## Letter to the Editor

# Molecular observations of comets C/2012 S1 (ISON) and C/2013 R1 (Lovejoy): HNC/HCN ratios and upper limits to PH<sub>3</sub>\*,\*\*

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#### **ABSTRACT**

We present molecular observations carried out with the IRAM 30 m telescope at wavelengths around 1.15 mm towards the Oort cloud comets C/2012 S1 (ISON) and C/2013 R1 (Lovejoy) when they were at ~0.6 and ~1 au, respectively, from the Sun. We detect HCN, HNC, and CH<sub>3</sub>OH in both comets, together with the ion HCO<sup>+</sup> in comet ISON and a few weak unidentified lines in comet Lovejoy, one of which might be assigned to methylamine (CH<sub>3</sub>NH<sub>2</sub>). The monitoring of the HCN J = 3-2 line showed a tenfold enhancement in comet ISON on November 14.4 UT due to an outburst of activity whose exact origin is unknown, although it might be related to some break-up of the nucleus. The set of CH<sub>3</sub>OH lines observed was used to derive the kinetic temperature in the coma, 90 K in comet ISON and 60 K in comet Lovejoy. The HNC/HCN ratios derived, 0.18 in ISON and 0.05 in Lovejoy, are similar to those found in most previous comets and are consistent with an enhancement of HNC as the comet approaches the Sun. Phosphine (PH<sub>3</sub>) was also searched for unsuccessfully in both comets through its fundamental  $1_0$ – $0_0$  transition, and  $3\sigma$  upper limits corresponding to PH<sub>3</sub>/H<sub>2</sub>O ratios 4–10 times above the solar P/O elemental ratio were derived.

Key words. comets: general – comets: individual: C/2012 S1 (ISON) – comets: individual: C/2013 R1 (Lovejoy)

## 1. Introduction

Radio spectroscopic observations of comets during their visit to the inner solar system have allowed us to detect a wide variety of molecules in their coma (e.g., Bockelée-Morvan & Crovisier 2002). These observations have provided significant constraints on the chemical nature of comets coming from the two main solar system reservoirs, the Oort cloud and the Kuiper belt, whose composition is expected to reflect to some extent that of the regions of the protosolar nebula where they were once formed.

Two bright comets coming from the Oort cloud approached the Sun in late 2013, allowing us to perform sensitive radio spectroscopic observations and to probe their volatile content. C/2012 S1 (ISON) –hereafter ISON– was discovered on September 2012 at 6.3 au from the Sun using a 0.4-m telescope of the International Scientific Optical Network (Nevski et al. 2012). It is a sungrazing comet, which at perihelion, on 2013 Nov. 28.8 UT, passed at just 0.012 au from the Sun (MPEC 2013-Q27). Its orbital elements are consistent with a dynamically new comet, with fresh ices not previously irradiated by sunlight. A worldwide observational campaign has extensively followed this comet from heliocentric distances beyond 4 au (O'Rourke et al. 2013; Li et al. 2013) to disappearance around perihelion (Knight & Battams 2014). C/2013 R1

(Lovejoy, so referred to hereafter) was discovered in September 2013 at  $r_h = 1.94$  au by Terry Lovejoy using a 0.2-m telescope (Guido et al. 2013). This comet reached perihelion on 2013 December 22.7 UT. According to its orbital elements (MPEC 2014-D13), this is not its first perihelion passage.

In this Letter we report IRAM 30m spectroscopic observations of the comets ISON and Lovejoy carried out when they were at heliocentric distances of  $\sim 0.6$  and  $\sim 1$  au, respectively.

## 2. Observations

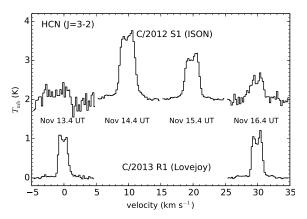
The observations of comets ISON and Lovejoy were carried out with the IRAM 30m telescope during the period of Nov. 13–16, 2013. At these dates (before perihelion for both comets) ISON spanned a heliocentric distance of 0.67–0.58 au and a geocentric distance of 0.93–0.89 au, while Lovejoy was at 1.09–1.06 au from the Sun and 0.43–0.41 au from the Earth. The position of the comets was tracked using the orbital elements from JPL Horizons<sup>1</sup>.

The EMIR 230 GHz dual polarization receiver (Carter et al. 2012) and the FTS spectrometer (Klein et al. 2012) were used to obtain spectra in the frequency ranges 249.0–256.7 GHz and 264.7–272.4 GHz with a spectral resolution of 0.2 MHz (~0.23 km s<sup>-1</sup> if expressed as equivalent radial velocity). Important molecular lines such as HCN J=3-2, HNC J=3-2, HCO<sup>+</sup> J=3-2, PH<sub>3</sub>  $1_0-0_0$ , and various CH<sub>3</sub>OH rotational transitions fall within the spectral range covered. Most of the observations were carried out using the wobbler-switching observing mode, with the secondary mirror nutating by  $\pm 90''$  at a rate of 0.5 Hz. Pointing and focus were regularly checked on

<sup>\*</sup> Based on observations carried out with the IRAM 30 m telescope. IRAM is supported by INSU/CNRS (France), MPG (Germany) and IGN (Spain).

<sup>\*\*</sup> Tables 3 and 4 are available online at http://www.aanda.org and also at the CDS via anonymous ftp to cdsarc.u-strasbg.fr (130.79.128.5) or via http://cdsarc.u-strasbg.fr/viz-bin/qcat?J/A+A/564/L2

See http://ssd.jpl.nasa.gov/horizons.cgi



**Fig. 1.** Monitoring of the HCN J = 3-2 line on ISON and Lovejoy during Nov. 13.4–16.4 UT. Lines are shifted in velocity by multiple integers of 10 km s<sup>-1</sup> and in  $T_{\rm mb}$  by 2 K for a better visualization. The line intensity shows strong time variations in ISON but remains nearly constant from Nov. 13.4 to 16.4 UT in Lovejoy.

Mars and nearby quasars. Weather conditions were rather poor on Nov. 13 and 14, with 6–12 mm of precipitable water vapour (pwv), quite good on Nov. 15 (pwv 1–3 mm), and excellent on Nov. 16 (pwv < 1 mm). The half-power beam width of the IRAM 30 m telescope at the observed frequencies ranges from 8.9 to 9.8", and the pointing error is typically lower than 2". Line intensities were converted from antenna temperature  $T_{\rm A}^*$  to main beam brightness temperature  $T_{\rm mb}$  by dividing by  $B_{\rm eff}/F_{\rm eff}$  (e.g., Kramer 1997), where  $B_{\rm eff}$  is in the range 0.50–0.54 and  $F_{\rm eff}$  is 0.88 at the observed frequencies. The data were reduced using the software GILDAS<sup>2</sup>.

The bright HCN J=3-2 line was observed to monitor cometary activity and to locate the position of maximum molecular emission. In both comets the maximum intensity of the HCN J=3-2 line was found slightly offset from the presumed position of the comet nucleus, at offsets, in (RA, Dec), of (-8'', +4'') for ISON (i.e., in the direction of the tail) and of (0'', +5'') in the case of Lovejoy. Due to the more favourable weather conditions on Nov. 15 and 16, the highest quality data for both comets were acquired during these dates, on Nov. 15.4 UT for ISON and Nov. 16.4 UT for Lovejoy. The  $T_{\rm mb}$  rms noise levels reached, per 0.2 MHz channel, were 0.013–0.017 K for ISON and 0.008–0.010 K for Lovejoy, after averaging the two polarizations.

## 3. HCN monitoring

A strong variation of the HCN J=3-2 intensity was observed in comet ISON during November 13.4-16.4 UT, with a tenfold intensity enhancement from Nov. 13.4 to 14.4 UT and a progressive decline afterwards (see Fig. 1 and Table 1). The outburst of activity of comet ISON on Nov. 14 was reported by various teams observing at different wavelengths. The dramatic increase of the production rate of HCN reported by Biver et al. (2013) and presented here was matched by enhancements in the production rates of other molecules such as OH, CN, and  $C_2$  (Crovisier et al. 2013; Opitom et al. 2013a), an increase in the visual brightness, and the appearance of wings in the coma, which may suggest that the outburst was caused by some splitting of the nucleus (Boehnhardt et al. 2013). Another outburst of activity was reported on Nov. 19 by Opitom et al. (2013b). Whether these outbursts were caused by nucleus splitting, delayed sublimation

**Table 1.** HCN J = 3-2 line parameters and HCN production rates

$r_{ m h}$	Δ	$\int T_{\rm mb} { m d} v^a$	$\Delta v^b$	Q(HCN)		
(au)	(au)	$(K \text{ km s}^{-1})$	$(km s^{-1})$	$(s^{-1})$		
C/2012 S1 (ISON)						
0.67	0.93	0.46(14)	1.5(6)	$6.5 \times 10^{25}$		
0.64	0.92	4.69(3)	2.37(5)	$6.0 \times 10^{26}$		
0.61	0.90	2.87(2)	2.22(4)	$3.6 \times 10^{26}$		
0.58	0.89	1.31(7)	2.21(10)	$1.5 \times 10^{26}$		
C/2013 R1 (Lovejoy)						
1.09	0.43	1.92(3)	1.52(7)	$6.0 \times 10^{25}$		
1.06	0.41	2.06(2)	1.69(4)	$6.1 \times 10^{25}$		
	0.67 0.64 0.61 0.58	(au) (au)  C/2  0.67 0.93  0.64 0.92  0.61 0.90  0.58 0.89  C/20  1.09 0.43	(au) (au) (K km s <sup>-1</sup> ) C/2012 S1 (ISON 0.67 0.93 0.46(14) 0.64 0.92 4.69(3) 0.61 0.90 2.87(2) 0.58 0.89 1.31(7) C/2013 R1 (Lovejo 1.09 0.43 1.92(3)	$ \begin{array}{c ccccccccccccccccccccccccccccccccccc$		

**Notes.** Numbers in parentheses are  $1\sigma$  uncertainties in units of the last digits. <sup>(a)</sup> Additional error due to calibration is estimated to be 10–20%. <sup>(b)</sup> Line width measured as FWHM.

(e.g., Altenhoff et al. 2009), a change in the orientation of the rotation axis, or some other reason is not clear.

In the case of the comet Lovejoy, the intensity of the HCN J=3-2 line remained nearly constant (within 10%) from Nov. 13.4 to 16.4 UT (see Fig. 1 and Table 1).

## 4. Observed molecules

In addition to the bright J = 3-2 HCN line, some other weaker lines were detected in ISON and Lovejoy within the covered frequency range. We restricted the analysis of lines other than J = 3-2 HCN to the dates of more favourable weather conditions, when acquired spectra were significantly more sensitive, i.e., Nov. 15.4 UT for ISON ( $r_h = 0.61$  au) and Nov. 16.4 UT for Lovejoy ( $r_h = 1.06$  au). A plethora of CH<sub>3</sub>OH lines and the J = 3-2 line of HNC were detected in both comets, while the J = 3-2 line of HCO<sup>+</sup> was only detected in ISON. The  $1_0-0_0$  rotational transition of PH<sub>3</sub> at 266.9 GHz was searched for in both comets without success, and here we report upper limits for this P-bearing molecule (see Sect. 4.3). Observed lines are shown in Fig. 2, while line parameters and derived production rates are compiled in Table 2. Some weak unidentified lines were also detected in Lovejoy (see Sect. 4.4).

Line widths are ~2.2 km s<sup>-1</sup> in ISON and ~1.7 km s<sup>-1</sup> in Lovejoy (see Table 2), which imply outflow velocities of 1.1 and 0.85 km s<sup>-1</sup>, respectively, in good agreement with the typical values expected at their heliocentric distances, 0.85 km s<sup>-1</sup>  $(r_h/au)^{-1/2}$  according to Budzien et al. (1994). The line profiles of HCN and HNC are quite similar, but that of HCO+ in ISON seems to be distinct within the limited signal-to-noise ratio (S/N) reached (see Fig. 2). Observations of HCO+ in comet C/1995 O1 (Hale-Bopp) indicate that this product species has a complex and variable spatial and kinematical distribution (Lovell et al. 1998; Milam et al. 2004). The interpretation of HCO+ data in ISON is beyond the scope of this Letter as it would require to model the chemistry and dynamics of the coma.

## 4.1. Methanol: kinetic temperature in the coma

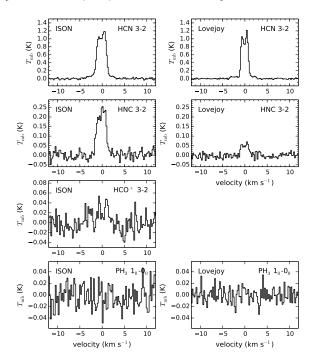
A large number of methanol lines were observed in both comets within the 249–267 GHz range, most of them belonging to the  $J_3$ – $J_2$  series of the  $A^{\pm}$  and  $A^{\mp}$  torsional states (see Table 3). The observed line intensities were used in a non-LTE excitation model (Biver et al. 2006) to derive the gas kinetic temperature in the coma, which resulted in 90 K for ISON at  $r_h = 0.61$  au and 60 K for Lovejoy at  $r_h = 1.06$  au. Production rates derived for methanol imply  $Q(\text{CH}_3\text{OH})/Q(\text{HCN})$  ratios of 12 and 18 for ISON and Lovejoy, respectively, within the typical range

<sup>2</sup> See http://www.iram.fr/IRAMFR/GILDAS

**Table 2.** Observed lines and inferred molecular production rates in comets ISON at  $r_h = 0.61$  au and Lovejoy at  $r_h = 1.06$  au.

Molecule	Transition	ν	$\int T_{\rm mb} { m d} v^a$	$\Delta v^b$	$Q^{c}$	$\int T_{\rm mb} { m d} v^a$	$\Delta v^b$	$Q^{c}$
		(MHz)	$(K \text{ km s}^{-1})$	$(km s^{-1})$	(molecule s <sup>-1</sup> )	$(K \text{ km s}^{-1})$	$(km s^{-1})$	(molecule s <sup>-1</sup> )
			C/2012 S1 (ISON), Nov. 15.4 UT			C/2013 R1	(Lovejoy),	Nov. 16.4 UT
HCN	J = 3-2	265 886.4	2.87(2)	2.22(4)	$3.6 \times 10^{26}$	2.06(2)	1.69(4)	$6.1 \times 10^{25}$
HNC	J = 3-2	271 981.1	0.57(2)	2.21(8)	$6.4 \times 10^{25}$	0.11(2)	1.80(7)	$2.9 \times 10^{24}$
$HCO^{+}$	J = 3-2	267 557.6	0.09(2)	2.9(10)	_			
$CH_3OH^d$	$11_0 - 10_1 \text{ A}^+$	250 507.0	0.132(8)	1.9(2)	$4.3 \times 10^{27}$	0.101(7)	1.5(1)	$1.12 \times 10^{27}$
$PH_3^e$	$1_0 - 0_0$	266 944.5	< 0.036		$< 8.8 \times 10^{26}$	< 0.019		$< 5.9 \times 10^{25}$

**Notes.** Numbers in parentheses are  $1\sigma$  uncertainties in units of the last digits. (a) Additional error due to calibration is estimated to be 10-20%. (b) Line width measured as FWHM. (c) Production rates are computed using the model by Biver et al. (2006). For PH<sub>3</sub> we proceeded similarly to NH<sub>3</sub> in Biver et al. (2012). (d) The full list of CH<sub>3</sub>OH lines detected is given in Table 3. (e)  $3\sigma$  upper limit.

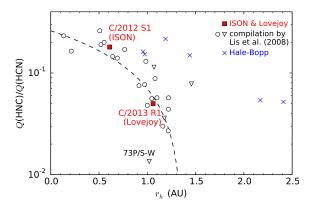


**Fig. 2.** Molecular lines observed in comet ISON on Nov. 15.4 UT (*left panels*) and in comet Lovejoy on Nov. 16.4 UT (*right panels*). The HCN J = 3-2 and HNC J = 3-2 lines are clearly detected in both comets, the HCO<sup>+</sup> J = 3-2 line only in comet ISON, and the PH<sub>3</sub>  $1_0$ – $0_0$  line is not detected in either of the comets.

of values observed in other comets (e.g., Crovisier et al. 2009; Bockelée-Moryan 2011).

## 4.2. HNC/HCN ratio

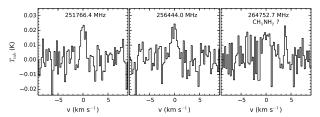
Hydrogen isocyanide (HNC), a metastable isomer of HCN, was first detected in comet C/1996 B2 (Hyakutake) by Irvine et al. (1996) and has later on been observed in about a dozen of comets. These observations have served to establish that the HNC/HCN ratio in comets increases as the heliocentric distance reduces, as observed in comet Hale-Bopp (Biver et al. 1997; Irvine et al. 1998) and indicated by the empirical correlation found by Lis et al. (2008) in a sample of 14 moderately active comets spanning heliocentric distances in the range 0.1-1.5 au (see Fig. 3). It is remarkable that most HNC/HCN ratios derived in comets can be accounted for by a simple expression that solely depends on  $r_h$  and not on any intrinsic property of the comet. A few comets show important deviations from this simple relation, however. For example, in the case of 73P/Schwassmann-Wachmann (fragment B) the sensitive upper limit obtained at



**Fig. 3.** HNC/HCN ratios observed in comets as a function of heliocentric distance. Values derived in comets ISON and Lovejoy are indicated as red squares. We also show the values (empty circles) and upper limits (empty triangles) derived in the sample of 14 moderately active comets compiled by **Lis et al.** (2008). The empirical relation found by these authors is shown as a dashed line. Values derived at various heliocentric distances before perihelion in comet Hale-Bopp (Biver et al. 1997; Irvine et al. 1998) are also shown as blue crosses.

 $r_{\rm h} \sim 1$  au (Lis et al. 2008) points to a HNC/HCN ratio well below that of other comets at similar heliocentric distances. Moreover, for Hale-Bopp the HNC/HCN ratio derived at heliocentric distances beyond 2 au is much higher than expected from extrapolating the behaviour of most other comets. In any case, the variation of the HNC/HCN ratio with  $r_{\rm h}$  indicates that HNC is not directly released from the cometary nucleus but formed in situ in the coma, although its exact origin is still a mystery. It has been argued that HNC may be formed by thermal degradation of organic polymers or dust grains (Rodgers & Charnley 2001; Lis et al. 2008), although the high HNC/HCN ratios observed in Hale-Bopp at large heliocentric distances seem to require a different source of HNC. Formation of HNC by radiative isomerization from HCN (Villanueva et al. 2013) does not seem efficient enough to explain the observed HNC/HCN ratios.

The HNC/HCN ratio in ISON is 0.18 at  $r_h = 0.61$  au, while in Lovejoy this ratio is significantly lower, 0.05 at  $r_h = 1.06$  au (see Fig. 3). These values agree with those found in most previous comets and are consistent with a higher HNC/HCN ratio at shorter heliocentric distances. Moreover, the values derived in ISON and Lovejoy match quite well the empirical linear relation found by Lis et al. (2008) between the HNC/HCN ratio and  $r_h$ , which strengthens the idea that in most comets the HNC/HCN ratio is mainly controlled by the heliocentric distance and not by intrinsic properties of the comet.



**Fig. 4.** Unidentified lines in comet Lovejoy at  $r_h = 1.06$  au.

# 4.3. PH<sub>3</sub> upper limits

Phosphine is most likely one of the major carriers of phosphorus in comets, although detecting it remains challenging. The search for it in the very active comet Hale-Bopp while it was at 3.6 au from the Sun yielded an upper limit to  $Q(PH_3)$  of  $3.2 \times 10^{26}$  molecule s<sup>-1</sup> (Crovisier et al. 2004), which corresponds to  $PH_3/CO < 3.2 \times 10^{-3}$  at 3.6 au (Biver et al. 1997) and translates into  $PH_3/H_2O < 7.4 \times 10^{-4}$  at 1 au (Bockelée-Morvan et al. 2000), that is, somewhat above the solar P/O elemental ratio of  $5.2 \times 10^{-4}$  (Asplund et al. 2009).

Our search for PH<sub>3</sub> in comets ISON and Lovejoy results in PH<sub>3</sub>/HCN ratios <2.4 and <1, respectively (see Table 2). Water production rates for these two comets during the relevant dates are not yet accurately known, but based on preliminary estimates (Bonev et al. 2013; Combi et al. 2013)  $Q(H_2O) \sim 1-3 \times 10^{29}$  molecule s<sup>-1</sup> for ISON on Nov. 15.4 UT, which implies an HCN/H<sub>2</sub>O ratio in the range 0.12–0.36%. Adopting a mean HCN/H<sub>2</sub>O ratio of 0.2% for ISON and Lovejoy, the resulting PH<sub>3</sub>/H<sub>2</sub>O ratios are <5 × 10<sup>-3</sup> and <2 × 10<sup>-3</sup>, respectively. These values are 10 and 4 times higher than the solar P/O elemental ratio and thus do not allow us to conclude whether or not PH<sub>3</sub> is the main phosphorus species in these comets.

#### 4.4. Unidentified lines and tentative assignment

In addition to the lines of HCN, HNC, and CH<sub>3</sub>OH observed in comet Lovejoy, a few weak lines with no obvious assignment were also observed in the spectral range covered (see Table 4 and Fig. 4). One of these lines coincides in frequency with the rotational transition 7<sub>2,3</sub>–7<sub>1,2</sub> of methylamine (CH<sub>3</sub>NH<sub>2</sub>), an organic molecule that is a plausible cometary constituent. In fact, this species has been detected in samples of comet Wild 2 returned by the mission Stardust (Glavin et al. 2008). Accurate rotational spectroscopic data for this molecule was available just recently (Ilyushin et al. 2005), preventing a search for it in previous comets such as Hale-Bopp (Crovisier et al. 2004). The inferred production rate of CH<sub>3</sub>NH<sub>2</sub> in Lovejoy is  $3-4 \times 10^{26}$ molecule s<sup>-1</sup>, that is, well above that of HCN. We note, however, that detailed LTE excitation calculations of CH<sub>3</sub>NH<sub>2</sub> in the coma of Lovejoy predict that within the spectral range covered there should be a line at 255 997.8 MHz with a similar intensity to the tentatively identified one at 264 752.7 MHz. This line is lacking in our observed spectra although it might be within the noise. The low S/N of the observed line at 264 752.7 MHz and the lack of the line at 255 997.8 MHz in our data make us to be cautious about the tentative identification of CH<sub>3</sub>NH<sub>2</sub> in Lovejoy.

## 5. Summary

We have carried out IRAM 30m observations of the comets C/2012 S1 (ISON) and C/2013 R1 (Lovejoy) at heliocentric

distances of  $\sim$ 0.6 and  $\sim$ 1 au, respectively. We detected HCN, HNC, and CH<sub>3</sub>OH in both comets, plus the ion HCO<sup>+</sup> in ISON and a few weak unidentified lines in Lovejoy, one of which might be assigned to CH<sub>3</sub>NH<sub>2</sub>. A tenfold enhancement of the HCN J=3–2 line was observed in comet ISON within less than 24 h on Nov. 14, indicating an outburst of activity whose origin could be related to nucleus splitting. The large number of CH<sub>3</sub>OH lines observed was used to derive kinetic temperatures in the coma of 90 and 60 K in ISON and Lovejoy, respectively. The HNC/HCN ratios derived, 0.18 in ISON and 0.05 in Lovejoy, are similar to those found in most previous comets and are consistent with an enhancement of HNC as the comet approaches the Sun. PH<sub>3</sub> was also searched for unsuccessfully in both comets so that only upper limits to the PH<sub>3</sub>/H<sub>2</sub>O ratio 4–10 times above the solar P/O elemental ratio were derived.

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#### References

Altenhoff, W. J., Kreysa, E., Menten, K. M., et al. 2009, A&A, 495, 975
Asplund, M., Grevesse, N., Sauval, A. J., & Scott, P. 2009, ARA&A, 47, 481
Biver, N., Bockelée-Morvan, D., Colom, P., et al. 1997, Science, 275, 1915
Biver, N., Bockelée-Morvan, D., Crovisier, J., et al. 2006, A&A, 449, 1255
Biver, N., Crovisier, J., Bockelée-Morvan, D., et al. 2012, A&A, 539, A68
Biver, N., Agúndez, M., Santos-Sanz, P., et al. 2013, Central Bureau Electronic Telegrams, 3711, 2

Bockelée-Morvan, D. 2011, IAU Symp., 280, 261
Bockelée-Morvan, D., Lis, D. C., Wink, J. E., et al. 2000, A&A, 353, 1101
Bockelée-Morvan, D., & Crovisier, J. 2002, Earth Moon Planets, 89, 53
Boehnhardt, H., Tubiana, C., Oklay, N., et al. 2013, Central Bureau Electronic Telegrams, 3715, 1

Bonev, B. P., DiSanti, M. A., Gibb, E. L., et al. 2013, Central Bureau Electronic Telegrams, 3720, 2

Budzien, S. A., Festou, M. C., & Feldman, P. D. 1994, Icarus, 107, 164
Carter, M., Lazareff, B., Maier, D., et al. 2012, A&A, 538, A89
Combi, M. R., Bertaux, J.-L., Quemerais, E., et al. 2013, IAU Circ., 9266, 1
Crovisier, J., Bockelée-Morvan, D., Colom, P., et al. 2004, A&A, 418, 1141
Crovisier, J., Biver, N., Bockelée-Morvan, D., et al. 2009, Earth Moon Planets, 105, 267

Crovisier, J., Colom, P., Biver, N., & Bockelée-Morvan, D. 2013, Central Bureau Electronic Telegrams, 3711, 1

Glavin, D. P., Dworkin, J. P., & Sanford, S. A. 2008, Meteor. Planet. Sci., 43, 399

Guido, E., Howes, N., Sato, H., et al. 2013, Central Bureau Electronic Telegrams, 3649, 1

Ilyushin, V. V., Alekseev, E. A., Dyubko, S. F., et al. 2005, J. Mol. Spec., 229, 170

Irvine, W. M., Bockelée-Morvan, D., Lis, D. C., et al. 1996, Nature, 383, 418 Irvine, W. M., Bergin, E. A., Dickens, J. E., et al. 1998, Nature, 393, 547 Klein, B., Hochgürtel, S., Krämer, I., et al. 2012, A&A, 542, L3 Knight, M. M., & Battams, K. 2014, ApJ, 782, L37

Kramer, C. 1997, Calibration of spectral line data at the IRAM 30 m radio telescope, IRAM Internal Report

Li, J.-Y., Kelley, M. S. P., Knight, M. M. et al. 2013, ApJ, 779, L3
Lis, D. C., Bockelée-Morvan, D., Boissier, J., et al. 2008, ApJ, 675, 931
Lovell, A. J., Schloerb, P., Dickens, J. E., et al. 1998, ApJ, 497, L117
Milam, S. N., Savage, C., Ziurys, L. M., & Wyckoff, S. 2004, ApJ, 615, 1054
Nevski, V., Novichonok, A., Burhonov, O., et al. 2012, Central Bureau Electronic Telegrams, 3238, 1

Opitom, C., Jehin, E., Manfroid, J., & Gillon, M. 2013a, Central Bureau Electronic Telegrams, 3711, 3

Opitom, C., Jehin, E., Manfroid, J., & Gillon, M. 2013b, Central Bureau Electronic Telegrams, 3719, 2

O'Rourke, L., Bockelée-Morvan, D., Biver, N., et al. 2013, A&A, 560, A101 Rodgers, S. D., & Charnley, S. B. 2001, MNRAS, 323, 84

Villanueva, G. L., Magee-Sauer, K., & Mumma, M. J. 2013, J. Quant. Spectr. Rad. Transf., 129, 158

**Table 3.** Observed lines of CH<sub>3</sub>OH in comets ISON at  $r_h = 0.61$  au and Lovejoy at  $r_h = 1.06$  au.

Transition	ν	$\int T_{\rm mb} { m d} v^a$	$\Delta v^b$	$\int T_{ m mb} { m d} v^a \qquad \Delta v^b$
	(MHz)	$(K \text{ km s}^{-1})$	$(km s^{-1})$	$(K \text{ km s}^{-1}) \text{ (km s}^{-1})$
		C/2012 S1	(ISON)	C/2013 R1 (Lovejoy)
$15_3 - 15_2 A^{\mp}$	249 419.9	0.023(6)	2.4(6)	
$13_3 - 13_2 A^{\mp}$	250 291.2	0.047(8)	1.4(4)	
$11_0 - 10_1 \text{ A}^+$	250 507.0	0.132(8)	1.9(2)	0.101(7) 1.5(1)
$12_3 - 12_2 A^{\mp}$	250 635.2	0.057(8)	1.9(2)	
$11_3 - 11_2 A^{\mp}$	250 924.4	0.059(8)	1.8(3)	0.038(7) 1.6(2)
$10_3 - 10_2 \text{ A}^{\mp}$	251 164.1	0.075(10)	2.4(3)	0.034(5) 1.5(2)
$9_3 - 9_2 A^{\mp}$	251 359.9	0.070(8)	1.9(3)	0.063(5) 1.2(1)
$8_3 - 8_2 A^{\mp}$	251 517.3	0.126(8)	1.7(2)	0.072(5) 1.4(1)
$7_3 - 7_2 A^{\mp}$	251 641.7	0.118(8)	2.2(2)	0.088(5) 1.4(1)
$6_3 - 6_2 \text{ A}^{\mp}$	251 738.5	0.139(8)	2.2(3)	0.116(5) 1.5(1)
$5_3 - 5_2 A^{\mp}$	251 811.9	0.088(8)	1.8(2)	0.110(5) 1.5(1)
$4_3 - 4_2 A^{\mp}$	251 866.6	0.090(10)	1.8(3)	0.098(7) 1.5(1)
$5_3 - 5_2 A^{\pm}$	251 890.9	0.129(10)	2.1(2)	0.121(7) 1.7(1)
$6_3 - 6_2 A^{\pm}$	251 895.7	0.141(10)	2.2(2)	0.102(7) 1.4(1)
$4_3-4_2 \text{ A}^{\pm}$	251 900.5	0.129(10)	2.1(2)	0.100(7) 1.5(1)
$3_3 - 3_2 A^{\mp}$	251 905.8	0.084(8)	1.8(3)	0.061(8) 1.4(3)
$3_3 - 3_2 A^{\pm}$	251 917.0			0.062(8) 1.7(3)
$7_3 - 7_2 A^{\pm}$	251 923.6	0.108(10)	2.3(3)	0.095(7) 1.5(1)
$8_3 - 8_2 A^{\pm}$	251 984.7	0.077(8)	2.1(3)	0.064(7) 1.7(2)
$9_3 - 9_2 A^{\pm}$	252 090.4	0.089(10)	2.1(2)	0.051(7) 1.3(2)
$10_3 - 10_2 \text{ A}^{\pm}$	252 252.8	0.097(10)	2.2(2)	0.036(5) 1.1(1)
$11_3 - 11_2 \text{ A}^{\pm}$	252 485.6	0.095(13)	2.9(6)	0.036(7) 1.2(4)
$12_3 - 12_2 A^{\pm}$	252 803.4	0.053(12)	1.8(3)	0.016(5) 0.9(3)
$2_{+0}-1_{-1}$ E	254 015.3			0.061(8) 2.1(4)
$6_{+1}$ – $5_{+2}$ E	265 289.6			0.060(7) 1.9(3)
$5_{+2}$ $-4_{+1}$ E	266 838.1	0.17(2)	2.1(2)	0.184(9) 1.5(1)
$9_{+0}$ $-8_{+1}$ E	267 403.4	0.077(12)	1.9(3)	0.071(7) 1.6(2)

**Notes.** Numbers in parentheses are  $1\sigma$  uncertainties in units of the last digits. <sup>(a)</sup> Additional error due to calibration is estimated to be 10–20%. <sup>(b)</sup> Line width measured as FWHM.

**Table 4.** Unidentified lines in comet Lovejoy at  $r_h = 1.06$  au

ν (MHz)	$\int_{\rm C} T_{\rm mb} dv$ (K km s <sup>-1</sup> )	$\Delta v$ (km s <sup>-1</sup> )	S/N <sup>a</sup>	Note
251 766.4	0.026(6)	1.0(2)	4.3	
256 444.0	0.034(7)	1.5(3)	4.9	
264 752.7	0.029(7)	1.4(4)	4.1	$CH_3NH_2 7_{2,3}-7_{1,2} ?$

**Notes.** Numbers in parentheses are  $1\sigma$  uncertainties in units of the last digits. (a) Line area signal-to-noise ratio.