overproduction of the protein, and not blocked in secretiondefective strains. The two processes could share the same translocation mechanism but utilize different receptor proteins; FBPase import may be greatly facilitated by a glucose-induced receptor.

The mechanism of these translocation events remains to be deciphered. Import of FBPase could by a unimolecular event, such as is well-known for mitochondrial and secretory protein translocation. If so, this would require unfolding of the transported molecule which could involve an hsc70 isozyme^{25,26}. Alternatively, protein aggregates clustered on the surface of the vacuole/lysosome could be taken up by a micro- or macroautophagic process, and then degraded along with the internalized membrane. These possibilities may be distinguished by the isolation and characterization of yeast mutants deficient in catabolite inactivation of FBPase.

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- 1. Hershko, A. J. biol. Chem. 264, 15237-15240 (1988).
- Driscoll, J. & Goldberg, A. L. Proc. natn. Acad. Sci. U.S.A. 86, 787-791 (1989)
- Watanabe, N., Van de Woude, G., Ikawa, Y. & Sagata, N. Nature 342, 505-511 (1989).
- Holzer, H. & Heinrich, P. A. Rev. Biochem. 49, 63-91 (1980).
- Teichert, U., Mechler, B., Muller, H. & Wolf, D. J. biol. Chem. 264, 16037-16045 (1989)
- 6. Zubenko, G. & Jones, E. Genetics 97, 45-64 (1981).
- Guerra, R., Valdes-Hervia M. D. & Gancedo, J. M. FEBS Lett. 242, 149-152 (1988).
- Schäfer, W., Kalisz, H. & Holzer, H. Biochim. biophys. Acta 925, 150-155 (1987).
- 9. Ammerer. G. et al. Molec. cell. Biol. 6, 2490-2499 (1986).
- Funayama, S., Gancedo, J. & Gancedo, C. Eur. J. Biochem. 109, 61-66 (1980).
 Stevens, T., Esmon, B. & Schekman, R. Cell. 30, 439-448 (1982).
- 12. Roger, D., Hiller, E., Mitsock, L. & Orr, E. J. biol. Chem. 263, 6051-6057 (1988).
- Deshales, R. & Schekman, R. J. Cell Biol. 109, 2653-2664 (1989).
 Kaiser, C. A. & Schekman, R. Cell 61, 723-733 (1990).
- 15. Franzusoff, A. & Schekman, R. EMBO J. 8, 2695-2702 (1989).
- 16. Novick, P., Ferro, S. & Schekman, R. Cell 25, 461-469 (1981)
- 17. Yamashiro, C., Kane, P., Wolczyk, D., Preston, R. & Stevens, T. Molec. cell. Biol. 10, 3737-3749 (1990)
- 18. Funaguma, T., Toyota, Y. & Sy, J. Biochem. biophys. Res. Commun. 130, 467-471 (1985)
- 19. Burlini, N., Facheris, P., Tortora, P. & Guerritore, A. Biochim. biophys. Acta 972, 353-356 (1988).

- 20. Rittenhouse, J., Moberly, L. & Marcus, F. J. biol. Chem. 262, 10114-10119 (1987)
- Lamponi, S., Galassi, C., Tortora, P. & Guerritore, A. FEBS Lett. 216, 265–269 (1987).
 Chiang, H.-L. & Dice, J. F. J. biol. Chem. 263, 6797–6805 (1988).
 Dice, J. F. Trends biochem. Sci. 15, 305–309 (1990).
- 24. Chaing, H.-L., Terleckey, S., Plant, C. & Dice, J. Science 246, 382-385 (1989).
- 25. Deshaies, R. J., Koch, B. D., Werner-Washburne, M., Craig, E. A. & Schekman, R. Nature 332, 800-805 (1988).
- Chirico, W., Waters, M. G. & Blobel, G. Nature 332, 805–810 (1988).
 Yoshihisa, T. & Anraku, Y. J. biol. Chem. 265, 22418–22425 (1990).
- 28. Rothman, J., Hunter, C., Valls, L. & Stevens, T. Proc. natn. Acad. Sci. U.S.A. 83, 3248-3252 (1986).
- 39 ito, H., Fukuda, K., Murata, K. & Kimura, A. J. Bact. 153, 163-168 (1983).
 30. Sedivey, J. & Fraenkel, D. J. molec. Biol. 186, 307-319 (1985).
 31. Rothblatt, J. & Schekman, R. Meth. Cell Biol. 32, 3-36 (1989).
- 32. Roberts, C., Raymond, C., Yamashiro, C. & Stevens, T. Meth. Enzym. 194, 644-661 (1990).

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LETTERS TO NATURE

Microwave detection of hydrogen sulphide and methanol in comet Austin (1989c1)

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INFRARED and microwave spectroscopy can be used to identify and study the parent molecules directly sublimed from cometary nuclei. Here we report spectroscopic observations of comet Austin (1989c1) at millimetre wavelengths using the 30-m telescope of the Institut de Radio Astronomie Millimétrique (IRAM). We detected the rotational transitions of hydrogen cyanide and formaldehyde, which were previously observed in comets Halley and Brorsen-Metcalf. In addition, we identified hydrogen sulphide and methanol, neither of which has previously been detected in a comet. The presence of hydrogen sulphide provides severe constraints on the formation of cometary nuclei, whereas that of methanol supports the hypothesis that cometary nuclei have retained, at least in part, some primitive material originating from the solar nebula.

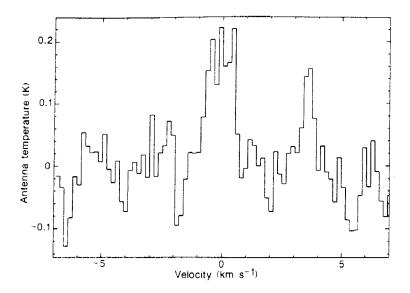
The observations reported here were made from 21 to 25 May 1990, when comet Austin was at 1.1 AU from the Sun and at its closest approach to Earth (0.24 AU), with the IRAM 30-m radio telescope at Pico Veleta (Spain). Three receivers could be used simultaneously, allowing us to search for different lines at the same time. The spectrometers were chosen from two banks of 128×100-kHz channels and two banks of 512×1-MHz channels. The telescope beam diameter is 14" at 169 GHz. To allow for possible ephemeris uncertainties and tracking errors, and to study the coma extension, we made observations at 6" and 12" north, east, south and west from the nucleus in addition to those aimed at the nucleus.

We detected hydrogen cyanide (HCN) through its J(1-0) and J(3-2) rotational transitions at 89 and 266 GHz, respectively. The formaldehyde (H₂CO) 3₁₂-2₁₁ transition at 226 GHz was observed with a signal-to-noise ratio larger than 10. (A detailed analysis of these results will be presented elsewhere.) Table 1 gives the resulting production rates and abundances relative to water. The HCN production rate is smaller than those we observed previously in comets P/Halley and P/Brorsen-Metcalf (19890)^{2,3}. The H₂CO relative production rate is comparable with that estimated for P/Brorsen-Metcalf³.

To detect hydrogen sulphide (H2S), we searched for the l_{10} - l_{01} transition at 168.762 762 GHz, which is expected to be the most favourable millimetre transition of this molecule because it occurs between low energy levels. We used a double-(superconductor-insulator-superconductor) sideband SIS mixer receiver (the image band being 7.8635 GHz higher); the system temperature was ~1,500 K. The line was unambiguously detected with an area of 0.30 ± 0.04 K km s⁻¹ (Fig. 1). The line is centred at the comet nucleus rest velocity, and the line width is 1.4 km s⁻¹, which is typical of all confirmed cometary radio lines. The line was observed on two days with different local oscillator settings, which excludes a spurious detection due to a receiver or spectrometer flaw. Figure 1 is the average of the two days of observation. The weaker and narrower feature at 3.5 km s^{-1} (corresponding to a frequency of 176.6283 GHz in the image band) only appeared in the first day of observation. On the second day, a similar feature appeared at 8.5 km s (176,6277 GHz in the image band). Both features may therefore come from the same signal in the image band, but its origin (internal interference or cometary line) is unknown.

Hydrogen sulphide has not previously been identified in a comet, although its presence was suspected from the tentative detection of H₂S⁺ in the visible spectrum of comet IRAS-Araki-Alcock 1983 VII (ref. 4) and from a mass spectrometer signal

FIG. 1 The H $_2$ S 1_{10} – 1_{01} spectrum of comet Austin (24–25 May 1990). The abcissa scale has been converted to Doppler velocities assuming a line rest frequency of 168.762 762 GHz in the frame of the comet nucleus. Thus the line profile represents the radial velocity distribution of the gas. The frequency resolution is $100\,\mathrm{kHz}$, corresponding to $0.18\,\mathrm{km\ s^{-1}}$. The intensity scale is main-beam antenna brightness temperature. The telescope beam diameter is 14". The spectrum is an average of observations made toward the nucleus and at positions offset by 12" north, east, south and west.



at mass 35 attributed to H_3S^+ in the Giotto investigations of comet P/Halley⁵. From the H_2S laboratory ultraviolet absorption spectrum of ref. 6 and the solar reference spectrum of ref. 7, we calculate a lifetime of 4,000 s before photodestruction at 1 AU from the Sun. We assume that this species is expanding from the nucleus with a velocity of $0.8 \, \mathrm{km \, s^{-1}}$ (which is in agreement with the observed line width). H_2S is thus confined in the inner coma, and its excitation is governed by collisions. For a preliminary estimate of the production rate, we assume rotational local thermodynamic equilibrium at a temperature⁸ $T_{\rm rot} = 50 \, \mathrm{K}$. This assumption is not critical, because the derived production rate is roughly proportional to the rotational partition function and scales as $T_{\rm rot}^{-1.5}$. The resulting H_2S production rate is $9 \times 10^{25} \, \mathrm{s}^{-1}$.

From the cometary water production rate estimated at the time of our observations, we tentatively infer a relative abundance $[H_2S]/[H_2O]$ of ~ 0.002 . This is an order of magnitude less than the estimated sulphur abundance in cometary volatiles, which is close to the cosmic relative abundance [S]/[O] = 0.02. The only other sulphur species definitely identified in comets are S_2 and CS (ref. 10), with relative abundances still smaller than that of H_2S . Thus, cometary sulphur might be retained in molecular species so far undetected.

In the analysis of the Giotto mass spectrometer data⁵, an unreasonably large H₂S production rate was obtained when a parent molecule distribution for this molecule was assumed, and a distributed source had to be invoked to interpret the observation. In fact, this problem arose because too short a lifetime for H₂S was used. With the lifetime we have derived, the Giotto data are consistent with an H₂S relative abundance similar to that observed here.

We investigated methanol (CH₃OH) using the same receiver as for H₂S, but with a rejection of 6 dB on the image band; the

TABLE 1 Molecular production rates and relative abundances in comet Austin (1989c1)

Molecule	Transition	Production rate (molecules per s ⁻¹)	Abundance	Ref.	
H ₂ 0	OH (ultraviolet)	6.0×10^{28}	1.00	IUE ¹⁸	
H ₂ O	OH (18 cm)	4.0×10^{28}		Nançay19	
HĈN	J(1-0)89 GHz	2.5×10^{25}	4×10^{-4}	IRAM	
H ₂ CO	3 ₁₂ -2 ₁₁ 226 GHz	4×10^{26} *	6×10^{-3}	IRAM	
H ₂ S	1 ₁₀ -1 ₀₁ 169 GHz	9×10^{25}	2×10^{-3}	IRAM	
CH₃OH	145 GHz	5 × 10 ²⁶	1×10^{-2}	IRAM	

^{*} Assuming a daughter density distribution with a parent scale length of 10^4 km (the production rate would be 10 times smaller if H_2CO were directly sublimed from the nucleus)

system temperature was \sim 750 K. The spectrometer was a 512 \times 1-MHz bank centred on 145.110 GHz, allowing us to search for several of the J(3-2) $\Delta K = 0$ transitions simultaneously, but not to resolve the lines (velocity resolution: 2.1 km s⁻¹). We detected two lines with signal-to-noise ratios of 5 and 3 and tentatively detected two other lines at the 2-sigma level (Fig. 2 and Table 1). Observation of other spectral regions with the same spectrometer during this run allowed us to rule out the possibility of faulty channels at these line positions. We also observed the 96 GHz spectral region, where two lines of the J(2-1) $\Delta K = 0$ transitions are marginally present. Observing several rotational lines of the same species simultaneously is fascinating because it provides clues to its rotational distribution and excitation conditions. In a preliminary calculation, we assumed a unique rotational temperature and obtained the best least-square fit to the data for $T_{\rm rot}$ = 22 K. Table 2 gives the relative line intensities expected for $T_{\rm rot} = 20$ and 70 K. This suggests that methanol is rotationally relaxed, as is observed for other cometary species such as water8. It is interesting to note that for this temperature, the other CH₃OH transitions falling in the frequency range of the spectra we observed occur between higher rotational levels and are too weak to be detected. In other words, there are no missing lines in our spectra, and we can have more confidence in our detection. From the CH₃OH laboratory ultraviolet absorption spectrum¹¹ we evaluate a lifetime of 7.7×10^4 s at 1 AU from the Sun. For $T_{\rm rot} = 20$ K, the resulting CH₃OH production rate is $\sim 5 \times 10^{26}$ s⁻¹, corresponding to an abundance of 0.01 relative to water.

TABLE 2 Methanol lines in the 96.7 and 145 GHz spectral regions

				Line ratio			
		Frequency	Line area		Expected		
Line		[GHz]	$[mK km s^{-1}]$	Observed	20 K	70 K	
(2, -1)- $(1, -1)$	E	96.7394	73 ± 38	0.28	0.23	0.22	
(2,0)-(1,0)	A +	96.7414	79 ± 38	0.30	0.40	0.32	
(2,0)-(1,0)	E	96.7446	< 105	< 0.40	0.21	0.27	
(2.1)-(1.1)	Ε	96.7555	<105	< 0.40	0.11	0.18	
(3,0)- $(2,0)$	Ε	145.0937	88 ± 37	0.34	0.53	0.85	
(3, -1)- $(2, -1)$	E	145.0975	$143 \pm 52^*$	0.55	0.69	0.84	
(3,0)-(2,0)	A	145.1032	$262 \pm 52*$	1.00	1.00	1.00	
(3, 2)- $(2, 2)$	A -	145.1244	< 105	< 0.40	0.08	0.32	
(3. 2)-(2. 2)	E	145.1264	<105	< 0.40	0.18	0.40	
(3, -2)- $(2, -2)$	Ε	145.1264			0.15	0.38	
(3, 1)-(2, 1)	E	145.1319	126 ± 37	0.48	0.31	0.66	
(3, 2)- $(2, 2)$	A +	145.1335	<105	< 0.40	0.08	0.32	

Observed intensities, intensities relative to the (3,0)-(2,0) A line and the expected relative intensities at thermal equilibrium are listed.

^{*} Sum of two adjacent channels.

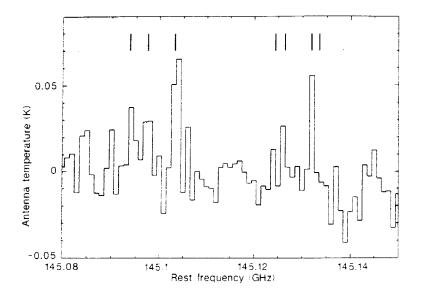


FIG. 2 Transitions of CH $_3$ OH observed around 145 GHz in comet Austin (25 May 1990). The frequency scale is with respect to the frame of the comet nucleus. The resolution is 1 MHz, corresponding to 2.1 km s $^{-1}$. Tick marks indicate the expected positions of methanol lines (see Table 2). As the resolution is close to the expected line width, the methanol lines may fall in either a single channel, or two adjacent channels. The non-detection of some of the lines is consistent with a low rotational temperature (see text and Table 2). The telescope beam diameter is 16". The spectrum is an average of observations made toward the nucleus and at positions offset by 12" north, east, south and west.

As one of the main photodissociation channels of methanol is ⁷

 $CH_3OH + h\nu \rightarrow H_2 + H_2CO$,

this molecule may be one of the sources of cometary formaldehyde. Methanol has a strong infrared band at $3.3-3.5 \,\mu m$, and the broad $3.4 \,\mu m$ emission band observed in several comets ^{12,13} may be due in part to methanol fluorescence. But with an abundance of 0.01, CH₃OH would account for only a small part of the observed infrared band.

Methanol is known to be an abundant constituent of the interstellar medium: its abundance relative to water in the solid phase was recently¹⁴ evaluated as 0.07 in the protostellar source W33A. Methanol cannot survive at high temperatures or in the presence of an ultraviolet field. It has not so far been identified in other solar-system bodies. Therefore, the identification of abundant cometary methanol would provide strong evidence that cometary nuclei retained some of the original matter of the pre-solar nebula. Hydrogen sulphide is not usually an abundant molecule in the interstellar gas, but we should note that it is also present in the solid phase where its abundance is unknown¹⁵. Hydrogen sulphide only condenses at very low temperatures (less than 57 K according to ref. 16). Therefore, its presence in comets would constrain their formation environment.

In addition to the ubiquitous OH radical, four molecular species have now been unambiguously identified in cometary atmospheres by radio spectroscopy. This technique proved to be able to study relatively complex organics such as methanol, or relatively minor species such as HCN or H₂S. It may be anticipated that radio astronomy could achieve an important breakthrough in the near future in the chemical study of comets. This was indeed verified very recently by observations of comet Levy (1990c) which confirmed and extended the present study¹⁷. A more complete analysis of these results will be published elsewhere.

 Encrenaz, T. & Knacke, R. in Comets in the Post-Halley Era (eds Newburn, R. et al.) (Kluwer Academic Dordrecht) (in the press).

Baas, F., Grim, R. J. A., Geballe, W., Schutte, W. & Greenberg, J. M. in *Dust in the Universe*, 55–60 (eds Bailey, M. E. & Williams, D. A.) (Cambridge University Press, 1988).

15. Geballe, T. R., Baas, F., Greenberg, J. M. & Schutte, W. Astr. Astrophys. 146, L6-L8 (1985).

16. Yamamoto, T. Astr. Astrophys. 142, 31-36 (1985).

Colom, P., Crovisier, J., Paubert, G., Bockelée-Morvan, D. & Despois, D. IAU Circ. No. 5087 (1990).
 Budzien, S. A., Feldman, P. D., Roettger, E. E., A'Hearn, M. F. & Festou, M. C. in Observations of Recent Cornets (ed. Huebner, W. F. et al.) 64–68 (Southwest Research Institute, San Antonio, Texas. 1990).

 Bockeiée-Morvan, D., Crovisier, J., Gérard, E. & Bourgois, G. in Observations of Recent Comets (ed. Huebner, W. F. et al.) 75–79 (Southwest Research Institute, San Antonio, Texas, 1990).

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Conducting films of C₆₀ and C₇₀ by alkali-metal doping

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THE recent syntheses 1,2 of macroscopic quantities of C₆₀ have suggested possible applications in host-guest and organic chemistry, tribology, electrochemistry and semiconductor technology. Here we report the preparation of alkali-metal-doped films of C₆₀ and C₇₀ which have electrical conductivities at room temperature that are comparable to those attained by n-type doped polyacetylene. The highest conductivities observed in the doped films are: $4 \, \mathrm{S \, cm^{-1}}$ (Cs/C₆₀), 100 (Rb/C₆₀), 500 (K/C₆₀), 20 (Na/C₆₀), 10 (Li/C₆₀), 2 (K/C₇₀). The doping process is reversed on exposure of the films to the atmosphere. At high doping levels, the films become more resistive. We attribute the conductivity induced in these films to the formation of energy bands from the π orbitals of C_{60} or C_{70} , which become partially filled with carriers on doping. The smaller alkali metal ions should be able to fit into the interstices in the lattice without disrupting the network of contacts between the carbon spheroids. In the case of C₆₀, this would allow the development of an isotropic band structure, and we therefore propose that these materials may constitute the first three-dimensional 'organic' conductors.

Previous highly conducting organic charge-transfer systems have had low-dimensional (quasi-one-dimensional or -two-dimensional) electronic structures. In extended systems, the

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Bockelée-Morvan, D. et al. Astr. Astrophys. 180, 253-262 (1987).

Marconi, M. E., et al. Astr. J. 352, L17-L20 (1990)
 Lee, E. C., Wang, X. & Suto, M. J. chem. Phys. 86, 4353-4361 (1987).

Crovisier, J. & Schloerb, F. P. in Comets in the Post-Halley Era leds Newburn, R. et al.) (Kluwer Academic, Dordrecht) (in the press).

Colom, P., Despois, D., Bockelée-Morvan D., Crovisier, J. & Paubert, G. in Observations of Recent Cornets (ed. Huebner W. F. et al.) 80–85. Southwest Research Institute, San Antonio, Texas, 1990).

^{4.} Cosmovici, C. B. & Ortolani, S. Nature 310, 122-124 (1984).

^{7.} Huebner, W. F. & Carpenter, C. W. Los Alamos Informal Report LA-8085-MS (1979).

^{8.} Bockelee-Morvan, D. & Crovisier, J. Astr. Astrophys. 187, 425-430 (1987).

Azoulay, G. & Festou, M. C. in Asteroids Cornets Meteors II (eds. Lagerkvist, C.-I., Lindblad, B. A., Lundstedt, H. & Rickman, H.) 273-277 (Uppsala University Press, 1986)

A'Hearn, M. F., Feldman, P. D. & Schleicher, D. G. Astr. J. 274, L99-L103 (1983).
 Nee, J. B., Suto, M. & Lee, L. C Chem. Phys. 98, 147-155 (1985).

^{12.} Combes et al. icarus 76, 404-436 (1988).