

HIGHLY DEPLETED ETHANE AND MILDLY DEPLETED METHANOL IN COMET 21P/GIACOBINI-ZINNER: APPLICATION OF A NEW EMPIRICAL ν_2 -BAND MODEL FOR CH₃OH NEAR 50 K

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ABSTRACT

We obtained infrared spectra of Comet 21P/Giacobini-Zinner (hereafter 21P/GZ) using NIRSPEC at Keck II on UT 2005 June 3, approximately one month before perihelion, that simultaneously sampled H₂O, C₂H₆, and CH₃OH. Our production rate for H₂O ($3.885 \pm 0.074 \times 10^{28}$ molecules s⁻¹) was consistent with that measured during other apparitions of 21P/GZ as retrieved from optical, infrared, and radio observations. Our analysis also provided values for rotational temperature ($T_{\text{rot}} = 51 \pm 3$ K) and the abundance ratio of ortho and para spin populations for water (OPR = 2.99 ± 0.23 , implying a spin temperature exceeding 50 K). Six Q -branches in the ν_7 band of C₂H₆ provided a production rate ($5.27 \pm 0.90 \times 10^{25}$ s⁻¹) that corresponded to an abundance ratio of $0.136 \pm 0.023 \times 10^{-2}$ relative to H₂O, confirming the previously reported strong depletion of C₂H₆ from IR observations during the 1998 apparition, and in qualitative agreement with the depletion of C₂ known from optical studies of 21P/GZ. For CH₃OH, we applied our recently published quantum model for the ν_3 band to obtain a rotational temperature (48^{+10}_{-7} K) consistent with that obtained for H₂O. In addition, we developed a new empirical model for the CH₃OH ν_2 band, based on observations of Comet 8P/Tuttle with NIRSPEC. The application of our ν_2 model to 21P/GZ yielded a production rate in agreement with that obtained from the ν_3 band. Combining results from both ν_2 and ν_3 bands provided a production rate ($47.5 \pm 4.4 \times 10^{25}$ s⁻¹) that corresponded to an abundance ratio of $1.22 \pm 0.11 \times 10^{-2}$ relative to H₂O in 21P/GZ, indicating mild depletion of CH₃OH. Together with observations of 21P/GZ in 1998, our study provides a measure of primary volatile production rates for this Jupiter family comet over multiple apparitions using high-resolution IR spectroscopy.

Key words: comets: general – comets: individual (21P/Giacobini-Zinner) – techniques: spectroscopic

Online-only material: color figures

1. INTRODUCTION

Comet 21P/Giacobini-Zinner (hereafter 21P/GZ) was discovered in 1900 by Michel Giacobini, was re-discovered independently by Ernst Zinner in 1913, and was recovered in all apparitions since its discovery with the exception of the unfavorable ones in 1907, 1920, and 1953. Its Tisserand parameter with respect to Jupiter ($T_J = 2.46$) classifies 21P/GZ dynamically as a Jupiter Family comet (JFC), the predominant “feeding zone” for which is the scattered Kuiper disk, as predicted by the pre-eminent Nice model (Gomes et al. 2005; Morbidelli et al. 2008). This comet has the distinction of being the first to be visited by a spacecraft—in 1985 September, the International Cometary Explorer (originally the International Sun–Earth Explorer-3) flew through its plasma tail, passing within 8000 km of the nucleus. Here we report production rates for simultaneously observed C₂H₆, CH₃OH, and H₂O in 21P/GZ during its 2005 apparition, using the cross-dispersed high-resolution IR echelle spectrometer (NIRSPEC) at Keck II, applying our latest fluorescence models for H₂O, C₂H₆, and CH₃OH, including a new empirical model for the ν_2 band of methanol.

Observational studies indicate substantial chemical diversity among comets (e.g., see Mumma & Charnley 2011, and references therein). The most comprehensive work reported optical narrow-band photometric observations of radical (photo-dissociation product) abundances spanning some three decades (A’Hearn et al. 1995). This survey established “typical” and “depleted” classes depending on their abundances of C₂ (and C₃) relative to CN and OH. It was argued that this may reflect

differences in carbon-chain chemistry (i.e., differing abundances of progenitor ices for C₂ and/or C₃), with inferred carbon-chain depletion being considerably more pronounced in JFCs compared with nearly isotropic comets (i.e., dynamically new or long-period returning comets, from the Oort cloud; see also Fink & Hicks 1996; Schleicher et al. 2007; Fink 2009; Cochran et al. 2012). Comet 21P/GZ is often regarded as the prototypical carbon-chain depleted comet (A’Hearn et al. 1995).

While highly diagnostic, these findings do not necessarily translate to a similar dichotomy in native ice abundances, primarily due to uncertainties in the parentages of fragmentation products (daughter or granddaughter species). Compared with optical observations, parent species have been studied in relatively few JFCs, owing mostly to their typically lower overall gas production relative to nearly isotropic comets. However, in recent years advances in technology have permitted more detailed studies of native ice abundances in JFCs, in both radio (Biver et al. 2002; Crovisier et al. 2009; Biver et al. 2012) and infrared regimes (Weaver et al. 1999; Mumma et al. 2000, 2005, 2011; Dello Russo et al. 2007, 2008, 2009, 2011; DiSanti et al. 2007a; Kobayashi et al. 2007, 2010; Villanueva et al. 2006; Paganini et al. 2012).

Through the use of modern high-resolution spectrometers, the IR offers the unique capability of measuring trace molecules simultaneously with H₂O, the most abundant ice in comet nuclei and the principal driver of cometary activity for heliocentric distances (R_h) less than ~ 3 AU. Symmetric hydrocarbons (e.g., C₂H₂, CH₄, C₂H₆, etc.) have no electric dipole moment and so are not observable at radio wavelengths since pure rotational

Table 1
Observing Log for Comet 21P/Giacobini-Zinner on UT 2005 June 3^a

NIRSPEC Setting	UT Start–End	Molecule (Order) ^b	T_{int}^c (minutes)
KL1	14:45–15:24	H ₂ O (26, 27) C ₂ H ₆ (23) CH ₃ OH (22, 23)	24

Notes.

^a $R_h = 1.116$ AU, $\Delta = 1.454$ AU, $d\Delta/dt = -5.4$ km s⁻¹, $dR_h/dt = -8.8$ km s⁻¹. Solar phase angle (β) = 44°.

^b Quantified primary molecules and NIRSPEC echelle order (in parentheses) in which their emissions occur.

^c Total on-source integration time.

transitions are forbidden, leaving their infrared vibrational bands as the sole means of measuring their abundances in comets through remote sensing.

In this study, we investigate whether the C₂ depletion observed in 21P/GZ carries over to primary (parent) volatiles, in particular to C₂H₆, which we quantify through application of a comprehensive fluorescence model for the ν_7 band near 3.35 μm (Villanueva et al. 2011a). For CH₃OH we present our newly developed empirical fluorescence model, incorporating more than 100 lines in the ν_2 band that are interspersed with C₂H₆ ν_7 emissions. Application of our empirical g -factors for ν_2 together with our recently published quantum model for the ν_3 band near 3.52 μm (Villanueva et al. 2012a) enables us to retrieve a highly precise production rate for methanol in 21P/GZ.

We compare our results for 21P/GZ with those reported from the IR (for C₂H₆ and CH₃OH) and radio (for CH₃OH) during its previous apparition in 1998. We compare our abundances in 21P/GZ with those measured in other JFCs, and also compare measured abundances of C₂H₆ and C₂ (from optical studies) among seven member comets in this dynamical population. We end with a discussion of prospects for measuring native ice abundances in 21P/GZ during its next favorable apparition in 2018.

2. OBSERVATIONS AND DATA PROCESSING

We obtained spectra of 21P/GZ on UT 2005 June 03.63 using the near-infrared cross-dispersed echelle spectrograph (NIRSPEC; McLean et al. 1998) and 10 m Keck II telescope on Mauna Kea, HI. NIRSPEC delivers simultaneous coverage of six echelle orders (at L -band) at sufficiently high spectral resolving power ($\lambda/\Delta\lambda \sim 24,000$, using the 0'43 wide slit) to measure emission intensities of individual lines or groups of blended lines for a given molecule.

One half-night (second half) was granted to obtain baseline measurements of Comet 9P/Tempel 1 approximately one month prior to the Deep Impact encounter. Comet 21P/GZ was accessible in the east toward the end of the night, permitting us to dedicate the final 40 minutes of available clock time to the study reported here. Its limited availability and modest brightness ($m_v = 10$ –12) meant that only one instrument setting was possible—this was chosen so as to simultaneously encompass C₂H₆ (in order 23), CH₃OH (in orders 22 and 23), and H₂O (in orders 26 and 27; Table 1).

The telescope was nodded in our standard ABBA cadence, with A- and B-beams each containing comet signal and the telescope nodded by ± 6 arcsec relative to the slit center for the two beam positions. For our observations, the slit was oriented at position angle 157° (Figure 1(a)), approximately

perpendicular to the Sun–comet direction (P.A. = 260°). A total of six ABBA sets were obtained, corresponding to 24 minutes on source. Individual echelle orders were processed as described previously (Villanueva et al. 2011b; Bonev 2005; Mumma et al. 2001a).

Signals from A and B beams were combined, and spectra were extracted over nine spatial pixels (1'78, or 1880 km) centered on the peak intensity as determined by the measured molecular emission profiles (Figures 1(b)–(d); also see Table 2, note “b”). The emission line spectrum was isolated by subtracting the cometary dust continuum multiplied by the modeled atmospheric transmittance function (Figures 3 and 5). Flux calibration was accomplished by obtaining spectra of an IR standard star (HR-5487). Absolute line fluxes were referred to the top-of-the-atmosphere by ratioing measured intensities to the monochromatic transmittance at each Doppler-shifted line-center frequency (based on geocentric velocity $\Delta\dot{\nu} = -5.42$ km s⁻¹). Transmittances were modeled using the Line-By-Line Radiative Transfer Model (Clough et al. 2005) and the latest HITRAN database with updated parameters (Rothman et al. 2010; see Villanueva et al. 2011a for detailed discussion and application). We used the NIRSPEC Slit-viewing CAMera to maintain 21P/GZ in the slit, thereby ensuring that loss of flux (slit spillover) was due primarily to seeing. We applied a measured slit-loss correction factor (denoted as GF in Equation (1) below) to convert our nucleus-centered production rates to global (or “total”) production rates (Section 4.1).

3. MOTIVATION FOR A ν_2 -BAND MODEL OF CH₃OH

Methanol is a molecule that is routinely observed in comets, both at IR and radio wavelengths. It has three fundamental vibrational bands in the 3.3–3.6 μm spectral region, ν_3 (parallel band; symmetric CH₃ stretching mode, centered near 2844 cm⁻¹), ν_2 , and ν_9 (predominantly perpendicular bands; asymmetric CH₃ stretching modes centered near 2990 and 2970 cm⁻¹, respectively). (The terms “parallel” and “perpendicular” refer, in the symmetric top approximation, to the orientation of the transition moment associated with the vibrational mode relative to the top axis; Herzberg 1945, p. 414.) Of these three bands, ν_3 has traditionally been targeted for measuring CH₃OH in comets, primarily because it is relatively free of blends with emissions from other species and also because it is spectrally more compact compared with the asymmetric bands, having a single strong, well-delineated Q -branch. The ν_2 and ν_9 bands exhibit several sub-band Q -branches dispersed in frequency and interspersed with P - and R -branch lines (e.g., see Herzberg 1945, Figure 128, p. 425).

In addition to providing an alternate means of quantifying CH₃OH in comets, the ability to interpret ν_2 -band emissions has a practical application. Prior to the commissioning of NIRSPEC in 1999, the only available high-resolution IR spectrometer was CSHELL at the NASA-IRTF 3 m telescope (Tokunaga et al. 1990; Greene et al. 1994). This heritage instrument revolutionized the field of gas-phase spectroscopy from 1 to 5 μm , albeit with relatively small spectral coverage per setting (within a single echelle order), for example encompassing only about 7 cm⁻¹ in the “cometary organics” region (~ 3.2 –3.6 μm). CSHELL is adequate for measuring the ν_3 Q -branch (having a total width of ~ 1.5 cm⁻¹), however this required a dedicated, stand-alone setting for CH₃OH, and a second setting for measuring other parent molecules, for example C₂H₆ through its ν_7 band centered near 2985 cm⁻¹. A fluorescence model for the methanol ν_2 band permits prominent emission features of C₂H₆ and CH₃OH

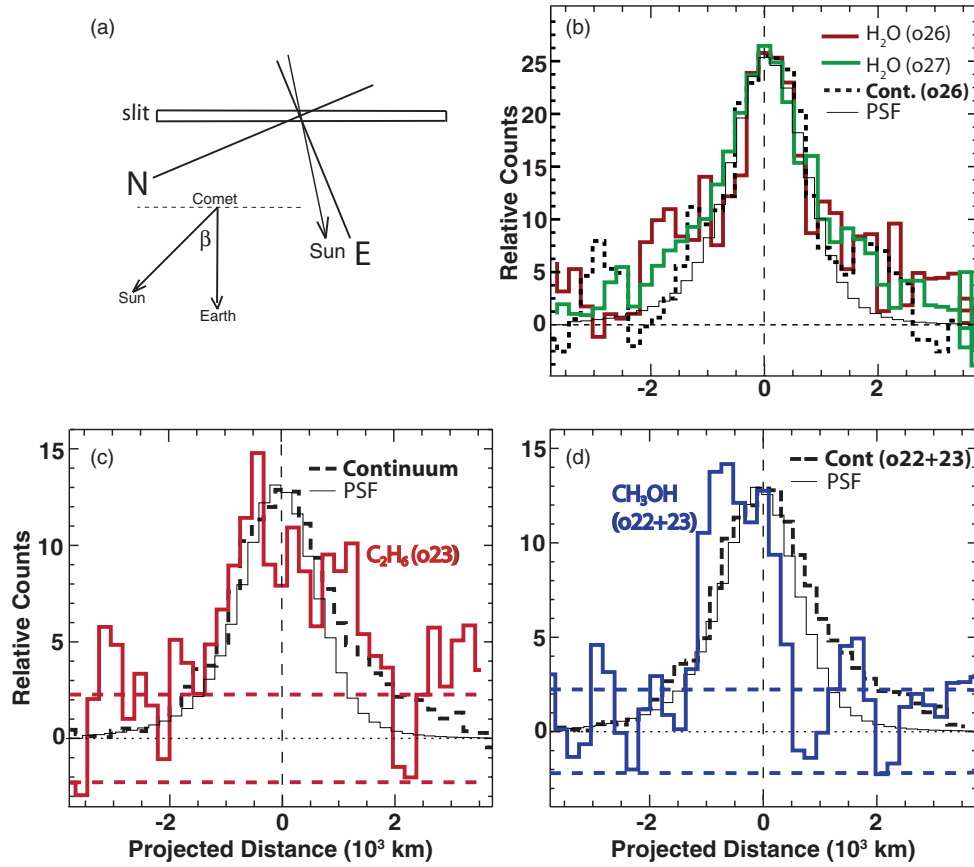


Figure 1. (a) Schematics showing the observing geometry for 21P/GZ on UT 2005 June 03. Upper: position angle (P.A.) of the extended Sun–comet vector (260°) and slit orientation (157° , or 23° W of N) projected onto the sky plane, with the comet located at the origin. Lower: solar phase angle ($\beta = 44^\circ$) for 21P/G-Z. (b)–(d) Comparison of spatial profiles in Comet 21P/G-Z. Projected distance is reckoned with respect to the peak of the observed continuum profile. For comparison, a representative point-spread function (PSF) is also shown.

(A color version of this figure is available in the online journal.)

to be measured simultaneously; even very modern instruments such as CRIRES (Käufl et al. 2004) at the VLT cannot measure C₂H₆ ν_7 and CH₃OH ν_3 emissions in a single setting.

Although since superseded by NIRSPEC, and more recently by CRIRES/VLT, CSHELL/IRTF retains a unique niche by virtue of its daytime capability and its greater flexibility in scheduling observing time compared with Keck or VLT, further emphasizing the need for quantifying CH₃OH through ν_2 emissions. Finally, regardless of instrument, adequate interpretation of cometary spectra in the region from ~ 2970 to 3000 cm^{-1} requires disentangling emissions arising from different molecules, most notably C₂H₆ and CH₃OH, with lesser contributions from CH₄ and OH prompt emission. A major step involves characterizing CH₃OH in this region, which is dominated by ν_2 -band emission. Toward this end, we developed a fluorescence model for this band (Section 4.3.4).

4. PRODUCTION RATES AND MOLECULAR ABUNDANCES

4.1. Methodology for Measuring Production Rates

Global (or total) production rates (Q_{tot}) for parent molecules were calculated using our well-documented methodology (Villanueva et al. 2011b; Bonev 2005; Mumma et al. 2003; DiSanti et al. 2001; Dello Russo et al. 1998). In applying our formalism, we measure a growth factor (GF), relating Q_{tot} for a primary volatile to that obtained from signal summed over nine

spatial pixels centered on the peak emission intensity (we refer to this as the “nucleus-centered” production rate, Q_{nc}):

$$Q_{\text{tot}} \equiv Q_{\text{nc}} GF. \quad (1)$$

The GF (>1) corrects for loss of flux, due primarily to atmospheric seeing as explained in Section 2. In our analysis of 21P/GZ, the majority of spectral regions (intervals) we selected for determining our production rates consisted of blends of multiple lines. Within each chosen interval, Q_{nc} for that interval (denoted as $Q_{\text{nc,int}}$) is proportional to the measured line flux (F_{int} , W m^{-2}) divided by the product of rest frequency (ν_i , cm^{-1}), fluorescence g -factor ($g_{1,i}$, photon s^{-1} molecule $^{-1}$, evaluated at $R_h = 1$ AU), and atmospheric transmittance (T_i) at the Doppler-shifted frequency of each encompassed line, summed over all contributing lines (numbering “ n ”):⁴

$$Q_{\text{nc,int}} = \frac{4\pi\Delta^2}{hc\tau_1 f(x)} \left[\frac{F_{\text{int}}}{\sum_{i=1}^n (\nu_i g_{1,i} T_i)} \right]. \quad (2)$$

In Equation (2), τ_1 (s) is the photo-dissociation lifetime at $R_h = 1$ AU, $f(x)$ is the fraction of all molecules in the coma contained in the nucleus-centered beam (assuming native release and spherically symmetric outflow; see the Appendix in Hoban

⁴ For the case of only one line within an interval, the quantity in square brackets in Equation (2) is equivalent to $(F_{\text{line}}/T)/(\nu_{\text{line}} g_{1,\text{line}})$, where F_{line}/T is the top-of-atmosphere line flux as described in Section 2.

Table 2
Primary Volatiles in 21P/G-Z on 2005 June 3.6

Molecule	Order	Band(s)	$T_{\text{rot}}^{\text{a}}$ (K)	Q_{nc}^{b} (10^{25} s^{-1})	GF ^c	$Q_{\text{tot}}^{\text{d}}$ (10^{25} s^{-1})
H ₂ O	26,27	(e)	51 ± 3	$2398 \pm 34(46)$	1.62 ± 0.059	3885 ± 74
C ₂ H ₆	23	ν_7	[50]	$3.25 \pm 0.39(0.56)$	[1.62]	5.27 ± 0.90
CH ₃ OH ^f	23	ν_2	[~50]	$30.1 \pm 3.1(4.4)$	[1.62]	48.8 ± 7.1
CH ₃ OH ^f	22	ν_3	48^{+10}_{-7}	$28.6 \pm 2.8 (3.4)$	[1.62]	46.3 ± 5.5

Notes.

^a Rotational temperatures, as measured for H₂O using lines in orders 26 and 27 (Figure 2) and for CH₃OH from the ν_3 band (Figure 5). Quantities in square brackets denote adopted values. Uncertainties here and in all subsequent tables represent 1σ .

^b Nucleus-centered production rate based on emission contained in an aperture subtending $0''.43 \times 1''.78$ (approximately 460×1880 km), and centered on the position of peak intensity for each molecule. The H₂O emission (Figure 1(b)) was coincident with the continuum peak, while maximum emission intensities for C₂H₆ and CH₃OH (see Figures 1(c) and 1(d), respectively) were displaced by ~ 400 km (projected onto the sky plane) from that for H₂O. For each tabulated entry, the first uncertainty is the stochastic noise and the second (in parentheses) is the standard error among the lines (i.e., spectral intervals) sampled.

^c Growth factor (GF, Equation (1)) used to correct Q_{nc} for slit losses, which are due primarily to atmospheric seeing. In our analysis we assume the value measured for H₂O applies to the other molecules.

^d Total or global Q (Equation (1)). For each entry, the uncertainty incorporates the (dominant) standard error in Q_{nc} and the error in GF measured for H₂O (σ GF contributes a relatively small amount). Using the GF measured for C₂H₆ (1.90 ± 0.285 , based on the profile in Figure 1(c)) increases its global Q (and hence the ethane abundance, see Table 3) by 17%, to $(6.17 \pm 1.40) \times 10^{25} \text{ s}^{-1}$; however, this is within 1σ of that obtained using the GF from H₂O, and does not change our conclusion of highly depleted C₂H₆ in comet 21P/GZ. Combining CH₃OH from orders 22 and 23 results in $Q_{\text{tot}}(\text{CH}_3\text{OH}) = (47.5 \pm 4.4) \times 10^{25} \text{ s}^{-1}$. For the combined CH₃OH profile (Figure 1(d)) we measured GF = 1.65 ± 0.241 ; using this GF increases the combined $Q_{\text{tot}}(\text{CH}_3\text{OH})$ by only a negligible amount (1.9%). For CH₃OH in order 23, σQ_{nc} and σQ_{tot} also include uncertainties in empirical g -factor summed over each interval, based on stochastic noise levels in the 8P/Tuttle residuals (Figure 4; see also Table 4).

^e The 28 H₂O lines included in our analysis arise from eight distinct non-resonant (“hot”) bands: 101–100, 101–001, 200–001, 200–100, 111–110, 210–110, 003–002, and 201–200 (see Table 5).

^f For CH₃OH in order 23, Q_{nc} and Q_{tot} correspond to the weighted mean of all intervals in Figure 3 excluding number “5,” due primarily to (unknown) uncertainties in g -factor for the co-measured OH* P12.5 2[−] line, both for 8P/Tuttle and 21P/GZ as discussed in Section 4.3.2. Including interval “5” lowers the global Q for CH₃OH in order 23 by about 18%, to $(40.1 \pm 6.6) \times 10^{25} \text{ molecules s}^{-1}$, and lowers the mean $Q(\text{CH}_3\text{OH})$ (and hence the abundance of CH₃OH from combining orders 22 and 23) by approximately 10% (also see Table 3, note “g”).

et al. 1991), Δ is expressed in meters, and $hc = 1.99 \times 10^{-23} \text{ W s cm}$. The overall Q_{nc} represents the mean of values from all intervals, weighted by their respective stochastic errors (see Section 4.2). For CH₃OH in order 23, the uncertainty in our equivalent empirical g -factor for each interval is also included in this weighting (Table 4). The factor $f(x)$ includes photo-decay, gas outflow speed (taken to be $v_{\text{gas}} = 800 R_{\text{h}}^{-0.5} \text{ m s}^{-1} \sim 759 \text{ m s}^{-1}$), and geometrical parameters.

We calculate our global production rates using GF = 1.62 (Table 2), based on the spatial emission profile summed from several bright water lines (Figure 1(b)). Although noisier, the GF for CH₃OH was in agreement with this value, and that for C₂H₆, although somewhat larger, was also consistent (within 1σ uncertainty) with that measured for H₂O. Details are given in Table 2 (in particular, see note “d”).

4.2. Measurement Uncertainties

The errors associated with all reported parameters (production rates, rotational temperatures, and the ortho–para ratio for H₂O) account for sources of uncertainty including but not limited to stochastic (i.e., photon) noise, for example, uncertainties in fluorescence g -factors of modeled lines, telluric transmittance corrections, and the assumption of a single T_{rot} over the field of view. This is reflected in scatter about the mean of each measured parameter (e.g., production rate) that cannot be accounted for by photon noise alone. We quantify this scatter in terms of a “standard error” for each distribution. In general, and in our analysis of 21P/GZ, the standard error dominates the stochastic error, as exemplified in Figures 2(d) (for H₂O), 3(c) (for C₂H₆),

3(d) (for CH₃OH), and 5(c), 5(d) (for CH₃OH). In Table 4, we tabulate line fluxes and production rates from application of our ν_2 empirical model for CH₃OH (see Section 4.3.4.2), and in Tables 5–7 from our studies of H₂O, C₂H₆, and CH₃OH ν_3 emission, respectively. For detailed discussions regarding our treatment of errors, see Bonev (2005, Chapter 4), Dello Russo et al. (2006, Section 4.2), Bonev et al. (2007, p. L100), Villanueva et al. (2011b; Section 2.3), and Bonev et al. (2012, Section 3).

4.3. Results for Individual molecules in 21P/GZ

4.3.1. H₂O

We measured 29 water lines contained within 24 spectral intervals in orders 26 and 27, of which 18 are ortho (parallel nuclear spins of the two H-atoms) and 11 are para (anti-parallel spins; see Figure 2 and Table 5). These sample a large range in rotational energy ($>300 \text{ cm}^{-1}$; Figures 2(b)–(d)), allowing the rotational temperature to be determined with high precision ($T_{\text{rot}} = 51 \pm 3 \text{ K}$). We incorporated all but one ortho line (see below) and used our improved fluorescence model for H₂O (Villanueva et al. 2012b). Analysis of relative ortho- and para-line intensities resulted in a measure of the ortho-to-para ratio (OPR = 2.99 ± 0.23) consistent with equilibrated spins, thereby implying a spin temperature (T_{spin}) exceeding 50 K (e.g., see Bonev et al. 2007). Our method for decoupling T_{rot} and T_{spin} provides a highly precise (and accurate) measure of the global production rate for H₂O in 21P/GZ ($Q(\text{H}_2\text{O}) = 3.885 \pm$

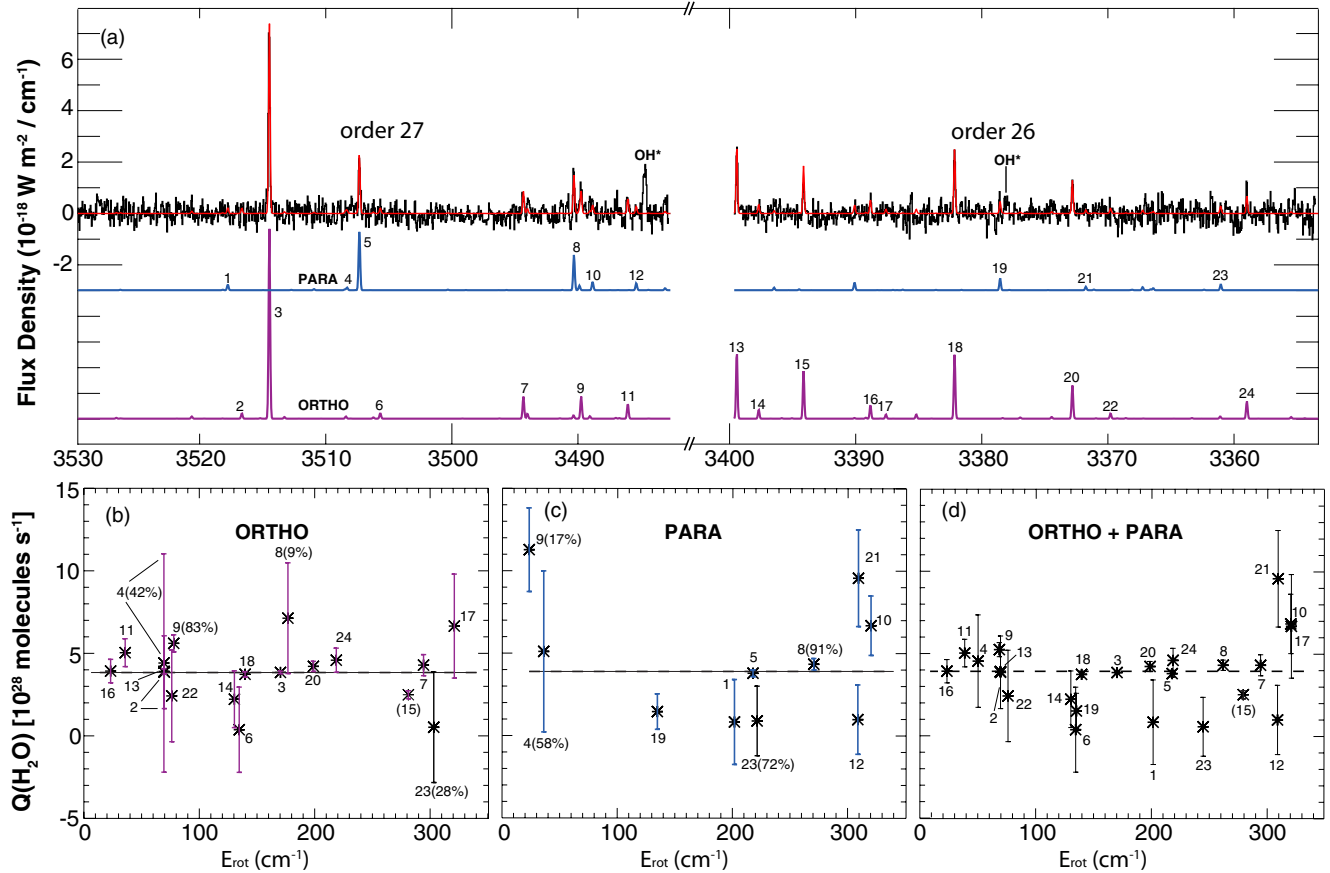


Figure 2. (a) Spectral extracts of H₂O in Comet 21P/G-Z, with best-fit fluorescence models for ortho and para spin species shown separately and corresponding to $T_{\text{rot}} = 51$ K and $\text{OPR} = 2.99$. The prominent feature near 3485 cm⁻¹ corresponds to two blended prompt OH lines (OH* $\nu = 1-0$, P2.5 1⁻ and P2.5 1⁺ at 3484.59 and 3484.74 cm⁻¹, respectively). The weaker feature in order 26 corresponds to OH* $\nu = 1-0$, P4.5 2⁺ and P4.5 2⁻ (3377.89 and 3378.07 cm⁻¹). (b) and (c) Line-by-line production rates for numbered ortho and para emissions, respectively. Features with percentages in parentheses indicate fractional intensities for ortho-para blends. For example, feature ‘8’ is comprised of 9% ortho and 91% para line flux for our measured T_{rot} and OPR. (d) Production rates for combined ortho, para distributions. Line ‘15’ is not well fit by our H₂O fluorescence model in 21P/GZ, and so is excluded from our analysis (see Section 4.3.1).

(A color version of this figure is available in the online journal.)

0.074×10^{28} molecules s⁻¹); see Bonev et al. (2012) for detailed discussion and application of our methodology.

In our rotational analysis, we omitted the strong ortho line at rest frequency 3394.08 cm⁻¹ (200,2₂₁ – 100,3₃₀; labeled ‘15’ in Figure 2; also see Table 5). This line appears to be affected by one or more bad pixels; its predicted (modeled) intensity is considerably larger than that measured in 21P/GZ, causing its calculated production rate to fall well below the mean $Q(\text{H}_2\text{O})$ as determined from the full suite of water lines in orders 26 and 27 (by ~ 4.9 times its stochastic error), as shown in Figures 2(b) and (d). Rotational temperature and OPR were highly correlated in our data, and including this line made it difficult to obtain unambiguous values for either parameter, and also increased the standard error associated with the distribution by a factor of nearly two. Fortunately, however, this line has a very minimal effect on our retrieved H₂O production rate—its inclusion decreased $Q(\text{H}_2\text{O})$ (and hence increased our retrieved abundance ratios for C₂H₆ and CH₃OH) by only $\sim 2\%$.

4.3.2. OH Prompt Emission in Order 23

Our observations encompassed four strong lines of OH in order 23. These lines arise through ‘prompt emission’ (denoted OH*) in the $\nu = 1-0$ band, radiating within milliseconds from vibrationally and rotationally excited states following their

production from photo-dissociation of H₂O molecules in the coma (Bonev et al. 2006 and references therein). The OH* P12.5 2⁻ line is blended with C₂H₆ ν_3 , and also with the strong A⁺ $\nu = 1 \rightarrow 0$ Q-branch of the CH₃OH ν_2 band (plus a few weaker ν_2 lines, Table 4). We estimated an effective g -factor for the P12.5 2⁻ line through comparison with OH* lines from adjacent multiplets. We also estimated its g -factor empirically from NIRSPEC observations of Comet C/1999 S4 (LINEAR) in 2000 July. This comet was very highly depleted in virtually all primary volatiles, including C₂H₆ and CH₃OH (Mumma et al. 2001b), leaving the OH* lines as the only discernable emissions in excess of the continuum in order 23. These two independent approaches led to g -factors for the P12.5 2⁻ line in the ratio 1.19 (the one based on LINEAR S4 being larger), exemplifying the uncertainties associated with obtaining accurate g -factors for these lines when comparing comets observed at different times, in particular during different phases of the solar cycle.

We verified that including this spectral interval (number ‘5’ in Figures 3 and 4) does not alter our conclusions regarding the abundances of C₂H₆ and CH₃OH in 21P/GZ. Because we encompass many emissions from both ethane and methanol, the spectral confusion from OH* (which affects only one feature) has a minor influence on their production rates. Including this blend lowers $Q(\text{C}_2\text{H}_6)$ by only $\sim 2\%$ (Section 4.3.3) and

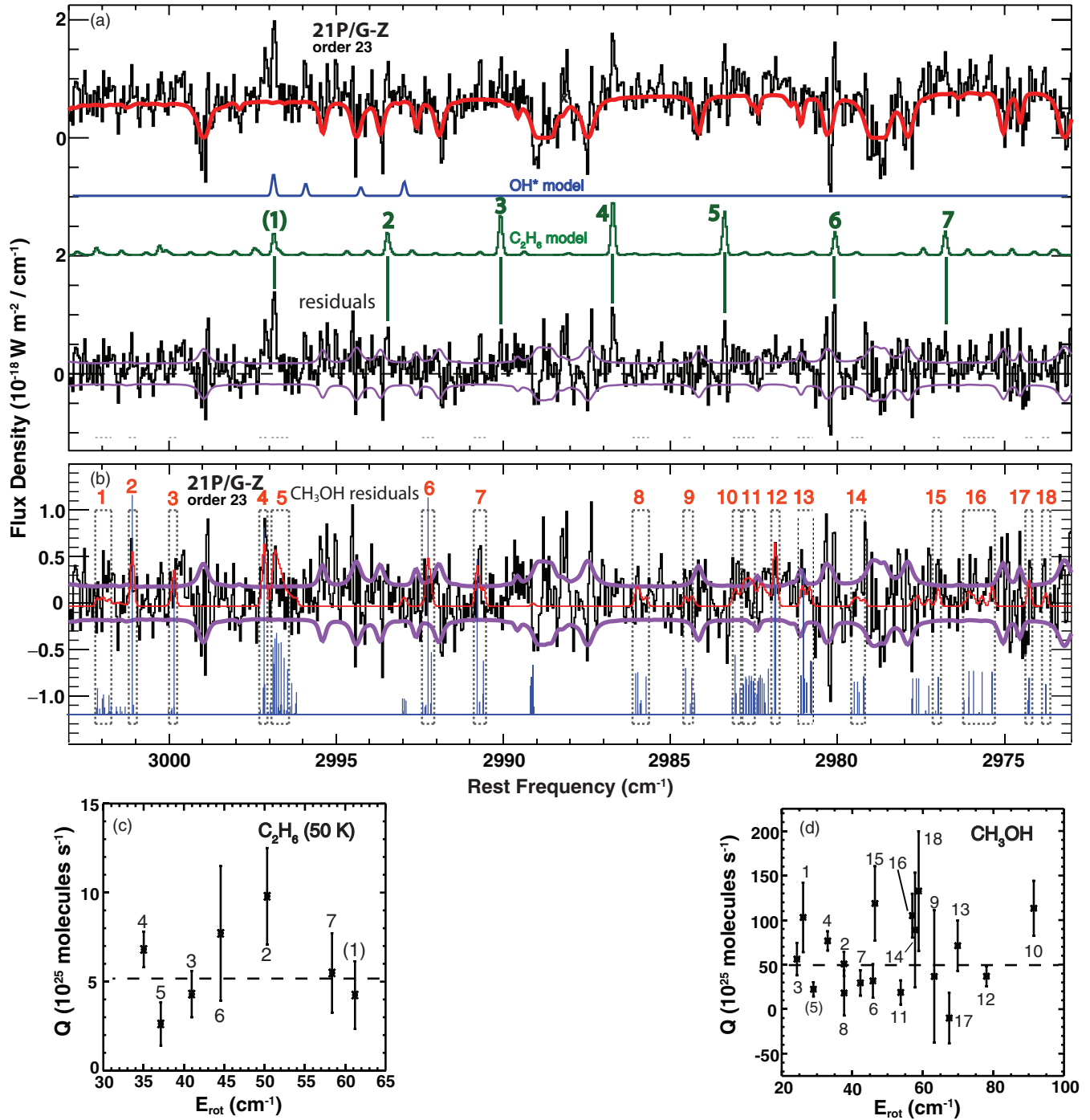


Figure 3. (a) Order 23 spectrum of 21P/GZ (top trace) with modeled transmittance function convolved to $\lambda/\Delta\lambda = 24,000$ and scaled to the observed continuum intensity. Lower traces: continuum-subtracted spectrum together with quantum model for C_2H_6 (with seven ν_7 Q -branches indicated by number; Villanueva et al. 2011a), and empirical model for OH prompt emission, both multiplied by the appropriate line-by-line transmittances and then convolved to 24,000. (b) Application of our new empirical ν_2 model to 21P/G-Z. Subtraction of modeled C_2H_6 and OH* yields the “CH₃OH residual” emission spectrum, shown with our new empirical model super-imposed. (c) Production rates derived from individual C_2H_6 Q -branches at the assumed T_{rot} (50 K), and the mean Q_{tot} (dashed line) based on points “2” through “7” (i.e., excluding “3”, point “1”). (d) Similar plot for the 18 spectral intervals used in our analysis of CH₃OH in order 23 from panel B. (See Section 4.3.4.2.) (A color version of this figure is available in the online journal.)

$Q(CH_3OH)$ by $\sim 10\%$ (approximately 1σ uncertainty in the production rate; see Section 4.3.4.2, and Table 2, note “f”). Because of this spectral confusion, together with uncertainty in the equivalent g -factor for the P12.5 2^- line, we exclude interval “5” from order 23 in determining our most reliable values for $Q(C_2H_6)$ and $Q(CH_3OH)$.

4.3.3. C_2H_6

Order 23 is dominated by emissions from ethane (ν_7 band) and methanol (primarily the ν_2 band). One motivation for our study of 21P/GZ is to investigate (and, in the case of C_2H_6 , to confirm) whether the depletion of C_2 observed in this comet

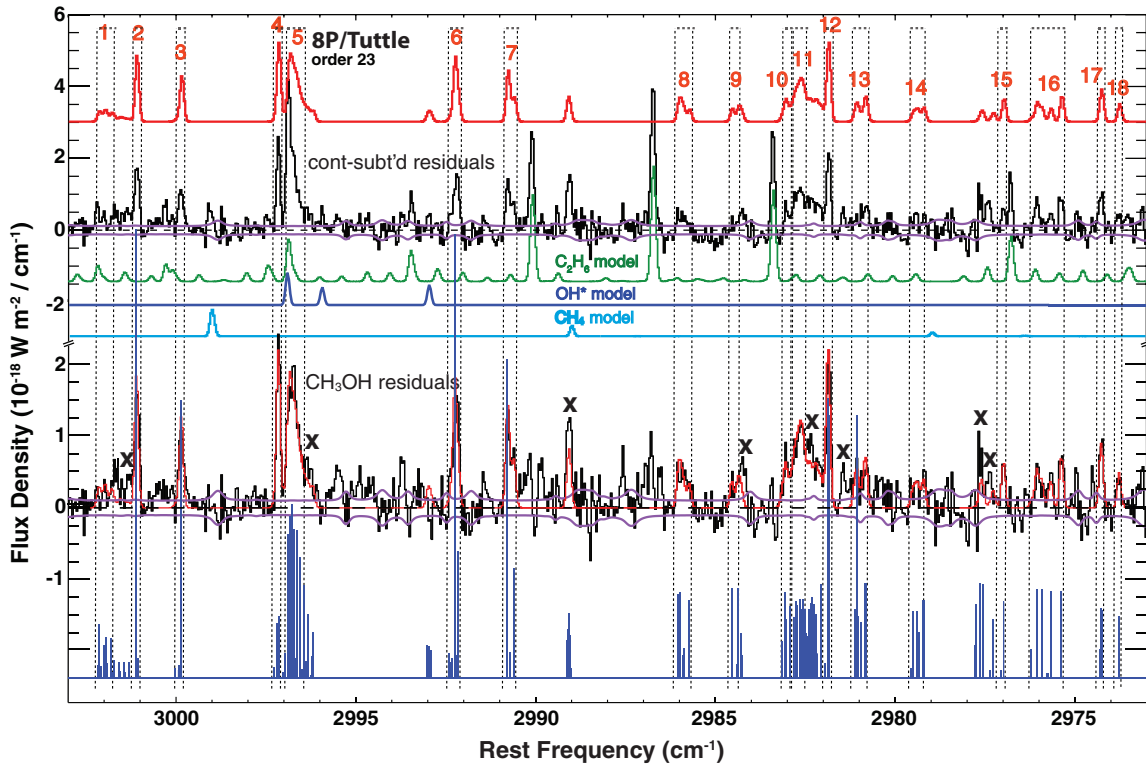


Figure 4. Top traces: continuum-subtracted residuals (black trace) from order 23 in Comet 8P/Tuttle, together with our empirical fluorescence model for CH_3OH (convolved to $\text{RP} = 24,000$; heavy red trace). Subtracting modeled emissions for C_2H_6 , OH^* , and CH_4 (shown below the comet residuals) leaves emissions dominated by ν_2 lines (hence the label “ CH_3OH residuals”), shown with our convolved empirical model superimposed. Regions marked “x” contain excess intensity, perhaps due to unaccounted-for CH_3OH ν_9 emissions, and so are omitted from our ν_2 analysis (see Appendix A). A stick spectrum for all lines included in the model is also shown, both here and for Comet 21P/GZ (Figure 3). For direct comparison with *observed* emissions, the modeled intensity for each line is multiplied by the monochromatic transmittance at its Doppler-shifted frequency.

(A color version of this figure is available in the online journal.)

(A’Hearn et al. 1995; Fink 2009) carries over to ethane. Depleted C_2H_6 was reported from CSHELL observations of 21P/GZ during the 1998 apparition (Weaver et al. 1999; Mumma et al. 2000). This might be expected if acetylene (C_2H_2) is the dominant source of C_2 , as the most efficient means of producing C_2H_6 is H-atom addition to C_2H_2 on the surfaces of interstellar icy grains at low temperatures (Mumma & Charnley 2011; also see Section 5.1.3).

We obtained production rates from the intensities of seven Q -branches of the C_2H_6 ν_7 band (1Q_3 , 1Q_2 , 1Q_1 , 1Q_0 , pQ_1 , pQ_2 , pQ_3) and identify these by numbers 1–7, respectively, in Figure 3(a) (also see Table 6). Our production rates were based on a full quantum model for the ν_7 band of C_2H_6 that includes P -, Q -, and R -branch intensities as well as contributions from the $\nu_7 + \nu_4 - \nu_4$ combination band (Villanueva et al. 2011a). Because each Q -branch encompasses many lines spanning a range of rotational energies, and because there is considerable overlap in the energies sampled among these Q -branches, the resulting production rate is relatively insensitive to T_{rot} . For this reason, we adopt $T_{\text{rot}} = 50$ K for C_2H_6 , consistent with (to well within 1σ) those we measured for H_2O and for CH_3OH (based on analysis of the ν_3 band; see Section 4.3.4.3 and Figure 5).

Global production rates for the seven Q -branches were calculated using their integrated line fluxes and applying the growth factor measured for H_2O ($\text{GF} = 1.62$); these are indicated in Figure 3(c). However, because the g -factor for the blended $\text{P}12.5\ 2^- \text{OH}^*$ line is uncertain (Section 4.3.2), 1Q_3 (labeled “1”

in Figures 3(a) and (c)) is excluded from our quantitative analysis of C_2H_6 . The global production rate is then the mean of the remaining six points, weighted by their individual stochastic uncertainties (denoted by the error bars in Figure 3(c)). We obtained a global production rate [$Q(\text{C}_2\text{H}_6) = 5.27 \pm 0.90 \times 10^{25} \text{ s}^{-1}$] that translates to an abundance ratio of $(0.136 \pm 0.023) \times 10^{-2}$ relative to H_2O (Tables 2 and 3). This is well below the current “normal” abundance among comets ($\sim 0.6 \times 10^{-2}$; Bockelée-Morvan et al. 2004; DiSanti & Mumma 2008; Mumma & Charnley 2011), confirming highly depleted C_2H_6 in 21P/GZ, in analogy with its observed C_2 depletion (A’Hearn et al. 1995; Fink 2009; see also Table 3).

4.3.4. CH_3OH

4.3.4.1. CH_3OH ν_2 Emission in Order 23: A New Empirical Fluorescence Model

We developed an empirical model that includes 157 individual lines of the ν_2 band, with assignments and frequencies adopted from jet-cooled laboratory spectra (Xu et al. 1997) and lower state energies taken from Mekhtiev et al. (1999, Section 3; also see note “b” of Table 4). We incorporated approximately 70% of these (109 lines) to quantify CH_3OH in order 23 (see Figures 3 and 4, and related discussion below).

Fluorescence efficiencies (g -factors) for our empirical model are based on higher signal-to-noise spectra of Halley Family Comet 8P/Tuttle, which we observed with NIRSPEC on UT 2007 December 22, approximately 2.5 years following our

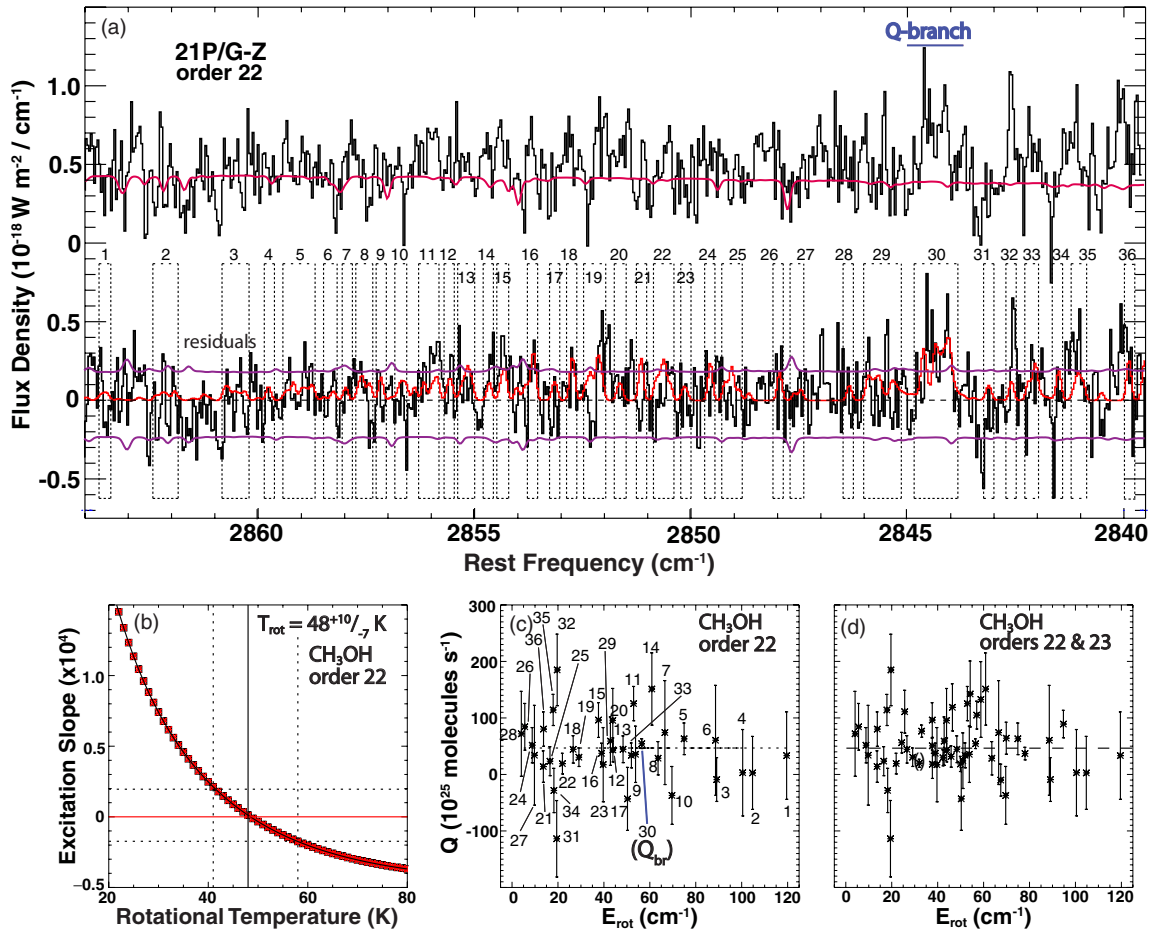


Figure 5. (a) Top: extracted spectrum for order 22, showing emissions from the ν_3 band of CH_3OH in Comet 21P/G-Z, with the Q -branch indicated. Bottom: continuum-subtracted residuals with (convolved) quantum band model (Villanueva et al. 2012a) superimposed. Based on modeled line intensities, 36 spectral intervals were selected. (b) Best-fit slope for a range of rotational temperatures, indicating optimal T_{rot} (corresponding to zero slope) and its $\pm 1\sigma$ uncertainties (based on corresponding uncertainty in slope; see DiSanti et al. 2006 for detailed formalism). (c) Measured (total) production rates derived from each of the 36 intervals, with that from the Q -branch (interval “30”) indicated (Q_{br}). (d) Similar plot for the combined ensemble of 54 intervals in orders 22 (Figure 5(c)) and 23 (Figure 3(d)). The dashed line represents the overall mean $Q(\text{CH}_3\text{OH})$ excluding interval “5” from order 23 (point shown in parentheses).

(A color version of this figure is available in the online journal.)

observations of 21P/GZ reported here. Comet Tuttle exhibited a high abundance ratio $\text{CH}_3\text{OH}/\text{C}_2\text{H}_6$ and a rotational temperature near 50 K (Bonev et al. 2008; also see Bönnhardt et al. 2008; Kobayashi et al. 2010), making it an excellent “template” for our study. Figure 4 shows the resulting model compared with the 8P/Tuttle residuals from order 23. After accounting for emissions from other species (specifically C_2H_6 , CH_4 , and OH^*), we judiciously identified 18 separate spectral intervals in which identified CH_3OH ν_2 emissions are isolated. Values for our empirical g -factors were assigned such that the production rate for each interval, based on a spectral extract centered on the nucleus ($Q_{\text{nc,int}}$; see Equation (2)), agreed with that obtained independently from application of our quantum model (to 8P/Tuttle) for the simultaneously observed ν_3 band in order 22 (Villanueva et al. 2012a).⁵

⁵ The production rate of CH_3OH initially published for 8P/Tuttle ($Q_{\text{tot}} = 49.65 \times 10^{25}$ molecules s^{-1} ; Bonev et al. 2008) was based on $Q_{\text{nc}} = 33.1 \times 10^{25} \text{ s}^{-1}$ (using the ν_3 Q -branch intensity) combined with a (measured) GF of 1.5. The value obtained using our new band model for ν_3 as presented in Villanueva et al. (2012a) revises Q_{nc} downward by $\sim 12\%$, to 29.0×10^{25} molecules s^{-1} .

4.3.4.2. CH_3OH Abundance in 21P/GZ Based on ν_2 Emissions in Order 23

Subtracting modeled C_2H_6 (and OH^*) emissions from the (continuum-subtracted) spectrum in Figure 3(a) results in a net emission spectrum dominated by methanol (labeled “ CH_3OH residuals” in Figure 3(b)). Application of our empirical model then provides a production rate for each spectral interval (see Table 4), and thereby an additional measure of CH_3OH production. In Figure 3(d) we show the resulting global production rates for CH_3OH in 21P/GZ based on signal contained in each of the 18 spectral intervals in order 23. The mean from all intervals (excluding number “5”) results in $Q(\text{CH}_3\text{OH}) = (4.88 \pm 0.71) \times 10^{26} \text{ s}^{-1}$ or an abundance ratio $\text{CH}_3\text{OH}/\text{H}_2\text{O} = (1.26 \pm 0.18) \times 10^{-2}$, while including interval “5” results in $\text{CH}_3\text{OH}/\text{H}_2\text{O} = (1.03 \pm 0.17) \times 10^{-2}$, based on CH_3OH in order 23 alone.

4.3.4.3. Measurement of CH_3OH ν_3 Emission in 21P/GZ: T_{rot} and Abundance

We identified 36 spectral intervals in order 22 and, applying our new ν_3 quantum band model (Villanueva et al. 2012a), we measured a rotational temperature for CH_3OH

Table 3
Volatile Abundances in 21P/G-Z and Other Jupiter Family Comets

Comet	Year ^a	$\frac{\text{C}_2\text{H}_6}{\text{H}_2\text{O}}$ ^a	$\frac{\text{CH}_3\text{OH}^a}{\text{H}_2\text{O}}$	$\text{Log } \frac{\text{C}_2^b}{\text{OH}}$	C_2/OH^c (%)	$\frac{\text{C}_2\text{H}_6^c}{\text{C}_2}$
21P/GZ	1998	0.22 ± 0.13^d				
	1998	$<0.05-0.08^e$	$0.9-1.4^e$	$-3.41^{(1)}$	.056	
	1998		1.6 ± 0.4^f	$-3.14^{(2)}$		
	2005	0.136 ± 0.023^g	1.22 ± 0.11^g			2.7
9P/Tempel 1	2005	0.23 ± 0.04^h	1.4 ± 0.2^h	$-2.90^{(1)}$	.097	2.6
		0.55 ± 0.09^i	1.1 ± 0.2^h	$-3.17^{(2)}$		
73P/SW3-B	2006	$<0.3^j$		$-3.29^{(2)}$	.051	2.7
73P/SW3-B		0.14 ± 0.01^k	0.25 ± 0.04^k			
73P/SW3-C		0.15 ± 0.04^j	$<0.38^j$			
73P/SW3-C		0.11 ± 0.01^k	0.21 ± 0.04^k			
17P/Holmes	2007	1.78 ± 0.26^l	3.2 ± 0.6^l	$-2.42^{(3)}$	0.38	5.2
6P/d'Arrest	2008	0.26 ± 0.06^m	1.99 ± 0.42^m	$-2.37^{(1)}$	0.28	1.0
				$-2.90^{(2)}$		
103P/Hartley 2	2010	0.75 ± 0.03^n	1.87 ± 0.13^n	$-2.36^{(1)}$	0.35	2.3
		0.65 ± 0.09^o	1.72 ± 0.11^o	$-2.59^{(2)}$		
10P/Tempel 2	1999		1.8 ± 0.2^p			
	2010	0.39 ± 0.04^q	1.58 ± 0.23^q	$-2.70^{(1)}$ $-2.71^{(2)}$	0.20	2.1

Notes.

^a Year observed (excluding optical observations; see note “b”) and abundances of ethane and methanol with respect to $\text{H}_2\text{O} = 100$ (all uncertainties represent 1σ , and upper limits are 3σ). Previously published values for $Q(\text{CH}_3\text{OH})$ from IR observations using the ν_3 Q -branch intensity are inter-normalized to $g(Q\text{-br}) = 1.5 \times 10^{-5}$ photons s^{-1} molecule $^{-1}$ (Villanueva et al. 2012a).

^b Abundances of C_2 are taken from the following papers: (1) A’Hearn et al. (1995), (2) Fink (2009), and (3) Schleicher (2009). With the exception of 17P, the optical observations refer to apparitions different from those listed under “year”; e.g., years of observation for Fink et al.: 21P, 1985; 9P, 1994; 73P, 1990 and 1995; 6P, 1995; 103P, 1997 and 1998; 10P, 1988. A’Hearn et al. (1995) classify comets having $-1.22 < \log(\text{C}_2/\text{CN}) < -0.21$, and $-4.13 < \log(\text{C}_2/\text{OH}) < -2.98$ as “carbon-chain depleted”, and those having $-0.09 < \log(\text{C}_2/\text{CN}) < 0.29$ and $-2.90 < \log(\text{C}_2/\text{OH}) < -2.10$ as “typical”. The values for 17P refer to the mean of 2007 November 01.16, November 20.12, and 2008 January 01.23, during the decline from its spectacular outburst in late 2007 October. Its rapidly evolving coma complicates comparison of abundances for primary (parent) and product species, and in this sense 17P represents a special case.

^c For comets with multiple entries for $\log(\text{C}_2/\text{OH})$, the quantity C_2/OH refers to their mean value. In calculating $\text{C}_2\text{H}_6/\text{C}_2$, the relation $Q(\text{H}_2\text{O}) = 1.1 \times Q(\text{OH})$ is assumed. The entry for 21P is based on the value for $\text{C}_2\text{H}_6/\text{H}_2\text{O}$ reported here (0.136×10^{-2}). The entry for 9P is for the pre-impact abundance ratio $\text{C}_2\text{H}_6/\text{H}_2\text{O}$ (note “h”). The entry for 73P uses the weighted mean value from the three measurements of $\text{C}_2\text{H}_6/\text{H}_2\text{O}$ having 1σ errors ($\sim 0.14 \times 10^{-2}$). The entry for 103P uses the weighted mean value from the two measurements listed for $\text{C}_2\text{H}_6/\text{H}_2\text{O}$.

^d Mumma et al. (2000).

^e Weaver et al. (1999). Their value for $Q(\text{CH}_3\text{OH})$ was reported as a 3σ upper limit. It was based on the entire ν_3 band using $g(\nu_3) = 1.5 \times 10^{-4} \text{ s}^{-1}$, therefore no re-scaling of production rate from the published value is required.

^f Biver et al. (2002).

^g This work. The value listed for C_2H_6 is based on six ν_7 Q -branches; i.e., excluding rQ_3 —interval/point “1” in Figures 3(a) and (c) (see related discussion in Section 4.3.3). Including rQ_3 modifies its abundance very little, to $(0.133 \pm 0.021) \times 10^{-2}$. The value listed for CH_3OH is based on signal in 36 spectral intervals in order 22 (Figure 5) and 17 spectral intervals in order 23 (i.e., with interval/point “5” in Figures 3(b) and 3(d) omitted). Including interval “5” from order 23 results in a mean CH_3OH abundance of $(1.12 \pm 0.11) \times 10^{-2}$.

^h Mumma et al. (2005). The first row corresponds to pre-impact, the second row to the DI ejecta.

ⁱ DiSanti et al. (2007b).

^j Villanueva et al. (2006).

^k Dello Russo et al. (2007) and Kobayashi et al. (2007) reported consistent values for fragment B, based on independent measurements.

^l Dello Russo et al. (2008).

^m Dello Russo et al. (2009).

ⁿ Mumma et al. (2011), as revised by Villanueva et al. (2012a).

^o Dello Russo et al. (2011), as revised by Villanueva et al. (2012a).

^p Biver et al. (2012).

^q Paganini et al. (2012).

($T_{\text{rot}} = 48^{+10}_{-7}$ K; Figure 5) consistent with that measured for H_2O in 21P/GZ. Our production rate for CH_3OH from order 22 alone ($4.63 \pm 0.55 \times 10^{26} \text{ s}^{-1}$) translates to an abundance ratio $\text{CH}_3\text{OH}/\text{H}_2\text{O} = (1.19 \pm 0.14) \times 10^{-2}$ (Table 2).

We note that although the residuals in Figure 5(a) are noisy, including this many spectral intervals actually improves our detection of CH_3OH in order 22 over that obtained by considering the Q -branch alone. The Q -branch is clearly detected, how-

ever its stochastic uncertainty ($8.58 \times 10^{25} \text{ s}^{-1}$; see Table 7) is considerably larger than either stochastic ($4.57 \times 10^{25} \text{ s}^{-1}$) or standard ($5.53 \times 10^{25} \text{ s}^{-1}$) uncertainties associated with the ensemble of 36 spectral intervals.

Combining CH_3OH from orders 22 and 23 (but excluding interval “5” in order 23) results in $Q_{\text{tot}}(\text{CH}_3\text{OH}) = (47.5 \pm 4.4) \times 10^{25} \text{ s}^{-1}$, or $(1.22 \pm 0.11) \times 10^{-2}$ relative to H_2O . We take this to represent our most reliable measure of CH_3OH in

21P/GZ. Global production rates for each of the 54 spectral intervals included in these two orders are shown graphically in Figure 5(d).

5. ABUNDANCE COMPARISONS

5.1. Comparisons with Other Observations of 21P/GZ

5.1.1. Water Production

The global production rate we measure for H_2O in 21P/GZ (3.88 , expressed in 10^{28} molecules s^{-1}) compares favorably with values reported elsewhere. In their optical photometric survey, A'Hearn et al. (1995) reported $Q_{\text{OH}} = 3.2$ (corresponding to $Q_{\text{H}_2\text{O}} \sim 3.5$) at the same heliocentric distance as our 2005 observations ($R_h = 1.12$ AU), and estimated 4.2 for the maximum $Q_{\text{H}_2\text{O}}$ at perihelion ($R_h = 1.03$ AU). Fink (2009) gave a range (1.6 – 4.2) from optical spectra encompassing $1.05 < R_h < 1.21$ AU during the 1985 apparition. Weaver et al. (1999) reported $Q_{\text{H}_2\text{O}} \sim 2$ – 3 from 1998 for $1.05 < R_h < 1.11$ AU based on IR spectra using CSHELL. Crovisier et al. (2002) reported a maximum $Q_{\text{H}_2\text{O}} = 5.1$ at $R_h = 1.05$ AU, and Crovisier et al. (2009) reported $Q_{\text{H}_2\text{O}} = 3$ at $R_h = 1.2$ AU, based on Nançay observations of fluorescent OH during the 1998 apparition.

5.1.2. Infrared Observations of C_2H_6 and CH_3OH in 21P/GZ

Strongly depleted C_2H_6 in 21P/GZ was reported in two papers from the 1998 apparition based on observations with CSHELL. Mumma et al. (2000) measured an abundance ratio ($\text{C}_2\text{H}_6/\text{H}_2\text{O} = 0.22 \pm 0.13 \times 10^{-2}$) that is consistent with ours, albeit with larger uncertainty owing to the lower sensitivity afforded by CSHELL compared with NIRSPEC. Weaver et al. (1999) reported a range of (3σ) upper limits, the maximum of their range (0.08×10^{-2}) being only $\sim 60\%$ of our value (0.136×10^{-2} ; Table 3). Taken together, these two papers suggested possible compositional heterogeneity in 21P/GZ.

For methanol, Weaver et al. reported a range for the abundance ratio $\text{CH}_3\text{OH}/\text{H}_2\text{O}$ (0.9 – 1.4×10^{-2}), based on the entire ν_3 -band intensity and $g_{\text{band}} = 1.5 \times 10^{-4}$ photon s^{-1} molecule $^{-1}$. This encompasses our combined value of $(1.22 \pm 0.11) \times 10^{-2}$ (from orders 22 and 23), as well as our values from each order separately, whether or not interval “5” in order 23 is included.

5.1.3. Production of C_2H_6 and CH_3OH through Grain Surface Chemistry

Infrared measurements such as those presented here can provide information on conditions in the environment where comets formed. Because gas phase formation of C_2H_6 is highly inefficient, a mechanism was proposed (Tielens 1992) involving H-atom addition reactions to C_2H_2 on the surfaces of interstellar grains, and this was later borne out by the discovery of abundant cometary C_2H_6 in C/1996 B2 (Hyakutake; Mumma et al. 1996). The now-routine measurement of C_2H_6 in comets suggests that such processing is ubiquitous in pre-cometary environments.

Similarly, gas-phase formation of CH_3OH , through reaction of the methyl ion (CH_3^+) with water followed by dissociative recombination of the product species (CH_3OH_2^+), cannot explain the abundances of CH_3OH observed in interstellar sources (Geppert et al. 2006; Garrod et al. 2006; Wiström et al. 2011). In addition, chemical models that trace the evolution of material from dark molecular clouds through proto-planetary disks have not found a viable formation pathway for CH_3OH in the gas phase (Walsh et al. 2010; Willacy & Woods 2009; Willacy 2007). However, as with C_2H_6 , methanol is synthesized

efficiently via grain surface chemistry through low-temperature hydrogenation of condensed CO. This was addressed theoretically (Charnley & Rodgers 2009 and references therein) and demonstrated by laboratory irradiation of pure CO and CO/ H_2O ice mixtures at ~ 10 – 20 K (Hudson & Moore 1999; Hiraoka et al. 2002; Watanabe et al. 2004).

5.1.4. Implications from Previous IR Studies of 21P/GZ

In this context, our measurements of strongly depleted C_2H_6 and modestly depleted CH_3OH in 21P/GZ lead naturally to questions regarding its abundances of C_2H_2 and CO. Weaver et al. (1999) reported an abundance ratio $\text{C}_2\text{H}_2/\text{H}_2\text{O} < 0.3$ – 0.4×10^{-2} (3σ); the (current) “normal” abundance of C_2H_2 among comets (~ 0.2 – 0.3×10^{-2} ; Mumma & Charnley 2011; DiSanti & Mumma 2008; Bockelée-Morvan et al. 2004) indicates that this does not provide a stringent constraint on the acetylene abundance in 21P/GZ. Mumma et al. (2000) reported a high abundance ratio $\text{CO}/\text{H}_2\text{O}$ ($\sim 10 \times 10^{-2}$), however this was based on a very marginal detection of H_2O ($< 2\sigma$) together with an abundance ratio $\text{C}_2\text{H}_6/\text{CO} = 2.1 \pm 0.6 \times 10^{-2}$. Our current result for C_2H_6 ($0.136 \pm 0.023 \times 10^{-2}$) then implies an abundance ratio $\text{CO}/\text{H}_2\text{O} = 6.5 \pm 2.2 \times 10^{-2}$, if scaled from the Mumma et al. ratio for $\text{C}_2\text{H}_6/\text{CO}$.

Results from the Weaver et al. (1999) and Mumma et al. (2000) studies, separated by approximately three weeks, are at odds. Weaver et al. detected H_2O yet neither C_2H_6 nor CO were seen, and both papers mentioned compositional heterogeneity as a possible explanation for these differences. Assuming a (modest) R_h^{-2} dependence, the upper limit reported for $Q(\text{CO})$ at $R_h = 2.4$ AU from 2005 *Spitzer* observations of 21P/GZ (6.0×10^{26} molecules s^{-1} ; Pittichová et al. 2008) scales to $\sim 2.8 \times 10^{27}$ molecules s^{-1} at $R_h = 1.12$ AU (corresponding to R_h for the observations reported here). Based on our measured $Q(\text{H}_2\text{O})$ (3.88×10^{28} molecules s^{-1}), this corresponds to $\text{CO}/\text{H}_2\text{O} < 7.3 \times 10^{-2}$, consistent with the revised Mumma et al. value (6.5×10^{-2}).

5.1.5. Millimeter Observations of CH_3OH in 21P/GZ

Biver et al. (2002) included 21P/GZ in a survey of molecular abundances in 24 comets based on millimeter wavelength observations with the Institut de Radio Astronomie Millimétrique (IRAM) 30 m and other radio telescopes. They reported $\text{CH}_3\text{OH}/\text{H}_2\text{O} = 1.6 \pm 0.4 \times 10^{-2}$, with $Q(\text{H}_2\text{O})$ based on measurements of fluorescent OH from Nançay (Crovisier et al. 2002). Our measured abundance ratio for CH_3OH falls within 1σ of the Biver et al. value, albeit near the low end. The agreement between IR and millimeter results provides a validation of our models for both the ν_2 and ν_3 bands. It is also notable, considering that the radio measurements of CH_3OH and OH were conducted with different telescopes having different beam sizes that sample temporal release averaged over different intervals, while our observations measured both CH_3OH and H_2O simultaneously with the same instrument and beam size.

5.2. Abundance Comparisons of C_2H_6 and CH_3OH Among Jupiter Family Comets

An ensemble of comets (both nearly isotropic comets and JFCs) measured with IR spectroscopy reveals an emerging taxonomy based on the diversity of primary volatile abundances (specifically C_2H_6 , CH_3OH , C_2H_2 , and HCN) among its members. Seven of 14 comets are conditionally classified “organics-normal,” while two are “enriched” and two are

“depleted,” particularly regarding their abundances of C_2H_6 and CH_3OH , for which “normal” values are, respectively, approximately 0.6×10^{-2} and 2×10^{-2} relative to H_2O (e.g., see Figure 8 in Mumma & Charnley 2011). A key question regards the extent to which comets fall into these three categories as opposed to forming a more continuous distribution in volatile organic compositions, and also whether the extreme examples (both enriched and depleted) represent end members or even if the “normal” group reflects a representative mean composition. Indeed, this classification scheme is being challenged as additional comets are characterized. For example, neither 8P/Tuttle (Bönnhardt et al. 2008; Bonev et al. 2008; Kobayashi et al. 2010) nor C/2007 N3 (Lulin; Gibb et al. 2012) fit neatly into any of the three categories.

The overall sample is dominated by nearly isotropic comets (delivered from the Oort cloud), however the JFC population (primarily from the scattered Kuiper disk) contributes in significant ways. An important finding revealed even in this relatively small sample of comets is that members from nearly isotropic comet and JFC populations are present both in enriched and depleted categories, as predicted by the Nice model (Gomes et al. 2005; Morbidelli et al. 2008).

Table 3 exemplifies this through abundance comparisons among JFCs. Comet 17P/Holmes was clearly enriched (Dello Russo et al. 2008) and 73P/Schwassmann-Wachmann 3 was depleted in both C_2H_6 and CH_3OH (Villanueva et al. 2006; Dello Russo et al. 2007), although 17P was measured during/following a large outburst, making such comparisons uncertain given its rapidly evolving coma (also see Section 5.3). Infrared spectra of 10P/Tempel 2 from 2010 (Paganini et al. 2012) revealed mild depletions in both C_2H_6 and CH_3OH , as did rotational spectra of CH_3OH in 1999 (using CSO) and 2010 (using IRAM; Biver et al. 2012). Comet 9P/Tempel 1 showed similar mild depletions (except for the material ejected by the Deep Impact event, which revealed “normal” C_2H_6 ; Mumma et al. 2005; DiSanti et al. 2007b). Our observations confirm that 21P/GZ was strongly depleted in C_2H_6 yet was only mildly depleted in CH_3OH . Comet 6P/d’Arrest had mildly depleted C_2H_6 and normal CH_3OH (Dello Russo et al. 2009), while in 103P/Hartley 2 both molecules had abundances consistent with normal (Mumma et al. 2011; Dello Russo et al. 2011; Kawakita et al. 2012). Clearly there are examples that do not fit the proposed relatively simple three-tiered classification scheme, even based on this small sample of seven JFCs.

5.3. Comparisons with C_2 Abundances from Optical Observations of JFCs

An additional comparison involves the potential relation between primary volatile abundances (in particular C_2H_6 for the present study) and C_2 . In an initial optical survey (A’Hearn et al. 1995), approximately one-third of 85 comets were classified as “carbon-chain depleted,” with this classification being considerably more pronounced in JFCs compared with nearly isotropic comets. This dichotomy with dynamical class is reinforced by other surveys (Fink & Hicks 1996; Fink 2009; Langland-Shula & Smith 2011; Cochran et al. 2012), including an extensive taxonomic compilation of over 150 comets that identified up to nine compositional groupings when abundances of NH , a potentially important tracer for NH_3 , are included (Schleicher et al. 2007).

Five of seven comets in Table 3 (including 21P/GZ) have similar values for the ratio $\text{C}_2\text{H}_6/\text{C}_2$. One exception is 17P/Holmes, however measurements of both C_2H_6 (Salyk et al. 2007; Dello Russo et al. 2008) and C_2 (Schleicher 2009) were

obtained following its spectacular outburst in 2007 October, and so uncertainties associated with a rapidly evolving coma might be expected when comparing abundances of native species and photo-dissociation fragments. Furthermore, given its relatively large heliocentric distance ($R_h \sim 2.6$ AU), preferential sublimation of ices more volatile than H_2O (e.g., C_2H_6 , which was particularly enriched; Dello Russo et al. 2008) from the large amount of released grains may not be representative of the bulk volatile composition of its nucleus. This leaves 6P/d’Arrest as a notable outlier, with mild depletion of C_2H_6 (by approximately a factor of two relative to “normal”; Dello Russo et al. 2009) but with C_2 near the midpoint of the range for comets classified as “typical” by A’Hearn et al. (1995).

While the majority of JFCs in Table 3 exhibit similar $\text{C}_2\text{H}_6/\text{C}_2$, the inter-relationship between these two species is far from secure. C_2 is produced directly from C_2H_2 with a branching ratio of approximately 20% (Huebner et al. 1992), but some comets produce more C_2 than can be accounted for by C_2H_2 alone, for example 8P/Tuttle (Bonev et al. 2008) and C/2007 N3 (Lulin; Gibb et al. 2012), both of which were depleted in C_2H_2 . An analogous situation may hold for the JFC 6P/d’Arrest, with strongly depleted C_2H_2 ($< 0.052 \times 10^{-2}$, 3σ) suggesting the need for an additional source of C_2 (Dello Russo et al. 2009).

Photo-dissociation of C_2H_6 can lead to C_2 , however, multiple steps are required (including production of C_2H_2) and branching ratios are highly uncertain (Helbert et al. 2005; Kobayashi et al. 2010). Indeed, Weiler (2012) used a coma chemistry model to compare radial column densities of C_2 and C_3 observed in three comets, and concluded that C_2H_6 was not a significant parent of C_2 . The similar values for $\text{C}_2\text{H}_6/\text{C}_2$ among five of the seven JFCs in Table 3 may indicate a common source of (and efficiency for producing) C_2 and C_2H_6 (such as C_2H_2) that dominates contributions from other sources (e.g., grains) in these five comets. The problem of relating abundances of fragment species to potential parents is not resolved, and parentages may vary among comets. Clearly, in general both gas and grain sources need to be considered.

6. IMPLICATIONS FOR FUTURE STUDIES OF 21P/GIACOBINI-ZINNER

Because of its non-integral orbital period (6.6 years), apparitions of 21P/GZ provide widely varying observational opportunities as viewed from Earth. This is particularly true when comparing those in 2012 and 2018. Near perihelion, the geocentric distance Δ was > 1.8 AU in 2012, but Δ will be only ~ 0.4 AU in 2018. Moreover, the geocentric velocity in 2018 exceeds 10 km s^{-1} (and thus is adequate for studying CO and CH_4) when Δ reaches ~ 0.48 AU. Assuming gas production rates (and rotational temperatures) similar to those measured during previous apparitions, line intensities in 2018 are expected to be larger by factors of three to four compared with those observed from 2005, and by factors of two to three compared with those from 1998 (for which $\Delta \sim 0.9\text{--}1.1$ AU). Combined with anticipated improvements in instrumentation (e.g., higher spectral resolving power and sensitivity), the 2018 apparition will enable deep searches for trace species in 21P/GZ—for example, detection of C_2H_2 or, if severely depleted, establishing stringent upper limits for its abundance—and will allow the question of potential compositional heterogeneity in the nucleus to be addressed in greater detail.

7. CONCLUSIONS

We used NIRSPEC at Keck II to obtain infrared spectra of 21P/GZ on UT 2005 June 03.6 that allowed simultaneous measurement of H_2O , C_2H_6 , and CH_3OH . For H_2O , we obtained a production rate $(3.885 \pm 0.074 \times 10^{28} \text{ molecules s}^{-1})$ consistent with that reported previously for 21P/GZ from optical, IR, and millimeter-wavelength observations. Our water analysis also provided values for rotational temperature ($T_{\text{rot}} = 51 \pm 3 \text{ K}$) and spin temperature ($T_{\text{spin}} > 50 \text{ K}$, based on OPR = 2.99 ± 0.23).

For C_2H_6 we applied our quantum-mechanical fluorescence model for the ν_7 band that includes contributions from the Q -, P -, and R -branches and also from a combination band. We obtained an abundance ratio $\text{C}_2\text{H}_6/\text{H}_2\text{O} = 0.136 \pm 0.023 \times 10^{-2}$, indicating nearly five-fold depletion of ethane in 21P/GZ relative to the current median value in comets ($\sim 0.6 \times 10^{-2}$).

For CH_3OH , we applied our recently published fluorescence model for the ν_3 band to obtain a rotational temperature ($T_{\text{rot}} = 48^{+10}_{-7} \text{ K}$) consistent with the value we measured for H_2O . The first application of our newly developed empirical model for the ν_2 band provided a CH_3OH production rate consistent with that obtained from ν_3 . Combining results for both bands (ν_2 and ν_3) resulted in an $\sim 11\sigma$ detection of CH_3OH , and an abundance ratio $\text{CH}_3\text{OH}/\text{H}_2\text{O} = 1.22 \pm 0.11 \times 10^{-2}$ in 21P/GZ, somewhat below its current median value (2×10^{-2}).

Our results therefore confirm strongly depleted C_2H_6 and mildly depleted CH_3OH in 21P/GZ, as reported previously from observations during the 1998 apparition. Together with those results, our study provides a measure of primary volatile abundances from ground-based IR spectroscopy for this JFC over multiple apparitions. It is also a comparator for more extensive studies of 21P/GZ during future apparitions, beginning with that in 2018.

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APPENDIX A

APPLICATION OF THE CH_3OH EMPIRICAL ν_2 BAND MODEL TO 21P/GZ

For our empirical model of the CH_3OH ν_2 band, we adopt notation according to the G_6 molecular symmetry group, as this takes into account the large amplitude torsional tunneling

between the three equivalent CH_3 orientations relative to OH (Xu et al. 1997, 2008). Under the G_6 group representation, the rotational structure is described using three quantum numbers (J, K, l), where J (≥ 0) is the usual total angular momentum, K is its projection along the symmetry a -axis of the molecule (such that $0 \leq K \leq J$), and l is related to the parity of the states involved in the transition. The G_6 symmetry group uses the representations A_1, A_2, E_1 and E_2 , where subscript “1” is associated with positive parity of a ro-vibrational state and “2” with negative parity, thereby leading to the representations A^+, A^-, E^+ , and E^- . Following Mekhtiev et al. (1999), we differentiate between E^+ to E^- states by associating the latter with negative K values. Using the standard convention, a single-prime denotes the upper vibrational state ($v = \nu_2$) and a double-prime denotes the lower (ground) vibrational state ($v = 0$). Then, for example (see Table 4), the designation $A^+ (1 \rightarrow 0)P4$ corresponds to $J' = 3, K' = 1, l' = 1$, and $J'' = 4, K'' = 0, l'' = 1$, while $E^- (-1 \rightarrow -2)R5$ corresponds to $J' = 6, K' = -1, l' = 2$, and $J'' = 5, K'' = -2, l'' = 2$.

To establish spectral intervals for determining the CH_3OH production rate using our empirical model, we first identified regions in the order 23 spectrum of Comet 8P/Tuttle having residual intensity after accounting for emissions due to C_2H_6 , OH, and CH_4 (see Figure 4, in particular the bottom trace labeled “ CH_3OH residuals”). We next incorporated line assignments and frequencies from the compilation in Xu et al. (1997) based on supersonic (jet) spectra of CH_3OH measured at low temperature ($\sim 17 \text{ K}$). We assigned fluorescence g -factors for lines contained in each spectral interval such that their sum reproduced the nucleus-centered production rate ($Q_{\text{nc,int}}$ in Equation (2)) retrieved for 8P/Tuttle ($= 29.0 \times 10^{25} \text{ molecules s}^{-1}$), based on application of our recently published ν_3 quantum band model to its molecular emissions in order 22 (the “revised” Q_{tot} for 8P/Tuttle, which includes $GF = 1.5$ as discussed in Bonev et al. 2008, is presented in Table 4 of Villanueva et al. 2012a; also see Section 4.3.4.1 in this 21P/GZ paper).

Rigorous calculation of line g -factors requires a full quantum-mechanical fluorescence model for the ν_2 band, in which solar pumps from all (dipole-allowed) contributing levels in the ground vibrational state ($v = 0$) into each upper level (in $v = \nu_2$) are summed (with potential cascades from higher ro-vibrational levels included). Each particular line g -factor is then given by this summed pump rate multiplied by the rotational branching ratio for the line in question. However, such a treatment is beyond the scope of the present paper.

Instead, in our empirical treatment, we preformed checks on lines having similar rotational designation (J, K) and symmetry (A, E). This approach provided more consistent g -factors, and also provided insights as to which spectral regions *not* to include in our measurements. To accomplish this, we examined the intensities of spectral lines, which for a given transition can be expressed as a proportionality with respect to line parameters and rotational temperature:

$$S_{\text{line}} \propto \frac{\nu}{\nu_0} L_{\text{HL}} [1 - \exp(-h\nu/kT_{\text{rot}})] [(2J+1) \times \exp(-hE/kT_{\text{rot}})]. \quad (\text{A1})$$

Here, and in the formulae below, ν is the line frequency (cm^{-1}), ν_0 is the band frequency (2999 cm^{-1}), J, K , and E (cm^{-1}) are respectively lower state rotational quantum numbers and energy (denoted by “ E_{low} ” in Table 4, and taken from Mekhtiev

Table 4
CH₃OH ν_2 empirical model results applied to 21P/Giacobini-Zinner on UT 2005 June 03

Int	$\nu_{\max} - \nu_{\min}^a$	Rot ID ^b	Rest ν^b		E_{low}^b	F_{line}^c	T^d	$g\text{-fac}^e$	Q^f
	(cm ⁻¹)		tabulated	wtd mean	(cm ⁻¹)	(10 ⁻²⁰ W m ⁻²)		(10 ⁻⁷ s ⁻¹)	(10 ²⁵ s ⁻¹)
1	3002.18 – 3001.70	A ⁺ (0→0) P3	3002.154		9.68				
		A ⁺ (1→0) P4	3002.121		16.13				
		E(1→2) R6	3002.054		49.35				
		E(1→0) R2	3001.975		13.96				
		A ⁺ → − (3→3) Q ^g	3001.940		~50.00				
		E(−1→ −2) R5	3001.905		42.21				
		E(−3→ −3) R6	3001.799		11.73				
		A [−] (1→1) R1	3001.775		14.90				
		A ⁺ (0→1) R2	3001.777		77.47				
		A ⁺ (1→1) R1	3001.735		11.70				
				3001.954	25.65	7.77 ± 2.65	0.935	15.72 ± 1.91	111.0 ± 37.9(40.4)
2	3001.21 – 3000.97	E(−1→0)Q ^g	3001.080		38.50				
		E(0→0)R3	3001.042		18.80				
				3001.079	37.65	7.40 ± 1.97	0.937	32.69 ± 1.51	50.73 ± 13.49(13.82)
3	3000.01 – 2999.77	A ⁺ (2→1)P4	3000.002		26.10				
		A ^{+/−} (2→2)R5	2999.912		50.41				
		E(−1→ −1)P4'	2999.894		50.41				
		E(−1→ −1)P4''	2999.836		78.34				
		E(0→ −1)Q ^g	2999.83		20.32				
				2999.854	24.31	5.89 ± 1.91	0.942	23.36 ± 1.36	56.19 ± 18.20(18.61)
4	2997.31 – 2997.07	E(1→2)R3	2997.250		25.14				
		A ⁺ (0→1)P7	2997.161		45.16				
		E(1→0)Q ^g	2997.14		32.51				
		E(0→1)R4	2997.130		30.76				
		E(−2→ −2)P3	2997.116		27.68				
				2997.139	33.02	13.18 ± 1.86	0.973	37.21 ± 1.30	76.59 ± 10.82(11.49)
5 ^h	2996.95 – 2996.42	A ⁺ → − (1→0)Q2	2996.870		43.69				
		A ⁺ → − (1→0)Q1	2996.847		11.73				
		A ⁺ → − (1→0)Q3	2996.811		14.99				
		A ⁺ → − (1→0)Q4	2996.763		19.87				
		E(−1→ −1)P6''	2996.715		26.38				
		A ⁺ → − (1→0)Q5	2996.702		37.75				
		A ^{+/−} → +/− (2→2)R3	2996.674		34.52				
		E(0 → −1)P2'	2996.639		35.89				
		A ⁺ → − (1→0)Q6	2996.626		35.89				
		E(−1→ −1)P6'	2996.626		44.28				
		E(0 → −1)P2''	2996.611		8.72				
		E(2→2)P5	2996.542		8.72				
		A ⁺ → − (1→0)Q7	2996.537		37.75				
		E(1→1)R2	2996.470		55.67				
		A ⁺ → − (0→1)Q8	2996.431		39.67				
				2996.675	32.01	7.59 ± 2.61	0.938	85.88 ± 1.98	19.82 ± 7.08(7.13)

Table 4
(Continued)

Int	$\nu_{\max} - \nu_{\min}^a$	Rot ID ^b	Rest ν^b		E_{low}^b	F_{line}^c	T^d	$g\text{-fac}^e$	Q^f
	(cm ⁻¹)		tabulated	wtd mean	(cm ⁻¹)	(10 ⁻²⁰ W m ⁻²)		(10 ⁻⁷ s ⁻¹)	(10 ²⁵ s ⁻¹)
6	2992.44 – 2992.08	A ⁻ (1→2)R5 E(0→1)R1 E(1→0)P3 E(-1→-2)Q ^g A ⁺ (1→1)P4 A ⁺ (0→1)P3	2992.389 2992.324 2992.294 2992.23 2992.153 2992.131		50.41 16.24 18.80 55.46 26.10 19.70				
				2992.224	45.85	5.35 ± 3.18	0.776	45.83 ± 2.67	31.68 ± 18.81(18.94)
7	2990.89 – 2990.53	E(1→2)Q ^g A ⁻ (1→2)R4 E (1→0)P4 A ⁺ (1→1)P5 A ⁺ (0→1)P4	2990.76 2990.693 2990.684 2990.580 2990.575		48.69 42.34 25.25 26.10 34.10				
				2990.715	42.30	4.86 ± 2.34	0.951	36.60 ± 1.67	29.43 ± 14.19(14.29)
8	2986.14 – 2985.65	A ⁺ (0→1)P7 E (-2→-3)R5 E(1→2)P3 E(0→1)P2' E(1→0)P7 E(0→1)P2'' E (-1→-2)P4	2986.017 2985.956 2985.956 2985.887 2985.859 2985.859 2985.708		54.89 25.14 67.79 19.47 19.47 54.27 34.14				
				2985.907	37.69	1.91 ± 2.66	0.956	23.36 ± 1.90	18.10 ± 25.19(25.24)
9	2984.62 – 2984.33	A ⁺ (0→1)P8 E(-2→-3)R4 E(1→2)P4	2984.524 2984.382 2984.342		67.68 42.35 31.60				
				2984.403	52.40	1.27 ± 2.57	0.819	13.61 ± 1.76	24.15 ± 48.88(49.33)
10	2983.14 – 2982.90	A ⁻ -> ⁺ (1→2)Q10 A ⁻ -> ⁺ (1→2)Q9 A ⁺ (0→1)P9 A ⁻ -> ⁺ (1→2)Q8	2983.131 2983.010 2983.044 2982.898		96.13 98.82 82.07 84.30				
				2983.0197	92.44	7.23 ± 1.97	0.958	17.91 ± 1.43	89.16 ± 24.32(25.54)
11	2982.86 – 2982.48	A ⁺ → ⁻ (1→2)Q7 E(-2→-3)R3 E(1→2)P5 A ⁺ → ⁻ (1→2)Q6 E(0→1)P4 E(1→0)P9 A ⁺ → ⁻ (1→2)Q5 A ⁺ → ⁻ (1→2)Q4 E(-1→-2)P6' E(-1→-2)P6'' A ⁺ → ⁻ (1→2)Q3	2982.797 2982.797 2982.726 2982.705 2982.635 2982.635 2982.624 2982.555 2982.573 2982.487 2982.501		53.27 71.39 39.67 60.10 81.64 30.76 50.41 51.89 42.35 35.89 51.89				
				2982.647	49.90	3.72 ± 2.68	0.838	50.57 ± 1.89	18.55 ± 13.39(13.43)

Table 4
(Continued)

Int	$\nu_{\max} - \nu_{\min}^a$ (cm ⁻¹)	Rot ID ^b	Rest ν^b		E_{low}^b (cm ⁻¹)	F_{line}^c (10 ⁻²⁰ W m ⁻²)	T^d	$g\text{-fac}^e$ (10 ⁻⁷ s ⁻¹)	Q^f (10 ²⁵ s ⁻¹)
			tabulated	wtd mean					
12	2981.99 – 2981.74	E(1→1)P6	2981.941		48.51				
		A ⁺ → ⁻ (2→3)Q ^g	2981.86		81.24				
		A ⁻ → ⁺ (2→3)Q ^g	2981.83		76.24				
				2981.848	78.03	6.55 ± 1.97	0.958	39.17 ± 1.40	36.89 ± 11.14(11.30)
13	2981.21 – 2980.76	E(1→2)P6	2981.106		49.35				
		E(0→1)P5	2981.012		38.83				
		E(-1→ -2)Q*q	2981.04		30.00				
		E(-1→ -2)P7	2980.924		63.19				
		A ⁻ → ⁺ (3→4)Q ^g	2980.825		115.1				
		A ⁺ → ⁻ (3→4)Q ^g	2980.793		103.8				
				2980.918	69.87	8.71 ± 3.84	0.733	44.96 ± 4.91	71.10 ± 31.33(32.38)
14	2979.56 – 2979.15	E(0→ ⁻ 1)P12	2979.549		129.6				
		E(1→2)P7	2979.479		60.65				
		E(0→1)P6	2979.380		48.51				
		E(-1→ -2)P8	2979.332		76.10				
		A ⁺ (1→2)P2	2979.181		31.05				
		A ⁻ (1→2)P2	2979.204		31.05				
				2979.352	54.16	8.80 ± 3.61	0.538	24.33 ± 3.06	142.4 ± 58.34(61.25)
15	2977.16 – 2976.92	E(1→1)P9	2977.044		87.24				
		A ⁻ (2→3)P3	2976.965		44.29				
		A ⁺ (2→3)P3	2976.966		44.29				
				2976.973	46.42	5.94 ± 2.09	0.932	11.36 ± 1.58	118.7 ± 41.78(45.13)
16	2976.25 – 2975.30	E(-1→ -2)P10	2976.192		88.09				
		E(0→1)P8	2976.043		72.72				
		A ⁻ (1→2)P4	2976.047		42.34				
		A ⁺ (1→2)P4	2975.909		42.35				
		A ⁺ (2→2)P9	2975.750		98.82				
		A ⁻ (2→2)P9	2975.735		98.80				
		E(2→3)P7	2975.656		78.34				
		A ⁻ (2→3)P4	2975.356		50.75				
		A ⁺ (2→3)P4	2975.357		50.75				
				2975.732	57.00	16.69 ± 3.91	0.928	36.29 ± 2.81	105.0 ± 24.61(26.20)

Table 4
(Continued)

Int	$\nu_{\max} - \nu_{\min}^a$ (cm^{-1})	Rot ID ^b	Rest ν^b		E_{low}^b (cm^{-1})	F_{line}^c ($10^{-20} \text{ W m}^{-2}$)	T^d	$g\text{-fac}^e$ (10^{-7} s^{-1})	Q^f (10^{25} s^{-1})
			tabulated	wtd mean					
17	2974.35 – 2974.14	E (0→1)P9	2974.282		87.24				
		A ⁺ (1→2)P4	2974.260		50.41				
		A ⁺ (3→4)P4	2974.240		71.98				
		A [−] (3→4)P4	2974.239		71.98				
				2974.251	67.48	−0.720 ± 2.03	0.912	16.63 ± 1.95	−10.01 ± 28.30(28.33)
18	2973.89 – 2973.64	A [−] (2→3)P5	2973.748		58.81				
		A ⁺ (2→3)P5	2973.751		58.81				
				2973.750	58.81	4.69 ± 2.37	0.863	8.70 ± 1.70	132.6 ± 67.07(72.06)

Notes.

^a Range of rest frequencies encompassed by each spectral interval in Figure 3(b).

^b Rotational designation and tabulated rest frequencies are taken from Xu et al. 1997. The asterisk in interval 13 denotes an E-type Q -branch of the ν_9 band; its frequency and energy are only approximate. The heading “wtd mean” for each spectral interval denotes the mean rest frequency weighted by contributing line-by-line empirical g -factors (multiplied by atmospheric transmittance at each Doppler shifted line center frequency, using $\Delta\text{-dot} = -5.42 \text{ km s}^{-1}$), based on the “CH₃OH residuals” in 8P/Tuttle (bottom trace in Figure 4). Equations (A1) and (A2) were used as a guide for modeling intensities of lines having similar rotational designation and symmetry, as discussed in Appendix A. Lower state energies (E_{low}) were taken from Mekhtiev et al. (1999), in particular see the anonymous ftp link listed in Section III of that paper.

^c Measured nucleus-centered line flux and 1σ stochastic error for each interval, based on signal contained within an aperture of size 460 x 1880 km at the distance of 21P/GZ.

^d Weighted mean atmospheric transmittance for all encompassed lines within each interval.

^e Summed fluorescence-efficiency g -factor (at $R_h = 1 \text{ AU}$) for each interval. Uncertainties in g represent 1σ and are based on the stochastic noise summed within each spectral interval in the 8P/Tuttle order 23 spectrum.

^f Global (total) production rate based on the signal contained in each interval. The first uncertainty incorporates the 1σ error in line flux (plus σ_{GF} , which adds only a minor contribution). The second uncertainty (in parentheses) includes these errors plus the 1σ uncertainty in empirical g -factor for each interval.

^g Because the lines comprising these Q -branches are closely spaced in frequency, entries for individual J 's are not presented. Instead, the equivalent integrated g -factor and approximate rotational energy for each Q -branch are listed. The approximate spectral dispersion per pixel = 0.041 cm^{-1} in order 23; correspondingly one resolution element is $\sim 0.2 \text{ cm}^{-1}$ (5 pixels). The spectral widths of these Q -branches range from approximately 0.04 cm^{-1} for $E(1\rightarrow 2)Q(J)$ to 0.2 cm^{-1} for $E(0\rightarrow -1)Q(J)$ or $E(-1\rightarrow 0)Q(J)$, including transitions having $J \leq 8$.

^h Bold-faced entries for interval “5” are shown in italics since we excluded this interval in determining our most reliable Q for CH₃OH in order 23, as discussed in the text.

Table 5
Line Fluxes and Production Rates for Comet 21P/GZ on UT 2005 June 3: H₂O Analysis

Int ^a	Individual Lines ^b					By Interval ^c				
	Line Id	Rest Frequency (cm ⁻¹)	<i>g</i> -factor (10 ⁻⁷ s ⁻¹)	<i>T</i>	<i>E</i> _{rot} (cm ⁻¹)	<i>F</i> _{line} ± <i>σ F</i> _{line} ^d (10 ⁻²⁰ W m ⁻²)	Σ <i>g</i> ^e (10 ⁻⁷ s ⁻¹)	(<i>T</i>) ^f	(<i>E</i> _{rot}) ^g (cm ⁻¹)	<i>Q</i> _{tot} ± <i>σ Q</i> _{tot} ^h (10 ²⁶ molecule s ⁻¹)
1	P 101(2 ₂₁)/100(3 ₂₂)	3517.70	0.433	0.32	201.8	0.64 ± 2.00				82.56 ± 256.9
2	O 101(2 ₁₁)/001(2 ₀₂)	3516.59	0.285	0.52	69.28	3.22 ± 1.84				386.0 ± 220.6
3	O 101(2 ₁₁)/100(3 ₁₂)	3514.41	12.60	0.42	170.3	114.4 ± 2.19				384.3 ± 7.35
4	O 200(3 ₀₃)/001(2 ₀₂)	3508.34	0.403	0.15	69.28	3.54 ± 2.19	0.723	0.20	50.31	453.9 ± 281.0
	P 200(0 ₀₀)/100(1 ₁₁)	3508.25	0.320	0.25	36.24					
5	P 101(3 ₀₃)/100(4 ₀₄)	3507.27	0.327	0.50	218.0	34.56 ± 1.87				377.6 ± 20.48
6	O 111(2 ₀₂)/110(3 ₀₃)	3505.62	1.38	0.13	134.7	0.35 ± 2.47				37.1 ± 258.3
7	O 101(3 ₂₂)/100(4 ₂₃)	3494.26	0.960	0.57	294.3	12.92 ± 1.93				428.6 ± 63.90
8	O 210(2 ₂₁)/110(3 ₁₂)	3490.29	0.154	0.63	174.6	25.06 ± 1.83	1.62	0.65	262.0	428.7 ± 31.30
	P 101(3 ₁₂)/100(4 ₁₃)	3490.26	1.46	0.65	270.8					
9	P 200(2 ₀₂)/001(1 ₀₁)	3489.82	0.272	0.50	23.56	22.90 ± 1.87	1.28	0.62	68.70	523.6 ± 42.83
	O 200(1 ₀₁)/100(2 ₁₂)	3489.68	1.01	0.65	77.84					
10	P 101(4 ₁₄)/100(5 ₁₅)	3488.78	0.543	0.39	320.9	8.03 ± 2.13				679.6 ± 180.4
11	O 200(2 ₁₂)/001(1 ₁₁)	3485.99	1.12	0.42	35.77	12.95 ± 2.16				502.7 ± 83.84
12	P 003(3 ₁₂)/002(4 ₁₃)	3485.35	0.0052	0.48	268.0	0.96 ± 2.11	0.376	0.48	308.9	96.23 ± 210.4
	P 101(3 ₂₁)/100(4 ₂₂)	3485.31	0.371	0.48	309.5					
13	O 200(1 ₀₁)/001(2 ₀₂)	3399.37	2.09	0.91	69.28	40.03 ± 1.62				390.8 ± 15.78
14	O 101(1 ₁₁)/001(2 ₂₀)	3397.63	0.696	0.37	131.2	3.10 ± 2.40				222.1 ± 172.2
15	O 200(2 ₂₁)/100(3 ₃₀)	3394.07	1.66	0.83	278.28	19.45 ± 1.74				262.6 ± 23.85
16	O 201(0 ₀₀)/200(1 ₀₁)	3388.77	0.447	0.94	23.04	8.87 ± 1.60				392.4 ± 70.96
17	O 101(4 ₀₄)/001(5 ₁₅)	3387.54	0.123	0.85	321.0	3.72 ± 1.76				665.1 ± 315.0
18	O 200(2 ₁₂)/001(3 ₁₃)	3382.10	2.09	0.92	139.7	38.33 ± 1.66				373.2 ± 16.18
19	P 200(2 ₀₂)/001(3 ₀₃)	3378.48	0.431	0.80	134.9	2.80 ± 1.99				150.8 ± 107.5
20	O 200(2 ₂₁)/001(3 ₂₂)	3372.75	1.07	0.92	200.7	22.30 ± 1.63				421.1 ± 30.69
21	P 200(3 ₁₃)/100(4 ₂₂)	3371.69	0.102	0.95	309.5	4.92 ± 1.51				954.1 ± 293.4
22	O 201(1 ₁₁)/200(2 ₁₂)	3369.73	0.266	0.59	76.15	2.02 ± 2.32				242.2 ± 277.7
23	O 210(2 ₂₁)/110(3 ₃₀)	3361.03	0.0913	0.71	303.8	0.67 ± 2.19	0.317	0.73	244.7	54.66 ± 178.9
	P 200(3 ₁₃)/001(4 ₁₄)	3360.99	0.230	0.73	221.3					
24	O 200(3 ₀₃)/001(4 ₀₄)	3358.92	0.605	0.81	218.7	12.00 ± 1.91				458.4 ± 73.08

Notes.^a Spectral interval as numbered in Figure 2.^b For each H₂O line, its spin (O/P) and vibrational (and rotational) designation are given as *V*(upper)/(*J*_{KaKc}(upper))/*V*(lower)/(*J*_{KaKc}(lower)), followed by its rest frequency, transmittance, upper state rotational energy, and line *g*-factor.^c For the five spectral intervals containing blends, the contributions from encompassed lines are combined.^d Measured line flux and its 1 σ error.^e Sum of model *g*-factors (i.e., not multiplied by transmittance) within interval.^f Mean modeled atmospheric transmittance over each spectral interval.^g Mean lower state rotational energy, weighted by individual line *g*-factors multiplied by corresponding atmospheric transmittances.^h Calculated production rate and its 1 σ error based on signal contained within each spectral interval (Figure 2(d)).

Table 6
Line Fluxes and Production Rates for 21P/GZ on UT 2005 June 3: C₂H₆ ν_7 Band

Int ^a	No. of Lines ^a	Rest Frequency ^b (cm ⁻¹)	<i>F</i> _{line} ± <i>σ F</i> _{line} ^c (10 ⁻²⁰ W m ⁻²)	Σ <i>g</i> ^d (10 ⁻⁷ s ⁻¹)	(<i>T</i>) ^e	(<i>E</i> _{rot}) ^f (cm ⁻¹)	<i>Q</i> _{tot} ± <i>σ Q</i> _{tot} ^g (10 ²⁵ molecule s ⁻¹)
1	27	2996.85	4.28 ± 1.91	221.9	0.954	61.21	4.24 ± 1.90
2	22	2993.44	9.70 ± 2.69	278.4	0.748	50.31	9.79 ± 2.71
3	22	2990.06	6.86 ± 2.07	367.8	0.913	40.96	4.30 ± 1.30
4	23	2986.74	14.55 ± 2.13	497.4	0.906	35.01	6.81 ± 0.996
5	23	2983.37	4.44 ± 2.05	376.4	0.948	37.13	2.63 ± 1.21
6	22	2980.08	6.76 ± 3.31	281.1	0.659	44.55	7.71 ± 3.78
7	32	2976.77	5.05 ± 2.05	209.4	0.930	58.36	5.49 ± 2.23

Notes.^a Spectral interval (from Figures 3(a) and (c)) and the number of encompassed C₂H₆ ν_7 lines.^b Measured mean rest frequency for encompassed lines.^c Measured integrated line flux.^d Sum of modeled *g*-factors (i.e., not multiplied by transmittance) within interval.^e Integrated line flux as measured within interval.^f Mean lower state rotational energy, weighted by individual line *g*-factors multiplied by corresponding atmospheric transmittances.^g Global production rate (points in Figure 3(c)).

Table 7
Line Fluxes and Production Rates for Comet 21P/GZ on UT 2005 June 3: CH₃OH ν_3 Band

Int ^a	No. of Lines ^a	Rest Frequency ^b (cm ⁻¹)	$F_{\text{line}} \pm \sigma F_{\text{line}}^c$ (10 ⁻²⁰ W m ⁻²)	Σg^d (10 ⁻⁷ s ⁻¹)	$\langle T \rangle^e$	$\langle E_{\text{rot}} \rangle^f$ (cm ⁻¹)	$Q_{\text{tot}} \pm \sigma Q_{\text{tot}}^g$ (10 ²⁵ molecule s ⁻¹)
1	25	2863.54	0.982 ± 2.28	6.60	0.983	119.6	33.34 ± 77.44
2	32	2862.14	0.146 ± 3.45	12.74	0.924	104.7	2.727 ± 64.58
3	28	2860.50	-0.779 ± 3.32	19.03	0.994	89.11	-9.075 ± 38.74
4	7	2859.72	0.0879 ± 2.19	6.40	0.986	100.4	3.070 ± 76.45
5	24	2859.05	8.27 ± 3.67	29.63	0.976	74.93	63.05 ± 27.99
6	10	2858.31	1.59 ± 2.57	6.91	0.843	88.61	60.41 ± 97.22
7	4	2857.92	1.99 ± 2.47	7.83	0.757	66.56	74.13 ± 92.00
8	14	2857.53	2.68 ± 2.75	21.13	0.975	63.58	28.68 ± 29.49
9	4	2857.13	1.58 ± 2.21	9.97	0.981	53.78	35.63 ± 49.79
10	8	2856.70	-1.75 ± 2.41	10.52	0.986	69.64	-37.13 ± 51.21
11	10	2856.04	12.36 ± 2.99	22.33	0.974	52.94	125.4 ± 30.31
12	6	2855.57	3.04 ± 2.21	11.78	0.967	42.83	58.98 ± 42.83
13	12	2855.17	5.48 ± 2.91	28.02	0.969	48.35	44.57 ± 23.68
14	5	2854.66	5.46 ± 2.31	8.67	0.919	60.88	151.2 ± 63.99
15	7	2854.35	7.98 ± 2.55	19.33	0.947	37.64	96.30 ± 30.76
16	9	2853.64	4.95 ± 2.37	31.61	0.926	38.97	37.34 ± 17.88
17	4	2853.13	-1.77 ± 2.28	9.28	0.976	50.27	-43.24 ± 55.74
18	10	2852.74	3.98 ± 2.17	19.93	0.995	26.62	44.41 ± 24.24
19	12	2852.22	5.96 ± 3.20	44.87	0.963	29.12	30.47 ± 16.38
20	3	2851.64	3.93 ± 2.33	9.15	0.994	43.88	95.57 ± 56.61
21	4	2851.12	1.10 ± 2.20	17.71	0.985	13.62	13.97 ± 27.84
22	12	2850.61	3.26 ± 3.11	39.50	0.951	21.94	19.16 ± 18.30
23	5	2850.10	0.575 ± 2.18	7.39	0.995	39.70	17.30 ± 65.73
24	4	2849.55	3.62 ± 2.19	15.61	0.992	8.78	51.76 ± 31.27
25	10	2849.03	2.84 ± 3.11	27.32	0.980	16.53	23.47 ± 25.66
26	6	2847.97	4.55 ± 2.23	12.17	0.982	5.55	84.30 ± 41.33
27	5	2847.53	1.15 ± 2.98	7.94	0.943	9.76	33.97 ± 88.29
28	37	2846.35	2.12 ± 2.21	6.58	0.991	4.04	71.93 ± 75.12
29	59	2845.56	8.59 ± 4.19	45.81	0.957	43.93	43.39 ± 21.20
30	319	2844.33	27.98 ± 4.41	117.8	0.968	56.49	54.41 ± 8.58
31	66	2843.10	-3.83 ± 2.28	7.71	0.969	19.44	-113.8 ± 67.63
32	46	2842.59	6.72 ± 2.30	8.41	0.957	19.66	185.0 ± 63.24
33	50	2842.11	3.88 ± 2.53	25.66	0.993	51.97	33.72 ± 22.05
34	33	2841.51	-1.73 ± 2.39	14.33	0.944	18.23	-28.35 ± 39.15
35	29	2841.04	11.20 ± 2.70	22.13	0.983	17.91	114.1 ± 27.56
36	16	2839.85	6.19 ± 23.46	18.11	0.945	13.71	80.30 ± 30.42

Notes.^a Spectral interval (Figure 5(a)) and the number of encompassed CH₃OH ν_3 lines that were included in our analysis.^b Measured mean rest frequency for encompassed lines.^c Integrated line flux as measured within interval.^d Sum of modeled g -factors (i.e., not multiplied by transmittance) within interval.^e Mean transmittance within interval.^f Mean lower state rotational energy, weighted by individual line g -factors multiplied by corresponding atmospheric transmittances.^g Global production rate (points in Figure 5(c)).

et al. 1999), T_{rot} is rotational temperature, and L_{HL} is the Hönl–London factor. For a perpendicular band such as ν_2 , the intensity of which is dominated by lines having “A” symmetry in b-type sub-bands (for which $\Delta K = \pm 1$; e.g., see Xu et al. 1997), L_{HL} is given by

$$L_{\text{HL}} = \frac{(J - 1 \mp K)(J \mp K)}{J(2J + 1)}$$

for $\Delta J = -1$ (P – branch lines),

$$L_{\text{HL}} = \frac{(J + 1 \pm K)(J \mp K)}{J(J + 1)}$$

for $\Delta J = 0$ (Q – branch lines),

$$L_{\text{HL}} = \frac{(J + 2 \pm K)(J + 1 \pm K)}{(J + 1)(2J + 1)}$$

for $\Delta J = +1$ (R – branch lines), (A2)

where the upper sign in each equation refers to $\Delta K (=K_{\text{upper}} \rightarrow K_{\text{lower}}) = +1$, and the lower sign refers to $\Delta K = -1$ (Herzberg 1945, p. 426).

An example is provided by P -branch lines in the $A(\Delta K = 1 \rightarrow 2)$ sub-band. In the Comet 8P/Tuttle “CH₃OH residual” spectrum (Figure 4), the intensity contained in the left-most (highest frequency) peak in interval 16 (near 2976.0 cm⁻¹) is dominated by $A^{-/+} \rightarrow -/+$ P_4 components. The corresponding P_3 components at ~ 2977.6 cm⁻¹ coincide approximately with a feature having strong residual intensity (additionally, a second feature near 2977.4 cm⁻¹ has lower intensity but no viable corresponding ν_2 line). Using Equations (A1) and (A2) (and assuming $T_{\text{rot}} = 50$ K) suggests an intensity ratio $P_3/P_4 = 1.07$, and this is reflected in the model shown in Figure 4. (We note that the modeled “ P_3 ” feature appears weaker than the feature in interval 16; this results from its relatively poorer transmittance ($\sim 50\%$) compared with that of the “ P_4 ” feature

(~95%).] However, to account for the intensity in the CH₃OH residuals near 2977.6 cm⁻¹ requires an unrealistically large ratio (~1.8), and we therefore exclude this region from our analysis. Similar reasoning pertains to other excluded spectral regions (marked “x” in Figure 4), and this approach will be used as our empirical model is improved through extension to other comets in our database encompassing a range of rotational temperatures. Table 4 provides a summary of our empirical model as applied to Comet 21P/Giacobini-Zinner.

APPENDIX B

LINE-BY-LINE RESULTS IN 21P/GZ: H₂O, C₂H₆ (ν_7), AND CH₃OH (ν_3)

Tables 5–7 present fluxes and production rates for spectral intervals included in our analysis of 21P/GZ.

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