

CHEMICAL PROCESSES IN COMETARY COMAE

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Abstract. Recent developments in the chemical modelling of cometary comae are described. We discuss the cyanide chemistry and present new HCN observations of the recent comet C/2002 C1 (Ikeya-Zhang). The connection between interstellar and cometary organic molecules is discussed from the perspective of recent theories of interstellar gas-grain chemistry.

Keywords: Comets, general-comets, individual, (Hale–Bopp)

1. Introduction

Comets are the most volatile-rich and pristine objects in our solar system. Although comets will have undergone some processing during their ~ 4.5 Gyr lifetime, their chemical composition will fundamentally reflect the conditions in the outer solar nebula when they were formed (Mumma et al., 1993; Irvine et al., 2000). Determining molecular abundances in cometary ices therefore allows us to place important constraints on models of the protosolar nebula, and planetary formation in general. A key question, when considering exactly when, where and how comets formed, is to what extent comets consist of relatively pure interstellar material? Detailed studies of interstellar solid state absorption bands made with the *Infrared Space Observatory (ISO)*, theoretical and observational progress in the understanding of interstellar gas-grain chemistry, and the recent apparitions of bright comets, particularly Hale–Bopp, have all contributed to a deeper understanding of the chemical similarities and differences between interstellar and cometary material (Table 1; Ehrenfreund and Charnley, 2000). Until the *Rosetta* and *Deep Impact* space missions, we have no direct way to determine the composition of the nucleus and must rely on gas phase observations of coma molecules to estimate nuclear molecular abundances. However, a great deal of chemical processing can occur in the coma and so accurate chemical models are of importance when using coma observations to derive nuclear ice composition.



TABLE I

Representative compositions of the gas in a cold molecular cloud (L134N), protostellar ices (NGC7538: IRS9), protostellar hot core gas (Sgr B2(N)), and in a cometary coma (Hale–Bopp)

Molecule	L134N	NGC7538: IRS9	Sgr B2(N)	Hale–Bopp
H ₂ O	<3	100	>100	100
CO	1000	16	1000	20
CO ₂	–	20	–	6–20
H ₂ CO	0.25	5	>0.005	1
CH ₃ OH	0.04	5	2	2
NH ₃	2.5	13	–	0.7–1.8
CH ₄	–	2	–	0.6
C ₂ H ₂	–	<10	–	0.1
C ₂ H ₆	–	<0.4	–	0.3
HCOOH	0.004	3	>0.003	0.06
CH ₂ CO	<0.009	–	0.002	<0.03
CH ₃ CHO	0.008	–	0.002	0.02
<i>c</i> -C ₂ H ₄ O	–	–	0.001	–
CH ₃ CH ₂ OH	–	<1.2	0.01	<0.05
CH ₃ OCH ₃	–	–	0.03	<0.45
HCOOCH ₃	<0.02	–	0.02	0.06
CH ₃ COOH	–	–	0.0008	–
CH ₂ OHCHO	–	–	0.003	–
OCN [–]	–	1	–	–
HNCO	–	–	0.006	0.06–0.1
NH ₂ CHO	<0.001	–	0.002	0.01
HCN	0.05	–	>0.05	0.25
HNC	0.08	–	>0.001	0.04
CH ₃ CN	<0.01	–	0.3	0.02
CH ₃ NC	–	–	0.015	–
HC ₃ N	0.002	–	0.05	0.02
C ₂ H ₃ CN	–	–	0.6	–
C ₂ H ₅ CN	–	–	0.006	–
H ₂ S	0.01	–	–	1.5
OCS	0.02	0.05	>0.02	0.5
H ₂ CS	0.008	–	0.2	0.02
SO	0.25	–	0.2	0.2–0.8
SO ₂	0.005	–	0.3	0.1

Abundances for interstellar ices and volatiles in comet Hale–Bopp are normalized to H₂O. Gaseous abundances for the Sgr B2(N) hot core and L134N are normalized to CO. Adapted from Ehrenfreund and Charnley (2000) and Charnley et al. (2002).

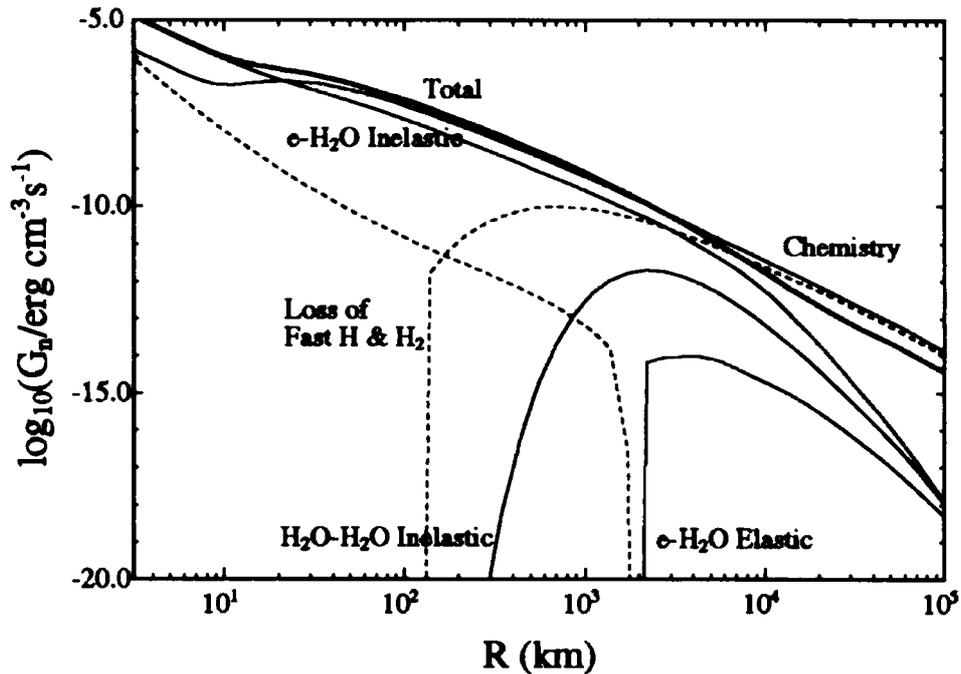


Figure 1. Major heating (full lines) and cooling (broken lines) mechanisms for coma neutrals (from Rodgers and Charnley, 2002a).

2. Modelling Coma Chemistry

Following sublimation from the nucleus, parent molecules are exposed to the solar UV field and they are photodissociated and ionized, creating distinct plasma and neutral fluid components, as well as populations of supra-thermal hydrogen atoms and molecules. The initial expansion of the gas is adiabatic and the temperature falls. Further out, photodissociation and ionization reactions heat the gas and the temperatures rise. A rich chemistry can ensue in the coma, involving processes such as electron impact ionization/dissociation, charge transfer, proton transfer, ion-atom interchange, and neutral rearrangement (see Schmidt et al., 1988). Also, sublimation from and/or photodestruction of dust injects new molecules into the coma.

Hydrodynamics and chemistry are intimately linked. Figure 1 shows that many processes affect the thermal balance of the neutral fluid. Chemistry can affect hydrodynamics: exothermic (~ 1 eV) proton transfer reactions are an important heat source in the inner coma, and cause the ion temperature to decouple from the neutral and electron temperatures (Körösmezey et al., 1987). Hydrodynamics can affect the chemistry: large variations in the electron temperature throughout the coma strongly affect the local rates of ion-electron recombination reactions.

We have developed a hydrodynamical-chemical model of the coma (Rodgers and Charnley, 2002a). A multifluid treatment is necessary and the model calculates the coupled chemical and dynamical evolution in the outflowing coma, computing in a self-consistent fashion molecular abundances, individual densities and temperatures for the plasma components and neutrals, as well as the inclusion of fast hydrogen atoms as a distinct component. It is similar to earlier models which also employed multifluid hydrodynamics (e.g., Huebner, 1985; Körösmezey et al., 1987) but, more pragmatically, we have the capability to study a wide range of different chemistries with relative ease. This model has been the basis of several recent chemical studies (Rodgers and Charnley, 1998, 2001b, c).

3. HCN and HNC in Comets

The HNC/HCN ratio varies greatly in different regions of the interstellar medium, with an inverse temperature dependence: In cold dark clouds the ratio can be higher than unity, whereas in hot cores it is small. At present we are unable to explain the excess of HNC in cold clouds (see Talbi et al., 1996). HCN has been seen in many comets, but HNC was detected for the first time in comet Hyakutake, where it was present with an abundance relative to HCN of 6% (Irvine et al., 1996). HNC was subsequently detected in comets Hale–Bopp and Lee, and the HNC/HCN ratio in Hale–Bopp showed a strong increase as the comet approached perihelion, from <2% at 2.5 AU to ~16% at 1 AU (Irvine et al., 1998). The Hyakutake results were originally interpreted as proof that cometary ices contain unprocessed material from the ISM, but the observations of Hale–Bopp proved conclusively that HNC must be a daughter species, and that its production is related to the solar photon flux and/or coma temperature.

Theoretical models can provide insight into possible chemical production routes for HNC in the coma (Rodgers and Charnley, 1998, 2001c). One must be careful to consider proton transfer reactions and to add or exclude all exoergic or endoergic reactions of this type (Hunter and Lias, 1998). This has the important consequence that ion-molecule chemistry is unable to synthesise the observed quantities of HNC since, for example, HCNH^+ will react with methanol to form HCN, but not HNC, thus quenching HNC production in methanol-rich comets (Rodgers and Charnley, 1998). However, endoergic isomerisation reactions of HCN, driven by suprathreshold H atoms produced in the photodissociation of parent molecules, may be efficient in large, active comets such as Hale–Bopp.

The observed HNC/HCN ratio in Comet Lee, of about 12%, effectively excludes bimolecular gas-phase reactions as the source of HNC in comets less active than Hale–Bopp. Detailed theoretical modelling indicates that the HNC observed in comets Hyakutake and Lee must be produced via photodissociation of some unknown parent(s), either organic dust particles or large molecules (Rodgers and Charnley, 2001c). Most small molecular candidates can be ruled out (e.g., HNCO,

CH₂NH). Photo-fragmentation of large organic molecules/particles has been proposed as an explanation of extended coma distributions of several molecules and radicals, e.g., CO, C₂, C₃, H₂CO, CN and NH₂. It appears likely that this process is also a common source of HNC, as well as perhaps accounting for the extended sources of HCN and CN. Potential candidates for the unknown parent(s) include hexamethylenetetramine (Bernstein et al., 1995) and polyaminocyanomethylene (Rettig et al., 1992).

These analyses suggest there may be two viable sources of HNC in comets. Photo-degradation being the most common, but with isomerisation reactions driven by fast H atoms playing an important role in large, active comets. Clearly, one would wish to know the HNC/HCN ratio, and its heliocentric variation, in many more comets. Mapping the spatial distribution of HCN and HNC (e.g., Veal et al., 2000; Blake et al., 1999) may also shed light on their origin and relationship with other coma molecules.

3.1. HCN IN COMET IKEYA-ZHANG

Using the Kitt Peak 12m telescope and the Submillimeter Telescope Observatory (SMTO) we have mapped the HCN emission from the coma of the recent bright Comet C/2002 C1 (Ikeya-Zhang). The comet ephemerides used were based on IAU Circulars and were calculated and updated as new circulars were released. The millimeter observations at the 12 m had typical system temperatures of less than 800 K for 1 mm observations. The backends used were 100 kHz filterbanks and 250 kHz filterbanks in parallel configuration. Calibration was done with a vane observation every 6 to 10 min. Submillimetre observations at the SMTO used either of the single channel, double-sideband, receivers (1.3 mm or 0.87 mm). Backends include the 250 kHz filterbanks, which is used to display the results in this paper. System temperatures varied from 400 K to 1000 K depending on weather conditions. Pointing/focus was done on a nearby planet and is accurate to better than 2 arcsec. Calibration was done with a hot vane observation every 10 minutes.

Figure 2 shows a superposition of coma maps in the $J = 3-2$ and $J = 4-3$ lines of HCN. The data was taken on different days (March 31 2002 for the HCN(4-3) map and April 10 2002 for the HCN(3-2) map). Both maps have been integrated between -2 and 2 km/s of the line center, which represents the maximum line extent seen in either line. The HCN(4-3) data are in the form of T_A^* (which should be multiplied by 0.50 to convert to T_R^*) and the HCN(3-2) data are in the form of T_R^* . To convert the HCN(4-3) data to T_R^* , 1 sigma equals 1.02 K km/s. The beams were 21 arcsec with 20 arcsec spacing for $J = 4-3$, and 24 arcsec with 15 arcsec spacing for $J = 3-2$.

The difference between the centre of the map (0,0) and the HCN(4-3) peak is real – about 10 arcsec. We can rule out differences in rotational emission for the observed J levels since one would expect that the HCN(3-2) emission would be more extended as one moves away from the inner coma, where the gas density is

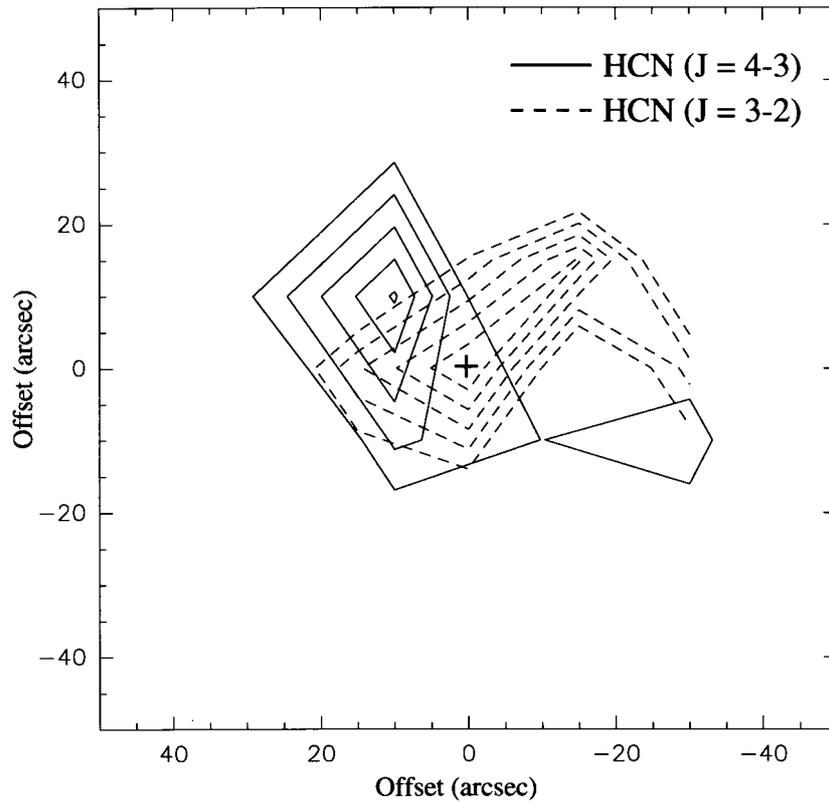


Figure 2. Maps of HCN emission in the coma of comet Ikeya-Zhang. Solid lines are HCN $J = 4-3$ and broken lines are HCN $J = 3-2$. The cross marks the nucleus position. For the $J = 4-3$ map, the lowest contour is 3 times the rms value and the contours are in steps of one sigma (i.e., 3, 4, 5, 6 and 7 sigma). The peak flux is 3.6 K km/s (7 sigma) and one sigma equals 0.51 K km/s. For the $J = 3-2$ map, the lowest contour is 20 times the rms value and the contours are in steps of 3 sigma each. The peak flux is 0.9 K km/s (35 sigma) and one sigma equals 0.026 K km/s. In both cases the sigma is the baseline rms per channel divided by the number of channels that are covered in the integration.

falling. The most likely explanation is that when the HCN(4-3) observations were made an extended source of HCN existed in the coma, whereas about 10 days later this had dissipated and the major contributor to HCN emission, as determined by the 3-2 line, was from molecules coming directly from the nucleus. This interpretation supports the idea that there are two sources of HCN in cometary comae. One source is pristine interstellar HCN from the nucleus, the other is photolytic decomposition of some organic parent molecule. This parent may be the same as that which is responsible for cometary HNC and hence, depending on the product branching ratios for photolysis of this unknown molecule, the HNC/HCN ratio in comets may actually reflect the nuclear ratio [organic parent]/HCN.

We have also measured the HCN production rates at several epochs and measured the HNC/HCN ratio. These results will be reported elsewhere (Butner et al.,

2002), however we note here that the HNC/HCN ratio in Ikeya–Zhang underwent a sharp increase between 0.96 AU and 0.73 AU, rising from $\sim 3\%$ to around 20%.

4. Organic Interstellar Molecules in Comets

Table I shows that, although there are some discrepancies, there is a strong correspondence between cometary molecules and those detected in interstellar ice mantles or in warm gas containing these evaporated ices – so-called “hot cores” (e.g., Charnley et al., 1992). We can strengthen this connection both by modelling coma organic chemistry and by exploring the implications interstellar grain chemistry theories have for cometary composition.

The brightness of comet Hale–Bopp allowed many organic molecules to be positively detected (Bockelée-Morvan et al., 2000). Many of the organic species detected, such as HCOOCH_3 , HC_3N , and CH_3CN , are also seen in hot cores where they are thought to be daughter species formed by gas-phase reactions (Rodgers and Charnley, 2001a). Thus, it is possible these molecules were actually created in the coma of Hale–Bopp. Coma modelling utilising the interstellar organic chemistry of these molecules indicates that chemical reactions *cannot* form sufficient quantities of HCOOH , HCOOCH_3 , HC_3N and CH_3CN (Rodgers and Charnley, 2001b). This result confirms that these species originate in the nuclear ices and suggests that, prior to incorporation into cometesimals, primordial interstellar grain mantle ices were evaporated, perhaps within the protosolar nebula, underwent a hot core-like phase of chemical processing, and then recondensed.

Figure 3 depicts chemistry driven by single atomic addition reactions on grains, with the further constraint of *radical stability* imposed on the intermediate organic radicals (Charnley, 1997, 2001). This scheme accounts for the presence in hot core precursor ices, and presumably also cometary ices, of small organic molecules containing the carbonyl group. The basic organic chemistry is driven primarily by C and N additions. Further H additions lead to a saturated mantle rich in alcohols although energy barriers for H additions to double and triple bonds mean that complete saturation does not occur and some aldehydes can persist. Acetaldehyde has been tentatively observed in Hale–Bopp (Crovisier et al., 1999) and this theory suggests that, depending on the reduction state of the cometary ices, ketene and/or ethanol should also have been present. Comets should also contain the ring isomer of acetaldehyde, ethylene oxide ($\text{c-C}_2\text{H}_4\text{O}$). Ethylene oxide is formed by O atom addition to the C_2H_3 radical, which is formed as an intermediate in the reduction of acetylene to ethene and ethane; this sequence has been proposed as the origin of cometary ethane (Mumma et al., 1996). The HCOOH , HNCO and NH_2CHO observed in both hot cores and comets are also accounted for by the theory. Stronger support for a connection to cometary material comes from PUMA mass spectrometry data of comet Halley. Kissel and Krueger (1987) identified the

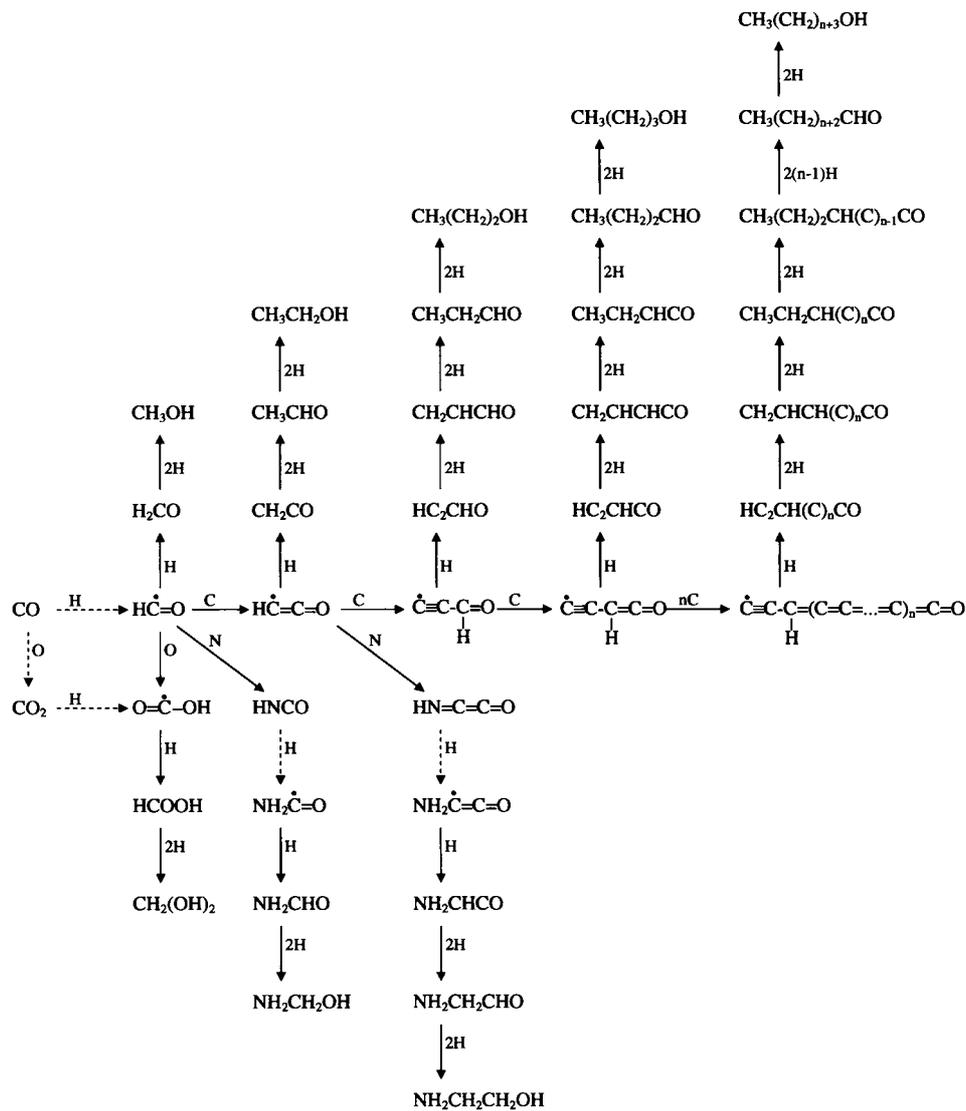


Figure 3. Interstellar grain surface chemistry (adapted from Charnley, 2001). Hydrogen atom addition to unsaturated molecules creates reactive radicals and a rich organic chemistry seeded by carbon monoxide ensues. Broken arrows indicate reactions with activation energy barriers; where 2H is shown, a barrier penetration reaction followed by an exothermic addition is implicitly indicated.

mass peaks at $m/Z = 44, 46$ and 48 with protonated HNC (or HOCN), NH_2CHO and $\text{NH}_2\text{CH}_2\text{OH}$ (aminomethanol).

A'Hearn et al. (1995) demonstrated that short-period comets are much more likely to be depleted in the carbon chains C_2 and C_3 than long-period comets. The current consensus is that Kuiper belt comets most probably formed near their current location, whereas Oort cloud comets originally formed somewhere in the

giant planet region of the protosolar nebula. Understanding this differentiation may therefore provide important cosmogonic information. Recent work suggests that C_2 and C_3 could be produced in the coma from C_2H_2 , C_2H_6 and C_3H_4 (Helbert et al., IAU Colloquium 186 presentation, Tenerife 2002). Alternatively, the chemistry of Figure 3 lends support to the idea that photolysis of nuclear propynal (HC_2CHO) could be the parent of C_3 and some C_2 (Krasnopolsky, 1991). Observational upper limits on the nuclear abundance of propynal are not very restrictive (Crovisier et al., 1993). One may speculate that C_2/C_3 differentiation amongst comet families, as well as other relative molecular depletions (CO , CH_3OH , CH_4 , C_2H_2 , C_2H_6 ; Mumma et al., 2000, 2001; Bockelée-Morvan et al., 2001), could be traced back to differences on the environment in which the chemistry of Figure 3 originally occurred.

Ion-molecule chemistry at the temperatures of molecular clouds ($\sim 10 - 30K$) leads to significant isotopic fractionation of D, ^{13}C and ^{15}N in interstellar molecules (Tielens and Hagen, 1982; Langer et al., 1984; Millar et al., 2000; Terzieva and Herbst, 2001). Hence, measuring these ratios in cometary parent molecules can strengthen the link with an interstellar provenance, and also offers the possibility of extracting important information regarding the origin, pristinity and formation temperature of the nuclear ices. The only deuterated molecules observed in comets are HDO and DCN. The observed HDO/ H_2O ratios lie in the range $5.7-6.6 \times 10^{-4}$ (e.g., Meier et al., 1998a) and a DCN/HCN ratio of 0.002 was determined in Hale-Bopp (Meier et al., 1998b). However, rapid chemical reactions in the coma could in principle alter D/H ratios, and this would compromise any comparisons with interstellar chemistry. Comet modelling of deuterium chemistry in the coma has demonstrated that, as in hot cores, post-evaporation chemistry does not significantly alter the initial D/H ratios (Rodgers and Charnley 2002a). Therefore, for parent species we can use the observed coma ratios to infer the nuclear D/H ratio, and for daughter species we can use these ratios to constrain the nature of the parent and the chemical mechanism by which the species are formed. In particular, if the DNC/HNC ratio can be determined in a comet, we may be able to ascertain the origin of cometary HNC, which is currently not well understood (see above).

5. Conclusions

Modelling of coma chemistry can constrain nuclear composition and isotopic fractionation, as well as the identification of the most important formation processes for individual molecules. We have highlighted this approach in studies of the important HNC/HCN ratio. More measurements of this ratio as a function of heliocentric distance are needed, as are maps of the individual molecules. Reactions involving suprathermal hydrogen atoms is an efficient pathway for HNC production in some comets. Fast H atoms may play an important general role in inner coma chemistry,

particularly so in the sulphur chemistry where the barrier for H abstraction from H₂S is the lowest amongst the most abundant parent molecules.

Existing measurements of the ¹⁵N/¹⁴N ratio in CN and HCN (Crovisier, 1999) show them to be consistent with bulk Solar System values. The measurement of an enhanced ¹⁵NH₃/¹⁴NH₃ ratio in a comet would provide positive evidence for the interstellar fractionation scenario proposed by Charnley and Rodgers (2002) which also gives a possible explanation of the widespread depletion of N₂ found in comets.

The detection of even more deuterated species would greatly constrain the connection with interstellar molecules. In particular, recent observations of low-mass protostellar cores yield very large HDCO/H₂CO and D₂CO/H₂CO ratios (Loinard et al., 2001) – measuring formaldehyde deuteration should be an important goal for the future. Determination of the DNC/HNC ratio would constrain some coma chemistry scenarios (Rodgers and Charnley, 2002a).

Anomalous water emission has recently been discovered in the inner envelope of the carbon-rich AGB star IRC+10216 (Melnick et al., 2001). This has been attributed to the sublimation of a population of comets, residing at a radius corresponding to that of the Kuiper Belt in the Solar System. The discovery of HDO molecules in IRC+10216 would be the definitive test of this scenario, as stars on the AGB have consumed their deuterium (Rodgers and Charnley, 2002b). As HDO molecules would also be present during the O-rich phase of evolution, it would also be an excellent general probe of extrasolar cometary material at the final stages of stellar evolution.

Finally, cometary ortho:para spin ratios have been measured for H₂O in a number of comets (Mumma et al., 1993; Irvine et al., 2000) and for H₂CO, CH₄, NH₃(NH₂) and CH₃OH in Hale–Bopp (Crovisier, 1999; Kawakita et al., 2001). The observed ratios imply formation temperatures for cometary molecules of typically 25–35 K; this range has important cosmogonic implications. However, it is not certain that the observed values accurately reflect the ratios in the nucleus. The presence of chemically significant abundances of H⁺ and protonated ions in the inner coma leads to the possibility that rapid ion-molecule spin-exchange (Dalgarno et al., 1973) and proton transfer reactions (Kahane et al., 1984) could alter these ratios from those originally present in the nucleus. Detailed models of the coma chemistry are necessary in order to ensure that coma observed ortho:para ratios accurately reflect the nuclear values.

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