New trends in cometary chemistry

Jacques Crovisier

This paper presents some of the implications of new comet observations for cometary chemistry: recent observations of bright comets, space missions, and especially the first results of the *Deep Impact* experiment. Topics which are discussed are the molecular complexity of cometary material, the evidence for molecular diversity from the infrared observations by *Deep Impact*, possible relations between cometary nuclei and carbonaceous chondrites, the sites of ices in cometary nuclei, the problem of interpretation of the spin temperatures observed in cometary molecules.

1. Introduction

Comets are unique chemical factories. Their chemical composition can be investigated by remote sensing observations of the numerous species released in the coma by the sublimation of nucleus ices. This technique has been in use since the beginnings of molecular spectroscopy in the 19th century. In the near future, direct *in situ* investigations will be possible by space missions such as *Rosetta*. Although comets are believed to be among the most primitive objects of the Solar System, cometary material exposed nowadays to our investigation experienced several steps of chemical processing:

1. Interstellar cloud chemistry.

2. Primitive solar nebula chemistry.

3. Possible alteration during storage in the comet nucleus (including internal 35 radiogenic heating as well as heating by external collisions¹).

4. Radiation processing at the surface of the nucleus.

5. Condensation/sublimation fractionation at several stages (in the interstellar cloud, in the primitive solar nebula, during periods of cometary activity).

6. Photolysis and chemical reactions within the cometary atmosphere.

A good knowledge of all these processes is necessary to evaluate how the observed, final material, is representative of primitive material.

In 1998, we presented in *Faraday Discussion* No. 108 (Chemistry and Physics of Molecules and Grains in Space) a discussion of results on cometary molecular chemistry just obtained from the observations of the exceptionally bright comets C/ 45 1996 B2 (Hyakutake) and C/1995 O1 (Hale–Bopp).² Since that time, the data gathered on these two comets have been thoroughly analysed, further results have been obtained on further comets, including especially 153P/Ikeya–Zhang, C/2001 Q4 (NEAT), C/2002 T7 (LINEAR) and C/2004 Q2 (Machholz), and three comets have been explored by space missions: 19P/Borrelly by *Deep Space 1*, 81P/Wild 2 by *Stardust* and 9P/Tempel 1 upon which an active experiment was performed by *Deep Impact* last summer. The present paper discusses some of the new implications of these recent observations for cometary chemistry.

Observatoire de Paris, 5 place Jules Janssen, F-92195 Meudon, France. E-mail: jacques.crovisier@obspm.fr

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Species	Origin ^b	Observation ^c	Notes ^d
Water and related spe	ecies		
H_2O	Р	R, IR, MS	
H_2O^+	S	V	
H_2O^+	S	R	
он	S	R IR UV	
н	S	V UV	
.1 U	S		
2	3		
) 2+	5	V, UV	
)'	S	UV	
CO and related specie	25		
20	P,S	R, IR, UV, MS	E
CO_2	Р	IR, MS	
20+	S	R, V, UV	
$2O_2^+$	S	V	
Aydrocarbons and rel	ated species		
CH4	· P	IR	
C ₂ H ₂	Р	IR. MS	
	P	MS	TBC
24 СаН.	P	IR MS	ibe
2116 1 LI	D	ID.	TDC
24112 CLI	r	IN ID V	IDU
л. л.	3	IK, V	
'H '	S	V	
CH ₂	S	MS	TBC
	S	UV	
2	S	IR, V, UV	
3	S	V	
CHO species			
H ₂ CO	Р	R. IR	Е
CH-OH	Р	R. IR. MS	
асоон	р	R	
сно	P	P	TRC
	I D	D	TDC
CUOCH ₃	r P	R	IBC
$(H_2OH)_2$	P	ĸ	
ICO '	S	R	
litrogen species			
√H ₃	Р	R, IR, MS	
ICN	Р	R, IR, MS	
INC	?	R	
CH ₃ CN	Р	R, MS	
IC ₃ N	Р	R	
INCO	р	R	
IH-CHO	p	R	
N	r C		
-1N	3	к, 1к, V V	
H H	5	V ID V	
H ₂	S	IR, V	
J	S	UV	
N_2^+	S	V	TBC
Sulfur species			
LS	Р	R, MS	
		,	
-2 	Р	V	TRC

 Table 1
 Molecules, radicals, ions and atoms observed in cometary comae^a

Table 1 (Continued)			
Species	Origin ^b	Observation ^c	Notes ^d
SO	р	R	
SO2	S	R	
OCS	P	R. IR	Е
H ₂ CS	Р	R	TBC
NŠ	?	R	TBC
S_2	?	UV	
S	S	UV	1
Others			
Na	S	V	
K	S	V	
Ar	S	UV	TBC 1
Metals ^e	S	V	

^{*a*} The species detected by mass spectroscopy of comet 1P/Halley are taken from the compilation of ref. 56 (Table 3); also listed as "probably detected" were CS, OCS, CH₃CHO, C₃H₂ and C₂H₅CN(ref. 56, Table 5). ^{*b*} Origin: P -primary (or parent) molecule coming from nucleus ices or from an extended source such as dust; S—secondary molecule coming from photolysis of a primary molecule, or from chemical reactions within the coma. ^{*c*} Observations: R—radio; IR infrared; V—visible; UV—ultraviolet; MS—mass spectroscopy. ^{*d*} Notes: TBC—the detection or identification of this species needs to be confirmed (*e.g.*, observation of a single line in a single comet). E—this species is suspected to come (at least partly) from an extended source such as cometary dust. ^{*e*} Various metal atoms were only observed in the sun grazing comet C/1965 S1 (Ikeya–Seki).

2. Molecular complexity in comets

Table 1 lists all cometary gas-phase species observed in cometary comae, withindications of their possible origin: from the sublimation of nucleus ices, fromphotolysis/chemistry in the coma, or released from still ill-defined *extended sources* in35the coma (possibly organic grains).

About two dozen stable volatile species, believed to be sublimated from cometary ices, have now been identified (they are noted "P" in Table 1) and their relative abundances have been measured. Significant upper limits are also available for many other species.^{3–7}

Altogether, about 45 molecules, radicals and molecular ions are identified in cometary atmospheres (Table 1). This is to be compared with about 130 species (including radicals and molecular ions, but not counting isotopologues) which are now known in the interstellar medium. But to be fair we must take into account that all these interstellar molecules are not observed in the same classes of objects: some are specific to interstellar hot cores, or dark clouds, or circumstellar envelopes. For instance, in protoplanetary discs, whose composition could be directly relevant to comets, only a handful of molecules are observed in the gas phase (CO, HCN, HNC, CN, CS, H₂CO, HCO⁺, C₂H . . .). Indeed, these small objects are difficult to investigate with the sensitivity of present instrumentation; furthermore, most molecules are trapped as ices and escape detection by gas-phase spectroscopy.⁸

The census of cometary molecules is also to be compared with chemical investigations of meteorites. Of course, chemical analyses performed in terrestrial laboratories achieve a much better sensitivity than remote sensing, and many more molecules, including complex organic molecules, can be identified in meteorites. In the Murchison meteorite (a carbonaceous chondrite) 140 aliphatic hydrocarbons, 87 30

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Fig. 1 The relative abundances of linear cyanopolyynes and alkanes in comet Hale–Bopp as a function of the number of carbon atoms. Power laws $X \propto n^{-\alpha}$ are drawn.

aromatic hydrocarbons (PAHs), no less than 74 amino acids have been identified.9,10 For several classes of species (e.g. amino acids), an "homologous decline" is observed, *i.e.* the abundances decrease when complexity (as measured by the number of carbon atoms) increases (cf. Fig. 10.5.1 of ref. 9).

As shown in Fig. 1, a similar trend is observed in cometary molecules for cyanopolyynes (HCN, HC₃N and upper limit on HC₅N^{3,5}) and for aliphatic hydrocarbons (CH₄, $C_2H_6^{11}$).

A random graphs model was proposed for simulating complex chemical astrophysical systems.^{12,13} It was applied to hydrocarbons in planetary atmospheres (Saturn, Uranus and Titan). This model predicts that the relative abundances of C_n hydrocarbons are following a power law $n^{-\alpha}$, with $\alpha \approx 13$. This is to be compared with $\alpha \approx 10$ for hydrocarbons observed in Titan and $\alpha \approx 8$ for laboratory simulations. For cometary molecules, if such a law applies, its slope is much less steep: $\alpha \approx 1.3$ for [C₂H₆]/CH₄], and $\alpha \approx 2.3$ for [HC₃N]/[HCN] (Fig. 1).

Surprisingly, for ethylene glycol, $(CH_2OH)_2$, which is the most complex gas-phase molecule identified in a comet, a relatively high abundance is observed.¹⁴ The abundance of this species is no less than 0.25% relative to water, making it the third CHO species by order of abundances, after methanol and formaldehyde. In contrast, ethanol is undetected with an upper limit of 0.1%.5

3. Statistics on cometary molecular abundances

The cumulative histogram of the number of cometary species as a function of their abundance is shown in Fig. 2. It bears on only the two dozen species observed in 45 comet Hale-Bopp. It is stalling for small abundances, obviously showing the effect of limited sensitivity. The power law indicated in the figure, which has a slope of -0.4, suggests that more than 100 species should be present at an abundance level of 0.001%.

It would be interesting to compare this histogram with similar distributions for 50 other astrophysical objects, or for complex chemical systems (e.g., living organisms, blood, wine . . .), if suitable homogeneous databases could be found. The problem for plotting such an histogram for astrophysical objects comes from the difficulty to find homogeneous samples; only column densities are measured, in different direc-55 tions, with different fields of view. This drawback is circumvented for comets, for which *production rates* can be derived in a consistent way, allowing us to obtain

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Fig. 2 Filled histogram: cumulative distribution of the number of cometary species as a function of their abundance relative to water (adapted from ref. 5). Thick line histogram: cumulative distribution of the number of molecular species in a cell (thick line) (from data of ref. 15, see text).

relative abundances; moreover, most of the data come from a single object, comet Hale–Bopp.

As a first try, Fig. 2 shows the histogram derived from data pertaining to the approximate chemical composition of a rapidly dividing cell (*Escherichia coli*), from ref. 15. Interestingly, it shows a slope similar to that of the cometary species, which suggests that such systems obey the same general law. It also fits with the extrapolation of the cometary histogram (which we may regard as being fortuitous).

Of course, Fig. 2 was not drawn to put forward any relation between comets and life, but just to investigate whether distributions of abundances in different complex chemical systems could obey similar laws.

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4. Deep Impact observations and molecular complexity

The *Deep Impact* mission allowed us to investigate the inner composition of the nucleus of comet 9P/Tempel 1 by excavating matter from $\approx 10-30$ m under the surface.¹⁶ The goal was to check whether material released by sublimation in the coma is representative of inner nucleus material.

Infrared spectra observed by *Deep Impact*[†] just before and just after the impact¹⁷) showed a tremendous increase of the relative intensity of the CH–X band around 3.2 μ m compared to the H₂O and CO₂ bands at 3.7 μ m and 4.25 μ m (Fig. 3). This was readily interpreted in ref. 17 as a surge of material with an enhanced abundance of organic matter from the inner nucleus.

† The analysis presented here is limited to results publicly available at the time of writing.



Fig. 3 Deep Impact spectra taken 4 min before (left) and 10 min after (right) the impact. The 15 spectra were observed by limb sounding at a projected distance of about 4 km from the impact region. (Adapted from ref. 17).

To be realistic, the interpretation should take into account optical thickness effects, which was not performed in ref. 17. Already, the 2.5-5.0 µm spectrum of comet 1P/Halley observed at a small distance by VEGA/IKS showed optically thick bands of H₂O and CO₂.^{18,19}

Table 2 shows evaluations of molecular production rates from the infrared pre-25 impact spectrum. Lines were assumed here to be optically thin. The water production rate is lower than evaluations from other observations (e.g. by $Odin^{20}$) by about a factor of 2 to 4. This may be due to flaws in our assumptions on the geometry of the observation or the coma gas distribution, or more probably, to optical depth effects. The ratio $[CO_2]/[H_2O] \approx 10$ is similar to that observed in the short-period comet 103P/Hartley 2 by ISO.21

The relative abundance for CH–X species ($\approx 15\%$ relative to water) is more or less in line (or rather larger) with that observed (CHO species and hydrocarbons) in other comets. Typical abundances of 5-10% relative to water were derived for the progenitors of the 3.2-3.6 µm band in several comets.²² The total production rate of identified hydrocarbons and CHO species in comet Hale-Bopp was $\approx 6.5\%$ by number relative to water.4

A discussion of the 3.2-3.6 µm cometary band as a whole is provided in ref. 2 and 22. The fluorescence rates of the bands of CH-X molecules in this spectral domain are roughly the same, which justifies our choice of the g-factor of the methanol ν_2 band as representative. (However, PAHs, which could contribute to the emission at

 Table 2
 Pre-impact production rates of 9P/Tempel 1 from Deep Impact observation, assuming
 optional thin fluorescence

		g-factor/s ⁻¹	$Flux/W m^{-2} sr^{-1}$	Q/s^{-1}	
Molecule	Band				
Water	ν_3	2.8×10^{-4}	1.5×10^{-4}	2.5×10^{27}	
CH–X		7.0×10^{-4}	4.0×10^{-5}	3.4×10^{26}	50
Carbon dioxide	ν_3	2.9×10^{-3}	1.0×10^{-4}	2.5×10^{26}	

Fluxes are taken from Fig. 13 of ref. 17. A miss-distance $\rho = 6$ km from comet nucleus, spherical symmetry and a coma expansion velocity of 0.5 km s⁻¹ are assumed. g-Factors are given for $r_{\rm h} = 1$ AU. For CH–X species, the total g-factor of the methanol bands ν_2 , ν_3 , ν_9 around 3.4 µm is assumed.

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Table 3 CH	O species and c	others—op	bacifies of infra	red lines				1
Molecule	Z _{rot} At 37.5 K	$g_{\rm I}$	$Band/\mu m \\$	A_{ij}/s^{-1}	$\sum \tau$	$\tau_{\rm max}$	$\langle \tau \rangle$	
H_2O	8.58	1, 3	ν ₃ 2.66	74	79	25	2.4	5
CO_2	33.5	0, 1	$\nu_3 4.26$	380	111	14	3.7	
CH ₃ OH	283.5	1, 1	$\nu_2 \ 3.33$	40	1.2			
$(CH_2OH)_2$	31 060	7, 9	≈ 3.3	≈ 50	0.15			

 $g_{\rm I}$: Spin degeneracies for ortho, para or A, E species. Optical depths τ are evaluated for $Q[{\rm H_2O}]$ = 10^{28} s^{-1} , $\rho = 6 \text{ km}$, $v_{\text{exp}} = 0.5 \text{ km s}^{-1}$ (corresponding to $N[\text{H}_2\text{O}] = 8 \times 10^{16} \text{ cm}^{-2}$), line 10 widths $\Delta v = 1 \text{ km s}^{-1}$ and a rotational temperature $T_{rot} = 37.5 \text{ K}$. Relative abundances of 100, 10, 2.5 and 0.25 are assumed for H_2O , CO_2 , CH_3OH and $(CH_2OH)_2$, respectively. $\Sigma\tau$ is the sum of the optical depths for all ro-vibrational lines in the band. τ_{max} is the optical depth for the strongest excitation line. $\langle \tau \rangle$ is defined from eqn (4). For H₂O and CO₂, Σ_{τ} , τ_{max} and $\langle \tau \rangle$ were computed from the GEISA database.⁵⁵ For CH₃OH and (CH₂OH)₂, Σ_{τ} was evaluated from 15 eqn (2). For $(CH_2OH)_2$ we have assumed a band of strength similar to that of CH_3OH .

 $3.28 \,\mu\text{m}$, could be excited by UV, followed by internal energy conversion, with much higher rates.

20 Quantitative evaluations of the optical depths of these bands are reported in Table 3. For a single ro-vibrational line:

$$\tau_{ij} = \frac{c^2}{8\pi\nu^2} \frac{\omega_{\rm u}}{\omega_{\rm l}} A_{\rm ul} \frac{N_{\rm l}}{\Delta\nu},\tag{1}$$

and for the whole vibrational band:

$$\Sigma \tau \approx \frac{c^2}{8\pi\nu^2} \langle A_{\rm ul} \rangle \frac{N_{\rm tot}}{\Delta\nu},\tag{2}$$

where N_1 is the lower level column density and N_{tot} the total column density. At a 30 miss-distance ρ from the nucleus:

$$N_{\rm tot}(\rho) = \frac{1}{4} \frac{Q}{\rho v_{\rm exp}}.$$
(3)

one can also define an *equivalent optical depth* $\langle \tau \rangle$ for the whole band by:

$$\sum [g_{ij} \exp(-\tau_{ij})] = [\sum g_{ij}] \exp(-\langle \tau \rangle), \tag{4}$$

where g_{ii} is the excitation g-factor for each ro-vibrational line and $\sum g_{ii}$ is the total g-factor of the band. In this simplified model, only one vibrational band is considered for each molecule, neglecting excitation by combination bands and the subsequent cascades. $\langle \tau \rangle$ scales roughly as $N_{\rm tot}/\sqrt{T_{\rm rot}}$.

These quantities have been evaluated in Table 3 for several molecules in the conditions of the pre-impact spectrum. The bands of H₂O and CO₂ had several thick lines, and the bands as a whole were moderately thick. On the other hand, methanol, 45 ethylene glycol, and presumably all heavy organic molecules, had optically thin bands: not only their bands have smaller $\sum \tau$, but they are distributed over much more individual ro-vibrational lines, as can be expected from their much larger partition functions.

In the post-impact spectrum, the intensities of the H₂O and CO₂ bands are 50 observed to increase by a factor of 10-20. This means that these bands are now heavily thick, and that the column densities for these molecules increased by several orders of magnitude. On the other hand, the CH–X band increased by a factor \approx 100, but given the very low level of saturation of this band in the pre-impact spectrum (taking methanol as an extreme case), this band is presumably still 55 optically thin.

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We conclude that the increase of the CH–X band relative to the H_2O and CO_2 bands is not due to a relative increase of the abundances of the organic molecules, but is rather an effect of the optical depths of the bands.

Further modelling of the optically thick infrared bands of comets is necessary. Such modelling will also be useful for the preparation and analysis of *in situ* observations of comet 67P/Churyumov–Gerasimenko with the *Rosetta* infrared spectrometer *VIRTIS*.²³

An infrared spectrum observed by *Deep Impact* just 0.6 s after the impact is shown in ref. 17 (their Fig. 11). This spectrum is that of the vapour plume, presumably at a hot temperature. The CH–X feature at 3.3 µm is remarkably smooth, broad and Gaussian-like. One can conjecture that this feature is due to a large number of different species at fairly high rotational temperatures, whose ro-vibrational lines add stochastically to form this smooth feature. Of course, no composition information can be retrieved from such a feature.

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5. Carbonaceous chondrites and cometary nuclei

Could some meteorites be pieces of cometary nuclei? Carbonaceous chondrites are the best candidates.²⁴ Indeed, it has been shown that the entry orbit of the Orgueil meteorite is compatible with a cometary orbit.²⁵ It is also compatible with those of near-Earth asteroids (NEAs)—but it is known that disguised cometary nuclei may possibly be present among NEAs.²⁶

Densities of carbonaceous chondrites, for the very few objects which were studied, are close to 2000 kg m⁻³.²⁷ This is much higher than what is expected for cometary nuclei—in the range 100–1000 kg m⁻³, this crucial parameter is not known very well. A density of 620^{+470}_{-330} kg m⁻³ was recently measured by *Deep Impact* for 9P/ Tempel 1.¹⁷

It is doubtful that a low-density, fragile cometary nuclei could survive an atmospheric entry. On the other hand, assuming a fractal model of cometary nuclei, the bulk density of the nucleus could be smaller than that of smaller pieces. Carbonaceous chondrites might be small pieces of cometary nuclei, with enough density and tensile strength to survive.

Could carbonaceous chondrite material be representative of cometary material? Organic matter in carbonaceous chondrites consists of a soluble fraction containing a complex mixture of compounds, and an insoluble macromolecular fraction.^{28,29} Carbonaceous chondrites also contain refractory inclusions (chondrules and calcium–aluminium inclusions). Such inclusions are apparently not present in meteors of cometary origin³⁰).

The insoluble macromolecular fraction could be akin to cometary semi-refractories. This is crucial for the explanation of the extended sources of cometary molecules. An alternative is polyoxymethylene and similar polymers which have also been invoked to explain the distributed source of formaldehyde.³¹

6. Where are cometary ices?

Exposed water ice, when freely sublimating under solar insolation at ≈ 1 AU, is expected to equilibrate at a temperature ≈ 180 K. It has a high albedo. Surprisingly, the *IKS* instrument aboard *VEGA 1* observed a surface temperature ≈ 400 K on the nucleus of comet 1P/Halley.³² The nucleus of the same comet was found to be very dark with an albedo ≈ 0.04 .

Since that time, albedos and temperatures of cometary nuclei have been mapped (albedos in comets 19P/Borrelly, 81P/Wild 2 and 9P/Tempel 1^{17,33,34} —temperatures in 9P/Tempel 1¹⁷). As for comet Halley, they do not show any sign of cometary ice, which should show up as regions of high albedo and low temperature. This is in contradiction with the idea that cometary activity arises from regions of exposed ice, the so-called "active regions".

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Reflectance spectra, either from the ground (several comets; see *e.g.*, ref. 35) or from space (19P/Borrelly³⁶), of cometary nuclei do not show any sign of ices. (Indeed, further analysis of the *Deep Impact* results revealed the presence of exposed water ice, but with a very small surface which can in no way explain the sublimation rate of water observed in this comet.³⁷) This contrasts with distant, icy objects of the Solar System (TNOs, several satellites, Centaurs) which show spectral features of different kinds of ices (*e.g.*, ref. 38) and especially water ice at 1.5 and 2.05 μ m.

So where is cometary ice? It could be mixed up with dust particles or boulders, whose albedo and temperature would be dominating on a macroscopic scale. Or it could be situated under a mantle of dust or a refractory crust, of low albedo and small thermal inertia. This surface layer should not be thick enough to prevent heating and sublimation of the underlaying ice. The sublimated gases should percolate through this layer, which should be porous.

Percolation through a dust layer would be a crucial process for cometary physics and the interface between nucleus and atmosphere. Gas temperature could equilibrate with the surface temperature (300–400 K at 1 AU), which is much higher than the sublimation equilibrium temperature (about 180 K for water ice). Is this compatible with the observed gas expansion velocities? Current hydrodynamical models assume a *cold* initial velocity.³⁹ This process would also be crucial for cometary chemistry, since during this short percolation travel, the gas is maintained at a relatively high density (and presumably temperature), with the opportunity of many collisions with the walls of the mantle pores. Conditions for a rich chemistry could be met.

7. The puzzle of the spin temperatures

Molecules such as H_2O , NH_3 , CH_4 ... which have several identical hydrogen atoms exist in different spin species (*ortho-para*, A-E...). Spin transitions are forbidden, so that spin temperatures could be preserved for a long time. The *ortho*-to-*para* ratios (OPR) and spin temperatures observed now for water or for other species might thus be primordial. First remarks on this topic were made in ref. 40 and 41.

First determinations of the water OPR were made from airborne infrared observations of comets 1P/Halley and C/1986 P1 (Wilson).⁴² Then accurate measurements were obtained with the *Infrared Space Observatory* on comets C/1995 O1 (Hale-Bopp) and 103P/Hartley 2.^{21,43} Further results on water were obtained by observing vibrational hot bands of water from the ground on bright comets.

These results were extended to ammonia. The OPR of NH_3 itself cannot (yet) be directly observed, but can derived from the OPR of NH_2 determined from its visible spectrum.⁴⁴ The spin temperature of methane can also be determined from the *E*, *A*, *F* spin species relative populations measured from its infrared spectrum.

All these results were recently reviewed in ref. 45 (see also ref. 46 for recent results on methane and ref. 47 for further results on water spin temperatures). These results are quite puzzling: the observed spin temperatures are remarkably close to 30 K, whatever the molecule, the heliocentric distance of the comet or its dynamical history. (The only departing value, obtained for C/1986 P1 (Wilson), may be erroneous, as was discussed in ref. 48, see also Table 4).

What is the significance of this temperature? It seems that any possible explanation can be ruled out (Table 5):

1. Equilibration within the coma would lead to spin temperatures depending on the heliocentric distance, as is observed for the rotational temperatures of cometary molecules. Similar spin temperatures were observed for comets at $r_{\rm h} \approx 1$ AU and $r_{\rm h} \approx 2.9$ AU. Laboratory experiments confirm that spin temperatures are preserved in molecular jets.

2. Equilibration at the comet surface would also lead to spin temperatures depending on the heliocentric distance, since surface temperatures vary roughly as $r_{\rm h}^{-1/2}$. If equilibration occurs at sublimation, one would rather expect $T_{\rm spin} \approx$

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Table 4 Spin temperatures observed in comets. Adapted from the compilation of ref. 45, and updated with recent results from ref. 46 and 47

Comet	H_2O/K	NH_3/K	CH_4/K	Orbital period/yr	4
IP/Halley C/1986 P1 (Wilson) C/1995 O1 (Hale–Bopp) 103P/Hartley 2 C/1999 H1 (Lee) C/1999 S4 (LINEAR) C/2001 A2 (LINEAR) 153P/Ikeya–Zhang C/2001 Q4 (NEAT)	$\begin{array}{c} 29 \pm 2 \\ > 50 \\ 28 \pm 2 \\ 34 \pm 3 \\ 30^{+15}_{-6} \\ \ge 30 \\ 23^{+4}_{-3} \end{array}$	26^{+10}_{-4} 27^{+3}_{-2} 25^{+1}_{-2} 32^{+5}_{-4}	33^{+3}_{-2}	76 Dynamically new 4000 6.4 Dynamically new Dynamically new 40 000 365 Dynamically new	10

 Table 5
 Possible processes for re-equilibration of spin temperatures

Process	Age^{a}	Duration ^b	Temperature/K
Formation in IS cloud	>4.5 Gyr	с	10-100
Chemical processing in PSN	4.5 Gyr	с	10-300
Condensation in PSN	4.5 Gyr	с	<180
Storage in nucleus	4.5 Gyr	4.5 Gyr	10-150
Sublimation	0-80 000 s	с	150-200
Percolation through dust mantle	0-80 000 s	<1 s	300-400
Expansion in the coma	0-80 000 s	80 000 s	10-100

Numerical values pertain to water." Time before observation." Time available for OPR reequilibration. ^c The process itself—chemical reaction or phase transition—is instantaneous.

150-200 K, the equilibrium temperature of sublimating water ice in cometary 30 conditions. However, it would be interesting to investigate in the laboratory whether the OPR is preserved during phase transitions.

3. A spin temperature in equilibrium with the internal temperature of the nucleus would nicely explain why the spin temperatures are the same for different molecules. However, the comet nucleus internal temperatures depend upon the comet orbital 35 history and are expected to differ between short-period and long-period comets, whereas both classes of comets show the same T_{spin} .

4. Although inter-spin conversions are forbidden, preservation of the spin state over cosmological times seems to be highly unlikely. This is unfortunately difficult to test in the laboratory! If indeed the present spin temperatures reflect the temperatures at the formation or condensation of the molecules this would imply that all comets formed in very similar physical conditions. This is inconsistent with the current view of cometary formation, where different classes of comets formed in different regions of the Solar System, translate into different chemical compositions. Note, also that H₂O, NH₃ and CH₄ have very different condensation temperatures: equilibrium at condensation would lead to different T_{spin} for these different molecules.

Conclusion 8.

We now return to the table of cometary molecules (Table 1). Most of the stable species can be explained by molecules sublimated from the nucleus ices and their subsequent photodegradation. Two-body reactions within the coma, although important, cannot lead to species of significant abundances.49

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The presence of some molecules, such as NS or S_2 , is still mysterious: they are unlikely to be present in cometary ices, but chemistry within the coma fails to account for them.^{50–52}

The nature, or even the existence of *extended sources* of cometary molecules is subject to raging debates. For instance, the source of extended CO which was observed from the CO infrared bands in comet Hale–Bopp⁵³ is not so obvious in interferometric radio observations.⁵⁴ These extended sources are presumably semirefractory organics of high molecular weight, similar to the insoluble macromolecular fraction of carbonaceous chondrites. Their very nature will be very difficult to characterize by remote sensing; it should rather be assessed by *in situ* analysis.

Mid-infrared spectroscopy is an invaluable remote sensing technique for studying the composition of gas-phase cometary species. However, it reaches its limits when the vibrational bands are getting optically thick, and when the spectral resolution is limited. This was the case for the *Deep Impact* observations, and we must bear this in mind for future investigations with *Rosetta*.

The homogeneity of the spin temperatures observed for different molecules of different comets under different conditions is an unsolved puzzle. Maybe we are missing insight into a key process.

Finally, the conclusion of our paper presented at *Faraday Discussion* No. 109 (Chemistry and Physics of Molecules and Grains in Space)² is still valid: recent 20 observations of comets have given some answers to old questions, but they have also brought new enigmas to be solved.

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