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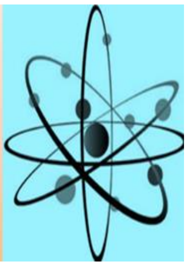

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Linear Reaction of Ca Atom with HCl Molecule in the Ground Electronic State: Hartree-Fock Method

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Abstract

The interaction of the Ca atom with HCl molecule in the ground electronic state is a very difficult reaction. Creating the halide of unstable HCl and then separating the H atom can take place with highly effective external energy. Therefore, the reaction takes place with a threshold energy of about 0.5 eV. To be able to understand this situation in more detail, the reaction was worked on 6-311G (3df, 3pd) basis set with Hartree-Fock Method in Gaussian09. Hartree-Fock Theory is a theory widely used for atom, molecule and nuclear studies. In this study, only electrons interacting with the static nucleus are related to Coulombic Hamiltonian. In this reaction, which is a long-time reaction, H atom decomposition were examined by means of infrared oscillations, dipole moment (representing electronic charge distributions) and oscillation frequencies (acting infrared oscillations-only stretching modes).

Key Words: Infrared, Long term interaction, Hartree-Fock

1. Introduction

In a reaction dynamics study, it is necessary to know the potential energy of the system in order to better understand the oscillation states that may occur during the reaction. In particular, explaining the dynamics of atoms in long-lived structures is the main subject of dynamic problems. In a reaction process, free radicals are the most important factor in determining the reaction time. The subject reaction is a harpoon system that is used very often experimentally to determine free radical fields [1, 2]. The Ca + HCl reaction has valuable findings both on the orientation of the reactants, influencing the outcome of the reaction and on the laser-induced gas systems related to the excited states of particles in the system as experimentally seen from resulting of works up to date. Experimentally, at low energy region with the time-of-flight technique under crossed-molecular beam conditions, chemiluminescence and fluorescence events were very important for this reaction because the subject reaction tended to react in excited electronic conditions [3-8]. In all of the cases mentioned above, it is described the events that show how unstable structures are formed. The position of the atoms forming the system is the fundamental condition that determines the inter-atomic forces. Charge distributions belonging to the system are the basis of these inter-atomic forces. During the course of a reaction, except for the reactant and product structures, any stable formations include vibrations and rotational structures. Infrared and Raman oscillations are fed by these vibration and rotational structures. Therefore, any molecular quantum oscillations that may occur during the reaction vary according to the positions of the atoms. In order to understand which infrared and Raman transitions are suitable for which vibration and rotation band ranges, a more realistic potential energy calculation is required. It is thus provided more accurate information about the electrical dipole moments that are important in infrared scattering calculations. This simplification of the approach puts the question of how it works in heavy atomic groups. The Ca + HCl reaction discussed is a reaction involving two heavy atoms. In order to obtain dynamic variables in the reaction dynamics, it is necessary to accurately determine the potential changes resulting from the movements of the nuclei. The real potential will lead to real and precise results. Electron density (number of orbital) can be a lot of difficulty in obtaining a real potential energy in an excess reaction. However, the effects of such a simple approach are the subject of curiosity.

The remaining of the study will give you a brief overview of the Hartree-Fock theory. Finally, conclusions of study will be interpreted in the Results and Discusses section.

2. Theory

In order to examine the neutral atom and molecular structures in reactants and product regions and the positive ion and free radicals in the transition state region, it is necessary to minimize the Hartree-Fock energy. This case is achieved by the solution of Hartree-Fock equations. This theory is based on Coulombic Hamiltonian states of electrons interacting with stationary nucleus movement. Also, the system has a positive charge after removing an electron. it can also explain this phenomenon occurred especially in transition situations [9]. These charge exchanges are created to define a potential area representing the movement of all electrons at a certain point in space. Electrons are presented in a certain area, such as a solid structure, and electrons move only in these areas. With this approximation, the Hartree-Fock method gets a great simplicity. High electron density systems or systems with heavy atoms may increase the margin of error.

The Hartree equation is obtained by modifying one-electron wave function $u_1(x), u_2(x), \dots\ u_n(x)$. The main purpose is to create the energy of Hartree.

$$\int u_1^*(x_1) \dots u_n^*(x_n) H u_1(x_1) \dots u_n(x_n) dx_1 \dots dx_n \tag{1}$$

Here, the *H* operator is the energy generated by the electrons under the influence of the nuclei. u (x) are wave functions that must be normalized. Furthermore, the integration therein includes summing over the spin. Thus, the Hartree-Fock equation can be rewritten as

$$H_1 u_1(x_1) + \left[\sum_{k=1}^{n} \int u_k^*(x_2) u_k(x_2) \left(\frac{e^2}{4\pi\epsilon r_{12}}\right) dx_2\right] u_i(x_1) - \sum_{k=1}^{n} \left[\int u_k^*(x_2) u_i(x_2) \left(\frac{e^2}{4\pi\epsilon r_{12}}\right) dx_2\right] u_k(x_1) = E_i u_i(x_1) \tag{2}$$

Where H_1 consists of the total of the kinetic and potential energies of the electron that are thought to be active. The integrations cover spin movements. This equation is Schrödinger Wave Equation for an electron moving in potential energy with $(e^2/4\pi\epsilon r_{12})$. The movement of the molecular system defined on the surface of the potential energy is regulated in accordance with the Born-Oppenheimer Approach. Energy eigenvalues that are suitable for molecular oscillation can be determined [10]. At the beginning, the Ca atom has a distance from the Cl atom of 4.0 Å while the HCl molecule was distance of 1.29 Å. Then the Ca atom is linearly approached in steps of 0.05 Å up to 1.0 Å toward the Cl atom [11, 12]. Some of the optimized parameters are given in Table1 in the part of Results and Discussions.

3. Results and Discussion

Table 1. Some of the parameters optimized.

Distances (Å)		**Ca-Cl**		**H-Cl**		**Dipole**	**Group**
Ca-Cl	**H-Cl**	**Freq.(cm^{-1})**	**IR int.**	**Freq.(cm^{-1})**	**IR int.**	**Ca-Cl-H (Debye)**	
3.90	1.2671	68.69	3.52	3113	12.38	2.137	
3.85	1.2673	71.09	4.01	3110	9.82	2.202	
3.80	1.2676	73.51	4.55	3107	7.42	2.271	
3.75	1.2679	75.95	5.16	3103	5.23	2.343	
2.95	1.2752	149.10	20.41	3002	66.31	4.215	
2.90	1.2760	160.44	20.69	2991	78.16	4.366	
2.85	1.2766	173.44	20.68	2982	89.62	4.518	A
2.80	1.2766	188.24	20.35	2978	98.97	4.671	
2.75	1.2772	204	19.64	2969	107	4.82	
2.70	1.2774	223	18.56	2960	113	4.96	
2.65	1.2784	244	17.10	2950	116	5.10	
2.60	1.2785	267	15.29	2948	112	5.24	
2.55	1.2790	293	13.15	2938	104	5.36	
2.50	1.2790	321	10.74	2936	90	5.48	
2.45	1.2791	351	8.15	2934	70	5.58	B
2.40	1.2790	384	5.50	2935	47	5.67	
2.35	1.2789	419	3.0	2937	24	5.73	
2.30	1.2785	457	0.99	2944	5	5.78	
2.25	1.2772	497	0.008	2962	0.41	5.80	C
2.20	1.2763	541	0.99	2978	16.6	5.78	

2.15	1.2753	587	5.38	2998	61.57	5.73	
2.10	1.2743	635	15.37	3020	136	5.63	
2.05	1.2734	687	34.12	3042	234	5.47	
2.0	1.2727	741	65.8	3062	329	5.24	D
1.95	1.2728	797	115	3073	386	4.93	
1.90	1.2730	856	118	3077	370	4.53	
1.85	1.2745	917	288	3062	271	4.02	
1.80	1.2774	980	418	3025	125	3.40	
1.75	1.2820	1045	574	2965	13	2.67	
1.70	1.2887	1113	736	2878	31	1.81	
1.65	1.2982	1187	854	2766	231	0.86	
1.60	1.312	1275	840	2619	555	0.12	
1.55	1.329	1385	629	2460	795	1.04	
1.50	1.351	1525	343	2297	837	1.78	
1.45	1.377	1694	170	2141	787	2.30	E
1.40	1.407	1885	291	1999	611	2.67	

Table 1 shows that, by Hartree-Fock method, the Ca atom approaches towards Cl atom in the HCl molecule. In this study, some of the results obtained from the calculations are given. As can be seen from the table, in each approach of the Ca atom, the infrared density of the system and the corresponding frequency and dipole moments were determined. 5 steps only are taken care of from these working steps. These are five groups represented with A, B, C, D and E letters.

In the immediately preceding step from group A, ie, the distance between the Ca and Cl atom was 2.90 angstrom, while the Ca-Cl infrared intensity was increased as long as the Ca atom approached the Cl atom. In Group A, the Ca and Cl atoms form a chemical bond. The Ca atom began to share an electron with the Cl atom. However, this charge shift is not sufficient to separate the H atom. After from this group, there is a decrease in the infrared density of the Ca-Cl molecule.

When the distance between the Ca and Cl atoms is 2.45 angstroms (the equilibrium bond distance for the Ca-Cl molecule, in group B), the effective distance for the H atom is started. Because, during the movement of the system, the forced H atom to separate started to approach again to the Cl atom after this group step. This behavior also affects the infrared oscillation frequency. That is, the oscillation frequency decreased during the movement tended to increase again after this step. Group B is the initial step of the transition state in the system. From this step, the H and Ca atoms tend to remain bound to the Cl atom.

If in the case of group C, Ca-Cl and H-Cl infrared oscillations have the best lowest values during the reaction duration. But the electrical dipole moment of the system has the best highest value. In this group, the H atom still wants to be bound to the Cl atom and this group is the center of the transition state. After group C, H atom tends to come equilibrium bound distance with Cl atom although the Ca atom is so close. Since the ground electronic state of this reaction has a very high endothermic value and barrier, the H atom is still bound and in order to distinguish it, it will be necessary to bring the Ca atom, thus increases the energy in the environment. After group D, H atom starts to separate, is completely separated at the group E.

the H atom forced to decompose from Group B up to group E, the changes in its infrared emissions shows that the Ca atom does not have enough energy. For this reason, the H atom showed an example of long-distance interaction.

4. Conclusions

Until the H atom is separated from Cl atom, there are charge transitions in the system. The variation of the amplitude of the electrical dipole moments and the fluctuations in the infrared oscillation frequencies explain that the system is a system that displays a long-distance example. Also, this case clarifies that the formation of the Ca-Cl ionic product was not sufficient to decompose the unstable H-Cl anion.

5. Acknowledgement

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