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Structure and Vibrational study of Entrance Channel of Monomer $C_2H_2 + Cl$ via *ab initio* calculation

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ABSTRACT

Theoretical calculations are reported to predict the geometrical structures and IR vibrational frequencies of entrance channel of $C_2H_2 + Cl$ interaction in the ground state. The calculations are performed via *Ab initio* calculations at perturbation theory (MP2) with Dunning correction-consistent basis set (aug-cc-pVDZ). The results show that attaching acetylene molecule with radical chlorine via van der Waals bonds has two equilibrium structures. These structures have IR active of harmonic vibrational frequencies. In one of these structures; Cl atom bonded to a particular H atom which has a single IR active of C-H asymmetric stretching vibration at 3428 cm^{-1} . The other structure, in which Cl atom attached to both of H atoms (T- shape), predicted harmonic vibration at 3424 cm^{-1} for asymmetric C-H stretch. The rear geometrical structure is lower minimum energy than the former one by 11.78 KJ/mol . Finally, the barrier for the interconversion from one minimum to the other is also computed in this study.

Introduction

Shape of the reaction potential energy surface is well known to have a significant influence on reaction dynamics [1]. It can steer the reaction from reactants to products via the transition state [1, 2]. Long range interactions in ion- molecule systems have been studied widely [1]. In contrast, few studies have focused on the van der Waals minima of neutral reactions on reacting potential energy surfaces [3-9]. For instance, research of $Cl + HD$ reaction indicates that these minima can have a major impact on the reaction process: entrance channel minima have a role in orientating reactants prior to the transition state [6-9], while exit channel minima can affect the quantum state populations of the products [2]. Therefore, atoms with different types of molecules show that the potential energy surfaces are becoming accessible to realistic quantum mechanics simulation. A significant study of the entrance and exit channel have been studied theoretically for $Cl + CH_4$ reaction using *ab initio* calculations, which showed the importance of channels on the reaction dynamics [10]. Since halogen atoms have a great role in chemistry environment, many research had been done to predict the minimum equilibrium structure for the halogen atoms – molecule, especially of Cl attached to HCl [11-19]. These studies predicted that the minimum

equilibrium structure for the $Cl - HCl$ system is T-shaped instead of the linear shape that was concluded via previous studies [11-19]. However, these studies did not include vibrational of C_2H_2 attached to Cl. Since C_2H_2 is important complex in the organic and industrial chemistry, many spectroscopic experimental studies concentrate on it [20-27]. Therefore, it is worth to study spectroscopy of C_2H_2 attached with halogen atoms particularly Cl atom. Recently, investigations have been reported for interaction Cl atom with C_2H_2 [28]. The results explored reaction coordinates of the transition states of $Cl + C_2H_2$ [28], however the work did not predict IR vibrational frequencies and equilibrium structures. The goal of this paper is to probe the structure of the entrance channel of $C_2H_2 + Cl$ and utilise for first the time its C-H stretching vibration in the IR region via *ab initio* harmonic frequencies.

Method

GAUSSIAN 03 software (2003) was used for the *ab initio* calculations. This software depends on theoretical calculations, which is one of the most advanced simulation of theory in recent year [29]. The methodology was second order perturbation theory (MP2) together with basis set of aug-cc-pVDZ (Dunning correlation-consistent basis set) to

incorporate electron correlation [30]. This level of theory and basis set was used only for predicting the potential energy minima and corresponding vibrational frequencies in the entrance channels for $\text{Cl} + \text{C}_2\text{H}_2$ reactions. However, barrier energy between both minima has been calculated using OPT (optimisation) = QST (Gaussian the Synchronous Transit-guide Quasi-Newton method) with 6-311G** basis set instead of aug-cc-pVDZ. Here, the 6-311G** basis set is used to calculate highest energy for the structure (transition states) since this basis set adds diffuse functions to heavy atoms and a diffuse 'S' orbital to Hydrogens.

Results and discussion

Before presenting the results for the entrance channel complex, the results for calculations on the isolated acetylene molecule are presented. These calculations serve to give some indications of the quality of the methodology employed. *Ab initio* calculation of C_2H_2 predicted $\text{C}\equiv\text{C}$, C-H bond lengths, and C-C-H angle as 1.23 Å, 1.07 Å and 179.9° , respectively. These values are in quite agreement with experimental results which were recorded 1.203 Å, 1.06 Å and 180° of $\text{C}\equiv\text{C}$, C-H bond lengths and C-C-H angle, respectively [31]. Given the high symmetry of acetylene there is only one observable band in the IR spectrum in a CH stretching region (Figure 1). The IR active mode corresponds to C-H stretching mode. Theoretical calculations in this work are predicted 3432 cm^{-1} vibration frequency for asymmetric mode (Figure 1). The experimental value of asymmetric C-H stretching is 3374 cm^{-1} [31]. *Ab initio* calculations predicted C-H IR stretching higher by 58 cm^{-1} than the observed value. There are two main reasons to explain the differences between theoretical prediction and the experimental results, one reason is related to that the theoretical calculations predicts a harmonic vibration oscillator only while the practical case includes anharmonic oscillator. Other cause is that our calculations have been done by using MP2 method, which is not covers all electron correlation, although it includes majority of electron correlation. The intensity of C-H stretching vibration relates to the larger size of the transition dipole moment of C-H IR stretching of C_2H_2 (strong band absorption).

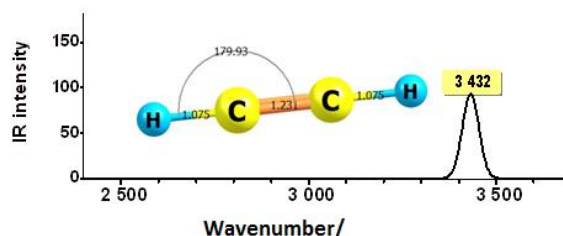


Fig. 1: Structure and vibration frequency of C_2H_2

Ab initio calculations on $\text{Cl} + \text{C}_2\text{H}_2$ predict entrance channel complex with two possible equilibrium structures where the chlorine atom is bonds to a specific hydrogen atom in one structure (Figure 2.a) and in the other structure the Cl atom connects to

both C atoms of the C_2H_2 (Figure 2. b). The second of these minima is calculated to have the deeper minimum. The calculations predicted well depths in the entrance channel region of 1.22 kJ mol^{-1} and 13 kJ mol^{-1} for the structures in Figure 2.a and Figure 2.b, respectively, as summarized in Figure 3. In addition, transition state which is the highest potential energy [32] between both structures is predicted using 6-311G** basis.

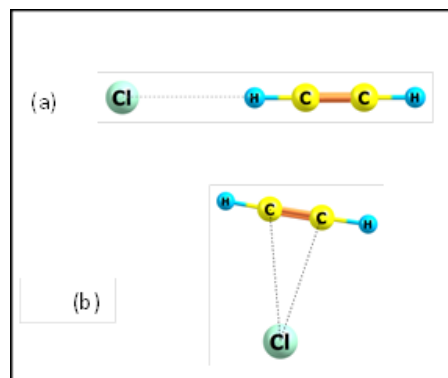


Fig. 2: Calculated equilibrium structures for the entrance channel complex (a) with the Cl bound to a particular H atom ($\text{Cl}-\text{C}_2\text{H}_2$), (b) Cl bound to both C atoms of C_2H_2 .

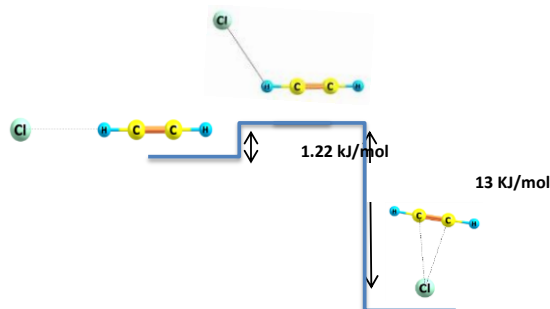


Fig. 3: Schematic of potential energy surface of the $\text{Cl} + \text{C}_2\text{H}_2$ reaction. The minimum energies are calculated via pVDZ basis sets while the transition state is predicted by using 6-311G** basis set. Energies are relative to $\text{Cl} + \text{C}_2\text{H}_2$. Note that this diagram is not scaled.

Vibrational frequencies have been calculated for both structures in entrance channel for $\text{Cl} + \text{C}_2\text{H}_2$ (Figures 4 and 5) in CH stretching region in a range from 2400 to 3600 cm^{-1} . For the first structure (Figure 2 (a)), the highest vibrational frequency is related to asymmetric C-H stretching and is predicted in the entrance channel at 3428 cm^{-1} (Figure 4). It is lower than the C-H stretching vibration of C_2H_2 alone (3432 cm^{-1}) (Figure 1) by about 4 cm^{-1} . It could be said that the line 3428 cm^{-1} is not easy to distinguish during an experimental work because the difference is only 4 cm^{-1} between CH asymmetric of pure acetylene and that of $\text{Cl} + \text{C}_2\text{H}_2$. However, it could be used techniques of testing the change in IR intensity before and after adding Cl atoms to C_2H_2 . In addition, it is possible to distinguish these IR spectra of the entrance channel in C-H as those in most recent experiments [33].

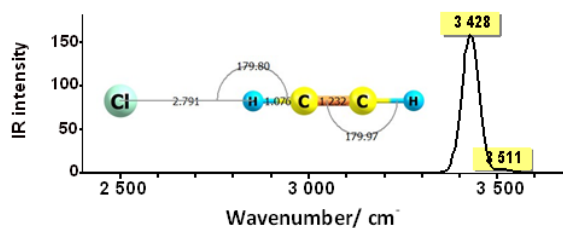


Fig. 4: Predicted of IR spectrum of C_2H_2 -Cl entrance channel complex with the Cl bound to a particular H atom ($Cl-C_2H_2$).

The second structure $Cl-C_2H_2$ (Figure 2 (b)) has a C-H stretching 3424 cm^{-1} which is less than C-H stretching of C_2H_2 alone (Figure 1) by 8 cm^{-1} . This could be easier than the first structure (Figure 2 (b)) to distinguish as the differences in C-H stretching vibrations more than those for the first structure. In addition, its intensity is acceptable in comparison to the intensity of C-H stretching in C_2H_2 (Figure 1). Overall, the $Cl-C_2H_2$ structure (Figure 2 (b)) will be distinguished easier than the first structure $Cl-C_2H_2$ (Figure 2 (a)) because it has the 3424 cm^{-1} (Figure 5)

C-H stretching with 4 cm^{-1} difference from the IR (Figure 4) of C-H stretching of the first structure (Figure 2 (a)). Mass spectroscopy could be used to solve the challenging in distinguish between the C-H stretching of the pure C_2H_2 and C-H stretching of the entrance channel [34]. All Bond lengths and bond angles for all structures concluded in this work are explored in table (1).

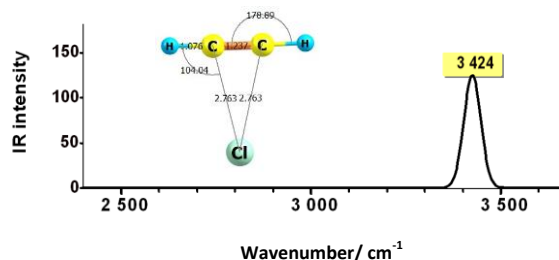


Fig. 5: Predicted of IR spectrum of C_2H_2 -Cl entrance channel complex with the Cl bound to both C atoms of C_2H_2 .

Table 1: Bond length, bond angle and cartesian coordinates of all structures that predicted in this work.

Structure	Bond length (Å)	Bond angle	Cartesian Coordinates				
	C-H = 1.075	H-C-H=179.9°	Sequence	Atomic number	x	y	z
	C≡C = 1.232		1	6	0.000162000	0.615617000	0.000000000
	H-C = 1.076	Cl-H-C=179.80	2	6	0.000162000	-0.615632000	0.000000000
	C-C-H = 179.97	C-C-H=179.97	3	1	-0.001123000	-1.690765000	0.000000000
	Cl-H = 2.791		4	1	-0.000819000	1.690854000	0.000000000
	C≡C = 1.232						
	H-C = 1.076	H-C-C = 178.9	Sequence	Atomic Number	x	y	z
	C≡C = 1.237	Cl-C-H = 104	1	1	1.496027000	1.694680000	0.000162000
	C-Cl = 2.763		2	6	1.475373000	0.618543000	0.000112000
			3	6	1.475392000	-0.618527000	0.000038000
			4	1	1.496187000	-1.694652000	0.000367000
			5	17	-1.217459000	-0.000007000	-0.000084000
	Cl-H = 2.97	Cl-H-C = 125.64	Sequence	Atomic Number	x	y	z
	H-C = 1.076		1	1	-0.162653315	0.187191361	0.158981308
	C≡C = 1.231		2	6	-0.098250484	-0.009169949	1.228054181
			3	6	-0.018734557	-0.023530453	2.451328664
			4	1	0.042129378	-0.115352355	3.521192016
			5	17	-1.526709390	1.466323575	5.485949330

Conclusion

In the current work, structures, vibrational frequencies of $Cl + C_2H_2$ as a new work, transition state and the relative energies of the equilibrium structures are predicted. The $Cl+C_2H_2$ structure (T-Shape) of the entrance channel is easy to observe in

References

IR spectroscopy (Figure 5), while the $Cl - C_2H_2$ (linear shape) could be difficult to detect. Vibration frequencies of C_2H_2 attached with Cl are higher intensity than the intensity of C-H stretching in C_2H_2 structure.

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دراسة الشكل الفراغي وترددات الاهتزازية عند قناة المدخل لتفاعل C₂H₂+ Cl باستخدام الحسابات

الاساسية Ab-Initio

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قسم الفيزياء ، كلية التربية ، جامعة السليمانية ، السليمانية ، العراق

الملخص

تم اجراء الحسابات النظرية لتوقع الشكل الهندسي والترددات الاهتزازية في منطقة تحت الحمراء لتفاعل جزيئة اسيتيلين مع ذرة كلور في المستوى الارضي. تم استخدام الحسابات Ab-Initio مع الرتبة الثانية لنظرية الاضطراب ومجموعات الاساس (aug-cc-pVDZ) ضمن تصحيح Dunning. وظهرت النتائج شكلين هندسيين من اتحاد جزيئة اسيتيلين وذرة الكلور بواسطة اواصر فاندرفالز: ففي الشكل الاول اتحدت ذرة الكلور مع احدى ذرتي الهيدروجين، وظهرت تردد C-H هارموني عند 3428 سم⁻¹. اما في الشكل الهندسي الثاني فقد اتحدت ذرة الكلور مع كلا ذرتي الهيدروجين (شكل حرف T) وقيمة التردد 3424 سم⁻¹. وظهرت النتائج بان الشكل الهندسي الاخير ذو طاقة استقرار اقل من الشكل السابق. وقد تم حساب الشكل الهندسي الانتقالي بين الشكلين الاول والثاني ايضا في هذه الدراسة.