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IR Spectra of Entrance and Exit Channels of Methane Molecule and Oxygen Atom Reaction at MP2 Theory

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Abstract

IR spectra of entrance and exit channels of methane and radical oxygen reaction are predicted in the ground state energy. *Ab* initio calculations at perturbation theory (MP2) with Dunning correction- consistent basis set (aug-cc-pVDZ) have been used. The calculations predicted structures, vibrational frequencies and potential energy surface. Three van der Waals minima from three adiabatic potential energy surfaces have been predicted in entrance and exit channels. Vibration frequency of 3209 cm^{-1} and 3212 cm^{-1} of C-H stretching in entrance structures are predicted while O-H vibrational frequency is predicted to be at 3673 cm^{-1} in the other channel. The lowest energy structure in entrance channel has - 0.18 kJ/ mol minimum energy.

Keywords: IR spectra ; vibrational frequency; entrance channel; exit channel; Ab initio calculations.

اطياف تحت الحمراء لقناتي المدخل والمخرج لتفاعل جزيئة ميثان مع ذرة اوكسجين

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الخلاصة

تم اجراء حسابات نظرية لايجاد اطياف اشعة تحت الحمراء لقناتي المدخل والمخرج لتفاعل جزيئة الميثان مع ذرةالاوكسجين في المستوى الارضي. استخدم الحاسابات Ab–initio مع المرتبة الثانية لنظرية الاظطراب MP2 ومجموعات الاساس (aug–cc–pVDZ). تم حساب الشكل الفراغي و الترددات الاهتزازية و مستوى طاقة الجهد .حيث اظهرت الحسابات شكلين هندسيين عند المستوى الطاقي الارضي لقناة المدخل حيث يتحد ذرة الاوكسجين مع احد ذرات الهيدروجين في جزيئة الميثان باواصر فاندرفالز وبترددات 3202.9 و 3212سم$^{-1}$, اما في الشكل الهندسي الثاني ,يلتقي ذرة الهيدروجين مع اجد واجهات جزيئة CH_4 وبترددات 3205.4 و 3209.6 سم $^{-1}$. اقل طاقة لاشكال الهندسيه في قناة المدخل هي −0.18 كيلوجول \مول .

1. Introduction

The study of entrance and exit channels is worth in physical chemistry ambience. As the entrance channels minima have a role in orientating reactants before the transition state[1-4], exit channel minima influence quantum state populations of the products [5]. Character of the reaction potential energy surface can navigate the reaction from reactants to products over the

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transition state [5]. Consequently, it has a major effect on reaction dynamics [6]. Therefore, molecules with different atoms show that the potential energy surfaces are becoming accessible to realistic quantum mechanics simulation [7]. CH_4 + (X) complex was used to study entrance and exit channels via Photo-detachment work; however, the work showed limited information [8]. A significant study of the entrance and exit channels has been done for Cl + CH_4 reaction using ab initio calculations, which showed the importance of channels on the reaction dynamics [3,10]. The reaction of O (^{3}P) atoms with methane has been studied that it is a prototypical atom + poly atom reaction. The full potential energy surface of this reaction has recently been generated [4]. Three energy minima have been predicted, one minimum in the exit channel and two in the entrance channel at CCSDT theory [4]. The results of our current study of potential energy surface are similar to the previous study [4]. However, our results of the current study are extended to predict the vibrational frequency of the minimum structure at MP2 theory.

The aim of the current study is to prop both the entrance and exit channels and predict IR vibrational frequency for CH_4 +O at MP2 theory, the previous studies included only potential energy surface using CCSDT theory. The importance of the current study is that it represents the theory part of future work that will be an experimental work on the entrance and exit channels of this reaction.

2. Methods and Materials

Theoretical calculations have been done via GAUSSIAN 03 software [11] which was used for the *ab initio* calculations. The methodology used was second order perturbation theory (MP2) to incorporate electron correlation, together with the Dunning correlation-consistent basis set, aug-cc-pVDZ. This level of theory was used for predicting the potential energy minima and corresponding vibrational frequencies in the entrance and exit channels for O + CH_4 reaction.

3. Results and discussion:

Calculations for the entrance and exit channel complexes were started with calculations on the isolated methane molecule. These calculations assist in providing accuracy of the methodology employed in the present work.

Ab initio calculation of CH_4 predicted C-H bond length and the angle of H-C-H as 1.098 A^o and 109.47A^o, respectively. These numbers agree with experimental results, which showed 1.087 A^o and 109.471° of CH bond length and H-C-H angle for methane [8]. There are only two observable bands in the IR spectrum of methane because of its high symmetry. The IR active modes are both of t2 symmetry and correspond to C-H stretching and bending modes. The theoretical calculations of this work predicted 3204cm^{-1} vibrational for antisymmetric mode and 1325 cm-^{1} vibrational for bending mode (Figure 1). The experimental values of C-H stretching and bending modes are 3019 cm^{-1} and 1306 cm^{-1}, respectively [9]**.** *Ab initio* calculations predicted C-H IR stretching to be higher by 185 cm^{-1} than the observed value, while there was a good agreement with a slight difference of 19 cm^{-1} for the bending mode. The difference between the results of theoretical calculations and the experimental work is related to that harmonic and non-harmonic vibrations oscillation. The theoretical calculations contain only harmonic vibration, while the experiment records IR of harmonic and non-harmonic oscillations. In addition, it could be the MP$_2$ theory that causes this difference in results since it does not cover all electron correlations.

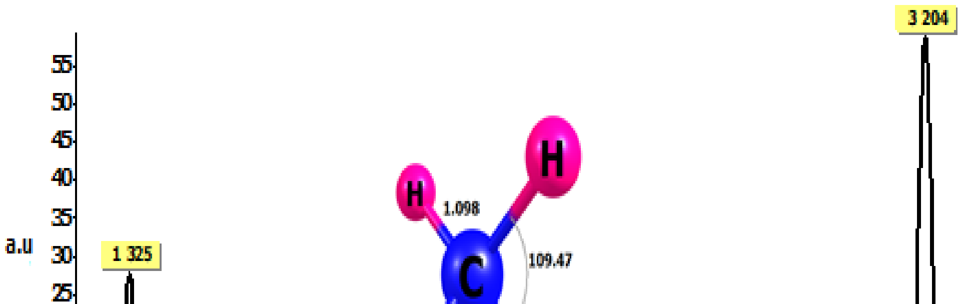


Figure 1: Structure and vibration frequency of CH_4

3.1 *Entrance channel of $CH_4 + O \rightarrow CH_3 + OH$*

Theoretical calculation predicts two possible minima in the entrance channel for O+CH_4. The O atom is bound to a specific H atom (O-CH_4) (Figure- 2) in one of the structures, while O atom is bound to one face of CH_4 in the other structure (O_{Fac}-CH_4) (Figure 3). The O_{Fac}-CH_4 structure has a well depth of 0.18 kJ/mol, while O-CH_4 structure has a lower minimum of 1.4 kJ/mol. Therefore, 0_{Fac}+CH_4 (Figure 3) has less energy than the O+CH_4 structure (Figure 2) in entrance region of O-CH_4.

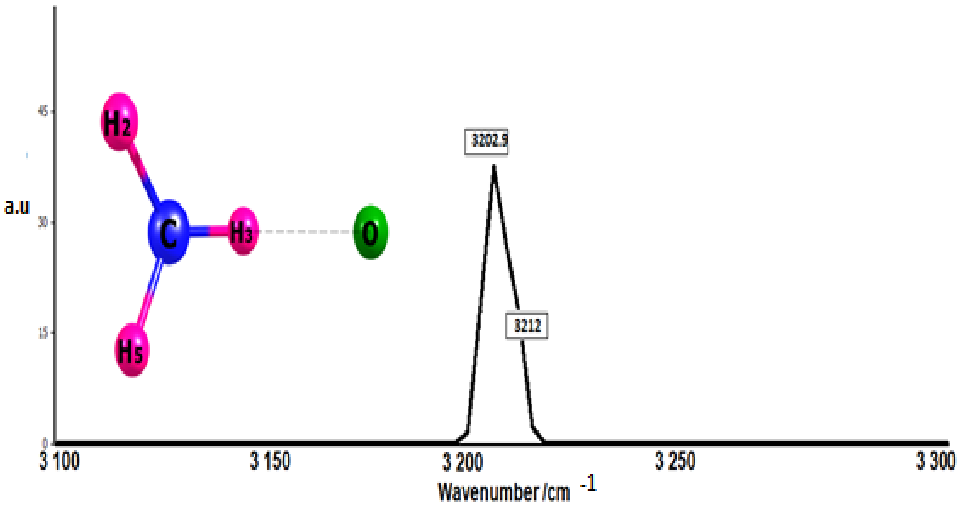


Figure 2: Predicted IR spectrum of CH_4-O entrance channel complex (O+CH_4 structure)

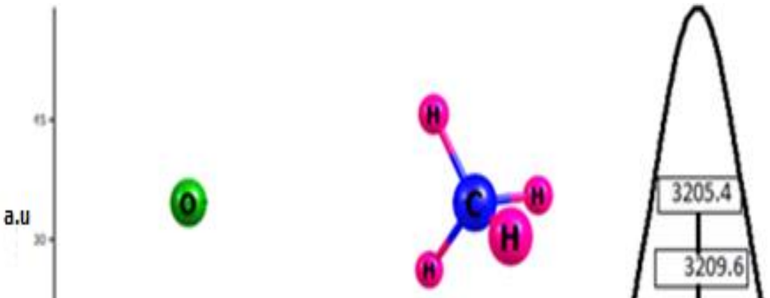


Figure 3: Predicted IR spectrum of CH_4-O entrance channel (O_{Fac}+ CH_4).

Ab-initio calculations of the IR spectra of the entrance channel complexes are shown in the C-H stretching region in Figure 2 and Figure 3 which are compared with the calculated spectrum of isolated CH_4 in Figure 1. Firstly, the band 1325 in Figure 1 has disappeared or became of very low intensity that it cannot be seen in the spectrum in Figure 2 and 3. This relates to the effect of radical O atom on the vibration of bending mode. In the O-CH_4 structure (Figure 2) vibration frequency was 3202.9 cm^{-1} and C-H stretching was 1 cm^{-1} higher than C-H stretching in Figure 1 which shows the experimental work for this reaction. In case of future experimental work, detecting IR spectra in laboratory requires a high resolution detector as described in the experimental part of previous studies [12, 13]. Therefore, the vibration frequency at 3202.9 cm^{-1} will not be distinguished. On the other hand, frequency at 3212 cm^{-1} vibration is higher than the C-H stretching frequency (Figure-1) by 8 cm^{-1} which is not difficult to distinguish.

The C-H stretching of the second entrance channel structure (Figure 3) is more difficult to distinguish than the first entrance structure (Figure 2), because the differences between its C-H stretching spectra and CH_4 stretching is about 5 cm^{-1}, although it includes 3063.5 cm^{-1} but it is a very weak band.

3.2 Exit channel of CH_4+ O →CH_3 + OH

The *ab initio* calculations in this work predicted one possible minimum in the exit channel region of OH with CH_3 (Figure 4) with an energy of 18.8 kJ mol^{-1} relative to CH_3+OH. There is good agreement of relative energies minima in entrance and exit channels of OH with CH_3 of this work and that of Czakó and Bowman[4] although they used different theory and large basis set (CCSD (T)/aug-cc-pCVTZ) (Table 1). This agreement makes results of the vibrational frequencies trustable.

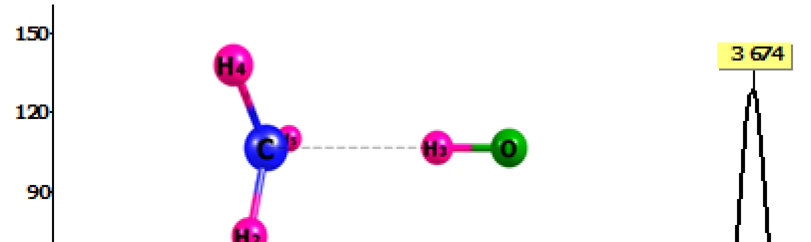


Figure 4: Predicted IR spectrum of CH_3-OH exit channel

The O-H vibrational frequency is predicted to be 3768 cm^{-1} of a pure OH (Figure 5), while in a complex with CH_3 it occurs at 3674 cm^{-1}. This is a large shift and therefore it should be easy in future experimental work to distinguish OH-CH_3 from free OH pure using IR spectroscopy. Table 1 shows the Cartesian coordinates of all structures.

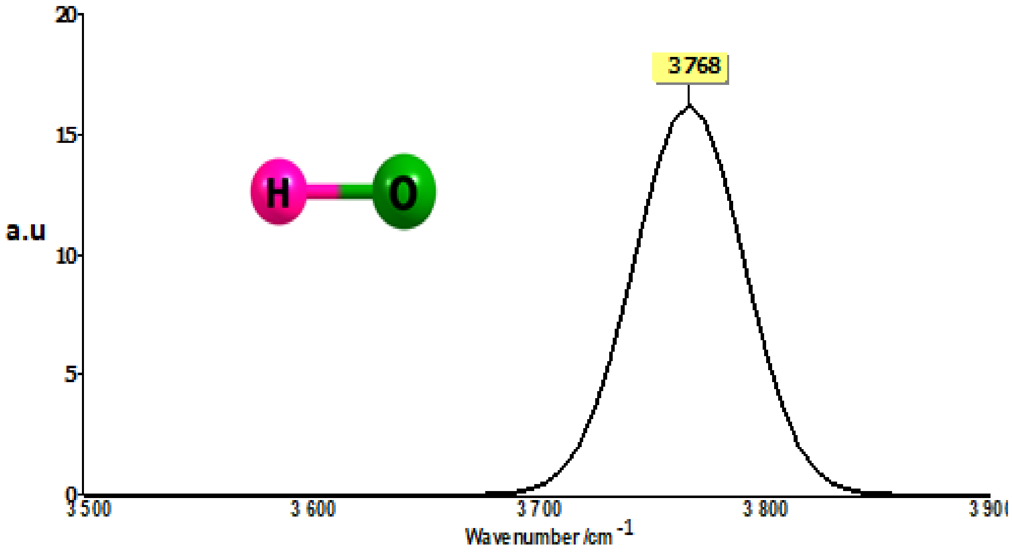
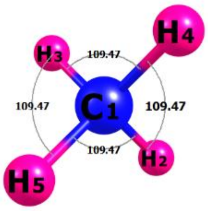
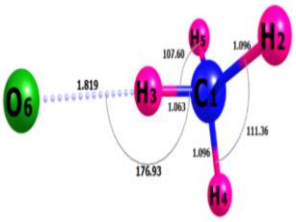
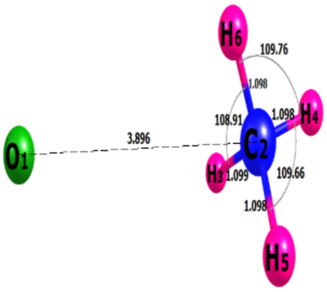
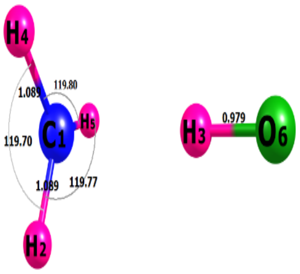
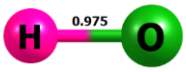


Figure 5: Calculated IR spectrum of pure OH.

Table 1: Structures and Cartesian coordinates of entrance and exit channels of O and CH4 reaction

Structure	Bond length(A°)	Bond angle	Cartesian Coordinates
	C-H=1.09	H-C-H=109.47	**Sequence Atomic number** 1 6 0.00000000 0.000000000 0.000000000 2 1 0.63421600 0.634216000 0.634216000 3 1 -0.63421600 -0.634216000 0.634216000 4 1 0.63421600 -0.634216000 -0.634216000
	$O-H_3=1.819$ $H_3-C=1.063$ $C-H_4=1.096$ $C-H_2=1.096$	$O-H_3-C=176.93$ $H_3-C-H_5=107.60$ $H_2-C_1-H_4=111.36$	**Sequence Atomic number** 1 6 -0.1167470 -1.520139000 -2.966337000 2 1 0.3230570 -2.522995000 -2.910290000 3 1 0.6773040 -0.81900900 -2.879633000 4 1 -0.8108820 -1.341780000 -2.137341000 5 1 -0.6014310 -1.353738000 -3.935365000 6 8 1.97491100 0.441123000 -2.685302000
	$C-H_6=1.098$ $C-H_3=1.099$ $C-H_4=1.098$ $C-H_5=1.098$ 0-C=3.8960	$H_3-C-H_6=108.91$ $H_6-C-H_4=109.76$ $H_4-C-H_5=109.66$ $H_3-C-H_5=109.47$	**Sequence Atomic number** 1 8 1.03901500 -1.979910000 -3.92924200 2 6 0.50311300 0.523178000 -0.99264900 3 1 1.42611500 -0.072427000 -0.98120100 4 1 0.60662300 1.380370000 -0.31487200 5 1 -0.34023400 -0.102518000 -0.67095400 6 1 0.32151500 0.878729000 -2.0157690
	O-H= 0.979 $C-H_2=1.089$ $C-H_4=1.089$	$H_2-C-H_4=119.7$ $H_2-C-H_5=119.77$ $H_4-C-H_5=118.80$	**Sequence Atomic number** 1 6 -0.342342000 -1.714208000 -2.9907930 2 1 0.357185000 -2.544270000 -2.9041440 3 1 1.364969000 -0.134859000 -2.7778800 4 1 -0.866308000 -1.355642000 -2.1061170 5 1 -0.634400000 -1.353781000 -3.9759310 6 8 2.085782000 0.520265000 -2.6770230
	O-H=0.975		**Sequence Atomic number** 1 8 0.0000000 0.000000000 0.108352000 2 1 0.0000000 0.00000000 -0.866819000

4. Conclusion

In this work, calculations of vibrational frequencies of the entrance and exit channel complexes were done as a new work for $CH_4 + O \rightarrow CH_3 + OH$ at MP2 theory.

IR spectra of the $O+CH_4$ structure of the entrance channel is possible to be observed in case of experimental future work because there is a suitable difference in C-H stretching in entrance channel from that of pure CH_4 ($8 cm^{-1}$). On the other hand, the difference is less than ($5 cm^{-1}$) for the $O_{Fac}+CH_4$ structure (Figure 3) that could be difficult to distinguish. Its exit channel can be distinguished without difficulty, because there is a considerable difference between O– H vibration alone and O– H stretching vibration in the exit channel as a result of CH_3. The lowest energy complex of entrance channel is for O-HCl bonding while the HCl-O species represent the most weakly bound. The present work can motivate and help future experimental investigations of O + methane reaction in helium nano- droplets**.**

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