OBSERVATIONS OF MOLECULES IN COMETS

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ABSTRACT. Ultraviolet and visible spectroscopy of comets has identified a large number of species in the coma, most of which appear to be the photodissociation and photoionization products of the "parent" molecules evaporated directly from the cometary nucleus. Analyses of cometary spectra support the icy conglomerate model of the nucleus with H_2O as the dominant ice species. Two molecules detected in the ultraviolet, CO and S_2, are of particular interest to the study of the cosmogonic evolution of cometary grains. CO appears to be a highly variable constituent from comet to comet, while S_2, first observed in comet IRAS-Araki-Alcock in 1983, is found in no other celestial source. Both of these molecules appear to be parent molecules.

1. INTRODUCTION

Much recent interest in the study of comets, as exemplified by the current spacecraft missions to Comet Halley, is the result of recognition of these objects as probable pristine remnants of the primordial solar system (Weissman 1985). By virtue of having spent most of their history in the "Oort cloud" at a mean distance of ~40,000 AU from the sun, the comets preserve a record of the volatile component of the original solar nebula that is missing from the abundance determinations based on analyses of meteoritic material whose volatile constituents may have vaporized upon entry into the Earth's atmosphere. Chemical modelling of the visible emissions of cometary comae (Huebner <u>et al</u>. 1982) has furthermore suggested that this volatile component is compositionally similar to that of interstellar molecular clouds, rather than that of the giant planets, thus strengthening the argument for comets as cosmic refrigerators of the material of the primordial nebula.

Observationally, the problem is difficult as the icy nucleus is not directly detected. Rather, the gaseous and solid components of the extended coma surrounding the nucleus are observed and it is from the spectral and spatial information about the coma, together with photochemical modelling, that the composition of the cometary ice must

417

be inferred.   The modelling is necessary since, with a few exceptions,
the spectroscopically observed species are radicals, atoms or ions which
are the products of successive photodissociations or photoionization of
the "parent" molecules, the species directly vaporized from the surface
of the nucleus.   Photochemistry in the cometary coma is discussed in the
papers by Huebner and van Dischoek in this volume.

2.   SPECTROSCOPY OF THE COMA

Perhaps the poorest spectral region for the study of the molecular
composition of the cometary coma is the visible (3000-8000 A).   By the
1940's, several radical species, including CH, C_2, C_3, CN, NH, NH_2 and
OH, had been identified in cometary spectra (Swings and Haser 1956), in
the case of C_3 before the observation of this spectrum in the laboratory
(Douglas, 1951).   Since the OH emission band at 3085 A is severely
attenuated by the atmosphere, the high abundance of hydroxyl in the coma
was not appreciated until the first observations from space (Code et al.
1972), and the early "icy-conglomerate" models of Whipple (1950, 1951)
contained nearly equal amounts of H_2O, CH_4, NH_3 and CO_2 as likely
parents of the observed radicals.   Stable molecules were inferred from
the presence of ionic emissions of CO^+, CO_2^+, and N_2^+, and much later H_2O^+
(Wehinger et al. 1974), in visible spectra.   Whipple's model was based
more on his association of the water ice vaporization as a function of
heliocentric distance with the "non-gravitational" parameters deduced
for the orbital evolution of the very short period comet P/Encke than on
the spectroscopic identification of OH in the coma.   Twenty years later,
when the water production rate required to account for the OH and HI
Lyman-α emission from comet Bennett (1970 II) observed by OGO-5 was
calculated (Bertaux et al. 1973) it was found to be exactly of the order
of magnitude as Whipple's dynamical analysis had required.
     Huebner et al. (1982) have summarized the difficulties that arise
with photochemical models based on ices containing only H_2O, CO_2, NH_3
and CH_4 in various proportions.   These models fail to reproduce the
observed column abundances of C_2, C_3 and CN, in some cases by several
orders of magnitude.   Much better agreement with observations was
obtained by using ice compositions based on the relative abundances
found in typical interstellar molecular clouds (Mitchell et al. 1981;
Biermann et al. 1982) implying that these radicals result from
straightforward dissociation of complex parent molecules.   Reaction
chains involving single or multiple neutral-neutral collisions do not
appear to have a significant effect on composition at the low densities
found in the gaseous coma of most comets.   The total abundance of all of
the parents of the observed radicals (except OH, of course) appears to
be less than 1% that of water, which is again consistent with the
general trend of molecular cloud abundances.
     Radioastronomical searches for parent molecules in comets have,
with few exceptions, been largely unsuccessful (Snyder 1982) due to the
relatively small column densities of the species of interest compared
with those that obtain in the giant molecular clouds.   The exceptions
are the reported detections of H_2O and NH_3 in comet IRAS-Araki-Alcock

(1983 VII) (Altenhoff et al. 1983), where the effective column densities
were geometrically enhanced by the small geocentric distance to the
comet at the times of observation (0.032 and 0.044 AU). Of course, the
18 cm transitions of OH, which is not a parent molecule, have been
observed in a large number of comets (Despois et al. 1981), although
there still remains a significant discrepancy between OH production
rates derived from these data and those based on UV observations. The
infrared is also potentially useful for identifying small parent
molecules (e.g. H_2O or CO_2) but attempted observations have so far
proved unsuccessful with several comets through 1984 (Weaver and Mumma
1984).

3. ULTRAVIOLET OBSERVATIONS

The visible emissions of cometary radicals result from the resonance
fluorescence in sunlight of these molecules. Biermann (1968) suggested
that similar resonance scattering of HI Lyman-α radiation at 1216 A in
the vacuum ultraviolet would produce a large signal, observable from
space, due to the preponderance of hydrogen-bearing molecules in the
coma. His prediction was borne out by the first earth-orbit
observations of comets Bennett (1970 II) and Tago-Sato-Kosaka (1969 IX)
(Code et al. 1972). The ultraviolet also contains the resonance
transitions of many of the cosmically abundant species (e.g. C, O, N and
S) as well as the strongest electronic transitions of a number of simple
molecules such as CO, H_2, NO and CS. Most of these species were first
identified in comets Kohoutek (1973 XII) and West (1976 VI) in spectra
obtained from a handful of sounding rocket experiments (Opal et al.
1974, Feldman et al. 1974, Feldman and Brune 1976, Smith et al. 1980).
     Systematic studies of ultraviolet spectra of a large number of
comets were made possible with the International Ultraviolet Explorer
(IUE) satellite observatory placed into a geosynchronous orbit in
January 1978. Nearly two dozen comets have been observed to date and a
summary of significant results has been given by the author in previous
reviews (Feldman 1982, 1983). It should be noted that during the eight
years of IUE operation so far there has not been an apparition of a
bright, new (in the Oort sense) comet similar to comets Bennett or West.
Nevertheless, it appears that all of the comets observed are water ice
dominated as evidenced by the strong H I and OH emissions detected and,
when possible, the corresponding O I 1304 A multiplet. Even comets
Bowell (1982 I) and Cernis (1983 XII), both observed near 3.3 AU from
the sun, showed detectable OH emission, indicative of an H_2O source
(A'Hearn et al. 1984).
     The ultraviolet spectral range also makes possible the detection of
the two dominant constituents of molecular clouds, H_2 and CO, which can
be observed in fluorescence of solar radiation (Feldman and Fastie 1973,
Feldman and Brune 1976). The data on comet West (1976 VI) do not show
any H_2 emission near 1600 A and a derived upper limit to the H_2
production rate (assuming it to be a parent molecule leaving the nucleus
with an outflow velocity of ~1 km s^{-1}) is comparable with the deduced
value of the water production rate. There is also a component of H_2

produced by the dissociation of H_2O into $O(^1D)$ and H_2, which occurs in about 7% of the photodissociations produced by solar ultraviolet radiation. This component is more difficult to detect as the excess energy of dissociation results in a mean H_2 velocity of ~13 km s^{-1} so that these molecules quickly escape from the spectrometer's field-of-view. Thus, in the cometary nucleus hydrogen exists principally in the form of water, molecular hydrogen, being extremely more volatile, having escaped during the condensation of the solar nebula.

Another possible indication of the temperature of the region of formation of comets in the primordial nebula is the comparative abundance of CO and CO_2. CO has been positively identified in only two comets, West (1976 VI) and Bradfield (1979 X), but the abundance of CO relative to H_2O in these two comets differs by a factor of ~20 (Feldman 1986). However, this difference may simply reflect the different histories of these two comets since their expulsion from the Oort cloud. CO_2 has not been detected directly even though possible in the ultraviolet since photodissociation of CO_2 leads to a significant population of the $CO(a^3\pi)$ state which is the upper level of the Cameron band system which is a prominent feature of the dayglow on Venus and Mars (Conway 1981). Feldman and Brune (1976) estimated an upper limit to the CO_2 production rate in comet West which was less than that derived for the observed CO. However, CO_2 must be present in the cometary nucleus as the CO_2 ion is a common feature in the spectra of many comets (Festou et al. 1982), including comet West, and moreover, appears in roughly constant abundance relative to water in these comets.

Finally, we note the utility of the ultraviolet for the detection of sulfur and sulfur-containing molecules. In particular, both S I and CS are common features of cometary spectra (Smith et al. 1980, Jackson et al. 1982) and CS appears to be present in roughly the same abundance relative to H_2O in most comets (Weaver et al. 1981). The close approach to Earth of comet IRAS-Araki-Alcock (1983 VII) in 1983 enabled the IUE discovery of S_2 which appeared confined to a region of ~500 km around the nucleus and was deduced to be a parent molecule (A'Hearn et al. 1983). However, the sulfur dimer has not yet been detected in any other comet and it is not known if it is a universal feature of cometary spectra. This molecule is not known to be present in any other celestial source. Two other molecules containing sulfur, SH and SO, also have their resonance transitions in the ultraviolet but have so far not been detected in cometary spectra.

A summary of atomic, ionic and molecular species detectable in the ultraviolet is given in Table I.

4. RELATION TO MOLECULAR CLOUDS

The presence of S_2 in the cometary ice remains somewhat of a mystery. At the temperatures of cometary formation according to various scenarios of the evolution of the solar nebula, sulfur is highly unlikely to be in the form of S_2, but based on laboratory data, probably exists as S_8. This appears to be consistent with the non-detection of this species in any molecular cloud or other celestial source. A'Hearn and Feldman

(1985) have considered the possibility that the S_2 is formed in the ice in the solid phase as a result of reactions among free sulfur atoms which are detached from molecules such as CS_2 and SO_2 by cosmic ray irradiation occurring over geologic time scales. However, such irradiation would affect only the outer meter or so of the cometary nucleus, and in the case of comet IRAS-Araki-Alcock whose orbital period is about 1000 years, the affected layer would be vaporized in a very short time. Thus, if irradiation was the source of the observed sulfur dimers, then it must have occurred to the pre-existing cometesimal grains in the precursor molecular cloud of the solar nebula.

TABLE I. Ultraviolet Emission Features

Observed Species	Wavelength (Å)	Possible Species	Wavelength (Å)
H I (Lyman-α)	1216	H_2	1608
O I	1304	NO	2150
C II	1335	CO_2	2000 - 2200
C I	1561, 1657	SO	2635
S I	1813	SH	3261
C I (^{1}D)	1931		
CO	1475 - 1600		
C_2	2313		
CS	2576		
S_2	2850 - 3050		
OH	3085		
CO^+	2188		
CO_2^+	2890		

Carbon monoxide, because of its high volatility, is also not expected to survive the cometary condensation phase at the solar nebula temperatures at the orbit of Saturn or Uranus so that the dominant carbon oxide expected in the cometary ice is CO_2. However, Greenberg and his collaborators (see Greenberg 1983) have demonstrated in the laboratory that ultraviolet irradiation of water ice containing either CO or CO_2 results in the rapid formation of the other oxide. Thus, the difference between a "new" comet such as West (1976 VI) and all of the comets observed by IUE may be that the higher concentration of CO in the water ice may reside entirely in the outer layer of the cometary nucleus (Feldman 1986). Such a composition, with the highly volatile CO in the outer skin, may also explain the initial high level of activity and subsequent decline of the "famous" comet Kohoutek (1973 XII). Further support is provided by the association of extensive (CO^+) ion tails with "new" comets, assuming that a high CO^+ abundance requires a similarly high concentration of CO in the nucleus.

Many of these questions are likely to be answered in the near future as a result of the in situ measurements to be provided by the various encounter missions to comet Halley and by the extensive ground-based and Earth-orbiting programs planned for this period. Observations of both CO and S_2 will be much enhanced by the high spatial resolution and sensitivity of the spectrographs on the Hubble Space Telescope. However, definitive answers may need to await the results of comet rendezvous and sample return missions planned for the last decade of this century.

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DISCUSSION

JACKSON: Does the measured scale length of CO allow one to predict the photochemical lifetime?

P.D. FELDMAN: No. In this case the spatial distribution is dominated by the r^{-2} variation in density of a parent molecule with a long photo-dissociation lifetime.

HUEBNER: You mentioned that the production rate variation with heliocentric distance is different for various comets, i.e., $Q \sim r^{-n}$, where n changes from comet to comet. Have you tried to correlate the values of n with the dustiness of comets? Very dusty comets may heat the nucleus quite differently than dust-free comets. There may be some feedback from the solar radiation scattered by the dust in the coma onto the nucleus.

P.D. FELDMAN: This has been investigated in some detail by Werssman and Kieffer who found that a large amount of dust increased the value of n. However, the variation of n that I mentioned was for a sample of comets all of which had very little dust.

SOMERVILLE: It is of interest to compare cometary dust and inter-
stellar dust. Is there any suggestion in the spectra of a broad
feature around 2200 Å?
P.D. FELDMAN: This has not yet been measured because the solar UV flux
decreases rapidly below ~2600 Å. However, in general, cometary grains
are very dark (albedo as low as 1%) which appears to be a distinct
difference from interstellar grains.

GREENBERG: I should like to point out that your comment on the very
low albedo of cometary dust compared to interstellar dust is easily
reconciled by my aggregated dust model. A loose fluffy aggregate of
particles whose individual albedo is α and whose scattering asymmetry
factor is g = <cosθ> presents an ensemble surface with a Bond albedo
(the albedo of comet dust) of $A_B \cong \alpha(1-g)$. For the fully accreted
interstellar grains the value of g in the ultraviolet is g $\cong$ 0.95
while α is its asymptotic value of 0.5. Thus the Bond albedo in the
ultra violet is $A_B \cong$ 0.5 (1-0.95) $\cong$ 0.025, which is indeed quite low.
P.A. FELDMAN: Regarding your comments on interstellar S_2, I would just
like to point out that we know almost nothing about the interstellar
abundance of this molecule. The 3 mm lines of S_2 are, of course,
magnetic dipole transitions and hence are $\sim 10^{-4}$ of typical electric
dipole lines of interstellar molecules. The only observation I know
of these S_2 lines are those of Liszt, made more than 5 years ago. I
can't recall the exact numbers, but it is unlikely that Liszt's upper
limits to $N(S_2)$ were better than $10^{16} - 10^{17}$ cm^{-2}.

P.D. SINGH: (i) Does S_2 as a 'parent' molecule react with other
cometary species? (ii) You consider CO molecule as a 'parent'. As
far as I remember, photodissociation of CO_2 by solar photon flux at
r_h = 1 AU (Huebner and Carpenter, 1979) yields CO in ground state
$X^1\Sigma^+$ and in an excited state $a^3\pi$ (perhaps). How will you differentiate
the two contributions in an UV cometary spectra?
P.D. FELDMAN: (i) There is no evidence, for comets with Q $\leq 10^{29}$
molecules s^{-1}, that neutral-neutral reactions have any significant
effect on the composition of the coma. Even so, the S_2 is destroyed
by photodissociation in <500 seconds, so the possibility of a reaction
is even smaller. (ii) There will certainly be a component of CO due
to photodissociation of CO_2. However, it will have a very different
spatial distribution than that of the CO vaporized directly from the
nucleus.