# PART 8.

# Comets

# Molecules in Comets: An ISM-Solar System Connection?

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Abstract. Our knowledge of the volatile composition of comets has advanced considerably since the last IAU Astrochemistry Symposium, in large part due to the apparition of comet Hale-Bopp and its study with both new ground-based instruments and from spacecraft. Some 23 or 24 coma molecules are now known which are probably, at least in part, volatile constituents of the nucleus. Relative abundances have been measured for rarer isotopomers of molecules containing <sup>13</sup>C, <sup>15</sup>N, <sup>34</sup>S, and D, and significant isotopic fractionation is observed for D-containing species. There are striking similarities in both relative abundances of molecular constituents and in isotopic fractionation between material in dense interstellar clouds and that in cometary comae. Whether this indicates that cometary nuclei consist of relatively unprocessed interstellar matter is less clear, since the observed coma composition is not simply related to the nuclear composition, and since recent chemical models of the outer solar nebula mimic interstellar chemistry in important respects.

#### 1. Introduction

Comets are believed to be relics of the icy planetesimals which accreted in the outer solar nebula at the time that the solar system was forming. Since they clearly have a higher volatile content than other small bodies in the solar system, they have been less thermally processed and hence should preserve a clearer record of conditions and processes at that early epoch. This record may be sought in the chemical composition, isotopic composition, mineralogy, and physical structure of comets, at both microscopic and macroscopic levels.

The chemistry of comets has been discussed at all the previous IAU astrochemistry symposia (e.g. Feldman 1987; Vanysek 1987; Huebner et al. 1987; A'Hearn 1992; Snyder 1992; Despois 1992; Weaver 1997; Bockelée-Morvan 1997). However, there has been important progress in the last three years, both observationally and theoretically. The apparition of comet Hale-Bopp (C/1995 O1), one of the most intrinsically active comets of this century, very fortunately coincided with the availability of spacecraft observatories such as ISO and with the advent of powerful new instruments for ground-based observations. Unlike the situation of just over a decade ago, the major and many minor "parent"

molecules (ices present in the nucleus) can now be directly detected in the coma through their rotational and rovibrational spectra at millimeter through infrared wavelengths. Moreover, emission from these species can be mapped, which is crucial to determining accurate production rates and abundances, and to distinguishing actual nuclear constituents from products of photochemistry or other processes in the coma.

Likewise, chemical models of the region of comet formation and of the coma itself are becoming more complete and, hopefully, more realistic. This has led, i.a., to the realization that in situ chemistry may have observable effects on the composition of the comae of active comets, and that processes in the cold, outer portions of the solar nebula may be similar to those that govern the composition of dense interstellar clouds.

The present review is necessarily limited in scope, and readers are referred to other recent discussions of comets (Irvine et al. 2000; Altwegg & Geiss 1999; A'Hearn et al. 1999; Bockelée-Morvan & Rickman 1999; Bockelée-Morvan et al. 1999; Crovisier 1998, 1999; and references therein) and to the other invited papers on comets at this symposium (Kim et al. this volume; Crovisier, this volume). We shall review here recent detections of new volatile constituents of cometary comae (primarily from observations of comet Hale-Bopp), discuss measurements of isotopic ratios in the coma, comment on some of the problems involved in deducing the composition of the nucleus from measurement of abundances in the coma (manifested in part by improved techniques for mapping the distribution of molecular emission, and by the wealth of data from Hale-Bopp on molecular production rates versus heliocentric distance), and describe some recent theoretical models of chemistry in the coma and in the outer solar nebula. Within this context we shall comment on a question that is much discussed at present, the extent to which cometary nuclei consist of relatively unprocessed interstellar grains. For a comparison of the silicate components of comets with interstellar and circumstellar grains, see Crovisier (this volume).

### 2. An Historical Note

One of the interesting aspects of planetary science, including the study of comets, is the long historical tradition. The linkage of cometary observations to historical events is well known in the case of comet Halley (e.g. Olson & Pasachoff 1987) and in ancient Chinese records (e.g. Yau 1996). It recently came to our attention that comets may be mentioned in some of the oldest extant written records in the world, the so-called pyramid texts in Egypt. In particular, the hieroglyphs in the tomb of the pharaoh Pepi I, which date from about 2200 BC, might even have been inspired by the previous (first?) apparition of comet Hale-Bopp (Weeks 1998)!

# 3. Chemical and Isotopic Composition

#### 3.1. Molecular abundances

Observations of comet Hale-Bopp at millimeter and sub-millimeter wavelengths have led to the discovery of 8 new neutral molecular species in the coma (cf.

Despois 1999; Irvine et al. 1999) and to the confirmation of the presence of two others (OCS, HNCO) first tentatively detected in comet Hyakutake (C/1996 B2). A list of detected cometary volatiles is given in Table 1. Obvious "daughter" products (observed species that are clearly produced by dissociation, normally by solar photons, of heavier molecules) such as CH, NH, etc., have been omitted (a complete list is given by Rauer 1999). Some of the included species may well be, at least in part, such daughter products (CO, SO, NS) or the result of chemistry in the coma (see below).

Among the striking aspects of the volatile composition evident from Table 1 are the coexistence of reduced with oxidized species, and the similarity to the inventory of molecules found in interstellar clouds (see Sec. 5). Both these points emphasize the key role of non-equilibrium (kinetically controlled) chemistry in producing the observed composition (cf. Irvine et al. 2000; Fegley 1999). The carbon volatile inventory is dominated by such oxidized molecules as CO and  $\rm CO_2$ , although the abundance of hydrocarbons like  $\rm CH_4$  and  $\rm C_2H_6$  is not negligible. In contrast, reduced sulfur and nitrogen compounds such as  $\rm H_2S$  and  $\rm NH_3$  appear to be more abundant volatile constituents than the corresponding more oxidized species (SO<sub>2</sub>, SO, N<sub>2</sub>, etc.). Many molecules of an intermediate oxidation state are present.

The low temperature and density in interstellar clouds, together with the presence of a high temperature component (cosmic rays), are well known to lead to a characteristic, very non-equilibrium chemistry. It is thus striking to see that essentially all of the cometary molecules are also found in the dense ISM (excluding only the non-polar and hence difficult to detect ethane and S<sub>2</sub>), including some of those most characteristic of the interstellar environment, such as HNC, HCO<sup>+</sup>, and methyl formate (HCOOCH<sub>3</sub>); see, e.g. Watson (1980); Herbst & Klemperer (1973); Millar, Herbst, & Charnley (1991); or, more recently, van Dishoeck & Blake (1998).

# 3.2. Isotopic ratios

Prior to comet Hale-Bopp, accurate measurements of isotopic ratios in comets were rare (Vanysek 1991). Although a non-terrestrial ratio was widely reported for  $^{12}\text{C}/^{13}\text{C}$  in comet Halley, that result was subsequently shown to be incorrect (Kleine et al. 1995). Determination of such isotopic ratios from visible spectra is very difficult, because of the relatively low spectral resolution. At millimeter wavelengths the lines of different isotopomers are clearly resolved. Nonetheless, problems arise, as is evident from the low (heavy) result for  $^{12}\text{C}/^{13}\text{C}$  reported for comet Hyakutake by Lis et al. (1997), which probably is a consequence of blending of the observed H<sup>13</sup>CN line with a transition of SO<sub>2</sub>. The most convincing isotopic measurements were those for D/H and  $^{18}\text{O}/^{16}\text{O}$  for protonated water from comet Halley by the Giotto mass spectroscopy experiments and for HDO/H<sub>2</sub>O for comet Hyakutake (Bockelée-Morvan et al. 1998; Eberhardt et al. 1995; see below).

Submillimeter wavelength observations of comet Hale-Bopp showed that, to within an accuracy of order 10%, the ratios  $\rm H^{13}CN/H^{12}CN$ ,  $\rm HC^{15}N/HC^{14}N$ , and  $\rm C^{34}S/C^{32}S$  agreed with the mean solar system values for  $\rm ^{13}C/^{12}C$ ,  $\rm ^{15}N/^{14}N$ , and  $\rm ^{34}S/^{32}S$  (Jewitt et al. 1997), as did the Halley  $\rm ^{18}O/^{16}O$  ratio (Eberhardt et al. 1995). The corresponding values in the local ISM are some 20–30% lower than

Table 1. Molecular volatiles detected in comets.<sup>1</sup>

Molecule	Abundance	Notes <sup>2</sup>
H <sub>2</sub> O	100	
CO	1-20	$\mathbf{a}$
$CO_2$	3-20	
$H_2CO$	0.1-1	$\mathbf{a}$
$\mathrm{CH_{3}OH}$	1-7	
HCOOH	$\sim 0.05$	b
HNCO	0.1	$\mathbf{c}$
$NH_2CHO$	$\sim 0.01$	b
$HCOOCH_3$	$\sim 0.05$	b
$\mathrm{CH_4}$	$\sim 0.6$	
$\mathrm{C_2H_2}$	$\sim 0.1$	c
$\mathrm{C_2H_6}$	$\sim 0.3$	
$\mathrm{NH_3}$	0.6	
HCN	0.05 – 0.2	
HNC	0.04 – 0.12	$\mathbf{a}$
$\mathrm{CH_{3}CN}$	0.02	$\mathbf{c}$
$\mathbf{HC_3N}$	0.03	Ъ
NS	$\geq 0.02$	b
$\mathrm{H_2S}$	0.2 - 1.5	
$\mathbf{H_{2}CS}$	$\sim 0.02$	b
$\mathbf{CS}$	0.2	from $CS_2$ ?
OCS	0.5	a?, c
SO	$\sim 0.5$	$\mathbf{a}, \mathbf{b}$
$\mathbf{SO}_2$	$\sim 0.1$	b
$S_2$	0.005	С

<sup>&</sup>lt;sup>1</sup>From review by Irvine et al. (2000), augmented by recent IAU Circulars on comet Lee (1991 H1). Bold face indicates first detection in comet Hale-Bopp. Analysis of Giotto mass spectrometer data indicates the presence in comet Halley of CH<sub>2</sub> and C<sub>2</sub>H<sub>4</sub> and the "probable" presence of N<sub>2</sub>, CH<sub>3</sub>CHO, C<sub>3</sub>H<sub>2</sub>, and CH<sub>3</sub>CH<sub>2</sub>CN (Altwegg et al. 1999).

<sup>&</sup>lt;sup>2</sup>a: extended source b: observed only in one comet c: observed only in 2 comets

the solar system values, presumably reflecting spatial and temporal differences from the epoch and site where the Sun formed (e.g. Irvine 1999 and references therein). In contrast, HDO/H<sub>2</sub>O in Hale-Bopp was found to be about  $3\times10^{-4}$ ; that is, about twice the value in terrestrial ocean water and an order of magnitude larger than the D/H ratio for the Jovian atmosphere or the solar wind (presumed to be the primordial value for the solar system; Meier et al. 1998b; Irvine et al. 2000). This deuterium fractionation observed for Hale-Bopp agrees quite closely with the values found earlier for comets Hyakutake and Halley (see Table 2). An even larger fractionation was observed for DCN/HCN (Meier et al. 1998a), where the ratio was about  $2\times10^{-3}$ .

Differing isotopic ratios among samples may reflect either differing nucle-osynthetic sources (e.g. the "anomalous" values found for some noble gases and refractory phases in meteorites have been traced to contributions from supernovae and/or AGB stars; e.g. Bernatowicz 1997), isotopic fractionation (kinetic effects), or both. Isotopic fractionation is clearly responsible for the very large deuterium fractionation observed in a variety of molecular species in molecular clouds. Such fractionation is a hallmark of classical low temperature, gas phase, ion-molecule chemistry, but can also take place on interstellar grains (Watson 1980; Millar et al. 1989; Tielens 1983). The values found for DCN/HCN and HDO/H<sub>2</sub>O in Hale-Bopp are in the same range as the ratios found for these molecules in interstellar "hot cores", where massive stars are forming and have presumably caused the sublimation of icy, fractionated grain mantles (Rodgers & Millar 1996).

# 4. Chemistry at the Nucleus and in the Coma

The traditional view of cometary chemistry was a simple one. The nucleus was assumed to consist of ices of simple molecules plus refractory dust; as the nucleus was warmed by sunlight, the ices sublimed to form the inner coma (carrying some dust with them), and then were photodissociated and photoionized as they flowed outward. Water was long suspected to be the principal volatile constituent, and this was directly confirmed for comet Halley. The activity of some comets at large heliocentric distances suggested, however, that under such conditions a more volatile constituent than H<sub>2</sub>O must control the activity. Carbon monoxide (CO) was indeed found to play this role in P/Schwassmann-Wachmann 1 (Senay & Jewitt 1994).

Detailed models of comet Halley predicted that gas phase chemistry could modify the coma composition, but direct evidence for this was limited (e.g.

Table 2. Deuterium fractionation measured in comets (Irvine et al. 2000).

Observed Ratio	Derived [D]/[H]	Comet
H <sub>2</sub> DO <sup>+</sup> /H <sub>3</sub> O <sup>+</sup> HDO/H <sub>2</sub> O HDO/H <sub>2</sub> O DCN/HCN	$3.2 \pm 0.3 \times 10^{-4}$ $2.9 \pm 1.0 \times 10^{-4}$ $3.3 \pm 0.8 \times 10^{-4}$ $2.3 \pm 0.4 \times 10^{-3}$	1P/Halley Hyakutake (1996 B2) Hale-Bopp (1995 O1) Hale-Bopp (1995 O1)

Schmidt et al. 1988). Likewise, models of the evolution of the nucleus and laboratory study of multicomponent ice formation and sublimation predicted that chemical fractionation should accompany comet formation, evolution, and volatile sublimation, but evidence remained scanty (cf. the discussion and many references in Mumma et al. 1993; Crovisier 1999; and Irvine et al. 2000). Spacecraft in situ measurements of comet Halley also showed that for parent molecules such as CO the nuclear source might be augmented by a "distributed" source, i.e., a source within the coma (for CO perhaps from the organic CHON grains; see below).

### 4.1. New data and new techniques

The situation has changed dramatically as a result of the observational campaign for comet Hale-Bopp. Firstly, because the comet was so intrinsically active, molecular emission was detected when the comet was still far from the Sun (6.7 AU for CO; Jewitt et al. 1996), and production rates of molecular species were monitored over a wide range of heliocentric distances, both pre- and postperihelion (Biver et al. 1997, 1999). Models of the complexities relating the observed coma composition to that deduced for the nucleus are also progressing (e.g. Huebner & Benkhoff 1999).

These data show a number of interesting features (e.g. Bockelée-Morvan & Rickman 1999). The composition of the coma changes dramatically with heliocentric distance  $r_h$ , with CO being considerably more abundant than  $H_2O$  for  $r_h \geq 4$  AU. The gradient of production rate with  $r_h$  is not a simple power law for most species, presumably as a consequence of the control of sublimation shifting from CO (and to a lesser extent  $CO_2$ ) to  $H_2O$  as the comet approaches the Sun. Even within the range where sublimation seems to be controlled by water, the production rate gradients differ for certain species such as HNC and  $H_2CO$ , probably indicating the existence of distributed sources for these molecules.

Although the increased sensitivity of instrumentation at millimeter and submillimeter wavelengths first allowed the direct detection of a variety of parent molecules, radio telescopes until recently were severely limited in their ability to map extended cometary emission. Weak signals required lengthy observations, and radio receivers typically observed only a single position on the sky at a time. Comets Hyakutake and particularly Hale-Bopp provided the first opportunities to employ sensitive new focal plane array receivers as well as aperture synthesis telescope arrays to image the molecular emission at short radio wavelengths (cf. Despois 1999). Key information on the distribution of emission was also obtained at infrared wavelengths, using long-slit spectroscopy. Such data are crucial to determining accurate production rates for molecular species, since such calculations require knowledge of the distribution of molecules in the coma. This distribution is also needed to distinguish between nuclear and extended sources of volatiles in the coma.

#### 4.2. Coma chemistry

The first detection of the HCO<sup>+</sup> ion in comets was shortly followed by the first maps of the distribution in Hale-Bopp, obtained with the QUARRY focal plane array at the University of Massachusett's Five College Radio Astronomy Observatory. The images revealed much more extended emission than that from

HCN, a distinct offset in the peak emission from the position of the nucleus, dramatic day-to-day and intraday variations, and a velocity gradient within the coma (Lovell et al. 1998, 1999; Lovell 1998). HCO<sup>+</sup> is clearly primarily a product of gas phase chemistry in the coma, and the maps are in general agreement with models of coma chemistry and interaction with the solar wind. Thus, the offset in peak emission is in accord with estimates of the variation of electron temperature in the coma (which controls the recombination of electrons with the positive ion) from the collision-dominated inner coma to the lower density, solar heated outer coma. Similar maps obtained by the "on-the-fly" mapping technique at NRAO Kitt Peak have been presented by Womack et al. (1999).

Although the production of HCO<sup>+</sup> in the coma was expected and other protonated ions were detected by the Giotto mass spectrometers in comet Halley (e.g. H<sub>3</sub>O<sup>+</sup> and HCO<sub>2</sub><sup>+</sup>; Huebner et al. 1991), the detection of HNC in comet Hyakutake (Irvine et al. 1996) was certainly not predicted. As a higher energy isomer of HCN, the relatively high HNC abundances found in cold interstellar clouds exemplify the dramatic departure from equilibrium chemistry in the ISM. The initial suggestion that most cometary HNC might simply be preserved interstellar ice was shattered by the observation that in Hale-Bopp the HNC/HCN ratio varied dramatically with heliocentric distance (Irvine et al. 1998). The same chemical model which produces sufficient HCO+ to match the Hale-Bopp data also matches the variation of HNC/HCN versus  $r_h$ , however, showing that HNC is the first neutral, closed shell molecule in the coma whose presence seems to be a result of gas phase chemistry (Rodgers & Charnley 1998; Irvine et al. 1998, 1999). This result raises the question of whether other minor constituents detected in the coma of Hale-Bopp might also be produced in the coma. It would be useful to extend coma models to the degree of chemical complexity necessary to test this possibility. A nagging problem remains — the same models which match the observed HNC in Hale-Bopp do not produce enough for the less active comet Hyakutake. Perhaps, as is the case for some other molecules, HNC can have more than a single source in comets.

#### 4.3. Extended or nuclear sources

The perplexing question of which molecules have a distributed source and which sublime directly from the nucleus is, of course, key to efforts to determine the nature of the nucleus. The issue is complicated by the possibility that species that are unstable in the laboratory may nonetheless be present in the cold nuclear ices. The Giotto results suggest, for example, that the CH<sub>2</sub> radical may be a nuclear constituent (Altwegg et al. 1999). There is in fact very little relevant data to address the problem of whether and/or how long such radicals might be stored in the nucleus.

Interferometric observations provide the high angular resolution needed to address the question of extended sources, and the OVRO, BIMA, and IRAM instruments all observed comet Hale-Bopp at short millimeter wavelengths. The IRAM data show that SO is, at least in part, a daughter molecule, probably produced by photodissociation of SO<sub>2</sub> (Despois 1999). BIMA observations (Wright et al. 1998) of HCN and HCO<sup>+</sup> show, as expected, that the predominant source of HCN is the nucleus, while the HCO<sup>+</sup> map is consistent with the lower resolution FCRAO data.

OVRO measurements are consistent with a source for HNC that is more extended than that for HCN, consistent with at least some HNC being produced in the coma (Blake et al. 1999), as discussed above (see also Hirota et al. 1999). In addition, the OVRO observations reveal jets of emission that may result from sublimation from icy grains and that show substantially higher HNC/HCN ratios and D/H fractionation compared to larger scale data. Blake et al. suggest that gases subliming from the nucleus might be chemically and isotopically altered by hydrogen exchange in the thin liquid water layer which, at least in the laboratory, exists at the surface of water ice even at temperatures in the 140-210 K range (Jenniskens et al. 1997; the potential importance of this layer was also pointed out by Irvine et al. 2000). In this view, the true D/H fractionation in nuclear HCN and H<sub>2</sub>O might be approximately that seen for the jets and thus might be an order of magnitude larger than that observed on the 10-15 arcsec scales observed by current submillimeter telescopes. This would make the DCN/HCN ratio larger than that in hot cores and much closer to that observed in cold, dark interstellar clouds. Whether or not this interpretation is correct, it provides an example of the complexity of the microphysics and chemistry which may relate actual nuclear abundances to those observed in the coma.

Both CO and  $\rm H_2CO$  have been known since the study of comet Halley to have distributed sources (Crovisier & Bockelée-Morvan 1999; Rauer 1999; and references therein). When Hale-Bopp was close to the Sun ( $\sim 1.5$  AU), long-slit infrared spectroscopy showed that about half of the CO came from an extended source, and half from the nucleus. This is consistent with results obtained by similar techniques in the ultraviolet (McPhate et al. 1999). The nature of the extended source, whether larger gas phase molecules or grains, is unclear (DiSanti et al. 1999). There is also evidence from such infrared spectroscopy that the source of OCS was extended in comet Hale-Bopp (Dello Russo et al. 1998).

The detection of water ice grains in the coma of Hale-Bopp at large heliocentric distance (Davies et al. 1997) implies that such grains can be an extended source of volatiles, including H<sub>2</sub>O. Small icy grains can achieve higher temperatures than the nucleus itself, so that sublimation of these grains is particularly important when the comet is too far from the Sun for water sublimation to occur on the nucleus (a more detailed discussion is given by Bockelée-Morvan & Rickman 1999).

#### 5. Relation to Interstellar Material

To what degree do cometary nuclei consist of interstellar material that has been preserved throughout the formation of the solar nebula, the accretion of the comets, and the history of the solar system? On the one hand, Greenberg (1982; Greenberg & Li 1999) argues that comets consist of accumulations of essentially unaltered interstellar grains, including silicate cores, refractory organics, and icy mantles. At the other extreme, the "classical" view was that comets condensed in the outer regions of a nebula which had been heated and mixed so as to lose any chemical "memory" of presolar molecular material.

As has been discussed by several authors (e.g. Altwegg & Geiss 1999; van Dishoeck & Blake 1998; Langer et al. 2000; Ehrenfreund et al. 1997; Despois

1999; Rauer 1999; Mumma 1997), the chemical composition of comets, particularly after the new detections in comets Hyakutake and Hale-Bopp, shows remarkable similarities to both that of interstellar icy grain mantles and to the gas in young star formation regions. Perhaps even more diagnostic, because less subject to modification, is the similar deuterium fractionation observed for HDO/H<sub>2</sub>O and DCN/HCN between comets and hot cores (Bockelée-Morvan et al. 1998; Meier & Owen 1999; Irvine et al. 2000).

It seems inevitable that some presolar molecular material is preserved in comets, since such material is found in components of certain meteorites (e.g. Kerridge 1999; Bernatowicz & Zinner 1997), and comets have been almost certainly less processed since their formation than meteorites. Moreover, interplanetary dust particles (IDPs) of presumed cometary origin show deuterium enhancements and amorphous silicate inclusions which both suggest an interstellar origin (e.g. Messenger, this volume; Bradley 1999).

# 6. Models of Nebular Chemistry

Nonetheless, the overall picture remains unclear. Molecular-ice-coated grains falling supersonically onto the outer solar nebula will undergo some processing due to an accretion shock. A sample of the relevant physical processes are frictional heating induced by gas-grain drag, non-thermal sputtering of grains due to grain-grain collisions, and radiative heating of infalling grains. Each of these processes has been modeled in the literature (Lunine et al. 1991; Neufeld & Hollenbach 1994; Chick & Cassen 1997), typically examining the effect on the water ice mantle at smaller nebular distances (< 50 AU), where the accretion shock is faster (Neufeld & Hollenbach 1994). However, the grain cooling and the depletion timescales are very short; therefore, to be an effective contributor to nebular chemistry, these mechanisms require a constant supply of material infalling onto the outer nebular disk. Other important questions such as the importance and chemical effect of radial mixing of material from the hot inner nebula to the cold outer nebula need to be investigated (Drouart et al. 1999). For a review of these and other relevant processes, see Lunine (1997).

Moreover, although models remain incomplete, the environment in the outer solar nebula probably mimicked that in dense interstellar clouds in many respects. Recent advances include the recognition that the cosmic-ray chemistry that is active in the interstellar medium could also be important in the dense mid-plane of proto-planetary disks (e.g. Aikawa et al. 1997). The importance of cosmic ray ionization to nebular chemistry is underscored by recent models which show that cosmic-ray initiated deuterium chemistry can significantly enhance the ratio of DCN/HCN (Aikawa & Herbst 1999). One crucial parameter, if ion-molecule reactions are to proceed in the disk, is the nebular thermal structure. If dust temperatures are greater than the CO sublimation temperature of 23 K in the outer nebula, then a rich chemistry ensues (Aikawa et al. 1999); however, if temperatures are colder, then ion-molecule chemistry is halted (Willacy et al. 1998). Here we can be guided by theoretical investigations of nebular thermal structure that attempt to model the spectra energy distributions of young solar-like protostars (Calvet et al. 1991; Calvet et al. 1992; Chiang & Goldreich 1997; D'Alessio et al. 1998). These models show that there will be thermal structure within the nebula both radially and also vertically, as a function of disk scale height, which can have a controlling influence on the chemistry. An additional complication for cosmic-ray chemistry is that in the present day solar system the cosmic rays responsible for ionization do not penetrate due to the solar wind. Given that T Tauri stars have strong winds, this also might have been true at the earlier stages of the proto-solar nebula. However, other sources of ionization have been isolated, such as extinct radionuclides (Umebayashi & Nakano 1981) or X-rays (Glassgold, Najita, & Igea 1997), which could still power the ion-molecule chemistry.

Given the array of possible contributors to the chemistry, it is likely that cometary constituents were processed in some fashion prior to comet formation. In the future we can look forward to theoretical models with more complexity and predicting power. In addition, the next generation of array instruments, such as ALMA, will be able to examine stellar nurseries with greater resolution and sensitivity, offering opportunities to study the physical structure and chemical composition in the zones of cometary formation. Direct observations probing the "snow lines" for various molecular species, or even resolving chemically isolated regions surrounding extra-solar proto-planets, have the potential to greatly improve our understanding of processes relevant in our own solar system and to aid in deciphering the puzzle of cometary origins.

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#### Discussion

- C. Qi: Comment: The observed comets have travelled a long way to the Earth, so the surface of the nucleus must be very old and the composition might have been changed already. Also, the volatiles detected by mm telescopes might not be the same material as inside the nucleus. Without direct sampling by satellites landing on comets, jets are the only sources that can give us information on the chemical composition inside the comet nucleus. Actually our OVRO measurements of the D/H ratio in HCN and H<sub>2</sub>O in the jets of Hale-Bopp are one order of magnitude larger than those measured by single dishes, but comparable to our measurement of the D/H ratio in circumstellar disks. So we should be very careful using millimeter line data in the comet's coma to compare with molecular clouds.
- W. M. Irvine: I agree. It is interesting that the higher DCN/HCN ratio that you measure in the jets is closer to the ratio in cold, dark clouds like TMC-1 than to the ratio in hot cores. It is also important to remember that comets may be inhomogeneous in the nucleus, as suggested in the poster by Woodney et al., and to remember the differing D/H ratios in different components of meteorites and even within a single IDP.
- J. Crovisier: HNC was recently observed in comet C/1999 H1 Lee (IAU Circ. N° 7203). The HNC/HCN ratio was found to be  $\approx 12\,\%$ , i.e., higher than in comet Hyakutake. Since comet Lee was moderately productive ( $\psi[H_2O]\approx 10^{27}~s^{-1}$ ), formation of HNC by chemical processing within the coma might be difficult.
- S. Charnley: Comment: high HNC/HCN ratios in comets with relatively low gas production rates put pressure on models in which HNC is produced by coma gas-phase chemistry. The coma of Comet Lee needs to be modelled to see if these mechanisms remain viable and can reproduce HNC/HCN  $\sim 12\,\%$ , as reported here by Crovisier.
- W. M. Irvine: I agree.
- J. H. Black: Is the excitation temperature of CH<sub>3</sub>OH in Comet Hale-Bopp equivalent to the kinetic temperature of the coma gas?
- W. M. Irvine: Presumably yes, in the dense inner coma sampled by the mm-submm observations.
- M. Guélin: Due to sensitivity and UV plane coverage requirements, it takes time (i.e. a good faction of the rotation period) to map a comet with interferometers. Could you comment on the effect of the corresponding smearing on the conclusions you can draw from such maps?
- W. M. Irvine: I suggest that Mr. Qi comment on this.
- C. Qi: With the OVRO sensitivity, we need 3-4 hours integration to map comet Hale-Bopp. Clearly the tricks of observing a comet and its jets are: First, integration time should not be long compared to the period of rotation of the comet nucleus, otherwise the image will be smeared. Second, the beam size should be small enough to detect small-scale jet features.