

The organic composition of Comet C/2001 A2 (LINEAR) I. Evidence for an unusual organic chemistry

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Abstract

We used the NIRSPEC instrument on the Keck-2 telescope atop Mauna Kea, HI to observe Comet C/2001 A2 (LINEAR) in a Target of Opportunity campaign on UT 2001 July 9.5, 10.5 August 4.4, 10.5. We measured seven organic parent volatiles (C₂H₆, C₂H₂, HCN, CH₄, CO, CH₃OH, H₂CO) simultaneously with H₂O. We obtained absolute production rates and relative abundances for parent volatiles, and also measured rotational temperatures for several of these species. The chemical composition of C/2001 A2 differs substantially from any comet we have observed to date. The abundances we measure (relative to H₂O) for C₂H₆, C₂H₂, HCN, and CH₃OH are enriched by a factor of ~2 to 3 in C/2001 A2 compared with most comets in our database. Other molecular species were detected within the typical range of measured abundances. C/2001 A2 presented a unique opportunity to study the chemistry of a fragmenting comet where pristine areas are exposed to the Sun.
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1. Introduction

C/2001 A2 (LINEAR) was discovered on UT 2001 January 15.3 and identified as a comet on January 16.9, when a diffuse coma was observed (Green, 2001). The visible magnitude (m_V) upon discovery was 15.8 and early predictions suggested the comet could reach a maximum brightness of 10 near perihelion, on May 20, 2001.

However, the brightening of C/2001 A2 was not typical. In late March 2001, the comet's brightness rapidly increased by 5 magnitudes to $m_V \sim 8$, already 4–5 times its originally predicted maximum brightness. The comet continued to brighten through its perihelion passage with several major outbursts that

were linked to fragmentation events (Sekanina et al., 2002). C/2001 A2 was noteworthy in that it shed six observable fragments during its perihelion passage. The maximum brightness achieved ($m_V \sim 3$) was almost 7 magnitudes greater than originally predicted. The discovery and subsequent brightening/fragmentation of C/2001 A2 occurred after normal telescope proposal due dates and so a "Target of Opportunity" (TOO) proposal was submitted to the W.M. Keck Observatory. TOO time was awarded for post-perihelion observations during July and August 2001.

C/2001 A2 is classified as an Oort-cloud comet. Oort-cloud comets are believed to have originated (mainly) in the giant-planets region of the solar nebula where temperatures ranged from ~150 to 40 K. Because of this temperature gradient, we expect the volatile fractions of comets to differ depending on their region of formation. Once formed, icy planetesimals are predicted to diffuse radially (a dynamical effect)

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in the proto-planetary disk and some are transported to the Oort cloud by gravitational scattering (Charnoz and Morbidelli, 2003; Levison and Morbidelli, 2003; Dones et al., 2004). Radial diffusion could lead to internal chemical heterogeneity if cometesimals formed in chemically distinct disk regions are later incorporated into a final cometary nucleus.

Searching for chemical heterogeneity within an individual cometary nucleus, and measuring the compositional diversity among comets are two principal objectives of cometary science. By examining temporal variations in two parent volatiles (CH₄ and H₂CO), Gibb et al. (2007) obtained evidence for chemical heterogeneity within the nucleus of C/2001 A2. The present paper is a study of the overall organic composition of this fragmented comet as revealed at infrared (IR) wavelengths. We measured seven organic parent volatiles (C₂H₆, C₂H₂, HCN, CH₄, CO, CH₃OH, H₂CO) simultaneously with H₂O and we show that their mixing ratios reveal a distinct chemistry compared with other comets in our IR database.

2. Observations and data analysis

C/2001 A2 became accessible to northern latitude observatories in late June 2001. We observed the comet on UT 2001 July 9.5 and 10.5, and August 4.4 and 10.5, immediately before and approximately one month after its fourth observed brightness outburst (on July 12). Two components were seen in the first observed outburst, but only the larger component (B) remained detectable at the time of our observations. Poor weather conditions limited the time available for conducting the observations in July. Other details are given in Table 1.

The observations were conducted using NIRSPEC on the 10-m Keck-2 telescope atop Mauna Kea, Hawaii. NIRSPEC is a cross-dispersed echelle spectrograph (covering wavelengths from ~ 1 to ~ 5.5 μm) equipped with a 1024×1024 pixel (Aladdin-3) InSb detector array (McLean et al., 1998). Each detector pixel subtends 0.198 arcsec in the spatial direction and 0.144 arcsec in the spectral direction. Because the echelle grating is cross-dispersed, multiple spectral orders are sampled at once providing the ability to detect and compare parent volatiles either simultaneously or within only a few hours. This makes NIRSPEC a powerful tool for determining the composition of

cometary volatiles and tracking any changes in chemistry with time.

A 0.43 arcsec wide (3 pixel) slit was used for our comet observations leading to a spectral resolving power $\nu/\Delta\nu \sim 2.4 \times 10^4$. The slit length was 24 arcsec (oriented east–west). For each setting, the comet was nodded along the slit in an ABBA sequence. Using this mode of “on-chip” nodding, comet signal is present in both A and B beams (placed equidistant from the slit midpoint and separated by ~ 12 arcsec), thereby increasing the signal-to-noise ratio by a factor of up to $\sqrt{2}$ (compared with nodding to blank sky) after signals from both beams are combined. Flat-fields and dark frames were obtained prior to changing each echelle/cross-disperser setting. For each setting, spectra of infrared standard stars were obtained for absolute flux calibration. An aperture correction was applied to the standard star flux to account for slit losses.

Three instrument configurations (filter, echelle, and cross-disperser) were used. Two of these settings (“KL1” and “KL2”) encompassed much of the “organics” region, spanning ~ 3525 – 2750 cm^{-1} (2.83–3.64 μm), and another setting (“M-wide”) sampled primarily CO and H₂O between 4.62–5.00 μm . Table 2 lists emissions detected within specific orders of the three settings.

Data were processed using algorithms specifically developed for our comet observations (Dello Russo et al., 1998, 2000, 2001, 2004, 2005; DiSanti et al., 1999, 2001; Magee-Sauer et al., 1999, 2002; Mumma et al., 1996). A detailed description of all data reduction, flux calibration and spectral analysis steps is presented in Bonev (2005). We provide here only a brief summary of our methodology.

Initial processing of each individual order included removal of high dark current pixels and cosmic ray hits, along with spatial and spectral straightening. This resulted in a rectified frame, in which the spatial and spectral dimensions fell along registered columns and rows, respectively. Absolute spectral calibration and determination of column burdens of absorbers in the terrestrial atmosphere were achieved through use of the Spectrum Synthesis Program (SSP; Kunde and Maguire, 1974), which accesses the HITRAN molecular database (Rothman et al., 1992). The sum of background thermal continuum emission and superimposed sky emission lines was removed by subtracting B-frames from A-frames. The optimized SSP model was

Table 1
Log of observations C/2001 A2 (LINEAR)

Date UT (2001)	<i>R</i> (AU)	Δ (AU)	Δ_{dot} (km s^{-1})	Instrument setting	Time (min)
July 9.5	1.160	0.275	11.4	KL1	20
				KL2	28
July 10.5	1.173	0.282	12.4	KL1	16
				KL2	40
				M-wide	9
August 4.4	1.510	0.578	25.9	KL2	12
August 10.5	1.594	0.673	28.0	KL1	8
				KL2	20

Table 2
Instrument settings and detections

Grating setting	Order	Spectral grasp (cm^{-1})	Molecules sampled
KL1	23	2962–3002	C ₂ H ₆ ν_7
	22	2833–2872	CH ₃ OH ν_3
KL2	26	3404–3454	H ₂ O
	25	3273–3322	C ₂ H ₂ ν_3 HCN ν_3 CH ₄ ν_3
M-wide	23	3019–3056	H ₂ CO ν_1, ν_5
	21	2753–2794	
M-wide	16	2130–2166	CO
	15	1999–2032	H ₂ O

convolved to the spectral resolution of the comet data and normalized to the cometary continuum level. Molecular emissions were isolated by subtracting this normalized synthetic continuum model from the observed comet spectrum. The true line flux at the top of the atmosphere was then obtained by dividing the total observed flux of each cometary emission line by the fully resolved atmospheric transmittance at its Doppler-shifted line center frequency.

3. Results

In C/2001 A2, we detected (simultaneously, or nearly so) eight parent volatiles (H_2O , C_2H_6 , C_2H_2 , HCN , CH_4 , CO , CH_3OH , H_2CO), and one daughter fragment (OH). We obtained quantitative measures of rotational temperatures, thereby providing robust absolute production rates (and *ortho*-to-*para* ratios for H_2O ; Dello Russo et al., 2005) and hence relative abundances (i.e., mixing ratios) for these parent volatiles. Spectra for four orders are shown in Figs. 1A–1D. Sample spectra of H_2O are presented in Dello Russo et al. (2005), H_2CO and CH_4 in Gibb et al. (2007), and OH in Bonev et al. (2004).

3.1. Rotational temperatures

When using individual ro-vibrational lines to determine production rates, adequate sampling of the rotational distribution is critically important. If lines from only a few levels spanning a limited range of upper or lower state rotational energies are sampled, then the inferred total production rate (Q) is highly sensitive to the value assumed for T_{rot} . Conversely, if many ro-vibrational lines spanning a large range of rotational energies are sampled, then Q is relatively insensitive to T_{rot} . H_2O and HCN have well separated lines and good quantum band models, and for them NIRSPEC samples a large range of rotational energies within a single instrument setting. Consequently, the production rates for these molecules are not significantly sensitive to the explicit value used for T_{rot} in the analysis, but at the same time, T_{rot} is accurately determined.

We use the transmittance-corrected fluxes (F_{line}) of individual ro-vibrational lines to obtain rotational temperatures for H_2O , C_2H_6 , CO , and HCN via excitation analyses [details are given by Dello Russo et al. (2000, 2004) and (DiSanti et al., 2006)]. Rotational temperatures were retrieved using a nucleus-centered 3×9 pixel ($0.43'' \times 1.78''$) spectral extract. Nucleus-centered extracts allow for higher signal-to-noise ratios compared with extracts offset from the nucleus (see Dello Russo et al., 2004, 2005).

Spectral lines in the non-resonance fluorescence bands (hot bands) (after Dello Russo et al., 2005) near $2.9\text{-}\mu\text{m}$ were used to determine the rotational temperature for water and they show that the ratio of $F_{\text{line}}/(\nu_{\text{line}} g_{\text{line}})$ is independent of the average lower state energy at the correct rotational temperature (Table 3).

Relative Q -branch intensities of ethane, C_2H_6 , are not sensitive indicators of rotational temperature because each Q -branch

encompasses many rotational lines that together reflect a range of energies rather than a discrete value [see Dello Russo et al. (2001) for a more detailed discussion of methodology]. This also means that the production rate obtained for ethane is relatively insensitive to the specific value of T_{rot} invoked. Although ro-vibrational lines of C_2H_6 do not provide a sensitive measure of T_{rot} , we do retrieve T_{rot} for C_2H_6 for comparison with other parent volatile species. We detect seven ethane Q -branches in the ν_7 band near $3.35\ \mu\text{m}$ and use their relative intensities to determine the rotational temperature in the excited vibrational state ($\nu_7 = 1$). We find the rotational temperature determined for C_2H_6 on July 9.5 is consistent with that measured for H_2O (Table 3).

Seven lines of the 1–0 band of CO (R4, R3, R2, R1, R0, P2, P3) were measured on July 10.6, and these were used to extract T_{rot} . The P1 line fell near the core of a neighboring (stronger) water absorption and therefore was not included in the analysis. The retrieved T_{rot} is consistent with that determined from H_2O on UT July 10.5 (Table 3, Fig. 2), however the value for CO (126_{-36}^{+42} K) is poorly constrained due to the limited range of rotational energies sampled by the CO lines.

H_2CO is approximated structurally (to a high degree of accuracy) as a symmetric top molecule. The existing fluorescence model (Reuter et al., 1989) calculates line g -factors for the ν_1 and ν_5 bands based on a least-squares fit to experimental line strengths obtained from high-dispersion laboratory spectra. The distribution of predicted H_2CO line intensities varies greatly with temperature in the observed spectral region (KL2 order 21). Thus, despite the relatively poor signal-to-noise ratio of individual H_2CO lines, an accurate rotational temperature is measured for H_2CO (Table 3) using the excitation approach [see DiSanti et al. (2006) for methodology].

Thirteen lines of the ν_3 band of HCN were detected within order 25 of the KL2 grating setting (R2, R1, R0, P2, P3, P4, P5, P6, P7, P8, P9, P10, P11) for the July 9.5 and 10.5 dates and 9 lines (R2, R1, R0, P2, P3, P4, P5, P7, P8) were detected on August 4.4 and 10.5. We exclude the R2 and P4 lines from our analysis because R2 is blended with a relatively bright H_2O line ($101\text{-}001\ 3_{13}\text{-}4_{22}$) while P4 is blended with the R1 line of C_2H_2 (comprising $\sim 15\%$ of the total P4 intensity for $T_{\text{rot}} = 50$ K). We use the remaining 11 lines to measure T_{rot} for HCN in July and 7 lines for HCN in August. T_{rot} values measured for HCN in July differ from those measured for H_2O and C_2H_6 (Table 3).

Rotational temperatures should differ among molecular species if radiative cooling controls their rotational populations (Xie and Mumma, 1992; Bockelée-Morvan et al., 1994). We find that the rotational temperature measured for HCN differs from values measured for other parent volatiles, on the same date (Table 3). This is the first comet for which we find such a difference and could be indicative of a different distribution of HCN within our aperture. However, we emphasize that this difference does not influence our results for production rates and mixing ratios, because (as for C_2H_6 and H_2O) the use of many ro-vibrational lines makes the HCN production rate insensitive to the specific value adopted for T_{rot} . The detected lines repre-

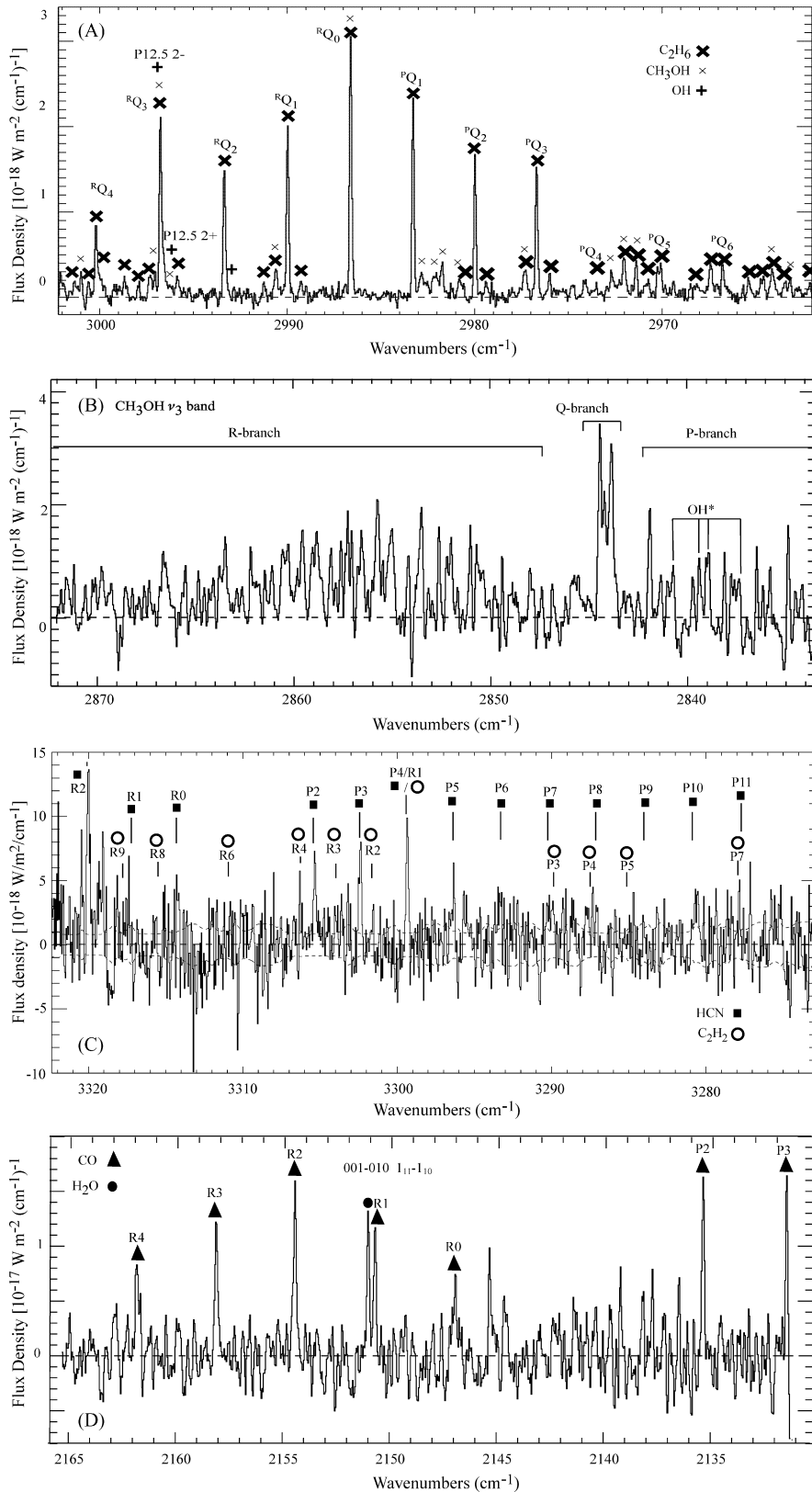


Fig. 1. Selected spectral extracts of C/2001 A2 (LINEAR) acquired with NIRSPEC on the Keck 2 telescope on UT 2001 July 9.5 (panels A–C) and 10.5 (panel D). Comet residuals are shown (after subtracting cometary continuum convolved with an atmospheric transmittance model). The dashed line in (C) shows a $1-\sigma$ noise envelope. The flux density refers to extracted signal contained within a 9 row aperture. The spectral resolving power is $\sim 25,000$. Doppler shifted positions of the cometary lines are marked. (A) KL1 order 23, (B) KL1 order 22, (C) KL2 order 25, (D) M-wide order 16. The noise level in (C) is higher than for other settings since for the July dates there was ice on the window of the instrument, and this affected the region near $3.0 \mu\text{m}$ the most. The presence of ice on the window does not affect the overall calibration since the standard star observations were similarly affected. The ice problem was resolved for the August observation dates.

Table 3
Rotational temperatures in C/2001 A2 (LINEAR)

Molecule	July 9.5 T_{rot} (K) ^a	July 10.5 T_{rot} (K) ^a	August 4.4 T_{rot} (K) ^a	August 10.5 T_{rot} (K) ^a
H ₂ O ^b	98 ⁺⁶ ₋₅	105 ⁺⁵ ₋₃	70 ^d	70 ^d
C ₂ H ₆	102 ⁺¹³ ₋₁₂	100 ^d	–	70 ^d
C ₂ H ₂	100 ^d	100 ^d	–	–
HCN	56 ⁺⁶ ₋₆	67 ⁺⁴ ₋₄	42 ⁺⁴ ₋₄	49 ⁺⁹ ₋₁₄
CH ₄	100 ^d	100 ^d	70 ^d	70 ^d
CO	–	126 ⁺⁴² ₋₃₆	–	–
CH ₃ OH	100 ^d	100 ^d	–	–
H ₂ CO ^c	104 ⁺²⁰ ₋₁₈	100 ^d	–	–

^a Based on a 3×3 -pixel nucleus-centered aperture for C₂H₆, and a 3×9 -pixel nucleus-centered aperture for H₂O, HCN, CO, and H₂CO.

^b Dello Russo et al. (2005).

^c Gibb et al. (2007).

^d Adopted rotational temperature.

sent 54% of the total band intensity for $T_{\text{rot}} = 56$ K and 49% of the band for $T_{\text{rot}} = 100$ K.

3.2. Production rates and relative abundances

To calculate the “global” production rate for each molecule we first generate a “ Q -curve” by measuring the spherical production rate as a function of distance from the nucleus and then forming a symmetric production rate from the east–west mean at each offset distance [for a detailed discussion of the methodology, see Bonev et al. (2006, Appendix B) and sources cited therein]. The symmetric Q is relatively insensitive to asymmetries in the coma, and it quickly reaches a terminal value (unless a distributed source is also present, DiSanti et al., 2001). From these Q -curves, we can determine the factor by which nucleus-centered extracts underestimate the global production rate. The apparent production rate measured on the nucleus is always smaller than its value in regions offset from the nucleus. Slit losses (primarily due to seeing) introduce a reduction in the apparent Q near the nucleus (the S/N ratio is, however, higher for nucleus-centered extracts). Production rates measured off the nucleus can sometimes be larger for other reasons (e.g., the release from extended sources such as icy grains or by dissociation of a precursor species, or opacity effects in the near-nucleus region), but we see no evidence of these effects in C/2001 A2.

To improve the accuracy of chemical comparisons, we use the production rate of each species extracted from a nucleus-centered aperture (3×9 pixel box, $0.43'' \times 1.78''$), because these spectral extracts feature the highest signal-to-noise ratios. These nucleus-centered values underestimate the true production rates, so we apply the correction factor based on the ratio of the terminal to nucleus-centered production rates determined from the Q -curve using the summed spatial profile for multiple lines. This methodology is discussed in detail in Dello Russo et al. (2005). The spatial distributions of eight species (H₂O, C₂H₆, C₂H₂, HCN, CH₄, CO, CH₃OH, and H₂CO) in C/2001 A2 are consistent with release directly from the nu-

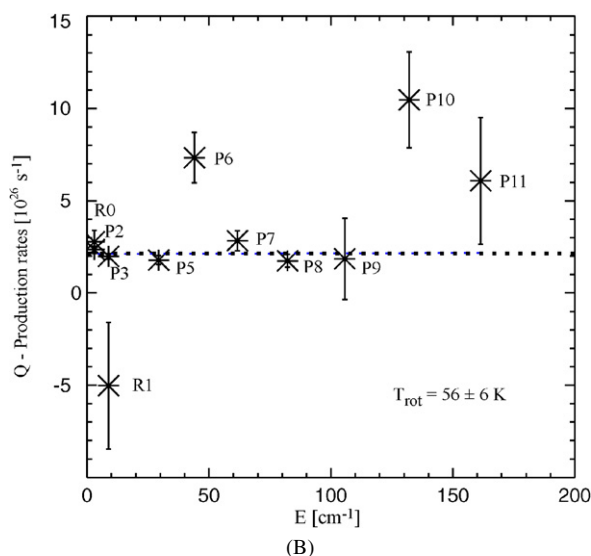
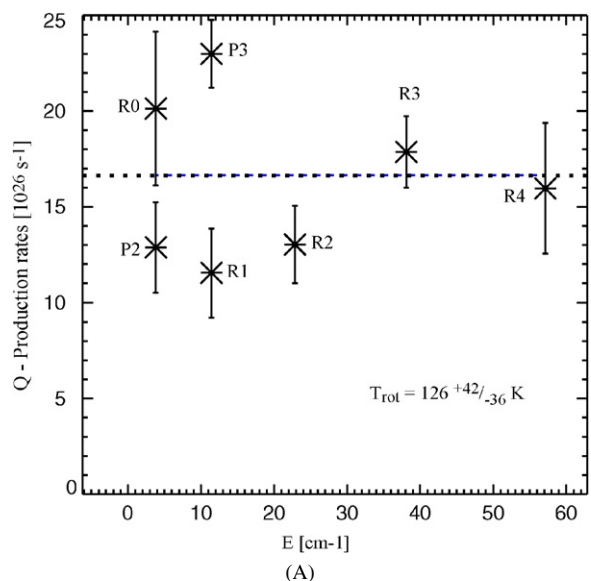


Fig. 2. Excitation analysis for CO and HCN. Line intensities extracted from a $0.43'' \times 1.78''$ ($85 \text{ km} \times 354 \text{ km}$) aperture centered on the nucleus are used to determine the rotational temperature. The production rate should be independent of the lower state energy of the individual transition at the correct T_{rot} [see Bonev (2005) and DiSanti et al. (2006) for detailed discussions]. (A) Seven ro-vibrational lines of CO on UT 2001 July 10.5 were included in the analysis to retrieve a rotational temperature ($T_{\text{rot}} = 126^{+42}_{-36}$ K). (B) Eleven ro-vibrational lines of HCN on UT 2001 July 9.5 were included in the analysis to retrieve a $T_{\text{rot}} = 56 \pm 6$ K. The greater uncertainty in T_{rot} for CO results from the relatively limited range of energies sampled (see text).

cleus with no significant contribution from extended sources (i.e., the correction factors are similar for all species observed simultaneously). For C₂H₂, the signal-to-noise ratio was not sufficient to determine the production rate for regions offset from the nucleus, so we applied the correction factor for HCN to the nucleus-centered production rate for C₂H₂ (which was detected simultaneously in the same spectral order as HCN). Table 4 lists our measured production rates and relative abundances (X:H₂O) from the July and August 2001 observations.

Table 4
Global production rates in C/2001 A2 (LINEAR) for UT July 9.5, 10.5, August 4.4, 10.5, 2001

Molecule	July 9.5 line flux ^a (10 ⁻¹⁸ W m ⁻¹)	July 9.5 <i>Q</i> (10 ²⁶ s ⁻¹)	July 10.5 line flux ^a (10 ⁻¹⁸ W m ⁻¹)	July 10.5 <i>Q</i> (10 ²⁶ s ⁻¹)	August 4.4 line flux ^a (10 ⁻¹⁸ W m ⁻¹)	August 4.4 <i>Q</i> (10 ²⁶ s ⁻¹)	August 10.5 line flux ^a (10 ⁻¹⁸ W m ⁻¹)	August 10.5 <i>Q</i> (10 ²⁶ s ⁻¹)
H ₂ O ^b	11.6 ± 1.0	377 ± 34	12.4 ± 1.1	430 ± 37	0.63 ± 0.10	109 ± 17	0.38 ± 0.09	62 ± 14
C ₂ H ₆	18.2 ± 1.7	6.3 ± 0.6	17.8 ± 1.7	6.4 ± 0.6	–	Not measured	1.11 ± 0.25	1.4 ± 0.2
C ₂ H ₂ ^c	1.58 ± 0.39	1.8 ± 0.5	1.04 ± 0.21	1.4 ± 0.3	–	Not detected	–	Not detected
HCN	7.8 ± 1.8	2.1 ± 0.2	6.72 ± 0.40	1.9 ± 0.1	0.5 ± 0.1	0.5 ± 0.1	0.21 ± 0.05	0.27 ± 0.07
CH ₄ ^d	2.17 ± 0.21	4.5 ± 0.4	2.98 ± 0.23	6.5 ± 0.5	0.73 ± 0.04	3.1 ± 0.2	0.34 ± 0.04	1.7 ± 0.2
CO ^e	–	Not measured	15.5 ± 1.0	16.6 ± 4.4	–	Not measured	–	Not measured
CH ₃ OH	2.8 ± 0.1	14.5 ± 0.4	2.88 ± 0.06	12.0 ± 1.0	–	Not measured	–	Not measured
H ₂ CO ^d	0.36 ± 0.03	0.89 ± 0.09	0.082 ± 0.044	0.21 ± 0.11	0.025 ± 0.022	0.19 ± 0.16	–	Not detected

^a Summed transmittance-corrected line fluxes are for a region 0.30 to 3.86 arcsec off the nucleus. The line flux for H₂O, C₂H₂, HCN was measured in a 0.43" × 1.78" aperture centered on the nucleus then scaled to a value for a region 0.30 to 3.86 arcsec off the nucleus. The line flux represents the flux from the sum of the lines used for each molecule.

^b *Q*(H₂O) measured from order 26 in KL2 [Dello Russo et al. (2005) gives details of the analysis]. Water was also measured in orders 15 and 16 of the M-wide setting and the weighted mean for *Q*(H₂O) [(424 ± 40) × 10²⁶, for *T*_{rot} = 100 K] is consistent with the value from KL2 order 26. Our mixing ratio for CO (Table 5) is based on the simultaneously measured *Q*(H₂O) from M-wide, thereby avoiding systematic uncertainties associated with slit losses and absolute flux calibration.

^c C₂H₂ lines included in July dates: R3, P3, P7.

^d Gibb et al. (2007).

^e The uncertainty in *Q*(CO) is dominated by the stochastic uncertainty in *T*_{rot} determined from the CO measurements.

4. Discussion

4.1. Individual production rates: Comparison with independent measurements

The apparent enrichment of C₂H₆, C₂H₂, HCN and to a lesser extent CH₃OH, is not due to anomalous measurements of H₂O. Our production rates for water are consistent with those obtained from the Odin (Lecacheux et al., 2003; Biver et al., 2007) and FUSE (Feldman et al., 2002) space observatories, considering the overall activity of the comet during July 2001 (Furusho et al., 2003). Moreover, our values for *Q*(H₂O) measured in different orders (observing a different hot-band) are consistent, e.g., the values from setting M-wide (orders 15 and 16; (353 ± 84) × 10²⁶ and (445 ± 46) × 10²⁶ molecules s⁻¹, respectively) are consistent with values from setting KL2 (order 26). We obtain the relative abundance of CO and H₂O from the weighted mean of *Q*(H₂O) values measured simultaneously with CO in the M-wide setting.

Our results for *Q*(CO) and *Q*(CH₃OH) (and their relative abundances with respect to H₂O on July 9.5 and 10.5) are consistent with IRAM (millimeter) production rates measured 1–2 days earlier (on 8 July <1.4 × 10²⁷ and 1.1 × 10²⁷ molecules s⁻¹ for CO and CH₃OH, respectively, Biver et al., 2006). We detected H₂CO on July 9.5, however on July 10.5 we obtained only a much-smaller upper limit (Table 4, Gibb et al., 2007). Measurements from IRAM provided a H₂CO production rate for July 10 of 0.95 × 10²⁶ molecules s⁻¹ (Biver et al., 2006), consistent with our value on July 9.5.

The rotational temperature derived from radio measurements of HCN in July 2001 (~50 K) agrees with those derived from our infrared measurements. This agreement may be fortuitous, because the IR and radio sample quite different regions of the coma and agreement in rotational temperature may not be expected. Moreover, our HCN production rates and relative abundance ratios (HCN:H₂O) ratios in July are higher (by a factor of 3–4) than those measured by IRAM (Biver et al., 2006). In most

comets observed to date, our infrared HCN production rates are larger by a factor of two compared with those measured at millimeter wavelengths (Biver et al., 1999a, 1999b, 2000, 2002; Magee-Sauer et al., 1999, 2002; Mumma et al., 2001a, 2001b, 2003).

4.2. Relative abundances: The “unusual” enrichment of organic molecules with respect to H₂O

The principal result of this study is that C₂H₆, C₂H₂, HCN, and CH₃OH are enriched relative to H₂O in C/2001 A2 while CO, CH₄, and H₂CO are within the ranges measured for other Oort-cloud comets in our database. The mixing ratios (relative to H₂O) for C₂H₆, C₂H₂, HCN, and CH₃OH in C/2001 A2 are higher by factors of ~2–3 compared to those in most other comets (Table 5). However, relative abundances among them are “normal,” i.e., C₂H₆/HCN, C₂H₂/HCN and CH₃OH/HCN are within the ranges measured in other comets (Table 6). CH₄/HCN, CO/HCN, and H₂CO/HCN are all smaller in C/2001 A2 than measured in other comets. Radio measurements also measure higher than usual relative abundances for CH₃OH and H₂S for C/2001 A2 (Biver et al., 2006).

The enrichment of C₂H₆, C₂H₂, HCN, and to a lesser extent CH₃OH in C/2001 A2 might be caused by several factors including (1) formation in a colder region of the nebula, (2) chemical processing of the ices after condensing onto grains, (3) exposure of interior material due to fragmentation. At this time the relationship between cometary chemistry and formative region in the nebula is poorly constrained. The fact that individual comets may have heterogeneous compositions complicates the identification of a specific formative region based on composition alone.

4.3. The relation between cometary composition and nebular processing

If temperature were the dominant factor controlling the volatile fraction in the cometary nucleus, we would expect

Table 5
Relative abundances of volatile molecules with respect to H₂O, as measured in the IR

Comet	C ₂ H ₆ :H ₂ O (%)	C ₂ H ₂ :H ₂ O (%)	HCN:H ₂ O (%)	CH ₄ :H ₂ O (%)	CO ^e :H ₂ O (%)	CH ₃ OH:H ₂ O (%)	H ₂ CO ^c :H ₂ O (%)
Hyakutake ^a	0.62 ± 0.07	0.16 ± 0.08	0.18 ± 0.04	0.79 ± 0.08	14.9 ± 1.9	1.7–2	<0.7 ^f
Hale–Bopp ^a	0.56 ± 0.04	0.31 ± 0.1	0.27 ± 0.04	1.45 ± 0.16	12.4 ± 0.4	2.1	<1.1 ^g
Lee ^a	0.67 ± 0.07	0.27 ± 0.03	0.29 ± 0.02	1.45 ± 0.18	1.8 ± 0.2	2.1 ± 0.5	–
Ikeya–Zhang ^{a,b,c}	0.62 ± 0.13	0.18 ± 0.05	0.18 ± 0.04	0.51 ± 0.06	4.7 ± 0.8	2.5 ± 0.5 ^e	0.62 ± 0.18
C/1999 S4 ^a	0.11 ± 0.02	<0.12	0.10 ± 0.03	0.18 ± 0.06	0.9 ± 0.3	<0.15	–
C/2001 A2 ^d	1.7 ± 0.2	0.5 ± 0.1	0.6 ± 0.1	1.2 ± 0.2	3.9 ± 1.1	3.9 ± 0.4	0.24 ± 0.05

^a Mumma et al. (2003) and references within.

^b Dello Russo et al. (2002).

^c DiSanti et al. (2002).

^d C/2001 A2 (LINEAR) from 2001 July 9.5 for all molecules except CO which was observed only on July 10.5 2001 (this paper), H₂O production rates from Dello Russo et al. (2005), CH₄ and H₂CO production rates from Gibb et al. (2007).

^e Native source only.

^f Biver et al. (1999a, 1999b), total H₂CO.

^g Biver et al. (1997), Bockelée-Morvan et al. (2000), total H₂CO.

Table 6
Relative abundances with respect to HCN, as measured in the IR

Comet	C ₂ H ₆ :HCN				C ₂ H ₂ :HCN				CH ₃ OH:HCN			
Hyakutake	3.4 ± 0.9				0.9 ± 0.5				9.4–11.1			
Hale–Bopp	2.1 ± 0.3				1.2 ± 0.4				7.8 ± 1.1			
Lee	2.3 ± 0.3				0.9 ± 0.1				7.2 ± 1.8			
Ikeya–Zhang	3.4 ± 1.1				1.0 ± 0.4				13.9 ± 4.1			
C/1999 S4	1.1 ± 0.4				<1.2				1.5 ± 0.5			
	July 9.5	July 10.5	August 4.4	August 10.5	July 9.5	July 10.5	August 4.4	August 10.5	July 9.5	July 10.5	August 4.4	August 10.5
C/2001 A2	3.0 ± 0.4	3.4 ± 0.4	–	5.2 ± 1.6	0.9 ± 0.2	0.7 ± 0.2	–	–	6.7 ± 0.6	6.5 ± 0.7	–	–

the relative abundances of highly volatile molecules to be correlated. Among comets in our database, we see no correlation in abundances (relative to H₂O) of the two most volatile molecules we measure routinely (CO and CH₄), suggesting that thermal processing alone likely did not control cometary chemistry (Gibb et al., 2003). While the relative abundances of CO, CH₄, and H₂CO with respect to H₂O fall within the range measured for other comets, the interpretations for CH₄ and H₂CO are complicated by observed variations found in the ratios H₂CO/H₂O and CH₄/H₂O, perhaps indicating heterogeneity within the nucleus of C/2001 A2 (Gibb et al., 2007).

The relative abundances of symmetric hydrocarbons provide an important clue to the past processing of cometary ices. Higher order hydrocarbons are produced in irradiated water-rich ices containing CH₄ or C₂H₂, respectively (Moore and Hudson, 1998). Furthermore, icy grain mantles may have been efficiently hydrogenated in regions of high H-atom density, thereby converting condensed phase C₂H₂ to C₂H₆ (cf. Mumma et al., 1996; Hiraoka et al., 2000, 2001). Similar hydrogenation of mixed CO–H₂O ice could produce both H₂CO and CH₃OH (Watanabe et al., 2003, 2004). The efficacy of such processing probably varied greatly with heliocentric distance and/or with time, enforcing corresponding differences in the volatile (icy) and refractory organic fractions in comets.

4.4. Comparison to other notable comets

C/2001 A2 is the first comet for which we measured an enrichment of organic volatiles with respect to water compared with “normal” volatile abundances measured to date. Previous “anomalous” abundances did not reflect enrichment, but rather a depletion of organic volatiles.

Among Oort-cloud comets, we first observed a depletion of organics in C/1999 S4 (LINEAR). Mumma et al. (2001b) argued that the observed abundances might indicate C/1999 S4 formed in the Jupiter–Saturn region where infalling ices vaporized and chemical processing of sublimated gases modified their composition in the nebula before they later re-condensed (Mumma et al., 2001b; see also Mumma et al., 2003).

Depletion of volatiles has also been observed in Jupiter Family Comets (JFCs). In JFCs, it is suggested that the surface layer of the cometary nucleus is preferentially “depleted” of volatile composition relative to “normal” (pristine?) cometary abundances within the comet due to the volatile losses from the surface as a result from numerous solar passages. Observations of 21P/Giacobinni–Zinner (where C₂H₆ was found to be depleted) first suggested evidence to support this hypothesis (Mumma et al., 2000). The hypothesis was further supported by results from the Deep Impact mission to 9P/Tempel 1, where the abundance of organics relative to water apparently increased in the ejecta (pending modeling of optical depth effects for H₂O

and CO₂; A'Hearn et al., 2005). Independently, Mumma et al. (2005) found that the abundance of C₂H₆ in the impact ejecta was in agreement with “normal” abundances measured from Oort-cloud comets, while the pre-impact quiescent release was severely depleted in C₂H₆ (by a factor of three). Mumma et al. noted that the observed difference could be the signature either of thermal fractionation of near-surface material, or of large-scale internal heterogeneity of the nucleus (perhaps associated with radial migration of chemically-distinct cometesimals in the proto-planetary disk).

Further insights are provided by the volatile composition of 73P/Schwassmann–Wachmann 3—a JFC noted for its spectacular fragmentation. If fragmentation exposes more pristine material (analogous to the Deep Impact ejecta), we might expect the freshly exposed volatiles to exhibit the characteristic chemistry of “normal” abundances. However, in 73P-C depleted C₂H₆ and CH₃OH, and a somewhat lower abundance of CH₄, yet “normal” abundances of HCN and C₂H₂ were found (Villanueva et al., 2006). Later observations also showed that CO was highly depleted in 73P-C (DiSanti et al., 2007). Sensitive measurements of the two separate fragments (73P-B and 73P-C) near closest approach to Earth found depletion of all measured volatiles with respect to H₂O (CH₃OH, H₂CO, CO, NH₃, C₂H₆ and C₂H₂) except HCN (Dello Russo et al., 2007). Also the chemistry within and between fragments was found to be homogeneous suggesting a primordial composition (Dello Russo et al., 2007). If the volatile abundance reflects formative conditions, then the region of formation of JFC 73P/SW3 is perhaps more similar to Oort-cloud Comet C/1999 S4 than to the formative regions of JFCs 21P/GZ and 9P/Tempel 1 (supposing a homogeneous composition for 9P).

5. Summary

The study of C/2001 A2 presented a unique opportunity to study the chemistry of a fragmenting comet, allowing ices in the interior of the nucleus to be sampled. Our findings are summarized as follows:

1. Three organic volatiles (C₂H₆, C₂H₂, HCN), and to a lesser extent CH₃OH are notably enriched relative to water. H₂O is measured simultaneously with each organic volatile removing most sources of systematic error and enabling robust measures of relative abundances. The high spatial resolution of our long-slit spectra samples volatiles within a small temporal window and does not average over substantial periods of cometary activity.
2. The relative production rates for CH₄, CO, and H₂CO measured with respect to H₂O fall within our normal range of variability measured for other comets.
3. Using Boltzmann and excitation analyses, we extract rotational temperatures for H₂O, HCN, CO, and C₂H₆. For H₂O, CO, and C₂H₆, these were consistent ($T_{\text{rot}} \sim 100$ K), however, T_{rot} for HCN differed ($T_{\text{rot}} \sim 60$ K). This is the first time we noted a significant difference in T_{rot} among parent volatiles. This may suggest a different spatial dis-

tribution of HCN within our aperture compared with other observed parent volatiles.

If one assumes that fragmentation exposes material indicative of the region of formation, then C/2001 A2 could be the first comet identified with a formative region rich in organics (Aikawa et al., 1999). However, a possible connection between fragmentation (with or without disruption) and volatile composition should not be dismissed. Of the comets that our group has observed at IR wavelengths, we have observed “unusual” chemistry (depletion or enhancement of volatiles) in comets that have displayed fragmentation (some disrupting completely). Whether all comets that fragment also display unusual organic chemistry is an important question.

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References

- A'Hearn, M.F., and 28 colleagues, 2005. Deep impact: A large-scale planetary experiment. *Science* 310, 258–264.
- Aikawa, Y., Umebayashi, T., Nakano, T., Miyama, S.M., 1999. Evolution of molecular abundances in proto-planetary disks with accretion flow. *Astrophys. J.* 519, 705–725.
- Biver, N., Bockelée-Morvan, Colom, P., Crovisier, J., Davies, J.K., Dent, W.R.F., Despois, D., Gerard, E., Lellouch, E., Rauer, H., Moreno, R., Paubert, G., 1997. Evolution of the outgassing of Comet Hale–Bopp (C/1995 O1) from radio observations. *Science* 275, 1915–1918.
- Biver, N., and 22 colleagues, 1999a. Long-term evolution of the outgassing of Comet Hale–Bopp from radio observations. *Earth Moon Planets* 78, 5–11.
- Biver, N., and 13 colleagues, 1999b. Spectroscopic monitoring of Comet C/1996 B2 (Hyakutake) with the JCMT and IRAM radio telescopes. *Astron. J.* 118, 1850–1872.
- Biver, N., and 12 colleagues, 2000. Spectroscopic observations of Comet C/1999 H1 (Lee) with the SEST, JCMT, CSO, IRAM, and Nançay radio telescopes. *Astrophys. J.* 120, 1554–1570.
- Biver, N., Bockelée-Morvan, D., Crovisier, J., Colom, P., Henry, F., Moreno, R., Paubert, G., Despois, D., Lis, D.C., 2002. Chemical composition diversity among 24 comets observed at radio wavelengths. *Earth Moon Planets* 90, 323–333.

- Biver, N., Bockelée-Morvan, D., Crovisier, J., Lis, D.C., Moreno, R., Colom, P., Henry, F., Herpin, F., Paubert, G., Womack, M., 2006. Radio wavelength molecular observations of Comets C/1999 T1 (McNaught-Hartley), C/2001 A2 (LINEAR), C/2000 WM1 (LINEAR), and 153P/Ikeya-Zhang. *Astron. Astrophys.* 449, 1255–1270.
- Biver, N., Bockelée-Morvan, D., Crovisier, J., Lecacheux, A., Baron, P., Frisk, U., Hjalmarson, A., Olberg, M., Florén, H.G., Sandqvist, A., Kwok, S., 2007. Submillimeter observations of comets with Odin: 2001–2005. *Planet. Space Sci.* 55, 1058–1068.
- Bockelée-Morvan, D., Padman, R., Davies, J.K., Crovisier, J., 1994. Observations of submillimetre lines of CH₃OH, HCN, and H₂CO in Comet P/Swift-Tuttle with the James Clerk Maxwell Telescope. *Planet. Space Sci.* 42, 662–665.
- Bockelée-Morvan, D., and 17 colleagues, 2000. New molecules found in Comet C/1995 O1 (Hale-Bopp): Investigating the link between cometary and interstellar material. *Astron. Astrophys.* 353, 1101–1114.
- Bonev, B.P., 2005. Ph.D. thesis, Univ. of Toledo.
- Bonev, B.P., Mumma, M.J., Dello Russo, N., Gibb, E.L., DiSanti, M.A., Magee-Sauer, K., 2004. Infrared OH prompt emission as a proxy of water production in comets: Quantitative analysis of the multiplet near 3046 cm⁻¹ in Comets C/1999 H1 (Lee) and C/2001 A2 (LINEAR). *Astrophys. J.* 615, 1048–1053.
- Bonev, B.P., Mumma, M.J., DiSanti, M.A., Dello Russo, N., Magee-Sauer, K., Ellis, R.S., Stark, D.P., 2006. A comprehensive study of infrared OH prompt emission in two comets. I. Observations and effective *g*-factors. *Astrophys. J.* 653, 774–787.
- Charnoz, S., Morbidelli, A., 2003. Coupling dynamical and collisional evolution of small bodies: An application to the early ejection of planetesimals from the Jupiter–Saturn region. *Icarus* 166, 141–156.
- Dello Russo, N., DiSanti, M.A., Mumma, M.J., Magee-Sauer, K., Rettig, T.W., 1998. Carbonyl sulfide in Comets C/1996 B2 (Hyakutake) and C/1995 O1 (Hale-Bopp): Evidence for an extended source in Hale-Bopp. *Icarus* 135, 377–388.
- Dello Russo, N., Mumma, M.J., DiSanti, M.A., Magee-Sauer, K., Novak, R., Rettig, T.W., 2000. Water production and release in Comet C/1995 O1 Hale-Bopp. *Icarus* 143, 324–337.
- Dello Russo, N., Mumma, M.J., DiSanti, M.A., Magee-Sauer, K., Novak, R., 2001. Ethane production and release in Comet C/1995 O1 Hale-Bopp. *Icarus* 153, 162–179.
- Dello Russo, N., Mumma, M.J., DiSanti, M.A., Magee-Sauer, K., 2002. Production of ethane and water in Comet C/1996 B2 Hyakutake. *J. Geophys. Res.* 107 (E11), doi:10.1029/2001JE001838. 5095.
- Dello Russo, N., DiSanti, M.A., Magee-Sauer, K., Gibb, E.L., Mumma, M.J., Barber, R.J., Tennyson, J., 2004. Water production and release in Comet 153P/Ikeya-Zhang (C/2002 C1): Accurate rotational temperature retrievals from hot-band lines near 2.9-mm. *Icarus* 168, 186–200.
- Dello Russo, N., Bonev, B.P., DiSanti, M.A., Mumma, M.J., Gibb, E.L., Magee-Sauer, K., Barber, R.J., Tennyson, J., 2005. Water production rates, rotational temperatures, and spin temperatures in Comets C/1999 H1 (Lee), C/1999 S4, and C/2001 A2. *Astrophys. J.* 621, 537–544.
- Dello Russo, N., Vervack, R.J., Weaver, H.A., Biver, N., Bockelée-Morvan, D., Crovisier, J., Lisse, C.M., 2007. Compositional homogeneity in the fragmented Comet 73P/Schwassmann–Wachmann 3. *Nature* 448, 172–175.
- DiSanti, M.A., Mumma, M.J., Dello Russo, N., Magee-Sauer, K., Novak, R., Rettig, T.W., 1999. Identification of two sources of carbon monoxide in Comet Hale-Bopp. *Nature* 399, 662–665.
- DiSanti, M.A., Mumma, M.J., Dello Russo, N., Magee-Sauer, K., 2001. Carbon monoxide production and excitation in Comet C/1995 O1 (Hale-Bopp): Isolation of native and distributed CO sources. *Icarus* 153, 361–390.
- DiSanti, M.A., Dello Russo, N., Magee-Sauer, K., Gibb, E.L., Reuter, D.C., Mumma, M.J., 2002. CO, H₂CO, and CH₃OH in Comet 2002 C1 Ikeya-Zhang. In: *Proceedings of Asteroids, Comets, Meteors, ACM 2002*, Berlin, Germany. ESA SP-500, pp. 571–574.
- DiSanti, M.A., Anderson, W.M., Villanueva, G.L., Bonev, B.P., Magee-Sauer, K., Gibb, E.L., Mumma, M.J., 2007. Depleted carbon monoxide in fragment C of the Jupiter-family Comet 73P/Schwassmann–Wachmann 3. *Astrophys. J.* 661, L101–L104.
- DiSanti, M.A., Bonev, B.P., Magee-Sauer, K., Dello Russo, N., Mumma, M.J., Reuter, D.C., Villanueva, G.L., 2006. Detection of formaldehyde emission in Comet C/2002 T7 (LINEAR) at infrared wavelength: Line-by-line validation of modeled fluorescent intensities. *Astrophys. J.* 650, 470–483.
- Dones, L., Weissman, P.R., Levison, H.F., Duncan, M.J., 2004. Oort Cloud Formation and Dynamics. In: *Festou, M.C., Keller, H.U., Weaver, H.A. (Eds.), Comets II*. Univ. of Arizona Press, Tucson, pp. 153–174.
- Feldman, P.D., Weaver, H.A., Burgh, E.B., 2002. Far ultraviolet spectroscopic explorer observations of CO and H₂ emission in Comet C/2001 A2 (LINEAR). *Astrophys. J.* 576, L91–L94.
- Furusho, R., Kawakita, H., Fujii, M., Kinugasa, K., Yamamuro, T., Takeyama, N., 2003. Spectroscopic observations of split Comet C/2001 A2 (LINEAR). *Publ. Astron. Soc. Jpn.* 55, 1153–1156.
- Green, D.W.E., 2001. *IAU Circ.* 7564.
- Gibb, E.L., Mumma, M.J., Dello Russo, N., DiSanti, M.A., Magee-Sauer, K., 2003. Methane in Oort-cloud comets. *Icarus* 165, 391–406.
- Gibb, E.L., DiSanti, M.A., Magee-Sauer, K., Dello Russo, N., Bonev, B.P., Mumma, M.J., 2007. The organic composition of C/2001 A2 (LINEAR). II. Search for heterogeneity within a comet nucleus. *Icarus* 188, 224–232.
- Hiraoka, K., Takayama, T., Euch, A., Handa, H., Sato, T., 2000. Study of the reactions of H and D atoms with solid C₂H₂, C₂H₄, and C₂H₆ at cryogenic temperatures. *Astrophys. J.* 532, 1029–1037.
- Hiraoka, K., Sato, T., Takayama, T., 2001. Interstellar chemistry: Tunneling reactions in interstellar ices. *Science* 292, 869–870.
- Kunde, V.G., Maguire, J.C., 1974. Direct integration transmittance model. *J. Quant. Spectrosc. Radiat. Trans.* 14, 803–817.
- Lecacheux, A., and 20 colleagues, 2003. Observations of water in comets with Odin. *Astron. Astrophys.* 402, L55–L58.
- Levison, H.A., Morbidelli, A., 2003. The formation of the Kuiper Belt by the outward transport of bodies during Neptune’s migration. *Nature* 426, 419–421.
- Magee-Sauer, K., Mumma, M.J., DiSanti, M.A., Dello Russo, N., Rettig, T.W., 1999. Infrared spectroscopy of the ν_3 band of hydrogen cyanide in C/1995 O1 Hale-Bopp. *Icarus* 142, 498–508.
- Magee-Sauer, K., Mumma, M.J., DiSanti, M.A., Dello Russo, N., 2002. Hydrogen cyanide in Comet C/1996 B2 Hyakutake. *J. Geophys. Res.* 107 (E11), doi:10.1029/2002JE001863. 5096.
- McLean, I.A., and 14 colleagues, 1998. The design and development of NIRSPEC: A near-infrared echelle spectrograph for the Keck II Telescope. In: *Proc. SPIE*, vol. 3354, pp. 566–578.
- Moore, M.H., Hudson, R.L., 1998. Infrared study of ion-irradiated water-ice mixtures with hydrocarbons relevant to comets. *Icarus* 135, 518–527.
- Mumma, M.J., DiSanti, M.A., Dello Russo, N., Fomenkova, M., Magee-Sauer, K., Kaminski, C.D., Xie, D.X., 1996. Detection of abundant ethane and methane, along with carbon monoxide and water, in Comet C/1996 B2 Hyakutake: Evidence for interstellar origin. *Science* 272, 1310–1314.
- Mumma, M.J., DiSanti, M.A., Dello Russo, N., Magee-Sauer, K., Rettig, T.W., 2000. Detection of CO and ethane in Comet 21P/Giacobini-Zinner: Evidence for variable chemistry in the outer solar nebula. *Astrophys. J.* 531, L155–L159.
- Mumma, M.J., and 17 colleagues, 2001a. A survey of organic volatile species in Comet C/1999 H1 (Lee) using NIRSPEC at the Keck observatory. *Astrophys. J.* 546, 1183–1193.
- Mumma, M.J., Dello Russo, N., DiSanti, M., Magee-Sauer, K., Novak, R.E., Brittain, S., Rettig, T., McLean, I.S., Reuter, D.C., Xu, L.-H., 2001b. The startling organic composition of C/1999 S4 (Linear): A comet formed near Jupiter? *Science* 292, 1334–1339.
- Mumma, M.J., DiSanti, M.A., Dello Russo, N., Magee-Sauer, K., Gibb, E.L., Novak, R., 2003. Remote infrared observations of parent volatiles in comets: A window on the early Solar System. *Adv. Space Res.* 31, 2563–2575.
- Mumma, M.J., DiSanti, M.A., Magee-Sauer, K., Bonev, B.P., Villanueva, G.L., Kawakita, H., Dello Russo, N., Gibb, E.L., Blake, G.A., Lyke, J.E., Campbell, R.D., Aycocock, J., Conrad, A., Hill, G.M., 2005. Parent volatiles in Comet 9P/Tempel 1: Before and after impact. *Science* 310, 270–274.
- Reuter, D.C., Mumma, M.J., Nadler, S., 1989. Infrared fluorescence efficiencies for the ν_1 and ν_5 bands of formaldehyde in the solar radiation field. *Astrophys. J.* 341, 1045–1058.
- Rothman, L.S., and 13 colleagues, 1992. The HITRAN molecular database: Editions of 1991 and 1992. *J. Quant. Spectrosc. Radiat. Trans.* 48, 469–507.

- Sekanina, Z., Jehin, E., Boehnhardt, H., Bonfils, X., Schuetz, O., Thomas, D., 2002. Recurring outbursts and nuclear fragmentation of Comet C/2001 A2 (LINEAR). *Astrophys. J.* 572, 679–684.
- Villanueva, G.L., Bonev, B.P., Mumma, M.J., Magee-Sauer, K., DiSanti, M.A., Slyk, C., Blake, G.A., 2006. The volatile composition of the split ecliptic Comet 73P/Schwassmann–Wachmann 3: A comparison of fragments C and B. *Astrophys. J.* 650, L87–L90.
- Watanabe, N., Shiraki, T., Kouchi, A., 2003. The dependence of H₂CO and CH₃OH formation on the temperature and thickness of H₂O–CO ice during the successive hydrogenation of CO. *Astrophys. J.* 588, L121–L124.
- Watanabe, N., Nagaoka, A., Shiraki, T., Kouchi, A., 2004. Hydrogenation of CO on pure solid CO and CO–H₂O mixed ice. *Astrophys. J.* 616, 638–642.
- Xie, X., Mumma, M.J., 1992. The effect of electron collisions on rotational populations of cometary water. *Astrophys. J.* 386, 720–728.