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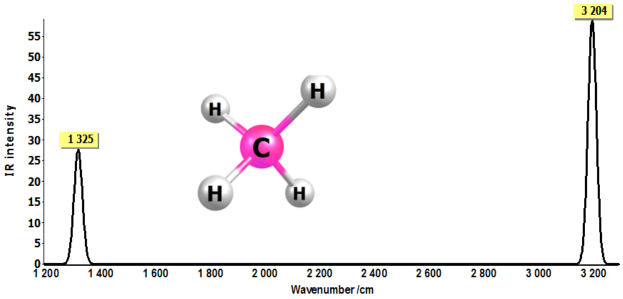

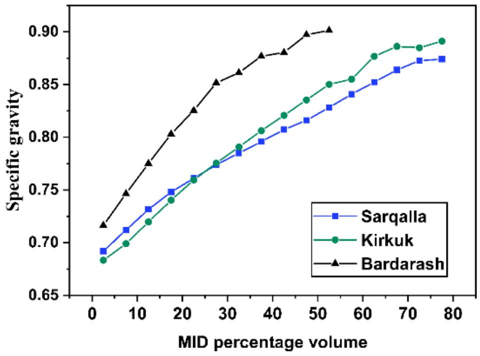

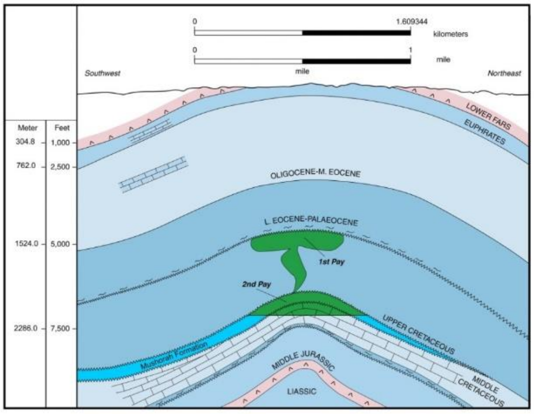

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Vibrational frequencies of entrance and exit channels of CH_4 with the radical Cl atom in the van der Waals region

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Abstract

Vibrational frequencies in the C-H stretching region, equilibrium structures, and the minimum energy of entrance and exit channels of radical chlorine attached to the methane molecule via van der Waals bonds are predicted via *ab initio* calculations. MP2 theory at the AUG-cc-pVDZ basis set is used for the calculations. Two equilibrium structures at minimum energies are predicted. A radical Cl atom attached by van der Waals bonds to a specific H atom in the CH 4 molecules in one structure. This structure has two bands of C-H vibration frequencies at 3212 cm^{-1} and 3222 cm^{-1} that are higher than the C-H vibration of pure CH_4. In the second structure at the entrance channel, the chlorine atom connects to a face (tetrahedron) of CH_4 by a van der Waals bond that has a deeper minimum of energy than the first structure. The rear structure has two C-H stretches of 3197 cm^{-1} and 3199 cm^{-1}. Finally, the minimum energy is predicted for both the first and second structures in the entrance channel, with relative energies of -2.2 kJ mol^{-1} and -4.6 kJ mol^{-1}, respectively. The structure of the exit channel shows a relative minimum energy of 25.7 kJ mol^{-1}. Our results of the IR spectrum of harmonic vibrational frequencies are original.

Introduction

The shape of van der Waals minima of neutral atoms and molecules reactions on potential energy surfaces greatly impacts the dynamics of chemical reactions in the physical chemistry environment (1). These entrance and exit channel minima can have a major influence on the full process of chemical reaction, entrance channel minima represent a guide to orient the reactants toward the transition state (1, 2**)**. The minima of the entrance channel of the reaction of chlorine and HF reaction has been previously studied (2). These spectra confirm that the complex in a ground state has a linear hydrogen-bonded structure, which is in agreement with theoretical results (2). Hydrogen abstraction from organic molecules by chlorine atoms has a vital role in understanding the process of several important reactions in atmospheric chemistry (1). *Experimental* and theoretical investigations have been reported on Cl (3, 4) atom interaction with CH_4, while fewer studies have been performed on this reaction's entrance and exit channel minima. However, the entrance and exit channels have been studied theoretically using *ab initio* calculation and their importance on the reaction dynamics has been investigated (4). Photo detachment work on the $X^-(CH_4)$ complex has been used to detect the entrance minima region of X + CH_4 via imaging spectra of the slow electron velocity-map process (5, 6). However, photo-detachment spectra provide limited structural information. Theoretical and experimental studies were performed on dynamics simulations to understand mechanisms of the atomic level of methane (7) and with hydroxyl radical (8). *Ab* initio calculations on Cl+CH_4 predict C_{3v} symmetry for the entrance minima predicted two structures of potential minimum energy, radical Cl is bound to a particular H atom in the first structure, while in the second structure the atom of chlorine is bound to a face of CH_4 tetrahedron (4, 9). The structure of the Cl atom connects to the face of methane and has lower energy (4, 9) Theoretical predictions on the CH_3-HCl complex predict C_{3v} symmetry and a depth of 840 cm^{-1}, which is much deeper than the entrance channel complex (5). Recent experimental work of collinear geometry Cl–H–C from reaction Cl + CH_4 in the transition state has been performed (10) and more studies have been done on the CH_4+Cl reaction (11, 12). The most recent research on the Methane molecule is to study C–H stretching via DFT theory (13), and also to study potential energy in the ground state of the entrance channel which is calculated at active space self-consistent field with the basis set of AVTZ for the reaction of methane and chlorine (14). In addition, the application of this reaction is studied recently through a thermal constant that is calculated using a Gaussian Process (15). A new study has been in the press to study the reaction of CH_4+ O in entrance and exit channels and also shows two structures in the entrance channel (16). However, these previous studies did not include any results of vibrational frequencies of Cl attached to CH_4 molecule in the van der Waals region which makes the current study original work. Our current work results agree with both previous studies (4, 9) in terms of structures and minimum energies. This agreement proves that our methodology is trustable to predict vibrational frequencies since previous studies did not concentrate on vibrational frequencies. The importance of the current study is that its results will be as a guide to perform experimental work to detect the IR spectrum in the He droplets technique. This technique is used to cool down reactants molecules and atoms to explore van der Waals minima on reaction potential energy surfaces (17). In addition, our current study's significance is to comprehend that this reaction proceeds in each step at the atomic and molecular levels. The current study aims to predicate the IR vibrational frequencies in the van der Waals region of $Cl+CH_4 \rightarrow HCl + CH_3$ in the ground state for the first time and characterize the entrance and exit channels of halogen atoms Cl with CH_4 via *ab initio* calculations.

Materials and Methods

Calculations of the current study have been done via GAUSSIAN 03 software. *Ab initio* calculation is used at MP2 theory (second-order perturbation theory) with the AUG-cc-pVDZ (Dunning correlation-consistent) basis set. Science-accurate results are obtained in a previous study [18] at this level (MP2) of methodology. Particularly, the MP2 theory was used to predict stabilized structures and harmonic vibrational frequencies of different types of molecules and compared them to accurate existing data from experiments (18). Therefore, second-order perturbation theory (MP2) is worth using in the current study. The correctness and applicability of this method are proved by obtaining results of calculations of structure-isolated CH_4 similar to previous studies (19).

Results and Discussion

Methane

Theoretical calculations are started with the study structure of pure methane. Results of calculations on pure CH_4 help to make us sure about the acutance of theoretical methodology.

These calculations serve to give some indications of the quality of the methodology that is used in the current work. *Ab Initio* calculations of CH_4 predicted C-H bond length and the angle of H-C-H as 1.098 A and 109.471^0, respectively (Figure 1). These results were similar to experimental values that showed 1.087 A and 109.471^0 of bond length of CH and angle of H-C-H for isolated methane, respectively (19). Since the CH_4 molecule has a high symmetry, there are only two vibrational frequency bands in the IR spectrum. The IR active modes are both of t_2 symmetry and correspond to C-H stretching and bending modes. Theoretical *Ab initio* calculations in the current study showed a 3204 cm^{-1} frequency for anti-symmetric vibration and a 1325

cm^{-1} frequency for bending vibration as shown in Figure 1, while the results of experiments of C-H vibration stretching and bending modes are 3019 cm^{-1} and 1306 cm^{-1}, respectively (20). Our theoretical results calculated stretching of CH higher by 186 cm^{-1} than the experimental results while the bending mode is mostly matched but with some difference of 18.5 cm^{-1}.

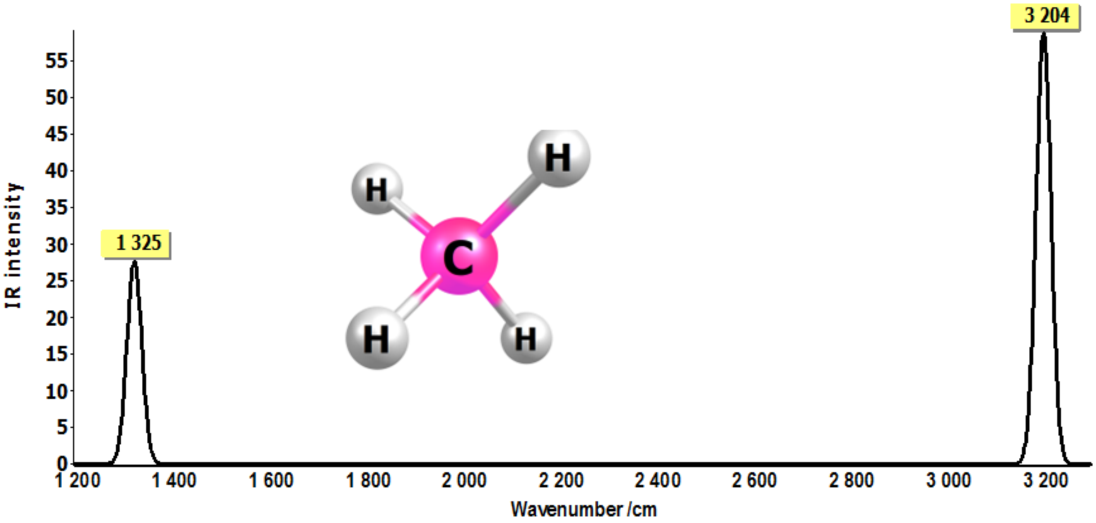


Figure 1. IR Vibrational frequency of Methane in the ground state is calculated at MP2 theory.

Entrance channel of $CH_4+Cl \rightarrow CH_3+HCl$

Theoretical calculations predict two possible minima in the entrance channel of CH_4+Cl that are attached via van der Waals bonds. In the first structure, which is a higher energy minimum than the second structure, the radical Cl bounds to a particular Hydrogen atom (Cl–CH_4) (Figure 2). In the second equilibrium structure, the Cl atom binds to one face of CH_4 (Cl_{fac}–CH_4) (Figure 3). These predictions agree with previous theoretical predictions (4, 9) (Table 1). However, in this work, any symmetry constraint was removed. The C_1 symmetry structure that resulted gave Cl-H-C angles of 179.8° (Figure 2) and 177.6° for Cl-C-H (Figure 3) instead of 180°. Previous studies expected well depths in the entrance minima region of 2.2 kJ mol^{-1} and 4.6 kJ mol^{-1} for the minimum energy structures in Figures 3 and 4, respectively (3). There are some differences in depths in the entrance region (Table 1). The differences are related to that the calculations of previous studies have been done using multi-reference configuration interaction (MRCI + Q) including electron correction of superposition error and spin-orbital correction in the previous study (4) while the current work is performed at Mp2 theory and the AUG-cc-pVDZ basis set**.**

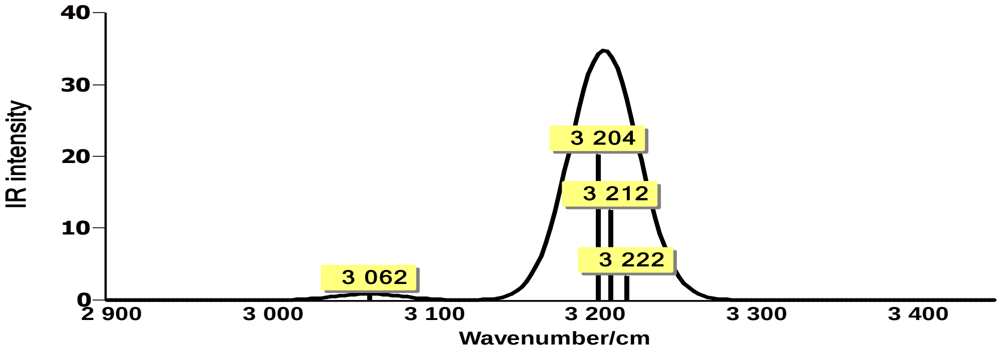


Figure 2. The Predicted vibrational frequency of CH_4-Cl entrance channel complex in the ground state at MP2 theory.

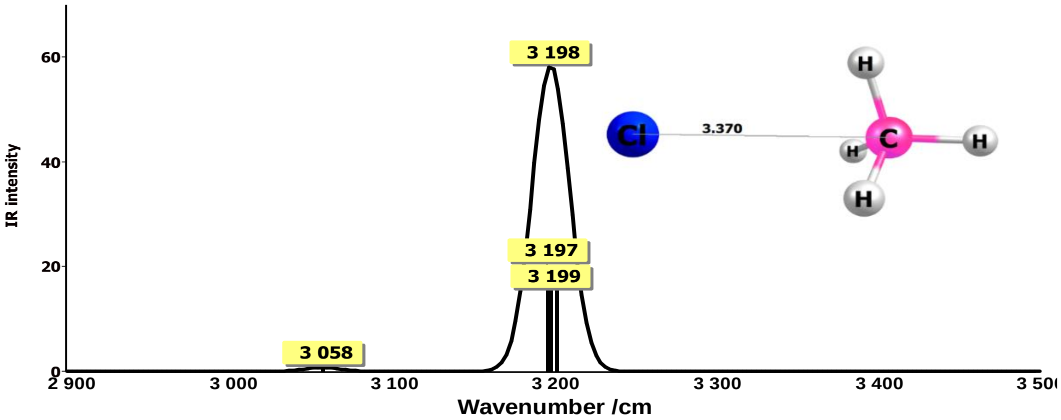


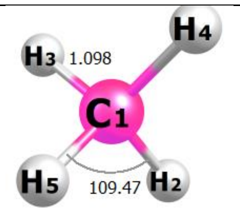
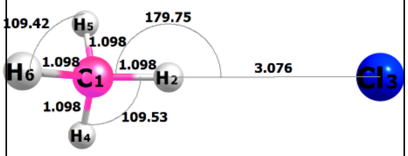
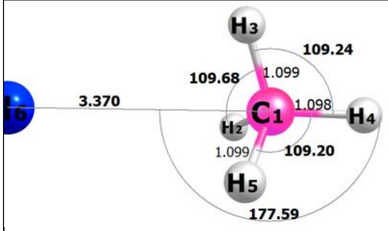
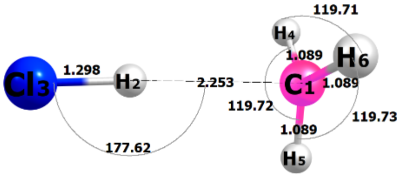
Figure 3.Vibrational frequency and structure of the second predicted structure in the entrance channel of CH_4 attached to Cl radical in the ground state at MP2 theory.

The current work intends to focus on the C-H stretching region in the IR spectra. Consequently, three antisymmetric vibrational C-H stretching are calculated in the entrance minima which are 3204 cm^{-1}, 3212 cm^{-1}, and 3222 cm^{-1} which is related to the Cl-CH_4 structure (Figure 2). Two of them are higher vibration frequencies than the stretching vibration of the CH bond of CH_4 alone (3204 cm^{-1}) (Figure 1) by about 18 cm^{-1} and 8 cm^{-1}, respectively. However, spectra at 3222 cm^{-1} are difficult to distinguish because of their low intensity, as a result, it will depend on the line 3212 cm^{-1} to explore the C-H stretching of the Cl+CH_4 structure in the entrance channel. Therefore, for future experimental work, it could be easy to recognize the spectrum of the minimum entrance channel in the C-H region for the structure in which the Cl atom is attached to a specific H atom as the line width of the OPO laser is mostly about 2cm^{-2} (17). The Cl_{Fac}–CH_4 structure of the entrance channel has three C-H stretching 3197 cm^{-1}, 3198cm^{-1}, and 3199 cm^{-1} which are lower frequency than C-H stretching of pure methane by 7cm^{-1}, 6cm^{-1}, and 5cm^{-1}, respectively. They could be distinguished as the differences in C-H stretching vibrations that are larger than an optical parametric oscillator (OPO) laser line width (17). The OPO laser is an advanced technique to detect the IR spectra during an experiment work. In addition, the intensity of C-H stretching is conventional in the evaluation of the intensity of the CH band of methane. Generally, the chlorine attached to the CH_4 structure (first structure) as in Figure 2, is more accurate than the Cl_{Fac}-CH_4 (second structure), science there is a 3212 cm^{-1} stretching vibration with a dissimilarity of 8cm^{-1} from those in Figure 3. In future experimental work, this work will be transferred from theoretical study to experimental work, then mass spectroscopy can be the best way to resolve the difficulty in distinguishing the C-H stretching of the CH_4 alone and the C-H of the minimum entrance energy. Via mass selectivity, the mass spectrum can forecast the formation of a complex in van der Waals minima (17) and focus on masses 51 and 53 of the Cl-CH_4 complex. This will give a trustable way to predict forming of complexes in helium nano-droplets.

Table 1. Calculated energy relative to Cl + CH_4 (kJ/mol*)*

Species	Relative energy (in this work)	Literature values (4)
CH_4-Cl (Cl bound to particular H)	-2.2	-1.2
CH_4-Cl (Cl bound to one face of CH_4	-4.6	-2.5
CH_3---HCl	14.4	15
HCl+CH_3	25.7	27

Table 2. Geometrical details about minima van der Waals structures of entrance and exit channels in ground state calculated in the current work.

Structure	Bond length(A°)	Bond angle	Cartesian Coordinates
	C-H=1.098	H-C-H=109.47°	**Sequence Atomic number x y z** 1 6 0.00000000 0.000000000 0.00000000 2 1 0.63421600 0.634216000 0.63421600 3 1 -0.63421600 -0.634216000 0.63421600 4 1 0.6342160 -0.6342160 -0.6342160 5 1 -0.6342160 0.6342160 -0.6342160
	C-H=1.098 H_2- Cl=3.076	H_2-C-H_4=109.47 ^{o} H_5-C-H_6=109.42 ^{o} C-H_2-Cl=179.75 ^{o}	**Sequence Atomic Number x y z** 1 6 -0.149157000 0.0523560 - 2.2462310 2 1 -0.12402300 0.0188880 - 1.1489780 3 7 -0.06269000 -0.0649300 1.9253650 4 1 0.8771070 0.0500230 -2.6371130 5 1 -0.6632730 0.9659100 - 2.5736170 6 1 -0.6871920 -0.8259870 -2.627351
	C-H_3=1.099 C-H_4=1.098 C-H_5=1.099 Cl-C=3.370	H_3-C-H_4=109.24 ^{o} H_5-C-H_4=109.20 ^{o} H_3-C-H_2=109.68 ^{o}	**Sequence Atomic number x y z** 1 6 -0.4953770 -0.8830210 - 0.6213540 2 1 0.2674850 -1.2151500 - 1.3386510 3 1 -0.1763210 0.0569180 - 0.1505760 4 1 -0.6230980 -1.6507540 0.1534070 5 1 -1.4515610 -0.7313860 - 1.1408130 6 17 -0.2433430 1.4710830 - 3.0198170
	C-H=1.089 Cl- H_2=1.298 H_2-C=2.253	H_4-C-H_6=119.71 ^{o} H_6-C-H_5=119.73 ^{o} H_5-C-H_4=119.72 ^{o} Cl-H_2-C=177.62 ^{o}	**Sequence Atomic number x y z** 1 6 -2.3122130 0.00159500 0.000200 2 1 -0.0593480 -0.032861 -0.0030550 3 17 1.2377610 0.0010380 0.0000530 4 1 -2.3766080 -0.8003150 - 0.7341280 5 1 -2.3635990 1.039075 - 0.3272180 6 1 -2.3690980 -0.23311200 1.0622930

Exit channel of CH_4+Cl → CH_3+HCl

One possible van der Waals minimum is predicted in the exit channel (HCl +CH_3) and it is deeper than the Cl + CH_4 entrance channel wells and is similar to previous studies ***[3,4,20]***. The exit channel relative energy is 25.7 kJ mol^{-1} (Figure 4). The Calculation of the IR spectrum in the C-H stretching region is very different from the C-H stretches predicted in the entrance channel region. There is no accompanying line to show the C-H stretching in Fig.4. Therefore, it can be depended on H-Cl stretching vibration to explore the exit channel which showed the high intensity of band absorption. Calculation of energy minima in exit region showed good agreement with previous studies (Table 1)

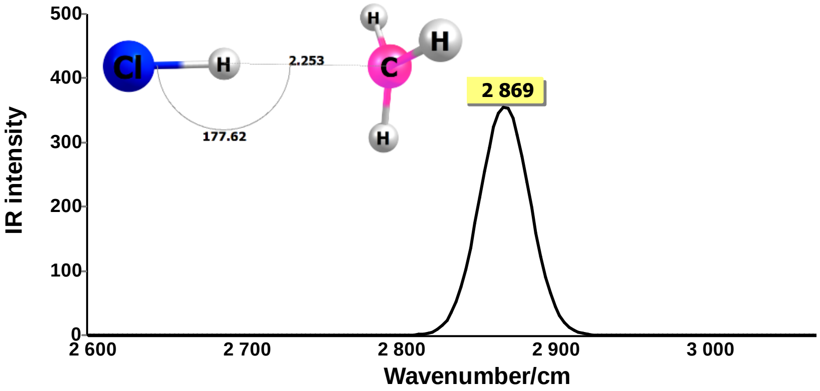


Figure 4. Structure and vibrations of exit channel HCl attached to CH_3 in the ground state at MP2 theory.

Conclusions

The current study predicted vibration frequencies of entrance and exit channels for CH_4+ Cl → CH_3+HCl in the ground state for the first time. Complexes of both channels are attached via van der Waals connections. Equilibrium structures and energy minima are calculated via *ab initio* calculations and compared with previous studies. The results agree quite well with other recent theoretical calculations in terms of the relative energies and minimum equilibrium structures. Predicted Infrared spectra at the entrance minimum energy for both structures could be recognized in experiments of infrared spectroscopy. However, the C-H stretching of IR spectra of the structure in Figure 3 can be appearing more accurate than those of the structure in Figure 4 It makes structure ClF_{ac} – CH4 difficult to distinguish in IR spectra because at its C-H stretching frequencies are different by 4 cm^{-1} and 6 cm^{-1} from those of the pure methane. Finally, the exit channel complex should be easily observable, it will depend on the change in H–Cl stretching vibration when it is alone and when it is in the exit region.

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