J. Am. Chem. Soc. **1990**, *112*, 7525–7528

Structure of Vinyl Alcohol: A Resolution of the Discrepancy between Theory and Experiment

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Abstract: Ab initio molecular orbital calculations have been used to derive a new theoretical r_0 structure for vinyl alcohol. In addition, a reanalysis of previously reported experimental data obtained from microwave spectroscopy measurements has led to new experimental r_0 and r_s structures. The theoretical and experimental r_0 structures are found to be in good agreement.

Vinyl alcohol, the unstable tautomer of acetaldehyde, is the prototypical enol. Its possible existence was first proposed by Erlenmeyer[1] in 1881, but it eluded detection for almost a century until 1973 when it was identified in an NMR photolysis experiment.[2] The first gas-phase observation was reported[3] in 1976. Since then, the microwave spectra of both syn[4] and anti[5] forms have been recorded, the matrix infrared spectrum has been measured,[6] and several photoelectron studies have been performed.[7] Since tautomerism plays a fundamental role in a wide variety of organic syntheses, understanding this simplest of enols is of quintessential importance. Vinyl alcohol is also of importance as a possible interstellar molecule.

One of the fundamental properties of vinyl alcohol that remains to be definitively established, despite several experimental and theoretical studies on the subject, is its detailed structure. The microwave spectrum of *syn*-vinyl alcohol was first recorded by Saito[3] in 1976, and a partial r_0 structure (CC length and CCO angle) was obtained. A full r_0 structure was estimated by Bouma and Radom[8] in 1978 using ab initio molecular orbital calculations. Subsequent microwave measurements on a range of isotopically substituted species led to the full r_s structure being determined by Rodler and Bauder (RB).[4] However, a striking difference of more than 8° was found between values from the experimental r_s structure[4] and the theoretical r_0 structure[8] for the CCH angle involving the H atom geminal to the OH group. Subsequent studies[5,9] that have dealt with this anomaly have been unable to resolve the discrepancy. An error of this magnitude would be quite unusual and suggests that a reexamination of both the theoretical and experimental structures would be desirable. We have addressed the problem by carrying out higher level ab initio calculations and by reanalyzing the existing experimental data. Our study, the results of which are reported here, has yielded new theoretical and experimental structures for vinyl alcohol. The theoretical and experimental r_0 structures are found to be in good agreement.

Method

Standard ab initio molecular orbital calculations[10] were performed with a modified version[11] of the GAUSSIAN 86 package of programs.[12] Geometries were fully optimized with the 6-31G(d) basis set and a variety of theoretical procedures including Hartree–Fock (HF) theory, Møller–Plesset perturbation theory terminated at second (MP2), third (MP3), and fourth (MP4) orders, and configuration interaction including all single and double excitations both with (CISD(Q)) and without (CISD) the Davidson correction for quadruple excitations. Core orbitals were frozen in the MP3 and MP4 calculations. Optimizations at the HF and MP2 levels were also carried out with the larger 6-311+G(d,p) basis set.

Results and Discussion

Spectroscopic techniques can yield four major structural types. Of these, r_0 and r_s structures are obtained from the observed rotational constants (r_0 structures) or differences in moments of inertia (r_s structures) for a collection of isotopic species; other than for diatomic molecules, r_0 and r_s parameters have no direct physical interpretation. Additional knowledge of the harmonic force field allows the determination of r_z structures that correspond to zero-point average structures. In a small number of cases, sufficient information is available to derive r_e structures that correspond to the structures of vibrationless molecules. The relationship between the different structural types is described in detail elsewhere.[13]

Theoretical ab initio treatments yield estimates of r_e structures whose quality depends on the level of theory employed. In order to obtain theoretical structures that may be usefully compared with experimental rotational constant data, we need to correct the raw ab initio structures both for the systematic deficiencies of the theory and for the difference between r_e and r_0. Several related approaches to deal with these issues have been investigated in the literature.[8,14] Of crucial importance is the recognition that the differences between calculated and experimental structural parameters at specific levels of ab initio theory are relatively constant for particular bond types and angles. This allows us to empirically adjust our calculated lengths and angles to produce improved sets of data. In previous studies, for example in our previous determination of the structure of vinyl alcohol,[8] we have adopted the approach of correcting *simultaneously* for the sys-

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Table I. Calculated and Experimental Geometries and Calculated Total Energies for Reference Molecules[a,b]

			6-31G(d)						6-311+G(d,p)	
		exptl r_0[c]	HF	MP2	MP3	MP4	CISD	CISD(Q)	HF	MP2
H_2O	O-H	0.957[d]	0.947 [0.010]	0.969 [-0.012]	0.967 [-0.010]	0.970 [-0.013]	0.966 [-0.009]	0.970 [-0.013]	0.941 [0.016]	0.959 [-0.002]
	<HOH	105.0	105.5 [-0.5]	104.0 [+1.0]	104.2 [+0.8]	104.0 [+1.0]	104.2 [+0.8]	104.0 [+1.0]	106.1 [-1.1]	103.5 [+1.5]
	E		-76.01075	-76.19924	-76.20271	-76.20733	-76.20027	-76.20964	-76.05331	-76.29372
$CH_2{=}CH_2$	C=C	1.339(1)[e]	1.317 [0.022]	1.335 [0.004]	1.334 [0.005]	1.342 [-0.003]	1.329 [0.010]	1.337 [0.002]	1.318 [0.021]	1.338 [0.001]
	C-H	1.085(2)	1.076 [0.009]	1.085 [0.000]	1.086 [-0.001]	1.089 [-0.004]	1.084 [0.001]	1.088 [-0.003]	1.077 [0.008]	1.085 [0.000]
	<CCH	121.1(3)	121.8 [-0.7]	121.7 [-0.6]	121.8 [-0.7]	121.8 [-0.7]	121.8 [-0.7]	121.8 [-0.7]	121.7 [-0.6]	121.4 [-0.3]
	E		-78.03172	-78.29429	-78.30598	-78.31991	-78.29969	-78.32448	-78.05608	-78.38370
CH_3OH	C-O	1.427(7)[f]	1.399 [0.028]	1.423 [0.004]	1.422 [0.005]	1.428 [-0.001]	1.416 [0.011]	1.423 [0.004]	1.400 [0.027]	1.420 [0.007]
	O-H	0.956(15)	0.946 [0.010]	0.970 [-0.014]	0.967 [-0.011]	0.972 [-0.016]	0.964 [-0.008]	0.969 [-0.013]	0.940 [0.016]	0.959 [-0.003]
	C-H_a	1.096(10)	1.081 [0.015]	1.090 [0.006]	1.091 [0.005]	1.094 [0.002]	1.089 [0.007]	1.092 [0.004]	1.082 [0.014]	1.089 [0.007]
	C-H_b	1.096(10)	1.088 [0.008]	1.097 [-0.001]	1.098 [-0.002]	1.101 [-0.005]	1.095 [0.001]	1.099 [-0.003]	1.088 [0.008]	1.096 [0.000]
	<HOC	108.9(20)	109.5 [-0.6]	107.4 [+1.5]	107.7 [+1.2]	107.2 [+1.7]	108.1 [+0.8]	107.7 [+1.2]	110.0 [-1.1]	107.4 [+1.5]
	<OCH_a		107.1	106.3	106.4	106.2	106.6	106.4	107.3	106.7
	<OCH_b		112.0	112.3	112.2	112.3	112.2	112.3	111.8	112.0
	<HOCH_b		61.2	61.5	61.5	61.5	61.4	61.5	61.2	61.4
	E		-115.03542	-115.35329	-115.36178	-115.37391	-115.34930	-115.37572	-115.08043	-115.48280

[a] Units are angstroms for bond lengths, degrees for angles, and hartrees for energies. [b] Numbers in square brackets are differences between calculated and experimental values. [c] Numbers in parentheses are cited estimates of uncertainty, where available. [d] Reference 15. [e] Reference 16. [f] Reference 17.

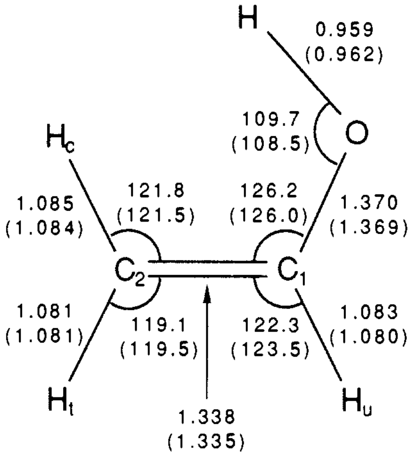

Figure 1. Theoretical and experimental (in parentheses) r_0 structural parameters for vinyl alcohol.

tematic deficiencies in the theoretical models *and* for the differences between r_e and r_0. We use such an approach again here. It involves initially generating comparative theoretical and experimental data for reference systems related to the molecule under investigation and then using these results to calculate appropriate correction terms.

Table I displays the optimized geometrical parameters and energies for a selection of systems that contain the specific structural units, i.e., bond lengths and angles, that are present in vinyl alcohol, obtained at a variety of levels of theory. Also tabulated are the experimental r_0 structures[15-17] and the calculated corrections to the theoretical structures required to reproduce the experimental values.

One of the difficulties associated with correcting the theoretical structural parameters on the basis of data for reference molecules is that the correction will depend to some extent on the environment of the particular structural unit. It is therefore important to select reference molecules in which the relevant environment is as similar as possible to that in the target molecule. Regression equations may sometimes be helpful in this regard[14b] but were not deemed necessary in the present case. Another problem occurs in the case of dependent parameters. For example, it is not clear how one should deal with the in-plane angles of the vinyl group where it is possible to make independent corrections to only two of the three angles at each carbon atom. We have adopted the practice of applying the corrections calculated for the ethylene CCH angle to each of the CCX (X = H or O) angles.

We report in Table II the optimized geometries of vinyl alcohol calculated at the same levels of theory as used in Table I. It can be seen that the sensitivity of the calculated geometries to basis set is relatively small: the results obtained with the 6-31G(d) and 6-311+G(d,p) basis sets in the two cases where comparisons can be made are very similar. The effect of electron correlation, on the other hand, is considerably larger, the range of predicted lengths and angles at the 6-31G(d) level being as large as 0.03 Å or 2° for some parameters. The variation in directly calculated structural parameters for different levels of theory is thus quite large.

Table III shows the effect of applying the corrections of Table I to the optimized structural parameters for vinyl alcohol of Table II. We can now see agreement between the different levels of theory that is quite extraordinary. Bond lengths vary by no more than 0.004 Å and angles by no more than 0.6°, and usually much less. Also reported in Table III and reproduced in Figure 1 is our best predicted r_0 structure, based on a subjective average of all the data. We believe that this structure represents the best

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Table II. Calculated Geometries and Total Energies for Vinyl Alcohol[a]

	6-31G(d)						6-311+G(d,p)	
	HF	MP2	MP3	MP4	CISD	CISD(Q)	HF	MP2
C=C	1.318	1.336	1.333	1.342	1.326	1.333	1.319	1.339
C-O	1.347	1.367	1.368	1.373	1.360	1.368	1.345	1.362
$C-H_u$	1.073	1.085	1.085	1.089	1.081	1.085	1.074	1.084
$C-H_t$	1.073	1.081	1.082	1.086	1.079	1.082	1.073	1.081
$C-H_c$	1.077	1.086	1.086	1.090	1.083	1.087	1.077	1.085
O-H	0.949	0.974	0.970	0.976	0.965	0.971	0.942	0.963
<CCO	126.9	126.8	126.7	126.8	126.8	126.7	126.8	126.6
<HOC	110.4	108.1	108.4	108.0	109.0	108.5	110.9	108.1
$<CCH_u$	122.4	122.9	122.9	123.0	122.8	123.0	122.2	122.6
$<CCH_t$	120.1	120.0	120.1	120.0	120.1	120.1	119.8	119.4
$<CCH_c$	122.4	122.3	122.5	122.3	122.4	122.5	122.3	122.1
E	-152.88889	-153.33216	-153.33832	-153.35972	-153.30795	-153.35473	-152.94202	-153.48692

[a] Units are angstroms for bond lengths, degrees for angles, and hartrees for energies. See Figure 1 for the labeling of hydrogen atoms.

Table III. Comparison of Corrected r_0 Geometrical Parameters for Vinyl Alcohol with r_0 and r_s Values Derived from Experimental Rotational Constants[a]

	6-31G(d)						6-311+G(d,p)					
	HF	MP2	MP3	MP4	CISD	CISD(Q)	HF	MP2	theor r_0[b]	exptl r_s[c]	exptl r_0[d,e]	exptl r_s[e,f]
C=C	1.340	1.340	1.338	1.339	1.336	1.335	1.340	1.340	1.338	1.326	1.335 (6)	1.327 (3)
C-O	1.375	1.371	1.373	1.372	1.371	1.372	1.372	1.369	1.370	1.372	1.369 (6)	1.365 (2)
$C-H_u$	1.082	1.085	1.084	1.085	1.082	1.082	1.082	1.084	1.083	1.097	1.080 (2)	1.092 (3)
$C-H_t$	1.082	1.081	1.081	1.082	1.080	1.079	1.081	1.081	1.081	1.079	1.081 (3)	1.077 (2)
$C-H_c$	1.086	1.086	1.085	1.086	1.084	1.084	1.085	1.085	1.085	1.086	1.084 (1)	1.091 (2)
O-H	0.959	0.961	0.959	0.960	0.957	0.958	0.958	0.960	0.959	0.960	0.962 (1)	0.961 (2)
<CCO	126.2	126.2	126.0	126.1	126.1	126.0	126.2	126.3	126.2	126.2	126.0 (1)	126.7 (3)
<HOC	109.8	109.6	109.6	109.7	109.8	109.7	109.8	109.6	109.7[g]	108.3	108.5 (5)	108.3 (2)
$<CCH_u$	121.7	122.3	122.2	122.3	122.2	122.3	121.6	122.3	122.3	129.1	123.5 (14)	125.3 (5)
$<CCH_t$	119.4	119.4	119.4	119.3	119.4	119.4	119.2	119.1	119.1	119.5	119.5 (2)	120.3 (3)
$<CCH_c$	121.7	121.7	121.8	121.6	121.7	121.8	121.7	121.8	121.8	121.7	121.5 (4)	121.1 (2)

[a] Units are angstroms for bond lengths and degrees for angles. See Figure 1 for the labeling of hydrogen atoms. [b] Obtained from empirical corrections from reference molecules, present work. [c] Obtained from Kraitchman's equations.[4] [d] Obtained from observed rotational constants by a least-squares procedure, present work. [e] Numbers in parentheses are standard deviations from least-squares fit, present work. [f] Obtained from differences in observed moments of inertia by a least-squares procedure, present work. [g] See ref 18.

theoretical r_0 structure presently available for vinyl alcohol.

Our theoretical r_0 structure for vinyl alcohol is generally quite similar to the previous theoretical structure of Bouma and Radom.[8] In particular, it continues to show some very marked differences to the experimental r_s structure of RB[4] derived with Kraitchman's equations, most notably the C=C (+0.012 Å) and $C-H_u$ (-0.014 Å) bond lengths and the CCH_u (-6.8°) angle.

There would appear to be three possible sources for these differences between our best theoretical r_0 structure and the experimental r_s structure. The discrepancies could, in the first place, reflect problems on the theoretical side. It may be that vinyl alcohol represents a pathological case that standard ab initio molecular orbital techniques are unable to describe properly. A second possibility is that there is an alternative interpretation of the experimental data. Finally, it is possible that the discrepancies reflect the differences in the origins of the two structural types, namely r_0 and r_s.

As far as the possibility that vinyl alcohol is a theoretically difficult molecule is concerned, the observation that the effects of electron correlation and improved basis set have only led to a small change compared with the previous theoretical r_0 structure[8] makes this unlikely. Alternatively, it is possible in principle that changes in the offending geometrical parameters are accompanied by only small changes in energy, which would mean that the energy minimization criterion of the ab initio structural calculations may lead to quantities that are poorly determined. However, examination of second derivatives from an analytical frequency calculation show that this is also not the case: the calculated force constants indicate that it should be possible to determine both the C=C lengths and CCH_u angle with at least the same degree of precision as the other parameters. The disagreement between experiment and theory therefore remains.

As part of a reexamination of the experimental data, we have refitted the rotational constants of all 10 isotopic species reported by RB[4] to obtain, for the first time, a complete r_0 structure. These results are included in Table III along with the estimated standard deviations. The A rotational constant for the $H_2C{=}^{13}CHOH$ isotopic species appeared inconsistent with the other experimental data and was therefore excluded from the least-squares refinement. Two points become very clear. There is good agreement for all the parameters, bond lengths, and angles, between this r_0 structure and our theoretical r_0 structure. Most significantly, the C=C length and CCH_u angle are now in satisfactory agreement with the theoretical predictions, although we note that there are relatively large uncertainties associated with these parameters. Comparing our best theoretical r_0 structure with our new experimental r_0 structure, the differences are within 0.003 Å for bond lengths and 1.2° for angles.[18] There is now no discrepancy between theory and experiment as far as the r_0 structure is concerned.

The problem that faces us now is that the experimental r_0 structure that we have just derived differs significantly from the r_s structure of RB,[4] including a 5.6° discrepancy in the CCH_u angle. Could this reflect a real (but unprecedentedly large) difference between r_0 and r_s structures? In order to tackle this problem, we have refitted the differences in moments of inertia associated with isotopic substitution to obtain a new experimental r_s structure. This is reported in the last column of Table III. Our r_s structure is close to that obtained (but not explicitly reported) by RB[4] from a similar least-squares approach. However, significant differences between our r_s structure (referred to as SR) and the preferred r_s structure of RB[4] (obtained using Kraitchman's equations) may be seen. For example, the RB and SR values for the CCH_u angle are 129.1° and 125.3°, respectively. Although

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(18) The difference of 1.2° between the theoretical and experimental estimates of the HOC angle in vinyl alcohol may actually be indicative that the experimental r_0 value for the HOC angle in the reference molecule, methanol, is about 1° too high. We note in this connection that the experimental r_s value for the HOC angle in methanol is 108.0°, 0.9° smaller than the r_0 value: Gerry, M. C. L.; Lees, R. M.; Winnewiser, G. *J.* Mol. *Spectrosc.* **1976**, *61*, 231. A very recent zero-point average structure for methanol gives <HOC = 107.6 ± 0.9°: Iijima, T. *J. Mol. Struct.* **1989**, *212*, 137.

Table IV. Comparison of Rotational Constants (*A*, *B*, *C*)[a] Calculated for Theoretical and Experimental r_0 Structures of Vinyl Alcohol with Observed Values

		theor[b]	exptl[c]	obs[d]
$H_2C=CHOH$	*A*	59 595	59 661	59 661
	B	10 504	10 559	10 562
	C	8 930	8 971	8 966
$H_2C=^{13}CHOH$	*A*	58 307	58 364	58 386
	B	10 502	10 557	10 561
	C	8 899	8 940	8 936
$H_2{}^{13}C=CHOH$	*A*	59 291	59 361	59 362
	B	10 177	10 230	10 233
	C	8 686	8 726	8 722
$H_2C=CH^{18}OH$	*A*	59 368	59 428	59 431
	B	9 970	10 021	10 026
	C	8 536	8 575	8 572
$H_2C=CHOD$	*A*	52 562	52 585	52 586
	B	10 254	10 317	10 320
	C	8 580	8 625	8 621
$H_2C=CDOH$	*A*	47 019	47 112	47 112
	B	10 504	10 559	10 561
	C	8 586	8 625	8 619
(*Z*)-HDC=CHOH	*A*	50 191	50 263	50 260
	B	10 136	10 192	10 195
	C	8 433	8 474	8 468
(*E*)-HDC=CHOH	*A*	58 830	58 914	58 912
	B	9 576	9 621	9 624
	C	8 236	8 270	8 267
$D_2C=CHOH$	*A*	49 224	49 313	49 316
	B	9 302	9 347	9 350
	C	7 823	7 858	7 854
$D_2C=CDOH$	*A*	40 124	40 226	40 226
	B	9 301	9 346	9 347
	C	7 550	7 584	7 579

[a] Units are megahertz. [b] Rotational constants calculated from the theoretical r_0 structure of the present work. [c] Rotational constants calculated from the experimental r_0 structure of the present work. [d] Observed rotational constants from ref 4.

Table V. Comparison of Differences in Moments of Inertia (ΔI_a, ΔI_b, ΔI_c)[a] Calculated for the r_s Structures of Vinyl Alcohol with Observed Values

		RB[b]	SR[c]	obs[d]
$H_2C=^{13}CHOH$	ΔI_a	0.186	0.183	0.185
	ΔI_b	0.008	0.008	0.003
	ΔI_c	0.195	0.190	0.189
$H_2{}^{13}C=CHOH$	ΔI_a	0.041	0.041	0.043
	ΔI_b	1.537	1.537	1.535
	ΔI_c	1.578	1.577	1.578
$H_2C=CH^{18}OH$	ΔI_a	0.034	0.033	0.033
	ΔI_b	2.556	2.557	2.557
	ΔI_c	2.590	2.590	2.590
$H_2C=CHOD$	ΔI_a	1.142	1.138	1.140
	ΔI_b	1.109	1.117	1.118
	ΔI_c	2.251	2.255	2.253
$H_2C=CDOH$	ΔI_a	2.260	2.262	2.256
	ΔI_b	0.010	0.001	0.005
	ΔI_c	2.271	2.263	2.270
(*Z*)-HDC=CHOH	ΔI_a	1.575	1.587	1.584
	ΔI_b	1.736	1.721	1.719
	ΔI_c	3.310	3.308	3.310
(*E*)-HDC=CHOH	ΔI_a	0.111	0.106	0.108
	ΔI_b	4.652	4.662	4.661
	ΔI_c	4.763	4.768	4.765
$D_2C=CHOH$[e]	ΔI_a	0.198	0.191	0.193
	ΔI_b	4.465	4.476	4.480
	ΔI_c	4.663	4.668	4.668
$D_2C=CDOH$[f]	ΔI_a	2.311	2.318	2.316
	ΔI_b	0.044	0.021	0.018
	ΔI_c	2.355	2.339	2.340

[a] Differences between the moments of inertia for the isotopically substituted species and those for the normal species ($H_2C=CHOH$) in units of u Å^2 unless otherwise noted. [b] Differences in moments of inertia calculated from the experimental r_s structure of ref 4. [c] Differences in moments of inertia calculated from the experimental r_s structure of the present work. [d] Observed differences in moments of inertia from ref 4. [e] Differences with respect to (*Z*)-HDC=CHOH. [f] Differences with respect to $D_2C=CHOH$.

our r_s structure is in better agreement than that of RB[4] with the theoretical and experimental r_0 structures, the differences are rather more than normally found.

A remaining question then is why do the RB and SR r_s structures differ from one another and from the r_0 structure? It would seem that the problem is at least partly associated with the well-known difficulty in locating atoms close to the inertial axis from information obtained from spectroscopic techniques. RB[4] appreciated this difficulty and were particularly careful in their attempts at locating the C_1 and H_u atoms, both sited close to the *a* inertial axis. However, the present study suggests that problems remained and emphasizes in particular dangers in the use of Kraitchman's equations in situations of this type. We have found also in our least-squares approach that the best least-squares fit is not very sensitive to the value of the CCH_u angle in particular.

Table IV compares the rotational constants calculated for both the theoretical and experimental r_0 structures derived in the present study with observed values for the 10 isotopic species that have been experimentally characterized.[4] As can be seen, the experimental r_0 structure fits the observed rotational constants very well, with differences typically less than about 5 MHz. The theoretical structure also reproduces the observed rotational constants very satisfactorily. The calculated rotational constants are all slightly smaller than the observed values, by 0.1–0.4% for *A*, 0.5–0.7% for *B*, and 0.4–0.5% for *C*.

In order to assess the quality of the r_s structure obtained by RB[4] and that obtained in the present work (SR), it is necessary to calculate differences (ΔI_a, ΔI_b, ΔI_c) in moments of inertia associated with isotopic substitution for the RB and SR structures and compare the values obtained with the observed differences. Such differences in moments of inertia, of course, form the basis for the calculation of r_s structures. The values for ΔI_a, ΔI_b, and ΔI_c for the nine isotopically substituted species calculated with the RB and SR r_s structures are compared with the experimental values in Table V. The agreement with experiment for our (SR) r_s structure is good. The root mean square deviation is 0.003 u Å^2 with a maximum error of 0.007 u Å^2. For the RB structure, the root mean square and maximum errors are 0.008 and 0.026 u Å^2, respectively. The present r_s structure is thus in somewhat better agreement with experimental data than the previous (RB) structure.

Concluding Remarks

Various workers have noted but not resolved discrepancies between the experimental r_s structure for vinyl alcohol in the literature and theoretical predictions of the r_0 structure. We have obtained a new theoretical r_0 structure for vinyl alcohol, and, through a reanalysis of the experimental rotational constant data, we have also obtained new experimental r_0 and r_s structures. We find small but significant differences between the experimental r_0 and r_s structures; these differences between r_0 and r_s structures have given rise to the previous problems in reconciling the theoretical and experimental structural data.[19] When the theoretical r_0 structure is compared with the experimental r_0 structure (rather than the experimental r_s structure), there is no longer a discrepancy between theoretical and experimental estimates of the structure of vinyl alcohol.

Acknowledgment. We gratefully acknowledge a generous allocation of computer time on the Fujitsu FACOM VP-100 of the Australian National University Supercomputer Facility.

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(19) **Note Added in Proof**: A very recent paper notes that there is a "slowly growing list of molecules for which very high quality r_s geometries appear to differ from their r_e geometries in a worrying manner". Williams, G. A.; Macdonald, J. N.; Boggs, J. E. *J. Mol. Struct.* **1990**, *220*, 321.