cometary impact with Jupiter, the observation of HNC in comets, and the probable relationship between cometary and interstellar chemistry.

Once stars form, they go through their main sequence existence, and then end their lives in a rather complicated sequence of red giant phases. Since molecules play a role even in the atmospheres of cool main sequence stars, we have learned about molecules in such environments. The role of vapor-phase water in stellar opacity is especially noteworthy and complex. The atmospheres, winds, and shells of post-main sequence stars are fertile grounds for astrochemical studies, and we have been presented with a variety of interesting studies, including observations of molecular abundances in AGB and post-AGB objects, chemical models of AGB winds, and observations of proto-planetary and planetary nebulae. The chemistry of the carbon-rich outflow in IRC+10216 remains a prime focus of attention, since this object is as rich in organic molecules as many interstellar clouds. Carbon-rich AGB envelopes such as IRC+10216 are the most likely source of PAHs although the "combustion" chemistry is far from well understood. Once produced, the PAHs may agglomerate into carbonaceous dust particles. Past the planetary nebula stage, stars become white dwarfs, which can produce novae if they exist near normal stars. Nova outflows are another environment in which molecules exist. High mass stars undergo Type II supernovae and, as most of us know, the remnant of Supernova 1987 is not bereft of molecules. Astrochemistry may even play a role in brown dwarfs which are objects not quite massive enough to form stars. Since brown dwarfs are prime candidates for the "missing" matter in galactic halos, astrochemistry may even tell us something about this dominant component of the universe.

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Given the diversity of galactic molecular environments, one can expect to find even more diversity in extragalactic sources. We have heard here about observations of the LMC and SMC, active galactic nuclei, low metallicity galaxies, starburst galaxies, and even quasars and other high redshift objects.

4. Diversity of chemical processes

The diversity of molecular environments has helped to stimulate interest in a variety of diverse chemical processes. Originally, interest in gas-phase processes focussed on low temperature ion-molecule reactions, with the ions produced by a low flux of cosmic rays. Chains of ion-molecule reactions form polyatomic molecular ions under low temperature conditions (as long as there is a source of ions), but until recently the neutral products formed from the recombination of molecular ions with electrons via so-called "dissociative recombination" reactions had not been measured. Recent experiments are addressing this question, and we have learned here about very exciting experiments using storage rings. Results for the polyatomic ions H_3O^+ and CH_3^+ were presented; the $H_3O^+ + e$ results differ somewhat from new results obtained in a flowing afterglow. The neutral products are produced in excited vibrational states which may lead to detectable radiation.

Thanks to a number of experiments involving the CRESU and other techniques, we now know that many reactions involving neutral reactants are also rapid at low temperature and must be included in interstellar models. These experiments do not tell us what the products of reaction are; for such information we can turn to crossed-beam experiments operating at higher collision energy, several of which we have learned about here. The perhaps pivotal reaction between C and C_2H_2 has now been studied with the crossed-beam technique, although there does appear to be some discrepancy with quantum chemical calculations.

Astrochemistry has outgrown its roots in low temperature chemistry, which involves (with certain rare exceptions) only exothermic reactions without activation energy; exothermic reactions with activation energy barriers as well as endothermic reactions will occur in energetic environments. The role of the endothermic reaction $C^+ + H_2 \longrightarrow CH^+ + H$ in the production of CH^+ is well known; the mechanism responsible for producing the 0.4 eV needed to power the reaction is still not.

Reactions between colliding gas-phase species are only part of the story; non-reactive inelastic collisions are critical to an understanding of the extent of excitation of molecular levels in regions not in thermodynamic equilibrium. Information on specific rates for rotationally inelastic collisions involving H_2 rather than He – both theoretical and experimental – has

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been slow in coming, but we have been told here about experiments and calculations that are beginning to give us the desired information.

Despite the strongest wishes of gas-phase enthusiasts, grains exist and play a major role in interstellar and circumstellar objects. The study of grain cores and mantles in the laboratory was discussed in several reviews this week. How dust grains coagulate and come apart, how surface layers form, and the fate of adducts were also explained. The complexity of small particles was detailed. The chemistry occurring on and even in interstellar grains, a topic of extreme interest, was touched upon. Besides photochemical pathways, modellers have considered a diffusive approach to grain surface chemistry – known as the Langmuir-Hinshelwood mechanism - and rather ignored a second approach known as the Eley-Rideal mechanism – but the role these play on grain surfaces of poorly known composition is still poorly constrained. It was interesting therefore to see the results of a quantum chemical study/molecular dynamics simulation of H_2 formation on amorphous ice. In gas-grain chemical models, there appears to be a problem with the equations used to describe the diffusive mechanism since these apply to tabletops rather than small particles, which may be closer to an "accretion" limit in which the order that species stick is more important than their diffusive rates.

In addition to the need for a better understanding of grain chemistry, it is also important to understand the processes and rates by which molecules can desorb from grains under cold interstellar conditions, where thermal evaporation is too slow to be significant. A new mechanism, in which infrared radiation from the well-known ice band at 3.05 μ is used to desorb molecules adjacent to excited water molecules, was presented. Under shock conditions, sputtering and grain-grain collisions become important mechanisms for desorption of significant amounts of material, as we also learned this week. The state of excitation of desorbed molecules is also of some interest.

The chemistry on and involving large molecules must be considered a distinct entity from grain chemistry and gas-phase chemistry. This week, we learned more about the photophysics of PAHs and their possible formation in shocks.

5. Diversity of experimental techniques

An understanding of the roles of molecules in space requires significant laboratory information, be it labelled laboratory astrophysics, chemistry, or physics. A host of important experimental results and techniques were mentioned this week. In addition to results on chemical processes, discussed above, spectroscopic experiments across the whole electromagnetic spec-

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trum remain critical for both gaseous and condensed-phase species. Several posters emphasized continuing work on the electronic spectroscopy of CO, and laboratory infrared spectroscopy was reviewed. Spectroscopic investigations of large molecules are especially crucial in determining the presence of these species in diverse astronomical environments. If large molecules are sufficiently stable, they are excellent candidates to be the carriers of the so-called visible diffuse interstellar bands (DIBs), which have been known but unassigned for many years. A variety of experiments are being undertaken on different types of large molecules, and we learned here about optical experiments both on carbon chains and on PAHs, including jet-cooled PAHs. A major difficulty in studying gas-phase large molecules is the need to cool the many vibrational degrees of freedom, although Thaddeus and co-workers, in a new series of microwave spectroscopic experiments on linear chains as large as $C_{11}H$, H_2C_6 and $HC_{13}N$, seem to have solved this problem for such species by use of a nozzle.

6. The role of theory

Theory is essential for many aspects of astrochemistry. Chemical models require chemical rates and these are not always available from experimentalists. The calculation of a gas phase rate typically involves quantum chemical calculations of the minimum energy pathway and dynamical calculations using that pathway. A variety of quantum chemical calculations were presented at the conference, and we presented dynamic calculations for several reactions. Quantum chemical calculations are also useful for the determination of photodestruction rates (an interesting study of the radical NH_2 was presented here) and for the determination of energy levels needed to predict the frequencies of spectral transitions. Of course, theory and experiment often work in a symbiotic relationship, correcting the mistakes of each other and leading to deeper interpretations. For example, our calculation for the rate of the reaction between CN and C_2H_2 confirms the unusual temperature dependence measured by Smith, Sims, Rowe and co-workers in the laboratory and offers an explanation for this dependence.

One area in which theory has dominated experiment in recent years is the topic of inelastic collision rates. Although some experimental results at low temperature are available, most results used to interpret spectral intensities are taken from theoretical results. The late Sheldon Green was a major figure in this field; his MOLSCAT program, co-authored with Jeremy Hudson, is used by many scientists. The tribute to Sheldon Green presented at the symposium was quite appropriate. Sheldon and I were collaborating on an analysis of HCO^+-H_2 collisions during the months before his untimely death; the results of this work have been strongly influenced by his critical

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intelligence.

In the area of chemical modelling, we heard this week about theoretical models of diffuse clouds including clumpiness and have seen a poster of how the chemistry is affected by magnetic turbulence. We have also seen posters concerning the chemical evolution of giant molecular cloud cores, collapsing clouds, protoplanetary disks, and star-forming regions. Special attention is being paid to PDRs, and we learned about time dependence, two-component modelling, and the effect of geometries on these objects, as well as the role of radiative transfer. Even standard ion-molecule models of one-phase interstellar cloud cores are no longer so simple; it is now well known (and was discussed in a poster on high latitude clouds) that a second solution – the "high" ionization solution – exists along with the more standard "low" ionization solution at steady state for a range of astrophysically interesting densities.

7. Some outstanding challenges

Here follows an idiosyncratic list of outstanding challenges in the field, some work on which we have heard discussed here. Although great progress has been made, much more remains to be done.

7.1. DEFINITIVE IDENTIFICATION OF LARGE MOLECULES IN SPACE

As molecules become larger, their spectral signatures tend to become more complex. In the microwave, the intensities of rotational transitions, which are often strongly related to molecular structure, become weaker as more and more states become thermally populated. In addition, large amplitude motions become prominent and interactions between these motions and end-over-end rotations complicate the spectra. These problems have made identification of glycine rather difficult, and have led to many unidentified lines especially in the submillimeter, where the laboratory base is not large. Interestingly, linear carbon-chain species are more identifiable because they possess relatively fewer levels and their motions are less complex. In the infrared, transitions are best ascribed to functional groups rather than individual molecules, so that identification of unique species is never easy. Visible and ultra-violet spectra, arising from electronic transitions, are perhaps the hardest to interpret, as can be seen from the DIB controversy. Although it is convenient to study large molecules in more-or-less inert matrices, it will eventually be necessary to use gas-phase species, and work in this area is progessing.

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7.2. HETEROGENEITY

There is ample evidence that interstellar clouds are inhomogeneous, even away from the complexity of star forming regions. The complexity of the formerly simple source TMC-1, well documented here, is a case in point. But the degree of inhomogeneity is unclear, and how to take it into account in models without overwhelming even the largest and fastest computers and the brains of the modellers is also unclear. From an observational standpoint, how accurate are current column densities, in which at least some degree of homogeneity is assumed? From a dynamics viewpoint, what are the smallest structures to be considered and how do they form and dissipate? When does self-similarity end? From a modelling standpoint, are simple homogeneous chemical models or slightly more complex slab models hopelessly inadequate? Do we need to include turbulence, mixing, collapse, etc for all situations? How are chemical and physical processes affected by inhomogeneous conditions? In some of these contexts, the temporal evolution of clumps may be even more crucial than their existence since sufficiently small time scales may diminish the importance of clumps.

7.3. UNCERTAINTIES IN CHEMISTRY/PHYSICS

Perhaps the largest uncertainties concern grains. Despite great increases in our understanding of interstellar grains in recent years described here, major uncertainties remain in our knowledge of grain chemistry and physics. Are we even sure in a quantitative sense of how grains nucleate and form? How important is photochemistry? What is the dominant mechanism of interstellar grain chemistry? How is the chemistry affected by grain shape and impurities on mantles? How does the chemistry involving small grains (large molecules) differ from that on and in classical grains? What is the role of tunneling in chemical reactions on interstellar grains? Reactions between radicals and H_2 on grain surfaces may be particularly important if tunneling is considered. How and at what rate do molecules desorb from cold grains? Several mechanisms have been advocated, but more detailed studies are surely needed.

Although relatively secure, our knowledge of gas-phase reactions still has large gaps. Despite a promising beginning, we still have little knowledge of neutral fragments for the vast majority of dissociative recombination reactions. Nor are we even sure that such reactions are more rapid in interstellar models than reactions between positive ions and large negative ions. Now that we know that neutral-neutral reactions may be rapid at low temperature even if one of the reacting species is stable, we still have little sense of their overall importance. We do know that models of large molecule formation are very sensitive to the rates of unmeasured neutral-

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neutral reactions involving oxygen atoms. Other uncertainties beset our understanding of how large molecules can grow, especially at high temperatures. The high-temperature combustion chemistry approach to PAH formation is plausible but the details are poorly understood. Even our knowledge of ion-molecule reactions is insufficient to model the low temperature growth of large molecules accurately, although laboratory studies suggest that growth proceeds through linear carbon clusters and unsaturated hydrocarbons to cyclic and tricyclic rings, and finally to fullerenes. Even if we know how to produce large molecules, we have little detailed understanding of their chemistry. For an understanding of the DIB problem, we must know how stable large molecules are in a strong radiation field, but except for a small amount of laboratory work, all we have at present are statistical estimates.

7.4. STAR FORMATION

Although many aspects of star formation including the infall of material are being studied, we still lack a general picture of the fate/fates of molecules during protostellar collapse and how observations of individual molecules can help us better understand the changing physical conditions. Accretion disks represent a particularly vital area for future astrochemical work, since these appear to be ubiquitous in low mass star formation and since the physical conditions are appropriate for molecular development. Some appropriate questions are whether the chemistry in accretion disks is dependent on what happened in earlier eras, how many of the gas phase species adsorb onto the dust, and what happens to them afterwards. Some chemical modelling work on accretion disks has already been undertaken and reported here, but much more can be done. The connection between the chemistry in accretion disks and the chemistry of the solar nebula is a very interesting link, which needs to be mapped out. Cometary and meteoritic studies often lead to the conclusion that pristine interstellar material has made its way into these bodies, but the connection among interstellar and circumstellar clouds, accretion disks, and primitive and not-so-primitive bodies has not been rigorously established.

7.5. EXTERNAL GALAXIES

Although the initial stage of astrochemistry was heavily devoted to galactic sources, this constraint is gradually being lifted, as discussed here especially for the Magellanic Clouds. As we study molecules in more galaxies, we will gain a better understanding of the different types of interstellar media and their relationships to galactic classifications. There is intense interest in active galactic nuclei among the astronomical community, and molecules

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provide an additional probe of these unusual objects. If molecular fractionation effects can be fully understood, the study of isotopomers in external galaxies can be turned into the study of isotopic abundance variations, which is of great interest to cosmologists. Molecules provide a handle on distant objects at large redshifts, close to the stage when the first molecules were made. Molecule formation in the early, pre-galactic universe may have had much to do with the formation of galaxies themselves. And molecules may even be found in the so-called "missing (baryonic) matter." Although some progress has been made on many of these topics, especially the chemistry of the early universe, the task ahead of us is not a small one.

8. Summation

We are living in a golden age of astronomy. New observations, aided by new observational instruments such as HST and ISO, are pushing back the frontiers of ignorance. The universe from its very beginning is becoming less mysterious if more complex. In this giant leap of understanding, molecules and astrochemistry are playing a significant role. As astrochemistry has evolved, it has broadened its scope to include a wide range of observational techniques and environments. Although its range may never be as great as that of astrophysics, astrochemistry has the advantage that the rich energy-level structure of molecules yields a great amount of information about the physical environments in which molecules are located. Astrochemistry may not tell us much about the first three minutes, but ultimately it should tell us our place in the universe.

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