brackets) and with equal populations of two rotamers with the H5–H6 dihedral angle equal to ~±150°. The overall fit to the data is good. The correlation time used in the analysis was verified by measuring the T_1^S/T_1^{NS} ratio. The NOE and T_1^S and T_1^{NS} data (Table II) support the conformations with the H5–H6 dihedral angle equal to ~±150°. The latter situation is preferred as it is consistent with the H5–H6 coupling constant and steric considerations.

Because the LTB_4 molecule is flexible, an analysis of all of the available parameters must be undertaken, together with conformational studies of model compounds, in order to evaluate the preferred conformations for LTB_4. This includes an analysis of the coupling constants, the T_1^S, T_1^{NS} and NOE data. By use of this combined approach, the conformational analysis of a complex molecule such as LTB_4 is possible.

Acknowledgment. We express our thanks to Drs. M. Bernstein, R. N. Young, and J. Rokach for useful discussions and to the Natural Sciences and Engineering Research Council of Canada, Merck Frosst Canada, Inc., and the University of Alberta for generous financial assistance.

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Structure of *syn*-Vinyl Alcohol Determined by Microwave Spectroscopy

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Abstract: The microwave spectra of *syn*-vinyl alcohol and nine isotopically substituted species have been measured and analyzed between 12 and 40 GHz. The compounds have been prepared by very low pressure pyrolysis of appropriately isotopically substituted species of cyclobutanol. The pyrolysis products have been pumped directly through the microwave Stark cell. Rotational constants and all quartic centrifugal distortion constants have been fitted to the measured transition frequencies. The complete substitution structure of *syn*-vinyl alcohol has been determined from the moments of inertia of all isotopic species.

Vinyl alcohol ($H_2C{=}CHOH$, ethenol), the simplest enol compound, is an unstable tautomer of acetaldehyde. Its existence as a reaction intermediate was proposed over 100 years ago.[1] In 1973, Blank and Fischer[2] observed its NMR spectrum by using the CIDNP technique during photolysis of acetaldehyde.

In 1976, Saito[3] reported the first identification in the gas phase. He produced vinyl alcohol by very low pressure pyrolysis of ethylene glycol and measured its microwave spectrum. Vinyl alcohol can exist in two planar conformations depending on the orientation of the hydroxyl group. Saito[3] showed from the rotational constants of the parent and the OD isotopic species that the syn conformer has been observed.

An indirect experimental estimate[4] of the difference between the heats of formation of vinyl alcohol and acetaldehyde in the gas phase at 25 °C gave 13.2 kcal/mol. Although vinyl alcohol is thermodynamically substantially less stable than its keto tautomer it has sufficient kinetic stability to be observed. A half-life of about 30 min at room temperature was reported[5] if vinyl alcohol was stored in a Pyrex flask.

In the most recent ab initio calculation Bouma and Radom[6] predicted the structure of vinyl alcohol. They showed that the syn conformer should be lower in energy than the anti form by 2.2 kcal/mol.

In this paper we report the measurements of the rotational spectra of *syn*-vinyl alcohol, all its singly substituted D, ^{13}C, and ^{18}O species, and two multiply substituted species. The vinyl alcohols have been produced by very low pressure pyrolysis of isotopic species of cyclobutanol. We have found recently that cyclobutanol or 3-thietanol are far better starting compounds than ethylene glycol for the preparation of vinyl alcohol.[7] The complete substitution structure of *syn*-vinyl alcohol has been deduced from the moments of inertia of the parent and all isotopic species.

Experimental Section

Pyrolysis. Very low pressure pyrolysis (thermolysis) allows cleavage of saturated four-membered rings at opposite bonds.[8] Thus, pyrolysis of cyclobutanol produced vinyl alcohol and ethylene with negligible side reactions. Temperatures above 800 °C were necessary in order to reach completion of the reaction. At these temperatures, however, it could not be avoided that a substantial fraction of vinyl alcohol isomerizes to acetaldehyde.

Cyclobutanol vapor was pyrolyzed in a quartz tube of 8-mm inner diameter heated over a length of 16 cm with an electric oven. The maximal yield of vinyl alcohol was obtained with the oven temperature around 800–900 °C. The emerging gases from the heated zone containing vinyl alcohol were pumped immediately through the Stark cell at pressures of 10 to 30 mtorr. The pressure and flow rate were adjusted with two valves, a needle valve between the sample reservoir and the oven and another valve between the Stark cell and the pump. The lifetime of vinyl alcohol in the Stark cell was 15–30 s.

Synthesis of Isotopic Cyclobutanols. Samples containing pure isotopic species or mixtures of isotopic species of cyclobutanol were prepared following known procedures.

$CH_2CH_2CH_2CHOD$: Direct exchange of cyclobutanol with D_2O produced cyclobutanol-*O-d*. The procedure was repeated in order to increase the deuterium content.

$CHDCH_2CH_2CHOH$, $CHDCH_2CHDCHOH$, $CD_2CH_2CH_2CHOH$, $CD_2CH_2CHDCHOH$, and $CD_2CH_2CD_2CHOH$: Acid-catalyzed exchange of cyclobutanone with a 1:1 mixture of $D_2O{:}H_2O$ gave a mixture of singly, doubly, triply, and quadruply deuterium substituted cyclobutanones in the *α* position. The mixture of cyclobutanones was reduced with $LiAlH_4$ to the corresponding cyclobutanols.

$CH_2CH_2CH_2CDOH$: Cyclobutanone was reduced with $LiAlD_4$ in an ethereal solution. The solution was treated with H_2O and gave cyclobutanol-*1-d*.

$CD_2CH_2CD_2CDOH$: $CD_2CH_2CD_2CO$ produced by acid-catalyzed exchange of cyclobutanone was reduced with $LiAlD_4$ as above.

$CH_2CH_2CH_2{}^{13}CHOH$: $CH_3{}^{13}COOH$ (0.5 g) was pyrolyzed in a quartz tube packed with quartz pieces and heated over a length of 35 cm

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Table I. Rotational Constants (MHz), Centrifugal Distortion Constants (kHz), and Moments of Inertia (u Å^2)[a] of Isotopomers of *syn*-vinyl Alcohol[b]

	$H_2C{=}CHOH$	$H_2C{=}{}^{13}CHOH$	$H_2{}^{13}C{=}CHOH$	$H_2C{=}CH^{18}OH$	$H_2C{=}CHOD$
A	59660.80 (2)	58385.65 (2)	59362.26 (2)	59430.52 (2)	52585.52 (2)
B	10561.665 (3)	10561.069 (3)	10233.319 (3)	10025.964 (3)	10320.499 (3)
C	8965.786 (3)	8935.768 (3)	8721.587 (2)	8571.915 (2)	8621.184 (3)
Δ_J	7.71 (2)	7.69 (2)	7.33[f]	7.02 (2)	7.80 (3)
Δ_{JK}	−61.6 (4)	−60.7 (3)	−60.1[f]	−58.8 (4)	−49.2 (5)
Δ_K	917 (1)	916.1 (8)	913.5[f]	918 (1)	607 (1)
δ_J	1.664 (2)	1.692 (2)	1.55[f]	1.458 (1)	1.785 (3)
δ_K	28.97 (5)	28.52 (5)	27.6[f]	27.05 (5)	27.88 (4)
I_a	8.470874 (3)	8.655878 (3)	8.513473 (2)	8.503695 (2)	9.610613 (3)
I_b	47.85032 (2)	47.85302 (2)	49.38564 (1)	50.40703 (1)	48.96847 (2)
I_c	56.36749 (2)	56.55687 (2)	57.94577 (2)	58.95755 (2)	58.62061 (2)
Δ^0[c]	0.04630	0.04797	0.04666	0.04683	0.04152
σ[d]	24	29	24	23	28
n[e]	36	30	9	32	33
	$H_2C{=}CDOH$	(Z)-$HDC{=}CHOH$[g]	(E)-$HDC{=}CHOH$[g]	$D_2C{=}CHOH$	$D_2C{=}CDOH$
A	47112.05 (1)	50260.32 (1)	58911.59 (2)	49315.77 (1)	40226.383 (8)
B	10560.543 (3)	10195.395 (3)	9624.171 (3)	9350.327 (3)	9347.259 (2)
C	8618.709 (3)	8468.432 (3)	8267.011 (2)	7854.079 (2)	7578.524 (2)
Δ_J	7.45 (4)	7.91 (3)	5.77 (2)	5.827 (9)	5.595 (9)
Δ_{JK}	−36.2 (5)	−43.7 (5)	−44.0 (3)	−28.0 (1)	−20.3 (1)
Δ_K	500.4 (6)	556.9 (8)	786 (1)	457.7 (4)	282.8 (1)
δ_J	1.864 (5)	1.853 (4)	1.142 (1)	1.268 (1)	1.400 (1)
δ_K	25.10 (4)	29.65 (3)	23.02 (4)	24.03 (4)	19.59 (3)
I_a	10.727171 (3)	10.055229 (3)	8.578602 (2)	10.247819 (3)	12.563373 (3)
I_b	47.85541 (1)	49.56934 (1)	52.51144 (1)	54.04934 (1)	54.06708 (1)
I_c	58.63744 (2)	59.67800 (2)	61.13202 (2)	64.34606 (2)	66.68568 (1)
Δ^0[c]	0.05486	0.05343	0.04198	0.04888	0.05523
σ[d]	31	28	22	28	27
n[e]	30	31	34	39	51

[a] Conversion factor of 505379.05 MHz u Å^2. [b] Numbers in parentheses represent one standard deviation. [c] $\Delta^0 = I_c - I_a - I_b$. [d] Mean residual error (kHz). [e] Number of measured transitions. [f] Estimated as described in text. [g] The prefix Z denotes isotopic species for which the heavier substituents at each carbon are located on the same side of the double bond. Otherwise the prefix E is used.

to 950 °C.[9] $CH_2{=}{}^{13}CO$ was formed together with H_2O. After freezing out H_2O in a trap at −78 °C $CH_2{=}{}^{13}CO$ was collected in a trap at −196 °C. It was transferred to an ethereal solution and reacted at −78 °C with an ethereal solution of CH_2N_2.[10] $CH_2CH_2CH_2{}^{13}CO$ formed was reduced with $LiAlH_4$ as above (yield 20–40 mg).

$^{13}CH_2CH_2CH_2CHOH$ and $CH_2{}^{13}CH_2CH_2CHOH$: $^{13}CH_3COOH$ (0.5 g) was pyrolyzed and reacted with CH_2N_2 as above. Since CH_2N_2 adds stepwise to $^{13}CH_2CO$ first forming cyclopropanone as an intermediate, a 1:1 mixture of $^{13}CH_2CH_2CH_2CO$ and $CH_2{}^{13}CH_2CH_2CO$ resulted, which then was reduced with $LiAlH_4$ (yield 20–40 mg).

$CH_2CH_2CH_2CH^{18}OH$: Acid-catalyzed exchange of cyclobutanone with $H_2{}^{18}O$ gave $CH_2CH_2CH_2C^{18}O$ which was reduced with $LiAlH_4$ as above. Further details of the isotopic syntheses are given in ref 11.

Microwave Spectra. The rotational spectra were recorded with conventional 30-kHz Stark modulated spectrometers over the range 12–40 GHz.[12] Phase-stabilized backward-wave oscillators were used as microwave radiation sources. The Stark cells of 2- or 4-m length were kept at 22 ± 2 °C. For accurate frequency measurements of rotational transitions the spectrometers were operated under control of a PDP-8/E computer. Several sweeps over a narrow frequency interval were added together in order to improve the signal-to-noise ratio. A parabola was fitted to the central part of an absorption line and its maximum was determined. Measured frequencies were averaged from sweeps in both directions and should be accurate within 20 kHz.

Assignment and Analysis of Rotational Spectra

Rotational transitions of all isotopic species were predicted from rotational constants based on the structure calculated by Bouma and Radom.[6] Low J μ_a-type R-branch transitions could easily be assigned on the basis of their typical Stark patterns. As an additional test in order to confirm that the transitions were due to vinyl alcohol the flow through the Stark cell was stopped by closing both valves. Transitions originating from vinyl alcohol decreased in intensity with a half-life of 15–30 s. Later μ_a- and μ_b-type, R- and Q-branch transitions with higher J values were added step by step.

The frequencies of 30–50 rotational transitions were measured accurately for all isotopic species except for $H_2{}^{13}C{=}CHOH$. The special situation during the isotopic synthesis of this species precluded an isotopic enrichment higher than 25%. More time was required to measure the weaker transitions with an adequate signal-to-noise ratio. Only nine transitions could be measured before the appropriate sample of cyclobutanol was exhausted.

Rotational spectra of the parent and the OD isotopic species of vinyl alcohol were reported by Saito.[3] In order to improve the accuracy of the rotational constants and to determine the quartic centrifugal distortion constants for these species, additional transitions with $J \leq 25$ were measured. The measured transition frequencies of all ten isotopic species and the differences from the calculated frequencies are collected in Tables IV–XIII available as supplementary material. The rotational constants and all quartic centrifugal distortion constants of each isotopic species were adjusted simultaneously to the measured transition frequencies in an iterative least-squares fit. The centrifugal distortion constants were defined according to Watson's asymmetric reduction in a prolate I^r basis.[13] The number of measured frequencies of $H_2{}^{13}C{=}CHOH$ did not allow the determination of the corresponding centrifugal distortion constants. They were estimated by adding calculated differences of the distortion constants between $H_2{}^{13}C{=}CHOH$ and the parent species to those observed for the parent species. The calculation was based on the force field from the normal coordinate analysis of ten isotopic species.[14] The mean residual errors between observed and cal-

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Table II. Cartesian Coordinates (Å) in the Principal Axis System of the Parent Molecule, Obtained by Kraitchman's Method and by the Least-Squares Fit

	Kraitchman's method[a]		least-squares fit[b]	
nucleus	*a*	*b*	*a*	*b*
C_1	(−0.0598) −0.0931[c]	−0.4353	−0.0885	−0.4327
C_2	−1.2504	0.2128	−1.2509	0.2076
O	1.1544	0.1355	1.1544	0.1358
H_1	1.0494	1.0902	1.0498	1.0907
H_2	0.0947 (0.0916)[d]	−1.5164	0.0470	−1.5161
H_3	−2.1732	−0.3464	−2.1736	−0.3473
H_4	−1.2963	1.2982	−1.2962	1.2974

[a] Reference 15. [b] Reference 18. [c] From the center-of-mass condition. [d] From multiply substituted species.

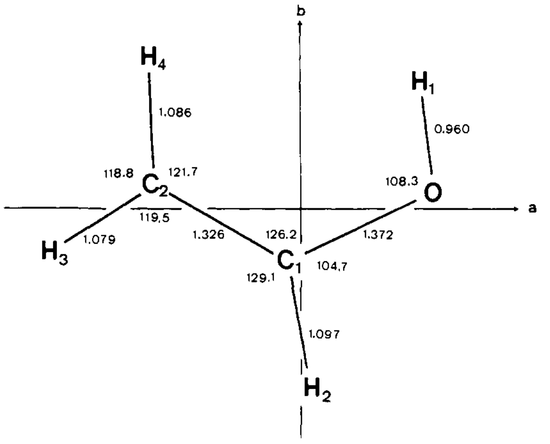

Figure 1. The atomic numbering scheme and substitution structure (bond lengths in Å, bond angles in deg) for *syn*-vinyl alcohol.

culated transition frequencies approach closely the estimated error of 20 kHz for the frequency measurements. The final results of the least-squares fits for all isotopic species are listed in Table I.

Molecular Structure

Moments of inertia and inertia defects $\Delta = I_c - I_a - I_b$ were calculated for all isotopic species from the rotational constants. The results are included in Table I. Small positive values of the inertia defects for all isotopic species establish the planarity of *syn*-vinyl alcohol. From differences between the moments of inertia of the singly substituted species and those of the parent species all substitution coordinates were calculated in the principal axis system of the parent molecule. The general three-dimensional equations of Kraitchman[15] were used but the *c* coordinates were disregarded. The results were numerically equal to those obtained from the equations of Rudolph[16] which consider all three moments of inertia for planar molecules in a balanced way. The substitution coordinates are given in Table II. The numbering of the nuclei of vinyl alcohol is shown in Figure 1.

Inspection of Table II shows that the absolute values of the *a* coordinates of the nuclei C_1 and H_2 are smaller than 0.1 Å. They are below the critical magnitude of 0.15 Å where the neglect of higher order vibrational contributions can introduce substantial systematic deviations from the true substitution coordinates. Furthermore, it is impossible on the basis of the equations of Kraitchman alone to affix the signs of these small coordinates. As an alternative in such a situation the center-of-mass and the product-of-inertia conditions have been applied for the calculation of small coordinates. In the present case only the center-of-mass condition can be used successfully since only the remaining *a* coordinates were determined with sufficient accuracy. However, the marginal accuracy of the *b* coordinates of the nuclei C_2 and O precludes the application of the product-of-inertia condition.

Additional information regarding the position of the nucleus H_2 could be gained from the two multideuterated species $D_2C{=}CHOH$ and $D_2C{=}CDOH$. The *a* and *b* coordinates of the nucleus H_2 of 0.1417 and 1.5339 Å, respectively, were determined in the principal axis system of $D_2C{=}CHOH$ with the equations of Kraitchman.[15] These coordinates were transformed to the principal axis system of the parent species. Knowing the coordinates of the nuclei H_3 and H_4 the shift and the rotation to the new system were calculated with equations derived by Wilson and Smith.[17] Depending on the sign of the original *a* coordinate of the nucleus H_2 two different solutions for this coordinate were obtained in the principal axis system of the parent species. Assuming a positive sign a value of 0.0916 Å was calculated which almost coincided with the value of 0.0947 Å determined from the singly substitued species. The other sign led to a value of −0.1870 Å at variance with the direct determination. This finding strongly supports the positive sign and confirms the *a* coordinate of 0.0947 Å of the nucleus H_2.

After having established unequivocally the position of the nucleus H_2 the center-of-mass condition was used to determine the a coordinate of the nucleus C_1. The result of −0.0931 Å should be more accurate than the directly determined value of −0.0598 Å from the equations of Kraitchman. It is included in Table II and will be used for the calculation of bond lengths and bond angles of *syn*-vinyl alcohol from the substitution coordinates. The resulting molecular structure is shown in Figure 1.

As a further check the geometry of syn-vinyl alcohol was determined with the molecular structure program GEOM.[18] Bond lengths and bond angles were fitted to the differences between the moments of inertia of all isotopic species and those of the parent species in an iterative least-squares procedure. Center-of-mass and product-of-inertia conditions are automatically fulfilled in the course of the calculations. The structural parameters were restricted to planar geometries. In order to allow a detailed comparison to the substitution structure the resulting coordinates of the least-squares structure are included in Table II. Large coordinates show close agreement. Coordinates with absolute values smaller than 0.1 Å exhibit considerable differences. Light nuclei like H are affected most. The *a* coordinate of the nucleus H_2 is reduced contrary to the expectation that vibrational contributions tend to decrease small coordinates. On the other hand, the *a* coordinate of the nucleus C_1 reveals the expected shift. As a consequence the positions of these two nuclei could not be determined with the usual accuracy.

Discussion

Vinyl alcohol is the only compound with an isolated enol group whose molecular structure has been determined accurately so far. The C–O bond length of vinyl alcohol is remarkably shorter than that of saturated alcohols. Values of 1.425 and 1.431 Å were reported for methanol[19] and ethanol,[20] respectively. This observation might be explained by a partial double bond character in the case of vinyl alcohol which originates from the interaction between the C=C double bond and the lone pairs on the oxygen. A comparably short C–O bond length of 1.343 Å was found in formic acid[21] which is isoelectronic to vinyl alcohol. A similar trend is found comparing the C–F bond length of vinyl fluoride[22] with that of ethyl fluoride.[23] The C=C bond length is slightly shortened compared to the corresponding bond lengths of 1.337 and 1.336 Å of ethylene[24] and propylene,[25] respectively. A similar

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Table III. Comparison of Structural Parameters of Monosubstituted Ethylenes, Determined by Microwave Spectroscopic Methods

parameter[a]	vinyl alcohol	vinyl fluoride[b]	vinyl chloride[c]	vinyl bromide[d]
		Lengths, Å		
C_1–C_2	1.326 (5)	1.329 (6)	1.332 (5)	1.330 (5)
C_1–X	1.372 (4)	1.347 (9)	1.726 (5)	1.882 (2)
C_1–H_2	1.097 (5)	1.082 (4)	1.079 (10)	1.079 (5)
C_2–H_3	1.079 (4)	1.077 (3)	1.078 (10)	1.087 (5)
C_2–H_4	1.086 (4)	1.087 (3)	1.090 (10)	1.084 (5)
O–H_1	0.960 (3)			
		Angles, deg		
C_2–C_1–X	126.2 (5)	120.8 (3)	122.3 (5)	122.7 (2)
C_2–C_1–H_2	129.1 (11)	129.2 (10)	123.8 (10)	123.8 (5)
H_4–C_2–C_1	121.7 (4)	120.9 (3)	121.0 (10)	121.2 (5)
H_3–C_2–C_1	119.5 (5)	119.0 (3)	119.5 (10)	119.2 (5)
C_1–O–H_1	108.3 (3)			

[a] Same numbering as in Figure 1. [b] Reference 22. [c] Reference 26. [d] Reference 27.

shrinkage was found in vinyl fluoride[22] but not in vinyl chloride.[26] A general comparison of the molecular structures of vinyl halides with vinyl alcohol is given in Table III.

The C–H bond length of vinyl alcohol in the trans position to the oxygen is considerably shorter than the bond in the cis position. This behavior is again reflected in vinyl fluoride[22] and vinyl chloride,[26] but it is inverted in vinyl bromide.[27] The variation of the C–H bond lengths with the nature of the halogen in the trans position was explained in terms of a repulsion between the bonding electron pairs in the C–H and the trans C–X bonds. This repulsion increases as the halogen relinquishes electron density in the sequence F, Cl, Br.[28] The data of vinyl alcohol are in agreement with this argumentation, the difference between the cis and trans C–H bond lengths being similar to that in vinyl fluoride.[22]

The most remarkable feature of the structure of *syn*-vinyl alcohol is perhaps the large value of 129.1° for the angle $C_2C_1H_2$ and the correspondingly small value of 104.7° for the angle OC_1H_2. The latter is an extremely small angle around a trigonal carbon nucleus. Vinyl fluoride exhibits the same value for the angle $C_2C_1H_2$. The angle C_2C_1F of vinyl fluoride is considerably smaller than the corresponding angle C_2C_1O of *syn*-vinyl alcohol. This might be traced back to a repulsion between the hydrogen nuclei H_1 and H_4 which opens the angle in *syn*-vinyl alcohol.

Bouma and Radom[6] predicted the structure of *syn*-vinyl alcohol from ab initio calculations. They corrected the structure for systematic deficiencies by the use of experimental rotational constants of the parent and the OD species. The bond lengths are in fair agreement with the exception of the C_1–H_2 distance which was predicted to be the shortest of all C–H distances. The main difference from the substitution structure, however, is found for the angle $C_2C_1H_2$. The predicted value is 8° smaller than the experimental value. Even considering the experimental difficulties in locating the nuclei C_1 and H_2 this discrepancy is much larger than anticipated. All other angles show deviations of 1.5° or less.

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Registry No. $H_2C=CHOH$, 557-75-5; $H_2C={}^{13}CHOH$, 90134-25-1; $H_2{}^{13}C=CHOH$, 90134-26-2; $H_2C=CH^{18}OH$, 90134-15-9; $H_2C=CHOD$, 64066-40-6; $H_2C=CDOH$, 90134-16-0; (*Z*)-$HDC=CHOH$, 90134-19-3; (*E*)-$HDC=CHOH$, 90134-18-2; $D_2C=CHOH$, 90134-17-1; $D_2C=CDOH$, 90134-20-6; $CH_2CH_2CH_2CHOD$, 55887-71-3; $CHDCH_2CH_2CHOH$, 90134-27-3; $CHDCH_2CHDCHOH$, 90134-28-4; $CD_2CH_2CH_2CHOH$, 24468-95-9; $CD_2CH_2CHDCHOH$, 90134-29-5; $CD_2CH_2CD_2CHOH$, 22696-03-3; $CH_2CH_2CH_2CDOH$, 22696-02-2; $CD_2CH_2CD_2CDOH$, 22696-04-4; $CH_2CH_2CH_2{}^{13}CHOH$, 90134-30-8; ${}^{13}CH_2CH_2CH_2CHOH$, 90134-31-9; $CH_2{}^{13}CH_2CH_2CHOH$, 90134-32-0; $CH_2CH_2CH_2CH^{18}OH$, 90134-33-1; $CH_3{}^{13}COOH$, 1563-79-7; ${}^{13}CH_3COOH$, 1563-80-0; cyclobutanol, 2919-23-5.

Supplementary Material Available: Listings of measured rotational transition frequencies of $H_2C=CHOH$, $H_2C={}^{13}CHOH$, $H_2{}^{13}C=CHOH$, $H_2C=CH^{18}OH$, $H_2C=CHOD$, $H_2C=CDOH$, (*Z*)-$HDC=CHOH$, (*E*)-$HDC=CHOH$, $D_2C=CHOH$, and $D_2C=CDOH$ in the vibrational ground state (Tables IV–XIII) (10 pages). Ordering information is given on any current masthead page.

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