New Insights into the Chemical Composition of Five Oort Cloud Comets after Re-analysis of Their Infrared Spectra

Manuela Lippi1,2, Geronimo L. Villanueva1, Michael J. Mumma1, Maria N. Camarca1,2, Sara Faggi1,2, and Lucas Paganini3

1 NASA Goddard Space Flight Center, 8800 Greenbelt Road, Greenbelt, MD 20771, USA; mlippi@american.edu, manuela.lippi@nasa.gov
2 American University, Department of Physics, 4400 Massachusetts Avenue NW, Washington, DC 20016, USA
3 NASA Headquarters, 300 E Street SW, Washington, DC 20546, USA

Received 2019 December 4; revised 2020 January 28; accepted 2020 January 29; published 2020 March 18

Abstract

We present revised results for the main molecular species in five Oort Cloud comets observed with near-infrared echelle grating spectrometer (NIRSPEC) at the Keck Observatory between 1999 and 2012 (C/1999 S4 (LINEAR), C/2001 A2 (LINEAR), C/2007 W1 (Boattini), C/2012 F6 (Lemmon), and C/2012 S1 (ISON)). The re-evaluation of these data shows the improvement of results in some of the data sets, in particular for comets observed and analyzed before the advent of new and revised fluorescence models and terrestrial retrieval methods introduced since 2011. We observe significant improvements in the resulting rotational temperatures and the production rates for all species, and in mixing ratios of minor species (relative to water). The re-analysis also allowed us to quantify species not analyzed previously, mostly due to the lack of molecular models (e.g., ammonia and formaldehyde). We note, however, that the improvement of these revised values is less substantial for comets observed (and/or analyzed) since 2010.

Unified Astronomy Thesaurus concepts: Comets (280); Astrobiology (74); Solar system formation (1530)

1. Introduction

Cometary nuclei are cryogenically preserved relics from the early solar system. Their compositional properties (molecular abundances, isotopic ratios, spin temperatures) are directly relevant to understanding the processes affecting material during solar system formation; moreover, they could test the hypothesis that small icy bodies have delivered prebiotic matter to early Earth. Current theories suggest that cometary nuclei probably formed from the ice and dust present in the protoplanetary disk at distances between 5 and 30 au from the proto-Sun; after their formation, they were ejected to their current reservoirs—the Kuiper Belt (KB) and the Oort cloud (OC)—as a result of gravitational interactions with the migrating giant planets (Gomes et al. 2005; Morbidelli et al. 2007). Even if diverse processes (such as energetic radiation and collisions) partially altered the chemical fingerprints of nucleus surface layers during their lifetime prior to injection into the inner solar system, the bulk nucleus is thought to preserve certain local chemical and mineralogical properties related to the protoplanetary disk where they formed. Our study seeks an accurate chemical classification of comets, to unveil important information regarding the origins and evolution of the early solar system and to understand the true heritage of these icy bodies.

A powerful technique to sample the organic composition of comets is the use of high-resolution spectroscopy in the infrared region between about 3 and 5 μm, where it is possible to sample emission lines produced by solar-pumped fluorescence of molecules released directly from the nucleus, such as H2O, CH4, C2H6, C2H2, HCN, NH3, CH3OH, H2CO, and CO. With this technique, we can investigate cosmogonic indicators like molecular abundances, isotopic ratios, ortho-para ratios, and spin temperatures that are expected to remain unaltered since the comet’s formation. Since 1996, high-resolution (∆λ/Δλ ≥ 25,000) spectra of comets in the infrared region were acquired using ground-based echelle spectrometers. We have created a database collecting all spectra obtained from more than 60 comets using state-of-the-art high-resolution infrared spectrometers (e.g., IRTF/CSHELL, Keck/near-infrared echelle grating spectrometer (NIRSPEC) and VLT/CRIRES). The correct modeling and analysis of these data is essential to interpreting important clues regarding the aforementioned cosmogonic indicators in comets, and to constraining the conditions present where (and when) a specific comet formed.

Recent taxonomic reviews (see, Mumma & Charnley 2011; Dello Russo et al. 2016; Bockelée-Morvan & Biver 2017) are based on primary volatiles in about 30 comets and have revealed a wide compositional diversity, but it is clear that an understanding of these bodies is far from complete. Some infrared results published before 2010 may contain systematic inaccuracies introduced by the use of immature algorithms and/or incomplete molecular models used to interpret the fluorescence excitation in comets.

In particular, fluorescence models for some individual ro-vibrational bands have evolved with time, affecting the production rates derived from measured line fluxes. In the past, certain molecular models made use of empirical line strengths when calculating the fluorescence efficiencies (g-factors) to interpret the infrared fluorescence excitation in comets. While these models were in part accurate, they were sometimes limited to only a few spectral lines and also did not fully describe the complexity of some observed spectra, often under-estimating or ignoring fluorescence cascades. The discovery of H2O hot-band emissions in 1P/Halley with the Kuiper Airborne Observatory revealed their importance (Weaver et al. 1986), and an early model of H2O fluorescence spectra included several hot bands (e.g., Bockelée-Morvan & Crovisier 1989). The (later) need to identify a method for the direct detection of cometary water from ground-based
observatories led to the use of hot-band emission as a way to circumvent telluric extinction (Mumma et al. 1995); its first general application used the 2 μm hot bands to characterize water in comet C/1996 B2 Hyakutake (Mumma et al. 1996). This initial success, and the team’s serendipitous detection of H2O hot-band emission near 4.7 μm in Hyakutake, led to the extended use of water hot bands in C/1995 O1 (Hale–Bopp) and later comets (Dello Russo et al. 2005). Searches for trace gases (HCN, H2CO, CH3OH, CH4, C2H2, C3H8) emphasized their fundamental bands (e.g., HCN, Magee-Sauer et al. 2002; H2CO, DiSanti et al. 2006; CH4, Gibb et al. 2003), leading to successful detections and increasingly robust interpretations. But, they too underwent successive improvements and updates as new band analyses emerged.

Since 2011, realistic quantum band models have been developed for many species, including complete line lists for specific vibrational bands, updated energy tables, and corrections for the Swings effect (i.e., the dependence on heliocentric velocity; e.g., Villanueva et al. 2011b, 2012b). Figure 1 shows an example of the remarkable differences between cometary fluorescence models before and after 2011. By providing more precise g-factors and including weak lines that were not considered in some of the previous analyses, these models now allow investigation of the spectra with unprecedented accuracy, thus enabling retrieval of more precise rotational temperatures. An improvement between predicted and observed line fluxes translates to a lower relative error for the rotational temperature (and consequently, for the temperature-dependent g-factors) and retrieved production rates. The development of quantum band models for many molecular species revealed also the remarkable complexity present in many spectral regions. This has increased the ability to recognize blended lines, which otherwise would lead to inaccurate production rates and mixing ratios (MR)—especially important for spectrally dense regions such as the CH-stretch near 3.32–3.54 μm. Furthermore, some molecules were not investigated in some comets analyzed before 2002, owing to the lack of specific molecular models (e.g., NH3 or H2CO), for instance, in comets C/1999 S4 (LINEAR) and C/2001 A2 (LINEAR); here, we provide the first analysis of NH3 and H2CO in them.

**Figure 1.** Example of the evolution of the molecular models used to interpret fluorescence in comets before (upper panel) and after (lower panel) 2011. The x-axis corresponds to the spectral region between 3050 and 2800 cm⁻¹, while the y-axis corresponds to molecular line fluorescence efficiencies scaled by typical molecular abundances and terrestrial transmittance (for Maunakea, HI). In the upper panel empirical g-factors corresponding to the CH3OH-v3 (purple), C2H6-v3 (cyan), and CH4-v3 (green) ro-vibrational transitions are shown. The same colors are used to represent full quantum molecular models for the same molecules considering also the CH3OH-v2 and C2H6-v5 ro-vibrational transitions; in the same panel H2CO (sand), CH3D (brown), and CH4 (red) quantum molecular models are also shown. References to the models are: C2H6–Mumma et al. 1996, Dello Russo et al. 2001, Villanueva et al. 2011b, Radeva et al. 2011; CH3OH–Reuter et al. 1992, Bockelée-Morvan et al. 1995, Villanueva et al. 2012c, DiSanti et al. 2013; CH4–Gibb et al. 2003, Villanueva et al. 2012c; H2CO–Villanueva et al. 2012c, DiSanti et al. 2006; CH3D–Gibb et al. 2013; C2H4–Villanueva et al. 2012c.
We recently updated our data reduction procedures used for the analysis of ground-based observations, which have greatly improved the spectral calibration through improved modeling of the Earth’s atmospheric transmittance and thus a better assessment of the terrestrial corrections needed for observed cometary spectra. In the past 20 years, different radiative transfer models have been used to synthesize the terrestrial atmospheric transmittance at high spectral resolution: the Spectrum Synthesis Program accessing HITRAN 1992 (Kunde & Maguire 1974; Rothman et al. 1992), the General Line-by-Line atmospheric transmittance and radiance model (GENLN; Edwards 1992), and the Line-By-Line Radiative Transfer Model (Clough et al. 2005), models that were further improved with the incorporation of complete and comprehensive databases for water (Villanueva et al. 2012b), ethane (Villanueva et al. 2011b), and carbon dioxide (Villanueva et al. 2008). We now use the Planetary and Universal Model of Atmospheric Scattering (PUMAS; Villanueva et al. 2018). PUMAS uses realistic profiles from the latest atmospheric database produced by NASA’s Modern-Era Retrospective Analysis for Research and Applications, Version 2 (MERRA-2; Clough et al. 2005, 2016), the General Line-by-Line atmospheric transmittance and radiance model (GENLN; Edwards 1992, 2001 A2, Villanueva et al. 2008), and the latest radiative transfer methods and spectroscopic parameters to calculate a line-by-line, layer-by-layer, radiative transfer model for the terrestrial atmosphere under the specific observational conditions.

Considering that data analysis techniques and molecular and atmospheric models have evolved and improved greatly since 1996, a chemical classification of comets may be affected by systematic uncertainties introduced by different reduction and retrieval approaches. This is expected to impact mostly comets that were observed before 2011—when we introduced the new analysis approaches—which constitute the majority of targets in our database (see Figure 2).

Here, we present updated rotational temperatures and production rates (and MR relative to water) for five OC comets (C/1999 S4 (LINEAR), C/2001 A2 (LINEAR), C/2007 W1 (Boattini), C/2012 F6 (Lemmon), and C/2012 S1 (ISON), hereafter 99S4, 01A2, 07W1, 12F6, and 12S1, respectively), using data selected from our rich archival data set. By the re-analysis of five OC comets, we seek an initial evaluation to quantify these inaccuracies. The comparison of current and earlier results for 07W1, 12F6, and 12S1 confirm the validity of the current reductions, while the current results for 99S4 and 01A2 present updated or even entirely new values for them. Thanks to the aforementioned improvements in the data retrieval process, our re-analysis of these spectra demonstrates that we can now unlock new and improved information from these data sets, especially for comets observed and analyzed prior to 2011.

2. Data Acquisition and Reduction

The data presented in this paper were obtained with NIRSPEC at the W. M. Keck Observatory (McLean et al. 1998), located on Maunakea, Hawai. In Table 1, we summarize the observing logs for the five comets along with a list of sampled molecules. For more details, we refer the reader to the original publications: Mumma et al. (2001) for 99S4, Magee-Sauer et al. (2008) and Gibb et al. (2007) for 01A2, Villanueva et al. (2011a) for 07W1, Paganini et al. (2014) for 12F6, and DiSanti et al. (2016) for 12S1.

We processed all data sets in a systematic way using semi-automated tools to improve processing speed and minimize possible human errors. These tools include the latest procedures for flat-fielding, removal of high dark current pixels and cosmic ray hits, along with spatial and spectral straightening with milli-pixel precision. Spectral calibration and compensation for telluric absorption is achieved by comparing the data with highly precise atmospheric radiance and transmittance models obtained with PUMAS. Flux calibration was obtained using the archived observations of a suitable standard star (observed closely in time with the comet) and our current data reduction algorithms.

To retrieve rotational temperatures ($T_{\text{rot}}$) and production rates ($Q$) we performed two different and independent analyses: a $\chi^2$ minimization technique (using a Levenberg–Marquardt fitting algorithm) and a correlation analysis (for more details on these methodologies see Villanueva et al. 2008 and Boney 2005, respectively). It has been demonstrated that these two methods are highly complementary, and they converge to a unique solution for $T_{\text{rot}}$, validating the robustness of the retrieval approach (see Boney et al. 2013).

Once $T_{\text{rot}}$ is determined, we calculate line production rates ($Q_{\text{line}}$) using

$$Q_{\text{line}} = GF \frac{4\pi \Delta F_{\text{line}}}{\tau_{\text{mol},f(x)} g_{\text{line}}},$$

where $F_{\text{line}}$ is the line flux (W m$^{-2}$, corrected for telluric transmittance), $\Delta$ is the geocentric distance (au), $\tau_{\text{mol}}$ is the molecular photodissociation lifetime of the considered molecule (in seconds and calculated for a heliocentric distance of 1 au), and $f(x)$ is a function representing the fraction of all molecules in the coma contained in the beam (spherically symmetric uniform outflow is assumed, see the appendix in Hoban et al. 1991); $g_{\text{line}}$ is the line g-factor (W molecule$^{-1}$) calculated at the correct rotational temperature (and for a heliocentric distance of 1 au), while $GF$ is a growth factor, accounting for slit losses and aperture effects, and derived by comparing the column abundance measured at discrete nucleocentric distances with outflow and photolysis models for the molecule in question (for detailed discussions of the Q-curve formalism see Villanueva et al. 2011a; Appendix B2 in Boney et al. 2006; Dello Russo et al. 1998; Mumma et al. 2003). The final production rate for a certain molecular species is computed as the weighted average of total production rates resulting from individual emission lines.

We report rotational temperatures, production rates, and MR of (minor) volatile species with respect to water. For detections, the uncertainty in the production rate is taken as the larger of the stochastic and standard noise contributions; statistical uncertainties are then propagated quadratically. If lines are not clearly detected for a given molecule, we provide upper limits at $3\sigma$, calculated as three times the uncertainties retrieved through the covariance matrix of the Levenberg–Marquardt fitting algorithm scaled for the goodness of the fit (i.e., the square root of the reduced $\chi^2$).

3. Results and Comparison

3.1. C/1999 S4 (LINEAR)

Comet C/1999 S4 was discovered on 1999 September 27 (Durig et al. 1999), and after several outbursts it was declared extinct in 2000 mid-August. The retrieval of rotational temperatures and production rates for this comet was impacted.
by an unusually large water content in Earth’s atmosphere during the observing night, resulting in low transmittance in some spectral regions. Moreover, the comet showed a very bright dust continuum but weak emission lines. Even so, we identify multiple water lines resulting in a rotational temperature of \((75 \pm 5)\) K, and we measure different water production rates depending on the used setting. These measurements are consistent with an exponential decrease in the water production rate over time (see Figure 3), possibly related to the peculiar outgassing behavior of comet 99S4, which was characterized by the significant increase/decrease of its activity before disruption (e.g., a minor outburst on July 13; Bockelée-Morvan et al. 2001; Farnham et al. 2001, and references therein).

Unfortunately, we were not able to verify that other molecules exhibited a similar behavior.

In addition to water, we detect C2H6, C2H4, HCN, and CO, and retrieve \((3\sigma)\) upper limits for NH3, C2H5, H2CO, and CH3OH. Since water showed a strong variation during the night, our MR are calculated using the individual H2O production rates, depending on the considered setting. Production rates and MR (with respect to water) are summarized in Table 2, and an example of the extracted spectra for comet 99S4 is shown in Figure 4, panel A.

Our results differ in many ways from those presented in Mumma et al. (2001; see Figure 5 and Tables 3–5), owing largely to the maturation of molecular fluorescence models and

---

**Figure 2.** Observations through time of comets with selected infrared spectrometers (CSHELL in red, NIRSPEC in cyan, CRIRES in green). The pies in the upper part of the figure represent the percent of comets observed before (darker color) and after (lighter color) 2011, for each instrument and considering the total (gray pie). The lower graphic shows the number of comets observed for each year, from 1996 until 2017. The acronyms and full comet names are: 22P: 22P/Kopff, 95O1: C/1995 O1 Hale Bopp, 96B2: C/1996 B2 Hyakutake, 96Q1: C/1996 Q1 Tabur, 21P: 21P/Giacobini-Zinner, 99H1: C/1999 H1 Lee, 99S4: C/1999 S4 LINEAR, 9P: 9P/Tuttle, 99T1: C/1999 T1 McNaught, 00WM1: C/2000 WM1 LINEAR, 01A2: C/2001 A2 LINEAR, 19P: 19P/Tuttle, 153P: 153P/Ikeya-Zhang, 02T7: C/2002 T7 LINEAR, 01RX: C/2001 RX LINEAR, 02X5: C/2002 X5 Kudo-Fujikawa, 78P: 78P/Gehrels 2, 03K4: C/2003 K4 LINEAR, 04Q2: C/2004 Q2 Machholz, 73P: 73P/Schwassmann–Wachmann (B–C), 8P: 8P/Tuttle, 17P: 17P/Holmes, 06P1: C/2006 P1 McNaught, 6P: 6P/d’Arrest, 07N3: C/2007 N3 Lulin, 07W1: C/2007 W1 Boattini, 06W3: C/2006 W3 Christensen, 07Q3: C/2007 Q3 Siding Spring, 10P: 10P/Tuttle, 29P: 29P/Schwassmann–Wachmann 1, 81P: 81P/Wild 2, 103P: 103P/Hartley 2, 09P1: C/2009 P1 Garradd, 10G2: C/2010 G2 Hill, 45P: 45P/Honda–Mrkos–Pajdušáková, 206P: 206P/McNaught, 10S1: C/2010 S1 LINEAR, 11Q4: C/2011 Q4 Swan, 12J1: C/2012 J1 Catalina, 12K5: C/2012 K5 LINEAR, 12S1: C/2012 S1 ISON, 11L4: C/2011 L4 Pan-STARRS, 12F6: C/2012 F6 Lemenon, 13R1: C/2013 R1 Lovejoy, 13A1: C/2013 A1 Siding Spring, 12K1: C/2012 K1 Pan-STARRS, 13V5: C/2013 V5 Oukaimeden, 14E2: C/2014 E2 Jacques, 332P: 332P/Ikeya Murakami, 13US: C/2013 US10 Catalina, 13X1: C/2013 X1 Pan-STARRS, 14Q2: C/2014 Q2 Lovejoy, 252P: 252P/LINEAR, 14S2: C/2014 S2 Pan-STARRS, 14W2: C/2014 W2 Pan-STARRS, 41P: 41P/Tuttle–Giacobini–Kresák, 14E2: C/2014 E2 Jacques, 15V2: C/2015 V2 Johnson.
Note. $R_\odot$ is the heliocentric distance of the comet, $V_s$ is the comet–Sun relative velocity, $\Delta$ is the geocentric distance, and $V_A$ is the topocentric velocity; AM is the airmass. The values are given for the midpoint of the observing time interval.

of data reduction algorithms. The new quantum molecular models and the updated atmospheric models play important roles in the updated results for this comet. The ability to sample multiple lines of water yielded a higher rotational temperature (+50%), and distinct production rates for the three settings used. Previously, Mumma et al. (2001) identified and used two water lines in the MW setting and assumed a fixed $T_{\text{rot}}$ of 50 K, based on observations of only eight comets before 99S4. They did not reduce water lines from the KL1 and KL2 settings.

| Date  | Setting | Principal Molecules Sampled | $R_\odot$ (au) | $V_s$ (km s$^{-1}$) | $\Delta$ (au) | $V_A$ (km s$^{-1}$) | AM  | Slit (arcsec) |
|-------|---------|-----------------------------|---------------|---------------------|-------------|---------------------|-----|---------------|
| C/1999 S4 (LINEAR) |
| 2000 Jul 13 | KL1 | H$_2$O, CH$_3$OH, C$_2$H$_6$ | 0.804 | −10.33 | 0.547 | −54.58 | 2.697 | 0.72 |
| | KL2 | H$_2$O, HCN, C$_2$H$_2$, NH$_3$, CH$_4$, H$_2$CO | 0.804 | −10.31 | 0.546 | −54.51 | 2.281 | 0.72 |
| | MW  | H$_2$O, CO | 0.804 | −10.28 | 0.545 | −54.38 | 1.810 | 0.72 |
| C/2001 A2 (LINEAR) |
| 2001 Jul 9 | KL1 | H$_2$O, CH$_3$OH, C$_2$H$_6$, CH$_4$ | 1.160 | 22.41 | 0.275 | 11.39 | 1.120 | 0.43 |
| | KL2 | H$_2$O, HCN, C$_2$H$_2$, NH$_3$, CH$_4$, H$_2$CO | 1.161 | 22.42 | 0.276 | 11.57 | 1.020 | 0.43 |
| | MW  | H$_2$O, CO | 1.172 | 22.53 | 0.282 | 12.24 | 1.350 | 0.43 |
| C/2007 W1 (Boattini) |
| 2008 Jul 9 | KL1 | H$_2$O, CH$_3$OH, C$_2$H$_6$, CH$_4$ | 0.893 | 9.77 | 0.348 | 12.91 | 1.506 | 0.43 |
| | KL2 | H$_2$O, HCN, C$_2$H$_2$, NH$_3$, CH$_4$, H$_2$CO | 0.893 | 9.79 | 0.348 | 12.96 | 1.110 | 0.43 |
| | MW  | H$_2$O, CO | 0.898 | 10.34 | 0.356 | 12.92 | 1.534 | 0.43 |
| C/2012 F6 (Lemmon) |
| 2013 Jun 20 | KL1 | H$_2$O, CH$_3$OH, C$_2$H$_6$ | 1.737 | 24.29 | 1.790 | 5.26 | 1.787 | 0.43 |
| | KL2 | H$_2$O, HCN, C$_2$H$_2$, NH$_3$, CH$_4$, H$_2$CO | 1.738 | 24.29 | 1.790 | 5.38 | 1.308 | 0.43 |
| C/2012 S1 (ISON) |
| 2013 Oct 22 | MW  | H$_2$O, CO | 1.213 | −38.05 | 1.502 | −52.08 | 1.695 | 0.43 |
| | KL1 | H$_2$O, CH$_3$OH, C$_2$H$_6$ | 1.212 | −38.06 | 1.502 | −52.06 | 1.475 | 0.43 |
| 2013 Oct 24 | MW  | H$_2$O, CO | 1.168 | −38.75 | 1.443 | −51.70 | 1.906 | 0.43 |
| | KL1 | H$_2$O, CH$_3$OH, C$_2$H$_6$ | 1.168 | −38.77 | 1.442 | −51.65 | 1.574 | 0.43 |
| 2013 Oct 25 | KL2 | H$_2$O, HCN, C$_2$H$_2$, NH$_3$, CH$_4$, H$_2$CO | 1.146 | −39.14 | 1.413 | −51.41 | 1.620 | 0.43 |
| 2013 Nov 7 | KL2 | H$_2$O, HCN, C$_2$H$_2$, NH$_3$, CH$_4$, H$_2$CO | 0.829 | −45.91 | 1.086 | −42.08 | 1.905 | 0.43 |

**Table 2**

| Molecule | Setting | Total Production Rate$^a$ 10$^{26}$ mol s$^{-1}$ | Averaged Mixing Ratios% |
|----------|---------|---------------------------------|-----------------------|
| H$_2$O   | KL1    | 735 ± 50                         | 100                   |
|         | KL2    | 495 ± 40                         |                       |
|         | MW     | 303 ± 56                         |                       |
| CH$_3$OH | KL1    | <1.38                           | <0.19                 |
|         | KL2    | 0.20 ± 0.08                      | 0.04 ± 0.01           |
| HCN     | KL1    | <5.64                           | <1.14                 |
|         | KL2    | <0.56                           | <0.11                 |
| NH$_3$  | KL1    | <0.36                           | <0.07                 |
| H$_2$CO | KL1    | 0.81 ± 0.16                      | 0.11 ± 0.02           |
| C$_2$H$_2$ | KL1 | 1.48 ± 0.55                      | 0.22 ± 0.06           |
| C$_2$H$_4$ | KL1 | 1.17 ± 0.55                      | 1.36 ± 0.32           |
| CO      | MW     | 4.11 ± 0.89                      |                       |

Notes. All the production rates are calculated for a common rotational temperature of (75 ± 5)K.

$^a$ Total production rate, after applying a measured growth factor (GF) of (1.47 ± 0.03) retrieved from water.
since suitable fluorescence models were not available then. If we use their rotational temperature to retrieve water from the KL1 spectra, the production rate that we obtain is $(650 \pm 50) \times 10^{26} \text{ mol s}^{-1}$, lower than the weighted mean from OH$^+$ (prompt emission) in the KL1 and KL2 settings presented in Mumma et al. (2001; $(730 \pm 50) \times 10^{26} \text{ mol s}^{-1}$).
Values in parenthesis are assumed. Computing mixing ratios for UT 2000 July 13. (Molecule Mumma et al. 2001)

Comparison of Previous and Updated Water Production Rates for Comet 99S4

| Molecule | Previous Results | This Work | Relative Difference% |
|----------|-----------------|-----------|----------------------|
| H2O      | (50)            | 73.8 ± 5  | 75 ± 5               |

Notes. Values in parenthesis are assumed.

Comparing Previous and Updated Rotational Temperatures for Comet 99S4

| Molecule | Mumma et al. (2001) | Dello Russo et al. (2005) | This Work |
|----------|---------------------|--------------------------|-----------|
| H2O      | (50)                | 73.8 ± 5                 | 75 ± 5    |

Notes. Values in parenthesis are assumed.

Figures 5. Comparison of results presented in Mumma et al. (2001; yellow bars) and this work (cyan bars), for comet 99S4. Mixing ratios for detected molecules are shown and reported together with the corresponding confidence limits, while 3σ upper limits are indicated with a downward arrow.

Table 3
Comparison of Previous and Updated Rotational Temperatures for Comet 99S4

| Molecule | Mumma et al. (2001) | Dello Russo et al. (2005) | This Work |
|----------|---------------------|--------------------------|-----------|
| H2O      | (50)                | 73.8 ± 5                 | 75 ± 5    |

Notes. Values in parenthesis are assumed.

Table 4
Comparison of Previous and Updated Water Production Rates for Comet 99S4

| Setting | Mumma et al. (2001) | Dello Russo et al. (2005) | This Work |
|---------|---------------------|--------------------------|-----------|
| KL1     | 730 ± 50 (OH')      | 673 ± 56                 | 735 ± 50  |
| KL2     | 730 ± 50 (OH')      | 673 ± 119                | 495 ± 40  |
| MW      | 446 ± 72            | 303 ± 56                 | 303 ± 56  |

Notes. 
* Mumma et al. (2001) retrieved a water production rate of (446 ± 72) × 10²⁶ mol s⁻¹ using two H₂O lines in the MW setting. For the KL1 and KL2 settings their reported production rate of (730 ± 50) × 10²⁶ mol s⁻¹ was computed from spectral lines of OH⁺ (prompt emission). They used the weighted mean of the MW and KL values ([638 ± 44] × 10²⁶ mol s⁻¹) when computing mixing ratios for UT 2000 July 13.

Table 5
Comparisons of Previous and Current Mixing Ratios for Comet 99S4

| Molecule | Previous Results | This Work | Relative Difference% |
|----------|-----------------|-----------|----------------------|
| CH₃OH    | <0.17          | <0.19     | 12%                  |
| HCN      | <0.15          | <0.15     | 12%                  |
| NH₃      | 0.07 ± 0.04    | 0.04 ± 0.01 | 56%              |
| H₂CO     | <1.14          | <1.14     | 0%                   |
| C₂H₂     | <0.14          | <0.07     | 50%                  |
| C₂H₆     | 0.13 ± 0.02    | 0.11 ± 0.02 | 15%              |
| CH₄      | 0.15 ± 0.02    | 0.15 ± 0.02 | 0%               |
| CO       | 0.45 ± 0.34    | 1.36 ± 0.32 | 202%             |

Notes.
* Mumma et al. (2001).
* Dello Russo et al. (2005).
* Gibb et al. (2003).

Dello Russo et al. (2005) re-analyzed the 99S4 spectra using a then-updated water fluorescence model, retrieving a corresponding rotational temperature of 73 ± 5 K and a water production rate of (677 ± 51) × 10²⁶ mol s⁻¹ (see Tables 3 and 4). To our knowledge, values for trace gases were not re-analyzed with the updated temperature, excepting methane: for an assumed rotational temperature of 70 K, Gibb et al. (2003) reported a production rate of (1.0 ± 0.3) × 10²⁶ mol s⁻¹ and a mixing ratio of (0.18 ± 0.06)%. The current analysis is the first to update values for all trace gases using self-consistent and modern algorithms and procedures.

In the 3310 cm⁻¹ spectral region, our analysis of C₂H₂ and HCN gives production rates that are substantially lower than those in previous publications. This spectral region contains several spectral lines from different molecular species, whose overlap, if not accounted for, can lead to erroneous production rates. Moreover, before 2001 several specific molecular models did not exist (e.g., NH₃) or were deficient (e.g., H₂O), resulting in an incomplete picture of the spectra. For example, the water line at about 3320 cm⁻¹ was not modeled in the previous analysis of 99S4, so its potential blend with a spectral line of
HCN (R2) resulted in a higher production rate for HCN. Later studies omitted the R2 line from HCN analyses for this reason (for example, the study of 01A2 by Magee-Sauer et al. 2008, see below). With the mature post-2011 algorithms, we can include it since we solve for all molecules simultaneously using the Levenberg–Marquardt formalism. The production rate retrieved including the updated water molecular model and using a rotational temperature of 50 K results in \((0.10 \pm 0.04) \times 10^{26} \text{ mol s}^{-1}\) a lower value than the previous result of \((0.61 \pm 0.17) \times 10^{26} \text{ mol s}^{-1}\).

Finally, we report the first upper limits for NH3 and H2CO; their fluorescence models were lacking in 2001 and thus their production rates were not reported in previous work.

### 3.2. C/2001 A2 (LINEAR)

Comet 01A2 was discovered on 2001 January 15 (Pravec et al. 2001); this comet was characterized by several outbursts and breakups, offering the possibility to study fresh organic material released from the nucleus. Observations and data reduction were complicated by poor weather conditions and by a reduced sensitivity of the spectrometer, especially in the region near 3.0 \(\mu\)m, due to the presence of water ice on a mirror within the instrument. Nevertheless, 01A2 showed many bright molecular emission lines, allowing us to retrieve individual rotational temperatures for H2O, C2H6, CH3OH, and HCN (Table 6). The rotational temperatures for H2O, C2H6, and CH3OH are consistent with the weighted mean of \((85 \pm 5) \text{ K}\), and adopting this value for all molecular species results in the production rates and corresponding MR shown in Table 7; Figure 4, panel B shows the detection of CH3OH on 2001 July 9.

Our re-analysis of data from comet 01A2 presents important new insights into its chemical composition. Like comet 99S5, the new quantum molecular models and the updated atmospheric transmittance play important roles in our analysis. We retrieved rotational temperatures for H2O, C2H6, and HCN are slightly smaller and less dispersed than those of Magee-Sauer et al. (2008; see Table 6), and they agree with our newly retrieved \(T_{\text{rot}}\) for CH3OH. Our rotational temperature for HCN is significantly lower than that for H2O (and other trace species), in agreement with previous findings. The lower temperature for HCN suggests that it arose farther from the nucleus than the native species, perhaps owing to extended release; our measured growth factors for HCN and H2O are similar, and this is consistent if the release is centered along the line of sight. Further discussion will be given elsewhere.

Our production rates for H2O are smaller than those of Magee-Sauer et al. (2008; about 30% lower, see Table 8). Using the modern algorithms, the current MR are smaller for HCN, H2CO, CO, and C2H2, but greater for CH3OH, C2H6, and CH4 (see Table 9 and Figure 6). The lower production rate for water is noticeable even when we run our models with the rotational temperatures used in previous publications. For example, if we use the rotational temperature of 105K reported by Magee-Sauer et al. (2008) for observations of UT 2001 July 10.5, we obtain a water production rate of \((343 \pm 26) \times 10^{26} \text{ mol s}^{-1}\). This is about 20% lower than the previously reported value of \((430 \pm 37) \times 10^{26} \text{ mol s}^{-1}\) (Magee-Sauer et al. 2008).

---

### Table 6

**Comparison of Rotational Temperatures for Comet 01A2**

| Molecule     | Date (2001 UT) | Magee-Sauer et al. (2008) | This Work |
|--------------|----------------|---------------------------|-----------|
| H2O          | Jul 9          | 98 \(\pm\) 6             | 88 \(\pm\) 6 |
|              | Jul 10         | 105 \(\pm\) 9            | 78 \(\pm\) 9 |
| C2H6         | Jul 9          | 102 \(\pm\) 13            | 86 \(\pm\) 5 |
|              | Jul 10         |                          | 82 \(\pm\) 4 |
| CH3OH\(a\)  | Jul 9          | 82 \(\pm\) 6             | 79 \(\pm\) 4 |
|              | Jul 10         |                          |            |
| HCN          | Jul 9          | 56 \(\pm\) 6             | 66 \(\pm\) 4 |
|              | Jul 10         | 67 \(\pm\) 4             | 67 \(\pm\) 4 |
| CO           | Jul 10         | 126 \(\pm\) 26            |            |
| H2CO         | Jul 9          | 104 \(\pm\) 20            |            |

**Note.**

\(a\) Villanueva et al. (2012a) retrieved a rotational temperature of \((78 \pm 5) \text{ K}\) on UT 9.5 July for CH3OH, using the updated molecular model, in agreement with current results.

### Table 7

**Production Rates and Mixing Ratios with Respect to Water for Comet 01A2**

| Date (UT 2001) | Molecule | Total Production Rates \(10^{26} \text{ mol s}^{-1}\) | Averaged Mixing Ratios %
|----------------|----------|--------------------------------------------------------|-----------------------|
| Jul 9          | H2O\(c\) | 284 \(\pm\) 29                                        | 100                   |
| Jul 10         |          | 278 \(\pm\) 18                                        |                       |
| Jul 10         | H2O\(d\) | 293 \(\pm\) 77                                        |                       |
| Jul 9          | CH3OH    | 14.5 \(\pm\) 0.6                                       | 4.11 \(\pm\) 0.25     |
| Jul 10         |          | 10.6 \(\pm\) 0.5                                       |                       |
| Jul 9          | HCN\(e\) | 0.86 \(\pm\) 0.09                                       | 0.30 \(\pm\) 0.02     |
| Jul 10         |          | 0.84 \(\pm\) 0.05                                       |                       |
| Jul 9          | NH3      | <2.60                                                  | <0.77                 |
| Jul 10         |          | <2.13                                                  |                       |
| Jul 9          | H2CO     | 0.23 \(\pm\) 0.08                                       | 0.08 \(\pm\) 0.02     |
| Jul 10         |          | <0.17                                                  |                       |
| Jul 9          | C2H2     | 0.41 \(\pm\) 0.11                                       | 0.14 \(\pm\) 0.02     |
| Jul 10         |          | 0.38 \(\pm\) 0.06                                       |                       |
| Jul 9          | C2H6     | 9.11 \(\pm\) 0.24                                       | 2.73 \(\pm\) 0.15     |
| Jul 10         |          | 7.16 \(\pm\) 0.25                                       |                       |
| Jul 9          | CH4      | 4.74 \(\pm\) 0.75                                       | 1.79 \(\pm\) 0.17     |
| Jul 10         |          | 5.10 \(\pm\) 0.44                                       |                       |
| Jul 10         | CO       | 9.0 \(\pm\) 2.0                                        | 3.07 \(\pm\) 0.96     |

**Notes.**

All the production rates are calculated for a common rotational temperature of \((85 \pm 5) \text{ K}\).

\(b\) Global production rates, after applying the following measured growth factors: July 9—(1.60 \(\pm\) 0.03) (retrieved from H2O, CH3OH, C2H6, and HCN), July 10—(1.50 \(\pm\) 0.03) (retrieved from H2O, CH3OH, C2H6, and HCN).

\(e\) The averaged mixing ratio is calculated as the weighted average of the singular mixing ratios obtained for the different observing nights.

\(d\) Obtained combining KL1 and KL2 settings.

\(c\) MW setting.

\(e\) The HCN mixing ratio for a temperature of \((67 \pm 4) \text{ K}\) is about \(0.29 \pm 0.03\), which is comparable within \(1\sigma\) with the value extracted for \(T_{\text{rot}} = (85 \pm 5) \text{ K}\).

### Table 8

**Comparison of Water Production Rates for Comet 01A2**

| Date (2001 UT) | Settings    | Magee-Sauer et al. (2008) | This Work |
|----------------|-------------|---------------------------|-----------|
| Jul 9          | KL1+KL2     | 377 \(\pm\) 34            | 284 \(\pm\) 29 |
| Jul 10         | KL1+KL2     | 430 \(\pm\) 37            | 278 \(\pm\) 18 |
| Jul 10         | MW          | 424 \(\pm\) 40            | 293 \(\pm\) 77 |

---

Lippi et al.
We retrieve rotational temperatures for H$_2$O, C$_2$H$_6$, CH$_3$OH, and HCN (Table 11), and using an averaged value of (83 ± 3) K we report revised production rates and MR for H$_2$O, C$_2$H$_6$, CH$_3$OH, HCN, C$_2$H$_2$, NH$_3$, CH$_4$, and CO, and an upper limit (3σ) for H$_2$CO (see results in Table 10 and a spectrum from 07W1 in Figure 4, panel C). In our analysis we scaled the nucleus-centered production rates with the retrieved growth factors; we then applied an additional correction factor of 2.5 to
production rates of water and methanol are shown and reported together with the corresponding confidence limits, while 3σ upper limits are indicated with a downward arrow.

Table 11: Comparison of Previous and Updated Rotational Temperatures for Comet 07W1

| Molecule | Date (2008 UT) | Villanueva et al. (2011a) | This Work |
|----------|----------------|--------------------------|-----------|
| H_2O     | Jul 9          | 80 ± 2                   | 83 ± 4    |
|          | Jul 10         | 79 ± 3                   | 83 ± 3    |
| C_2H_6   | Jul 9          | 79 ± 3                   | 80 ± 3    |
|          | Jul 10         | 78 ± 3                   | 78 ± 5    |
| HCN      | Jul 9          | 84 ± 5                   | 84 ± 7    |
| CH_3OH   | Jul 9          | 83 ± 5                   | 83 ± 4    |
|          | Jul 10         |                         |           |

Table 12: Comparison of Previous and Updated Water Production Rates for Comet 07W1

| Date (UT) | Settings | Villanueva et al. (2011a) | This Work |
|-----------|----------|--------------------------|-----------|
| Jul 9     | KL1+KL2  | 301 ± 22                 | 272 ± 15  |
| Jul 10    | KL1+MW   | 306 ± 23                 | 264 ± 20  |

production rates of water and methanol (see footnote “d” in Table 3 of Villanueva et al. 2011a).

Given that Villanueva et al. (2011a) used some of the latest reduction techniques and fluorescence models, we note minor differences in the two results (see Figure 7 and Tables 11–13). We obtain similar rotational temperatures for all the molecular species, and a lower production rate for water (about −10%); the trace species show MR that are consistent (within ±1σ confidence limits) with the previous results, except for CH_3OH (about +11%) and C_2H_6 (about +18%).

The observed differences in MR are mainly related to our lower value for the water production rate. For example, Villanueva et al. (2011a) reported the modeling of only the Q-branch of CH_3OH ν_3 band—as opposed to the full rovibrational band model that we apply for the current analysis; moreover, they do not include Q-scale uncertainties propagation in the calculation of the MR.

If we follow a similar approach, limiting our analysis to the Q-branch observed on UT 2008 July 9 and before applying the 2.5 correction factor, we obtain a methanol production rate of (4.49 ± 0.34) × 10^{26} mol s^{-1}—comparable to the value reported previously (4.42 ± 0.34) × 10^{26} mol s^{-1} and only about 4% smaller than the value we retrieve by considering the complete ν_3 band (4.67 ± 0.36) × 10^{26} mol s^{-1}. If we use our Q-branch value along with the previously published water production rate, we retrieve a methanol mixing ratio of (3.73 ± 0.12)%, which is similar to the one published in Villanueva et al. (2011a; 3.67 ± 0.11%).

### 3.4. C/2012 F6 (Lemmon)

Comet 12F6 was discovered on 2012 March 23 and belongs to the nearly isotropic long-period comet group, originating from the OC. For observations on 2012 June 20, we retrieve a water rotational temperature of (53 ± 3) K, production rates for H_2O, C_2H_6, CH_3OH, HCN, and NH_3, and 3σ upper limits for...
C$_2$H$_2$ and H$_2$CO. Observations of methane were precluded by the small geocentric velocity of the comet and CO was not sampled. The results are summarized in Table 14 and a sample extracted spectrum is shown in Figure 4, panel D. These data were originally presented in Paganini et al. (2014), which used similar procedures and molecular models. Thus, as expected, our values are consistent within 1$\sigma$ confidence limits (see Figure 8 and Tables 15–17), excepting formaldehyde for which we found a smaller upper limit. This difference is probably related to the fact that for non-detections our 3$\sigma$ upper limits are calculated using the uncertainties retrieved through the covariance matrix of the Levenberg–Marquardt fitting algorithm, while previous reductions consider the uncertainties retrieved from the correlation analysis.

3.5. C/2012 S1 (ISON)

Discovered on 2012 September 21, C/2012 S1 (known as D/2012 S1 after its disruption) was a dynamically new Sun-grazing comet that disintegrated as it passed close to the Sun; NIRSPEC observing runs are listed in Table 1. Except on the night of November 7, the comet did not show very bright lines and the spectra were quite noisy, limiting the possible...
In Figure 4, panel E, we show the detection of water on November 7. We report our results in Table 18. Even though comet 12S1 was observed and analyzed quite recently, we find some differences between our results and those presented in DiSanti et al. (2016; see Figure 9 and Tables 19–21). We obtained robust water rotational detections. In Figure 4, panel E, we show the detection of water on November 7. We report our results in Table 18.

![Figure 9](image)

**Figure 9.** Comparison of results presented in DiSanti et al. (2016; yellow bars) and this work (cyan bars), for comet 12S1. Mixing ratios for detected molecules are shown and reported together with the corresponding confidence limits, while 3σ upper limits are indicated with a downward arrow.

### Table 18

| Date (UT 2012) | Molecule | Production Rates $10^{26}$ mol s$^{-1}$ | Averaged Mixing Ratios % |
|---------------|----------|----------------------------------------|--------------------------|
| Oct 22        | H$_2$O   | 116 ± 15                                | 100                      |
| Oct 24        | HCN      | 85 ± 8                                  | < 1.78                   |
| Oct 25        | NH$_3$   | 71 ± 19                                 | 0.10 ± 0.02              |
| Nov 7         | CH$_3$OH | 395 ± 34                                | 100                      |
| Oct 22        | CH$_3$OH | < 0.06                                  | < 1.78                   |
| Oct 24        | HCN      | < 0.80                                  | < 1.78                   |
| Oct 25        | NH$_3$   | 0.38 ± 0.11                             | < 1.78                   |
| Nov 7         | H$_2$CO  | < 0.05                                  | < 1.78                   |
| Oct 25        | C$_2$H$_2$ | < 0.28                                | 0.11 ± 0.05              |
| Nov 7         | C$_2$H$_2$ | 0.43 ± 0.19                          | 0.11 ± 0.05              |
| Oct 22        | C$_2$H$_6$ | 0.45 ± 0.14                         | 0.41 ± 0.09              |
| Oct 24        | CH$_4$   | 0.37 ± 0.12                             | 0.41 ± 0.09              |
| Oct 25        | CH$_4$   | 0.41 ± 0.06                             | 0.41 ± 0.06              |
| Nov 7         | CO       | 1.85 ± 0.35                             | 3.78                     |
| Oct 24        | CO       | < 3.21                                  | < 3.78                   |

Notes. Production rates are calculated using an average temperature of 50 K (assumed) for the first two nights, (53 ± 5) K for the third night, and (63 ± 4) K for the last night.

a Global production rates after applying measured growth factors of (1.72 ± 0.12) for the October 22, (1.61 ± 0.10) for the October 24, (1.42 ± 0.22) for the October 25, and (1.98 ± 0.30) for the November 7.

b Mixing ratios are calculated as the weighted average of the singular mixing ratios obtained for the different observing nights.

c Obtained from the combination of KL1 and MW settings.
temperatures for October 25 and November 7, showing a slight increase of temperature in November, and our production rates for water are consistent with those of DiSanti et al. (2016). Our MR for HCN, C2H6, and CH4 are higher, while we get the same value for C2H2. Due to the low signal-to-noise ratio, we report only upper limits for CH3OH and H2CO, that are consistent with values reported previously, as well as upper limits for CO and NH3. Despite these differences, our results are in agreement within 1σ confidence limits with DiSanti et al. (2016).

4. Discussion

In the previous section we showed that for comets 99S4 and 01A2, observed and analyzed before 2011, the results obtained with the updated models and procedures differ significantly from previous work. For comets 07W1, 12F6, and 12S1, we notice some differences with respect to previous rotational temperatures, production rates, and MR, but the results are in general consistent within confidence limits. We find that these discrepancies are likely due to the inherent uncertainties related to the noise of the astronomical observations and (slight) human interaction in the data analysis. However, we observe improvements to pre-2011 work, and we attribute these changes to the following factors.

1. New and improved quantum fluorescence molecular models. Using the new models, the rotational temperatures, production rates, and MR are better constrained thanks to more precise g-factors, more complete molecular line lists, and availability of improved molecular constants. These breakthroughs have facilitated the analysis of spectral regions characterized by overlapping of emission lines from different molecules (e.g., the HCN spectral region). Furthermore, the development of new models has allowed the characterization of species not reported in previous studies.

2. Implementation of updated atmospheric models. An accurate model of the terrestrial transmittance at the times of observation is necessary to assist in the reduction and calibration of spectroscopic data collected using ground-based observations. Inaccuracies in the atmospheric models translate into an improper removal of terrestrial features, which affects the characterization of the comet’s continuum and can critically affect the modeled atmospheric transmittance at the Doppler-shifted position of an individual line.

3. Novel approaches for the retrieval of the molecular properties. The χ2 minimization technique and the correlation analysis are two different and independent methods that can be used for the analysis of the spectral features. When used together, their convergence to a common solution for rotational temperatures and production rates is a test that can verify the self-consistency of the results. The χ2 minimization technique could not be used before the advent of advanced quantum molecular models.

4. A systematic study of the flux calibration. Flux calibration is one of the key steps in reducing spectra: for this reason, we have recalculated the flux calibration factors for each observation, using the semi-automatic procedure and the updated atmospheric transmittance...
models; we then compared all the calibration factors from different observing campaigns, cross-checking for their consistency.

The significant differences observed in pre-2011 results could bring strong implications to our understanding of cometary taxonomy, and the addition of new molecular species (e.g., NH$_3$ and H$_2$CO) in the infrared database can further our understanding of cometary origins. For example, in Figure 10, we show how the relationship between HCN and C$_2$H$_6$ MR investigated in previous reviews (e.g., Mumma & Charnley 2011; Dello Russo et al. 2016) changes if we consider the results presented in our new analysis. Since the MR retrieved from about 58% of comets present in our database need revision (see Figure 2), we expect that the updated results will impact on molecule-to-molecule relationships, with the greater impact for those species that are at the moment poorly determined (e.g., NH$_3$ and H$_2$CO). But, to infer more definite conclusions we will first need to complete our revisions, as exemplified by the sample results presented here.

4.1. Comparison and Classification of Comets

We can make use of the updated results to retrieve some information about the possible origins of the analyzed comets. When comparing abundances of trace species, two comets can
share the same relative amount of the individual molecules, although absolute values of MR can appear very different. For this reason, we decided to consider pie charts to show how the elements are proportionally distributed in a given comet (see Figure 11). In theory these proportions are related to the processes that affected a comet during its formation and its history and can give valuable clues on cometary taxonomy. For the trace species we created multilevel pies, where the inner level takes into consideration a possible chemical formative origin, resulting in the following four representative subgroups:

1. Group 1—CO (red): it is one of the most hyper-volatile species in cometary coma and most likely has interstellar origin;
2. Group 2—CH3OH, H2CO and CH4 (yellow): methanol and formaldehyde may form through hydrogenation of condensed CO, while hydrogenation of atomic C trapped in CO ice can produce methane (Hiraoka et al. 1994, 1998);
3. Group 3—C2H2 and C2H6 (blue): hydrogenation of acetylene can produce ethane (Hiraoka et al. 2000);
4. Group 4—HCN (green).

The outer band of each pie shows the proportional amount of individual molecular species using corresponding color shades; the proportion between water and all other species considered here is also reported in an additional pie. The NH3 molecule was not included because for comets 99S4, 01A2, and 12S1 it is not detected with NIRSPEC, and the corresponding retrieved upper limits are not significant if compared with the NH3 average found in other OC comets, leading to possible bias in the pies.

If we organize the multilevel pies with decreasing CO, we can see a gradient in their redox ratio (sum of H2CO, CH3OH, and CH4 relative to CO) that ranges from 0.37 (99S4) to 2.25 (07W1): the five comets are quite distinct in redox ratio, excepting 12F6 and 12S1 with redox ratios of 0.58 and 0.61 respectively.

Considering the second group (CH3OH, H2CO, and CH4), comet 12F6 is more similar to 12S1 and 99S4, even though the proportion of methanol in the latter is lower; for 01A2 and 07W1 the contribution of this group to the total composition is much higher than the other comets.

In the third group (C2H2 and C2H6), we see that comets 99S4, 12S1, and 12F6 again look similar, showing lower abundance fractions for C2H6, opposite to 07W1 and 01A2 that show much higher contributions for this molecule—especially in comet 01A2. Finally, HCN looks quite the same for four compared comets while 99S4 displays a lower value.

Effective hydrogenation of simple compounds (e.g., CO, C2H2) is favored in relatively cold formation environments, where atomic hydrogen is better retained on grain surfaces, and this affects the hydrogenation ratios in pre-cometary ices (Mumma et al. 1996, 2001). If we assume that MR are cosmogonic indicators of chemical conditions in a given comet’s birthplace, the higher redox ratio for C2H6 in 01A2 and 07W1 suggests that they formed in a colder region of the disk than that where 99S4, 12S1, and 12F6 formed. In this colder region, the retention and hydrogenation of CO on pre-cometary grain should also have been more efficient, and indeed the COH4 redox ratio is higher for 01A2 and 07W1 compared with 99S4, 12S1, and 12F6. The intermediate hydrogenation product (C2H4) has not been detected in any comet, consistent with much faster hydrogenation rates for adsorbed C2H4 than for C2H2 (see, Hiraoka et al. 2000). 01A2 shows a higher proportion of C2H4 and a lower one for CH3OH, consistent with a different hydrogenation history or a different endowment of initial C2H2 versus CO with respect to 07W1. The gradual decrease of the proportion of CO in the compared comets may also suggest a gradient in temperature in the protoplanetary disk.

5. Conclusions and Future Steps

We presented updated production rates, MR of minor species (relative to water), and rotational temperatures for five comets observed with NIRSPEC at the Keck Observatory since 1999, obtained using more complete fluorescence quantum band models and stand-alone analysis techniques. Our results for these comets allowed us to identify certain drawbacks in previous analyses that could limit a true understanding of cometary taxonomy. In particular, we showed that it is possible to obtain significant improvements in data sets that were analyzed before the advent of recent fluorescence models and terrestrial retrieval methods (i.e., before 2011). For instance, we quantified results for ammonia and formaldehyde in comets 99S4 and 01A2.

We are now revisiting the 60+ comets in our database to build an updated chemical classification of comets. In addition to the updated MR, our chemical classification would include comparisons with other cosmic indicators, such as isotopic ratios, ortho-to-para ratios, and spin temperatures. Ultimately, a self-consistent, revised chemical taxonomy would allow the removal of inconsistencies added by dissimilar retrieval strategies and inaccurate (or absent) information due to missing fluorescence efficiencies. As already mentioned, a better understanding of cometary compositions and their possible groupings can help us understand the conditions that shaped our planetary system during its formation, and with this work we demonstrated the need to revisit existing (pre-2011) cometary data. We expect that a re-assessment of certain data sets could provide a more accurate picture of the chemical taxonomy of comets.

This work was supported by the NASA Astrobiology Institute (13-13NA17-0032 to Goddard Space Flight Center, PI: M. J. Mumma) and the NASA Emerging Worlds Program (EW15-57 to Goddard Space Flight Center, PI: G. L. Villanueva). This research has made use of the Keck Observatory Archive (KOA), which is operated by the W. M. Keck Observatory and the NASA Exoplanet Science Institute (NExScI), under contract with the National Aeronautics and Space Administration.

The authors wish to recognize and acknowledge the very significant cultural role and reverence that the summit of Maunakea has always had within the indigenous Hawaiian community. We are most fortunate to have the opportunity to conduct observations from this mountain.

ORCID iDs
Manuela Lippi https://orcid.org/0000-0001-9185-878X
Geronimo L. Villanueva https://orcid.org/0000-0002-2662-5776
Michael J. Mumma https://orcid.org/0000-0003-4627-750X
Maria N. Camarca https://orcid.org/0000-0003-3887-4080
Sara Faggi https://orcid.org/0000-0003-0194-5615
Lucas Paganini https://orcid.org/0000-0002-4639-5488

References
Boattini, A., Snodgrass, C., Guido, E., & Sostero, G. 2007, IAU, 8899, 1
Bockelée-Morvan, D., & Biver, N. 2017, RSPTA, 375, 20160252
