Astrochemistry: Historical Perspective and Future Challenges

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Abstract. A review is presented of some of the developments in astrochemistry that have occurred in the past three years, ranging from the chemistry of the early Universe to the chemistry of planetary systems.

1. Introduction

Astrochemistry is a blending of astronomy and chemistry in which each area of research enriches the other in a mutually stimulating interaction. Astrochemistry began sixty years ago with the observation of visible absorption lines in the interstellar gas attributable to the diatomic molecules CH, CN and CH^+, coupled with experiments in laboratory spectroscopy and with theoretical attempts to identify the processes through which molecules are formed and destroyed in the diffuse interstellar medium. It has grown into a unified discipline of extraordinary power that reaches into all corners of astronomy beginning with the recombination era. It involves observations across a major fraction of the electromagnetic spectrum of molecules ranging from the simple diatomic hydrogen molecule to complex organic species. In addition to providing diagnostic probes of unique capability, molecules play a controlling role in determining the ionization and thermal balance of the plasmas in which they are formed and their presence is a fundamental aspect of the dynamics and evolution of astronomical objects.

In addition to stellar and planetary atmospheres and diffuse, translucent and dense interstellar clouds, molecules in the gas phase and on grain surfaces have been detected in circumstellar shells, HII regions, emission nebulae, planetary nebulae, Herbig-Haro objects, supernova remnants, supernova ejecta, novae, shocked gas subjected to outflows, photodissociation or photon-dominated regions, star-forming regions, accretion disks, cooling flows and external galaxies as distant as a red-shift of 4.69. Because of the extreme nature of the environments, often hostile, in which molecules are found to survive, a detailed understanding of the chemical reaction mechanisms is needed to identify the critical molecular processes and to apply properly the results of laboratory measurements which are made in entirely different physical conditions of density, temperature and radiation fields. It was the recognition that progress depended upon an intimate collaboration between the two disciplines that led to the creation of the IAU Working Group on Astrochemistry and to the series of symposia of which this is the fourth.

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The last three years have seen extraordinary progress. I have space to mention only a few of the major advances. I will begin with a brief account of the early history of Astrochemistry.

2.   Early History

The first consideration of molecules in interstellar space may have been reported in the Bakerian lecture by Eddington in 1926 on Diffuse Matter in Interstellar Space. Eddington remarked, apparently in response to a question from the audience, that "it is difficult to admit the existence of molecules in interstellar space because once a molecule becomes dissociated there seems no chance of the atoms joining up again. The atoms will be ionized and unable to combine." Eddington added that "if this seemingly fatal objection is overruled might we not find some traces of band spectra in stars which are partially dimmed by the nebula?"

Such spectra were found a decade or so later by Adams, Dunham, & McKellar (Dunham 1937; Dunham & Adams 1937; McKellar 1940; Adams 1941) which established the presence of CH, CH^+ and CN, though the identification of CH^+ waited upon laboratory measurements of Douglas & Herzberg (1941). The relative strength of absorption lines originating in the lowest two rotational levels of CN yielded a rotational temperature of 3 K. The level populations are controlled mainly by spontaneous emission and stimulated emission and absorption by the cosmic background radiation and, though not recognized at the time, the interstellar observations provided the earliest measurement of the radiation temperature.

Initial theoretical attempts by Swings (1942) and by ter Haar (1943) and Kramers & ter Haar (1946) were superseded by the study of Bates & Spitzer (1951) which included most of the processes we employ today. The Bates-Spitzer discussion was extended by Solomon & Klemperer (1972) to explain CN by the reaction of CH and CH^+ with N atoms and by Black & Dalgarno (1973a) to explain CH as the product of the dissociative recombination of CH_2^+ formed by the radiative association of C^+ and H_2. None of the studies was successful in reproducing the abundance of CH^+, a problem that remains with us to this day. The explosion in observational studies that has occurred in the last 35 years was triggered by the discovery of OH at radio wavelengths by Weinreb, Barrett, Meeks, & Henry (1963). Ammonia was the first polyatomic molecule to be found (Rank, Townes, & Welch 1973) and OH was the first extragalactic molecule (Weliachew 1971). The spectral range of molecular observations has been extended to far-infrared and submillimeter wavelengths and particularly informative about molecules on grains have been data gathered with instrumentation on the ISO satellite which covered wavelengths from 2.5 μm to 200 μm.

Well over 100 distinct molecular species have been detected subsequently in interstellar clouds and circumstellar shells and evidence has accumulated that very large molecules may be present in the diffuse interstellar medium.

Early attempts to explain the abundances of molecules more complex than the diatomic species involved formation on the surfaces of grains but with the identification of X-ogen as HCO^+ by Klemperer (1970) attention focused more on ion-molecule chemistry driven by cosmic rays (Herbst & Klemperer 1973;

Watson 1973; Black & Dalgarno 1973b). The importance of grain chemistry is now widely recognized and gas phase and grain surface chemistries have been extended to incorporate hundreds of species and thousands of reactions (Herbst 1995; van Dishoeck 1998).

## 3. Recent Advances

3.1. Early Universe

There has been progress in the determination of molecular abundances in the early Universe in the sense that the various theoretical predictions are mostly in reasonable agreement (Stancil et al. 1998; Galli & Palla 1998). The predicted abundances of LiH and LiH$^+$ are very small though there remain questions over the rates of the reactions (Stancil et al. 1996)

$$\text{LiH} + \text{H} \rightarrow \text{Li} + \text{H}_2$$

$$\text{LiH}^+ + \text{H} \rightarrow \text{Li} + \text{H}_2^+$$
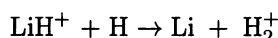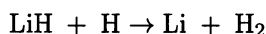
and of the dissociative recombination of LiH$^+$,

$$\text{LiH}^+ + e \rightarrow \text{Li} + \text{H} ,$$
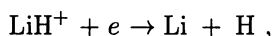
which may be quite slow. In the case of the deuterium chemistry, the differences between the calculations of Galli & Palla (1998) and Stancil et al. (1998) stem from assumptions about the rate coefficients of the radiative associations

$$\text{H}_2^+ + \text{H} \rightarrow \text{H}_3^+ + \nu$$

$$\text{H}^+ + \text{H}_2 \rightarrow \text{H}_3^+ + \nu.$$
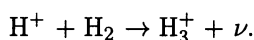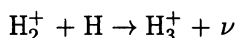
The formation of the first cosmological objects that separated out of the cosmic flow has been the subject of much attention (Haiman, Thoul, & Loeb 1996; Tegmark et al. 1997; Haiman, Rees, & Loeb 1996, 1997; Parravano & Pech 1997; Ferrara 1998; Omukai & Nishi 1998; Abel et al. 1998; Brown, Coppi, & Larson 1999; Nakamura & Umemura 1999), but the chemistry has been limited to reactions involving hydrogen. The production of the collapsed objects led to the reheating and re-ionization of the Universe and exerted a profound influence on the subsequent structure. It also led to the production of heavy elements that were distributed into the Universe by winds and explosions. The first heavy molecule was OH followed probably by H$_2$O and CO.

3.2. Interstellar clouds

Central to ion-molecule chemistry in dense interstellar clouds is the molecular ion H$_3^+$ produced by the reaction of H$_2^+$ with H$_2$, as first noted by Martin, McDaniel, & Meeks (1971). The long-awaited detection of H$_3^+$ in interstellar space has been achieved through a brilliant combination of laboratory and astronomical

spectroscopy (Geballe & Oka 1996; Geballe et al. 1999; McCall et al. 1998, 1999). Though the chemistry of H_3^+ is simple, the observations of it in an apparently diffuse region towards the star Cygnus OB 12 No. 2 present some problems of interpretation (Geballe et al. 1999). A model of clumps of density 10^2 cm^{-3} in a diffuse interclump medium has been proposed (Cecchi-Pestellini & Dalgarno 1999).

The deuterated version H_2D^+ has now been definitely detected but in emission, not absorption, from the young stellar object NGC1333 IRAS 4A (Stark, van der Tak, & van Dishoeck 1999). The abundance is enhanced by chemical fractionation.

The central importance of H_3^+ stems from its reactivity with neutral atoms which initiates chemical sequences that terminate by dissociative recombination and create complex molecules (Herbst & Klemperer 1973; Watson 1973). A major uncertainty attends the branching ratios of the different channels open in dissociative recombination, though some data were available from afterglow measurements (Herd, Adams, & Smith 1990; Adams et al. 1991). In important cases, the uncertainties have been removed by experiments using heavy ion storage rings (Vejby-Christensen et al. 1997; Larson et al. 1998; Semaniak et al. 1998; Vikor et al. 1999; Derkatch et al. 1999). Herbst & Lee (1997) and Bergin et al. (1997) have explored the effects of the revised branching ratios.

Important laboratory and theoretical studies of gas phase and grain surface reactions have been carried out. Some examples are the investigations of Scott et al. (1997a,b), Brownsword et al. (1997), Hiraoka et al. (1998), Dartois et al. (1998), Kaiser et al. (1998), Kaiser et al. (1999), Bergeat et al. (1999), and Fukuzawa, Osamura, & Schaeffer (1999). However, there remain large uncertainties in the details of many of the reactions comprising the interstellar chemical network. It was pointed out by Amin, Shalabiea, & Herbst (1997) and Ruffle et al. (1999) that the UMIST (Millar, Farquhar, & Willacy 1997) and NSM (Terzieva & Herbst 1998) compilations of reactions yield very different molecular compositions. Still greater uncertainties attach to the processes of grain chemistry.

The explanation of the abundances of CH$^+$ in diffuse clouds remains elusive though the suggestion that it arises in turbulently heated gas has been proposed (Joulain et al. 1998).

Another kind of uncertainty of basic importance is introduced by the existence of multiple solutions of the chemical network (Pineau des Forêts, Roueff, & Flower 1992; Le Bourlot et al. 1993, 1995a,b; Shalabiea & Greenberg 1995; Lee et al. 1998).

There are still no detections of molecular oxygen. Severe upper limits of 0.04 and 0.05 have been placed on the O_2/CO ratio by searches with a balloon-borne telescope (Oloffson et al. 1998). Constraints on the abundance of solid O_2 have been obtained from ISO data (Vandenbussche et al. 1999). It appears that much of the oxygen is in atomic form (Poglitsch et al. 1996; Baluteau et al. 1997; Caux et al. 1999). We await the results of the Sub-millimetre Wave Astronomical Satellite.

Dark regions in which the CO in the gas phase contains only a small fraction of the elemental carbon have been identified (Gibb & Little 1998). The chemistry

of such highly depleted regions provides a valuable diagnostic of the dynamics of stellar birth (Ruffle et al. 1999).

3.3. Warm gas

In astronomical environments, warm gas is created by shocks, non-dissociative and dissociative, and by the action of intense ultraviolet and X-ray radiation. A complex interplay of gas phase and grain surface chemistry occurs in which atoms and molecules are accreted onto grains, are processed on the grain surfaces and injected back into the gas where they participate in a gas phase chemistry in which endothermic and exothermic reactions with H_2 initiate sequences of chemical reactions.

Warm regions arising from intense ultraviolet radiation fields are called PDRs, photon-dominated regions or photodissociation regions. In PDRs, molecular formation is driven by photoionization and molecular destruction by photodissociation. XDRs are X-ray dominated regions in which molecular formation is driven by photoionization and molecular destruction by X-ray induced photoelectrons. The radiation creates a warm zone in the gas where reactions with H_2, both exothermic and endothermic, dominate the chemistry. The OH radical is produced by reaction of O with H_2 and becomes the heart of the chemical network (Sternberg & Dalgarno 1995). Ionization is created at greater depths into molecular clouds and the formation of molecules is enhanced. The intense flux also enhances the destruction and the resulting chemical composition provides specific diagnostics. Much evidence has accumulated that demonstrates the existence of PDRs. Recent examples may be found in papers by Rodriquez-Franco, Martín-Pintado, & Fuente (1998), Ceccarelli et al. (1998), Luhman, Engelbracht, & Luhman (1998), Pak et al. (1998), Apponi, Pesch, & Ziurys (1999), Yan et al. (1999), Jackson & Kramer (1999) and Kemper et al. (1999). Theoretical models of increasing refinement have been developed (Diaz-Miller, Franco, & Shore 1998; Bakes & Tielens 1998; Störzer & Hollenbach 1998; Bolatto, Jackson, & Ingalls 1999).

One indication of a PDR is the presence of the molecular ion CO^+ which in a warm gas is produced by the sequence

$$O + H_2 \rightarrow OH + H$$

$$C^+ + OH \rightarrow CO^+ + H.$$
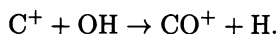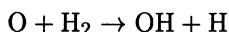
Other indications are rotationally excited CO, OH, CH and CH^+, all of which have been detected (Cernicharo et al. 1997; Liu et al. 1997; Ceccarelli et al. 1998; Kemper et al. 1999).

The chemical response of molecular clouds to X-rays has been investigated (Lepp & Dalgarno 1996; Maloney, Hollenbach, & Tielens 1996; Yan & Dalgarno 1997). The multiply-charged ions that are created by the absorption of energetic X-rays undergo sequential charge transfer and are quickly reduced to the singly-charged and neutral states. The X-rays heat the gas and the resulting chemistry reflects the presence of warm H_2.

A possible diagnostic of an XDR is the presence of the molecular ion HeH^+. However, the emission line of the pure rotational 1–0 transition lies at 149.14 μm

near the two lines of CH at 149.09 μm and 149.39 μm. This near coincidence may have prevented the detection of HeH$^+$ in the planetary nebula NGC 7027 (Liu et al. 1997). The quantal calculations of excitation by Rabadan, Sarpal, & Tennyson (1998) encourage the possibility that HeH$^+$ might be more readily detected by its 2–1 emission line at 74.8 μm.

Shock-heated gas has a similar chemistry to a PDR and they are not readily distinguished by their chemical composition. However detailed analysis with appropriate modeling has led Ceccarelli et al. (1998) to conclude that the CO$^+$ they detected towards the protostar IRAS 16293-2422 arises from gas subjected to a dissociative shock. Non-dissociative shocks are surely responsible, possibly in conjunction with PDRs, for the large abundance of water. In hot molecular gas, most of the oxygen is driven into H$_2$O.

Hot cores of high density gas at temperatures between 100 K and 200 K and masses of 100 M$_\odot$ are found in the vicinity of young high-mass stars. The cores are heated by radiation and by interactions with the stellar winds. At an earlier stage the hot cores may have been highly-depleted regions but subsequent chemical processing on grain surfaces and desorption has created high gas phase abundances of saturated molecules with large enhancements of deuterated species (Charnley 1997; van Dishoeck 1998; Viti & Williams 1999; Teixeira et al. 1999). Thus, the chemical composition may provide an astronomical clock.

3.4.   The Red Rectangle

The red rectangle is an unusual source of nebulosity associated with a circumstellar disk-like structure around an evolving binary pair. The object has an unusual visible spectrum whose origin is unclear. The allowed fourth positive system and the forbidden Cameron system are present in the emission spectrum as are the ^3P–$^3P^0$ and ^1D–$^1P^0$ lines of atomic carbon (Glinski et al. 1996, 1997) and the $A^1\Pi$–$X^1\Sigma^+$ band system of CH$^+$ (Balin & Jura 1992). There are weaker features attributable to OH (Reese & Sitko 1996). The first positive system of CO is probably produced by fluorescence but the Cameron system is not. Glinski et al. (1997) suggested that charged particle impact is responsible for the excitation of the upper $a^3\Pi$ state of the Cameron system of CO, but it may be a product of the dissociative recombination of HCO$^+$ (Yan, Dalgarno, & Klemperer 1999) as suggested by the experiments of Adams & Babcock (1994). It may be a unique example in astrophysics beyond the solar system of visible or ultraviolet emission produced by a chemical reaction.

3.5.   Large molecules

Large polycyclic aromatic hydrocarbon (PAH) molecules were proposed fifteen years ago (Puget & Leger 1984) as the source of the unidentified infrared (UIR) bands at 3.3, 6.2, 7.7, 8.6 and 12.7 μm discovered by Gillett, Forrest, & Merrill (1973). The bands and many others between 3 and 21 μm have been detected subsequently in a diverse range of astronomical objects. Attempts to establish their explicit identification have stimulated numerous experimental and theoretical studies. Recent examples are papers by Jochims, Baumgartel, & Leech (1999), Pauzat, Talbi, & Ellinger (1999) and Hudgins & Allamandola (1999a,b). The PAH molecules usually have low ionization potentials so that a substantial fraction of them should be ionized. Observational evidence supporting the

presence of PAH$^+$ molecular ions has been obtained from the analysis of emission features between 11 and 14 μm (Hudgins & Allamandola 1999b; Sloan et al. 1999). PAH molecules have been proposed also as the carriers of the diffuse interstellar bands (DIBs) (Puget & Léger 1989; Salama et al. 1996) but Thaddeus (1994, 1995) has argued that long carbon chains are more likely candidates. His view is supported by the remarkable experiments of Tulej et al. (1999) who measured the visible absorption spectrum of C$_7^-$, finding five coincidences with DIBs. The distribution of ionization amongst large molecules has been investigated (Lepp & Dalgarno 1988a). For carbon chains a substantial fraction may exist as anions as well as in neutral form. The anions are formed by attachment of electrons and destroyed by photodetachment, associative detachment and mutual neutralization. Estimates are available of the rate coefficients but nothing is known of the branching ratios. The presence of the negative ions enhances the heating efficiency of the interstellar gas (Lepp & Dalgarno 1988a; Bakes & Tielens 1994) and changes the chemistry (Lepp & Dalgarno 1988b; Lepp et al. 1988; Bakes & Tielens 1998) as molecular ions are removed by mutual neutralization rather than by dissociative recombination. If the total anion abundances approach a fraction of 10^{-7}, discussions of ionization in molecular clouds will have to be modified (Williams et al. 1998; Bergin et al. 1999).

4. The Chemistry of Brown Dwarfs, Comets and Planetary Systems

Developments in our understanding of the chemistry of star-forming regions (van Dishoeck & Hogerheijde 1999) and the chemistry of protoplanetary accretion disks (cf. Aikawa & Herbst 1999) point to deep connections between interstellar chemistry and the chemistries of comets and of planetary systems, as the title of this symposium emphasises. The chemistry of planetary atmospheres has its own history and its own considerable literature (Yung & DeMore 1999). The integration of chemistries is an exciting developing activity of increasing interest with the discovery of extrasolar giant planets and the detection of numerous brown dwarf stars. It opens up a new realm of astrochemistry. Warm brown dwarfs show absorptions due to FeH, TiO and VO (Kirkpatrick et al. 1999) and cool brown dwarfs show absorption due to H$_2$, CH$_4$ and H$_2$O, indicating a chemistry similar to that of the Jovian planets (Burrows et al. 1997; Griffith & Yelle 1999; Tsuji, Ohnaka, & Aoki 1999). Thus as brown dwarfs cool their chemical composition changes.

The atmospheres of the extrasolar giant planets, many of which orbit close to their parent stars, are subjected to intense radiation which modifies their composition (Seager & Sasselov 1999).

The connection between the interstellar medium and comets in an important question of astrochemistry. Comets may have condensed in the interstellar medium or the solar nebula. Comets originate in the Oort cloud and in the Kuiper Belt. There may be differences in chemical composition arising from the varying degrees of processing experienced by the two kinds in interactions with the Sun (Mumma et al. 2000).

5.   Future Developments

I was asked to comment on the future challenges. It is difficult enough to predict the past and impossible to guess the future, though one thing is certain. Our greatest challenge will be to find the research funds that are needed if we are to exploit the extraordinary opportunities that lie in front of us as new telescopes of enhanced sensitivity and spatial spectral resolutions, both ground-based and in space, are introduced; as advances in the sophistication and precision of laboratory techniques continue; and as theory develops more comprehensive models in which chemistry and dynamics are integrated in computer simulations of complex events.

   I think that in the past three years, particularly with the observations made with ISO, and with millimetre and sub-millimetre telescopes, and the conclusions that have been drawn about star formation, Astrochemistry has come of age. I recall questioning in 1986 whether or not interstellar chemistry was useful, useful in the sense that it taught us something about astronomy that we did not already know. I concluded then that the answer was yes, it was useful but not very. It was intellectually interesting that molecular observations could more or less be accommodated by conventional models and that was all. My answer now is quite different. Today Astrochemistry is a powerful, unified and unifying discipline, reaching into all areas of astronomy and making unique contributions to the answers of deeply significant questions of galaxy, star and planet formation and evolution. One of the most challenging questions of cosmology today is in fact star formation.. In a longer view the most significant scientific question for the new millennium is the origin of life. Progress in Astrochemistry in all its varied aspects of observation, measurement and theory is an essential component of the search for the answer.

References

Abel, T., Anninos, P., Norman, M.L., & Zhang, Y. 1998, ApJ, 508, 518
Adams, W.S. 1941, ApJ, 93, 11
Adams, W.G. & Babcock, L.M. 1994, J. Phys. Chem., 98, 4564
Adams, N.G., Herd, C.R., Geoghegan, M., Smith, D., Canosa, A., Gomet, J.C., Rowe, B.R., Queffelec, J.L., & Morlais, M. 1991, J. Chem. Phys., 94, 4852
Aikawa, Y. & Herbst, E. 1999, ApJ, 526, 314
Amin, M.Y., Shalabiea, O.M., & Herbst, E. 1997, MNRAS, 290, 347
Apponi, A.J., Pesch, T.C., & Ziurys, L.M. 1999, ApJ, 519, L89
Bakes, E.L.O. & Tielens, A.G.G.M. 1994, ApJ, 427, 822
————— 1998, ApJ, 499, 258
Balin, S.P. & Jura, M. 1992, A&A, 261, L25
Baluteau, J.P., Cox, P., Cernicharo, J., et al. 1997, A&A, 322, L33
Bates, D.R. & Spitzer, L. 1951, ApJ, 113, 441
Bergeat, A., Calvo, T., Dorthe, G., & Loison, J.C. 1999, Chem. Phys. Lett., 308, 7

Bergin, E.A., Goldsmith, P.F., Snell, R.L., & Langer, W.D. 1997, ApJ, 482, 285

Bergin, E.A., Plume, R., Williams, J.P., & Myers, P.C. 1999, ApJ, 512, 724

Black, J.H. & Dalgarno, A. 1973a, Ap. Lett., 15, 79

————— 1973b, ApJ, 184, L101

Bolatto, A.D., Jackson, J.M., & Ingalls, J.G. 1999, ApJ, 513, 275

Brown, V., Coppi, P.S., & Larson, R.B. 1999, ApJ Letters, in press

Brownsword, R.A., Canosa, A., Rowe, B.R., Sims, I.R., Smith, I.W.M., Stewart, D.W.A., Symonds, A.C., & Travers, D. 1997, J. Chem. Phys., 106, 1662

Burrows, A., Marley, M., Hubbard, W.B., Lunine, J.T., Guillot, T., Saumon, D., Freedman, R., Sudarsky, D., & Sharp, C. 1997, ApJ, 491, 856

Caux, E., Ceccarelli, C., Castets, A., Vastel, C., Liseau, R., Molinari, S., Nisini, B., Saraceno, P., & White, G.J. 1999, A&A, 347, L1

Ceccarelli, C., Caux, E., Wolfire, M., Rudolph, A., Nisimi, B., Saraceno, P., & White, G.J. 1998, A&A, 331, L17

Cecchi-Pestellini, C. & Dalgarno, A. 1999, MNRAS, in press

Cernicharo, J., Liu, X.-W., González-Alfonso, E., Cox, P., Barlow, M.J., Lim, T., & Swinyard, B.M. 1997, ApJ, 483, L65

Charnley, S.B. 1997, ApJ, 481, 396

Dartois, E., d'Hendecourt, L., Boulanger, F., Jourdain de Muizon, M., Breitfellner, M., Puget, J.L., & Habing, H.J. 1998, A&A, 331, 651

Derkatch, A.M., Al-Khalili, A., Vikor, L., Neau, A., Shi, W., Danared, H., af Ugglas, M., & Larsson, M. 1999, J. Phys. B., in press

Diaz-Miller, R.I., Franco, J., & Shore, S.N. 1998, ApJ, 501, 192

Douglas, A.E. & Herzberg, G. 1941, ApJ, 94, 381

Dunham, T. 1937, Pub. Astron. Soc. Pac., 49, 26

Dunham, T. & Adams, W.S. 1937, Pub. Am. Astron. Soc., 9, 5

Eddington, A.S. 1926, Proc. Roy. Soc. Lond. A., 111, 424

Ferrara, A. 1998, ApJ, 499, L17

Fukuzawa, K., Osamura, Y., & Schaefer, H.F. 1999, ApJ, 505, 278

Galli, D. & Palla, F. 1998, A&A, 335, 403

Geballe, T.R., McCall, B.J., Hinkle, R.H., & Oka, T. 1999, ApJ, 510, 251

Geballe, T.R. & Oka, T. 1996, Nature, 384, 334

Gibb, A.G. & Little, L.T. 1998, MNRAS, 295, 299

Gillett, F.C., Forrest, W., & Merrill, K.M. 1973, ApJ, 183, 87

Glinski, R.J., Nuth, J.A., Reese, M.D., & Sitko, M.L. 1996, ApJ, 467, L109

Glinksi, R.J., Lauroesch, J.T., Reese, M.D., & Sitko, M.L. 1997, ApJ, 490, 826

Griffith, C.A. & Yelle, R.V. 1999, ApJ, 512, 843

Haiman, Z., Rees, M.J., & Loeb, A. 1997, ApJ, 476, 458 & 484, 985

————— 1996, ApJ, 467, 522

Haiman, Z., Thoul, A., & Loeb, A. 1996, ApJ, 464, 323

Herbst, E. 1995, Ann. Rev. Phys. Chem., 46, 27

Herbst, E. & Klemperer, W. 1973, ApJ, 185, 505

Herbst, E. & Lee, H-H. 1997, ApJ, 485, 689

Herd, C.R., Adams, N.G., & Smith, D. 1990, ApJ, 349, 388

Hiraoka, K., Mijagoshi,T., Takayana, T., Yamamoto, K., & Kihara, Y. 1998, ApJ, 498, 701

Hudgins, D.M. & Allamandola, L.J. 1999a, ApJ, 513, L41

————— 1999b, ApJ, 513, L69

Jackson, J.M. & Kramer, K.E. 1999, ApJ, 512, 260

Jochims, H.W., Baumgartel, H., & Leach S. 1999, ApJ, 512, 500

Joulain, K., Falgarone, E., Pineau des Forets, G., & Flower, D., 1998, A&A, 340, 241

Kaiser, R.I., Ochsenfield, C., Stranges, D., Head-Gordon, M., & Lee, Y.T. 1998, Faraday Disc., 109, 183

Kaiser, R.I. Ochsenfeld, C., Head-Gordon, M., & Y.T. Lee 1999, ApJ, 510, 784

Kemper, C., Spaans, M., Jansen, D.J., Hogerheijde, M.R., van Dishoeck, E.F., & Tielens, A.G.G.M. 1999, ApJ, 515, 649

Kirkpatrick, J.D. et al. 1999, ApJ, 519, 802 and 834

Klemperer, W. 1970, Nature, 227, 1230

Kramers, H.A. & ter Haar, D. 1946, Bull. Astron. Inst. Netherlands, 10, 137

Larson, A., Le Padellec, A., Semanek, J., Stromholm, C., Larsson, M., Rosen S.N., & Peverall, R. 1998, ApJ, 505, 459

LeBourlot, J., Pineau des Forêts, G., & Roueff E. 1993, ApJ, 416, L87

————— 1995a, A&A, 297, 251

————— 1995b, A&A, 302, 870

Lee, H-H., Roueff, E., Pineau des Forets, G., Shalabiea, O.M., Terzieva, R., & Herbst, E. 1998, A&A, 334, 1047

Lepp, S. & Dalgarno, A. 1996, A&A, 306, L21

————— 1988a, ApJ, 324, 553

————— 1988b, ApJ, 335, 769

Lepp, S., Dalgarno, A., van Dishoeck, E.F., & Black, J.H. 1988, ApJ, 329, 418

Liu, X-W., Barlow, M.J., Dalgarno, A. et al. 1997, MNRAS, 290, L71

Luhman, S.K., Engelbracht, C.W., & Luhman, M.L. 1998, ApJ, 499, 793

Maloney, P.R., Hollenbach, D.J., & Tielens, A.G.G.M. 1996, ApJ, 461, 298

Martin, D.W., McDaniel, E.W., & Meeks, M.L. 1961 ApJ, 134, 1012

McCall, B.J., Geballe, T.R., Hinkle, K.H., & Oka, T. 1998, Science, 279, 1910

————— 1999, ApJ, 522, 338

McKellar, A. 1940, Pub. Astron. Soc. Pac. 52, 187; Pub. Dom. Astrophys. Obs. 52, 307

Millar, T.J., Farquhar, P.R., & Willacy, K. 1997, A&AS, 121, 139

Mumma, M.J., DiSanti, M.A., Russo, N.D., Magle-Sauer, K., & Peltig, T.W. 2000, ApJ Letters, in press

Nakamura, F. & Umemura, 1999, ApJ, 515, 239

Oloffson, G. et al. 1998, A&A, 339, L81

Omukai, K. & Nishi, R. 1998, ApJ, 508, 141

Pak, S., Jaffe, D.T., van Dishoeck, E.F., Johannson, L.E.B., & Booth R.S. 1998, ApJ, 498, 735

Parravano, A. & Pech, C. 1997, A&A, 327, 1262

Pauzat, F., Albi, D., & Ellinger, Y. 1999, MNRAS, 304, 241

Pineau des Forêts, G., Roueff, E., & Flower, D.R. 1992, MNRAS, 258, 45

Poglitsch, A., Hermann, F., Genzel, R., et al. 1996, ApJ, 462, L43

Puget, J.L. & Leger, A. 1989, ARAA, 27, 161

Rabadan, I., Sarpal, B.K., & Tennyson, J. 1998, MNRAS, 299, 171

Rank, D.M. Townes, C.H., & Welch, W.J. 1973, Science, 174, 1083

Reese, M.D. & Sitko, M.L. 1996, ApJ, 467, L105

Rodriquez-Franco, A., Martín-Pintado, J., & Fuente, A. 1998, A&A, 329, 1097

Ruffle, D., Hartquist, T.W., Caselli, P., & Williams, D.A. 1999, MNRAS, 308, 691

Salama, F., Bakes, E.L.O., Alamandola, L.J., & Tielens, A.G.G.M. 1996, ApJ, 458, 621

Scott, G.B., Fairley, D.A., Freeman, C.G., McEwan, M.J., Spanel, P., & Smith, D. 1997a, J. Chem. Phys., 106, 3982

Scott, G.B.I., Fairley, D.A., Freeman, C.G., & McEwan, M.J., 1997b, Chem. Phys. Lett., 269, 88

Seager, S. & Sasselov, D.D. 1999, ApJ, 502, L157

Semaniak, J., Larson, A., Le Padellec, A., Stromholm, C., Larsson, M., Rosen, S., Peverall, R., Dnared, H., Djuric, N., Dunn, G.H., & Datz, S. 1998, ApJ, 498, 886

Shalabiea, O.M. & Greenberg, J.M. 1995, A&A, 296, 779

Sloan, G.C., Hayward, T.L., Allamandola, L.J., Bregman, J.D., DeVito, B., & Judgins, D.M. 1999, ApJ, 513, L65

Solomon, P.M. & Klemperer, W. 1972, ApJ, 178, 389

Stancil, P.C., Lepp, S., & Dalgarno, A. 1996, ApJ, 458, 401

————— 1998, ApJ, 509, 1

Stark, R., van der Tak, F.F.S., & van Dishoeck E.F. 1999, ApJ, 521, L67

Sternberg, A. & Dalgarno, A. 1995, ApJS, 99, 565

Störzer, H. & Hollenbach, D. 1998, ApJ, 495, 863

Swings, P. 1942, ApJ, 95, 270

Tegmark, M., Silk, J., Rees, M.J., Blanchard, A., Abel, T., & Palla, F. 1997, ApJ, 474, 1

Teixeira, T.C., Devlin, J.P. Buch, V., & Emerson, J.P. 1999, A&A, 347, L19

ter Haar, D. 1943, Bull. Astron. Inst. Netherlands, 10, 1

Terzieva, R. & Herbst, E. 1998, ApJ, 501, 207

Thaddeus, P. 1994 in Molecules and Grains in Space, ed. I. Nenner, AIP Conf. Proc. 312, New York, 711

————— 1995, in The Diffuse Interstellar Bands, ed. A.G.G.M. Tielens & T.P. Snow (Kluwer), 369

Tsuji, T., Ohnaka, K., & Aoki, W. 1999, ApJ, 520, L119

Tulej, M., Kirkwood, D.A., Pachkov, M., & Maier, J.-P. 1999, ApJ, 506, L69

van Dishoeck, E.F. 1998, in Molecular Astrophysics of Stars and Galaxies, eds. T.W. Hartquist & D.A. Williams (Oxford University Press)

van Dishoeck, E.F. & Hogerheijde, M.R. 1999, in The Physics of Star Formation and Early Stellar Evolution, eds. C.J. Lada & N.D. Kylafis (Dordrecht: Kluwer)

Vandenbussche, B., et al. 1999, A&A, 346, L57

Vejby-Christensen, L., Andersen, L.H., Heber, O., Kella, D., Pedersen, H.B., Schmidt, H.T., Zajfman, D. 1997, ApJ, 483, 531

Vikor, L., Al-Khalih, A., Danared, H., Kjuric, N., Dunn G.H., Larsson, M., Le Padellec, A., Rosen, S., & af. Ugglas, M. 1999, A&A, 344, 1027

Viti, S. & Williams, D.A. 1999, MNRAS, 305, 755

Watson, W.D. 1973, ApJ, 183, L17

Weinreb, S., Barrett, A.H. Meeks, M.L., & Henry, J.C. 1963, Nature, 200, 829

Weliachew, L. 1971, ApJ, 187, L47

Williams, J.P. Bergen, E.A. Caselli, P., Myers, P.C., & Plume, R. 1998, ApJ, 503, 689

Yan, M. & Dalgarno, A. 1997, ApJ, 481, 286

Yan, M., Dalgarno, A., & Klemperer, W.B. 1999, in preparation

Yung, Y.L. & DeMore, W.B. 1999, Photochemistry of Planetary Atmospheres (Oxford University Press)

Discussion

D. A. Williams: Can you please describe the density structure that is necessary to account for H_3^+ abundances detected in regions that are apparently diffuse?

A. Dalgarno: The density must be at least 50 cm^{-3} in order to produce enough H_2 and hence enough H_3^+. The measured visual extinction together with other observational restrictions appear to require that the medium consists of individual clumps in a diffuse interclump gas. A model put together by Cecchi-Pestellini and myself has nine clumps of mean extinction 1.2 mag. With a cosmic ray flux of 6×10^{-17} s^{-1} we obtain the measured abundance of H_3^+ of Geballe et al.

E. Herbst: The measured fractional abundance of C_7^- along several lines of sight is $\sim 10^{-9}$, which is rather small compared with the fractional electron abundance of $\sim 10^{-4}$.

A. Dalgarno: The fractional ionization will be much less in denser regions and C_7^- is unlikely to be the most abundant of the cations.