Theoretical Study of the Electronic Spectrum and ESR of the CH_2OH Radical

Feiwu Chen and Ernest R. Davidson*

Department of Chemistry, Indiana University, Bloomington, Indiana 47405-7102

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The structure of the CH_2OH radical was optimized at the UHF, UB3LYP, and MP2 levels. The calculated ionization potential was very close to the experimental one. The transition dipole moments from the ground state to the first four lowest excited states were calculated with and without C_s symmetry using the multireference single and double configuration interaction method (MRSD). The first four lowest excited states were also optimized with the single excitation configuration interaction method (CIS). The adiabatic excitation energies and transition dipole moments for vertical emission were calculated at the same level. None of these calculations lead to the assignment of the first excited Rydberg *p* state as $^2A''(3p_z)$ as suggested in a recent paper (*Chem. Phys. Lett.* 318, *393*, **2000**). Some results of multireference perturbation theory are also presented. The isotropic hyperfine parameters calculated with MRSD were in good agreement with the experimental values.

I. Introduction

The hydroxymethyl radical (CH_2OH) has been known for a long time[1] and plays an important role in combustion chemistry[2] and atmospheric chemistry.[3] This radical was first detected during electron spin resonance (ESR) studies in methanol liquid.[4] A complete resolution of the hydroxyl hydrogen hyperfine splitting was achieved later by Livingston and Zeldes.[5] The isotropic hyperfine splitting parameters of the alpha and beta hydrogen are 17.4 and 1.15 G in magnitude (sign not determined), respectively. The spin densities of both hydroxyl and alpha hydrogen increased slightly with a decrease of temperature to 243 K. A much lower temperature ESR study was performed by Hudson.[6] Under the lower temperature of 220 K, the two alpha hydrogen atoms (CH_2) were shown to be inequivalent. The torsional barrier height for OH rotation was estimated as 9.5 kJ/mol. The ESR study in an argon matrix at 4 K was carried out by Cochran et al.[7] The temperature effect on the hyperfine splitting was studied in detail by Krusik, Meakin, and Jesson.[8] The torsional barrier height was determined to be about 4 kcal/mol, which is larger than that obtained by Hudson. The above experimental data indicate that CH_2OH has a nonplanar structure. The radical electron is delocalized between the carbon and the oxygen atoms in a π^* orbital. The infrared spectroscopy studies of the CH_2OH radical were carried out by Jacox et al.[9,10] The frequency of the CO stretch was shown to be 1183 cm^{-1}, which is much larger than that which is typical for a CO single bond and indicates partial double-bond character in the CO bond. The photoelectron spectrum of the radical was observed by Dyke et al.[11] The adiabatic ionization potential was determined to be 7.56 eV. Early theoretical work on the CH_2OH radical was done by Gordon and Pople with the approximate INDO method.[12] A systematic calculation was done by Saebo et al.[13] The geometry was optimized at the UHF level with the basis sets 3-21G, 6-31G* and 6-31G**. A nonplanar structure was found. Several transition states were identified. The torsional barriers 2.75 and 3.98 kcal/mol were determined using UHF/6-31G** and MP2/6-31G**, respectively.

In contrast with the early work on the CH_2OH radical ground state, studies on the excited electronic states were begun much later. The first observation of the excited electronic state was by resonance-enhanced multiphoton ionization (REMPI) in 1983.[14] The REMPI spectrum showed an extensive band system with a strong origin at 486.7 nm corresponding to a transition energy of 5.10 eV. On the basis of the then accepted ionization potential, 8.10 eV,[15,16] the band origin was proposed to be due to either a two-photon resonance with the 3*s* Rydberg state or a low-lying valence excited state. However, this interpretation was revised later[17] by the same authors with the improved ionization potential provided by Dyke et al.[11] The resonant state was assigned to be a *3p* Rydberg state. The 2+1 REMPI spectra of the vibrationally excited CH_2OH radical were also investigated by Bomse et al.[18] Ultraviolet absorption spectra of the $^2A''\rightarrow{}^2A'(3s)$ and $^2A''\rightarrow{}^2A'(3p)$ transitions were reported by Pagsberg et al.[19] A full analysis of the vibrational spectroscopy of the CH_2OH radical was due to experimental and theoretical studies by Hudgens et al.[20] Ab initio calculations on the excited states of the CH_2OH radical were carried out by Rettrup et al.[21] The geometry was taken from reference,[13] although a different basis set was used. The first four lowest excited states from a single excited CI calculation were chosen as reference configurations, and then, a multireference CI with the size of 53 472 was performed. In comparison with the experimental data,[14,19] the first excited state was assigned as $\pi^*\rightarrow 3s$, whereas the second was $\pi^*\rightarrow 3p_y(a')$ (with y along the CO axis). However, by considering the spectroscopic behavior of the CH_2OH radical in accordance with a C_s symmetry, a different assignment of the *3p* Rydberg state, $3p_z\ ^2A''$, was reported very recently based on REMPI experimental results.[22]

It is known that the ground state of the CH_2OH radical has a A'' symmetry if C_s symmetry is assumed for the radical. Therefore, the excited *3p* Rydberg state has a A'' symmetry if the transition dipole moment has a A' symmetry and vice versa. However, the equilibrium position of the ground-state radical has no symmetry in either the theoretical calculations or the ESR experimental results described above. Thus, it is much more difficult to assign a correct symmetry type for the excited state

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* To whom correspondence should be addressed: davidson@indiana.edu.

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in this no symmetry case. To make a correct assignment of the excited *3p* state, both the excitation energy and the transition dipole moments should be taken into account. In this paper, we calculated both the vertical and the adiabatic excitation energies and transition dipole moments of CH_2OH radical with and without C_s symmetry. The results are opposed to the $3p_z$ assignment. We also calculated the isotropic hyperfine splitting constants, which are in good agreement with the ESR experimental data. In addition, the results of the multireference perturbation theory are presented.

II. Computational Method

All calculations in this work were performed using MELD[23] and Gaussian 98.[24] The basis set used in the calculations is 6-311++G(*3d*,*3p*), which comes from 6-311++G(3*df*,3*pd*) without *f* and *d* for heavy and light atoms, respectively. To describe the single free electron in the radical, additional *sp* diffuse orbitals are augmented to oxygen and carbon nuclei with exponents 0.0146 and 0.02817, respectively. The geometry optimizations are carried out at three levels: density functional theory with Becke's three-parameter exchange functional[25] and the gradient-corrected Lee−Yang−Parr correlational functional[26] (B3LYP), unrestricted Hartree−Fock (UHF), and second-order Møller−Plesset perturbation theory (MP2). The vertical excitation energies and transition dipole moments are calculated with MRSD implemented in the MELD program. The adiabatic excitation energies and transition dipole moments are computed with CIS of Gaussian 98. In addition, the vertical excitation energies and transition dipole moments of the CH_2OH radical with the C_s symmetry are also calculated with MRSD for comparison. On the other hand, it is well-known that multireference perturbation theory (MRPT) provides another way to calculate the properties of the excited states.[27] The MRPT second- and third-order energies[28] defined in eq 1 are computed for comparison

$$E(\lambda, p) = \epsilon_p^{(0)} + \sum_{i,j\le n}\sum_{a=n+1}\frac{u_p^{(0)}(i)H_{ia}H_{aj}u_p^{(0)}(j)}{\epsilon_p^{(0)} - H_{aa}}\lambda^2 + \sum_{i,j\le n}\sum_{a,b=n+1,a\neq b}\frac{u_p^{(0)}(i)H_{ia}H_{ab}H_{bj}u_p^{(0)}(j)}{(\epsilon_p^{(0)} - H_{aa})(\epsilon_p^{(0)} - H_{bb})}\lambda^3 + ... \quad (1)$$

where λ is a perturbation parameter and is set to 1 in final results; n is the dimension of the reference space; $\epsilon_p^{(0)}$ and $u_p^{(0)}$ are the p-th eigenvalue and corresponding eigenvector of the Hamiltonian within the reference space, respectively; and, H_{ij} is the matrix element.

Electron spin resonance spectroscopy is one of the most widely used techniques to study the unpaired electron density within a molecule. The interaction of the electron spin with neighboring magnetic nuclei accounts for the magnetic spin hyperfine splitting. In this paper, the canonical virtual orbitals obtained from the restricted open-shell Hartree−Fock (ROHF) are converted to the *K*-orbitals[29] to carry out the hyperfine splitting parameter calculation.[30,31] All of these calculations are performed over three optimized structures of the CH_2OH radical.

III. Results and Discussion

TABLE 1: Geometry Parameters of CH_2OH Radical Optimized at UHF, B3LYP and MP2 Levels[a]

	UHF	B3LYP	MP2	MP2[b]
r(C−O)	1.354	1.365	1.368	1.365
r(O−H_1)	0.939	0.961	0.960	0.959
r(C−H_2)	1.075	1.081	1.079	1.074
r(C−H_3)	1.071	1.078	1.075	1.071
$\angle COH_1$	110.8	110.0	109.3	109.4
$\angle OCH_2$	118.0	119.9	118.4	120.4
$\angle OCH_3$	113.4	113.7	113.1	115.0
$\angle H_2COH_1$	29.7	21.4	24.7	0.0
$\angle H_3COH_1$	176.5	175.3	174.3	180.0
IP(eV)[c]	7.06	7.70	7.44	

[a] The last column is the transition state of CH_2OH optimized at the MP2 level. The last row shows the adiabatic ionization potential (eV) calculated with UHF, B3LYP, and MP2. The bond length is in Å, the angle in degrees. [b] Geometry of the planar transition state. [c] Exp. 7.56 eV ref 11.

TABLE 2: Geometry Parameters of CH_2OH^+ Cation Optimized at UHF, B3LYP, and MP2 Level[a]

	UHF	B3LYP	MP2
r(C−O)	1.227	1.245	1.249
r(O−H_1)	0.958	0.983	0.981
r(C−H_2)	1.080	1.091	1.086
r(C−H_3)	1.078	1.089	1.084
$\angle COH_1$	116.8	116.0	114.9
$\angle OCH_2$	121.7	121.8	121.5
$\angle OCH_3$	116.5	115.8	115.6

[a] The bond length is in Å, the angle in degrees.

To study the possible assignment of the Rydberg *p* state of the CH_2OH radical, the geometry structure of the radical was optimized at the UHF, B3LYP, and MP2 levels. Table 1 shows the optimized geometry parameters. The hydroxyl hydrogen is H_1, whereas the two alpha hydrogen atoms (CH_2) are H_2 and H_3, respectively, where H_1 is cis to H_2 and trans to H_3. The H_1, carbon, and oxygen nuclei together determine the x−y plane with the *y*-axis pointing from the carbon nucleus to the oxygen nucleus. It can be seen that the radical is not planar. The largest deviation from the plane is from the UHF calculation, whereas the smallest one is from B3LYP. The CO bond length 1.368 Å is smaller than the corresponding CO bond length 1.423 Å in methanol optimized with the same basis set at MP2 level. This contraction indicates the CO bond's partial double-bond character. The last column in Table 1 is the optimized geometry parameters of the CH_2OH radical with a C_s symmetry in a transition state. The structure of the CH_2OH^+ cation is also optimized at three levels as above. The results are listed in Table 2. The cation has a C_s symmetry; however, the two alpha hydrogen atoms are still not equivalent because of the hydroxyl. The CO double bond character is much more significant than in the radical, in agreement with the π^* character of the electron removed during ionization. The adiabatic ionization potential (IP) is calculated with the zero-point energy included and is listed in the last row of Table 1. It is easy to see that the IPs with MP2 and B3LYP optimized structures are in good agreement with the experimental data.

In Table 3 are the vertical excitation energies and transition dipole moments of the four lowest excited states calculated with MRSD in three geometric structures described above. The dimensions of the MRSD CI matrix are listed in parentheses in Table 3. The singly occupied orbital in the ground state is π^*.[20,21,22] First, the results with UHF geometry are examined. It is found that the first excited state is $\pi^* \rightarrow 3s$ by checking the CI coefficients and the orbital components. If the radical is assumed to have approximately C_s symmetry, then the ground state has A'' symmetry, and the first excited 3s state has A' symmetry. Therefore, the transition dipole moment of the *3s* state should be A''. This is in accordance with the calculated transition moment, of which the largest component has the

TABLE 3: Vertical Excitation Energies, Transition Dipole Moments, and Oscillatory Strengths of the CH_2OH Radical Calculated with MRSD (Equilibrium Positions Are Located at UHF, B3LYP, and MP2 Levels without Symmetry[a,b])

	energy	transition	ΔE	transition moment (eao) x	y	z	strength
1. UHF geometry (199,978)[c]							
1	−114.720 611	$A_1(\pi) \rightarrow A_2(s)$	4.72	0.0772	0.0309	−0.3209	0.012 71
2	−114.547 150	$A_1(\pi) \rightarrow A_3(y)$	5.48	0.0390	−0.0730	−0.3013	0.013 10
3	−114.519 389	$A_1(\pi) \rightarrow A_4(x)$	5.84	0.0440	0.0115	−0.0657	0.000 91
4	−114.506 134	$A_1(\pi) \rightarrow A_5(z)$	5.97	0.0349	−0.2943	−0.1188	0.014 92
5	−114.501 125						
2. B3LYP geometry (194,623)[c]							
1	−114.725 351	$A_1(\pi) \rightarrow A_2(s)$	4.60	0.0437	0.0351	−0.3165	0.011 64
2	−114.556 286	$A_1(\pi) \rightarrow A_3(y)$	5.35	0.0255	−0.0560	−0.3088	0.013 00
3	−114.528 651	$A_1(\pi) \rightarrow A_4(x)$	5.71	−0.0488	−0.0134	−0.0717	0.001 07
4	−114.515 356	$A_1(\pi) \rightarrow A_5(z)$	5.87	0.0228	−0.2850	−0.1075	0.013 44
5	−114.509 372						
3. MP2 geometry (201,183)[c]							
1	−114.722 837	$A_1(\pi) \rightarrow A_2(s)$		0.0541	0.0369	−0.3119	0.011 72
2	−114.549 755	$A_1(\pi) \rightarrow A_3(y)$		0.0260	0.0688	0.3082	0.013 45
3	−114.521 980	$A_1(\pi) \rightarrow A_4(x)$		0.0449	0.0175	0.0681	0.000 99
4	−114.508 905	$A_1(\pi) \rightarrow A_5(z)$		0.0284	−0.2881	−0.1129	0.014 15
5	−114.503 062						

[a] Experimental excitation energies 4.34 (eV) (ref 19), 5.10 (eV) (refs 14, 19), calculated energies in Hartrees, transition energies in eV, transition moments in $ea_{o,}$ oscillator strengths are dimensionless. [b] *y* is along CO and z is perpendicular to COH_1 plane. [c] The numbers in parentheses are the number of configurations in the MRSD expansion.

TABLE 4: Vertical Excitation Energies, Transition Dipole Moments, and Strengths of the CH_2OH Radical Calculated with MRSD[a,b]

	A''	A'	transition	energy (eV)	transition moment^2	oscillator strength
1	−114.757 885	−114.595 282	$1A'' \rightarrow 2A''$	5.76	0.100 97	0.014 24
2	−114.546 316	−114.567 415	$1A'' \rightarrow 1A'$	4.42	0.097 41	0.010 56
3		−114.552 095	$1A'' \rightarrow 2A'$	5.18	0.114 36	0.014 52
4			$1A'' \rightarrow 3A'$	5.60	0.010 46	0.001 44

[a] The radical is in a transition state and has a C_s symmetry optimized with MP2. Units: A.U. [b] A'' CI matrix dimension 190,856, A' CI matrix dimension 187 638.

required A'' symmetry. The character of the second excited state cannot be determined by the same analysis as the first excited state. The excitation energy 5.48 eV is close to the experimental value 5.10 eV.[14,19] Because the largest component of the transition moment is A'', the second excited state should be $^2A'$ ($3p_y$). The third state is also $^2A'$ and its small transition moment is consistent with $3p_x$. The fourth state is found to be $^2A''$ ($3p_z$) by the same analysis as above. However, its excitation energy is larger than the second state, whereas the magnitude of its oscillator strength is almost the same. Thus, neither excitation energy nor oscillator strength are in favor of the fourth excited state being assigned as the observed Rydberg *3p* state, as suggested in the experimental work.[22] The analyses of the results with B3LYP and MP2 structures in Table 3 lead to the same conclusion. In Table 4, there are results performed for the CH_2OH radical with C_s symmetry optimized at the MP2 level. It is not a minimum but a transition state for moving H_2 through the COH_1 plane. The purpose of this calculation is to make a clearer symmetry assignment for excited states. The first excited state is *3s*, the second and third states are still mixed, and the fourth $3p_z$. The first excitation energy 4.42 eV is in very good agreement with the experimental data 4.34 eV.[19] In comparison with the fourth excitation energy 5.76 eV, the second 5.18 eV is much closer to the experimental value 5.10 eV.[14,19] The oscillator strengths of the second and fourth excited states are almost the same. Therefore, it is almost impossible to assign the fourth excited state instead of the second one as the experimental observed Rydberg *3p* state,[14,19,22] if no other evidence is available.

Apart from the vertical excitation energies and transition dipole moments, the adiabatic counterparts are also calculated for a complete analysis. Table 5 shows the geometry parameters of the first four lowest excited states optimized with CIS. The four excited states all have planar structures, although the initial structures for optimization do not have planar structures. It is interesting to see that the second and third excited states have almost the same geometry. Table 6 lists the adiabatic excitation energies and transition dipole moments. All zero-point energies are taken into account. The first excited state is 3*s* $^2A'$, and its excitation energy 4.12 eV is very close to the experimental value 4.34 eV.[19] The second state is a mixture of *s*, p_x, and p_y states. The excitation energy 5.20 eV is also in very good agreement with the experimental value 5.10 eV.[14] The fourth state is again $3p_z$ $^2A''$. Its excitation energy is larger than the second state. On the other hand, its transition strength is slightly smaller than that of the second state. Therefore, no conclusion other than the above could be reached.

TABLE 5: Geometry Parameters of the First Four Excited States of the CH_2OH Radical optimized at CIS level[a]

	first	second	third	fourth
$r(C-O)$	1.207	1.230	1.230	1.217
$r(O-H_1)$	1.060	0.968	0.968	0.951
$r(C-H_2)$	1.083	1.075	1.075	1.069
$r(C-H_3)$	1.072	1.086	1.086	1.067
$\angle COH_1$	110.1	117.3	117.3	116.1
$\angle OCH_2$	118.8	122.0	122.1	121.7
$\angle OCH_3$	118.6	118.9	118.9	116.8
$\angle H_2COH$	0.0	0.0	0.0	0.0
$\angle H_3COH$	180.0	180.0	180.0	180.0

[a] The bond length is in Å, the angle in degrees.

The results of the second- and third-order MRPT energies with B3LYP geometry are presented for comparison. In Table

TABLE 6: CIS Adiabatic Excitation Energies, Vertical Transition Dipole Moments for Emission, and Oscillator Strengths of the CH_2OH Radical Calculated with CI Single Excitation Method[a,b]

	excited type		excitation energy (eV)	transition moment	oscillator strength
1	s	A'	4.12	0.193	0.0030
2	sp_xp_y	A'	5.20	0.392	0.0185
3	sp_xp_y	A'	5.72	0.028	0.0001
4	p_z	A''	5.80	0.311	0.0125

[a] Each state is optimized in CIS level. [b] Exp. 4.34 (eV) (ref 19), 5.10 (eV) (refs 14, 19).

TABLE 7: Excitation Energies of the First Four Excited States Calculated with the Second- and Third-order MRPT as Defined in Eq 2[a]

	98	305	527	645	exact
1. Zeroth-Order Energies + 114, Unit: a.u.					
1	−0.456 89	−0.483 88	−0.495 95	−0.500 65	−0.725 35
2	−0.283 28	−0.312 89	−0.325 47	−0.330 59	−0.556 26
3	−0.256 35	−0.285 71	−0.297 77	−0.302 71	−0.528 65
4	−0.239 41	−0.265 24	−0.276 45	−0.280 89	−0.515 36
5	−0.237 24	−0.263 54	−0.275 20	−0.279 37	−0.509 37
Excitation Energies, Unit: eV					
1→2	4.72	4.65	4.63	4.63	4.60
1→3	5.46	5.39	5.39	5.38	5.35
1→4	5.92	5.95	5.97	5.98	5.71
1→5	5.98	6.00	6.00	6.02	5.87
2. Second-Order Energies + 114, Unit: a.u.					
1	−0.788 47	−0.774 77	−0.769 94	−0.768 08	−0.725 35
2	−0.621 29	−0.596 88	−0.590 05	−0.587 40	−0.556 26
3	−0.596 15	−0.572 72	−0.566 17	−0.563 49	−0.528 65
4	−0.580 30	−0.557 99	−0.551 42	−0.549 16	−0.515 36
5	−0.569 92	−0.548 48	−0.542 11	−0.539 82	−0.509 37
Excitation Energies, Unit: eV					
1→2	4.54	4.84	4.90	4.92	4.60
1→3	5.23	5.50	5.54	5.57	5.35
1→4	5.66	5.90	5.95	5.96	5.71
1→5	5.94	6.16	6.20	6.21	5.87
3. Second- and Third-Order Energies + 114, Unit: a.u.					
1	−0.730 91	−0.732 30	−0.732 66	−0.732 87	−0.725 35
2	−0.562 23	−0.560 75	−0.560 07	−0.560 35	−0.556 26
3	−0.535 54	−0.535 10	−0.534 51	−0.534 47	−0.528 65
4	−0.523 02	−0.522 40	−0.521 27	−0.521 10	−0.515 36
5	−0.516 60	−0.515 48	−0.514 25	−0.514 16	−0.509 37
Excitation Energies, Unit: eV					
1→2	4.59	4.67	4.69	4.69	4.60
1→3	5.32	5.37	5.39	5.40	5.35
1→4	5.66	5.71	5.75	5.76	5.71
1→5	5.83	5.90	5.94	5.95	5.87

[a] The dimensions of the model space are 98, 305, 527, and 645, respectively. The dimension of MRSD space is 194 623. The last column is the exact matrix eigenvalue obtained by the Davidson method (ref 32).

TABLE 8: Isotropic Hyperfine Splitting Constant Calculated with ROHF, CI, and MRSD[a]

	ROHF	CI	MRSD	exp (ref 8)[b]
1. B3LYP Geometry[c]				
H_1	0.250	−3.269	−3.024	1.15
H_2	4.743	−13.723	−11.825	17.65
H_3	3.326	−15.902	−14.563	18.53
2. UHF Geometry[c]				
H_1	0.679	−2.472	−1.980	1.15
H_2	7.293	−9.126	−6.560	17.65
H_3	4.724	−12.970	−10.457	18.53
3. MP2 Geometry[c]				
H_1	0.314	−2.880	−2.361	1.15
H_2	6.167	−11.102	−8.433	17.65
H_3	4.327	−13.798	−11.232	18.53

[a] The geometry is optimized with B3LYP, UHF, and MP2. Unit: gauss. [b] Only absolute values determined at temperature 148 K. [c] The size of all CI matrices is 188 062. The sizes of MRSD matrix for B3LYP, UHF, and MP2 geometry are 180 255, 186 491, and 182 735, respectively.

7, the results determined according to eq 1 are displayed. The size of the reference space is 98. The corresponding results are listed in the second column. In the next three columns (Table 7), the results corresponding to the model space with larger sizes are given. The configurations in the model space come from the whole reference space plus those configurations outside the reference space, whose contributions to the required roots are considered to be largest according to the second-order MRPT energies. To select those configurations into the model space in a balanced way, the sum of the second-order MRPT energy from the selected configurations should be almost the same for each root so that the required roots are still reasonably separated in the model space. For example, if the 100 most important configurations are selected for the first root, their total contributions can be calculated by a simple sum. Then, configurations can be selected for other roots with almost the same contribution. In this way, the excitation energies calculated within the model space are close to the exact values obtained by the Davidson method,[32] as can be seen in Table 7. The absolute values are improved by the second-order correction and are slightly overestimated. Up to third order, both the absolute values and the excitation energies are very close to the exact values. The inaccuracy of the third-order estimate of the energy is only10^{-3} a.u. On the other hand, there are almost no improvements upon the absolute values and excitation energies with the increasing size of the model space. This is due to the slow convergence of the model space because the model space energies, even with the increasing size, are still well separated from the exact energies, as can be seen from the 0.2 au differences between the zeroth order energies in the model space and the exact values.

In Table 8 the isotropic hyperfine splitting constants of the three hydrogen nuclei calculated with ROHF, CI, and MRSD are shown. The ROHF results are poor because no correlation effect is taken into account. The CI and MRSD results with the three geometrical structures are all very close to the experimental results. These predict that all the proton hyperfine splitting constants are actually negative as would be expected for a radical with a delocalized π electron.

IV Conclusion

In this paper, the vertical excitation energies and transition dipole moments of the first four lowest excited states are calculated with CI and MRSD over four optimized structures with and without symmetry. The four excited states are also optimized with CIS. The transition dipole moments and the corresponding adiabatic excitation energies are determined at the same level. None of these calculations are in favor of the fourth excited state, $3p_z$ $^2A''$, as the experimental observed Rydberg $3p$ state, as suggested in a recent paper.[22] In addition, the CH_2OH^+ cation structures are optimized with UHF, B3LYP, and MP2. The ionization potentials calculated with B3LYP and MP2 structures are very close to the experimental value. The isotropic hyperfine parameters determined with CI and MRSD are all in good agreement with the experimental data. The preliminary results of MRPT are also presented. The test calculations indicate that very good excitation energies could be obtained with a relatively small effort in comparison with the large MRSD eigenvalue problem. As expected, intruder states do not appear in this so-called one-state-at-a-time theory.[27]

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