

The Effect of Basis Set on Quantum Tunneling Probability with the Case of trans-HCOH Isomerization

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Abstract. We investigate the effects of basis set in quantum tunneling probability in the case of trans-HCOH isomerization to H₂CO. Based on Density Functional Theory (DFT) calculation with B3LYP as functional exchange-correlation and 6-31G(d,p) as basis set, Rizka et al. found that trans-HCOH molecule has half life for 2.5 hours. The result has 0.7 hour longer than experimental result done by Schreiner et al. In this study, we used five variations of basis set which are: STO-3G, 6-31G, 6-31G(d,p), 6-31+G(d,p), and LANL2DZ. We started to investigate the effects of basis set on the electronic structure and vibrational frequency of the molecules. Then, we investigated the effects of basis set on quantum tunneling probability in molecule. Based on quantum tunneling probabilities, we could calculate half-life of trans-HCOH isomerization to H₂CO. We compare our results to the experimental result done by Schreiner et al. The results show that basis set increases the quantum tunneling probability of the isomerization.

1. Introduction

Description of the electronic structure of a system is given by two physical quantities, which are wave function (ψ) and energy (E). ψ and E of a system is obtained by solving the Schrödinger equation. [1] In predicting molecular electronic structure, one of the solutions is the Linear Combination of Atomic Orbitals (LCAO). Each atomic orbital is formed from linear combination of basis functions. [2] The two basis functions that commonly used are Slater and Gaussian functions. The atomic orbitals approached with Slater function are called Slater Type Orbital (STO). The atomic orbitals approached with Gaussian function are called Gaussian Type Orbital (GTO).

LCAO of atoms and molecules are constructed by basis set based on hydrogen atomic orbitals. Computationally, basis set formed from GTO is easier to solve than STO. Basis set contained the minimum number of basis functions needed for each atom is called minimal basis sets. The first way that a basis set can be made larger is to increase the number of basis functions per atom, such as polarized basis sets and diffuse functions. [3]



Basis set can affect the molecular energy calculations of trans-HCOH isomerization to H₂CO. The molecular energy calculations have been performed by Rizka et al. [4, 5] based on Density Functional Theory (DFT) with 6-31G(d,p) as basis set and B3LYP as functional exchange correlation. Rizka et al. found that trans-HCOH molecule has half-life 2.5 hours. Meanwhile, the experimental result done by Schreiner et al. [6] found that trans-HCOH molecule has half-life 1.8 hours at a temperature of 11 K. The half-life difference between DFT calculation and experiment becomes an interesting topic to study.

We attempt to study the effect of basis set on quantum tunneling probability of trans-HCOH isomerization using DFT. We calculate the quantum tunneling probability using Wentzel-Kramers-Brillouin (WKB) approximation [1] and Eckart Model [8] to get the half-life of its corresponding basis set. We verify that quantum tunneling probability is affected by the basis set.

2. Computational Detail

We study the isomerization of trans-HCOH to H₂CO in various basis set. We selected five basis set contained Gaussian function [3], which are STO-3G, 6-31G, 6-31G(d,p), 6-31+G(d,p), and LANL2DZ. We use B3LYP as an exchange-correlation functional.

We model trans-HCOH and H₂CO as shown in Figure 1a and 1b respectively. We determine their ground state electronic structures on singlet spin state using DFT. We compare our calculation results with other calculation using coupled cluster [6] and experimental data [7].

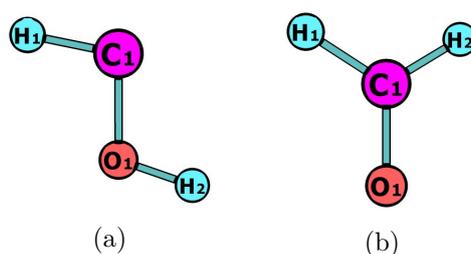


Figure 1: Molecular geometry of (a) trans-HCOH dan (b) H₂CO.

We predict the transition state structure using STQN method. We perform frequency calculation to confirm the existence of imaginary frequency on transition state structure.

We perform IRC calculation to map out the reaction path which connects trans-HCOH with H₂CO. We fit a function to IRC calculation data to obtain the potential barrier as function of position. Hence, we able to calculate the quantum tunneling probability using Wentzel-Kramers-Brillouin (WKB) approximation [1] and Eckart Model [8].

We perform DFT, frequency, and IRC calculations using Gaussian09 software package [9].

3. Results and Discussion

3.1. Molecular Structure

Figure 2 shows the relative energy diagram of H₂CO and trans-HCOH on singlet spin state. The results show that H₂CO is more stable than trans-HCOH in five selected basis set. It indicates that basis set does not affect the electronic energy of trans-HCOH isomerization.

Our DFT calculations obtain the geometrical structure parameters of H₂CO and trans-HCOH in five selected basis set which are listed in Table 1 and Table 2, respectively. The structure labeling is based on Figure 1. The results show that ground state electronic structure in STO-3G, 6-31G, and LANL2DZ basis set significantly affect the geometrical structure of H₂CO and trans-HCOH. Meanwhile, ground state electronic structure in 6-31G(d,p) and 6-31+G(d,p) basis set do not significantly affect the geometrical structure of H₂CO and trans-HCOH.

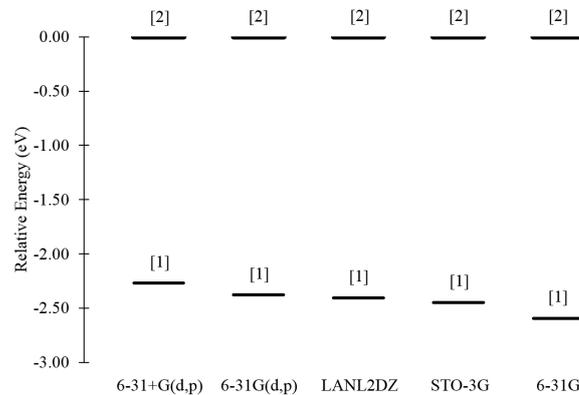


Figure 2: Relative energy diagram of [1] H_2CO and [2] trans-HCOH in various basis set. The total energy of trans-HCOH is used as reference point.

Table 1: Geometrical parameters of H_2CO from calculation results (Calc.), experimental data (Expr.) [7], and coupled cluster (CC.) [6]. " Δ " is the discrepancy between our calculation and experimental data and coupled cluster method, negative value means Calc. underestimates.

Basis Set	Parameter								
	C1-O1 (\AA)			C1-H1 (\AA)			H1-C1-H2 ($^\circ$)		
	Calc.	$\Delta(\text{Expr.})$	$\Delta(\text{CC.})$	Calc.	$\Delta(\text{Expr.})$	$\Delta(\text{CC.})$	Calc.	$\Delta(\text{Expr.})$	$\Delta(\text{CC.})$
STO-3G	1.250	0.042	0.046	1.125	0.009	0.014	113.5	-3.0	-
6-31G	1.231	0.023	0.027	1.102	-0.014	-0.009	115.7	-0.8	-
6-31G(d,p)	1.207	-0.001	0.003	1.110	-0.006	-0.001	115.2	-1.3	-
6-31+G(d,p)	1.209	0.001	0.005	1.108	-0.008	-0.003	116.1	-0.4	-
LANL2DZ	1.241	0.033	0.037	1.106	-0.010	-0.005	116.1	-0.4	-
Expr.		1.208			1.116			116.5	
CC.		1.204			1.111			-	

Table 2: Geometrical parameters of trans-HCOH from calculation results (Calc.) and coupled cluster (CC.) [6]. " Δ " is the discrepancy between our calculation and coupled cluster method, negative value means Calc. underestimates.

Basis Set	Parameter					
	C1-O1 (\AA)		C1-H1 (\AA)		H1-C1-O1 ($^\circ$)	
	Calc.	$\Delta(\text{CC.})$	Calc.	$\Delta(\text{CC.})$	Calc.	$\Delta(\text{CC.})$
STO-3G	1.368	0.057	1.161	0.050	97.7	-4.6
6-31G	1.354	0.041	1.125	0.014	101.3	-1.0
6-31G(d,p)	1.320	0.009	1.124	0.013	101.3	-1.0
6-31+G(d,p)	1.317	0.006	1.116	0.005	101.8	-0.5
LANL2DZ	1.362	0.051	1.127	0.016	101.8	-0.5
CC.		1.311		1.111		102.3

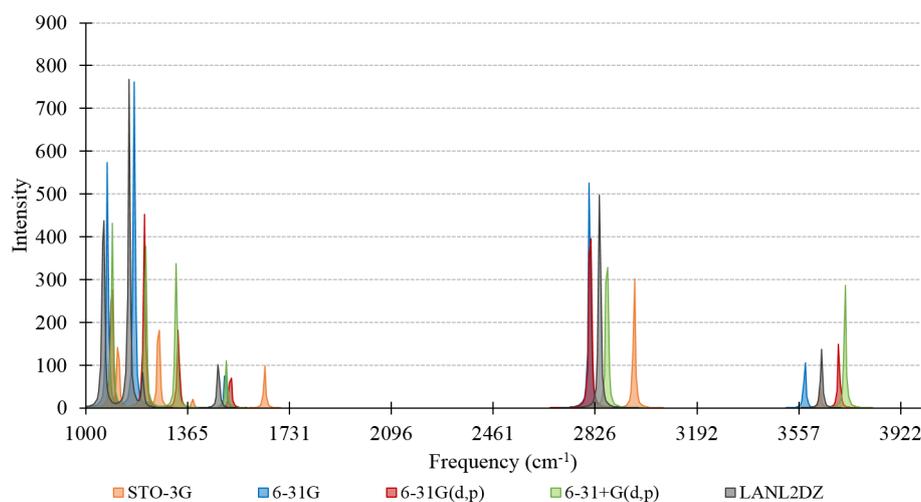


Figure 3: Vibrational frequencies of trans-HCOH in various basis set.

Beside ground state energy and geometrical structure, we obtain vibrational frequencies of trans-HCOH in five selected basis set as shown in Figure 3. The results show that there is significant difference in vibrational frequency. It indicates that the basis set significantly affect the vibrational frequency of molecule.

Table 3 lists the vibrational frequencies of trans-HCOH. Based on the type of motion, there are two vibrational modes that most possible to change geometry of trans-HCOH to H₂CO. There are mode 2 (ν_2) and mode 4 (ν_4). From those vibrational modes, the most possible one to change trans-HCOH into H₂CO is selected by the highest intensity, which is mode 2 (ν_2). We used this vibrational frequency to calculate isomerization rate (k) of molecule.

Table 3: Vibrational frequencies of trans-HCOH in 6-31G(d,p) basis set as the result of frequency calculation.

Mode	Calc.(1/m)	Type of motion	Intensity	Modes's name
1	1116.47	H1-H2 wagging	56.7342	ν_1
2	1261.34	H1-H2 rocking	75.6696	ν_2
3	1383.03	C1-O1 symmetrical stretching	6.2681	ν_3
4	1641.83	H1-H2 scissoring	28.5343	ν_4
5	2966.98	H1-C1 symmetrical stretching	92.986	ν_5
6	3634.44	H1-C1 symmetrical stretching	14.3356	ν_6

3.2. Energy Barrier

Figure 4 shows a potential barrier function of trans-HCOH. The potential barrier function acts as the reaction path which connects trans-HCOH to H₂CO through a transition state. We obtain eckart model to our IRC calculation data.

Table 4 shows the barrier parameter of isomerization of trans-HCOH to H₂CO. The results show that STO-3G, 6-31G, and LANL2DZ basis set significantly affect the barrier parameter of the isomerization. Meanwhile, 6-31G(d,p) and 6-31+G(d,p) basis set do not significantly affect the barrier parameter of the isomerization.

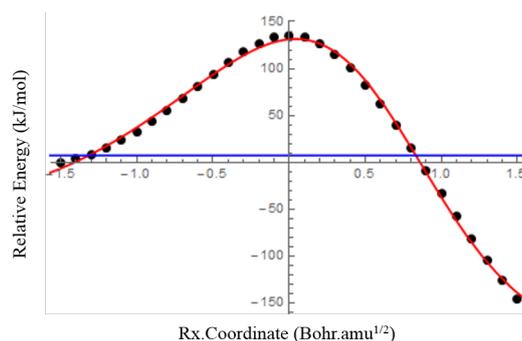


Figure 4: Potential energy curve is the reaction path of the isomerization of trans-HCOH to H₂CO in 6-31G(d,p). The blue line represents zero-point energy (ZPE). The red line is the fitted function which acts as energy barrier.

Table 4: Barrier parameters from calculation results (Calc.) and coupled cluster (CC.) [6]. "Δ" is the discrepancy between our calculation and coupled cluster method, negative value means Calc. overestimates.

Basis Set	Parameter					
	$V_b(x)$ (KJ/mol)		x (bohr \sqrt{amu})		E_{ZP} (KJ/mol)	
	Calc.	Δ(CC.)	Calc.	Δ(CC.)	Calc.	Δ(CC.)
STO-3G	181.96	-57.61	2.36	-	7.55	-0.25
6-31G	148.94	-24.59	2.25	-	7.03	0.27
6-31G(d,p)	138.41	-14.06	2.15	-	7.25	0.05
6-31+G(d,p)	143.14	-18.79	2.16	-	7.27	0.03
LANL2DZ	153.98	-29.63	2.28	-	6.92	0.38
CC.	124.35		-		7.30	

3.3. Quantum Tunneling Probability

Table 5 shows the quantum tunneling probability of isomerization of trans-HCOH to H₂CO using WKB approximation and Eckart model. Quantum tunneling probability increases as the size of basis set is increased.

Table 6 shows the half-life of isomerization of trans-HCOH to H₂CO using WKB approximation and Eckart model. We compared our results with experimental result [6]. The results show that 6-31G(d,p) has the best half-life to studying the isomerization of trans-HCOH to H₂CO.

4. Conclusion

This study reports that STO-3G, 6-31G, and LANL2DZ basis set significantly affect the geometrical structure and barrier parameter of the isomerization. Meanwhile, 6-31G(d,p) and 6-31+G(d,p) basis set do not significantly affect the geometrical structure and barrier parameter of the isomerization. Moreover, the basis set increases the quantum tunneling probability of the isomerization. 6-31G(d,p) basis set is the best basis set to studying the isomerization of trans-HCOH to H₂CO.

Table 5: Quantum tunneling probability of the isomerization of trans-HCOH to H₂CO based on WKB approximation and Eckart Model

Basis Set	Quantum tunneling probability	
	WKB	Eckart Model
STO-3G	2.92×10^{-23}	2.78×10^{-20}
6-31G	3.61×10^{-20}	5.69×10^{-18}
6-31G(d,p)	1.44×10^{-18}	4.52×10^{-19}
6-31+G(d,p)	5.34×10^{-19}	1.13×10^{-17}
LANL2DZ	7.39×10^{-21}	1.34×10^{-18}

Table 6: Half-life of the isomerization of trans-HCOH to H₂CO based on WKB approximation and Eckart Model

Basis Set	Half-life (Hour)	
	WKB	Eckart Model
STO-3G	174208.0	11887300.0
6-31G	151.6	1065.0
6-31G(d,p)	3.7	11.3
6-31+G(d,p)	9.9	33.1
LANL2DZ	751.1	4427.5

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