Microwave Observations of Hydrogen Sulfide and Searches for Other Sulfur Compounds in Comets Austin (1989c1) and Levy (1990c)

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We detected hydrogen sulfide through observations of its $1_{10}–1_{01}$ rotational line at 2 mm in Comets Austin (1989c1) and Levy (1990c) using the IRAM 30-m radiotelescope. In Comet Levy, the $2_{20}–2_{11}$ line of H_2S was also observed; the relative intensities of the two lines suggest a cold rotational distribution for H_2S. We also unsuccessfully searched for other sulfur molecular species in Comet Levy: SO_2, OCS, H_2CS. From these observations, we derive molecular production rates using an out-of-equilibrium excitation model which takes into account collisions and vibrational radiative excitation. The inferred hydrogen sulfide production rate is about 0.002 that of water for both comets. H_2S and the parent of the CS radical appear to be the main depositories of sulfur in cometary volatiles. This element seems to be depleted in cometary volatiles with respect to cosmic abundance. The presence in cometary nuclei of H_2S, which is a highly volatile molecule, is a clue that comets formed and remained stored at very cold temperatures. © 1991 Academic Press, Inc.

1. INTRODUCTION

Sulfur is a relatively abundant cosmic species with [S]/[O] = 0.021 and [S]/[C] = 0.050 (Anders and Grevesse 1989). Its presence in comets is testified by the ultraviolet emissions of SI and of the CS radical (Smith *et al.* 1980,

Azoulay and Festou 1986) and the $(m/q) = 32$ signal observed in P/Halley by the neutral mass spectrometer aboard *Giotto* attributed to S^+ (Balsiger *et al.* 1986). These species are secondary products coming from the grains or from the photodissociation of parent molecules contained in the nucleus. The observed distribution of the CS radical suggests that it comes from a short-lived parent molecule rather than from grains (Jackson *et al.* 1986). The nature of the sulfurous parent molecules is still debated. Indeed, the S_2 molecule was identified in the ultraviolet spectrum of Comet IRAS-Araki-Alcock 1983 VII (A'Hearn *et al.* 1983), but this molecule may result from radiation processing of the nucleus surface rather than coming from the inner nucleus.

Since water is the most abundant cometary volatile, and since sulfur and oxygen are chemically similar, it seems plausible that a significant part of cometary sulfur is contained in hydrogen sulfide. H_2S is a well-known interstellar molecule identified in the gas phase at radio wavelengths (Minh *et al.* 1991, and references therein) and possibly in the solid phase in the infrared (Geballe *et al.* 1985). Supports for the existence of cometary H_2S come from the tentative identification of H_2S^+ lines in the visible spectrum of Comet IRAS-Araki-Alcock 1983 VII (Cosmovici and Ortolani 1984) and, more recently, by the

TABLE I
Log of the Observations

Range of observation	$\langle \Delta \rangle$ [AU]	$\langle r_h \rangle$ [AU]	Species	Line	Frequency[a] [GHz]	Receiver[b]	Spectrometer[c]	Integ. [min]	T_{sys} [K]
Austin (1989c1)									
1990 May 23.09–23.42	0.24	1.12	H₂S	$1_{10}-1_{01}$	168.762781	2 mm LSB	1 MHz	260	1610
1990 May 24.06–24.40	0.24	1.13	H₂S	$1_{10}-1_{01}$	168.762781	2 mm LSB	1 MHz, 100 kHz	280	1550
1990 May 25.09–25.22	0.24	1.14	H₂S	$1_{10}-1_{01}$	168.762781	2 mm LSB	100 kHz	95	1710
Levy (1990c)									
1990 Aug. 30.85–31.00	0.46	1.33	H₂S	$1_{10}-1_{01}$	168.762781	2 mm USB	1 MHz, 100 kHz	202	2110
1990 Aug. 31.72–31.99	0.47	1.32	H₂S	$1_{10}-1_{01}$	168.762781	2 mm USB	1 MHz, 100 kHz	223	2160
1990 Aug. 31.72–31.99	0.47	1.32	H₂S	$2_{20}-2_{11}$	216.710391	1.3 mm SSB	AOS, 100 kHz	223	1590
1990 Aug. 28.74–29.00	0.44	1.35	SO₂	$5_{15}-4_{04}$	135.696016	2 mm SSB	1 MHz	219	940
1990 Aug. 29.73–30.00	0.45	1.34	SO₂	$5_{24}-5_{15}$	165.144656	2 mm SSB	1 MHz	217	1990
1990 Aug. 29.73–30.00	0.45	1.34	SO₂	$7_{17}-6_{06}$	165.225438	2 mm SSB	1 MHz	217	1990
1990 Aug. 28.74–29.00	0.44	1.35	OCS	18–17	218.903359	1.3 mm SSB	AOS, 100 kHz	219	3120
1990 Aug. 31.72–31.99	0.47	1.32	OCS	7–6	85.139102	3 mm SSB	1 MHz	223	495
1990 Aug. 28.74–29.00	0.44	1.35	H₂CS	$4_{14}-3_{13}$	135.298141	2 mm SSB	1 MHz	219	940

[a] From Lovas (1986).

[b] SSB: single-sideband mode with a rejection of about 6 dB applied to the image band (which is at a higher frequency). LSB: double-sideband mode; the image band is at a higher frequency. USB: double-sideband mode; the image band is at a lower frequency. In all cases, the two bands are separated by 7.8635 GHz.

[c] 100 kHz: 128 × 100 kHz filter bank; 1 MHz: 256 × 1 MHz filter bank; AOS: acousto-optic spectrometer.

detection of an ion of mass per charge 35 in the atmosphere of Comet P/Halley, using the heavy ion analyzer PICCA aboard *Giotto*, identified as H_3S^+ by Marconi *et al.* (1990). However, H₂S has never been directly observed up to now. The vibrational bands of hydrogen sulfide are excessively weak (see Section 3 and Table IV); its electronic transitions are dissociative and do not yield fluorescence. A remaining possibility to observe H₂S directly is to search for its rotational transitions, and especially its $1_{10}-1_{01}$ line at 168.762 GHz which occurs between low energy levels, and which is currently observed in the interstellar medium.

Two good targets for molecular cometary observations were offered in 1990: Comets Austin (1989c1) and Levy (1990c), which had total gas production rates of the order of 10^{29} sec^{-1}. They made relatively close approaches to Earth: 0.24 AU at the end of May for Austin and 0.43 AU at the end of August for Levy. At these moments, we observed these comets at millimeter wavelengths with the IRAM (Institut de Radio Astronomie Millimétrique) 30-m radiotelescope in order to search for parent molecules. We detected rotational transitions of HCN, H₂CO, H₂S, and CH₃OH in both comets. In addition, upper limits were obtained for several other molecules in Comet Levy. Preliminary accounts of these observations were published by Bockelée-Morvan *et al.* (1990a, 1991), Colom *et al.* (1990), and Crovisier *et al.* (1990a,b). A detailed analysis of the formaldehyde observations is given by Colom *et al.* (1991).

The present paper gives a detailed report of the IRAM observations of H₂S and other sulfur compounds in Comets Austin and Levy (Section 2). In Section 3, we analyze the excitation conditions of these molecules and we derive their abundances. Section 4 discusses the implications of the existence of cometary H₂S and how it constrains cometary formation scenarios.

2. OBSERVATIONS

The observations were made with the 30-m IRAM radiotelescope at Pico Veleta (Spain) during our cometary observing runs of May 21–25 and August 26–31, 1990. A log of the observations is given in Table I. The telescope characteristics are summarized in Table II. We took advantage of the possibility to use three receivers simultaneously to observe several lines at the same time. The receivers were SIS mixer receivers at 1.3, 2, and 3 mm. Their average system temperatures (which were degraded because part of the observations were made at low elevations) and their mode of operation (single- or double-sideband) are listed in Table I. Beam switching at a rate of 0.25 Hz with a throw of 4′ was made using a wobbling secondary mirror. The spectrometers were two 128 × 100 kHz filter banks, two 256 × 1 MHz filter banks and, for Comet Levy, an acousto optic spectrometer (AOS) of 864 channels and a total band of 505 MHz. They were used as listed in Table I (note that lines of species other than
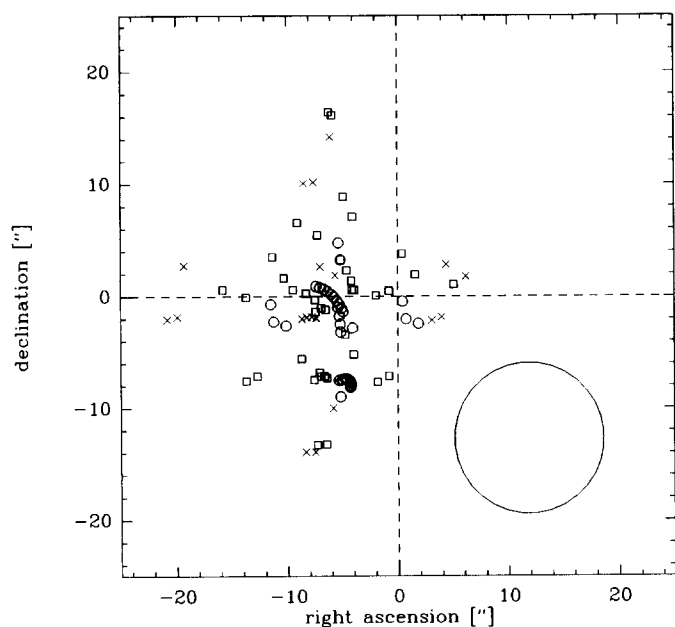
FIG. 1. The offsets of the observed positions in Comet Austin (1989c1), after correction for ephemeris uncertainties and pointing errors. Circles: May 23; squares: May 24; crosses: May 25. The large circle represents the instrumental beam at half-power. The pattern shows the five-point cross mapping (center and 6 or 12″ E, W, N, and S) with a systematic offset due to ephemeris errors and receiver misalignment, and a dispersion due to tracking errors.

sulfur compounds were observed simultaneously, but are not listed in this table).

The problems of the accuracy of the orbital elements and of the telescope pointing and tracking were discussed in our formaldehyde paper (Colom *et al.* 1991). For Comet Austin, we used orbital elements diffused by D. K. Yeomans (*Austin Newsletter* No 3); the resulting computed comet positions were off by about 6″ in right ascension (RA) and 1″ in declination (dec) (compared to those resulting from MPC 16551). For Comet Levy, the updated elements of MPC 16841 were communicated to us by D. W. E. Green and B. G. Marsden in advance of publication during our observing run, and the computed positions for the H_2S observations are estimated to be correct within 1″.

For Comet Austin, in order to study a possible extension of the coma and to cope with possible ephemeris and tracking errors, half of the integration time was spent aiming at the expected position of the nucleus and half of the time at 6″ and 12″ North, South, West, and East of the nucleus. The pointing errors were reevaluated after the observations from a thorough study of the pointing calibration observations, as explained by Colom *et al.* (1991). The resulting offsets from the comet nucleus position are shown in Fig. 1.

For Comet Levy, it was possible to observe, just before the rise of the comet, pointing calibration sources describ-

ing the path of the comet in azimuth and elevation. The resulting pointing corrections were therefore better. The rms offsets, for both tracking and ephemeris errors, are estimated to 2″ in right ascension and in declination, which is negligible compared to the 14″ half-power beamwidth.

The H_2S $1_{10}-1_{01}$ line was marginally detected with the low spectral resolution backend (1 MHz resolution) on the first day of its observation in Comet Austin (May 23). The observation was repeated the following days with the 100-kHz backends and the detection was confirmed (Fig. 2). The line appears centered at the expected rest frequency in the cometary frame, with a linewidth of 1.4 km sec^{-1} (Table III), which is typical of other radio linewidths observed in comets. On May 24, a weaker and narrower feature was present at 3.5 km sec^{-1} (in the comet velocity rest frame), corresponding to 168.7607 GHz in the principal band, to 176.6283 GHz in the image band. On May 25, a slight shift in frequency was applied to the local oscillator: the line attributed to H_2S was still present, the feature at 3.5 km sec^{-1} disappeared, but another one was present at 8.5 km sec^{-1} (Fig. 2, which is the average of both observations, shows both features), corresponding to 168.7574 GHz in the principal band, to 176.6277 GHz in the image band. Thus, these features, if real, might come from a single emission at 176.628 GHz. We have not identified any plausible molecular line near this frequency in the Lovas (1986) compilation. It cannot be excluded, however, that this emission is coming through spurious harmonics of the local oscillator.
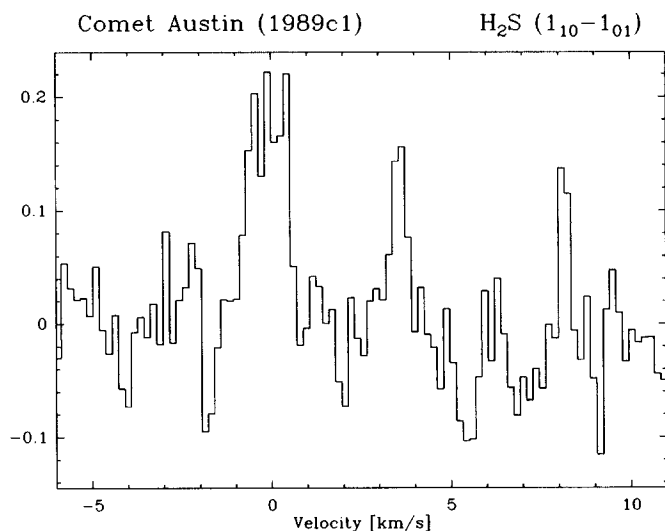

FIG. 2. The H_2S $1_{10}-1_{01}$ line of Comet Austin (1989c1), average of observations of May 24 and 25, 1990. The abscissa scale has been converted to Doppler velocities with respect to the comet nucleus frame. The frequency resolution is 100 kHz and corresponds to 0.18 km sec^{-1}. The intensity scale is main-beam antenna brightness temperature in K. The possible origin of the features at 3.5 and 8.5 km sec^{-1} is discussed in Section 2.

TABLE II
Characteristics of the IRAM 30-m Telescope

Frequency [GHz]	Beam width ["]	Main beam efficiency
85	27.5	0.60
135	17.5	0.60
166	14.5	0.60
217	13.0	0.45

In Comet Levy, the H_2S $1_{10}-1_{01}$ line was easily detected on each day of observation (Fig. 3 and Table III). Since the observations were made with a quite different setting (using the upper sideband rather than the lower sideband), it was not possible to check the 176.628 GHz emission. On August 31, we searched simultaneously for the H_2S $2_{20}-2_{11}$ line, which, according to model predictions, is the second best choice for observing this molecule in the millimeter range (and the only other H_2S line observed in the interstellar medium). The line was detected at the 5σ level (Fig. 4 and Table III).

Several other sulfur compounds were searched for in Comet Levy during our observing run: SO_2, OCS, H_2CS. These observations and their results, which were negative, are listed in Tables I and III.

3. EXCITATION CONDITIONS AND MOLECULAR ABUNDANCES

Converting the observed radio line intensities into column densities requires the knowledge of the rotational population distributions (Crovisier and Schloerb 1991).
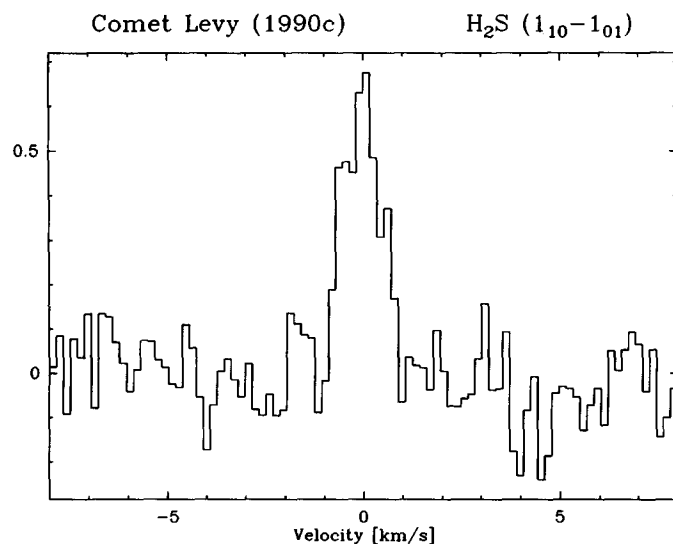
TABLE III
Parameters of the Observed Lines

Date	Species	Line	Area [K km sec⁻¹]	Center [km sec⁻¹]	Width [km sec⁻¹]
		Austin (1989c1)[a]			
1990 May 23[b]	H_2S	$1_{10}-1_{01}$	0.16 ± 0.05		
1990 May 24-25[c]	H_2S	$1_{10}-1_{01}$	0.26 ± 0.04	-0.09 ± 0.09	1.23 ± 0.21
		Levy (1990c)			
1990 Aug. 30	H_2S	$1_{10}-1_{01}$	0.69 ± 0.05	-0.14 ± 0.06	1.33 ± 0.10
1990 Aug. 31	H_2S	$1_{10}-1_{01}$	0.77 ± 0.06	-0.04 ± 0.04	1.15 ± 0.09
1990 Aug. 30-31[c]	H_2S	$1_{10}-1_{01}$	0.73 ± 0.04	-0.08 ± 0.03	1.26 ± 0.07
1990 Aug. 30	H_2S	$2_{20}-2_{11}$	0.15 ± 0.03	-0.05 ± 0.12	0.97 ± 0.21
1990 Aug. 28	SO_2	$5_{15}-4_{04}$	$<0.11^d$		
1990 Aug. 29	SO_2	$5_{24}-5_{15}$	$<0.17^d$		
1990 Aug. 28	SO_2	$7_{17}-6_{06}$	$<0.17^d$		
1990 Aug. 28	OCS	18-17	$<0.16^e$		
1990 Aug. 31	OCS	7-6	$<0.08^d$		
1990 Aug. 28	H_2CS	$4_{14}-3_{13}$	$<0.11^e$		

[a] Average of central and offset positions.
[b] No Gaussian fit was performed, because of the bad spectral resolution (1 MHz).
[c] Average of the two observations.
[d] 3σ upper limit for a 1-MHz channel.
[e] 3σ upper limit for a 1.5 km sec⁻¹ line.

This distribution is essentially out of equilibrium, since it is governed by collisions in the inner coma, radiative decay, and excitation by solar radiation. One has to solve the differential equations that govern the population distributions as the molecules move with the expanding gas from the nucleus. For this, we use models similar to those developed by Crovisier (1987) for linear molecules and by Bockelée-Morvan (1987) for the water molecule (except that optical thickness of the lines may be neglected here). The rotational energy levels and the Einstein A-coefficients for rotational transitions are taken from Poynter
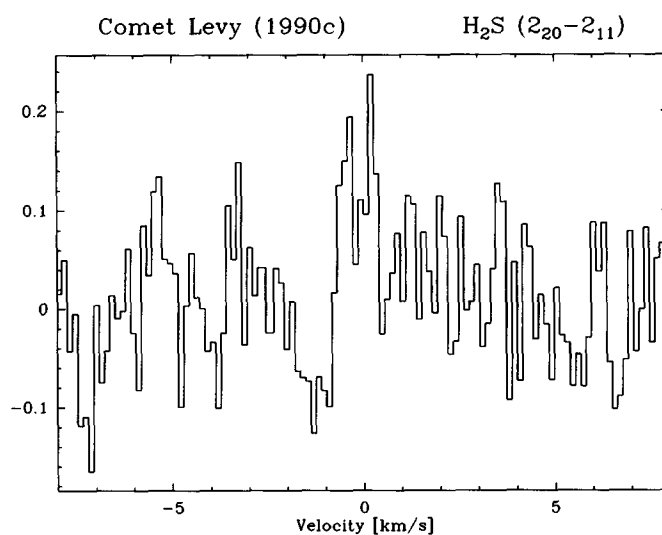

FIG. 3. The H_2S $1_{10}-1_{01}$ line of Comet Levy (1990c), average of observations of August 30 and 31, 1990. Scales, units and resolution are the same as in Fig. 2.

FIG. 4. The H_2S $2_{20}-2_{11}$ line of Comet Levy (1990c), observed on August 31, 1990. Scales and units are the same as in Fig. 2. The frequency resolution is 100 kHz and corresponds to 0.14 km sec⁻¹.

TABLE IV
Fundamental Vibrational Bands of Sulfur-Bearing Molecules, Their Strengths, and Excitation Rates

Molecule	Band	Frequency $[cm^{-1}]$	A^a $[sec^{-1}]$	g^b $[sec^{-1}]$	Ref.[c]
H_2S	ν_1	2615	0.10	6.0×10^{-7}	(1)
	ν_2	1183	0.08	1.3×10^{-6}	(2)
	ν_3	2627	0.025	1.5×10^{-7}	(1)
SO_2	ν_1	1151	3.6	5.8×10^{-5}	(2)
	ν_2	518	0.8	3.1×10^{-5}	(2)
	ν_3	1362	44.0	5.8×10^{-4}	(2)
OCS	ν_1	859	0.88	2.0×10^{-5}	(3)
	ν_2	520	0.05	4.2×10^{-6}	(3)
	ν_3	2062	370.0	3.0×10^{-3}	(3)
H_2CS	ν_1	2971			
	ν_2	1457			
	ν_3	1059			
	ν_4	990			
	ν_5	3025			
	ν_6	991			
CS_2	ν_1	658	0.0		
	ν_2	397	0.07	7.7×10^{-6}	(3)
	ν_3	1532	210.0	2.4×10^{-3}	(3)

[a] Einstein A-coefficients for the bands, evaluated from laboratory absorption spectra.

[b] Excitation rates by the radiation field of the Sun at 1 AU.

[c] References for laboratory absorption data: (1) Lechuga-Fossat et al. (1984); (2) GEISA, Husson et al. (1986); (3) Pugh and Rao (1976).

and Pickett (1984). Whereas there is no difficulty to model radiative excitation by the Sun, which depends only upon molecular constants and the solar radiation (Table IV), collisional excitation is more tricky to deal with because collisional cross sections and kinetic temperatures are not reliably known. As in our previous models, we assume cross sections of 10^{-14} cm^2 for rotational transitions induced by collisions between water and other polar molecules. This section, which is due to dipole–dipole interaction, is much larger than the geometric cross sections but is in agreement with line-broadening measurements. We also assume complete thermalization of the rotational distribution at each collision. We have adopted a constant coma kinetic temperature of 40 K. This temperature is in reasonable agreement with the intensity ratio of the $1_{10}-1_{01}$ and $2_{20}-2_{11}$ H_2S lines observed in Comet Levy, with the relative intensities of the methanol lines observed in the two comets (Bockelée-Morvan et al. 1990a), and with the predictions of thermodynamical models and the analysis of the KAO observations of the infrared water lines in P/Halley (Bockelée-Morvan and Crovisier 1987a,b). This assumption is not crucial: since the energy levels of the transitions observed during our program were low, there is no dramatic change in their relative populations if the

kinetic temperature is changed by, e.g., a factor of 2. This point is discussed further in Section 3.1.

Converting column densities into molecular abundances requires in turn the knowledge of the density distribution. We assume that the observed molecules are expanding from the nucleus with spherical symmetry and a constant velocity of 0.8 km sec^{-1}. Spherical symmetry is in contradiction with the slight velocity offset observed in the lines, but we expect that this assumption does not affect the determination of the average production rates. This adopted expansion velocity is in agreement with the observed linewidths of HCN and CH_3OH. The H_2S linewidths suggest a somewhat smaller velocity (see Section 4.1 below); adopting a smaller expansion velocity would somewhat diminish the derived production rates. The molecular lifetimes for each molecule are discussed below individually.

In order to convert the observed production rates into abundances relative to water, we use the water production rates deduced from the observations of the OH 18-cm lines at Nançay, using the method of Bockelée-Morvan et al. (1990b) and assuming $Q[H_2O] = 1.1\ Q[OH]$. For Austin, $Q[H_2O] = 4.0 \times 10^{28}$ sec^{-1} in the average for the May 21–25 period (Bockelée-Morvan et al. 1990c). IUE observations of OH in the UV were also available for May 24: from these, Budzien et al. (1990a) derived $Q[H_2O] = 6.0 \times 10^{28}$ sec^{-1}; this value was revised to $Q[H_2O] = 2.0 \times 10^{28}$ sec^{-1}, taking into account solar activity (Budzien et al. 1990b). For Levy, $Q[H_2O] = 2.5 \times 10^{29}$ sec^{-1} on August 30–31 (unpublished Nançay observations).

3.1. Hydrogen Sulfide

We have evaluated the photodissociation rate of H_2S using the recent ultraviolet absorption spectrum of Lee et al. (1987) and the solar reference spectrum of Huebner and Carpenter (1979). The resulting rate is $2.5\ 10^{-4}$ sec^{-1} at 1 AU and is mainly due to absorption in the 180–220 nm region. The contribution of solar Lyman α to this rate is only 1.5×10^{-5} sec^{-1} (for quiet Sun). Therefore, this rate is practically independent of solar activity. Huebner (1985) previously published a much larger rate (3.3×10^{-3} sec^{-1}), but he recently revised this rate to 3.3×10^{-4} sec^{-1} (Huebner 1990, private communication). With a lifetime of about 4000 sec, H_2S is not a very short-lived species, and its scale length is comparable to the IRAM telescope field radius.

The vibrational bands of H_2S are very weak, more than two orders of magnitude weaker than those of water, and their excitation rates are of the order of 10^{-6} sec^{-1} (Table IV). Electronic excitation leads to the destruction of the molecule. Therefore, rotational excitation of H_2S will be essentially governed by collisions and radiative decay.

The intensity ratio of the $1_{10}-1_{01}$ and $2_{20}-2_{11}$ lines is
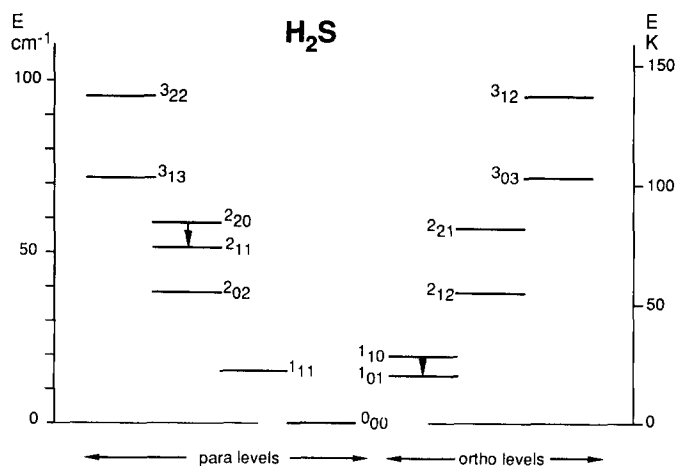
FIG. 5. Diagram of the first energy levels of H₂S (all levels lower than 100 cm⁻¹). The arrows show the observed rotational transitions.

interesting to study, since the two lines were observed simultaneously on August 31, with a comparable beam size. Thus, this ratio is not subject to variability or coma inhomogeneity effects and essentially depends on the rotational population distribution. Figure 5 shows the energy diagram of the lowest rotational states of H₂S. The two observed transitions belong to the *ortho* and *para* spin species, respectively. Since these two species are practically independent with respect to radiative and collisional transitions, their population ratio may differ from the statistical ratio 3 : 1, especially if they are in equilibrium with a very cold nucleus temperature. For instance, Mumma *et al.* (1988), from their infrared observations of water, found an *ortho*-to-*para* ratio of 2.2 ± 0.1 for P/ Halley and of 3.2 ± 0.2 for Comet Wilson 1987 VII. This result, however, was questioned by Bockelée-Morvan and Crovisier (1990) who retrieved different ratios from the same data. In any case, the energy separation of the *ortho* and *para* levels of H₂S is smaller than that for H₂O (the 1_{01} *ortho* level is 13.8 cm⁻¹ higher than the 0_{00} *para* level for H₂S, to be compared to 23.8 cm⁻¹ for H₂O). Thus, the H₂S *ortho*-to-*para* ratio should depend less critically on temperature than is the case for water. An equilibrium temperature less than 20 K is required to obtain a departure of the *ortho*-to-*para* ratio by more than 10% from the statistical ratio. In the absence of any other piece of information, we assume the statistical population ratio 3 : 1.

The observed transitions come from rotational levels of different energies (Fig. 5): whereas the $1_{10}-1_{01}$ line comes from the two lowest states of the *ortho* ladder, the $2_{20}-2_{11}$ line occurs between levels at about 55 cm⁻¹ (75 K) above the ground state. The observed ratio [$1_{10}-1_{01}$]/[$2_{20}-2_{11}$] is 4.6 ± 1.0, which corresponds to an excitation temperature between 36 and 48 K. This does not mean that H₂S has a rotational temperature of about 40 K, because models

predict that the rotational distribution is relaxing and out of equilibrium. However, it suggests that the coma kinetic temperature is higher than this excitation temperature and it helps to constrain the excitation conditions.

The most uncertain parameters in our excitation model are the coma temperature and the collisional cross section. In order to assess the dependence of the retrieved H₂S production rate on model assumptions, we have computed the predicted intensities of the $1_{10}-1_{01}$ and $2_{20}-2_{11}$ lines for a variety of values of these parameters and for the observing conditions of Comet Levy. The results are summarized in Fig. 6.

As shown by Fig. 6, the observed line intensities suggest that the kinetic temperature of the coma is at least 35 K. We have not included in the present model a temperature profile, but a uniform kinetic temperature. From the observations of the infrared bands of water in P/Halley, Bockelée-Morvan and Crovisier (1987b) retrieved a coma temperature of about 60 K, but at moments where P/ Halley was closer to the Sun and had a larger gas production rate than Comet Levy. The simultaneous observations of the methanol lines in Comet Levy also suggest a
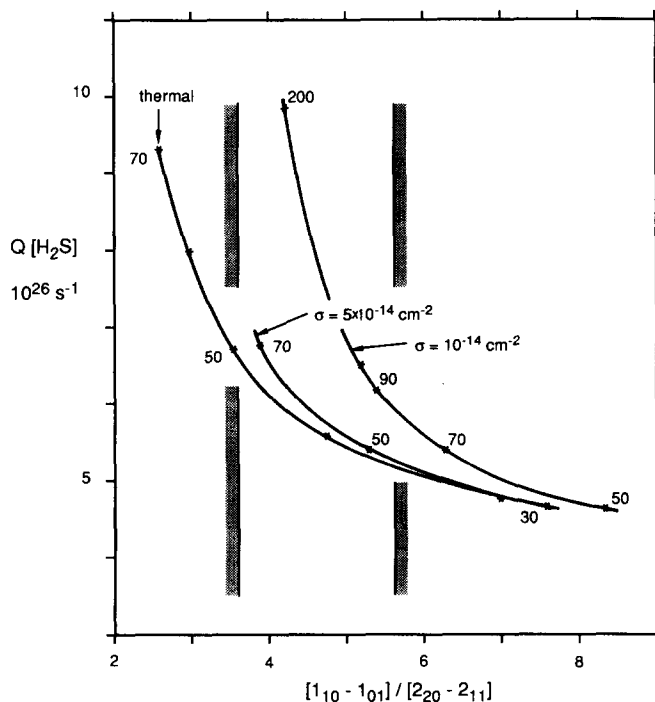

FIG. 6. An illustration of the dependence of the retrieved H₂S production rate on the model parameters. The abscissa is the intensity ratio of the $1_{10}-1_{01}$ and $2_{20}-2_{11}$ lines. The ordinate is the production rate corresponding to the observed $1_{10}-1_{01}$ line intensity. Each curve corresponds to a fixed value of the collisional cross section and to different values of the kinetic temperature (which are tagged on the figure). The other parameters correspond to the observation of Comet Levy at IRAM. The region corresponding to the observed $1_{10}-1_{01}$ to $2_{20}-2_{11}$ line ratio is indicated.

cool temperature (Bockelée-Morvan *et al.* 1990a, and in preparation). It therefore does not seem plausible that the coma mean kinetic temperature exceeds 100 K. Taking this constraint into account and the other constraint that is imposed by the limit case of a purely thermal rotational population, Fig. 6 shows that the H_2S production rate in Comet Levy is conservatively bracketed by 5×10^{26} and 8×10^{26} sec^{-1}. A production rate close to the lower limit 5×10^{26} sec^{-1}, which is compatible with cooler kinetic temperatures, seems to be more plausible. This corresponds to a $[H_2S]/[H_2O]$ ratio of 0.0020 in Comet Levy.

For Comet Austin, we have only observations of the $1_{10}–1_{01}$ line. We assume a coma kinetic temperature of 40 K and a collisional cross section of 10^{-14} cm^{-2}. We must take into account that the observations were not centered on the comet (Fig. 1). Grouping the observations into two sets according to their offset with respect to the nucleus, we obtain line areas of 0.32 ± 0.05 K km sec^{-1} at $\approx 5''$ from the center and of 0.18 ± 0.05 K km sec^{-1} at $\approx 11''$ from the center. This is consistent with the distribution of a parent molecule having a lifetime of 4000 sec at 1 AU from the Sun. We evaluate that, if the observations had been aimed at the center, the line area would have been 0.38 ± 0.05 K km sec^{-1}. From this value and our excitation model, we obtain an H_2S production rate of 1.1×10^{26} sec^{-1}, corresponding to a $[H_2S]/[H_2O]$ ratio of 0.0027 in that comet.

3.2. Sulfur Dioxide

SO_2 might be an important sulfur depository in cometary nuclei, since its abundance in the interstellar gas is close to that of H_2S (Irvine and Knacke 1989) and since it can condense at higher temperatures than H_2S (Yamamoto 1985).

The photodissociation rate of SO_2 is 2.5×10^{-4} sec^{-1} according to Huebner (1985) and 2.1×10^{-4} sec^{-1} according to Kim and A'Hearn (1991). The vibrational excitation rates are given in Table IV. In addition, SO_2 has two strong electronic systems, $A–X$ around 300 nm and $C–X$ around 280 nm, which are expected to show fluorescence (Kim and A'Hearn 1991) and which should contribute significantly to rotational excitation: the excitation rates of the vibronic bands of the $C–X$ system, as estimated from the band strengths measured by Ebata *et al.* (1988), are of the order of 5×10^{-4} sec^{-1} and comparable to the infrared excitation rates.

Our modeling of SO_2 is crude and includes only collisional excitation at a rotational temperature of 40 K. Even at this low temperature, many rotational levels are populated, since the energy separation of the levels of this heavy molecule is small. The three SO_2 lines that we tried to observe yielded upper limits $Q[SO_2] < 6 \times 10^{26}$ sec^{-1}, which corresponds to $Q[SO_2]/Q[H_2O] < 0.0025$. Kim and A'Hearn (1991) derived much lower limits on the SO_2

abundance from the search of the $C–X$ system in *IUE* spectra: $Q[SO_2]/Q[H_2O] < 1 \times 10^{-5}$ in Bradfield 1979 X and P/Encke 1980 XI, $<2 \times 10^{-5}$ in P/Halley, and $<10^{-6}$ in IRAS-Araki-Alcock 1983 VII. The ultraviolet observations are thus more sensitive than the radio observations, as is expected for species with strong nondissociative electronic transitions. Therefore, the development of a more sophisticated model to interpret the radio observations is hardly justified.

3.3. Carbonyl Sulfide

OCS was suggested by Azoulay and Festou (1986) to be one of the parents for the atomic S observed in comets (OCS dissociates into CO + S rather than CS + O). Its $J = 8–7$ transition was unsuccessfully searched for at IRAM in Comet P/Halley (Bockelée-Morvan *et al.* 1987), but the corresponding upper limit ($Q[OCS]/Q[H_2O] < 0.06$) was not very meaningful. In the infrared spectrum of P/Halley observed by the IKS-VEGA spectrometer (Combes *et al.* 1988), a feature was marginally present at the wavelength (4.85 μm) of the strong ν_3 band of OCS; this feature was cautiously interpreted by the authors in terms of an upper limit corresponding to $Q[OCS]/Q[H_2O] < 0.007$.

Our interpretation of the OCS observations is based upon the model of Crovisier (1987) for the excitation of linear molecules with the vibrational excitation rates given in Table IV and a kinetic temperature of 40 K. We have adopted the photodissociation rate of 8×10^{-5} sec^{-1} computed by Azoulay and Festou (1986); Huebner (1985) has estimated a larger value (6.5×10^{-4} sec^{-1}); a rough estimation from the UV absorption data compiled by Lee (1984), however, leads to 5×10^{-5} sec^{-1}, close to the value of Azoulay and Festou. During our observing run of Comet Levy, two OCS lines were observed: the $J = 18–17$ line during a dedicated search and the $J = 7–6$ line which was serendipitously observed during a search for the CH_3CCH lines around 85 GHz. The most meaningful upper limit is obtained for the $J = 18–17$ line: $Q[OCS] < 5 \times 10^{26}$ sec^{-1}, which corresponds to $Q[OCS]/Q[H_2O] < 0.002$.

3.4. Thioformaldehyde

Thioformaldehyde was searched for because of its analogy with H_2CO, which has been identified in cometary atmospheres (Colom *et al.* 1991), and because it might be a parent for the CS cometary radical. The properties of H_2CS, which is unstable in the laboratory at room temperature, are not as well known as those for H_2CO. Little is known about its photochemistry. Its $A–X$ electronic band at 610 nm is known to yield both fluorescence and dissociation (Kawasaki *et al.* 1985), but this band is weak (oscillator strength $f \approx 10^{-5}$, corresponding to an excitation rate by the Sun of the order of 10^{-3} sec^{-1}). We assume that

its lifetime against photodissociation is comparable to that of H_2CO (3300 sec) and, therefore, that the H_2CS scale length is larger than the IRAM telescope field of view. We could not find any laboratory measurements of the H_2CS vibrational band intensities. Our excitation model only includes collisional excitation with a kinetic temperature of 40 K. If H_2CS behaves as formaldehyde (Bockelée-Morvan and Crovisier 1991), it undergoes only a very few fluorescence cycles during its lifetime, which does not strongly affect its rotational population, especially in the inner coma region sampled by the IRAM beam.

The resulting upper limit on $Q[H_2CS]$ is 2.5×10^{26} sec^{-1}, corresponding to $Q[H_2CS]/Q[H_2O] < 0.01$. This is smaller than the abundance of CS typically observed in comets ($Q[CS]/Q[H_2O]$ is about 0.002). On the other hand, if the H_2CS lifetime were smaller than we assumed and comparable to the CS-parent lifetime (500 sec according to Jackson et al. 1986), we would obtain a higher upper limit which would not be in contradiction with H_2CS being the parent of cometary CS.

4. DISCUSSION

4.1. Lineshapes and Coma Kinematics

The observation of the H_2S $1_{10}-1_{01}$ transition in Comet Levy gives the line profile of a parent molecule with both high spectral resolution and reasonable signal-to-noise ratio (Fig. 3). It corresponds to a field of view of $r = 2200$ km and thus allows us to probe the kinematics of the inner coma. The profile is narrow, with a width of only 1.26 ± 0.07 km sec^{-1} at half intensity. A comparable width is observed for Comet Austin (Table III). This width suggests an expansion velocity of about 0.65 km sec^{-1} in the inner coma. This value is among the smallest of those inferred for water from radio OH observations, and is somewhat smaller than the predictions of most hydrodynamic models (see the discussion of Bockelée-Morvan et al. 1990b).

The H_2S lines in Comet Levy are marginally blue-shifted. The other molecular lines observed during the same run, as well as the OH radiolines observed at Nançay, are also blueshifted. At the moment of the observations, the comet phase angle was about 35°. Thus, these blueshifts may be due to anisotropic outgassing toward the Sun.

The implications of the H_2S lineshapes on the kinematics of the comet together with the data obtained for other molecules will be further discussed in another paper (Colom et al., in preparation).

4.2. Comparison with the PICCA Observation of H_3S^+

The PICCA instrument aboard Giotto measured the mass spectrum of the ions inside P/Halley's coma and observed a peak at $(m/q) = 35$ which was attributed to H_3S^+ (Marconi et al. 1990). This ion is presumably coming from H_2S through the exchange reaction:

$$H_2S + H_3O^+ \rightarrow H_3S^+ + H_2O.$$

Marconi et al. tried to infer the H_2S production rate from the PICCA observation. They estimate the H_2S density to be about 10^3 cm^{-3} at $r = 4200$ km from the nucleus. They assumed the H_2S photodissociation rate of 3.3×10^{-3} sec^{-1} published by Huebner (1985). With this rate, at the distance of about 4000 km from the nucleus where the PICCA measurement took place, H_2S coming from the nucleus would be practically completely destroyed. Therefore, Marconi et al. supposed that the H_2S they indirectly observed was coming from circumnuclear dust. However, as discussed in Section 3.1, the photodissociation rate given by Huebner (1985) is too high by an order of magnitude. With our estimation of 2.5×10^{-4} sec^{-1} for the photodissociation rate of H_2S, this molecule, when coming from the nucleus, is still significantly abundant at $r = 4000$ km. The H_2S density inferred from the PICCA observation then corresponds to a production rate from the nucleus of 9×10^{26} sec^{-1}, or 0.0013 relative to water. This is somewhat smaller than the relative abundances we observed in Comets Austin and Levy. It must be noted that the PICCA determination heavily relies on assumptions for the exchange rate between H_2S and H_3O^+, and for the recombination rate of H_3S^+, which are poorly known; therefore, a discrepancy between PICCA and IRAM determinations may not be due to a real difference of abundance in the comets.

4.3. The Abundance of Sulfur and Sulfur-Containing Molecules in Comets

There are four sulfur-containing species reliably identified by spectroscopy in cometary atmospheres: CS, S_2, atomic S, and now H_2S. The photodissociation product of H_2S, the SH radical, chemically akin to OH, has not been detected. Its lifetime is very short (about 150 sec at 1 AU) because its strong $A-X$ band at 325 nm is predissociative (Kim and A'Hearn 1991, private communication). The fluorescence rate of this band is small, and the upper limits to $Q[SH]$ derived from available spectra are well above those derived for $Q[H_2S]$ from our radio observations (Kim and A'Hearn 1991, private communication, Roettger 1991). The prospect to detect SH at radio or infrared wavelengths is also grim due to the short lifetime of this radical.

CS has been observed in many comets by IUE with abundances of the order of 10^{-3} relative to water (Feldman 1991). For instance, $Q[CS]/Q[H_2O]$ varied between 0.3×10^{-3} and 2.5×10^{-3} for Comet Halley (Feldman et al. 1987); it was 0.5×10^{-3} in Comet Austin at the end of

May (Budzien *et al.* 1990a). It is likely that the parent for the CS radical is CS_2, due to the agreement between the CS_2 lifetime (600 sec at 1 AU) and that expected for the CS parent from the CS spatial distribution (Jackson *et al.* 1986). Other parent candidates such as the interstellar molecules OCS, CH_3SH, and HNCS can be ruled out because they have much larger lifetimes and/or they do not have significant photodissociation channels yielding CS. Direct observation of CS_2 will be difficult: it has no rotational transitions because it is a nonpolar molecule; it has a strongly excited vibrational band at 6.5 μm (Table IV), but due to the small abundance of CS_2 and its short lifetime, this band would be at least two orders of magnitude weaker than the ν_2 water band at the same wavelength.

S_2 has only been observed in one comet, IRAS-Araki-Alcock 1983 VII, with a relative abundance $Q[S_2]/Q[H_2O] = 2 \times 10^{-4}$ according to the recent analysis of Kim *et al.* (1990). Upper limits have been obtained for other comets: $Q[S_2]/Q[H_2O] < 3 \times 10^{-4}$ for P/Halley (Feldman 1991) and $<0.5 \times 10^{-4}$ for Austin (1989c1) (Budzien *et al.* 1990a). It must be noted that S_2 is a relatively refractory molecule, and its release process from the cometary nucleus is not easy to predict (Grim and Greenberg 1987, Moore *et al.* 1988). This might explain its presence in Comet IRAS-Araki-Alcock and not in Comet Austin after its passage at perihelion. On another hand, it has been advanced (A'Hearn *et al.* 1983, Grim and Greenberg 1987) that S_2 is not accreted from the interstellar medium, but results from secular radiation processing of species such as H_2S on grain surface. Therefore, the S_2 abundance in cometary atmospheres has probably not the same meaning as that of other species.

Atomic sulfur has been observed in several comets by IUE at 147.4 and 181.4 nm (Feldman 1991). Azoulay and Festou (1986), who modeled SI emission, concluded that SI cannot be produced solely by CS_2 and that another parent with a much larger lifetime (about 10^5 sec) should be present. They proposed OCS as the other parent. Our millimeter observations revealed the existence of H_2S rather than of OCS. The question of whether H_2S and the CS parent can account for all the observed SI must now be examined. Azoulay and Festou (1986) estimated that $Q[SI]/Q[H_2O]$ is about 0.02 in several comets, but this abundance is still debated, because the SI relative line intensities are not well understood and the atomic oscillator strengths of sulfur are uncertain (Roettger *et al.* 1989, Roettger 1991).

From the present work, H_2S has been observed with similar abundances (about 0.002) in two comets: Austin (1989c1), which is apparently a new comet, and Levy (1990c), which according to Marsden (1990) is a long-period comet. The total production rate of sulfur coming from H_2S and CS_2 (assuming it is the parent of the observed CS) thus ranges from 3×10^{-3} to 8×10^{-3} that of

water, which is smaller than the abundance derived by Azoulay and Festou. Due to the lack of simultaneous determinations of production rates in the same comet and to the uncertainty on the atomic sulfur production rate, it is premature to conclude firmly that there are missing sulfur parent molecules. In any case, our millimeter observations have placed significant upper limits for the abundances of SO_2, OCS, and H_2CS. Still lower limits have been obtained from ultraviolet spectra by Kim and A'Hearn (1991) for SO (which might be stable in a cold nucleus) and SO_2.

Assuming that most of the oxygen is contained in water, the abundance of sulfur coming from *identified* volatile parent molecules is $[S]/[O] < 0.01$, significantly less than the cosmic abundance $[S]/[O] = 0.021$ (Anders and Grevesse 1989). Sulfur, however, is more abundant in dust particles, since the PUMA experiment aboard *Giotto* measured $[S]/[O] = 0.090$ in P/Halley (Jessberger *et al.* 1988). It is thus possible that the overall sulfur abundance in comets is close to the cosmic abundance.

4.4. Implications for Comet Formation

According to one of the two main scenarios of cometary matter formation (Yamamoto *et al.* 1983, Yamamoto 1985, 1991), cometary matter comes directly from the condensation of interstellar gas at very low temperature, followed by a partial sublimation in the outer solar nebula which released the most volatile species; a distinct but related proposal stresses the role of interstellar dust grains with mantles of organic refractories (Greenberg and Hage (1990). In the alternative model (e.g., Prinn and Fegley 1989; see Yamamoto 1991 for further references) material from the solar nebula and the outer planets' subnebulae, initially at high temperature (>1000 K), cools down, which first stops its chemical evolution and then makes it condense selectively. We present here a short discussion of the implication of the presence of H_2S for the origin of cometary matter and its probable link with interstellar medium; a more detailed account will be given elsewhere (Despois *et al.*, in preparation).

Hydrogen sulfide is a very volatile species. Pure H_2S only condenses at temperatures lower than 57 K for densities lower than 10^{13} cm^{-3}, such as those expected in the zone of cometary formation (Yamamoto 1985). Among identified cometary volatiles, only CO condenses at a lower temperature (25 K), but it is not known for certain whether the observed cometary CO is indeed coming from the nucleus or is a secondary product. For example, water condenses at 152 K, methanol at 99 K, hydrogen cyanide at 95 K, and formaldehyde at 64 K. Thus, the existence of cometary H_2S suggests that cometary matter formed and remained stored in cold regions (57 K is the equilibrium temperature of a rotating blackbody at 23 AU from the Sun). One should be aware, however, that H_2S may

be condensed together with other molecules in a structure where H_2O (amorphous ?) ice probably dominates. As the H_2O–H_2S bond is expected to be strong, the effective sublimation temperature could be higher than that of a layer of pure hydrogen sulfide. As an example of this phenomenon, Sandford and Allamandola (1988, 1990) have recently shown that, in the presence of H_2O ice, CO can condense at temperatures as high as 50 K, instead of 25 K. Conversely, substantial amounts of CO can remain trapped in water ice at temperatures as high as 130 K (Schmitt et al. 1989). On the other hand, if the comet nucleus is highly porous (cf. the low average density derived, ~0.3–0.7 g cm^{-3}, e.g., Rickman 1989), the relatively small H_2S molecule should not be too much affected by physical trapping in the ice. Laboratory simulations are needed to clarify these points.

Hydrogen sulfide is present in interstellar gas, but not very abundant in quiescent clouds ($\sim3 \times 10^{-9}$ and 0.7×10^{-9} relative to H_2 in the dark clouds L134N and TMC1; Minh et al. 1989). It is apparently more abundant in starforming regions, reaching its highest relative abundance ($\sim10^{-6}$) in Orion Hot Core and Plateau (Minh et al. 1990, 1991), suggesting that a large quantity of H_2S is trapped in grains in regions of sufficiently low temperature.

The existence of interstellar H_2S in the solid phase has been postulated in W33A from the presence of an absorption feature at 3.94 μm (Geballe et al. 1985). Tielens (1989) quotes an abundance $[H_2S]/[H_2O] = 0.003$ for that source (unfortunately without explaining how it is derived), which would be comparable to the abundance we observed for comets. This detection has, however, been recently questioned by Smith (1991), who gives for three other sources upper limits on the order of 2 to 4×10^{-3} with respect to solid H_2O, and who suggests that the 3.94-μm feature in W33A could be spurious. It is sure that one should search for the presence of solid H_2S in more galactic sources and evaluate its abundance by future infrared observations.

It is striking that H_2S is present in comets, but not SO_2, which condenses at a higher temperature (83 K, to be compared to 57 K for H_2S). From the present data set, the $[SO_2]/[H_2O]$ ratio is less than 3×10^{-3}. If one accepts the idea that chemical abundances do not vary strongly from comet to comet, one has an even more striking result including the upper limits on SO and SO_2 abundances in Comets IRAS-Araki-Alcock, P/Halley, and a few other ones recently obtained by Kim and A'Hearn (1991). They derive $[SO]/[H_2O] < 2 \times 10^{-4}$ in most cases, and a preliminary limit $[SO_2]/[H_2O] < 2 \times 10^{-5}$, which would lead to upper limits to the abundances relative to H_2S of 10^{-1} and 10^{-2}, respectively; in one comet (IRAS-Araki-Alcock) these latter ratios are even lower: 2.5×10^{-3} and 4×10^{-4}, respectively. In contrast, in the interstellar gas, SO_2 is usually observed with abundances not lower than onetenth of H_2S, and may be even more abundant in some

cases; a notable exception is Orion Hot Core, with $[SO_2]/[H_2S]$ and $[SO]/[H_2S] < \sim2 \times 10^{-3}$ (Blake et al. 1987, Minh et al. 1990). Chemical models also lead to $[SO_2]/[H_2S]$ and/or $[SO]/[H_2S]$ greater than 0.1 in most interstellar situations: pure gas phase ion-molecule chemistry (e.g., Millar and Herbst 1990), shock chemistry (e.g., Hartquist et al. 1980), and gas interacting with stellar winds (Charnley et al. 1989). However, grain surface reactions in the interstellar medium form HS and H_2S with a total abundance up to 50 times higher than both sulfur oxides according to Duley et al. (1980).

This again suggests the possible importance of grain surface chemistry in the formation of cometary matter, which is not unexpected. In addition, several species present in the gas phase of the interstellar medium like S, SH, etc., and the ions S^+, SH^+, etc., might also lead to H_2S when stuck on the grain surface. It is interesting to note the high abundance of S and/or S^+ expected from chemical modeling (e.g., $[S]/[H_2S] > \sim10^2$ in Millar and Herbst 1990).

As for the alternative scenario of comet formation from the protosolar nebula and outer planet subnebulae (Prinn and Fegley 1989), little can be said at present as sulfur compounds have not been included up to now in this model. The presence of H_2S rather than sulfur oxides in these hydrogen-rich nebulae would not be surprising. However, a detailed study is needed, taking into account the kinematics of the reactions, and the whole set of sulfur-bearing species already observed or suggested in comets (e.g., OCS, CS_2, H_2CS). This would lead to interesting new observational tests. Such a study is, however, beyond the scope of the present paper.

Thus, whatever the scenario is, H_2S provides us with a new constraint on the maximum temperature encountered by the cometary matter since its formation; it should be well below that of sublimation of H_2O ice, and possibly as low as ~57 K. In case of an interstellar origin of cometary volatiles, the abundance of hydrogen sulfide, when related to upper limits found for sulfur oxides SO and SO_2, constrains the kind of interstellar gas from which they might have condensed and, although the data relevant for comparison are very scarce, there is some indication in favor of H_2S formation on grain surfaces. On the other hand, the even rarer data on H_2S in the interstellar solid phase do not exclude an H_2S abundance on the order of that encountered in comets, and thus the possibility of aggregation of interstellar grains to form cometesimals. Clearly, more observations of sulfur species are needed in interstellar solid and gas phases as well as in comets.

5. CONCLUSION

We have detected the 1_{10}–1_{01} rotational line of hydrogen sulfide in Comets Austin (1989c1) and Levy (1990c). In Comet Levy, the 2_{20}–2_{11} line was also observed, and the

relative intensities of the two lines show that the rotational distribution of the molecule is cold, as expected from models. We derive a production rate of H_2S coming from the nucleus of about 0.002, relative to water, for both comets. This is in agreement with the abundance indirectly derived from the observation of H_3S^+ from mass spectrometry in P/Halley, provided one uses the lifetime of 4000 sec that we have estimated for H_2S.

Hydrogen sulfide is the most abundant of the known parent molecules containing sulfur, the other one being presumably CS_2, parent of the observed CS radical. It is possible that H_2S and CS_2 are the only significant depositories of sulfur among cometary volatiles. A more definite answer to this point should await a better understanding of the atomic SI ultraviolet emissions in comets. However, this point is supported by the unfruitful searches for other sulfur compounds such as SO, SO_2, OCS, and H_2CS (Kim and A'Hearn 1991, and this work). Sulfur is apparently depleted in cometary volatiles with respect to cosmic abundance, but this depletion is perhaps compensated by its higher abundance in cometary dust (Jessberger et al. 1988).

Although laboratory measurements of the condensation–sublimation of H_2S–H_2O mixtures are not yet available, the presence of hydrogen sulfide in cometary nuclei strongly suggests that these bodies formed and remained stored at cold temperatures. This is in agreement with the commonly proposed scenario of cometary formation from cold interstellar matter. Could comets also have formed from chemical evolution and selective condensation in the solar nebula? The answer should await the introduction of sulfur compounds in the presolar nebula chemical models.

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