

The organic composition of C/2001 A2 (LINEAR) II. Search for heterogeneity within a comet nucleus

Erika L. Gibb^{a,*}, Michael A. DiSanti^b, Karen Magee-Sauer^c, Neil Dello Russo^d,
Boncho P. Bonev^{e,f}, Michael J. Mumma^f

^a Department of Physics & Astronomy, University of Missouri–St. Louis, St. Louis, MO 63121, USA

^b Planetary Systems Laboratory, Solar System Exploration Division, NASA Goddard Space Flight Center, Code 693, Greenbelt, MD 20771, USA

^c Department of Chemistry and Physics, Rowan University, Glassboro, NJ 08028-1701, USA

^d Space Department, Planetary Exploration Group, Applied Physics Laboratory/Johns Hopkins University, 11100 Johns Hopkins Road, Laurel, MD 20723-6099, USA

^e Department of Physics, The Catholic University of America, Washington, DC 20064, USA

^f Solar System Exploration Division, NASA Goddard Space Flight Center, Code 690, Greenbelt, MD 20771, USA

Received 17 January 2006; revised 27 September 2006

Available online 26 December 2006

Abstract

The nucleus of Comet C/2001 A2 (LINEAR) split several times during its recent apparition, presenting an unusual opportunity to search for chemical differences in freshly exposed material. We conducted this search using NIRSPEC at the W.M. Keck Observatory on four dates in 2001: 9.5 and 10.5 July and 4.4 and 10.5 August. We detected the R0 and R1 lines of the ν_3 vibrational band of CH₄ near 3.3 μm on all dates. The R2 line was detected on 4.4 and 10.5 August. When we compare production rates of CH₄ to H₂O, we find evidence of a significant enhancement in August relative to that found in July. H₂CO was securely detected via its ν_1 and ν_5 bands on 9.5 July. On 10.5 July, H₂CO emission was much weaker, and its mixing ratio had dropped by a factor of about four. The mixing ratios for other detected volatile species did not change significantly over the course of the observations. We discuss the implications of this evidence for chemical heterogeneity in the nucleus of Comet C/2001 A2. © 2006 Elsevier Inc. All rights reserved.

Keywords: Comets, composition; Infrared observations; Spectroscopy

1. Introduction

Comets are arguably considered the most pristine bodies formed in the outer Solar System (beyond ~ 5 AU), and therefore studies of the chemical composition of comet nuclei have cosmogonic implications. Much work has been done in recent years to characterize the composition of nuclear ices in comets. One important question in cometary science is whether comet nuclei have heterogeneous compositions. There is increasing evidence of various processes that may have altered the primordial composition of comets since the time of their formation (cf. Stern, 2003; Weissman et al., 2004). The majority of these processes are believed primarily to affect a thin layer at the sur-

face of the nucleus. For example, the outer surface (to a depth of perhaps a few meters) may have been modified by cosmic rays during a comet's long storage in the Oort cloud or by thermal processing from repeated passes through the inner Solar System [see Stern (2003) for a discussion of evolution mechanisms in the Oort cloud]. As deeper layers are exposed through evaporation or disruption of the nucleus, the composition may change. Also, repeated passes through the inner Solar System or the passing of nearby hot (O or B) stars or supernovae can cause thermal modification of the top several meters of material, as can mechanical sputtering by interstellar grain collisions.

Another possible source of chemical heterogeneity may be bulk radial transport mechanisms in the early Solar System by, for example, gas drag, turbulence, or gravitational interactions with migrating planets/protoplanets (Tsiganis et al., 2005; Goldreich et al., 2004; Levison and Morbidelli, 2003;

* Corresponding author. Fax: +1 (314) 516 6152.
E-mail address: gibbe@umsl.edu (E.L. Gibb).

Weidenschilling, 1997). This may have resulted in cometesimals that formed at different radii in the protoplanetary disk accumulating into a single body. If this did occur, one might expect to observe different volatile compositions over time in a single comet. For example, chemical differences may be seen if gas jets originating from different cometesimals rotate into or out of view. Also, comets have been known to disrupt. If a comet is comprised of multiple cometesimals, studying the disrupted bodies or studying a comet before and after a disruption event will provide a good test of the level of chemical homogeneity within a comet nucleus.

Comet C/2001 A2 (LINEAR) is an Oort cloud comet discovered by the Lincoln Near Earth Asteroid Research (LINEAR) Project on 15 January 2001 (Pravec et al., 2001). The comet displayed an unusual light curve during its apparition, brightening dramatically on 29.5–30.5 March when it was still inbound 1.3 AU from the Sun (Mattiazzo et al., 2001; Seargent et al., 2001). It was later found to have disrupted into at least two nuclei (Hergenrother et al., 2001; Sekanina et al., 2001). Further outbursts and additional companion nuclei were observed in May (Broughton et al., 2001; Jehin et al., 2001) and June (Schuetz et al., 2001) with smaller outbursts on 12 July (Kysely et al., 2001; Morris et al., 2001) and 25 and 30 July (Kidger et al., 2001). These latter events were also attributed to disruption, though no separate nuclei were observed (Sekanina et al., 2002). With so many outbursts and disruption events, C/2001 A2 presented an excellent opportunity to investigate potentially pristine cometary material. Our team was granted observing time at the Keck Observatory for this unusual Target-of-Opportunity.

In Magee-Sauer et al. (2006; hereafter, Paper I) we presented an analysis of infrared detections of four parent volatiles in C/2001 A2 (H_2O , C_2H_6 , HCN, and C_2H_2), and showed that the abundances for C_2H_2 , C_2H_6 , and HCN are enriched by a factor of ~ 2 – 3 relative to H_2O compared with other comets in our database. In this paper we present a search for chemical heterogeneity within the nucleus of the fragmented Comet C/2001 A2. We report infrared spectroscopic observations on four dates of CH_4 and H_2CO and compare them to H_2O , revealing evidence for significant abundance variations for both molecules. The chemical composition of C/2001 A2 makes it a particularly interesting comet.

2. Observations and data analysis

We observed Comet C/2001 A2 on four nights in 2001 (Table 1) with NIRSPEC at the 10-m W.M. Keck Observatory, located at Mauna Kea, HI (McLean et al., 1998). Observations were performed with a 3-pixel ($0.43''$) wide slit, permitting acquisition of high spectral resolution data ($\lambda/\Delta\lambda \sim 25,000$). Details of the observing procedures and flux calibrations can be found in Gibb et al. (2003).

We detected the R0 and R1 lines of the ν_3 band of CH_4 on all four nights. Owing to the larger Doppler shifts, CH_4 R2 was also detected on 4.4 and 10.5 August but was included only in the analysis of data acquired on 10.5 August (discussed below). We firmly detected the ν_1 and ν_5 bands of H_2CO on 9.5 July but

Table 1
Summary of Comet A2 methane and formaldehyde observations

Date (UT)	R_h (AU)	Δ (AU)	Δ -dot (km/s)	t_{int} (s)
9.5 July	1.161	0.276	11.5	1680
10.5 July	1.173	0.282	12.4	2400
4.4 August	1.509	0.578	25.9	720
10.5 August	1.593	0.673	28.0	1200

Note. These are observations using the KL2 setting described by Magee-Sauer et al. (2006). R_h = heliocentric distance, Δ = geocentric distance, Δ -dot = geocentric velocity, t_{int} = integration time.

achieved only a marginal detection on 10.5 July and an upper limit on 4.4 August. Multiple transitions of H_2O , C_2H_2 , and HCN were observed simultaneously in different orders of the same grating setting (KL2) on each night (see Dello Russo et al., 2005, and Paper I). The CH_3OH ν_3 and C_2H_6 ν_7 vibrational bands were observed in our KL1 setting on three nights (the 4.4 August observations included only the KL2 setting) and CO was observed in our M-band setting only on 10.5 July (DiSanti et al., in preparation).

Data were processed using algorithms specifically tailored to our comet observations and include dark subtraction, flat fielding, and removal of high dark current pixels and cosmic ray hits. Detailed descriptions of our observing procedures and data processing techniques are given elsewhere (Dello Russo et al., 1998, 2000, 2001; Magee-Sauer et al., 1999, 2002; DiSanti et al., 1999, 2001; Bonev, 2005). Details of atmospheric model fitting and extraction of production rates for CH_4 were discussed in Gibb et al. (2003).

The resulting spectra for CH_4 are shown in Fig. 1 and for H_2CO in Fig. 3 (atmospheric fits appear as dashed lines). The residual cometary line fluxes (Table 2) were obtained by subtracting the atmospheric model from the comet row-by-row and then correcting for the monochromatic transmittance at the Doppler shifted line positions. Production rates were obtained using our standard methodology (Magee-Sauer et al., 1999; Dello Russo et al., 2000; DiSanti et al., 2001; Gibb et al., 2003). The highest signal-to-noise ratios were obtained for a 3-by-9 pixel aperture centered on the nucleus, and we used these to compare production rates for molecules that were observed simultaneously (i.e., CH_4 , H_2O , and H_2CO in our KL2 setting). Simultaneous observations are affected identically by seeing and drift, and this approach removes those effects from the relative production rates. These “nucleus-centered” (3 spectral by 9 spatial pixel or $0.43'' \times 1.78''$) values are given in Table 2. We also report the “global” production rate (i.e., corrected for slit loss effects in the “nucleus centered” extracts, cf. Dello Russo et al., 1998, 2005) for comparison with those observed at different times or in different settings in Table 3.

3. Evidence for variability in Comet C/2001 A2

3.1. CH_4

Methane (CH_4) was first securely detected via fluorescent emission of its ν_3 band near $3.3 \mu\text{m}$ in Comet C/1996 B2

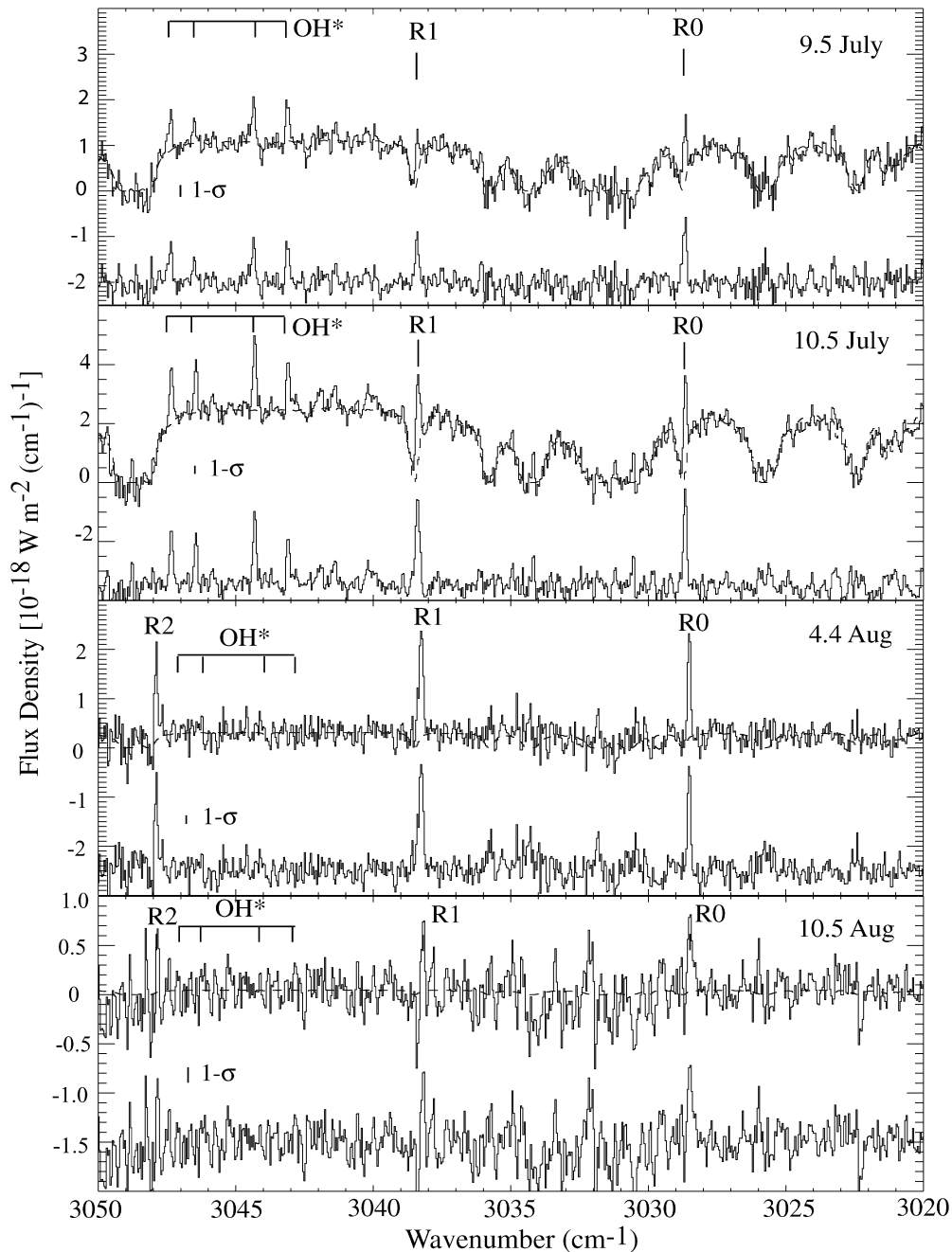


Fig. 1. Spectral extracts of Comet C/2001 A2 taken on four dates with NIRSPEC (setting KL2, order 23, 5 row extract centered on the nucleus). Doppler-shifted positions of the OH prompt emission (OH*) and CH₄ R0 and R1 lines are indicated. The dashed curve is the atmospheric model fit. Beneath the spectra are the residuals, not corrected for atmospheric transmittance, formed by subtraction of the model fit. The CH₄ R0 and R1 lines are present on all dates while the OH* lines are only seen in July and the CH₄ R2 line is visible only in August owing to the insufficient Doppler shift in July.

(Hyakutake) (Mumma et al., 1996) and has been routinely detected in comets since then, including C/1995 O1 (Hale-Bopp), C/1999 S4 (LINEAR), C/2001 A2 (LINEAR), C/1999 T1 (McNaught–Hartley), C/2000 WM1 (LINEAR), C/1999 H1 (Lee), 153/P Ikeya–Zhang (C/2002 C1) (Gibb et al., 2003), C/2002 T7 (LINEAR), C2001 Q4 (NEAT) (Kawakita et al., 2005) and C/2005 Q2 (Macholz) (Bonev et al., 2006). CH₄ is of primary interest because its abundance relative to H₂O has been found to vary from as little as ~0.18% in S4 to nearly 1.5% in Lee, Hale–Bopp, and McNaught–Hartley (Gibb et al., 2003). Thus far the only other molecule found to vary to this

extent is CO (DiSanti et al., 1999, 2001; see also Mumma et al., 2003), but the abundance ratios of these two hypervolatiles, both of which sublimate near 30 K, do not correlate within the reported sample of eight Oort cloud comets (Gibb et al., 2003).

Strong emissions due to the ν_3 R0 and R1 lines of CH₄ were present in Comet A2 on all four dates. The comet was less productive in August, but the Doppler shift was larger, increasing the atmospheric transmittance and making the CH₄ lines more apparent. This increased geocentric velocity also shifted the R2 line out of the corresponding telluric absorption line by a sufficient amount to be visible in a spectral extract (Fig. 1). How-

Table 2
Nucleus centered production rates and mixing ratios for CH₄ and H₂CO in Comet C/2001 A2

Date (UT)	T_{rot} (K)	Flux ^a		Q(H ₂ O) (10 ²⁶ s ⁻¹)	Q(CH ₄) (10 ²⁶ s ⁻¹)	Q(H ₂ CO) ^c (10 ²⁶ s ⁻¹)	CH ₄ /H ₂ O (%)	H ₂ CO/H ₂ O (%)
		CH ₄	H ₂ CO					
9.5 July	100	3.59(0.16)	0.651(0.053)	212(15)	3.24(0.22)	0.633(0.052)	1.53(0.15)	0.299(0.032)
10.5 July	100	4.78(0.25)	0.141(0.076)	269(16)	4.47(0.32)	0.143(0.077)	1.66(0.15)	0.053(0.029)
4.4 August	70	1.45(0.04)	0.0524(0.0466)	86(12) ^b	2.47(0.08)	0.149(0.131)	2.87(0.41)	0.173(0.154)
10.5 August	70	0.60(0.06)	–	45(10) ^b	1.29(0.13)	–	2.89(0.70)	–

^a The total transmittance-corrected line fluxes (in units of 10⁻¹⁸ W m⁻²) in a 0.43'' × 1.74'' (3 spectral by 9 spatial pixels) aperture centered on the nucleus (as opposed to the terminal production rates presented in Paper I and Table 3). The CH₄ fluxes are the sum of the R0 and R1 lines, and the H₂CO flux pertains to the nucleus-centered sum over five spectral lines, one of which encompasses the ν₁ Q-branch. All numbers in parentheses are 1-σ confidence limits.

^b From Dello Russo et al. (2005).

^c Q(H₂CO) is based on $T_{\text{rot}} = 104$ K as measured on 9.5 July, corresponding to the best fit from a Boltzmann excitation over the same spectral intervals used to measure the flux. This same rotational temperature was assumed on 10.5 July.

Table 3
Global production rates and mixing ratios for CH₄ and H₂CO in Comet C/2001 A2

Date (UT)	T_{rot} (K)	Flux ^a		Q(H ₂ O) (10 ²⁶ s ⁻¹)	Q(CH ₄) (10 ²⁶ s ⁻¹)	Q(H ₂ CO) (10 ²⁶ s ⁻¹)	CH ₄ /H ₂ O (%)	H ₂ CO/H ₂ O (%)
		CH ₄	H ₂ CO					
9.5 July	100	2.17(0.21)	0.363(0.030)	377(34)	4.54(0.43)	0.886(0.088)	1.20(0.17)	0.235(0.029)
10.5 July	100	2.98(0.23)	0.082(0.044)	430(37)	6.48(0.49)	0.207(0.112)	1.51(0.15)	0.048(0.026)
4.4 August	70	0.73(0.04)	0.025(0.022)	109(17) ^b	3.07(0.16)	0.186(0.164)	3.39(0.56)	0.171(0.153)
10.5 August	70	0.34(0.04)	–	62(14) ^b	1.70(0.22)	–	2.74(0.71)	–

^a The total transmittance-corrected line fluxes (in units of 10⁻¹⁸ W m⁻²) based on the signal summed from 0.29–3.76 arc-sec off the nucleus, averaged from both sides of the nucleus. The fluxes for CH₄ were summed over the R0 and R1 lines. Those for H₂CO were summed over five spectral lines, one of which encompasses the ν₁ Q-branch. All numbers in parentheses are 1-σ confidence limits.

^b From Dello Russo et al. (2005).

ever, we omitted the R2 line from the analysis on 4.4 August due to the long on-chip exposure time (180 s per frame). The NIRSPEC InSb ALADDIN detector has a linear response up to ~10,000 counts. This count level was exceeded in the cores of atmospheric emission lines (corresponding to transmittances less than about 60%) on 4.4 August. While the R0 and R1 lines were Doppler shifted to ~70% transmittance (corresponding to ~8000 counts on chip), the R2 line experienced only 44% transmittance and may have been affected by the detector's non-linearity. This is further suggested by the smaller-than-expected line intensity compared to the R0 and R1 lines on that night.

Several factors could affect the determination of production rates for methane, the most important of which is the rotational temperature. The R0 and R1 lines originate from different spin states and consequently are insufficient by themselves to meaningfully constrain the rotational temperature (Gibb et al., 2003). Instead, rotational temperatures for each date were derived from a population analysis of multiple lines of one or more of the following: HCN, CO, C₂H₆, H₂CO, and H₂O. It has been found that inner-coma rotational temperatures determined from different molecules are typically in agreement (Mumma et al., 2001; DiSanti et al., 2001; Dello Russo et al., 2000; Magee-Sauer et al., 1999). C/2001 A2 was somewhat unusual in that HCN was found in July to have a significantly lower rotational temperature (~60 K) than the ~100 K found for H₂O, H₂CO, CO, and C₂H₆ (Paper I). Possible causes for this difference are discussed in Magee-Sauer et al. (2006).

Since the signal-to-noise in August was insufficient to measure T_{rot} directly (except for HCN), we estimated T_{rot} for wa-

ter. Magee-Sauer et al. (2006) found that the heliocentric T_{rot} dependence for HCN in C/2001 A2 was consistent with the ~0.6 R_h^{-1} found by Biver et al. (2006). If we assume a similar R_h^{-1} dependence for the other molecules, then $T_{\text{rot}} \sim 70$ –80 K in August. To be conservative, the August values for CH₄ in Table 2 were calculated for 70 K. A T_{rot} of 80 K would increase the CH₄ abundance to 3.5%. We note that these results are consistent with the unusual enhancement of hydrocarbon abundances reported by Magee-Sauer et al. (2006) in C/2001 A2.

We also note that if we use the HCN rotational temperatures for CH₄, the abundance variation remains. The abundance for CH₄, assuming $T_{\text{rot}} \sim 60$ K, was 0.59% and 0.74% on July 9 and 10, respectively. In August, T_{rot} was determined to be ~40 K based on an analysis of six lines of HCN, resulting in CH₄ abundances of 1.9% and 1.5% on August 4 and 10, respectively. We emphasize that the comparison must be consistent. Whether we use the HCN T_{rot} in July and August or the ~100 K T_{rot} found for the other molecules in July with a R_h^{-1} dependence similar to that found for HCN and radio observations (Biver et al., 2006), CH₄ exhibited a significant change in abundance between July and August. In order to bring the CH₄ abundances into agreement on all dates, the T_{rot} for H₂O and the other molecules would have had to drop a factor of three faster than that for HCN. Alternatively, a drastically different heliocentric dependence (R_h^{-3}) would have to be assumed. Both scenarios are unrealistic and we conclude that the most likely explanation is that the CH₄ abundance changed between July and August.

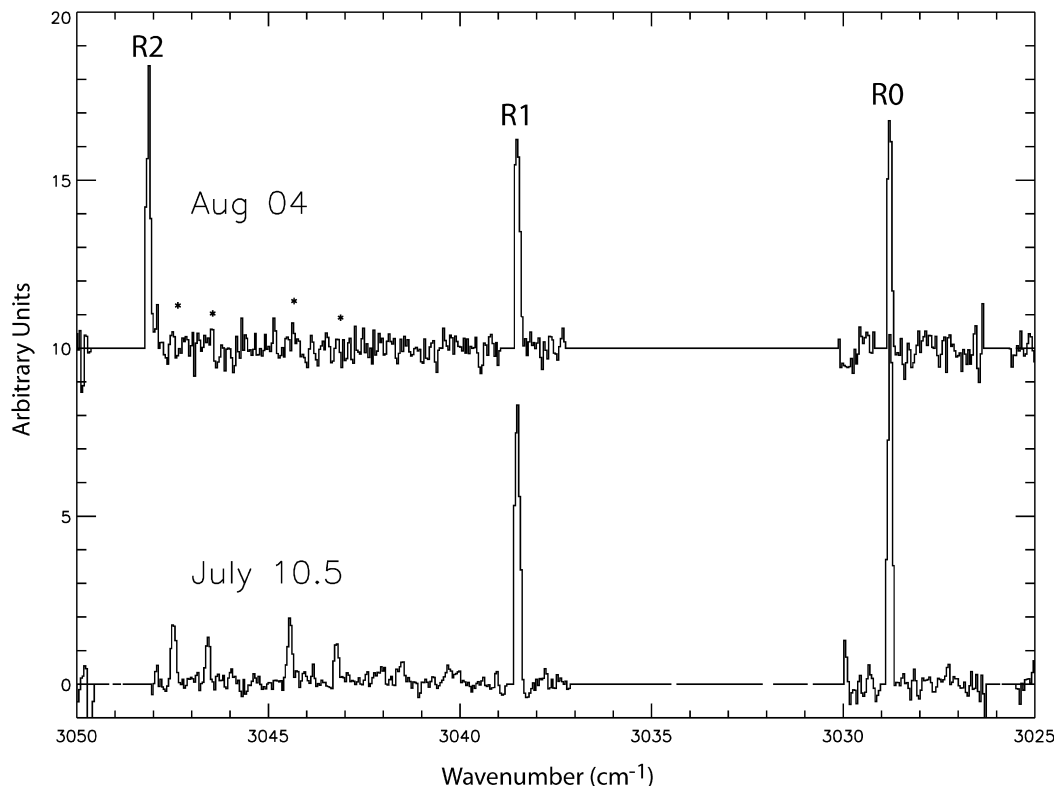


Fig. 2. The spectral extracts of the 3050–3025 cm^{-1} region of Comet C/2001 A2 on July 10.5 and August 4.4 after correction for terrestrial transmittance. Both spectra are shown in the comet's rest frame. Regions with no data correspond to low terrestrial transmittance ($<25\%$). The *'s mark the expected peak intensities of OH prompt emission lines (OH*) if CH_4 and H_2O were present in the same relative abundances on the two dates, taking into account the measured rotational temperatures. This implies that the CH_4 mixing ratio in August was enhanced relative to that found in July.

The production rate derived for CH_4 also depends on the quality of the atmospheric model fit. Stellar calibration spectra were taken immediately following the cometary observations for the KL2 setting and at similar air mass, except for 10.5 August where a KL2 calibration was unavailable. For this date, we applied the atmospheric water burden determined from the KL1 stellar calibration to the KL2 comet spectrum. We note, however, that the CH_4 R0 and R1 lines do not overlap strong atmospheric water lines for our redshifts and so are relatively insensitive to the atmospheric water content. The calibration star observations achieved very high signal-to-noise ratio, and we were able to fit the atmospheric model with high precision. The terrestrial methane burden is found to be constant to within 4% in our comet and stellar calibration database from 1996 to the present. We also fit the spectrum using the GENLN2 telluric spectrum package (Edwards, 1992) and obtained the same result, giving us confidence that we have accurately determined the transmittance at the Doppler-shifted positions of the methane lines, even for the low geocentric velocity ($\sim 12 \text{ km s}^{-1}$) of the July observations. This comparison demonstrates that the uncertainty in atmospheric transmittance will affect the CH_4 production rates by no more than 5% in C/2001 A2.

The H_2O production rate was measured using both hot-band emission lines near $2.9 \mu\text{m}$ and prompt emission (PE) from dissociatively-excited OH (Paper I), which is a proxy for water (Bonev et al., 2004, 2006; Bonev, 2005). We found a significant variation in CH_4 mixing ratio between the July and August

dates (see Table 2). The increased mixing ratio is made apparent by comparing the transmittance-corrected emission spectra on 10.5 July and 4.4 August (Fig. 2). The OH lines in Fig. 2 should exhibit the intensities shown (*) if the relative production rates ($\text{CH}_4/\text{H}_2\text{O}$) were the same on these two nights. Methane production was clearly enhanced (relative to H_2O) in August, compared to July. An alternative explanation might be the variation in the PE mechanism near 1.5 AU compared to smaller heliocentric distances as suggested by Kawakita et al. (2003). However, Bonev (2005) tested this hypothesis for C/2004 Q2 (Machholtz) observed at 1.2 and 1.5 AU; OH PE was detected at both heliocentric distances with no evidence for any significant changes in the OH emission efficiencies. Moreover, the change of the $\text{CH}_4/\text{H}_2\text{O}$ mixing ratio between July and August is confirmed from the directly measured H_2O production rate (via “hot-band” emission) within the same instrument setting (KL2) that sampled CH_4 .

3.2. H_2CO

Formaldehyde (H_2CO) is a nearly-symmetric top molecule that was first reported in Comet Halley in the radio and from the IKS infrared spectrometer aboard the Vega spacecraft (Combes et al., 1988; Snyder et al., 1989; Mumma and Reuter, 1989). Since then radio transitions of formaldehyde have been routinely detected in comets (Biver et al., 2002). Using improved infrared instrumentation, we detected H_2CO via its ν_1 and ν_5 bands near $3.6 \mu\text{m}$ in Comets C/2002 C1 (Ikeya–Zhang)

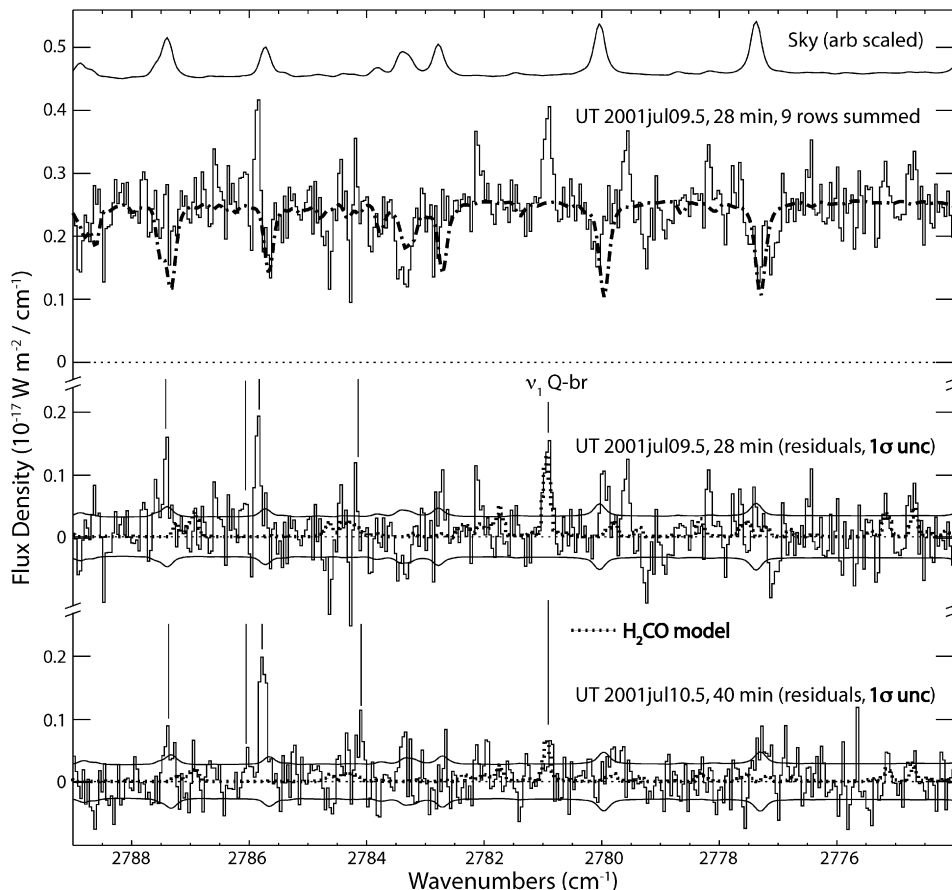


Fig. 3. H_2CO in C/2001 A2. The top panel shows the KL2, order 21 spectrum obtained with NIRSPEC on 9.5 July. The dashed line is the telluric model. The bottom panel shows the residuals from 9.5 and 10.5 July after subtraction of the atmospheric model. The $1\text{-}\sigma$ photon noise uncertainty level is indicated by the thin solid. The dotted line is the best-fit formaldehyde model ($T_{\text{rot}} = 104\text{ K}$). OH^* lines ($2784\text{--}2788\text{ cm}^{-1}$) are indicated by vertical tick marks. Note that while the OH^* lines were stronger on 10.5 July, consistent with the increased production rate noted in Paper I, the H_2CO Q-branch emission was absent on 10.5 July. This suggests heterogeneous composition of the nucleus.

(DiSanti et al., 2002), Lee (Dello Russo et al., 2006), and several other Comets (DiSanti et al., in preparation) in addition to Comet C/2001 A2. Observations of C/2002 T7 (LINEAR) in 2004 provided the first secure line-by-line detection of cometary H_2CO in these bands (DiSanti et al., 2006), enabling a robust measure of rotational temperature through comparison with a fluorescence model developed for interpretation of spectra of comets Halley and Wilson (Reuter et al., 1989; Mumma and Reuter, 1989).

H_2CO was securely detected on 9.5 July (Fig. 3). In the spectral regions we sampled, the ν_1 and ν_5 band line intensities are sensitive to temperature (Reuter et al., 1989; DiSanti et al., 2006). Fig. 3 shows a residual spectrum of H_2CO in C/2001 A2 on 9.5 and 10.5 July, along with a fluorescence model for formaldehyde at 104 K. The retrieved rotational temperature ($T_{\text{rot}} = 104_{-18}^{+20}\text{ K}$) is consistent with the rotational temperatures derived from other molecules in our spectra (Paper I). OH prompt emission near 2785 cm^{-1} (P16.5 2^+ , 2^- , P17.5 1^+ , 1^-) was measured simultaneously and traces (vertical tick marks, Fig. 3) water production (Bonev et al., 2004, 2006; Bonev, 2005). The OH^* P17.5 1^- line gives a water production rate of $4.2 \pm 0.2 \times 10^{28}$ molecules/s, in agreement with the $Q(\text{H}_2\text{O}) = 3.8 \pm 0.4 \times 10^{28}$ molecules/s derived by Dello

Russo et al. (2005). OH emission was somewhat stronger on 10.5 July, consistent with the general trend of increased production rates on that date for most molecules (Paper I), including H_2O (see Dello Russo et al., 2005), but the Q-branch of H_2CO is substantially weaker than on the previous night. The Q-branch of H_2CO falls in a region of good transmittance ($>95\%$ on both nights), so this variation cannot be due to transmittance effects, even though the terrestrial water burden was unusually high during our July observations. This is intriguing, particularly since other parent molecules that were observed on both dates did not show such a large variation relative to one another or to water (Table 2), although the chemically related species CH_3OH decreased slightly in abundance from July 9.5 to 10.5, from $(3.85 \pm 0.36)\%$ to $(2.79 \pm 0.33)\%$ relative to water. We suggest that the variations of both CH_4 and H_2CO are good evidence of chemical heterogeneity within the nucleus of Comet C/2001 A2.

4. Discussion

4.1. The variability of CH_4 between July and August

We find that the CH_4 abundance relative to other species changed significantly in Comet C/2001 A2 from July to Au-

gust and that the H_2CO abundance varied even between two consecutive nights (9.5 and 10.5 July). There might be a hint for CH_4 variability between July 9.5 and 10.5, though we cannot say conclusively as the results agree within their $1\text{-}\sigma$ errors. These changes could be evidence of chemical heterogeneity of parent species within the nucleus. Magee-Sauer et al. (2006) report that several organic species (HCN , C_2H_6 , C_2H_2) were enhanced in abundance in C/2001 A2 by approximately a factor of two over other comets observed in the infrared to date. However, in C/2001 A2 their abundance ratios did not vary significantly with time. In July, CH_4 in C/2001 A2 was consistent with abundances seen in several other comets (Gibb et al., 2003), but in August the higher abundance is consistent with the factor of two enhancement found for other organics in July, perhaps suggesting that the region active in July was depleted in methane (and was variable in formaldehyde).

C/2001 A2 disrupted prior to our July observations and also experienced an outburst on 12 July (Kysely et al., 2001; Morris et al., 2001), just after our July observations. There were additional minor events prior to our August observations as evidenced by a 0.4 (0.2) magnitude increase in the light curve on 25 (30) July, respectively (Kidger et al., 2001). These variations in the light curve have been interpreted to be most likely due to the separation of small, short-lived pieces of the comet that were not themselves directly observable (Sekanina et al., 2002). Two scenarios may explain the observed compositional differences in C/2001 A2. First, it is possible that in August, production was dominated by fresh, unaltered material from deeper within the comet nucleus that had been shielded from the effects of solar heating prior to disruption. We may have been sampling material from different depths into the nucleus in July and August. Alternatively, a different methane-rich region of the comet, perhaps a separate cometesimal (or vent), produced most of the emission in August but not in July. This may indicate that the comet nucleus is an assemblage of compositionally distinct cometesimals. At this time we cannot distinguish between the two scenarios.

Another possible explanation is related to the scale length for evaporation from icy mantles of grains. In August, C/2001 A2 was farther from Earth (~ 0.6 AU as opposed to ~ 0.3 AU in July), so the slit sampled a larger region around the nucleus. However, the comet was also farther from the Sun (Table 1), so the initial temperature of grains coming off the nucleus was lower as was the insolation. Observations of CH_4 ice and gas toward young stars embedded in molecular cloud material suggest that CH_4 is trapped in a polar ice matrix in the interstellar medium (Boogert et al., 1996, 1998). If CH_4 in comets were also trapped in a water-ice matrix, a possibility discussed in Gibb et al. (2003), then we would expect similar evaporation behavior for both species and the explanation for the enhanced production rates would be chemical heterogeneity. However, if hypervolatiles such as methane are not mixed with the polar species, as may be the case if the ice mantles were completely evaporated and then recondensed from the solar nebula according to their volatility prior to incorporation into a cometary body, then they may evaporate more quickly than water at a heliocentric distance of 1.5 AU, compared to 1.1 AU. If this were

the case, water would evaporate later than the hypervolatile species and would be observed as an extended source. Unfortunately, the signal-to-noise was not sufficient to determine whether the release of water was extended in August. However, this seems an unlikely explanation since we have not seen evidence of extended water in any other comet observed to date, though we note that our observations generally are made at heliocentric distances less than 1.3 AU. Nevertheless, the significance of extended vs. native release of parent volatiles from the comet surface is a question requiring further investigation.

4.2. The day-to-day variability of H_2CO in July

There were no known disruption or outburst events between our July 9.5 and 10.5 observations that included H_2CO . Formaldehyde has a relatively short photo-dissociation lifetime (~ 4500 s at $R_h = 1$ AU; Huebner et al., 1992), but our column density is weighted heavily toward molecules within about 100 km of the nucleus, so the short lifetime cannot explain the large difference in H_2CO production between 9.5 and 10.5 July. Formaldehyde could be released either as monomers or polymers (e.g., POM), but our measurements sample mainly the monomeric component. The measured change in H_2CO abundances between the two nights requires a major change in the monomeric production. We were unable to test the presence of a polymeric fraction (or its change), again because our beam was heavily weighted toward the nucleus and POM destruction would produce a more distributed source (Cottin et al., 2004). The signal-to-noise was not sufficient to determine whether the release of H_2CO included an extended component.

H_2CO was detected on 10.3 July at radio wavelengths (using IRAM) with a beam size of $10.9''$, much larger than ours (Biver et al., 2006). Biver et al. considered production of H_2CO from both native and distributed sources. They inferred a native production ratio of $0.05 \pm 0.01\%$ if H_2CO was a parent volatile, which is consistent with our measured value ($0.048 \pm 0.026\%$) for H_2CO on 10.5 July (Table 2). (Although our nucleus-centered beam is heavily weighted toward native H_2CO , molecules released in the coma along the line of sight also contribute somewhat to the measured column.) Given the large difference in the production of H_2CO we measured on these two dates, it is possible that we observed a H_2CO rich jet on 9.5 July.

5. Conclusion

We report evidence for chemical heterogeneity of two volatiles in Comet C/2001 A2. The H_2CO abundance, relative to water, decreased by a factor of nearly four between successive nights (9.5 and 10.5 July). The CH_4 abundance increased nearly a factor of two between July and August. These variations may reflect chemical heterogeneities within the nucleus and may be related to the repeated outburst events C/2001 A2 underwent during its apparition. Clearly, it is important to study parent volatiles over a wide range of heliocentric distances and to observe comets both before and after any outburst or disruption events. Snapshots of nuclear ice composition may not give us a comprehensive picture of the chemical composition of these primitive bodies.

Acknowledgments

E.L.G. gratefully acknowledges support from the NRC under her Resident Research Associateship at NASA's Goddard Space Flight Center. K.M.-S. was supported by the NSF Research at Undergraduate Institutions Program (AST-009841). We also acknowledge NASA's Planetary Astronomy program support for M.J.M. and B.P.B. (RTOP 344-32-30-07) and M.A.D. (RTOP 344-32-98, and NAG5-7905, NAG5-12208), and NASA's Planetary Atmospheres program support for N.D.R. (NAG5-10795, NAG5-12285) and M.A.D. (RTOP 344-33-55). We thank the NASA Keck TAC for awarding observing time to our Target-of-Opportunity proposal and the Observatory Director (F. Chaffee) for rescheduling Keck-2. We thank I. McLean and D. Sprayberry for acquiring the 4.4 August data. We also thank Geronimo Villanueva for providing GENLN2 telluric model spectra. Data presented herein were obtained at the W.M. Keck Observatory, which is operated as a scientific partnership among the California Institute of Technology, the University of California, and the National Aeronautics and Space Administration. The Observatory was made possible by the generous financial support of the W.M. Keck Foundation. The authors recognize and acknowledge the very significant cultural role and reverence that the summit of Mauna Kea has always had within the indigenous Hawaiian community.

References

- Biver, N., and 8 colleagues, 2002. Chemical composition diversity among 24 comets observed at radio wavelengths. *Earth Moon Planets* 90, 323–333.
- Biver, N., and 9 colleagues, 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.
- 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., 2005. Towards a chemical taxonomy of comets: Infrared spectroscopic methods for quantitative measurements of cometary water (with an independent chapter on Mars polar science). Ph.D. thesis. http://astrobiology.gsfc.nasa.gov/Bonev_thesis.pdf.
- 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.
- Boogert, A.C.A., Schutte, W.A., Tielens, A.G.G.M., Whittet, D.C.B., Helmich, F.P., Ehrenfreund, P., Wesseliuss, P.R., deGraauw, Th., Prusti, T., 1996. Solid methane toward deeply embedded protostars. *Astron. Astrophys.* 315, L377–L380.
- Boogert, A.C.A., Helmich, F.P., van Dishoeck, E.F., Schutte, W.A., Tielens, A.G.G.M., Whittet, D.C.B., 1998. The gas/solid methane abundance ratio toward deeply embedded protostars. *Astron. Astrophys.* 335, 352–358.
- Broughton, J., Sekanina, Z., Pearce, A., 2001. Comet C/2001 A2 (LINEAR). *IAU Circ.* 7625.
- Combes, M., Crovisier, J., Encrenaz, T., Moroz, V.I., Bibring, J.-P., 1988. The 2.5–12 micron spectrum of Comet Halley from the IKS-VEGA experiment. *Icarus* 76, 404–436.
- Cottin, H., Bénilan, Y., Gazeau, M.-C., Raulin, F., 2004. Origin of cometary extended source from degradation of refractory organics on grains: Polyoxymethylene as formaldehyde parent molecule. *Icarus* 167, 397–416.
- 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, B., 2001. Ethane production and release in Comet C/1995 O1 Hale–Bopp. *Icarus* 153, 162–179.
- 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., Mumma, M.J., DiSanti, M.A., Magee-Sauer, K., Gibb, E.L., Bonev, B.P., McLean, I.S., Li-Hong, Xu., 2006. A high-resolution infrared spectral survey of Comet C/1999 H1 Lee. *Icarus* 184, 255–276.
- 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., Novak, R., Rettig, T.W., 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*. ESA SP-500, pp. 571–574.
- 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 wavelengths: Line-by-line validation of modeled fluorescent intensities. *Astrophys. J.* 650, 470–483.
- Edwards, D.P., 1992. GENLN2: A general line-by-line atmospheric transmittance and radiance model. NCAR Tech. Note NCAR/TN-367+STR. National Center for Atmospheric Research, Boulder, CO.
- 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.
- Goldreich, P., Lithwick, Y., Sari, R., 2004. Final stages of planet formation. *Astrophys. J.* 615, 497–507.
- Hergenrother, C.W., Chamberlain, M., Chamberlain, Y., 2001. Comet C/2001 A2 (LINEAR). *IAU Circ.* 7616.
- Huebner, W.J., Keady, J.J., Lyon, S.P., 1992. Solar photo rates for planetary atmospheres and atmospheric pollutants. *Astrophys. Space Sci.* 195, 1–294.
- Jehin, E., and 10 colleagues, 2001. Comet C/2001 A2 (LINEAR). *IAU Circ.* 7627.
- Kawakita, H., Watanabe, J., Kinoshita, D., Ishiguro, M., Nakamura, R., 2003. Saturated hydrocarbons in Comet 153P/Ikeya–Zhang: Ethane, methane, and monodeuterio-methane. *Astrophys. J.* 590, 573–578.
- Kawakita, H., Watanabe, J., Furusho, R., Fuse, T., Boice, D.C., 2005. Nuclear spin temperature and deuterium-to-hydrogen ratio of methane in Comet C/2001 Q4 (NEAT). *Astrophys. J.* 623, L49–L52.
- Kidger, M., Ferrando, R., Manteca, P., Rodrigues, D., Ligustri, R., 2001. Comet C/2001 A2 (LINEAR). *IAU Circ.* 7679.
- Kysely, J., Baroni, S., Hornoch, K., Morris, C.S., 2001. Comet C/2001 A2 (LINEAR). *IAU Circ.* 7659.
- Levison, H.F., 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 Comet 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. Planets* 107 (E11), doi:10.1029/2002JE001863, 5096.
- Magee-Sauer, K., Mumma, M.J., DiSanti, M.A., Dello Russo, N., Gibb, E.L., 2006. The organic composition of Comet C/2001 A2 (LINEAR): A water-poor comet? *Icarus*. Submitted for publication.

- Mattiazzo, M., Bouma, R.J., Raymundo, P.M., Linnolt, M., Amorim, A., Nagai, Y., Rae, S.T., Cernis, K., 2001. Comet C/2001 A2 (LINEAR). IAU Circ. 7605.
- McLean, I.S., and 14 colleagues, 1998. Design and development of NIRSPEC: A near-infrared echelle spectrograph for the Keck II telescope. In: Fowler, A.M. (Ed.), Proc. SPIE, vol. 3354, pp. 566–578.
- Morris, C.S., Lehky, M., Pereira, A., Bouma, R.J., Hasubick, W., Spratt, C.E., Terbacz, A., 2001. Comet C/2001 A2 (LINEAR). IAU Circ. 7676.
- Mumma, M.J., Reuter, D.C., 1989. On the identification of formaldehyde in Halley's comet. *Astrophys. J.* 344, 940–948.
- 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., and 18 colleagues, 2001. 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., 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 (12), 2563.
- Pravec, P., Sarounova, L., Tichy, M., Kocer, M., 2001. Comet C/2001 A2 (LINEAR). IAU Circ. 7564.
- 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.
- Schuetz, O., and 16 colleagues, 2001. Comet C/2001 A2 (LINEAR). IAU Circ. 7656.
- Seargent, D.A.J., Baransky, A., Hasubick, W., Morris, C.S., 2001. Comet C/2001 A2 (LINEAR). IAU Circ. 7611.
- Sekanina, Z., Buso, V.A., Souza, W., Pearce, A., Seargent, D.A.J., 2001. Comet C/2001 A2 (LINEAR). IAU Circ. 7630.
- 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.
- Snyder, L.E., Palmer, P., de Pater, I., 1989. Radio detection of formaldehyde emission from Comet Halley. *Astron. J.* 97, 246–253.
- Stern, S.A., 2003. The evolution of comets in the Oort cloud and Kuiper belt. *Nature* 424, 639–642.
- Tsiganis, K., Gomes, R., Morbidelli, A., Levison, H.F., 2005. Origin of the orbital architecture of the giant planets of the Solar System. *Nature* 435, 459–461.
- Weidenschilling, S.J., 1997. The origin of comets in the solar nebula: A unified model. *Icarus* 127, 290–306.
- Weissman, P.R., Asphaug, E., Lowry, S.C., 2004. Structure and density of cometary nuclei. In: Festou, M.C., Keller, H.U., Weaver, H.A. (Eds.), *Comets II*. Univ. of Arizona Press, Tucson, pp. 337–357.