

Astrochemistry and the Role of Laboratory and Theoretical Support

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ABSTRACT

We emphasize some current needs of astrochemists for laboratory data. The data are urgently required both to detect molecules in assorted regions and to produce robust models of these regions. Three areas of laboratory-based research are particularly crucial and yet are not being studied in the United States: (i) reactions more complex than the formation of molecular hydrogen occurring on interstellar grain analogs, (ii) molecular spectroscopy in the THz (far-infrared) region of the electromagnetic spectrum, and (iii) gas-phase kinetics of reactions leading to complex molecules. Without solid knowledge of many unstudied but key reactions, both in the gas and on grains, astrochemists will not be in position to keep up with the large amount of new information expected to come from the next generation of telescopes.

1. Introduction: the Role of Spectroscopy

There would exist no astrochemistry, and very little astronomy, if there were no atomic and molecular spectroscopy. Spectroscopy, the study of the interaction of matter and radiation, lies at the heart of any detailed research concerning material in the heavens. In the interstellar medium of our galaxy and others, the rich molecular nature of the gas phase of dense objects has been discovered and studied mainly through the rotational spectroscopy of molecules, typically detected in the microwave, millimeter-, and submillimeter-wave regions. But, in order to use spectroscopy for remote sensing, one must know the spectra thoroughly from laboratory studies. The current generation of millimeter-wave and submillimeter-wave telescopes are useful for molecular research only because of relevant laboratory studies by

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groups such as our own, which pioneered the movement from the microwave to higher frequency regions.

In recent years, we have used our ultra-fast (“FASSST”) spectrometer, most often in the frequency range 100-400 GHz, to study organic molecules somewhat larger than those currently known to be in interstellar clouds in an attempt to help astronomers find these species in space. Typically located in warm regions associated with protostars, known as hot cores or hot corinos, the molecules are interesting in an astrobiological sense as prebiotic species and tell us information concerning the physical conditions of the sources. Although these molecules had been studied before at lower frequencies, it is very difficult to predict a higher-frequency spectrum from lower-frequency data because of the non-rigidity of the molecules. And yet it is the higher frequencies that are often associated with molecules in warm star-forming regions, since the higher temperatures allow excitation to higher molecular energy levels, which are typically separated more widely than the lower-lying rotational levels. Some of the species recently studied in our laboratory are the alcohols *n*-propanol ($\text{CH}_3\text{CH}_2\text{CH}_2\text{OH}$) and *iso*-propanol ($(\text{CH}_3)_2\text{CHOH}$), the ethers ethyl methyl ether ($\text{C}_2\text{H}_5\text{OCH}_3$) and diethyl ether ($\text{C}_2\text{H}_5\text{OC}_2\text{H}_5$), the ester ethyl formate (HCOOC_2H_5), and the pre-biotic species oxiranecarbonitrile (*c*- $\text{H}_2\text{COC(H)CN}$) and cyanofornamide (NCCONH_2) (Maeda et al. 2006; Fuchs et al. 2003; Medvedev et al. 2003; Behnke et al. 2004; Winnewisser et al. 2005). In addition to these studies, we have collaborated with the group at the University of Cologne in Germany to study molecular spectra in the 1-2 THz region for a small number of species, most importantly the radical methylene (CH_2), which was subsequently detected in the galactic center based on our measurements (Michael et al. 2003; Bruenken et al. 2004; Polehampton et al. 2005).

Although the Cologne group does study some molecules in the THz region, this group has lost both its long-term funding and its leader, Gisbert Winnewisser, who has retired. Moreover, it is probably the only group in the world that specializes in this arcane area of spectroscopy. Yet, with the advent in the near future of telescopes operating in the THz, or far-infrared, region of the electromagnetic spectrum, much more laboratory spectroscopic information will be required to make sense of the huge amounts of data to be taken. Both SOFIA, an airborne project developed by NASA in collaboration with the German Space Agency, and Herschel, a space telescope developed by ESA with the help of NASA, will operate in regions where little laboratory information has been obtained. Without a crash program in laboratory THz studies, a catastrophe may be in the making.

Since most rotational spectral lines in the interstellar medium are detected in emission, it is often necessary to understand the details of molecular excitation via rotationally inelastic collisions in order to convert a line of a given intensity into a column density. The laboratory study of rotational excitation is very difficult, and most of the needs of astronomers have been met by theoretical chemists. Since the death of the late Sheldon Green, the US has seen very little if anything in the way of such theoretical studies, which are performed mainly by groups in the United Kingdom and France.

2. Astrochemistry and Star Formation

By the analysis of molecular spectra and continua from dust particles, astrochemists have succeeded in understanding much of the evolution of cold cores of dense interstellar clouds into stellar and planetary systems. Each of the sources along the way, however, is likely to be heterogeneous and to have a complex history. In order to understand the sources in some detail, one must study the chemical processes that create and destroy molecules and use these processes in large simulations in which both chemistry and possibly dynamical changes take place. If the chemistry is to be used to try to unravel the history and heterogeneity of the sources, a secure knowledge of all of the chemical processes occurring is needed.

The evolutionary path to low-mass star formation goes through the following stages (Herbst 2005a): (i) *cold cores*, defined as stable regions characterized by a rich gas-phase chemistry, a density of 10^4 cm^{-3} chiefly composed of H_2 , and a temperature of 10 K; (ii) *prestellar cores*, which are collapsing regions maintaining a near constant temperature of 10 K but developing a central condensation of density 10^{5-6} cm^{-3} where gas-phase species heavier than hydrogen and helium are strongly accreted onto the dust particles, (iii) *protostars*, observed as regions in which the central condensation has started to heat up, a disk of gas and dust has formed in the equatorial plane, violent jets flow out along the poles, and the envelope warms to a temperature of 100-300 K, constituting what is now known as a “hot corino”; (iv) *protoplanetary disks and T Tauri stars* in which adolescent stars have formed surrounded by dense disks of gas and dust.

All of the objects along the path to low-mass star formation have been modeled using large chemical networks, mainly consisting of gas-phase processes. State-of-the-art gas-phase networks contain about 4000 reactions and 400 species. These networks include the UMIST collection (<http://www.udfa.net/>) and the Ohio State compendium (<http://www.physics.ohio-state.edu/~eric/research.html>), both of which are available for use by astrochemists. Use of these networks, however, is afflicted by the following four classes of chemical problems:

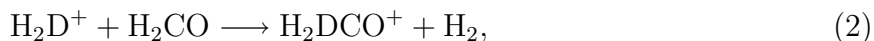
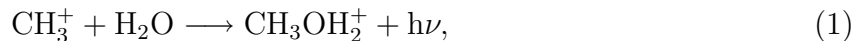
- uncertain rate coefficients
- incomplete chemistry (missing reactions, missing temperature ranges)
- incorrect chemistry or rate coefficients
- non-thermal chemistry (e.g. ortho/para effects).

Let us consider these problems in turn. The effect of uncertain rate coefficients can be quantified by a Monte Carlo analysis in which each rate coefficient and its uncertainty is treated as a log-normal distribution Wakelam et al. (2005). For any given simulation, each rate coefficient in the set of approximately 4000 is chosen randomly according to its distribution. The simulation is rerun many times, until good statistics are obtained. Unless non-linear effects occur, the calculated concentration for each molecule at any given time

is a distribution of values with a Gaussian or near-Gaussian shape. Thus, the output of the model calculation is an abundance and its uncertainty at all times for each species. Moreover, the important reactions leading to the uncertainties can be elucidated, so that improved measurements can be made.

The effect of incomplete chemistry is hard to deduce, since it is difficult to prove that a large model is incomplete. For temperatures higher than 300 K, however, it should be realized that many endothermic reactions and exothermic reactions with barriers will start to become competitive. The use of standard databases designed more for low temperatures can be fraught with error, although the UMIST data base makes some allowance for endothermic processes. In our view, two types of additional calculations can be considered. First, one can consider inclusion of the backwards reactions for all reactions in the networks, using a thermal equilibrium argument to deduce the rate coefficients for the reverse processes. If there is a significant difference in the results, other processes may also have to be taken into account. If there is no difference in the results, it is likely that the network is still valid. Secondly, at still higher temperatures one can consider the use of a true thermodynamic approach in which the global free energy is minimized.

Incorrect chemical processes or those with incorrect rates in the networks can only be discovered by laboratory or theoretical studies. Four examples to be considered are the three specific processes:



and the general case of dissociative recombination reactions. Reaction (1), a radiative association, has recently been measured to proceed orders of magnitude more slowly than predicted at temperatures under 100 K (Luca et al. 2002). This reaction was supposed to lead to the formation of methanol in cold cores by the dissociative recombination of protonated methanol with electrons. Reaction (2) was supposed to start the deuteration of formaldehyde, eventually leading to the isotopologs HDCO and D₂CO by cycles of deuteration and dissociative recombination reactions. It has been calculated, however, that the reaction proceeds to make the deuterated ion H₂COD⁺, with the deuteron on the opposite side of the molecule from the two protons (Osamura et al. 2005). The ensuing dissociative recombination produces H₂CO + D and possibly HCOD + H, neither of which set of products contains HDCO. The third reaction was supposed to lead to the production of protonated methyl formate in hot cores, starting from methanol that had earlier evaporated from grain mantles due to rising temperatures. The reaction does not occur because of a large activation energy barrier (Horn et al. 2004). Finally, storage-ring results indicate that a class of dissociative recombination reactions involving hydrogen-rich ions, designated AH⁺, tend to fragment strongly rather than to give off a single H atom to product the species A (Geppert et al. 2006). Examples include the CH₃OH₂⁺ + e⁻ reaction, in which the methanol

+ H channel is only 6%, and the $\text{CH}_3\text{OHCH}_3^+ + e^-$ reaction, in which no dimethyl ether + H is found. The latter reaction was considered to be critical in forming dimethyl ether in hot cores at temperatures of 100-300 K. New methods of synthesizing this and other complex hydrogen-rich species thought to form in hot cores via dissociative recombination will have to be studied. One possibility is to consider the chemistry occurring on warming grain surfaces (Garrod & Herbst 2006). Other possibilities involve high-energy processes such as irradiation on grain surfaces. Clearly, more work is needed to understand the formation of organic molecules in warm environments.

Non-thermal effects can strongly affect rates of reaction. Consider the reaction system



which is exothermic in the left-to-right direction by 230 K. In a 10 K cloud, the backwards, endothermic reaction is exceedingly slow and the equilibrium lies far to the right, so that H_2D^+ becomes highly abundant compared with H_3^+ , a process known as fractionation (Herbst 1982). Indeed, the equilibrium constant is larger than 10^9 . But, suppose that the system is not strictly thermal, and that a small portion of ortho- H_2 in its $J = 1$ state exists. This state can collide with H_2D^+ to exothermically excite that ion to its lowest ortho state, designated 1_{11} . The reaction between the lowest ortho states of H_2 and H_2D^+ to form $\text{H}_3^+ + \text{HD}$ is exothermic rather than endothermic, so is much faster than the thermal value. This non-thermal effect can possibly be quantified by actual measurements of deuteration in cold sources as a function of temperature (Maret 2006).

3. Grain-Surface Chemistry

Much of the chemistry that occurs in cold regions of the interstellar medium occurs on the surfaces of dust particles, probably by the well-known Langmuir-Hinshelwood, or diffusive, mechanism. The most important reaction, the production of molecular hydrogen from the surface recombination of two hydrogen atoms, has drawn the most attention, both theoretically and in the laboratory. Although other processes have received some study, much more work remains to fully quantify them. Among the most important reactions are those involving atomic hydrogen, since this atom is bound particularly weakly to surfaces and so diffuses readily, and is also quite reactive. Consider, for example, what happens to an oxygen atom that lands on and sticks to a grain surface. When a hydrogen atom lands on the same grain, it diffuses readily and eventually finds the rather stationary oxygen atom. Like the situation in the gas phase, an OH complex is formed. But, unlike the situation in the gas phase, the grain acts as a third body to remove sufficient energy from the complex to stabilize it. The newly formed OH radical is as reactive as its precursor, and associates with the next diffusing hydrogen atom to form water. Unlike the case of H_2 , which is weakly bound to the grain and so eventually desorbs back into the gas, water is strongly bound and remains on the surface. In cold regions, this conversion of O into H_2O continues and eventually

forms a sizable mantle of water ice, which is detected through infrared absorption. Similar processes result in the hydrogenation of carbon atoms into methane and of nitrogen atoms into ammonia, although competing reactions in the gas phase lower the amount of C and N available for accretion. As the cold cloud ages, copious amounts of carbon monoxide are produced in the gas, and some accretes onto grain surfaces. Despite the fact that the reaction possesses some activation energy, the hydrogenation of surface CO, designated CO(s), into HCO:



occurs. Once the radical HCO is formed, a second hydrogenation occurs facily to form formaldehyde, H₂CO. Subsequent hydrogenation to form the methoxy radical and finally methanol has been detected in one laboratory but not in others (Hidaka et al. 2004). The sequence of reactions is important because no mechanism is known to produce methanol efficiently in the gas. More work is clearly needed.

Not only are few surface reactions understood in any degree of detail, but the desorption of molecules back into the gas is also poorly understood. In the absence of star formation, the cloud remains cold so that no species heavier than hydrogen and helium can evaporate into the gas. Yet, to account for the gas-phase abundance of methanol in cold sources, there must be some non-thermal desorption mechanisms. Possible mechanisms considered are cosmic ray heating of the grains, photodesorption, and desorption via the energy generated in exothermic chemical reactions, but none has been studied in the degree of detail needed to understand fully what occurs in interstellar clouds. Once again, more work is clearly required.

So far, almost all experiments on analogs of interstellar dust particles have been undertaken with large surfaces rather than with actual dust particles. It has been shown that there are severe differences in the reaction mechanisms for processes on small particles and those on larger surfaces, especially when in the former case, there is on average less than one reactive surface species per grain (Herbst 2005b). Consequently, experiments that probe surface chemistry on and desorption from tiny particles would be most desirable.

4. Summary

Laboratory astrophysics has been and still is crucial for understanding star formation and other processes in the interstellar medium. At this time, some key projects can be identified, including the following:

1. the sustained study of molecular spectroscopy in the THz regime,
2. the calculation and measurement of rotationally inelastic rate coefficients,

3. the improvement of gas-phase chemical networks by (i) the reduction of uncertainties in rate coefficients, (ii) the correction of errors, and (iii) the inclusion of non-thermal processes when necessary,
4. the study of grain-surface chemistry, especially involving products more complex than molecular hydrogen.

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