*Astrochemistry: Recent Successes and Current Challenges*
*Proceedings IAU Symposium No. 231, 2005*
*D.C. Lis, G.A. Blake & E. Herbst, eds.*

doi:10.1017/S1743921306007551

# Astrochemistry: A Summary

**Alexander Dalgarno**

60 Garden Street, Cambridge, MA 02138

**Abstract.** A summary is given of the presentations delivered at IAU Symposium 231.

---

According to Big Bang cosmology the universe began as a very hot, weakly fluctuating, not quite uniform expanding plasma. It was not a promising scenario for the formation of structures. Yet as the Universe evolved, the baryons were distributed into clouds of gas and dust, condensed into stars, stellar remnants and planets, and assembled into groups and clusters of galaxies. On at least one occasion life emerged.

Astrochemistry deals with the molecules and the molecular processes that are central to the growth of complexity in the Universe. Because of their energy level structure molecules can be detected by observing transitions at wavelengths and frequencies ranging from the ultraviolet to the gigahertz, and they provide powerful unique diagnostic probes of astronomical environments. But they do much more than provide insight into the nature of astronomical events. In their control of the ionization balance and the thermal structure of cosmic gases, molecular processes are fundamental in bringing about the physical conditions in which gravitational collapse occurs and galaxies, stars and planets are formed.

The first International Astronomical Union Symposium in Astrochemistry took place twenty years ago in December 1985. This IAU symposium on Astrochemistry is the fifth. The series has charted the development of Astrochemistry into an extensive intellectual discipline in which Astronomy and Chemistry have merged and observers, experimenters and theorists have joined in a mutually enriching interaction. The future of Astrochemistry is assured by the exciting advances that have occurred since the last symposium in August 1999 and by the promise of new telescopes with improved spatial and spectral resolution operating over an extended range of frequencies. Results of observations with a wide range of telescopes have been presented here and we have the Atacama Large Millimetre Array (ALMA), the Herschel Space Observatory and SOFIA to look forward to, though we must take care not to be engulfed by the wave of data that we will be able to accumulate.

A major emphasis of this symposium has been star formation. Progress in understanding the several stages of star formation has been rapid, much of it stimulated by the ISO satellite. For low-mass stars a plausible picture has been constructed that begins with the collapse of a pre-stellar dense core in a molecular cloud. The collapse leads to a protostar embedded in an infalling envelope of gas and dust surrounded by an accreting protoplanetary disk. The infall is accompanied by an outflow driven by the evolving protostar. The outflows give rise to shocks and the dispersal of the envelope material exposes the gas to ultraviolet radiation from the parent protostar, creating photon-dominated regions (PDRs).

The several evolutionary stages are characterized by distinct spectral energy distributions (SEDs). They have been labelled Classes 0 and I (early and late), II and III. They are assumed to reflect an ordering in time. In a remarkable application of astrochemistry, the different continuum and line spectra arising from changes in molecular composition have been interpreted to yield a quantitative description of the density and temperature distribution and variations in velocity. There is chemical evidence for a freeze-out region in the envelope producing a fall in the molecular abundances. Depletion and desorption are critical elements in the modeling. A differential depletion of CO and $N_2$ appears necessary to explain the relative behavior of $HCO^+$ and $N_2H^+$, though recent experiments raise questions about the magnitudes of the binding energies.

Observations of low-mass protostars were reviewed by Cecilia Ceccarelli. She showed how chemical composition and SEDs could be employed to construct two-phase models consisting of a cold envelope around a hot core. She noted that the changing chemical composition might serve as a clock.

Observations of pre-stellar cores, dense condensations of dust and gas with no apparent sign of an interval energy source, were summarized by Mario Tafalla. He also stressed the usefulness of changes in chemical composition and in tracking the evolution of different objects.

Observations place new demands on the development of adequate theoretical models with which to interpret the data and to predict further observations. One such model of pre-stellar cores was advanced by Valery Shematovich.

The most direct evidence of depletion is the existence of abundant multiply-deuterated species. Because of depletion the destruction of deuterated molecular ions is slowed and the ions have time to undergo fractionation driven by reactions with HD molecules and with D atoms. Helen Roberts gave an enlightening discussion of the deuterium chemistry. Deuterium chemistry came up time and time again in the meeting.

Because of the large disruptive effect of the formation of high-mass stars, the sequence of events is less clear. High-mass Young Stellar Objects (YSOs) reveal large variations in chemical composition. They can be generally described as composed of a hot compact core surrounding an ultra compact H II region embedded in an envelope with an inner warm and outer cold region. The complex environment of young massive stars was discussed by Stan Kurtz. He identified a hot phase in which molecules that had been frozen onto grains during the collapse undergo sublimation back into the gas phase as the newly formed star warms its environment, and he drew attention to the occurrence of high-mass starless cores.

Steven Doty gave an instructive comparison of chemical models of the composition of low- and high-mass YSOs. The chemistry of hot cores was the subject of Serena Viti's talk. She demonstrated the value of molecules as evolutionary tracers. Hot cores are the places where complex organic molecules are found.

Geoff Blake gave us a broad instructive account of observations of circumstellar disks and their relationship to planetary formation. He discussed the diagnostics of infall and rotation and pointed out the importance of the ionization distribution. Inga Kemp described how models of the disk chemistry are similar to but different from those of interstellar chemistry. She showed in more detail how chemistry serves as a control of the structure of protoplanetary disks, as did Andrew Markwick-Kemper, who drew attention to the usefulness of observations of isotopic molecules.

Joan Najita demonstrated the value of infrared observations in understanding the formation of planets from disks and the circumstances in which terrestrial-like planets could come into existence.

Hans Olofsson reviewed the molecular abundances in the circumstellar envelopes of AGB stars and stressed the need for improved models and physical data. Jose Cernicharo examined the AGB star IRC + 10216 in which 60 molecular species have been detected from which the physical parameters of the gas and dust could be derived and Ciska

https://doi.org/10.1017/S1743921306007551 Published online by Cambridge University Press

Markwick-Kemper discussed the dust in the outflow of the Red Rectangle observed with the Spitzer Space Telescope.

Complex organic molecules are, by their connection to living organisms, of absorbing interest, though as yet no biological molecule has been found in interstellar space. Apparently the discovery of glycine has to be withdrawn. New mechanisms of the formation of complex molecules were proposed by Steve Charnley, who suggested that deuterated organic molecules would provide a test of the chemical sequences. Marla Moore described laboratory data on complex molecules resulting from proton bombardment of an icy surface and Mike Hollis reviewed observations and mechanisms for the production of isomers. The difficulties in spectroscopic identifications were discussed by Aldo Apponi. Their detection in star-forming regions was reviewed by Sheng-Yuan Liu who showed the value of interferometric observations and who drew attention to the large number of unidentified lines.

Shocks are a ubiquitous phenomenon in the interstellar medium and their effects on molecular gas are profound. In fast shocks the molecules are dissociated and the gas is ionized. The chemistry is that of a cooling recombining gas subject to precursor radiation. In slow shocks the gas is heated and not only is the chemistry modified by endothermic reactions, it is enhanced by materials released from grains. The chemistry is a valuable determinant of the physical parameters of the shock as shown by Malcolm Walmsley. The chemistry serves to differentiate shocks from PDRs, which are regions heated by intense ultraviolet radiation, and from X-ray dominated regions (XDRs), which are regions subjected to intense X rays. Amiel Sternberg reviewed the essential physics and chemistry of PDRs and XDRs and Maryvonne Gerin gave a more specialized talk on carbon chemistry in PDRs.

The basic data that enter into models of the composition of gases and dust were the subject of twelve presentations. Basic data are the identification and determination of spectroscopic lines and bands, calculations and measurements of cross sections for collisional excitation and ionization, charge transfer, photodissociation, photoionization and chemical processes in the gas phase and in and on grains. These studies are a vital component of astrochemistry and we must do what we can to encourage them. Remarkable progress has been made.

In the first session which was on gas-phase processes, Tom Millar summarized the present state of our knowledge, listed the available databases and identified some critical needs. Extraordinary technical skills were exhibited by four experimenters. Thomas Giessen reported measurements of spectral lines at teraherz frequencies expected from light hydrides, carbon chains and complex molecules. Experiments at low temperatures on neutral-neutral reactions were reported by Iam Sims. The variation with temperature of rate coefficients that he found was unexpected. Wolf Geppert measured rate coefficients of dissociative recombination of protonated methanol and Stephen Schlemmer measured rate coefficients of the deuterium fractionation reactions. As an example of theoretical contributions, Marie-Lise Dubernet presented her sophisticated calculations of heavy particle excitation cross sections.

The physics and chemistry of grains and of polycyclic aromatic hydrocarbons (PAHs) occupied the second session. Martin McCoustra described elegant careful measurements of desorption from grain-mantle analogues, Naoki Watanabe investigated grain reactions as a source of deuterated organic molecules and Thomas Henning gave a broad informative review of observations and experiments on silicates and their use as diagnostics, including their appearance in meteorites. Douglas Huggins reported on the Spectroscopy of PAHs (are PADs interesting?) and introduced the idea of possible contributions to the 6.2 $\mu$m emission feature of polycyclic aromatic nitrogen heterocycles (PANHs). Sven

https://doi.org/10.1017/S1743921306007551 Published online by Cambridge University Press

Thorwirth gave results of measurements of rotational transitions of specific PAHs. There was an enlightening contribution from Geerd-Jan Kroes on the theory of scattering and photochemistry of ice surfaces which yielded some unexpected interesting results.

Because of the exciting discoveries of extrasolar planets, the study of the solar system, and its relationship to its parent star and to the interstellar medium out of which it was formed, assumes a new importance as a nearby example of a planetary system, though the extrasolar planets detected so far appear to have highly unusual properties, as Sara Seager told us. Actually, Geoff Blake remarked that it is the solar system planets that are unusual. Sara discussed aspects of the photochemistry of their atmospheres. She made it clear that we are at the beginning of an exciting extension of astrochemistry which leads me to suggest we include more on the atmospheres of the planetary satellites such as Titan, Triton and Europa in our next symposium. There were two posters on reactions of CH and $C_4H$ with hydrocarbons by Bergeat *et al.* and Berteloite *et al.* that may occur in the atmospheres of Titan and Triton and in interstellar clouds.

Didier Despois reviewed a large amount of information on comets and explored the connection with the interstellar medium. He compared organic molecules and PAHs in comets and interstellar clouds with particular references to Hale-Bopp which is an abundant source of complex molecules. Oliver Botta discussed the molecular content of carbonaceous meteorites and described the procedures used to analyze them. He provided a list of amino acids found in meteorites and noted that two of them are not found on earth. He included a comparison of the cometary molecules and discussed pathways for the production of amino acids. Frank Bensch reviewed SWAS data on comets and reported new results on Tempel 1 and Deep Impact. He derived water production rates and showed they varied with time. Deep Impact was tracked. The analysis and interpretation continue. Don Brownlee gave a fascinating account of interplanetary dust particles. They offer an additional source of information of a unique character. He concluded with the idea that femto-rocks are the original building blocks of the planets. He pointed to hotspots of D/H as indicating an origin in molecular clouds.

Astrochemistry began as a discipline with the chemistry of diffuse clouds, and diffuse clouds present a continuing challenge. Ben McCall reported on optical and infrared observations, Harvey Liszt on millimeter observations and Ted Snow on ultraviolet observations. Ted spoke mostly on the FUSE data. He was not optimistic about the future of ultraviolet astronomy despite, as he showed, its considerable potential. Ben McCall showed some of his data on the diffuse interstellar bands (DIBs). Their origin is an outstanding spectroscopic mystery. Evelyne Roueff put forth new models of diffuse clouds which have three components with different densities and temperatures. They achieved general but not precise agreement with measured abundances of diatomic species. The abundances found by Harvey Liszt of species like $HCO^+$, HCN, HNC and $C_2H$ in what may be translucent clouds present an interesting challenge. The chemistry may be correct; it is the physical model and perhaps the assumption of a steady state that require attention. The simple models are successful in explaining the abundances of HF, unexpected though its discovery was. David Neufeld *et al.* went on to predict the presence of $CF^+$ (isoelectronic with CO). David reported here its detection towards the Orion Bar.

The observation of absorption by $H_3^+$ by Tom Geballe, Takeshi Oka and Ben McCall was a major advance, long anticipated. Despite the simplicity of its chemistry, interpretation may not be immediate. From measurements towards $\zeta$ Persei, McCall *et al.* (2004) inferred an ionization rate of $1.2 \times 10^{-15}$ s$^{-1}$. With a more elaborate model, Franck Le Petit, Evelyne Roueff and Eric Herbst derived the much lower rate of $2.5 \times 10^{-16}$ s$^{-1}$. The slower rate agrees with the value presented by Stephen Lepp at the IAU Symposium in Brazil in 1991, which was based on measurements of HD and OH. Stephen Lepp was quoting Ewine van Dishoeck who had obtained $2 \times 10^{-16}$ s$^{-1}$ using the now accepted faster rate for dissociative recombination of $H_3^+$. The lower ionization rates obtained at the time were based on a slow recombination rate. It would be interesting, Ewine, to know what you predicted for the abundance of $H_3^+$ in those models. Whatever, it seems that a larger ionization rate is appropriate. These rates are larger than the value of $5 \times 10^{-17}$ s$^{-1}$ that appears to be typical of dense clouds. That the rate in dense clouds could be less than in the intercloud region was pointed out years ago.

Extragalactic molecules offer an exciting project for chemically probing the universe. Molecules in external galaxies promise to become a major source of information about the evolution and structure of galaxies and should enable distinctions to be drawn between different galaxy types. Carbon monoxide has been detected in a quasar at a red shift of 6.42 when the universe was less than a billion years old. Cooling by collisional excitation of $H_2$ and HD was crucial to the formation of the first distinct cosmological objects, as Tom Abel noted in his simulations. Not much is yet understood about where and when the first heavy elements were made and still less is understood about the production of heavy molecules. One of the first heavy elements was probably oxygen and the first heavy molecule would have been OH.

I mention OH because it could provide limits on the variation in time and space of the proton gyromagnetic ratio. Observations of molecules in external galaxies and their interpretation were described by Suzanne Aalto, Pierre Cox, Christine Wilson, and Henrik Spoon. They demonstrated the value of chemical composition as a diagnostic probe. The $CO/H_2$ ratio is an important number which will depend on galaxy type.

There were five special talks, focusing on the unexpected lack of $O_2$ in molecular clouds. The SWAS data were examined by Ted Bergin who gave a comprehensive picture of the distribution of water. The ODIN data were examined by Rene Liseau. As both speakers made clear, we learn much from the near-absence of $O_2$. Klaus Pontoppidan introduced us to the idea and reality of mapping the ice distribution in star-forming regions. Neal Evans surveyed broadly the exciting results from Spitzer, and Eric Becklin told us what we can expect from SOFIA.

The special session was followed by a Panel Discussion presented by a distinguished assembly of older and, we hope, mature astrochemists. It was chaired by David Williams, who managed to keep control of a potentially unruly group.

The consensus of the panel was that grain-gas interactions were the major uncertainty in astrochemistry and that is primarily an experimental question. Tom Phillips raised the question—where is all the deuterium? It was agreed that theorists should attempt to predict what observers measure rather than have observers derive what theorists calculate. It is better apparently to have brilliant insights than to carry out large-scale calculations. In my personal view, they are not mutually exclusive and both can be attempted at the same time, each supporting and amplifying the other.

The fundamental question of the formation of $H_2$ and HD was addressed in several challenging experiments. Measurements were reported by Stephanie Cazaux, Liv Hornekær and Gianfranco Vidali, and a theoretical analysis of $H_2$ and HD was advanced by Ofer Biham. We need to understand not only the rates of formation, chemisorption, physisorption and quantum tunneling, but also the details of the energetics. There is astrophysical evidence that the velocity dispersion increases with the level of rotational excitation and observations of PDRs appear to indicate a more rapid rate for a warmer grain-gas interaction as Stephanie Cazaux noted.

The posters, both in number and in content, were a testament to the vitality of Astrochemistry today. Over 200 posters were presented, all directly relevant and interesting and all addressing real questions. Regrettably I cannot mention them individually. There were observational, experimental and theoretical papers relating to low- and high-mass star formation and to protoplanetary discs. PAH's, neutral and ionized, received much attention as did diffuse cloud chemistry, and the Red Rectangle was the favorite object, followed by DIBs and the Early Universe. There were extensive laboratory and theoretical posters on grain and gas phase processes and chemical schemes for the formation of organic molecules were proposed.

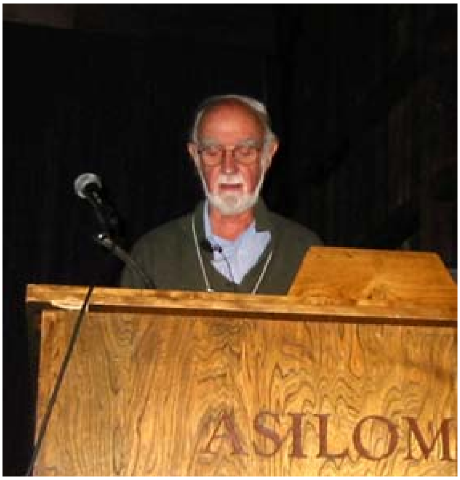


Photo: E. van Dishoeck

https://doi.org/10.1017/S1743921306007551 Published online by Cambridge University Press