COMETARY MOLECULES

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ABSTRACT. Which molecular species are firmly identified as cometary species and which are also interstellar? How may excitation effects bias the data interpretation?

1. Introduction

Because space is limited, only those molecules with observed and identified gas-phase spectra will be discussed. Thus, there can be no discussion of either the interesting mass spectra acquired by the Comet Halley spacecraft, or current work on the proposed polyoxymethylene identification (Huebner 1987). Modern theory links the composition of comets to that of the interstellar medium, with many uncertainties. Table 1 lists the known interstellar and circumstellar species by <u>number</u> of atoms, except for the polycyclic aromatic

TABLE 1. The 89 reported interstellar and circumstellar molecules as of July, 1991

<u>2</u> AlF AlCl C_2 CH CH^+ CN CO CP CS CSi HCl H_2
KCl NH NO NS NaCl OH PN SO SO^+ SiN SiO SiS
<u>3</u> C_2H C_2S HCN HCO HCO^+ HCS^+ H_3^+ H_2O H_2S HNC
HNO N_2H^+ OCS SO_2 c-SiC_2 <u>4</u> c-C_3H l-C_3H C_3N
C_3O C_3S C_2H_2 $HCNH^+$ H_2CO H_2CS H_3O^+ HNCO HNCS
$HOCO^+$ NH_3 <u>5</u> C_4H C_4Si c-C_3H_2 CH_2CN CH_4 HC_3N
HCOOH H_2C_2O H_2CHN H_2NCN SiH_4 <u>6</u> C_5H C_5O C_2H_4
CH_3CN CH_3NC CH_3OH CH_3SH $HCONH_2$ <u>7</u> C_6H CH_2CHCN
CH_3C_2H HC_5N $HCOCH_3$ NH_2CH_3 <u>8</u> CH_3C_3N $HCOOCH_3$
<u>9</u> CH_3C_4H CH_3CH_2CN $(CH_3)_2O$ CH_3CH_2OH HC_7N
<u>10</u> CH_3C_5N $(CH_3)_2CO$ <u>11</u> HC_9N <u>13</u> $HC_{11}N$

hydrocarbon (PAH) compounds. Ring structures are preceded by c-, but where the structure is also linear an l- is used. Mann and Williams (1980) and Lovas (1986; 1987) have prepared extensive frequency lists.

P. D. Singh (ed.), Astrochemistry of Cosmic Phenomena, 427–434.

2. Cometary Molecules

The cometary molecules with observed and identified gas-phase spectra are listed in Table 2. The known interstellar/

TABLE 2. The 27 reported cometary molecules as of July 1991

2	C_2 CH CH^+ CN CN^+ CO CO^+ CS N_2^+ NH OH OH^+ S_2
3	HCN H_2O H_2O^+ H_2S C_3 CO_2 CO_2^+ NH_2 OCS
4	H_2CO NH_3
5	CH_4
6	CH_3CN CH_3OH

circumstellar molecules are more chemically complicated than these; along with the Halley mass spectra and meteoritic chemistry, this suggests that comets are more chemically evolved than their gas-phase spectra indicate.

Two important questions are: how secure is a given cometary molecular identification; and what molecules are identified in multiple spectral regions? Several reviews have addressed these questions (e.g., A'Hearn 1983; Feldman 1983; Wyckoff 1983; Snyder 1982), so this will be a brief update. The ultraviolet region will be defined as $\lambda < 3200$ Å, optical as 3200-8000 Å, infrared as 8000 Å to 0.5 mm (20 cm^{-1}), and radio as $\lambda > 0.5$ mm wavelength. Table 3 lists ultraviolet molecules, approximate band centers, and assignments. All are

TABLE 3. Cometary molecules with ultraviolet spectra

C_2 (2313 Å, $D^1\Sigma^+_u - X^1\Sigma^+_g$) CN^+ (2181 Å, $f^1\Sigma - a^1\Sigma$; 3185 Å, $c^1\Sigma - a^1\Sigma$) CO (1510 Å, $A^1\Pi - X^1\Sigma^+$) CO^+ (2190 Å, $B^2\Sigma^+ - X^2\Sigma^+$) CS (2576 Å, $A^1\Pi - X^1\Sigma^+$) OH (3090 Å, $A^2\Sigma^+ - X^2\Pi_i$) S_2 (2957 Å, $B^3\Sigma^-_u - X^3\Sigma^-_g$) CO_2^+ (2890 Å, $B^2\Sigma^+_u - X^2\Pi_g$)

commonly found except for S_2, which was detected only in Comet IRAS-Araki-Alcock or I-A-A (A'Hearn 1983; Feldman 1983; 1991; Wyckoff 1983). Table 4 lists optical molecules, approximate band centers, and assignments (A'Hearn 1983; Wyckoff 1983).

TABLE 4. Cometary molecules with optical spectra

C_2 (5165 Å, $d^3\Pi_g - a^3\Pi_u$; 7715 Å, $A^1\Pi_u - X^1\Sigma^+_g$) $^{12}C^{13}C$ (4745 Å, $d^3\Pi_g - a^3\Pi_u$) CH (3889 Å, $B^2\Sigma^- - X^2\Pi_r$; 4315 Å, $A^2\Delta - X^2\Pi_r$) CH^+ (4225 Å, $A^1\Pi - X^1\Sigma^+$) CN (3883 Å, $B^2\Sigma^+ - X^2\Sigma^+$; 7873 Å, $A^2\Pi_i - X^2\Sigma^+$) CO^+ (3954 Å, $B^2\Sigma^+ - A^2\Pi_i$; 4273 Å, $A^2\Pi_i - X^2\Sigma^+$) N_2^+ (3914 Å, $B^2\Sigma^+_u - X^2\Sigma^+_g$) NH (3360 Å, $A^3\Pi_i - X^3\Sigma^-$) OH^+ (3565 Å, $A^3\Pi_i - X^3\Sigma^-$) H_2O^+ (6198 Å, $\tilde{A}^2A_1 - \tilde{X}^2B_1$) C_3 (4040 Å, $\tilde{A}^1\Pi_u - \tilde{X}^1\Sigma^+_g$) CO_2^+ (3509 Å, $\tilde{A}^2\Pi_u - \tilde{X}^2\Pi_g$; 3674 Å) NH_2 (5007 Å, $\tilde{A}^2A_1 - \tilde{X}^2B_1$)

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Table 5 lists cometary molecules observed in the infrared,

TABLE 5. Cometary molecules with infrared spectra

CO (4.7 μm/2143 cm^{-1}, 1-0)
OH (1.5-1.9 μm/6666-5263 cm^{-1}, 3-1, 4-2, 5-3, 12-9, 6-4, 7-5; 119.23 μm/83.9 cm^{-1}, $^2\Pi_{3/2}$ J=5/2-3/2,+ -)
H_2O (1.38 μm/7249.8 cm^{-1}, $\nu_1+\nu_3$; 1.88 μm/5331.3 cm^{-1}, $\nu_2+\nu_3$; 2.44 μm/4100 cm^{-1}, $\nu_1+\nu_3-2\nu_2$ (tent. assignment); 2.64 μm/3782.2 cm^{-1}, $\nu_2+\nu_3-\nu_2$; 2.66 μm/3755.9 cm^{-1}, ν_3)
CO_2 (4.3 μm/2349 cm^{-1}, ν_3) OCS (4.85 μm/2062 cm^{-1}, ν_3)
H_2CO(3.5 μm/2843 cm^{-1}, ν_5; 3.6 μm/2783 cm^{-1}, ν_1)
CH_4 (3.3 μm/3019 cm^{-1}, ν_3)

wavelengths (in μm/$cm^{-1)}$, and assignments. Encrenaz and Knacke (1991) and Weaver et al. (1991) have given recent reviews. The 1.38 μm H_2O band was detected in Halley by Knacke et al. (1986) and Krasnopolsky et al. (1986), and the 1.88 μm band by Knacke et al. (1986). The 2.44 μm band is a tentative H_2O hot band assignment in Halley (Maillard et al. 1987), but the 2.64 μm assignment is definite (Weaver et al. 1986). The 2.66 μm assignment (ν_3) is well confirmed (Mumma et al. 1986; Weaver et al. 1986; Combes et al. 1988). Larson et al. (1989) also detected 10 H_2O emission lines from ν_3 and a hot band line from $\nu_2+\nu_3-\nu_2$ in Comet Wilson. CO, CO_2, OCS, and H_2CO were identified in Halley by Combes et al. (1988), but CO and OCS were weak. Stacey et al. (1987) detected OH in Halley at 119.23 μm and Krasnopolsky et al. (1986) detected the 1.5-1.9 μm OH bands. CH_4 in Halley was reported by Kawara et al. (1988) and in Wilson by Larson et al. (1989). Table 6 lists the molecules observed in the radio region, wavelengths/ frequencies, and assignments. The radio CH line has been reported only in Comet Kohoutek (Black et al. 1974). Radio OH lines are routinely observed in comets. HCN detections in Kohoutek and Halley were followed by detections in Brorsen-Metcalf, Austin, and Levy (cf., Crovisier and Schloerb 1991; Colom et al. 1990; Schloerb and Ge 1990a;b). The 1.348 cm H_2O line was reported in comets Bradfield and I-A-A (Jackson et al. 1976; Altenhoff et al. 1983). H_2S and CH_3OH (3.099 and 2.066 mm) were detected in Austin (Bockelée-Morvan et al. 1991). CH_3OH (1.240 mm) also was detected in Levy (Schloerb and Ge 1990a). The 6.207 cm H_2CO line was detected in comets Halley and Machholz by Snyder et al. (1989; 1990), the 1.3283 mm line in Brorsen-Metcalf, Austin, and Levy by Colom et al. (1991), and the 0.8522 mm line in Levy by Schloerb and Ge (1990b). The 1.256 cm line of NH_3 was detected only in I-A-A (Altenhoff et al. 1983). Vibrationally excited CH_3CN (2.7079 mm) was observed only in Kohoutek (Ulich and Conklin 1974).

TABLE 6. Cometary molecules with radio spectra

CH	(8.988 cm/3,335.481 MHz, $^2\Pi_{1/2}$ J=1/2,F=1-1)
OH	(18.595 cm/1,612.2310 MHz $^2\Pi_{3/2}$ J=3/2,F=1-2; 18.001 cm/1,665.4018 MHz $^2\Pi_{3/2}$ J=3/2,F=1-1; 17.980 cm/1,667.3590 MHz $^2\Pi_{3/2}$ J=3/2,F=2-2; 17.424 cm/1,720.5300 MHz $^2\Pi_{3/2}$ J=3/2,F=2-1)
HCN	(3.3825 mm/88,630.4157 MHz J=1-0,F=1-1; 3.3824 mm/88,631.8473 MHz J=1-0,F=2-1; 3.3824 mm/88,633.9360 MHz J=1-0,F=0-1; 1.1285 mm/265,886.432 MHz J=3-2; 0.8457 mm/354,505.472 MHz J=4-3)
H_2O	(1.348 cm/22,235.120 MHz $J_{KaKc}=6_{16}-5_{23}$,F=5-4)
H_2S	(1.7764 mm/168,762.762 MHz $J_{KaKc}=1_{10}-1_{01}$)
H_2CO	(6.207 cm/4829.6639 MHz $J_{KaKc}=1_{11}-1_{10}$,F=2-1; 1.3283 mm/225,697.775 MHz $J_{KaKc}=3_{12}-2_{11}$; 0.8522 mm/351,768.639 MHz $J_{KaKc}=5_{15}-4_{14}$)
NH_3	(1.256 cm/23870.1296 MHz J(K)=3(3),F=4-4)
CH_3CN	(2.7079 mm/110,709.55 MHz v_8=1,J(K)=6(3)-5(3); 2.7079 mm/110,712.22 MHz v_8=1, J(K)= 6(0)-5(0))
CH_3OH	(3.0990 mm/96,739.39 MHz J(K)=2(-1)-1(-1)E; 3.0989 mm/96,741.42 MHz J(K)=2(0)-1(0)A+; 2.0662 mm/145,093.75 MHz J(K)=3(0)-2(0)E; 2.0661 mm/145,097.47 MHz J(K)=3(-1)-2(-1)E; 2.0661 mm/145,103.23 MHz J(K)=3(0)-2(0)A+; 2.0657 mm/145,131.88 MHz J(K)=3(1)-2(1)E; 1.2400 mm/241,767.224 MHz J(K)=5(-1)-4(-1)E; 1.2399 mm/241,791.431 MHz J(K)=5(0)-4(0)A+)

3. Excitation Effects in Comets

In the ultraviolet and optical spectral regions, the dominant excitation mechanism for electronic transitions is resonance fluorescence. The Doppler-shifted resonant transitions of cometary molecules absorb the solar spectrum and reradiate it via various electronic transitions. Typically, collisions play only a minor role in establishing the molecular population distributions in these spectra (cf., Arpigny 1976). In the longer wavelength spectral regions, a major excitation mechanism is believed to be infrared fluorescence, but radio excitation may be more complicated.

Because ultraviolet excitation mechanisms are fairly well understood, the detection of S_2 in I-A-A, as discussed by M. A'Hearn (this book), can be attributed both to the existence of an outburst at closest approach and to the remarkable 25 km/arcsec scale of the comet.

The intensities of the radio OH lines are determined by ultraviolet pumping called the Swings effect (cf., Schloerb and Gerard 1985; Crovisier and Schloerb 1991; de Pater et al. 1991). Briefly, solar ultraviolet Fraunhofer radiation pumps the cometary OH ultraviolet bands listed in Table 3 (3090 Å, $A^2\Sigma^+-X^2\Pi_i$). The OH cascades to the ground state, establishing the intensities of the 18 cm lines in Table 6. This effect determines whether radio OH will be observed in maser emission, absorption, or not at all! For example, when the projected densities of the unsplit upper and lower levels of the ground-state Λ doublet are almost equal, the cometary OH signal may vanish, even though the OH has not. Another point is that single radio antennas can make crude maps of cometary OH with a resolution of a few arcminutes, but radio interferometers can produce detailed imaging which can greatly affect the excitation modeling (cf., de Pater et al. 1991).

The evidence for an extended cometary dust coma that began to emerge with the measurements of Comet Halley is:

A. The in situ measurements made with the Giotto neutral gas mass spectrometer by Eberhardt et al. (1987) can be explained if CO is produced both directly from the nucleus and from extended dust in the inner coma.

B. The >60,000 km CN and C_2 jets observed by A'Hearn et al. (1986a,b) can be explained by dissociation directly from CHON particles in an extended dust coma.

C. The VLA detected the 6.207 cm line of H_2CO in emission from Halley and Machholz (Snyder et al. 1989; 1990). Interpreting this line requires an extended coma model.

D. The cometary H_2CO model of Bockelée-Morvan and Crovisier (1991) shows how H_2CO will behave if produced only by the cometary nucleus, with no further gas production in an extended gas/dust coma. This is an excellent model, but it does not explain (a) the VLA detections of the 6.207 cm H_2CO line; (b) the IRAM detections of the 1.3283 mm H_2CO line at a nuclear distance of 3500 km from Austin and 6300 km from Levy by Colom et al. (1991); or (c) the CSO detection of the 0.8522 mm H_2CO line at a 30" nuclear distance offset from Comet Levy by Schloerb (1991, private communication). These observations suggest that either specious comet lines are extremely common at different frequencies and times, or there is indeed an extended cometary dust coma which needs to be taken into account in future models.

4. Summary

Newly detected species include H_2O, H_2CO, CH_4 (Halley), CH_3OH (Austin and Levy), and H_2S (Austin). Cometary nuclei appear to be more chemically evolved than the current gas-phase spectroscopy suggests. Some of the excitation conditions are exemplified by the sudden appearance of S_2 in I-A-A, the ultraviolet pumping of radio OH lines, the extended dust coma, and the unexplained radio lines of H_2O and excited CH_3CN.

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5. References

A'Hearn, M. F. (1983) 'Spectrophotometry of comets at optical wavelengths', in Wilkening and Matthews (eds.), Comets, University of Arizona Press, Tucson, pp. 433-60.

A'Hearn, M. F. et al. (1986a) 'Cyanogen jets in Comet Halley', Nature 324, 649-51.

A'Hearn, M. F. et al. (1986b) 'Gaseous jets in Comet p/Halley', in 20th ESLAB Symp. Expl. Halley's Comet, SP-250, pp. 483-6.

Altenhoff, W.J. et al. (1983) 'Radio observations of Comet 1983d', A&A 125, L19-L22.

Arpigny, C. (1976) 'Interpretation of comet spectra', in Donn et al. (eds.), The Study of Comets, NASA SP-393, pp. 797-839.

Black, J. H. et al. (1974) 'Radiofrequency emission from CH in Comet Kohoutek (1973f)', ApJ 191, L45-7.

Bockelée-Morvan, D. et al. (1991) 'Microwave detection of hydrogen sulfide and methanol in Comet Austin (1989cl)', Nature 350, 318-20.

Bockelée-Morvan, D., and Crovisier, J. (1991) 'Formaldehyde in comets: excitation of the rotational lines', A&A, in press.

Colom, P. et al. (1990) 'Millimetre observations of Comets P/Brorsen/Metcalf (1989o) and Austin (1989cl) with the IRAM 30-m radio telescope' in Huebner et al. (eds.), Workshop on Observations of Recent Comets (1990), Southwest Research Inst., San Antonio, pp. 80-5.

Colom, P. et al. (1991) 'Formaldehyde in comets: microwave observations of P/Brorsen-Metcalf (1989X), Austin (1989cl), and Levy (1990c)', A&A, in press.

Combes, M. et al. (1988) 'The 2.2-12 μm spectrum of Comet Halley from the IKS-VEGA experiment', Icarus 76, 404–36.

Crovisier, J. and Schloerb, F. P. (1991) 'Study of comets at radio wavelengths', in Newburn et al. (eds.), Comets in the Post-Halley Era, Kluwer, Dordrecht, pp. 149-73.

de Pater, I. et al. (1991) 'A review of radio interferometric imaging of comets', Ibid., pp. 175-207.

Eberhardt, P., et al. (1987) 'The CO and N_2 abundance in Comet p/Halley', A&A 187, 481-4.

Encrenaz, T., and Knacke, R. (1991) 'Carbonaceous compounds in comets: infrared observations', in Newburn et al. (eds.), Comets in the Post-Halley Era, Kluwer, Dordrecht, pp. 107-37.

Feldman, P. D. (1983) 'Ultraviolet spectroscopy of comae', in Wilkening and Matthews (eds.), Comets, University of Arizona Press, Tucson, pp. 461-79.

Feldman, P. D. (1991) 'Ultraviolet spectroscopy of cometary comae', in Newburn et al. (eds.), Comets in the Post-Halley Era, Kluwer, Dordrecht, pp. 139-48.

Huebner, W. F. (1987) 'First polymer in space identified

in Comet Halley', Science 237, 628-30.
Jackson, W. M., Clark, T., and Donn, B. (1976) 'Radio detection of H_2O in Comet Bradfield' in Donn et al. (eds.), The Study of Comets, NASA SP-393, pp. 272-80.
Kawara et al. (1988) 'Infrared spectroscopic observation of methane in Comet P/Halley' A&A 207, 174-81.
Knacke, R. F. et al. (1986) 'Ground-based detection of water in Comet Halley' in Battrick et al. (eds.), 20th ESLAB Symp. Expl. Halley's Comet, SP-250, pp. 99-101.
Krasnopolsky, V. A. et al. (1986) 'Spectroscopic study of Comet Halley by the Vega 2 three-channel spectrometer', Nature 321, 269-71.
Larson, H. P. et al. (1989) 'Airbourne infrared spectroscopy of Comet Wilson (1986l) and comparisons with Comet Halley', ApJ 338, 1106-14.
Lovas, F. J. (1986) 'Recommended rest frequencies for observed interstellar molecular microwave transitions- 1985 revision', J. Phys. Chem. Ref. Data 15, 251-303.
_____, (1987) Ibid. 16, 153-4.
Maillard, J. P. et al. (1987) 'Spectrum of Comet P/Halley between 0.9 and 2.5 microns', A&A 187, 398-404.
Mann, A.P.C., and Williams, D.A. (1980) 'A list of interstellar molecules', Nature 283, 721-25.
Mumma, M. J. et al. (1986) 'Detection of water vapor in Halley's Comet', Science 232, 1523-28.
Schloerb, F. P., and Ge, W. (1991a,b) 'Comet Levy (1990c)', IAU Circs. No. 5081 and 5086.
Schloerb, F. P., and Gerard, E. (1985) 'Models of cometary emission in the 18-cm OH transitions: the predicted behavior of Comet Halley', AJ 90, 1117-35.
Snyder, L.E. (1982) 'A review of radio observations of comets', Icarus, 51, 1-24.
Snyder, L. E., Palmer, P., and de Pater, I. (1989) 'Radio detection of formaldehyde emission from Comet Halley', AJ 97, 246-53.
_____, (1990) 'Observations of formaldehyde in Comet Machholz (1988j)', Icarus 86, 289-98.
Stacey, G. J., Lugten, J. B., and Genzel, R. (1987) 'Detection of OH rotational emission from Comet P/Halley in the far-infrared', A&A 187, 451-54.
Ulich, B. L., and Conklin, E. K. (1974) 'Detection of methyl cyanide in Comet Kohoutek', Nature 248, 121-2.
Weaver, H. A., Mumma, M. J., and Larson, H. P. (1991) 'Infrared spectroscopy of parent molecules', in Newburn et al. (eds.), Comets in the Post-Halley Era, Kluwer, Dordrecht, pp. 93-106.
Weaver, H. A. et al. (1986) 'Post-perihelion observations of water in Comet Halley', Nature 324, 441-4.
Wyckoff, S. (1983) 'Overview of comet observations', in Wilkening and Matthews (eds.), Comets, University of Arizona Press, Tucson, pp. 3-55.

QUESTIONS AND ANSWERS

J.P.Maillard: You listed CO as a detected molecule in the IR (at 4.7 μm). As far I know it has not been detected. It has been looked for, of course, but only upper limit has been obtained.

L.E.Snyder: CO was identified in Halley by Combes et al (1988), but it was week.

T.J.Millar: If cometery particles are related to interstellar particles, one might expect them to contain significant fractionation in deuterium. Have there been sensitive searches for D-bearing molecules in comets?

L.E.Snyder: This question was answered by Mike A'Hearn.

T.J.Millar: What is the abundance of D?

M.F.A'Hearn: The Giotto NMS was used in its ion mode by Eberhardt to derive separate upper & lower limits on HDO/H_2O in Halley at something like 5×10^{-5} to 5×10^{-4} (I don't remember the exact numbers). Spectra from IUE have been searched for emission by OD and upper limits have been derived for 5 - 10 comets ranging from 10^{-2} to 4×10^{-4}, depending on signal-to-noise.

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