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Ethylene glycol in comet C/1995 O1 (Hale-Bopp)

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Abstract. We report the detection of ethylene glycol ($HOCH_2CH_2OH$) in comet C/1995 O1 (Hale-Bopp) from the analysis of archival radio spectra. Its production rate is ≈0.25% that of water, making it one of the most abundant organic molecules in cometary ices. This detection strengthens the similarity between interstellar and cometary material.

Key words. astrobiology – astrochemistry – comets: general – comets: individuals: C/1995 O1 (Hale-Bopp) – radio lines: solar system – solar system: formation

1. Introduction

Investigations of the composition of comets provide clues to the physical conditions and chemical processes which occurred in the primitive Solar Nebula. They could also help in understanding the origin of life on Earth, because comets might have played a crucial role in the first stages of the Solar System evolution by seeding the early Earth with prebiotic molecules. Decisive progress was made in the last decade with the identification of many cometary molecules, especially from radio spectroscopy (Bockelée-Morvan et al. 2000, 2004). The most complex species identified were acetaldehyde and methyl formate. However, the presence of more complex, still unidentified species was indicated in the exploration of comet Halley, from mass spectroscopy and from evidence of an organic refractory component in cometary grains (Mitchell et al. 1987; Fomenkova 1999).

We report here the detection of ethylene glycol in comet C/1995 O1 (Hale-Bopp) from an analysis of archival spectra. Ethylene glycol $HOCH_2CH_2OH$, also known as 1,2-ethanediol, is commonly used as antifreeze in coolant fluids for car engines. It was recently discovered in the interstellar medium by observing four of its rotational lines at millimetre wavelengths (Hollis et al. 2002).

2. Observations and analysis

C/1995 O1 (Hale-Bopp) was an exceptionally highly productive comet, with a water production rate reaching 10^{31} molec. s^{-1} at perihelion, in early April 1997. Its apparition offered the opportunity to investigate the chemical composition of a comet with unprecedented sensitivity. A spectral survey of the comet at radio wavelengths was undertaken with the Institut de Radioastronomie Millimétrique (IRAM) 30-m telescope and Plateau de Bure Interferometer (PdBI, used here in the single dish mode), and at the Caltech Submillimeter Observatory (CSO) 10-m telescope. Observations are described in detail by Bockelée-Morvan et al. (2000) and Crovisier et al. (2004).

At the time the observations were carried out, no line frequency predictions were available for ethylene glycol. Soon after line predictions were published by Christen & Müller (2003) and incorporated in the Cologne Database for Molecular Spectroscopy (Müller et al. 2001; `http://www.cdms.de`), we were able to assign to this molecule several of the unidentified lines in our survey as well as several previously unnoticed features (Table 1, Figs. 1 and 2). Theory predicts the existence of several (10) conformers (Christen et al. 2001). The conformer detected in the comet and in the interstellar medium is the one of lowest energy, aGg'.

Altogether, eight lines of ethylene glycol were detected with the IRAM 30-m telescope with a signal-to-noise ratio ranging from 3 to 7. The PdBI observed the 230.578 GHz line independently on two days (Fig. 2), with a S/N of 10 on the second day. Two more lines were observed at the CSO with a S/N of 3 and 6. All the observed spectral features coincide, within observational uncertainties, with the ethylene glycol line frequencies, and their widths are similar to other cometary lines (although most observations were made with low spectral resolution). The relative line intensities are reasonably consistent with model predictions (see below). No strong line is predicted, within the spectral range of our survey, that does not appear in the spectra. Therefore, the identification is secure.

The inner, collisional coma sampled here is close to thermal equilibrium. A convenient way to analyze the observations of several molecular rotational lines is then the *rotation diagram*

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Table 1. Lines of ethylene glycol observed in comet Hale-Bopp.

Transition [a]	Frequency	E_u	Telescope	Date	r	Δ	Int.[b]	$\int T_b dv$ [mK km s^{-1}]	
	[GHz]	[cm^{-1}]		dd/mm/yy	[AU]	[AU]	[min]	Model[c]	Observed
$12_{1,12,0}-11_{1,11,1}$	106.9074	25.3	IRAM 30-m	03/04/97	0.91	1.37	145	70	75 ± 16
$15_{7,9,0}-14_{7,8,1}$	147.1318	57.7	IRAM 30-m	08/04/97	0.92	1.42	130	72	181 ± 26
$15_{7,8,0}-14_{7,7,1}$	147.1324	57.7						92	
$16_{8,9,0}-15_{8,8,1}$	157.2863	68.3	IRAM 30-m	05/04/97	0.92	1.39	85	94	239 ± 58
$16_{8,8,0}-15_{8,7,1}$	157.2864	68.3						74	
$17_{2,15,0}-16_{2,14,1}$	168.3863	54.9	IRAM 30-m	03/04/97	0.91	1.37	205	198	194 ± 63
$25_{1,25,0}-24_{1,24,1}$	226.6433	102.7	IRAM 30-m	11/04/97	0.93	1.45	65	222	440 ± 76
$25_{0,25,0}-24_{0,24,1}$	226.6435	102.7						284	
$21_{5,16,1}-20_{5,15,0}$	227.3158	88.5	IRAM 30-m	05/04/97	0.92	1.39	310	178	135 ± 22
$23_{2,21,0}-22_{3,20,0}$	227.5035	96.2						54	72 ± 22
$22_{4,18,0}-21_{4,17,1}$	227.5871	94.0						214	114 ± 22
$24_{3,22,0}-23_{3,21,1}$	230.5771	104.0	IRAM PdBI	6, 11/03/97	1.00	1.40	34	116	192 ± 18
$22_{4,19,1}-21_{4,18,0}$	230.5783	92.3						98	
$25_{10,16,1}-24_{10,15,0}$	263.3025	144.4	CSO	08/04/97	0.92	1.42	44	52	53 ± 16
$25_{10,15,1}-24_{10,14,0}$	263.3026	144.4						40	
$29_{1,29,0}-28_{1,28,1}$	263.3921	136.4	CSO	08/04/97	0.92	1.42	44	62	121 ± 21
$29_{0,29,0}-28_{0,28,1}$	263.3921	136.4						82	

[a] The energy levels are noted here $J_{K_a,K_b,v}$, where v is the quantum number associated with OH tunneling motions (Christen & Müller 2003).

[b] Integration time (on comet + comparison field).

[c] Line area predicted by our LTE model (Crovisier et al. 2004) for a production rate of ethylene glycol of 0.002 relative to that of H_2O (which is 0.8 to 1.1 × 10^{31} molec. s^{-1}). A uniform rotational temperature of 110 K and a spherical coma expanding with a velocity of 1.04 km s^{-1} are assumed (Biver et al. 1999). β is set to 2×10^{-5} s^{-1} at 1 AU.

method (Goldsmith & Langer 1999). The plot of $\log(N_u/g_u)$ (where N_u is the column density of the upper state and g_u its statistical weight) for individual lines as a function of the upper state energy E_u should be distributed along a straight line related to the rotational temperature T_{rot} and the total column density. In the present case, this method is more difficult to apply because the lines were not observed simultaneously and may therefore be affected by short-term variations of cometary activity. Moreover, the observed line intensities must be corrected for the differences in the instrumental field of view. The rotation diagram for the glycol lines observed with the IRAM 30-m telescope (i.e., restricted to the 3−11 April period) is shown in Fig. 3. Column densities have been normalized to the same field of view, assuming a parent molecule spatial distribution with a photodestruction rate $\beta = 2 \times 10^{-5}$ s^{-1} at 1 AU (i.e., comparable to those of other CHO-containing molecules such as methanol or ethanol). The data are reasonably well fitted by a straight line. The linear regression corresponds to a rotational temperature of 77 ± 11 K (which is somewhat lower than the ≈110 K temperature derived at the same time from observations of other molecules by Biver et al. 1999) and a production rate of 0.29 ± 0.07% relative to water (all quoted errors are 1-σ). The choice of β, which is unknown for ethylene glycol, is not crucial as long as the molecular scale-length is much larger than the radius of the instrumental field of view. This condition is met for $\beta \ll 10^{-4}$ s^{-1}. Adopting β smaller than 2×10^{-5} s^{-1} would not significantly change T_{rot} and the retrieved production rate. However, adopting $\beta = 10^{-4}$ s^{-1} would result in a higher production rate (0.57 ± 0.13%) and a still lower temperature (T_{rot} = 65 ± 8 K) hard to reconcile with the temperature retrieved from other molecules.

If we use T_{rot} = 110 K determined from other molecules, the weighted average of the line area ratios [observed]/[model prediction] from Table 1 leads to a production rate of ethylene glycol 0.17 ± 0.05% relative to water (the *error* representing the dispersion between the individual lines). Together with our rotation diagram analysis for small β values, this provides a robust determination of the abundance of 0.25 ± 0.12%.

3. Discussion

The detection of ethylene glycol completes our inventory of “CHO” molecules in comet Hale-Bopp (Table 2). This molecule of 10 atoms is the most complex species ever identified in a comet by means of spectroscopy. With an abundance of 0.25% in number (or ≈1% in mass) relative to water, it is one of the most abundant CHO molecules in comet Hale-Bopp. It is 5−10 times less abundant than methanol, but at least 5 times more abundant than ethanol, for which only an upper limit has been established. Formaldehyde is the only CHO molecule, other than CH_3OH, which is more abundant than ethylene glycol. However, H_2CO is mainly coming from an extended source and the fraction directly coming from nuclear ices is small. Other known cometary CHO molecules ($HCOOH$, CH_3CHO, $HCOOCH_3$) are less abundant by factors 2.5 to 10. Upper limits at similar levels of abundances are set for c-C_2H_4O, C_2H_5OH and CH_3COOH.

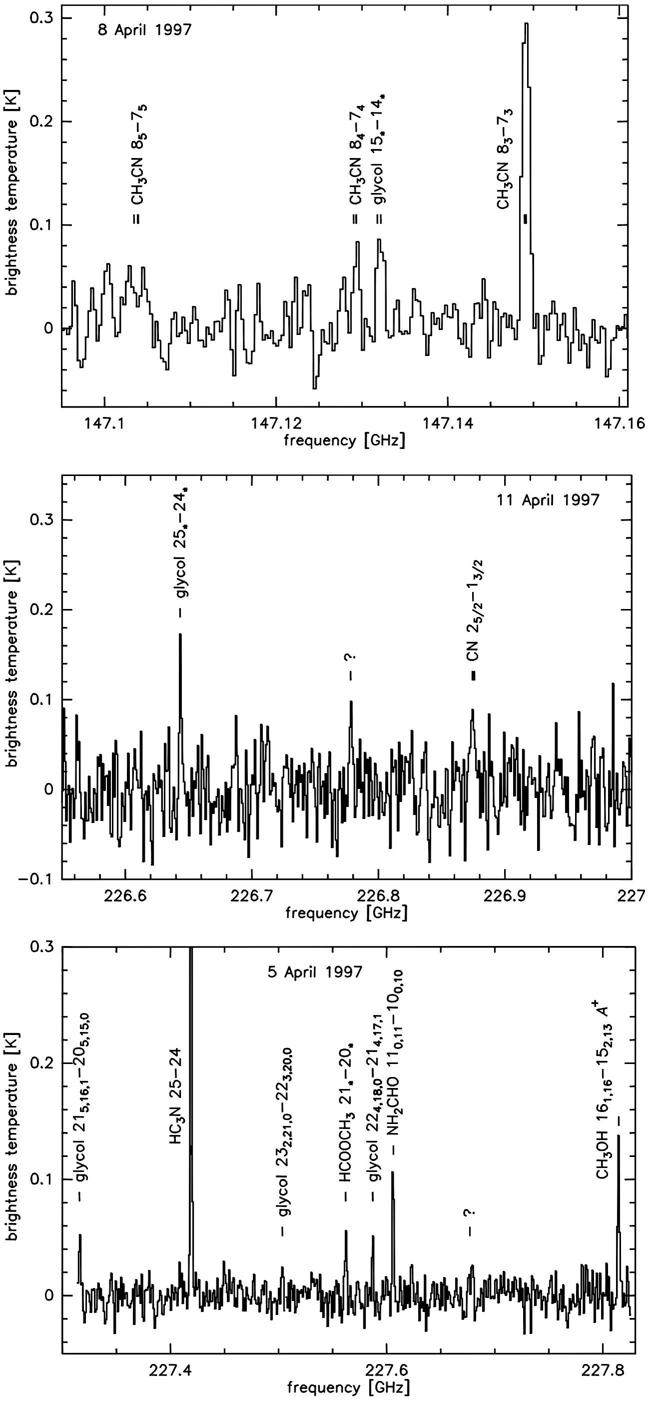

Fig. 1. Lines of ethylene glycol observed with the IRAM 30-m telescope. Lines from other molecules, as well as unidentified features, are also seen. The single sideband mode was used with spectral resolutions of 0.312 MHz (corresponding to 0.64 km s^{-1}) for the top spectrum and of 1 MHz (1.3 km s^{-1}) for the two other spectra.

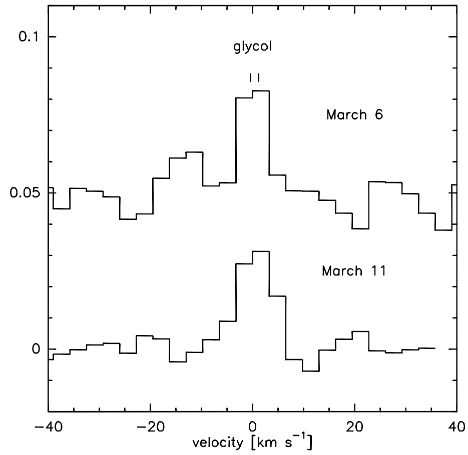

Fig. 2. The ethylene glycol line at 230.578 GHz observed on two different days with the IRAM PdBI. The spectral resolution is 2.5 MHz (3.25 km s^{-1}). The observations were made in the double sideband mode; the variation of the line frequency between the two days shows that the line is coming from the main sideband.

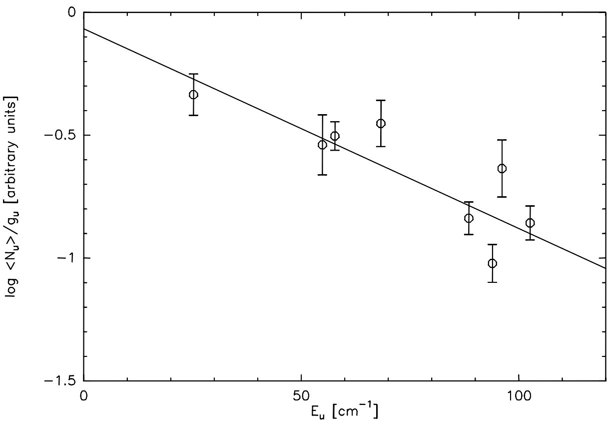

Fig. 3. The rotation diagram for ethylene glycol lines observed at IRAM 30-m. The linear regression corresponds to $T_{\rm rot}$ = 77 ± 11 K and a production rate of 0.29 ± 0.07% relative to water.

Ethylene glycol is the chemically reduced form of glycolaldehyde (CH_2OHCHO), the simplest member of the sugar family. This molecule was not detected in the comet with a 3-σ upper limit indicating that it is at least 5 times less abundant than ethylene glycol (Table 2; Crovisier et al. 2004). Together with the high [CH_3OH]/[H_2CO] abundance ratio in cometary ices (>30), this suggests that the chemistry favoured reduced alcohols with respect to their corresponding aldehydes. The upper limit [C_2H_5OH]/[CH_3CHO] < 4 is also consistent with this scenario.

Which formation mechanism could explain such a high abundance of ethylene glycol? Aldehyde/reduced alcohol pairs are apparently common in interstellar clouds. In the core Sgr B2(N) of the Sagittarius B2 molecular cloud complex, large [CH_3OH]/[H_2CO] and [C_2H_5OH]/[CH_3CHO] abundance ratios are observed (Nummelin et al. 2000). Chemical modelling as well as laboratory experiments argue for these species being formed by grain chemistry and released in the gas phase by the sublimation of grain mantles. Therefore, the overabundance of reduced alcohols seems to characterize molecular synthesis on grain surfaces, and could result from the saturation of aldehyde precursors by atomic hydrogen addition reactions, as proposed by Charnley (2001) for CH_3OH and C_2H_5OH. Glycolaldehyde and ethylene glycol were both detected in Sgr B2(N) (Hollis et al. 2000, 2002). Though there is no consensus as to how such large complex molecules form in interstellar clouds, Charnley (2001) suggested that these two molecules are produced on

Table 2. Comparative abundances of "CHO" molecules in comet Hale-Bopp and in the Galactic Centre Sgr B2(N).

Molecule	Relative abundance	
	C/1995 O1[a] $\times 100$	Sgr B2(N)[b] $\times 10^7$
H_2CO	$\approx 1^c$	>0.005
CH_3OH	2.4	2.
CH_3CHO	0.025	0.002
c-C_2H_4O	<0.2	0.001
C_2H_5OH	<0.1	0.01
HCOOH	0.09	0.001
CH_3COOH	<0.06	≈0.01
$HCOOCH_3$	0.08	0.01
CH_2OHCHO	<0.04	0.0007–0.0011
$HOCH_2CH_2OH$	0.25	0.0008–0.0015

[a] Cometary abundances are given relative to H_2O. They are taken from Bockelée-Morvan et al. (2000), Crovisier et al. (2004) and from the present work.

[b] Abundances are given relative to H_2 assuming $N[H_2] = 2.8 \times 10^{24}$ cm^{-2}. They are taken from Nummelin et al. (2000), from Mehringer et al. (1997) for CH_3COOH, from Hollis et al. (2000, 2001, 2002) for glycolaldehyde and ethylene glycol. Since the spatial distributions of the molecules differ, these relative abundances must be considered with some caution.

[c] Cometary formaldehyde is mainly coming from an extended source. Less than 0.07% relative to water is coming directly from the nucleus according to Wink et al. (1999).

grain surfaces from a hydrogenation-oxidation sequence starting from ketene (CH_2CO). Alternatively, these molecules could be produced by UV irradiation of grain mantles: laboratory experiments have shown that ethylene glycol (but not ethanol) can be easily formed in such environment from water-methanol ice mixtures (McDonald et al. 1996; Cottin et al. 1999; Hudson & Moore 2000). Unlike in comet Hale-Bopp, glycolaldehyde and ethylene glycol are observed with similar abundances in Sgr B2(N) within a 1′ region. On the other hand, the glycolaldehyde spatial distribution mapped in Sgr B2(N) with 10″ angular resolution (Hollis et al. 2001) shows that this molecule has a large spatial scale. It is not confined, like other large molecules, to an embedded (<5″) hot core source known as "Large Molecule Heimat" (LMH), where grain sublimation can proceed. Considering the highly reactive nature of sugars in general, the low abundance of glycolaldehyde in LMH might result from its chemical destruction after release into the gas phase (Hollis et al. 2001, 2002). Future interferometric observations might reveal that ethylene glycol is more abundant than glycolaldehyde in LMH, as observed in comet Hale-Bopp, and more consistent with a formation onto grains. Another explanation could be the destruction of glycolaldehyde before being incorporated into comets.

Primitive meteorites provide other clues to extraterrestrial organic chemistry. Ethylene glycol as well as several polyols were detected in the carbonaceous chondrites Murchison and Murray, but no aldehyde sugars (Cooper et al. 2001).

The discovery of ethylene glycol in comet Hale-Bopp makes it even more compelling that volatile cometary matter retains a significant interstellar signature. The molecular inventory of cometary volatiles matches the richness of star-forming regions (Bockelée-Morvan et al. 2000), and the present study shows that this extends to the most complex interstellar species. Likely, many cometary molecules are of interstellar origin, or formed in the Solar Nebula by low-temperature processes similar to those acting in interstellar clouds. However, ethylene glycol is found to be much more abundant, relative to methanol, in comet Hale-Bopp than in the interstellar medium. Possibly, comets accreted some molecules formed in the hot inner Solar Nebula. Pending the identification of efficient gas-phase processes for the synthesis of complex organic molecules in the Solar Nebula, the high abundance of ethylene glycol in comet Hale-Bopp supports models in which cometary volatiles formed in large part by grain surface chemistry.

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