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Theoretical calculations of the spectroscopy of CH_3OH

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ABSTRACT

The ground and low-lying excited states of Methanol(CH_3OH) have been studied. The geometric parameters, energies and frequencies of the ground state and the triplet exited state were calculated by using the MP2(full)/6-311++G(2d,2p) level of theory. Beginning with the triplet state structure, the repulsive nature of the triplet state potential energy surface is explained. The vertical excitation energies of the singlet excited states of CH_3OH are calculated. It is found that the theoretical results performed by the TD-DFT(b3p86/6-311++G**) method are in best agreement with the experimental results. In addition, the vertical ionization energy, the adiabatic ionization energy, the vertical electron affinity and the adiabatic electron affinity are calculated. The theoretical results could serve as a guidance for experimental investigations.

KEYWORDS

Methanol(CH_3OH);
Ground state and triplet state;
Excitation energies;
Ionization energies;
The electron affinities.

INTRODUCTION

Methanol(CH_3OH) is an important species in both the atmospheres of Earth[1] and comets[2,3], and in interstellar Media[4]. The photochemistry of CH_3OH has received considerable attention over the last two decades[5,6]. Numerous studies on the absorption spectra of methanol have been carried out. Nee et al.[7] reported an absorption spectrum of methanol in the region of 105–200 nm. The absorption spectrum of CH_3OH shows a weak continuous feature in the 163–220 nm region, two intense systems with vibronic structure in the 140–151 and 151–163 nm regions, and some weak features upon a rising continuum at wavelengths smaller than 140 nm[8]. Sominska et al.[9] reported the absorption spectra of CH_3OH, CH_3OD, and CD_3OD in a supersonic jet and assigned another vibrational mode (CH_3 rocking) for the system in the region of 151–163 nm. Philis[10] reported resonance-enhanced multiphoton ionization spectra of jet-cooled methanol which is in complete agreement with the VUV absorption spectra[9,11]. What is more, the absorption spectra in the vacuum ultraviolet region of methanol in condensed phases[12] which is substantially different from gas phase results was reported recently.

Despite many theoretical and experimental reports about CH_3OH[7,8], the studies of the ground and low-lying excited states' properties of methanol(CH_3OH) are needed. The geometric parameters, energies and the harmonic vibrational frequencies of the ground state and the triplet excited state are calculated. The vertical excitation energies of the singlet excited states of CH_3OH are calculated and the theoretical results are in better agreement with the experimental results. What is more, the vertical ionization energy, the adiabatic ionization energy, the vertical electron affinity and the adiabatic electron affinity of the methanol are calculated and compared with available experimental results. These results are valuable and could serve as a guide for both the theoretical and experimental research in the future.

This paper is outlined as follows. In Sec.2, the theory and the calculation details are introduced. In Sec.3, the calculated results of the geometric parameters, the vertical excitation energies, the vertical ionization energy, the adiabatic ionization energy, the vertical electron affinity and the adiabatic electron affinity of the methanol are discussed. We end with a summary in Sec.4.

THEORETICAL METHOD

The MP2(full)/6-311++G(2d,2p) level of theory is chosen after comparing various theoretical results with experimental results. The geometric parameters, energies and frequencies of the ground state and the triplet exited state of methanol(CH_3OH) were calculated. All the computed harmonic frequencies are scaled by a factor of 0.9427. The vertical excitation energies of the singlet excited states of CH_3OH are also calculated. After comparing the singlet excited states' vertical excitation energies calculated by different methods and basis sets with the experimental results, it is found that the theoretical results performed by the TD-DFT[13](b3p86/6-311++G**) method are in best agreement with the experimental results. What is more, the ionization energies and the electron affinities of methanol(CH_3OH) are calculated.

The ionization energy could be regarded as the energy variance of abstracting an electron from the molecule and the electron affinities could be regarded as the energy variance of adding an electron into the molecule. The ionization energy could be divided into the vertical ionization energy and the adiabatic ionization energy; accordingly, the electron affinities could be divided into the vertical electron affinities and the adiabatic electron affinities. We used the optimized geometry of the ground state of CH_3OH to calculate the vertical ionization energy which is obtained from the energy difference between the positive molecular ion and the neutral CH_3OH molecule. The calculated adiabatic ionization energy is obtained from the energy difference between the positive molecular ion and the neutral CH_3OH molecule under their respective optimized geometries. The vertical electron affinity is obtained from the energy difference between the negative molecular ion and the neutral CH_3OH molecule. The calculated adiabatic electron affinity is obtained from the energy difference between the negative molecular ion and the neutral CH_3OH molecule under their respective optimized geometries. All of the calculations were performed using the GAUSS09 quantum chemistry software[14].

RESULTS AND DISCUSSION

The optimized equilibrium structures of the ground state and the lowest excited state of methanol

TABLE 1 presents the calculated geometric parameters and experimental results of methanol at various methods and basis sets. It could be found that the results at the MP2(full)/6-311++G(2d,2p) level of theory is in best agreement with the experimental results[15]. Therefore, the MP2(full)/6-311++G(2d,2p) level of theory is chosen for methanol molecule. For the ground state of methanol, the C-O bond length of 1.425 °A is 0.0004 °A larger than the experimental value of 1.4246. °A The H-O bond length of 0.957 °A is 0.0119 °A larger than the experimental value of 0.9451 °A. The bond angle of $\angle$COH is 108.1368 ° and the experimental value is 108.53°. The dihedral angle D(H,C,O,H) is 179.9778° and the experimental value is 176.73°.

Figure 1 exhibits the optimized ground state geometry of methanol at the MP2(full)/6-311++G(2d,2p) level of theory. Figure 2 exhibits the optimized triplet state geometry of methanol at the MP2(full)/6-311++G(2d,2p) level of theory. The calculated results indicate strongly that the ground state of methanol molecule(11A) has Cs symmetry and the triplet state has C1 symmetry.

TABLE 1 : The calculated geometric parameters and experimental results of methanol at various methods and basis sets(the unit of the bond length is °A and the unit of the bond angle is °)

Level	r(C-O)	r(C-H)	r(O-H)	∠COH	∠HCH	D(H,C,O,H)
Observed[15]	1.4246	1.0936	0.9451	108.53	108.63	-176.73
CCSD/6-311++G**	1.4201	1.0983	0.9577	107.6002	108.5173	180.016
CCSD(full)/6-311++G**	1.4185	1.0978	0.9572	107.6555	108.4878	-180.1152
CCSD/ aug-cc-pVDZ	1.4324	1.1058	0.9636	108.1289	108.6398	-180.0255
MP2/6-311++G(d,p)	1.4218	1.0959	0.9594	107.3441	108.528	179.9845
MP2(full)/6-311++G(d,p)	1.4203	1.0955	0.9589	107.4103	108.488	179.9904
MP2/6-311++G(2d,2p)	1.4269	1.0887	0.9578	108.0564	108.6139	180.0436
MP2(full)/6-311++G(2d,2p)	1.425	1.0875	0.957	108.1368	108.5712	179.9778
MP2/aug-cc-pVDZ	1.4348	1.1031	0.9658	107.8985	108.6967	179.9611
MP2/aug-cc-pVTZ	1.4235	1.0913	0.9611	108.0291	108.5987	179.9247
B3LYP/6-311++G**	1.4238	1.097	0.9613	108.8337	108.4043	179.9291
B3LYP/6-31++G(d)…	1.4251	1.0996	0.969	109.0437	108.5793	-180.0071
B3LYP/6-31++G(d,2p)	1.4254	1.0975	0.9641	108.8731	108.4588	179.9577

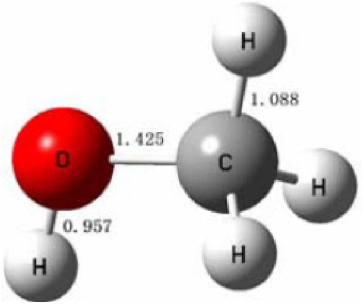

Figure 1 : The ground state geometry of methanol

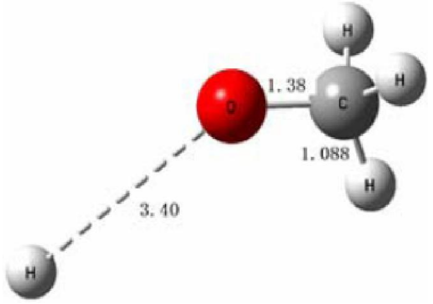

Figure 2 : The triplet state geometry of methanol

TABLE 2 : The geometric parameters and energies of the ground state(1^1A), triplet state(1^3A) of methanol(the unit of the bond length is °A,the unit of the bond angle is ° and the unit of energy is hartree)

State	r(C-H)	r(C-O)	r(O-H)	∠HCH	∠COH	D(H,C,O,H)	Energy
Observed[15]	1.0936	1.4246	0.945	108.63	108.53	176.73	
Ground	1.0875	1.425	0.957	108.57	108.14	179.98	-115.52
Triplet	1.0881	1.3795	3.390	107.57	94.12	-146.05	-115.34

TABLE 2 presents the optimized geometric parameters and energies of the ground state(11A) and triplet state(13A) of methanol at the MP2(full)/6-311++G(2d,2p) level of theory. The ground state geometric parameters are in good accordance with the experimental values. The triplet state's geometry and energy are compared with the counterpart of the ground state. The ground state energy of methanol at the MP2(full)/6-311++G(2d,2p) level of theory is -115.52hartree and the lowest triplet state energy of methanol is -115.34harstree. When the methanol molecule is excited to the triplet state(13A) optimized geometry, the O-H bond length is lengthened to 3.3895 $\overset{o}{A}$ and the C-O bond length is shortened to 1.3795 °A. The substantial increase in O-H bond length indicates strongly that the triplet state potential energy surface has repulsive nature. The corresponding product channel is to form H atom and CH_3O radical.

The calculated results of the excitation energies

The vertical excitation energies of the singlet excited states of CH_3OH are calculated. TABLE 3 presents the singlet excited states' vertical excitation energies calculated by different methods(TD-DFT and CIS) and basis sets at the MP2(full)/6-311++G(2d,2p) optimized geometry. It could be found that the TD-DFT results are more accurate

TABLE 3 : Vertical Excitation Energies(in nm) for Low-Lying Excited Electronic States of CH_3OH based on the geometry of MP2(full)/6-311++G(2d,2p) level along with the experimental results

CH_3OH	$X^1A'\rightarrow 1^1A''$	$X^1A'\rightarrow 2^1A''$
Experiment[9,11]	183.42	160.46
TD-pbepbe/6-311++G**	218.04	194.86
TD-pw91pw91/6-311++G**	219.97	195.60
TD-b3p86/6-311++G**	186.05	165.91
TD-b3lyp/6-31g(d)	160.77	128.90
TD-pbepbe/aug-cc-pVDZ	219.28	196.97
TD-pw91pw91/aug-cc-pVDZ	221.47	196.73
TD-b3p86/aug-cc-pVDZ	186.97	167.59
TD-b3lyp/6-311++G**	198.04	175.52
RCIS/6-311++G**	152.42	131.00

TABLE 4 : Vibrational frequencies of the ground and triplet state of methanol

State	Frequencies
Ground	271,994,1032,1123,1308,1422,1444,1456,2899,2964,3021,3607
Triplet	16,35,65,761,919,1054,1348,1357,1460,2854,2931,2968

TABLE 5 : Calculated vertical ionization potentials(VIP), adiabatic ionization potentials(AIP), vertical electron affinity(VEA) and adiabatic electron affinity(AEA) of CH_3OH

CH_3OH	VIP(in eV)	AIP(in eV)	VEA(in eV)	AEA(in eV)
MP2(full)/6-311++G(2d,2p)	11.32	11.18	0.893	0.888

than the CIS results compared with the experimental results. The theoretical results performed by different TD-DFT methods are quite different. It is found that the theoretical results performed by the TDDFT-b3p86 method are more adjacent to the experimental results than pbepbe and pw91pw91 methods. What is more, the excitation energies at different basis sets calculated by b3p86 are also different. The results calculated by b3p86/6-311++G** are much better than the counterparts calculated by b3p86/aug-cc-pVDZ compared with experimental results. In summary, the theoretical results performed by the TDDFT(b3p86/6-311++G**) method are in best agreement with the experimental results.

Harmonic frequencies

TABLE 4 presents the vibrational frequencies of the ground state and triplet state of methanol. It could be found that the vibrational strengths are the largest at wavenumbers of 271 and 994cm-1 which correspond to the rocking vibration and stretching vibration, respectively. As for the triplet state, the vibrational strength is the largest at wavenumber of 761cm-1 which corresponds to the rocking vibration. The calculated geometries of the ground and triplet states are stable because there are no imaginary frequencies.

Ionization energies

TABLE 5 presents the vertical ionization energy, the adiabatic ionization energy, the vertical electron affinity and the adiabatic electron affinity of methanol calculated at the MP2(full)/6-311++G(2d,2p) level.

The vertical ionization energy and the adiabatic ionization energy of methanol calculated at the MP2(full)/6-311++G(2d,2p) level are 11.32eV and 11.18eV,respectively. The calculated vertical electron affinity and the adiabatic electron affinity of the CH_3OH molecule are 0.893eV and 0.888eV, respectively. It could be concluded that the molecule needs more energy in losing an electron than obtaining an electron. That is to say, the ability of obtaining an electron is stronger than losing an electron. The calculated results could serve as a guidance for experimental observations.

CONCLUSIONS

The ground and low-lying excited states of methanol(CH_3OH) molecule have been studied. The MP2(full)/6-311++G(2d,2p) level of theory is chosen after comparing various theoretical results with the experimental results. The geometric parameters, energies and frequencies of the ground state and the triplet state were calculated. The results of the harmonic vibrational frequencies indicate strongly that the calculated geometries of the ground and triplet state are stable. Beginning with the triplet state structure, the repulsive nature of the triplet state potential energy surface is explained. The vertical excitation energy of the singlet excited states of CH_3OH are calculated. After comparing the singlet excited states' vertical excitation energies calculated by different methods and basis sets with the experimental results, it is found that the theoretical results performed by the TDDFT(b3p86/6-311++G**) method are in best agreement with the experimental results. The calculated vertical ionization energy and adiabatic ionization energy of the methanol at the MP2(full)/6-311++G(2d,2p) level are 11.32eV and 11.18eV while the calculated vertical electron affinity and the adiabatic electron affinity of the CH_3OH molecule are 0.893eV and 0.888eV, respectively. The calculated results could serve as a guidance for experimental observations.

REFERENCES

[1] E.Murad, W.Swider, R.A.Moss et al.; Geophys.Res. Lett., **11**, 147 **(1984)**.
[2] J.M.Greenberg; Astron.Astrophys.330(1998) 375.
[3] Y.L.Yung, W.B.De More; New York: Oxford University Press, **(1999)**.
[4] T.Jacq, C.M.Walmsley, R.Mauersberger et al.; Astron.Astrophys., **271**, 276 **(1993)**.
[5] Z.C.Chen, A.T.J.B.Eppink, B.Jiang et al.; Phys. Chem.Chem.Phys., **13**, 2350 **(2011)**.
[6] K.J.Yuan, Y.Cheng, F.Y.Wang et al.; Chin.Journ. Chem.Phys., **21**, 301 **(2008)**.
[7] J.B.Nee, M.Suto, L.C.Lee; Chem.Phys., **98**, 147 **(1985)**.
[8] D.R.Salahub, C.Sandorfy; Chem.Phys.Lett., **8**, 71 **(1971)**.
[9] E.Sominska, A.Gedanken; J.Mol.Spectrosc., **175**, 234 **(1996)**.
[10] J.G.Philis; Chem.Phys.Lett., **449**, 291 **(2007)**.
[11] B.M.Cheng, M.Bahou, W.C.Chen et al.; J.Chem. Phys., **117**, 1633 **(2002)**.
[12] Y.P.Kuo, H.C.Lu, Y.J.Wu et al.; Chem.Phys.Lett., **447**, 168 **(2007)**.
[13] N.A.Besley, A.Noble; J.Phys.Chem.C, **111**, 3333 **(2007)**.
[14] M.J.Frisch, G.W.Trucks, H.B.Schlegel et al.; Inc Pittsburgh PAÿGaussian, **(2009)**.
[15] M.D.Harmony, V.W.Laurie, R.L.Kuczkowski et al.; J.Phys.Chem.Ref.Data., **8**, 619 **(1979)**.