Cometary Chemistry

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Abstract.
The key problem in cometary chemistry is to observe abundances of species in the coma and to reassemble those species into the species that are present in the nucleus. The limitations are primarily due to poorly constrained models and the lack of uniqueness in reassembling parent species from the fragments when not all of the fragments are observable. These problems will be illustrated with several examples.

Key words: comets sulfur ammonia water grains

1. Introduction

Snyder(this volume) will provide a comprehensive survey of the molecules found in comets and Despois (this volume) will relate the composition of comets to that of the interstellar medium. I will therefore concentrate on determining the composition of the cometary nucleus from observations of the coma. This includes reconstruction of parent molecules that were frozen as ices in the nucleus and reconstruction of relatively refractory grains.

The standard paradigm is the dirty snowball model of Whipple (1950) in which ices evaporate from the nucleus, the resultant gas flows into the vacuum of space, and the gas drags sufficiently small solid grains with it. The outflow velocity is of order 1 km/s at r=1 AU and the density in the coma is sufficiently high for chemical reactions to occur only in the first few hundred to few thousand km. Beyond that distance, only photochemistry and reactions with the solar wind have significant rates. At a few thousand km from the nucleus of P/Halley, the total density of ions was $10^{-3}\times$ the total density of neutrals so the $10^{5}\times$ greater cross-section of reactions involving ions means that they can be significant at somewhat larger distances from the nucleus than neutral-neutral reactions. The rapid outflow yields only a short time during which a given particle can undergo an n-body reaction, whereas the time during which photoprocesses or solar wind reactions can take place is orders of magnitude longer.

Most measurements of cometary comae are made *via* remote sensing so the region sampled is dominated by the region in which photoprocesses dominate. Even *in situ* measurements, such as those made by the ICE, Suisei, Vega, and Giotto spacecraft, were made primarily in the region where photoprocesses dominate. Only Giotto clearly penetrated the region in which chemical reactions should occur. Thus I will emphasize the fragments that are seen in the outer coma and use of those to infer the composition that was released from the nucleus.

P. D. Singh (ed.), Astrochemistry of Cosmic Phenomena, 415–420.

2. Reassembling Parent Molecules

2.1. H_2O

In order to evaluate our ability to put the pieces together, I will first consider the relatively well understood case of H_2O and its frequently observed products – OH, H, $O(^1D)$, and H_2O^+. Direct measurements of H_2O are rare. There have been no measurements of the other dissociation product, H_2. There is no doubt that all the expected fragments of H_2O are present and the only question is whether we can reliably put the fragments together quantitatively to say that H_2O is the sole parent for all the fragments or conversely to derive the amount of H_2O from measurements of one or more of the fragments.

Remote measurements of OH (Festou *et al.*, 1986) showed roughly 35% more OH than expected from the amount of H_2O deduced almost simultaneously from the neutral mass spectrometer (NMS) on Giotto (Krankowsky *et al.*, 1986). The NMS also showed that H_2O was roughly 80% of the total gas. No subsequent study has clearly eliminated the discrepancy although much of the discrepancy is undoubtedly in the use of somewhat different models for the interpretation of the data. Thus an accuracy of 10% in reassembling the pieces is overoptimistic with our present knowledge. Two weeks later, infrared measurements of H_2O yielded a production rate 2× higher than nearly simultaneous measurements of OH (Weaver *et al.*, 1987). The lack of an adequate time-dependent model of the coma may play a role in the discrepancy as may uncertainties in the excitation of the two species. The uncertainties are highlighted by comparing measurements of the same species in different spectral domains as illustrated by Festou (1990, Figure 3). He shows the large discrepancy between ultraviolet and radiowave measurements of OH as well as the discrepancy between those results and the ultraviolet measurements of H. Taken as a whole, one must conclude that H_2O is the dominant parent of OH and H and, in most comets, of $O(^1D)$ but the uncertainties in the data and in the models prohibit any firm conclusion about additional minor parents of these species.

2.2. NH_3

NH_3 presents a particularly interesting example because there is only one direct measurement, a radio measurement for comet I-A-A which did not yield a reliable abundance (Altenhoff *et al.*, 1983), While in comet P/Halley, two mutually exclusive sets of products of NH_3 led to estimates of the NH_3 abundance which differ by an order of magnitude.

Allen *et al.* (1987) used the *in situ* measurements from the ion mass spectrometer (IMS) on Giotto in conjunction with a model for the ion-chemistry of the inner coma to interpret the radial profiles of the mass peaks

TABLE I
Sulfur-Bearing Species in Comets

Species	Technique	Comets	Abundance	Source	Comments
S	uv	all	?	various	
CS	uv	all	0.2%	CS_2	
S_2	uv	I-A-A	0.01-0.1%	grains?	only comet
H_2S	radio	Austin+Levy	0.2%	parent?	all comets?
H_3S^+	Giotto IMS	Halley	0.2% H_2S	H_2S	all comets?
SO	uv	several	$< 0.01\%$	parent, SO_2	no comets?
SO_2	uv	several	$< 0.01\%$	parent	no comets?
SH	optical	P/Bro-Met	$< 1\%$	H_2S	
OCS	radio	Levy	$< 0.2\%$	parent	
H_2CS	radio	Levy	$< 0.1\%$?	parent	

associated with H_2O^+, NH_3^+, and their associated compounds. Fitting these profiles with various assumed abundances of the corresponding neutrals, they concluded that an NH_3 abundance of 1-2% that of water provided the best fit to the data. It should be pointed out, however, that the resultant fit was still not a good one.

Remote observations of NH and NH_2, on the other hand, imply much lower abundances of NH_3. Wyckoff *et al.* (1991) have found from observations of NH_2 that the abundance of NH_3 is only 0.2% in P/Halley. They find somewhat lower but comparable values for three other comets. Analysis of narrow-band photometry of NH for comet P/Halley also suggests an NH_3 abundance of a few times 0.1% (Schleicher, A'Hearn, and Samarasinha, unpublished), comparable to the values found for other comets. Although the errors on all the results are large, the discrepancy between the interpretations of the ions and of the neutrals is beginning to strain the quoted uncertainties.

Since the primary dissociation channel of NH_3 is into NH_2 and NH, while direct ionization and protonization to NH_4^+ are minor channels for the destruction of NH_3, it seems likely that the results based on the neutrals are correct. Since all investigators agree on the primary destruction channel, the NH_3 abundance implied by the ions would require an unknown process to destroy NH_3 without producing NH_2 and NH. Thus this is a case in which one must make a judicious choice of which pieces to reassemble into the parent.

2.3. SULFUR COMPOUNDS

A quite different example of reassembly uses atomic column densitites to determine whether or not all molecules containing a given atom have been identified, as in the case of sulfur shown in Table I. It has been known for many years that in some comets the observed production of CS is insufficient to explain the observed column density of S if the CS comes from CS_2. With the discovery of H_2S in comets (Bockelee-Morvan *et al.*, 1991), Roettger (1991) has found that all the observations of S can be explained if one assumes amounts of H_2S less than or equal to that observed in comets Austin and Levy. At first glance, this seems to explain everything very well but there are several complications. One significant limitation is that S is always observed with a relatively small field of view. Thus the observed column density of sulfur is insensitive to any sulfur-bearing molecules with long lifetimes, say $\geq 10^5$ sec. An additional complication is indicated by the fact that some observations of very active comets yield a production of CS_2 which should produce more S than is observed. One way out of this is to assume that CS comes from a different (unknown) parent, thereby reducing the source of S atoms by a factor two. Another way out is suggested by the fact that in some spectra the sulfur triplet at 1812Å exhibits a profile inconsistent with the known intensity ratios of the three components implying that optical depth effects are important. These effects have not been modelled although in the simplest approximation the finite optical depth merely redistributes the flux among the three components without changing the net flux. Finally, the recently discovered lines of S at 1425/1474Å (Roettger *et al.*, 1989) yield abundances that are a factor of five greater, implying an error either in the model of the excitation or in the atomic parameters. Thus the possibility remains of a substantial amount of other sulfur bearing molecules.

3. Grains as Parents

The *in situ* observations of CO in comet P/Halley (Eberhardt *et al.*, 1987) were the first to provide solid evidence for an extended, non-gaseous source for an observed gaseous species. At least half the CO was released from the extended source. Although doubts have been expressed about the interpretation, suggesting that the spatial profile observed by Giotto was an artifact induced by passage through a CO-rich jet, the extended source interpretation is still more convincing. Since the lifetimes of icy grains would be much too short to explain the spatial distribution, and since the sum of all heavier gases was no more than the abundance of CO, it is generally hypothesized that the CO was released, either thermally or by photoprocesses, from refractory grains, presumably the CHON grains also detected *in situ*. Although no other observations provide such a convincing case, there are many observations that are most easily interpreted under this scenario. *E.g.*, Feldman *et al.* (1991) have used the extended source to explain the different production rates of CO in comet Levy deduced from instruments with different fields of view. Similarly Snyder (this volume) has pointed out that the radio observations of H_2CO require an extended source (either gaseous or refractory) in order to avoid a ridiculously high abundance while Krankowsky (1991) has pointed out that the radial profile observed with the Giotto NMS also implies an extended source with the same spatial characteristics as that of the CO source.

Additional evidence for refractory sources of gas comes from observations of CN. A'Hearn *et al.* (1986) originally suggested that the jets observed in CN images of P/Halley were so well collimated that a grain source (collisionless even very close to the nucleus) was required. More recent processing of those same images by Klavetter (private communication) shows a region of excess production of CN which is semicircular and at the same distance from the nucleus as was the extended source of CO. It therefore appears that, at least in some comets, very many different gaseous species are produced from refractory grains.

I suggest that this may also be the source of S_2 in comet I-A-A. The absence of SO and SO_2 from comets (Kim and A'Hearn, 1991) rules out our original hypothesis that S_2 was a residue of interstellar processing of sulfur compounds in the icy mantles of interstellar grains. An alternative procedure for producing S_2 is by sputtering of solid sulfur-bearing grains. Russell *et al.* (1987) pointed out that the interplanetary magnetic field had an unusual radial alignment when the S_2 was observed so that solar wind particles could penetrate unusually deeply into the coma. Boring *et al.* (1985) and Chrisey *et al.* (1987, 1988) showed that S_2 was readily produced by sputtering solid sulfur or solid H_2S. Sputtering from the nucleus requires a quantum yield at least an order of magnitude too high but spreading the material into grains reduces the required quantum yield. Grains of H_2S are unlikely because they are too volatile and no mechanism is know to produce solid S_8, but H_2S is readily converted to FeS in the presence of Fe and liquid water. Whether the process also works in the presence of ice is unclear but I suggest that the S_2 was produced by sputtering of either grains of FeS.

In summary, refractory grains are playing an increasingly important role in our understanding of the gases observed in comets. Unfortunately, the physical processes involving grains are less well understood than are gaseous processes so it is very difficult to reassemble grains from their fragments.

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QUESTIONS AND ANSWERS

S.Sandford: Given that methanol (CH_3OH) is now known to exist in interstellar ices and that it's been recently detected in comets, could its presence bear on the question of the extended sources of CO and H_2CO? (We know from lab experiments that photolysis of CH_3OH in H_2O-rich ices produces CO, H_2CO, CO_2, CH_4,...)

M.F.A'Hearn: If the CH_3OH leaves the comet in grains it may very well help explain the extended source of CO and H_2CO. If it evaporates directly from the nucleus it cannot explain the observations.

W.F.Huebner: The idea of sputtering sulfer off FeS grains is very interesting. Are FeS grains consistent with PIA and Puma experiments on Giotto and Vega?

M.F.A'Hearn: I have not yet checked this point.

L.d'Hendecourt: How is the oxygen distributed in the comet? 1) mostly in H_2O? 2) why not in molecular oxygen O_2? Some question for the nitrogen: 1) in NH_3, CN... 2) why not in molecuar nitrogen N_2?

M.F.A'Hearn: Oxygen is observed as [OI] at $\lambda 6300, 6363$ and brightness and spatial distribution are both consistent with prompt emission following dissociation of 5 - 10% of water via $H_2O + h\nu \rightarrow H_2 + O(^1D)$. It is also observed in the $\lambda 1304$ resonance line of OI which has been observed with small fields of view using IUE for many comets. The ensemble of $\lambda 1304$ data on all comets has not, to my knowledge, been checked for consistency with H_2O dissociation but I think that in some comets the results are consistent, within the usual factors of two, with production from H_2O. A.Delsemme will comment on the nitrogen and the abundance of N_2.