Sub-Doppler infrared spectroscopy of CH₂OH radical in a slit supersonic jet: Vibration-rotation-tunneling dynamics in the symmetric CH stretch manifold

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The sub-Doppler CH-symmetric stretch (ν_3) infrared absorption spectrum of a hydroxymethyl (CH₂OH) radical is observed and analyzed with the radical formed in a slit-jet supersonic discharge expansion ($T_{\text{rot}} = 18$ K) via Cl atom mediated H atom abstraction from methanol. The high sensitivity of the spectrometer and reduced spectral congestion associated with the cooled expansion enable first infrared spectroscopic observation of hydroxymethyl transitions from both $\pm$ symmetry tunneling states resulting from large amplitude COH torsional motion. Nuclear spin statistics due to exchange of the two methyl H-atoms aid in unambiguous rovibrational assignment of two A-type $K_a = 0 \leftarrow 0$ and $K_a = 1 \leftarrow 1$ bands out of each $\pm$ tunneling state, with additional spectral information obtained from spin-rotation splittings in P, Q, and R branch $K_a = 1 \leftarrow 1$ transitions that become resolved at low N . A high level *ab initio* potential surface (CCSD(T)-f12b/cc-pvTZ12 ($n = 2,3$)/CBS) is calculated in the large amplitude COH torsional and CH₂ wag coordinates, which in the adiabatic approximation and with zero point correction predicts ground state tunneling splittings in good qualitative agreement with experiment. Of particular astrochemical interest, a combined fit of the present infrared ground state combination differences with recently reported millimeter-wave frequencies permits the determination of improved accuracy rotational constants for the ground vibrational state, which will facilitate ongoing millimeter/microwave searches for a hydroxymethyl radical in the interstellar medium. *Published by AIP Publishing.* [<http://dx.doi.org/10.1063/1.4982803>]

I. INTRODUCTION

A hydroxymethyl radical (CH₂OH) appears as an intermediate in methanol combustion reactions, towards which there has been significant theoretical and experimental effort directed, in part due to the potential large-scale use of methanol as an oxygenated additive to gasoline and diesel fuels.^{1–3} As a fuel stock, methanol has several advantages compared with the more conventional ethanol additive, including lower cost of production, greater diversity of sources from which it can be produced (e.g., natural gas, coal, and biomass), and higher percentage of oxygen.⁴ The hydroxymethyl radical is produced directly in the early initiation stages of methanol combustion (CH₃OH + O₂/O → CH₂OH + HO₂/HO) as well as in subsequent propagation steps based on H-atom abstraction from CH₃OH by HO₂ and OH.^{2,3,5–7} While H-atom abstraction by O₂ or O can energetically occur in principle from either the methyl or hydroxyl end of the molecule, theory and experiment^{1,8–11} indicate the predominant channel for both reactions to be removal of methyl hydrogen to form CH₂OH. *In situ* remote sensing of the hydroxymethyl radical under actual combustion conditions would provide an invaluable spectroscopic test of potential reaction mechanisms.^{1,2}

In a very different albeit complementary direction, the search for and study of oxygen-containing complex organic molecules in the interstellar medium are also of significant interest, with such species postulated to be key precursors to the formation of important biological molecules.^{12,13} The formation of these species is likely not dominated by homogeneous gas phase chemistry, since theoretical production rates for complex organic molecules via gas-phase neutral/neutral and neutral/ion reactions are predicted to be significantly smaller than the values experimentally inferred from spectroscopic measurements.^{14–17} Such deficits in the gas phase kinetic models have been used to support the predominance of radical-radical reactions pathways on cold grain surfaces as an important additional source of complex organic molecules. Of particular relevance to the present efforts, recent surveys have determined that these interstellar grains are often coated with water/methanol ice.^{18,19} Indeed, laboratory studies replicating these ice grain conditions at low temperature have demonstrated that large organic molecules can be produced via surface chemical reactions,^{20–22} for which the hydroxymethyl radical has been identified as a crucial intermediate.

Despite a growing body of evidence for the relevance of the hydroxymethyl radical in astrochemistry, direct confirmation via mm/microwave detection of CH₂OH in the interstellar medium has yet to be reported. Obtaining definitive observational data promises to be particularly challenging, as the microwave spectroscopy of CH₂OH is significantly complicated by large amplitude COH torsional motion in this highly

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quantum mechanical species. Furthermore, the concentrations of the hydroxymethyl radical are expected to be considerably smaller than those of the much more abundant methanol, which has similar rotational constants and an extremely rich manifold of states due to large amplitude internal rotation of the COH moiety. Indeed, while methanol is also an extremely important interstellar oxygen-containing molecule, it exhibits such a congested spectrum that it has been referred to as an interstellar “weed.”^{22–26} As a result, positive identification of the hydroxymethyl radical in the interstellar medium will require highest quality predictions from precise ground vibrational state constants, the determination of which is a primary goal of this work.

The hydroxymethyl radical has four equivalent minimum energy non-planar geometries (see Fig. 1) connected by larger COH torsional rotation barriers and smaller CH₂ wag barriers. Significant theoretical and experimental effort has been invested in determining the potential energy surface and resultant molecular parameters. Schaefer and co-workers²⁷ provided some of the earliest calculations of the CH₂OH potential energy surface, specifically, predicting 1392 cm^{−1} and 322 cm^{−1} barriers associated with a coupled COH internal hindered rotation and CH₂ wag. Johnson and Hudgens²⁸ calculated comparable potential energy barriers for COH internal rotation (1643 cm^{−1}) and CH₂ wag (156 cm^{−1}), respectively. Furthermore, Johnson and Hudgens determined that the two lowest frequency vibrations in the radical, COH torsion (ν_8) and CH₂ wag (ν_9), are both highly anharmonic and strongly coupled. The authors also inferred that the presence of a predominantly 2-fold barrier to COH internal rotation will result in a spectral fine structure for each pair of tunneling states but predicted these splittings to be limited by convergence in

the eigenvalues (<1 cm^{−1}) for all states with $\nu_8 + \nu_9 \leq 2$. Marenich and Boggs^{29,30} provided improved estimates of vibrational energies using full 9D anharmonic calculations, with comparison of predicted experimental values yielding a $<1.7\%$ average error for the seven available frequencies. Interestingly, the experimental data for this comparison is not yet available for the CH-symmetric (ν_3) or CH-asymmetric (ν_2) stretch vibrations. Particular relevance to the present study is the CH-symmetric vibrational band predicted near 3060 cm^{−1}, with rotational constants in the ground ($\nu_3 = 1$) vibrational states of $A = 6.508$ (6.427) cm^{−1}, $B = 0.988$ (0.986) cm^{−1}, and $C = 0.862$ (0.859) cm^{−1}, respectively.

Although the hydroxymethyl radical has been a target of many experimental studies exploiting laser magnetic resonance,³¹ resonance enhanced multiphoton ionization,^{28,32–38} and infrared^{35,39–42} and millimeter-wave (mm-wave) spectroscopy,⁴³ the earliest experimental observations of hydroxymethyl have been made via electron spin resonance^{44–48} by Dixon and Norman.⁴⁵ In these studies, CH₂OH was generated by hydrogen abstraction from methanol in a liquid flow system, where OH is formed by titanium (III) ion catalyzed decomposition of hydrogen peroxide and in turn reacts with methanol via: $\text{OH} + \text{CH}_3\text{OH} \rightarrow \text{CH}_2\text{OH} + \text{H}_2\text{O}$. The ESR spectrum is consistent with a CH₂OH structure in which the π radical center is on the C atom with two equivalent methylene H atoms and no measurable coupling between the unpaired electron and the hydroxyl hydrogen atom. Livingston and Zeldes⁴⁶ later obtained the hyperfine-resolved ESR spectrum of hydroxymethyl produced by reacting methanol with UV irradiated hydrogen peroxide to generate OH in a liquid flow system. These studies provided adequate experimental resolution to observe both the larger splitting due to coupling of the radical electron spin with the two equivalent methylene H-atoms and a smaller hyperfine splitting due to coupling with the hydroxyl H-atom. Interestingly, the coupling strengths increased as the temperature was reduced below -50°C . At the lowest temperature (-130°C), Hudson observed the central doublet to split into two doublets attributed to nonequivalence of the two methylene H-atoms, which permitted the estimation of the internal rotor COH torsional barrier to be in excess of 800 cm^{−1}. Krusic *et al.*⁴⁷ obtained ESR spectra down to -150°C in a later study and used the temperature dependence of the hyperfine coupling constant and line shape analysis to determine an improved barrier estimate of 1400 cm^{−1} for COH internal rotation.

Resonance enhanced multiphoton ionization (REMPI) methods^{32–34,36–38,49} have also been used to provide valuable spectroscopic information about the hydroxymethyl radical in the gas phase, specifically mapping out the vibrational level structure in excited intermediate Rydberg electronic states. The Hudgens group³² reported the first REMPI observation of the hydroxymethyl radical via excitation to the 3p excited Rydberg state, with later studies²⁸ on both fundamental and hot band transitions allowing them to extract vibrational frequencies for multiple isotopomers in the ground and excited electronic states. Of particular relevance to motivating the present studies, the Reisler group^{34,36–38,49} contributed significantly to understanding hydroxymethyl photofragmentation dynamics via monitoring the dissociation products resulting

FIG. 1. 2D CH₂OH potential energy surface as a function of the COH torsional and CH₂ wag vibrations obtained from Molpro calculations at the CCSD(T)/avqz level.⁶² Note the four equivalent minimum energy structures separated by relatively small barriers (≈ 96 cm^{−1}) in the CH₂ wag and much larger barriers (≈ 1661 cm^{−1}) in the COH torsional coordinate.

from electronic excitation to 3s, 3p_x, and 3p_z Rydberg as well as highly energized (4v₁) OH stretch overtone states.

Infrared vibrational studies of CH₂OH were first obtained by Jacox and Milligan³⁹ via matrix isolation spectroscopy, with the radical species generated by the UV photolysis of methanol and permitting first identification of the hydroxymethyl CO stretch and COH torsion vibrations for which they reported frequencies of 1183.5 cm⁻¹ and 482.0 cm⁻¹, respectively. In later studies, Jacox⁴⁰ produced improved concentrations of the hydroxymethyl radical via methanol reactions with discharge generated fluorine and metastable argon atoms. These improvements in signal to noise facilitated detection and assignment for seven of the 3N - 6 = 9 total normal mode vibrations, although, interestingly, the CH-symmetric and CH-asymmetric vibrations again remained unobserved and unanalyzed. However, a detailed normal mode analysis of force constants obtained through the study of multiple hydroxymethyl H/D and ¹³C/¹²C isotopomers permitted Jacox and Milligan to predict fundamental vibrational frequencies for all nine modes of the hydroxymethyl radical, including a CH-symmetric stretch frequency at 2915.4 cm⁻¹.

The first rovibrational information on CH₂OH was reported by Reisler and co-workers,^{35,49} using a combination of depletion and double resonant ionization detected IR (DRID-IR) spectroscopy to identify the fundamental CH-symmetric (v₃), CH-asymmetric (v₂), and OH (v₁) stretch bands as well as the first overtone of the OH stretch (2v₁) band. One parallel band (K_a = 0 ← 0) was observed for each of the CH-symmetric and OH stretch fundamental and overtone bands, with K_a = 0 ← 1 and K_a = 1 ← 0 perpendicular bands also observed for the CH-asymmetric stretch fundamental. Experimental resolution in these studies was limited by laser linewidth (Δv ≈ 0.4 cm⁻¹), which, although permitting very useful band contour fits to estimate vibrational origins and rotational constants, precluded the observation of any high resolution information such as a asymmetry structure and/or COH torsion tunneling effects. However, such action spectroscopy methods could be quite nicely extended to higher vibrational excitation, with the second (3v₁) and the third (4v₁) overtones of the OH stretch vibration also explored.^{36,41,50} Indeed, the energy of the upper state for the third overtone approaches the threshold for dissociation to H + CH₂O, which permitted observation by monitoring the resulting H atom fragments. Of particular dynamical interest, the observed linewidths for the third overtone (Δv ≈ 1.3 cm⁻¹) proved to be significantly broader than those for the second overtone (Δv ≈ 0.4 cm⁻¹), thereby signaling rapid O-H bond rupture via quantum mechanical tunneling through the dissociation barrier.

The first fully rotationally resolved gas-phase infrared spectrum of CH₂OH in the K_a = 0 ← 0 CH-symmetric stretch band in the ground tunneling state has been recently reported from our group.⁴² In that study, high concentrations of jet cooled CH₂OH radicals were generated in a slit jet supersonic discharge expansion via both (i) direct dissociation (CH₃OH → CH₂OH + H) and (ii) gas-phase atomic chlorine mediated H-abstraction chemistry (Cl + CH₃OH → CH₂OH + HCl), with the latter pathway greatly reducing the number of methanol spectral interferences due to more selective

H atom abstraction. The current study builds on and extends this work significantly, in which we exploit optimized precursor chemistry, discharge voltages, and higher pulsed valve stagnation pressure to achieve increased signal to noise and colder rotational temperatures. These improvements now permit observation, resolution, and assignment of transitions out of multiple K_a levels and both ground (+) and excited (-) COH torsional tunneling states. Indeed, this work also builds synergistically on the very recent study of Bermudez *et al.*,⁴³ which itself took advantage of the preliminary ground state rotational constants from our group to facilitate the first mm-wave observation of hydroxymethyl. In particular, they have measured frequencies for 96 hyperfine components of 11 rotational transitions, with rotational constants now determined by simultaneously fitting 85 of the observed mm-wave transitions and three ground state K_a = 0 ← 0 combination differences (CDs) from Roberts *et al.*⁴² Furthermore, the mm-wave studies resolve transitions out of both (+) and (-) tunneling symmetries and provide invaluable information for unambiguous assignment of the high resolution infrared spectra. Most importantly, the new spectral information provided by the present infrared studies permits combined least squares fit to all mm-wave transitions and a large number of infrared-based ground state combination differences in both tunneling manifolds. The results of this combined fit significantly improve the precision of ground state rotational constants, which in turn should help facilitate spectroscopic search for the hydroxymethyl radical in the interstellar medium.

The organization of this paper is as follows. Experimental details relevant to this study are briefly summarized Sec. II, followed in Sec. III by detailed assignment and analysis of the multiple CH-symmetric stretch ΔK_a = 0 sub-bands observed. In Sec. IV, we discuss combined fits to 38 infrared ground state combination differences [18(+) and 20(-)] with the mm-wave transition frequencies reported by Bermudez *et al.*,⁴³ with additional details on analysis of a partially resolved spin-rotation fine structure and indications for the presence of perturbations from near resonant “dark” levels in the excited vibrational state. We extend this discussion by high level *ab initio* calculations for the internal COH torsional and CH₂ wag degrees of freedom, which permits first calculation of the converged ground state tunneling splittings. Conclusions and thoughts for further directions are briefly summarized in Sec. V.

II. EXPERIMENT

The CH-symmetric stretch absorption spectrum of the hydroxymethyl radical has been recorded using a high-resolution infrared slit-jet discharge spectrometer presented in detail elsewhere.⁵¹ The infrared light is produced by difference frequency generation via phase matching 514 nm light from a frequency stabilized Ar⁺ laser with a tunable light from a single mode ring dye laser, pumped with a frequency doubled Nd:YAG, in a temperature controlled, periodically poled lithium niobate crystal. The infrared light produced (~12 μW) is split into signal and reference beams with roughly equal IR power. The signal beam is multipassed 16 times through the detection region 5 mm downstream of

the pulsed slit-jet orifice ($4\text{ cm} \times 300\text{ }\mu\text{m}$) operating at a 19 Hz repetition rate. The signal and reference beams are monitored on matched liquid N_2 -cooled InSb detectors, with near shot-noise-limited levels ($\approx 10^{-6}/\text{Hz}^{1/2}$ in a 10 kHz detection bandwidth) achieved by fast electronic subtraction of the signal and reference beams. The Ar^+ and dye laser frequencies are determined via laser transmission fringes through a stabilized confocal Fabry-Perot (FSR $\sim 250\text{ MHz}$), which is locked to a polarization-stabilized HeNe laser to ensure long-term stability.⁵² Frequency measurements with a typical precision of $\sigma = 12\text{ MHz}$ are readily obtained via fringe interpolation on this stable optical transfer cavity, with a nearly comparable frequency accuracy achieved via comparison with well-known methane reference gas transitions doped into and measured simultaneously in the sub-Doppler slit jet expansion.⁵³

Hydroxymethyl radicals are produced in a 500 V pulsed discharge at the slit jet orifice with a gas mixture of 0.1% methanol, 0.2% Cl_2 in a buffer gas of 30% He, and 70% Ne at a total stagnation pressure of 250 Torr. Chlorine atoms form via dissociation of Cl_2 in the discharge and react with methanol via $\text{Cl} + \text{CH}_3\text{OH} \rightarrow \text{HCl} + \text{CH}_2\text{OH}$. The discharge is modulated at 50 kHz and monitored via phase-sensitive lock-in detection to permit radical transitions to be discriminated from those of the methanol precursor. Hydroxymethyl radicals are cooled in the expansion to a rotational temperature of 18 K, which compresses population into only the lowest few rotational states ($N \leq 9$). In conjunction with the intrinsic 5–10 fold suppression of Doppler widths in the slit jet expansion environment, this dramatically increases signal to noise, reduces spectral congestion, and greatly aids in the rotational, tunneling, and spin-orbit state assignments.

III. RESULTS

In the slit jet expansion, multiple bands in the CH_2OH fundamental CH-symmetric stretch (ν_3) absorption spectrum are readily detected at sub-Doppler resolution ($\approx 0.002\text{ cm}^{-1}$) between 3025 cm^{-1} and 3060 cm^{-1} . Thorough investigation of this spectral region over multiple scans clearly reveals two $K_a = 0 \leftarrow 0$ bands (Table I) and two $K_a = 1 \leftarrow 1$ bands (Table II), each observed with an additional splitting of all $N_{K_a K_c}$ asymmetric top energy levels due to internal rotor tunneling of the OH group through the COH torsional barrier.

The assignment and analysis of the internal rotor tunneling splittings utilizes straightforward application of Fermi-Dirac statistics, which requires that the *total* wavefunction be antisymmetric (–) with respect to any feasible exchange of the two equivalent spin 1/2 methylene H-atoms ($I = 1/2$). In CH_2OH , the exchange is most simply achieved by 180° internal rotation of CH_2 around the CO bond axis followed by a much lower barrier adjustment in the CH_2 wag coordinate. For the purpose of calculating nuclear spin weights, the overall wave function can be treated as a separable product: $\psi_{\text{tot}} = \psi_{\text{elec}} \times \psi_{\text{vib}} \times \psi_{\text{rot}} \times \psi_{\text{tun}} \times \psi_{\text{NS}}$, where Table III summarizes all symmetry contributions to the total wave function. The highest occupied molecular orbital (HOMO) contributing to the total electronic state wave function (ψ_{elec}) is singly occupied and therefore antisymmetric (–) under π internal rotation of the CH_2 group (see Fig. 2). The symmetries of the CH-symmetric

TABLE I. List of all a-type $K_a = 0 \leftarrow 0$ infrared transitions (cm^{-1}) out of both lower (+) and upper (–) torsional tunneling states. Residuals are determined from least squares fits to yield vibrationally excited state molecular constants reported in Table VI.

P-branch				
$N_{K_a K_c}(J)$	(+ Tunneling state		(– Tunneling state	
		(Obs-Pred)		(Obs-Pred)
	Observed	$\times 10^3$	Observed	$\times 10^3$
0 ₀₀ (0.5)–1 ₀₁ (1.5)	3 039.895 8	–0.3	3 039.367 2	0.1
1 ₀₁ (1.5)–2 ₀₂ (2.5)	3 038.034 1	–0.4	3 037.504 4	–0.5
2 ₀₂ (2.5)–3 ₀₃ (3.5)	3 036.173 6	–0.9	3 035.643 0	–0.6
3 ₀₃ (3.5)–4 ₀₄ (4.5)	3 034.317 7	–0.5	3 033.784 5	–0.6
4 ₀₄ (4.5)–5 ₀₅ (5.5)	3 032.466 9	–0.9	3 031.930 0	–1.0
5 ₀₅ (5.5)–6 ₀₆ (6.5)	3 030.624 6	–0.4		
6 ₀₆ (6.5)–7 ₀₇ (7.5)	3 028.790 7	–0.7	3 028.241 6	–0.5
7 ₀₇ (7.5)–8 ₀₈ (8.5)	3 026.967 7	–0.7		
8 ₀₈ (8.5)–9 ₀₉ (9.5)	3 025.155 4	–1.2		
R-branch				
1 ₀₁ (1.5)–0 ₀₀ (0.5)	3 043.614 2	1.2	3 043.084 0	0.6
2 ₀₂ (2.5)–1 ₀₁ (1.5)	3 045.466 3	0.5	3 044.935 5	0.6
3 ₀₃ (3.5)–2 ₀₂ (2.5)	3 047.311 4	0.7	3 046.778 0	0.5
4 ₀₄ (4.3)–3 ₀₃ (3.5)	3 049.145 9	0.6	3 048.609 2	0.6
5 ₀₅ (5.5)–4 ₀₄ (4.5)	3 050.967 6	0.4	3 050.425 6	0.4
6 ₀₆ (6.5)–5 ₀₅ (5.5)	3 052.774 8	0.7	3 052.224 9	0.2
7 ₀₇ (7.5)–6 ₀₆ (6.5)	3 054.565 2	1.1	3 054.005 5	0.4
8 ₀₈ (8.5)–7 ₀₇ (7.5)	3 056.336 8	0.9	3 055.764 9	–0.1

stretch and overall rotational wave function are (+) and (–) ^{K_a} , respectively. The OH torsional wave function controls the tunneling state symmetry, which can be labeled as symmetric (+) or antisymmetric (–) as a function of the internal rotation path connecting the two equivalent structures (see Fig. 1). Thus, for the total wave function to be antisymmetric with respect to CH_2 internal rotation, this requires ψ_{NS} to be symmetric (NS weight = 1, *para*) for $K_a'' = 0(-)$ and $K_a'' = 1(+)$ states and antisymmetric (NS weight = 3, *ortho*) for $K_a'' = 1(-)$ and $K_a'' = 0(+)$ states, where the $\pm$ signs in parentheses for the remainder of this paper will refer exclusively to even/odd symmetry of the tunneling wave function.

These nuclear spin weights provide a powerful aid in spectral assignment, as illustrated, for example, by the 3:1 intensity ratios in Fig. 3 between three tunneling split pairs of $N = 3 \leftarrow 2$ transitions out of $2_{02}(+):2_{02}(-)$, $2_{11}(-):2_{11}(+)$, and $2_{12}(-):2_{12}(+)$ pairs of *ortho:para* lower states. Indeed, this can be exploited more quantitatively in Boltzmann plots for separate contributions out of the $K_a = 0(+)$, $1(-)$ *ortho* and $K_a = 0(-)$, $1(+)$ *para* levels, with a series of multiple transitions from each of the four K_a'' and $\pm$ tunneling states shown in Fig. 4. Note that each series is individually well fit by a Boltzmann plot with a slope corresponding to a common rotational temperature ($T_{\text{rot}} \approx 18\text{ K}$), but with systematic shifts in the y-intercept. As a first test of consistency, the logarithmic differences between *ortho/para* Boltzmann intercepts for the same K_a state (3.0(3), 3.2(5) for $K_a = 0, 1$, respectively) correspond quite closely with the expected 3:1 ratio based on nuclear spin statistics.

TABLE II. List of all a-type $K_a = 1 \leftarrow 1$ infrared transitions (cm^{-1}) out of the (+) and (−) tunneling states. Residuals are determined from least squares fits to yield vibrationally excited molecular constants reported in Table VI.

$N_{K_a K_c}(J)$	(+) Tunneling state		(−) Tunneling state		$N_{K_a K_c}(J)$	(+) Tunneling state		(−) Tunneling state	
	Observed	(Obs-Pred)	Observed	(Obs-Pred)		Observed	(Obs-Pred)	Observed	(Obs-Pred)
		$\times 10^3$		$\times 10^3$			$\times 10^3$		$\times 10^3$
P-branch									
1 ₁₁ (1.5)–2 ₁₂ (2.5)	3 038.144 9	0.7	3 037.796 4	−0.5	1 ₁₀ (1.5)–2 ₁₁ (2.5)	3 037.885 7	^a	3 037.533 0	^a
1 ₁₁ (0.5)–2 ₁₂ (1.5)			3 037.800 2	−0.8					
1 ₁₁ (1.5)–2 ₁₂ (1.5)			3 037.788 4	0.5					
2 ₁₂ (2.5)–3 ₁₃ (3.5)	3 036.344 4	0.2	3 036.000 6	0.6	2 ₁₁ (2.5)–3 ₁₂ (3.5)	3 035.955 3	^a	3 035.595 9	^a
3 ₁₃ (3.5)–4 ₁₄ (4.5)	3 034.542 8	0.3	3 034.203 4	0.7	3 ₁₂ (3.5)–4 ₁₃ (4.5)	3 034.023 1	^a	3 033.648 1	^a
4 ₁₄ (4.5)–5 ₁₅ (5.5)	3 032.739 9	−0.1	3 032.405 6	0.1	4 ₁₃ (4.5)–5 ₁₄ (5.5)	3 032.108 9	^a	3 031.646 5	^a
5 ₁₅ (5.5)–6 ₁₆ (6.5)	3 030.937 2	−0.1	3 030.608 3	0.0					
6 ₁₆ (6.5)–7 ₁₇ (7.5)			3 028.810 9	−0.4					
7 ₁₇ (7.5)–8 ₁₈ (8.5)			3 027.013 6	−0.6					
Q-branch									
1 ₁₁ (1.5)–1 ₁₀ (1.5)	3 041.607 6	−0.3	3 041.259 1	−1.4	1 ₁₀ (1.5)–1 ₁₁ (1.5)	3 041.865 9	^a	3 041.513 2	^a
1 ₁₁ (0.5)–1 ₁₀ (0.5)	3 041.604 6	−0.3			1 ₁₀ (0.5)–1 ₁₁ (0.5)	3 041.868 9	^a		
2 ₁₂ (2.5)–2 ₁₁ (2.5)	3 041.342 8	0.0	3 040.998 3	−0.3	2 ₁₁ (2.5)–2 ₁₂ (2.5)	3 042.118 8	^a	3 041.759 5	^a
2 ₁₂ (1.5)–2 ₁₁ (1.5)	3 041.337 6	−0.2	3 040.994 1	0.4	2 ₁₁ (1.5)–2 ₁₂ (1.5)			3 041.764 5	^a
3 ₁₃ (3.5)–3 ₁₂ (3.5)			3 040.605 6	0.6	3 ₁₂ (3.5)–3 ₁₃ (3.5)	3 042.497 4	^a	3 042.123 3	^a
3 ₁₃ (2.5)–3 ₁₂ (2.5)			3 040.598 6	0.6	3 ₁₂ (2.5)–3 ₁₃ (2.5)			3 042.129 0	^a
4 ₁₄ (4.5)–4 ₁₃ (4.5)			3 040.080 6	1.2					
4 ₁₄ (3.5)–4 ₁₃ (3.5)			3 040.069 5	−0.9					
R-branch									
2 ₁₂ (2.5)–1 ₁₁ (1.5)	3 045.323 1	−0.2	3 044.978 4	−0.7	2 ₁₁ (2.5)–1 ₁₀ (1.5)	3 045.581 6	^a	3 045.222 6	^a
2 ₁₂ (1.5)–1 ₁₁ (0.5)	3 045.319 3	−0.1	3 044.976 0	0.7					
3 ₁₃ (3.5)–2 ₁₂ (2.5)	3 047.107 7	−0.1	3 046.768 2	0.2	3 ₁₂ (3.5)–2 ₁₁ (2.5)	3 047.496 5	^a	3 047.121 5	^a
4 ₁₄ (4.5)–3 ₁₃ (3.5)	3 048.888 0	0.1	3 048.553 9	0.5	4 ₁₃ (4.5)–3 ₁₂ (3.5)			3 048.959 9	^a
5 ₁₅ (5.5)–4 ₁₄ (4.5)	3 050.663 0	0.1	3 050.333 7	−0.2	5 ₁₄ (5.5)–4 ₁₃ (4.5)	3 051.323 9	^a	3 051.029 6	^a
6 ₁₆ (6.5)–5 ₁₅ (5.5)	3 052.432 1	−0.1	3 052.107 9	−0.6	6 ₁₅ (6.5)–5 ₁₄ (5.5)	3 053.222 0	^a	3 052.882 3	^a
7 ₁₇ (7.5)–6 ₁₆ (6.5)	3 054.195 6	0.1	3 053.875 8	−0.4	7 ₁₆ (7.5)–6 ₁₅ (6.5)	3 055.115 1	^a	3 054.740 3	^a
8 ₁₈ (8.5)–7 ₁₇ (7.5)			3 055.636 8	0.8					

^aTransitions that terminate in $v_3 = 1$ with $K_a = 1$ and $K_c = K_a - 1$ (right half of the table) are shifted by 0.02 to 0.14 cm^{-1} from the expected frequency due to upper vibrational state perturbations and thus are not been included in the fit in least squares fitting of data for the symmetric CH stretch excited vibrational state.

As a second test, the logarithmic shifts between the two *ortho* plots [$K_a = 0(+)$ and $1(-)$] or *para* plots [$K_a = 0(-)$ and $1(+)$] reflect the additional Boltzmann penalty due to $K_a = 1$ vs. 0 asymmetric top rotational excitation. The simple reason for this is that the collisional time scales for changing the nuclear spin state are much longer than the time between radical formation and achieving the optimal detection

TABLE III. Nuclear spin statistical analysis for torsional tunneling in CH_2OH . The total wave function, $\Psi_{\text{tot}} = \Psi_{\text{elec}} \Psi_{\text{vib}} \Psi_{\text{rot}} \Psi_{\text{tun}} \Psi_{\text{NS}}$, must be antisymmetric with respect to the exchange of the two indistinguishable methylene H atoms ($I = 1/2$). This yields nuclear spin weights of 3:1 for $K_a = \text{even}(+)/\text{odd}(-)$ vs. $K_a = \text{even}(-)/\text{odd}(+)$ states, where $\pm$ denotes the even/odd symmetry of tunneling wave function.

	Ψ_{elec}	Ψ_{vib}	Ψ_{rot}	Ψ_{tun}	Ψ_{NS}	Statistical weight
$K_a = \text{odd}(-)$	−1	+1	−1	−1	+1	3
$K_a = \text{odd}(+)$	−1	+1	−1	+1	−1	1
$K_a = \text{even}(-)$	−1	+1	+1	−1	−1	1
$K_a = \text{even}(+)$	−1	+1	+1	+1	+1	3

geometry. As a result, radicals can *only* cool through rotational manifolds of the same *ortho/para* symmetry, and thus one expects the *ortho* $K_a'' = 0(+)$ and $K_a'' = 1(-)$ states to

FIG. 2. CH_2OH radical with the electronic state wavefunction corresponding to the singly occupied highest occupied molecular orbital (HOMO). This electronic wave function has π -like radical character on the C atom and is antisymmetric with respect to the exchange of the two equivalent H atoms made feasible by internal rotation around the CO bond axis.

FIG. 3. Sample expanded section of CH₂OH symmetric CH stretch spectra revealing three pairs of R-branch transitions built on the $N = 3 \leftarrow 2$ and originating from (+, blue) and (-, red) tunneling states. Note the clear 3:1 intensity alternation arising from nuclear spin statistics due to identical methylenic H atoms. Based on the known ground state tunneling splitting ($\Delta E_T' = 0.004\,659\text{ cm}^{-1}$), the double headed arrow represents the difference in tunneling splittings between $K_a = 0$ ground and vibrationally excited states ($\Delta[\Delta E_T] = \Delta E_T' - \Delta E_T''$).

achieve thermal equilibrium as well as the *para* $K_a'' = 0(-)$ and $K_a'' = 1(+)$ states. Comparing transitions from lower states with the *same nuclear spin weights* reveals 2.0(3) and 2.1(2) more intense populations in $K_a = 0$ states for the (+) and (-) tunneling manifolds than in $K_a = 1$ states, respectively. This is in very good agreement with the 7.41 cm^{-1} energy differences between the $K_a = 0$ and $K_a = 1$ states,⁵⁴ which would predict a 1.8-fold population difference at the 18 K expansion temperature.

Finally, since *ortho:para* nuclear spin manifolds remain unchanged upon CH symmetric stretch excitation, the tunneling selection rules are (+) $\leftarrow$ (+) and (-) $\leftarrow$ (-); thus the splitting in each pair represents the difference in tunneling splitting between the ground and excited vibrational states. As a note for later discussion, the systematic *red-shift* of the (-) $\leftarrow$ (-) from the (+) $\leftarrow$ (+) transitions in Fig. 3 implies that the tunneling splitting must decrease significantly and indeed becomes *negative* in the upper state. This is clearly anomalous, since, for any separable 1D coordinate, the order of vibrational eigenvalues must increase monotonically with the corresponding number of vibrational nodes. Consequently, this reversal in sign from normal behavior must signal the presence of a tunneling state-selective coupling between bright and dark states in the upper vibrational manifold, which we explore further in Sec. IV.

FIG. 4. Boltzmann plot for *ortho* [$K_a = 0(+), 1(-)$] and *para* [$K_a = 0(-), 1(+)$] nuclear spin modifications of CH₂OH, yielding a common rotational temperature of 18.3(10) K. The intercept ratios [3.0(3), 3.2(5)] confirm the expected 3:1 nuclear spin weights for *ortho:para* transitions originating from the same K_a but different tunneling levels, i.e., 0(+):0(-) and 1(-):1(+). Conversely, intercept ratios for transitions from the same *ortho* or *para* state but with different K_a'' values are consistent with expected Boltzmann populations at these rotational energy differences.

All bands are purely a-type as indicated by observation $K_a = 0 \leftarrow 0$ bands composed of P and R-branches without a Q-branch and the $K_a = 1 \leftarrow 1$ bands composed of asymmetry doubled P- and R-branches with weak Q-branches. A

FIG. 5. Sample scan section in the CH₂OH R-branch, illustrating typical S/N levels and excellent agreement with the least squares fit simulations. Each $N' \leftarrow N''$ group has six transitions, three from each of the two different tunneling states. In the simulated spectrum (downward), blue and red transitions arise from (+) and (-) tunneling states.

total of 46/53 rovibrational transitions within the $\pm$ tunneling manifolds are observed, respectively, as summarized in Tables I and II. Rovibrational assignments for the 15 most intense transitions in the $K_a = 1 \leftarrow 1$ ($-$) tunneling manifold are unambiguously confirmed via four-line combination differences (Table S1, [supplementary material](#)), with an agreement consistent within the stated frequency precision (12 MHz) for a single measurement. With the tunneling levels for $K_a = 0(+)\leftarrow 0(+)$ well determined, assignments for other transitions out of the ($-$) tunneling state and all transitions in the $K_a = 1 \leftarrow 1$ and $0 \leftarrow 0$ ($+$) tunneling manifold can be readily made by inspection. Note that the difference in vibrational origins for the two tunneling progressions ($|\Delta[\Delta E_T]| \approx 0.52 \text{ cm}^{-1}$) is smaller than the spacing between adjacent transitions ($\approx 1.8 \text{ cm}^{-1}$), thus the spectrum demonstrates the P/R branch structure with up to six transitions for each ΔN cluster. A portion of the $\Delta N = +1$ (R-branch) spectrum is shown in Fig. 5 with the simulated fit spectrum, which illustrates accurate prediction of nuclear spin weights, thermal Boltzmann populations, and quantitative reproduction of the observed frequencies.

IV. DISCUSSION

A. Ground state vibrational analysis

The present high resolution infrared data provide important additional constraints on the energy levels in the ground vibrational state, which is relevant to the astronomical detection of the hydroxymethyl radical via microwave and mm-wave telescope methods. As one explicit goal is the determination of precision ground vibrational state constants, infrared two-line ground state combination differences (CDs) determined in this work have been analyzed in a combined fit with the extensive set of mm-wave transitions of Bermudez *et al.*⁴³ The reason for focusing on ground state CD's is not limited by spectroscopic resolution, but rather to isolate the ground state fits from potential perturbations in the upper vibrational state manifold. A total of 38 [18($+$), 20($-$)] infrared two-line combination differences (Table IV) for the $\pm$ tunneling manifolds are used in the fit, along with the 85 mm-wave transitions recently reported by Bermudez *et al.*⁴³ The PGOPHER program with a Watson asymmetric top Hamiltonian (A-reduction, Ir-representation) is used to fit the data,

TABLE IV. Hydroxymethyl CH-symmetric stretch two-line ground state combination differences for both ($+$) and ($-$) tunneling states. These combination differences are least squares fitted with mm-wave data of Bermudez *et al.*⁴³ to determine ground vibrational state molecular constants given in Table V. Transitions reported are for $J = K_c + 0.5$ states only.

Transition 1 $N_{K_a K_c}$	Transition 2 $N_{K_a K_c}$	(+) Tunneling state		(-) Tunneling state	
		Combination difference (cm^{-1})	Combination difference (MHz)	Combination difference (cm^{-1})	Combination difference (MHz)
R-P combination differences					
1 ₀₁ -0 ₀₀	1 ₀₁ -2 ₀₂	5.5801	167 287.2	5.5796	167 272.2
2 ₀₂ -1 ₀₁	2 ₀₂ -3 ₀₃	9.2927	278 588.1	9.2925	278 582.1
3 ₀₃ -2 ₀₂	3 ₀₃ -4 ₀₄	12.9937	389 541.3	12.9935	389 535.3
4 ₀₄ -3 ₀₃	4 ₀₄ -5 ₀₅	16.6790	500 023.8	16.6792	500 029.8
5 ₀₅ -4 ₀₄	5 ₀₅ -6 ₀₆	20.3430	609 867.8		
6 ₀₆ -5 ₀₅	6 ₀₆ -7 ₀₇	23.9841	719 025.2	23.9833	719 001.2
7 ₀₇ -6 ₀₆	7 ₀₇ -8 ₀₈	27.5975	827 352.2		
8 ₀₈ -7 ₀₇	8 ₀₈ -9 ₀₉	31.1814	934 794.9		
2 ₁₁ -1 ₁₀	2 ₁₁ -3 ₁₂	9.6264	288 592.2	9.6267	288 601.2
2 ₁₂ -1 ₁₁	2 ₁₂ -3 ₁₃	8.9788	269 177.7	8.9778	269 147.7
3 ₁₂ -2 ₁₁	3 ₁₂ -4 ₁₃	13.4734	403 922.4	13.4734	403 922.4
3 ₁₃ -2 ₁₂	3 ₁₃ -4 ₁₄	12.5648	376 683.2	12.5648	376 683.2
4 ₁₃ -3 ₁₂	4 ₁₃ -5 ₁₄			17.3134	519 042.7
4 ₁₄ -3 ₁₃	4 ₁₄ -5 ₁₅	16.1481	484 107.9	16.1483	484 113.9
5 ₁₅ -4 ₁₄	5 ₁₅ -6 ₁₆	19.7259	591 367.6	19.7254	591 352.6
6 ₁₆ -5 ₁₅	6 ₁₆ -7 ₁₇			23.2970	698 426.5
7 ₁₇ -6 ₁₆	7 ₁₇ -8 ₁₈			26.8622	805 308.5
Q-P combination differences					
1 ₁₀ -1 ₁₁	1 ₁₀ -2 ₁₁	3.9802	119 323.4	3.9802	119 323.4
1 ₁₁ -1 ₁₀	1 ₁₁ -2 ₁₂	3.4627	103 809.1	3.4627	103 809.1
2 ₁₂ -2 ₁₁	2 ₁₂ -3 ₁₃	4.9984	149 848.3	4.9977	149 827.3
3 ₁₃ -3 ₁₂	3 ₁₃ -4 ₁₄			6.4023	191 936.1
R-Q combination differences					
2 ₁₁ -1 ₁₀	2 ₁₁ -2 ₁₂	3.4629	103 815.1	3.4631	103 821.1
3 ₁₂ -2 ₁₁	3 ₁₂ -3 ₁₃			4.9982	149 842.3

TABLE V. Ground vibrational state CH₂OH rotational constants (in MHz (left panel) and in cm⁻¹ (right panel)) determined from a combined least squares fit of IR ground state combination differences given in Table IV with the mm-wave transition frequencies reported by Bermudez *et al.*⁴³

Fit of MW data and 36 IR ground state combination differences				
	+	-	+	-
$\Delta E''_T$		139.68 (8) ^a		0.004659(3)
A	194540.52(19)		6.4891733(63)	
B	29843.85(4)	29844.00 (4)	0.9954837(12)	0.9954887(12)
C	25947.854(15)	25947.579 (17)	0.8655272(5)	0.8655181(6)
Δ_N	0.06595(10)		$2.200(3) \times 10^{-6}$	
Δ_{NK}	0.605(13)		$2.02(4) \times 10^{-5}$	
Δ_K	5.6059 ^b		1.86993×10^{-4b}	
δ_N	0.0079 ^b		2.64×10^{-7b}	
δ_K	0.141(12)		$4.7(4) \times 10^{-6}$	
ϵ_{aa}	-512.5(17)		-0.01710(6)	
ϵ_{bb}	-125.2(3)		-0.004175(9)	
ϵ_{cc}	-3.7(3)		-0.000124(11)	
Δ^S_N	0.0272(17)		$9.07(57) \times 10^{-7}$	
$D^S_{NK} + D^S_{KN}$	1.03(4)		$3.42(15) \times 10^{-5}$	
OH proton				
a_F	-12.4 ^b		-0.000414 ^b	
T_{aa}	-1.9 ^b		-6.3×10^{-5b}	
$T_{bb} - T_{cc}$	16.96(11)		0.000566(4)	
CH ₂ protons				
a_F	-54.2(5)		-0.00181(2)	
T_{aa}	-21.5 ^b		-0.000717 ^b	
$T_{bb} - T_{cc}$	15.65(8)		0.000522(3)	

^aNumbers in parentheses represent one standard deviation uncertainty.

^bFor consistency, held fixed at the calculated values of Bermudez *et al.*⁴³

with relative 1:200 weights estimated from the corresponding frequency uncertainties for infrared and mm-wave measurements.⁵⁴ For consistency, the least squares fitting procedure has floated (or fixed) the same set of molecular constants in the ground vibrational state chosen by Bermudez *et al.*,⁴³ with results of this combined fit summarized in Table V. Note that the ground state tunneling splitting ($\Delta E''_T$) and A, B, and C asymmetric top rotational constants are in very good agreement (within 1 σ) with the previous mm-wave analysis. Indeed, increasing the number of ground state infrared combination differences from the three previously available from Roberts *et al.*⁴² to the 38 used herein reduces the uncertainty of almost all parameters and improves the quality of the mm-wave/IR combined fit significantly more robust. As this process involves a combined fit to data sources with quite different spectral resolution.

Observation and confirmation of the presence of the hydroxymethyl radical in the interstellar medium requires highly accurate transition frequencies. Since the above analysis includes all previous mm-wave data used by Bermudez *et al.*,⁴³ further enhanced by 10-fold more additional infrared ground state combination differences, the current fit represents the most accurate set of molecular constants for detection of the hydroxymethyl radical. By way of example, we have calculated frequency predictions (Table S2, [supplementary material](#)) for the same set of transitions of astronomical

relevance reported by Bermudez *et al.*,⁴³ with other transitions readily calculated from the fitted molecular constants reported in Table V. While the A, B, and C parameters and ground state tunneling splitting ($\Delta E''_T$) reported in Table V are in generally very good agreement with the constants determined by Bermudez *et al.*,⁴³ the revised frequency predictions (in Table S2 of the [supplementary material](#)) can differ by up to several MHz, which is quite significant in an astronomical mm/ μ -wave search. Of particular relevance is the frequency accuracy of these predictions, which we estimate to be $\sigma \approx 106$ kHz based on a standard deviation over all mm-wave observed-calculated values obtained in the mm-wave/IR combined fit. To facilitate further detailed calculations of individual frequency uncertainties, we also include the full correlation matrix for each of the parameters extracted from the final least squares fit (Table S3, of the [supplementary material](#)).

B. Upper state vibrational analysis

With improved spectroscopic parameters determined for the ground vibrational state from all available high resolution infrared and mm-wave data, we can now focus our attention on high resolution infrared analysis of the upper vibrational state. The reason for this separation of analysis efforts is to isolate the ground state fits from perturbations evident in the upper vibrational state manifold. Molecular constants in the symmetric CH stretch ($\nu_3 = 1$) vibrationally excited state are determined

TABLE VI. Rotational constants for the CH₂OH vibrational excited ($v_3 = 1$) state for the (+) and (−) tunneling states. A total of 32/31 transitions have been included in the fit of a Watson asymmetric top Hamiltonian for $\pm$ tunneling states, with the ground state constants fixed at the values in Table V. All results are reported in cm^{−1}, with 1 σ uncertainties shown in parentheses in the last digit.

	Current study		Results from Roberts <i>et al.</i> ⁴²	Results ^b from Feng, Wei and Reisler ³⁵
	(+) Tunneling states	(−) Tunneling states	(+) Tunneling states $K_a = 0 \leftarrow 0$ band	
A	6.4716(5)	6.6515(5)	6.45 ^a	6.48
B	0.9956(5)	0.9966(4)	0.9945(4)	0.98
C	0.8624(4)	0.8609(3)	0.8632(3)	0.88
Δ_N	$6.2(9) \times 10^{-7}$	$6.2(5) \times 10^{-6}$		
Δ_{NK}	$-6.9(19) \times 10^{-4}$	$-2.42(12) \times 10^{-3}$		
e_{aa}		$-1.74(8) \times 10^{-2}$		
v_3	3041.7561(3)	3041.2270(3)	3041.7563(1)	3043.4
Res. std. dev.	5.7×10^{-4}	6.0×10^{-4}	2.4×10^{-4}	

^aHeld fixed at *ab initio* values.

^bReported uncertainties <2%.

via separate fits of infrared transition energies to a Watson asymmetric top Hamiltonian (A-reduction, Ir-representation) for each of the two tunneling manifolds.⁵⁵ All ground state vibrational constants are fixed at the optimized values determined above, with (i) rigid rotor A, B, and C, (ii) low order centrifugal distortion constants, and (iii) vibrational band origins floated in the excited state. All higher order constants not floated in the upper state are held fixed at ground state values.

Initial fits of all the infrared transitions yield residual standard deviations of 692 MHz (0.0231 cm^{−1}) and 830 MHz (0.0277 cm^{−1}) for the (+) and (−) manifolds, respectively. Since the infrared frequency precision is 1-2 orders of magnitude smaller, this clearly signals the presence of perturbations in the excited symmetric CH stretch vibrational state. Indeed, if all transitions that terminate in the upper vibrational $v_3 = 1$ manifold with $K_a = 1$ and $K_c = N - 1$ are eliminated from the fit, the residual standard deviations drop to 18 MHz for both (+) and (−) tunneling states, i.e., comparable with the frequency measurement reproducibility. Upper vibrational state spectroscopic constants determined from these reduced data sets (a total of 33 (+) and 38 (−) rovibrational transitions) are summarized in Table VI. Comparison of observed vs. simulated spectra for a sample region in Fig. 5 provides visual confirmation of spectral assignments as well as the high S/N and quality of fit.

C. Spin-rotation effects

Due to the open shell nature of the CH₂OH radical, one expects additional spin-rotation splitting arising from the coupling of electron spin (*S*) with end-over-end rotation (*N*) angular momentum. Although such effects are typically outside the realm of Doppler limited infrared spectroscopy, the current sub-Doppler resolution of these slit jet discharge methods often makes such a fine (and sometimes even hyperfine) structure experimentally accessible.^{51,56–59} Indeed, closer inspection of low *N* transitions in the $K_a = 1 \leftarrow 1$ band reveals quite clear spin-rotation structure, due to splitting of $N_{K_a K_c}$ states into $J = N \pm \frac{1}{2}$ levels. By way of example,

Fig. 6 shows a high resolution blow up of the $1_{11}(-) \leftarrow 2_{12}(-)$ P-branch transition, for which all three allowed spin-rotation transitions ($J = 1.5 \leftarrow 2.5$, $1.5 \leftarrow 1.5$, and $1.5 \leftarrow 0.5$) are cleanly resolved. At low *N* values, we resolve the spin-rotation $K_a = 1 \leftarrow 1$ structure in ten $\Delta N = 0$, one $\Delta N = -1$, and two $\Delta N = +1$ transitions in the (−) tunneling manifold, the inclusion of which permits first insights into spin-rotation dynamics in the vibrationally excited state. However, due to $\Delta K_a = 0$, a-type selection rules in the CH-symmetric stretch band, spin-rotation splittings for the corresponding $K_a = 0 \leftarrow 0$, and high *N* transitions remain unresolved with sub-Doppler

FIG. 6. Sample high resolution scans over the $1_{11}(-) \leftarrow 2_{12}(-)$ spin rotation multiplet, indicating full resolution of a fine structure at low values of *N*.

instrumental resolution (60 MHz). Nevertheless, inclusion of low N , spin-rotation resolved ground state combination differences with the mm-wave data results in noticeable uncertainty improvement in the spin-rotation parameters reported by Bermudez *et al.*⁴³ Due to the predominance of ϵ_{aa} , such fine-structure splitting in CH_2OH is predicted to be much more highly pronounced in b- and c-type bands ($\Delta K_a = \pm 1$) infrared active in the asymmetric CH stretch and OH stretch manifolds, through which we will be able to achieve a more detailed spin-rotation analysis in the excited vibrational state.

D. Negative tunneling splittings in the upper state

For the a-type symmetric CH stretch band observed, only $\Delta K_a = 0$ transitions are allowed and thus only transitions that preserve the tunneling symmetry [i.e., $(+) \leftarrow (+)$ or $(-) \leftarrow (-)$] are infrared active. As a result, the symmetric CH stretch spectra are only sensitive to the *changes* in tunneling splittings between the ground and vibrational excited state. What is particularly surprising (see Fig. 3) is that the vibrational origin for the $K_a = 1 \leftarrow 1$; $(-) \leftarrow (-)$ band is *redshifted* from the $K_a = 0 \leftarrow 0$ $(+) \leftarrow (+)$ band by $\Delta[\Delta E_T] = 0.5290 \text{ cm}^{-1}$, which, based on the much smaller torsional splitting (0.0047 cm^{-1}) in the ground state, immediately implies a *reversal* in the $\pm$ symmetry order and thus a *negative* tunneling splitting of $\Delta E_T' = -0.5241 \text{ cm}^{-1}$ upper state (see Fig. 7). As this behavior is inconsistent with simple 1D predictions for a separable torsional vibration, this requires tunneling states in the CH symmetric stretch manifold to be coupling with a near

resonant “dark” state,⁶⁰ which systematically *pushes down* or *up* on the $(-)$ or $(+)$ manifold of rotational levels, respectively. Indeed, we can take this logic one step further by noting that any perturbative intramolecular rovibrational interaction between a bright and dark state must have essentially *identical* off-diagonal matrix elements for coupling the pairs of tunneling levels. Thus, in the limit of low state densities, reversal of tunneling level order requires a special circumstance. Specifically, the corresponding dark state levels must “straddle” the bright state tunneling pair in order to be able to push the $(+)$ and $(-)$ levels in *opposite* directions. Consequently, we can rigorously infer that the dark state must have tunneling splittings at least in excess of $|\Delta E_T| = 0.5241 \text{ cm}^{-1}$.

Since the CH_2OH radical has only five atoms and nine vibrational modes, only six of which have energetically accessible frequencies, the vibrational state density near ν_3 is quite sparse. Indeed, we can calculate these state densities using the efficient Kemper backtracking algorithm,⁶¹ based on the thorough diagonal/off-diagonal anharmonic frequency analysis by Marenich and Boggs.^{29,30} It is worth stressing that diagonal anharmonicity in the internal rotation coordinate is large and therefore crucial to take into account.^{29,30} Such explicit state counting analysis does predict a near resonant combination level [nominally labeled as ν_4 (CH_2 -scissor) + ν_5 (in-phase HCOH bend) + $2\nu_8$ (COH torsion)] to occur within a few cm^{-1} of the ν_3 band origin, with all energies calculated at the same level of theory. By way of comparison, there is a 1-2 order of magnitude larger average spacing ($\approx 50 \text{ cm}^{-1}$) *between* vibrational states, which makes tentative assignment of this as the perturbing dark state at least a reasonable suggestion. In further support, we also note that this resonant state nominally has two quanta of COH torsion. This excitation would contribute exponentially toward the enhancement of the tunneling splittings, for which such an extremely sparse set of dark state tunneling levels could statistically help facilitate “straddling” and thereby differentially shifting the bright state tunneling levels apart by as much as $|\Delta E_T| = 0.5241 \text{ cm}^{-1}$ observed experimentally.

E. *Ab initio* CCSD(T)-f12b/CBS potentials and tunneling predictions

This simple but physically plausible assignment motivates a closer theoretical look at the internal rotor tunneling energy level structure anticipated for the CH_2OH radical. As a final topic of discussion, we therefore consider an approximate calculation of the vibrational tunneling splittings from first principles, based on high level CCSD(T)-f12b *ab initio* potential surface calculations with explicitly electron correlated methods.⁶² What makes this particularly challenging is the fact that the tunneling path involves simultaneous motion of multiple internal coordinates over multiple, high barriers, for which accurate quantum mechanical calculation of tunneling splittings constitutes a state-of-the-art problem even for a relatively small 5-atom molecule. This can be readily seen in Fig. 1, which represents a 2D slice at the CCSD(T)/avqz level of the full potential energy surface in COH torsion and CH_2 wag coordinates, with the remaining degrees of freedom optimized at each point. This 2D potential surface exhibits large barriers ($E_{\text{max}} \approx 1661 \text{ cm}^{-1}$) in the COH torsional

FIG. 7. Schematic 1-D torsional tunneling potentials for the ground and vibrational excited symmetric CH stretch state in CH_2OH . The ground state tunneling splitting (0.0047 cm^{-1}) is positive and well determined in a combined fit to high resolution IR and mm-wave data. By way of contrast, tunneling splitting in the vibrational excited state is $\approx 10^2$ larger and *negative*, due to dark state coupling selectively pushing the $\nu_3 = 1 \pm$ tunneling levels up and down, respectively. For visual clarity, the tunneling splittings have been expanded with respect to barrier heights by $\approx 2.5 \times 10^4$.

FIG. 8. 2D contour plot (in cm^{-1}) for CH_2OH obtained from Molpro *ab initio* calculations at the CCSD(T)-f12b/cc-pvTZ-f12 ($n = 2,3$) level and extrapolated to the complete basis set (CBS) limit.^{62,68–70} Note the high barrier ($E_{\text{max}} = 1661 \text{ cm}^{-1}$) at the C_s transition state structure ($\phi_{\text{COH}} = 90^\circ, 270^\circ$), with a shallow trough along the CH_2 wag coordinate that runs over a much small barrier ($E_{\text{min}} = 96 \text{ cm}^{-1}$). The solid green line represents the intrinsic reaction path (projected in CH_2 wag and COH torsion coordinates) obtained by gradient following from each of the two transition states in the downhill direction. The high and low barriers with harmonic zero point correction at the CCSD(T)-f12b/cc-pvtZ-f12 level are 1521 cm^{-1} and 58 cm^{-1} , respectively.

angle, but also smaller yet critically important barriers ($E_{\text{min}} \approx 96 \text{ cm}^{-1}$) in the CH_2 wag angle. To simplify such calculations further, we note that the COH torsion ($\approx 330 \text{ cm}^{-1}$) and CH_2 wag ($\approx 530 \text{ cm}^{-1}$) vibrations are by far the lowest frequency modes in CH_2OH , with the next vibration (the in-plane CH_2/COH bend) at least 2-fold higher in frequency. This suggests the adiabatic approximation as a reasonable starting point,⁶³ with a reduced dimensional tunneling pathway localized along the corresponding COH torsion and out-of-plane CH_2 wag internal coordinates. The requirement for including multiple coordinates is particularly evident in a contour plot representation of the CCSD(T)/avqz potential surface (see Fig. 8), which suggests that the important regions of the PES for tunneling follow a path involving both COH torsion and CH_2 wag motion. This provides additional support for the present estimation of the tunneling splittings in an adiabatic, reduced dimensionality path that permits large amplitude motion in both torsion and wag degrees of freedom.

There are multiple paths connecting each transition state to the corresponding global minimum, each of which contributes to the tunneling amplitude. From a semiclassical perspective, the pathway with the most significant tunneling contribution is expected to be concentrated around the minimum energy path (MEP). This is the path corresponding to infinitely damped motion of the nuclei, though there is much theoretical support for important if not dominant contributions from nearby “corner-cutting” paths.^{64–66} For the present tunneling estimation purposes, we use Molpro *ab initio* codes⁶² at the explicitly electron correlated CCSD(T)-f12b/cc-pvtZ-f12 level to calculate the gradient downhill path in internal

FIG. 9. Intrinsic reaction path/gradient following potential for CH_2OH internal rotation on a high level CCSD(T)-f12b/cc-pvTZ-f12 ($n = 2,3$)/CBS, plotted in black as a function of the ϕ_{COH} torsional angle, along with the corresponding molecular geometries. The lowest 4 pairs of $\pm$ tunneling energy levels are shown in green, with the nodeless ground state (+) tunneling eigenfunction for this potential in red. With harmonic zero point energy corrections in the 3N-7 coordinates to the 1D path, the tunneling splittings grow nearly exponentially over the range of $v_8 = 0-3$ from $\Delta E_T = 0.0075 \text{ cm}^{-1}$ ($v_8 = 0$) to $\Delta E_T = 0.18 \text{ cm}^{-1}$ ($v_8 = 1$) to $\Delta E_T = 2.68 \text{ cm}^{-1}$ ($v_8 = 2$) to $\Delta E_T = 22.2 \text{ cm}^{-1}$ ($v_8 = 3$). See text for details.

coordinates (see z-matrix in Table S4, [supplementary material](#)) from each of the large and small barrier transition states to the global minimum. The internal coordinates along this pathway are then used to (i) calculate energies at the CCSD(T)-f12b/cc-pvtZ-f12 ($n = 2,3$) level and (ii) extrapolate to the complete basis set (CBS) limit.^{62,67–70} As this choice of path completely neglects zero point energy, we calculate frequencies at the CCSD(T)-f12b/cc-pvdZ-f12 level and thereby correct for differential zero point effects due to each of the 3N-7 seven high frequency modes.

The resulting zero-point corrected tunneling potential is shown as a 1D function of the COH torsional angle in Fig. 9, which reveals the expected double transition state barrier structure. The higher transition state barrier ($E_{\text{max}} \approx 1661 \text{ cm}^{-1}$ without ZPE and $\approx 1521 \text{ cm}^{-1}$ with ZPE) plays the more dominant role in the observed vibrational energy levels and corresponds to a C_s structure with the COH moiety perpendicular to the CH_2 plane. However, also clearly visible in Fig. 9 is the 10-fold weaker barrier ($E_{\text{min}} \approx 96 \text{ cm}^{-1}$ without ZPE and $\approx 58 \text{ cm}^{-1}$ with ZPE) associated with the fully planar CH_2OH (C_s) transition state, which arises from large amplitude motion along a shallow CH_2 wag potential trough (see Fig. 8) and which to a lesser extent also impacts the tunneling splitting.

Calculating accurate energy levels in this effective 1D adiabatic potential requires integration of the Schrödinger equation with the effective mass/moment of inertia along the corresponding large amplitude monotonic coordinate. This can be obtained from large amplitude Hamiltonian treatments of Hougen, Bunker, and Johns, and as previously implemented by Rush and Wiberg.^{71–73} Specifically, we calculate the $\mathbf{G}$ matrix as a function of the torsional coordinate

$$\mathbf{G}(\phi_{\text{COH}}) = \begin{pmatrix} I & X \\ X & Y \end{pmatrix}^{-1},$$

where $\mathbf{I}$, $\mathbf{X}$, and $\mathbf{Y}$ represent the instantaneous moment of inertia matrix, the 1×3 rotation-torsion coupling vector, and

the 1×1 diagonal vibration-vibration coupling contributions, respectively. The effective moment of inertia at a given torsional geometry along the tunneling path is given by $I(\phi_{\text{COH}}) = 1/G_{44}(\phi_{\text{COH}})$, which in turn can be extracted from the $\begin{pmatrix} I & X \\ X & Y \end{pmatrix}$ rotation-vibration coupling matrix by matrix inversion. The resulting values for I vary smoothly between $0.5379 \text{ amu } \text{\AA}^2$ and $0.5438 \text{ amu } \text{\AA}^2$ over the range of the high barrier, equilibrium, and low barrier geometries. By way of confirmation, this is consistent with an approximate reduced moment of inertia estimation ($\mu_{\text{eff}} \approx 0.564 \text{ amu } \text{\AA}^2$) based on independent rotation of CH_2 ($\mu \approx 1.85 \text{ amu } \text{\AA}^2$) and COH ($\mu \approx 0.812 \text{ amu } \text{\AA}^2$) moieties around the CO axis.

Rigorous application of the Hougen, Bunker, and Johns formalism requires solving the large amplitude Hamiltonian eigenfunction-eigenvalue equation, where the potential is modified by the dependence of $I|G|$ on the large amplitude coordinate of integration.⁷² However, as our primary goal is to estimate the tunneling splitting and the reduced moment of inertia changes by only $\approx 1\%$ with respect to the torsional coordinate, it suffices to numerically integrate the 1D Schrödinger equation with $I(\phi_{\text{COH}})$ from $\phi_{\text{COH}} = 0^\circ$ to 90° using 4th order Numerov methods.^{74,75} Furthermore, since the torsional coordinate is cyclic, we obtain the $\pm$ pairs of eigenfunctions and tunneling eigenvalues simply by applying suitable boundary conditions (either $\Psi = 0$ or $d\Psi/d\phi_{\text{COH}} = 0$) at $\phi_{\text{COH}} = 0^\circ$ and 90° . The numerical stability of the Numerov method and precision of the resulting eigenvalues is quite good ($<10^{-10}$ level) for an appropriate choice of integration away from the high transition state barrier at $\phi_{\text{COH}} = 0^\circ$.

The eigenvalues and eigenvalue differences tunneling splittings from these Numerov calculations are plotted in Fig. 9 and warrant several comments. First of all, although we do not expect quantitative agreement from a simple 1D tunneling model, the *ab initio* ground state tunneling splitting ($\Delta E_T = 0.00747 \text{ cm}^{-1}$) is nevertheless within a factor of 2 of the $\Delta E_T = 0.00466 \text{ cm}^{-1}$ value experimentally observed from the mm-wave studies.⁴³ Such results are particularly noteworthy based on the $>10^5$ fold larger height of the torsional barrier, for which one expects near exponential dependence in the tunneling splitting.⁷⁶ Second, the magnitude of the tunneling splitting grows quite rapidly (roughly 20-fold) with each integer increase in the torsional quantum number (see Table VII), which yields values already 5-fold in excess of the experimentally *inverted* tunneling splitting in the upper state ($|\Delta E_T| = 0.52 \text{ cm}^{-1}$) by $v_8 = 2$. It is worth noting that such tunneling splittings are now large enough to straddle and shift the tunneling order for the zeroth order “bright” vibrational state, which would therefore be consistent with our proposed assignment of the perturbing “dark” level to the $v_4 + v_5 + 2v_8$ combination state with 2 quanta of torsional vibration. However, additional

spectroscopic and theoretical efforts will clearly be necessary for unambiguous assignment of the perturber dark state identity.

V. SUMMARY AND CONCLUSIONS

Detailed high resolution spectroscopic investigation and analysis of the jet-cooled CH_2OH radical in the symmetric CH stretch region have been reported, as further stimulated by recent mm-wave studies by Bermudez *et al.*⁴³ Changes in slit-jet expansion conditions from those of an earlier report from our group to optimize the production of the hydroxymethyl radical now allow for the spectral assignment of 99 rovibrationally resolved transitions with $S/N \leq 50$ and at a rotational temperature of $T_{\text{rot}} = 18 \text{ K}$. Both $K_a = 0 \leftarrow 0$ and $K_a = 1 \leftarrow 1$ bands are observed, consistent with a nearly pure a-type transition moment for CH-symmetric stretch excitation. This study is the first high resolution IR report of spectroscopy out of both of the COH torsion tunneling states. A combined least squares fit of 38 ground vibrational state combination differences (accessing up to $N \leq 8$) and 85 mm-wave transitions from Bermudez *et al.*⁴³ is reported and which provides ground vibrational state constants and spectral predictions of unprecedentedly high accuracy. It is our hope that the availability of such high quality predictions will stimulate further laboratory characterization of this important combustion intermediate as well as mm-/microwave search for this crucially important radical species in the interstellar medium.

These spectroscopic studies have been extended to include explicitly correlated *ab initio* CCSD(T)-f12b/cc-pvnZ ($n=2,3$) calculations of the approximate tunneling potential energy, with eigenfunctions and splitting calculated at each position along the path, and extrapolated to the complete basis set (CBS) limit. This gradient following path has then been used to estimate tunneling splitting for a series of states in the torsional/ CH_2 wag manifold, based on the large amplitude quantum methods of Hougen, Bunker, and Johns. The agreement between the experiment and simple “zero-curvature” 1D adiabatic theoretical predictions⁷⁷ is not spectroscopic but still quite reasonable for such a deep tunneling process, with a 10^5 to 10^6 -fold dynamic range between ground state splitting ($\approx 0.005 \text{ cm}^{-1}$) and torsional barrier ($\approx 1600 \text{ cm}^{-1}$). Furthermore, this 1D theory indicates a trend with increasing excitation of the torsional mode which is consistent with the observed change in sign for tunneling splitting in the CH_2 symmetric stretch excited upper state and potential assignment of the perturbing “dark” level to the $v_4 + v_5 + 2v_8$ combination state with 2 quanta of torsional vibration.

Future work within the group is currently directed towards obtaining similar hydroxymethyl spectra in the CH-asymmetric stretch and OH stretch region. We have made precision theoretical predictions for the locations of these bands and expect both to have comparable or even larger integrated absorption intensities. Although the asymmetric CH stretch spectra will almost certainly be dominated by b-type bands, the OH stretch spectral region is predicted to have both b and c components to the transition dipole. We therefore expect the OH stretch bands to have mixed b- and c-type character, which will permit a direct measurement of

TABLE VII. *Ab initio* tunneling analysis (in cm^{-1}).

v_8	ΔE_T	E_{ave}
0	0.00747	153
1	0.177	482
2	2.68	842
3	22.2	1165

tunneling splittings in the ground and multiple vibrationally excited states. Both spectral regions will have $\Delta K_a = \pm 1$ transition band types, which for the present set of spin-rotation values ($|e_{aa}| \gg |e_{bb}| > |e_{cc}|$) should permit full resolution of a fine structure and inform redistribution of electron spin density in vibrationally excited states. Most importantly, such high resolution infrared studies offer novel spectroscopic opportunities for remote sensing and precision *ab initio* tests on highly reactive radical species, with applications relevant to a variety of disparate areas in chemical physics ranging from the combustion of oxygenated fuels to the chemistry of the interstellar medium.

From gradient following (reaction path) calculations on a reduced dimensionality *ab initio* potential surface (CCSD(T)-f12b/cc-pvnZ-f12 ($n = 2,3$)/CBS) with harmonic zero point energy (ZPE) corrections in the 3N-7 higher frequency modes at the CCSD(T)-f12b/cc-pvtZ-f12 level. Vibrational eigenvalues and tunneling splittings are obtained via 1D Numerov integration of the Schrödinger equation, based on large amplitude motion Hamiltonian methods developed by Hougen, Bunker, and Johns (see text for details).^{72,73,75} Note that despite neglect of vibrationally nonadiabatic motion along the reaction path and “corner cutting” due to the multidimensional nature of the tunneling dynamics, such 1D calculations are still at least in good qualitative agreement with the experimentally observed splittings for the ground state ($\Delta E_T'' = 0.004\,649(3)\text{ cm}^{-1}$).

SUPPLEMENTARY MATERIAL

See [supplementary material](#) for the following: Table S1 lists four-line ground state IR combination differences (cm^{-1}) confirming the spectral assignment, with predicted frequencies (MHz) for low N transitions of potential astrophysical interest reported in Table S2. Table S3 provides both the parameters and correlation matrix output from a non-linear least squares fitting of the combined mm-wave/IR ground state combination differences data set, with the explicit z-matrix parameters used for *ab initio* calculation of the potential energy surface and adiabatic COH torsion/CH₂ wag reaction path summarized in Table S4.

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