

**Studying Reactivity of a Chemical System using Computational Quantum
Chemistry**

McNair/ URP Scholar: Mayra Miranda

Faculty Mentor: Jorge A. Morales

Graduate Student Assistant: Patrick Mclaurin

Final Research Project

Texas Tech University

December 11, 2008

TABLE OF CONTENTS

ABSTRACT	1
INTRODUCTION	2
A. Statement of Research	2
B. Purpose of Research	2
C. Significance of Research	3
BACKGROUND OF RESEARCH	4
a) Experimental Background	4
b) Theoretical Background	4
METHODOLOGY	7
RESULTS	9
DISCUSSION	13
CONCLUSION	17
REFERENCES	19

ABSTRACT

Studies of atmospheric molecules colliding with solar particles (like protons) are scarce. Recently, it has been suggested that protons that come from the sun (solar wind) may modify the chemistry of the atmosphere. In that way, it is crucial to consider the atmosphere as a chemical system and study its reactivity and chemical composition by using experimental and theoretical techniques. In this study, we aim at determining whether carbon dioxide can react with proton projectiles at high energy ($H^+ + CO_2$ -30eV) as a function of the projectile impact parameter. Here, we want to emphasize that the single use of experimental techniques provide limited results because not all the microscopic details of a reaction can be accessed in that way. In that respect, the computer simulation of a reaction allows a complete inspection of its microscopic details. The employed computational method involves different atomic basis sets. Basis sets are set of functions to mathematically formulate the quantum chemistry description of a system. According to our results, the main process occurring in this system was non-(charge)-transfer scattering (NTS) process. However, the study also showed some collisional-induced vibration in the carbon dioxide and deflection by the proton. In conclusion, there is not a high level of reactivity for this chemical system ($H^+ + CO_2$ -30eV). The results from our simulations were compared with available experimental results.

INTRODUCTION

A. Statement of Research

The study of different chemical systems in natural settings has attracted considerable interest. In particular, recent reports on earth climate conditions emphasize the role of atmospheric chemical reactivity as being an indicator of atmosphere variability. Having in mind the earth's atmosphere, we consider the carbon dioxide molecule and a proton as reactants. From the experimental point of view, the study of such a chemical system had already been considered by the Toennies Research group. The Morales research group's approach focuses on the theoretical side, namely, the computational simulation of that system in terms of quantum chemistry.

B. Purpose of Research

This study is directed to provide insight into the reactivity of a target molecule that is present in the atmosphere; such is the case of the carbon dioxide.

Within the atmospheric sciences, it has been emphasized the crucial role of the chemical interaction between chemical compounds present in the earth's lower atmosphere, and cosmic rays coming from outer space to our planet. Those cosmic rays are made of energetic particles called protons. Among the processes that give place to such particles are the energetic processes on the Sun. Thus the mentioned interaction increases the possibility of an atmospheric chemical variability. One of the important chemicals that exist in the Earth's planet is carbon dioxide. Carbon dioxide is very important for the plant growth and development. Also, carbon dioxide is used by plants during photosynthesis

in order for them to make sugars. Finally, carbon dioxide is needed for other functions to produce organic compounds. It is really important to study the reactivity of a proton colliding with a target molecule. The target molecule will be carbon dioxide that belongs to atmosphere in the Earth planet. Depending of the results of this research in studying this particular chemical system, we will see how its reactivity varies in terms of the initial condition of the reactants.

C. Significance of Research

The study of this particular chemical system will be significant to understand recent changes in the earth's atmosphere. The carbon dioxide and proton reactions can make some impact on the atmosphere if a high level of reactivity is observed. Thus, studying the particular chemical system involving carbon dioxide in more detail and predict its products acquire great relevance.

BACKGROUND OF RESEARCH

a) Experimental Background¹

The experimental study¹ of the chemical system: $\text{H}^+ + \text{CO}_2$ focused on vibrationally inelastic scattering and the charge transfer reactions. This experiment measured the energy loss of either the scattered protons or the charge transfer of hydrogen atoms by using a Colutron ion beam source. A main focus of this experimental study was to analyze the reactivity of the scattering processes. Also, the charge transfer of the hydrogen atom with the target molecule can have different energy loss spectra depending of the states of the system. According to the experimental results, the energy loss can be measured by a collision system where the proton can be able to collide with target molecule. The target molecule is first affected by the incoming proton and then the collision makes the target molecule to vibrate. The strong vibration of the target molecule can lead to the breaking of one of the bonds. There are only three normal modes in which carbon dioxide can vibrate and they are the symmetric stretch, bending and asymmetric stretch. The experimental results show energy loss spectra interpretation between those three modes but still the reactivity of the system was low. From the theoretical point of view, the study of the chemical system was approached in a different way, namely by using the electron nuclear dynamics theory.

b) Theoretical Background²

There are several leading theories in quantum mechanics that treat the molecular degrees of freedom when a chemical system is being considered. In particular, the

Morales Research Group decided to explain a complete nuclear electronic dynamics (END) within the coherent-states dynamics (CSD) ². Computational quantum chemistry can explain many microscopic details that experimental chemistry can not. The combination of different theoretical methods using the ENDYNE program and other tools will contribute to study quantum mechanics properties of the system. A crucial task involves the programming of the quantum mechanics so that the simulated results can get closer to the experimental ones. Quantum chemistry leads to mathematical equations from which computer simulations are based.

Within the theoretical side, the chemical system is described by a total wave function ψ_{Total} for the target molecule and the proton. There, N_{nuclei} is the total number of nuclei in the system: three nuclei in the target (O=C=O) and one in the proton (H⁺). N_{electron} is the total number of electrons that at initial time are fourteen on the target and none on the proton. The wave function of the nuclei is denoted by ψ_{nuclei} and that for the electrons by $\psi_{\text{electrons}}$. ψ_{Total} is the product of ψ_{nuclei} and ψ_{electron} . The nuclear wave function ψ_{nuclei} is a product of Gaussian wave packets:

$$\psi_{\text{Nuc}}(\mathbf{X}; \mathbf{R}, \mathbf{P}) = \prod_{i=1}^{3N_{\text{Nuc}}} \exp \left\{ -\left(\frac{X_i - R_i}{2\Delta R_i} \right)^2 + \frac{iP_i}{\hbar} (X_i - R_i) \right\},$$

where the average positions are R_i , the average momentum are P_i , and the position normal deviation are $\Delta R_i \propto \hbar^{1/2}$. ψ_{nuclei} can be factorized into translational, rotational, and vibrational parts. For ψ_{ele} , K fermion creation operators b_i^\dagger (b_i) of N_{el} occupied $\{\phi_h\}$ and $K - N_{\text{el}}$ virtual $\{\phi_p\}$ orthogonal molecular spin-orbitals (MSO) can generate particle-hole pair of operators $b_p^\dagger b_h$ of U (K) Lie group. Taking as a fiducial state the Fermi Vacuum single determinant $|0\rangle = b_{N_{\text{el}}}^\dagger \dots b_1^\dagger |\text{vac}\rangle$, the non-quasi-classical, single-determinantal

Thouless electronic CS $|\mu; \mathbf{R}\rangle$, in terms of non-orthogonal Thouless MSO $\{\chi_h\}$, $\chi_h = \phi_h + \sum_{p=N_{el}+1}^K \phi_p \mu_{ph}$ ($1 \leq h \leq N_{el}$) is

$$\begin{aligned} \psi_{el} = |\mu; \mathbf{R}\rangle &= \det[\chi_h(\mu; \mathbf{R})] \\ &= \exp\left(\sum_{p=N_{el}+1}^K \sum_{h=1}^{N_{el}} \mu_{ph}(t) b_p^\dagger b_h\right) |0\rangle \end{aligned}$$

With ψ_{Total} CS-formulated, the quantum Lagrangian is

$$\mathcal{L}_{\text{CS}} = \langle \psi_{\text{Total}} | \left[\frac{i\hbar}{2} \left(\frac{\partial}{\partial t} - \frac{\partial}{\partial t} \right) - \hat{H} \right] | \psi_{\text{Total}} \rangle / \langle \psi_{\text{Total}} | \psi_{\text{Total}} \rangle$$

By imposing stationary to the quantum action A_{CS} , $\delta A_{\text{CS}} = \delta \int_{t_1}^{t_2} \mathcal{L}_{\text{CS}}(t) dt = 0$ with the nuclei in the semiclassical limit of $\hbar \rightarrow 0$, the END dynamical equations for the CS parameters R_b , P_b , μ_{ph} , and μ_{ph}^* are obtained below

$$\begin{bmatrix} i\mathbf{C} & \mathbf{0} & i\mathbf{C}_{\mathbf{R}} & \mathbf{0} \\ \mathbf{0} & -i\mathbf{C}^* & -i\mathbf{C}_{\mathbf{R}}^* & \mathbf{0} \\ i\mathbf{C}_{\mathbf{R}}^\dagger & -i\mathbf{C}_{\mathbf{R}}^\top & \mathbf{C}_{\mathbf{RR}} & -\mathbf{I} \\ \mathbf{0} & \mathbf{0} & \mathbf{I} & \mathbf{0} \end{bmatrix} \begin{bmatrix} \frac{d\mu}{dt} \\ \frac{d\mu^*}{dt} \\ \frac{d\mathbf{R}}{dt} \\ \frac{d\mathbf{P}}{dt} \end{bmatrix} = \begin{bmatrix} \frac{\partial E_{\text{Total}}}{\partial \mu^*} \\ \frac{\partial E_{\text{Total}}}{\partial \mu} \\ \frac{\partial E_{\text{Total}}}{\partial \mathbf{R}} \\ \frac{\partial E_{\text{Total}}}{\partial \mathbf{P}} \end{bmatrix},$$

where the left matrix is the inverse of Hamilton generalized symplectic matrix with dynamical sub-matrices containing non-adiabatic coupling terms:

$$\begin{aligned} (\mathbf{C}_{XY})_{ij,kl} &= -2\text{Im} \left. \frac{\partial^2 \ln S}{\partial X_{ik} \partial Y_{jl}} \right|_{\mathbf{R}'=\mathbf{R}}; \\ (\mathbf{C}_{X_k})_{\text{ph}} &= \left. \frac{\partial^2 \ln S}{\partial \mu_{\text{ph}}^* \partial X_k} \right|_{\mathbf{R}'=\mathbf{R}}; \quad \mathbf{C}_{\text{ph;qg}} = \left. \frac{\partial^2 \ln S}{\partial \mu_{\text{ph}}^* \partial \mu_{\text{qg}}} \right|_{\mathbf{R}'=\mathbf{R}}, \end{aligned}$$

where $S = \langle \mu'; \mathbf{R}' | \mu; \mathbf{R} \rangle$ is the overlap between two Thouless CS and

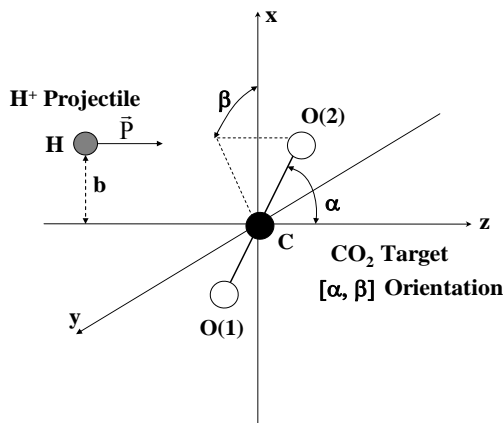
$E_{\text{total}} = \langle \psi_{\text{Total}} | \hat{H} | \psi_{\text{Total}} \rangle / \langle \psi_{\text{Total}} | \psi_{\text{Total}} \rangle = \sum_{i=1}^{3N_{\text{el}}} P_i^2 / 2M_i + \langle \mu; \mathbf{R} | \hat{H}_{\text{el}} | \mu; \mathbf{R} \rangle / \langle \mu; \mathbf{R} | \mu; \mathbf{R} \rangle$ the total energy. This complicated matrix with the big brackets express in a quantum

Hamilton symplectic format, the combined quantum electronic and quasi-classical CM, rotational, vibrational CS dynamics. It treats simultaneously both electron and nuclei and provides a direct dynamics not requiring pre-calculated potential energy surfaces to run. The CS parameters R_i^0 , and P_i^0 , and with electronic state μ_{ph}^0 , and μ_{ph}^{0*} evolving in time trace different reaction trajectories in a CS quantum phase space.

METHODOLOGY

All the simulations for the different orientations were simulated with the ENDyne program and with several auxiliary programs such as perl scripts, developed from the ENDyne software. UNIX Shell scripts were used to modify many of the parameters and make some changes in the initial conditions of the system. The nuclear CS parameters defining the reactants initial condition are shown in Figure # 1.

Fig # 1 $H^+ + CO_2$; Impact Parameter, and Orientation $[\alpha, \beta]$



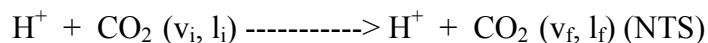
The target molecule, in this case carbon dioxide, is labeled in the following way: There are two oxygen atoms in the molecule: one is labeled O (1) and the other is labeled

O (3). The center atom, in this case carbon, is labeled C (2), and the incoming proton projectile is labeled as H^+ (4). The simulations were running using four different basis sets. The angular orientation $[\alpha, \beta]$ of the carbon dioxide is determined by the polar angle between $0 < \alpha < 180$ and the azimuthal angle that will be zero for all the orientations studied. The proton projectile will be located in x-z plane, with an impact parameter “b”, and initially placed at (b, 0.0, -15.00) a.u. The proton initially travels in the z direction with a momentum commensurate with $E_{lab}=30\text{eV}$. All the simulation lasted for 1000 a.u.

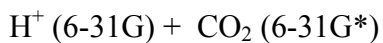
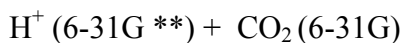
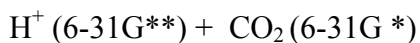
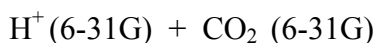
All the simulations and results reported therein were conducted during the summer 2008 in the Department of Chemistry and Biochemistry at Texas Tech University, under the close supervision of my mentor Dr. Morales and a graduate student assistant Patrick McLaurin.

RESULTS

Simulations of the chemical system ($H^+ + CO_2$) showed only one particular reactive process: non-(charge)-transfer scattering process, also called NTS.



The main results of the simulations include products analysis and the deflection functions (scattering angles) of the outgoing projectile. The basis sets used in every orientation are shown below:



We show two reactivity tables with different basis sets that show some reactivity (NTS) behavior for different impact parameters. Also, we show the two corresponding graphs that describe the scattering angle with different impact parameters. Both graphs and reactivity tables refer to the four orientations. In the discussion section, these results will be explained in more detail. The Reactivity tables are shown below:

Table 1.1

Non-Transfer Scattering for $H^+ + CO_2 - 30eV$

Set Basis: 6-31G (CO₂)/6-31G (H⁺)

Orientation α ,

<i>β</i>	<i>Impact Parameter</i>	<i>Reactive Process</i>
<i>[0,0]</i>	N/A	O1---O2 Vibration
	N/A	C2---O3 Vibration
	N/A	C2---O1 Vibration
	0.0-1.3 First	O1---H4 Deflection
	0.0-1.3 (C2 & H away from each other) Second	C2---H4 Deflection
	0.0-1.3 (O3 & H away from each other) Third	O3---H4 Deflection
<i>[45,0]</i>	0.0-0.5	O1---O2 Vibration
	0.0-1.3	C2---O3 Vibration
	0.0-1.3	C2---O1 Vibration
	0.5-1.3	O1---H4 Deflection
	0.0-0.5	C2---H4 Deflection
	0.0-1.3 (O3 & H away from each other)	O3---H4 Deflection
<i>[90,0]</i>	0.4-2.0	O1---O2 Vibration
	1.0-1.6	C2---O3 Vibration
	0.0-2.0	C2---O1 Vibration
	0.5-2.0	O1---H4 Deflection
	0.0-0.4	C2---H4 Deflection
	0.0-2.0 (O3 & H away from each other)	O3---H4 Deflection
<i>[135,0]</i>	0.0-0.7	O1---O2 Vibration
	0.0-0.9	C2---O3 Vibration
	0.9-2.2	C2---O1 Vibration
	0.0-0.9 Third & 1.0-1.4 Second & 1.5-2.2 First	O1---H4 Deflection
	0.0-1.4 First & 1.5-2.2 Second	C2---H4 Deflection
	0.0-0.9 Second & 1.0-2.2 Third	O3---H4 Deflection

Table 1.2

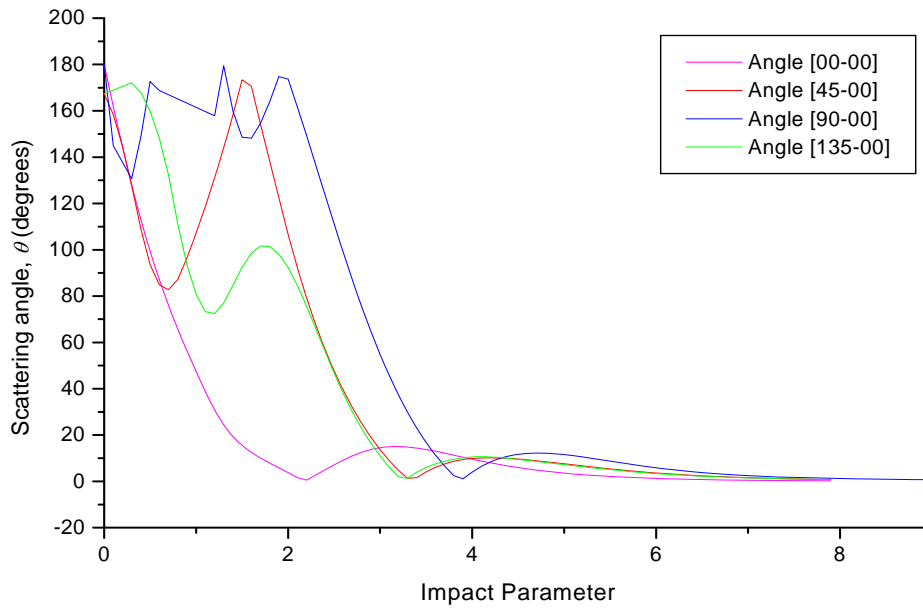
Non-Transfer Scattering for $H^+ + CO_2 - 30eV$

Set Basis: 6-31G* (CO₂)/6-31G** (H⁺)

<i>Orientation α, β</i>	<i>Impact Parameter</i>	<i>Reactive Process</i>
<i>[0,0]</i>	0.0-0.8	O1---O2 Vibration
	0.0-0.4	C2---O3 Vibration
	0.0-0.4	C2---O1 Vibration
	0.0-0.8 First	O1---H4 Deflection
	0.0-0.8 (C2 and & H4 away from each other) Second	C2---H4 Deflection
	0.0-0.8 (O3 and & H4 away from each other) Third	O3---H4 Deflection
<i>[45,0]</i>	0.0-0.7	O1---O2 Vibration
	0.0-1.2	C2---O3 Vibration
	0.0-1.2	C2---O1 Vibration
	0.6-1.2	O1---H4 Deflection
	0.0-0.5	C2---H4 Deflection
	0.0-1.2 (O3 & H away from each other)	O3---H4 Deflection
<i>[90,0]</i>	0.4-1.9	O1---O2 Vibration
	0.4-2.3	C2---O3 Vibration
	0.1-2.3	C2---O1 Vibration
	0.5-2.3	O1---H4 Deflection
	0.0-0.4	C2---H4 Deflection
	0.0-2.3 (O3 & H away from each other)	O3---H4 Deflection
<i>[135,0]</i>	0.0-0.8	O1---O2 Vibration
	0.0-2.5	C2---O3 Vibration
	0.0-2.5	C2---O1 Vibration
	0.0-0.9 Third & 1.0-1.6 Second & 1.7-2.5 First	O1---H4 Deflection
	0.0-1.5 First & 1.6-1.5 Second	C2---H4 Deflection
	0.0- 0.9 Second & 1.0-2.5 Third	O3---H4 Deflection

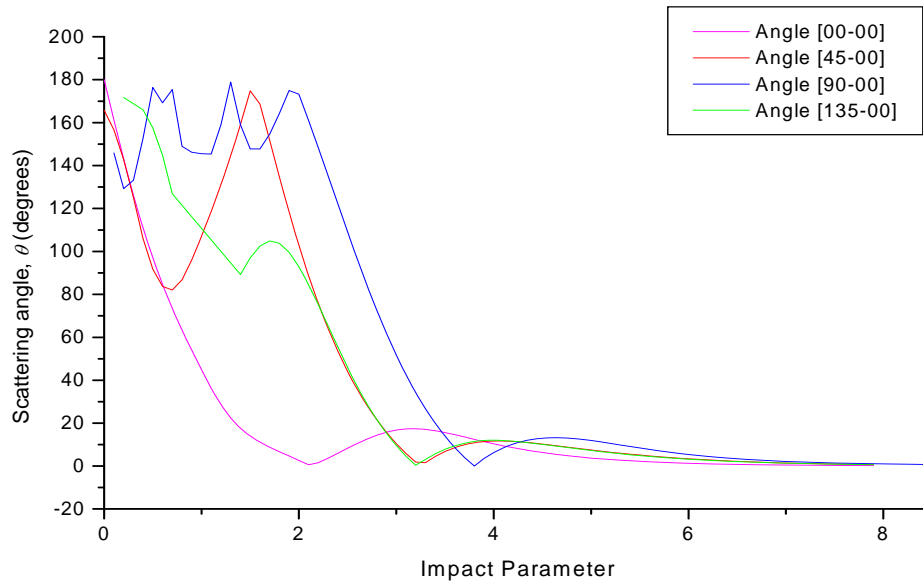
Non-Transfer Scattering for $H^+ + CO_2 - 30eV$

Set Basis: 6-31G (CO_2)/6-31G (H^+)



Non-Transfer Scattering for $H^+ + CO_2 - 30eV$

Set Basis: 6-31G (CO_2)/6-31G** (H^+)*



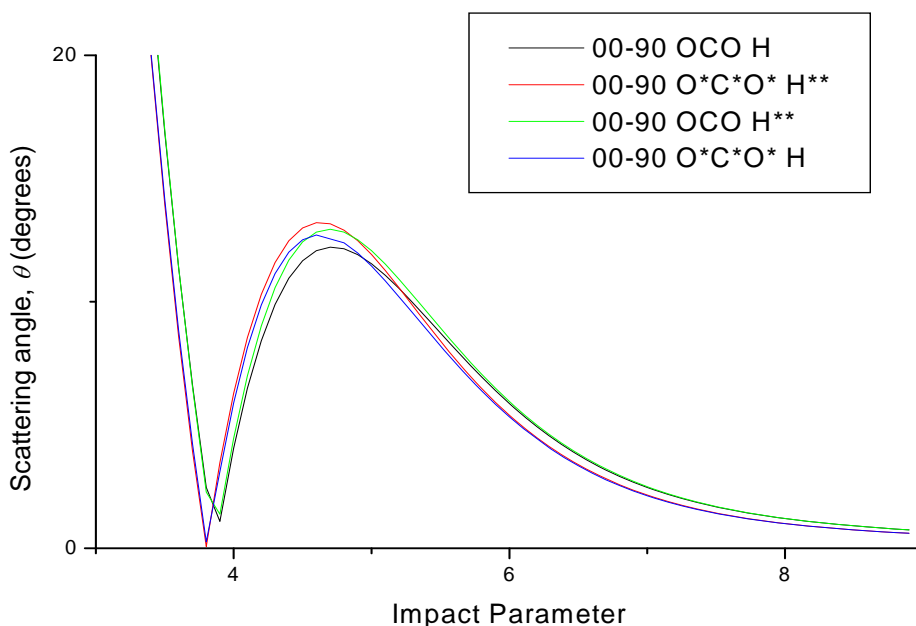
DISCUSSION

The simulations of this particular system did not show reactivity in the sense of forming a new compound. According to the results, the only reactivity process predicted was non-transfer scattering where the compounds are the same as the reactants. However some level of collision-induced vibrational excitation in the target molecule was observed. We had to select a particular orientation to observe those excitations more clearly. That selected orientation was [90, 0]. The Morales Research group decided to study the chemical system in more detail by using different basis sets so as to see if the same behavior occurred for all the orientations. These basis sets contain different types and number of mathematical functions to represent the total wave function. The results showed that the reactivity behavior was the same even if the basis set was changed. By comparing results from four basis sets, it was observed that the scattering angles do not depend much on the type of basis set.

The scattering angle was interpreted in the way a proton is getting closer to or farther from the target molecule. The proton can experience attractive and repulsive forces from the molecule target. The scattering results can be interpreted in the following graph that shows the scattering angle as a function of the impact parameter. The simulations used a range of impact parameters from 0.0 to 9.0 for different basis sets. The graph below (Non-Transfer Scattering for Orientation [90-00] for all the tested basis sets) exhibits a primary rainbow peak where it shows the maximum projectile attraction at high impact parameter (“b”). The meaning is that net attractive forces are acting at about that impact parameter. Also, the zero the glory angle corresponds to neither attractive nor

repulsive scattering processes. Usually the glory angle occurs at impact parameters lower than that of the primary rainbow angles. As shown below in the graph, the different orientation shows similar scattering angles at the same impact parameters even when the basis sets are different.

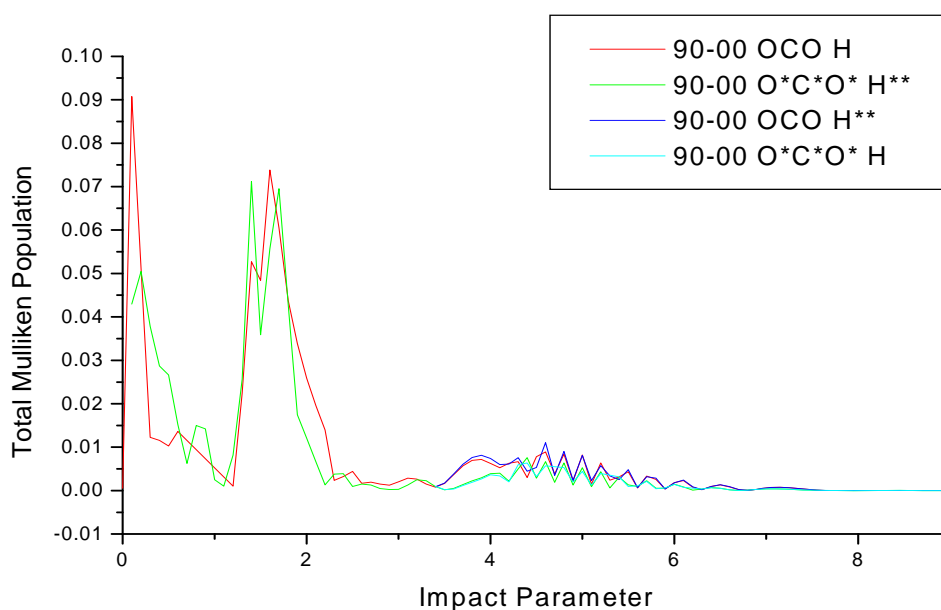
Non-Transfer Scattering for Orientation [90-00] in all the basis sets



There is another important variable in this analysis that is necessary to observe. The Mulliken Population of the orientation [90, 0]. The Mulliken population estimated the number of electrons on each atom. The proton is positively charged at initial times. There is a possibility that the electron density cloud of the target molecule get into the proton. The proton could become a neutral atom while the target molecule becomes charged. The results show that there was no charge in the proton at impact parameters from 0.0 to 2.5 a.u. where the Mulliken Population was studied only in two basis set as shown in the following graph (90-00 OCO H and 90-00 O6-31*C6-31*O6-31* H6-

31**). In the other two basis sets (90-00 O6-31C6-31O6-31 H6-31** and 90-00 O6-31*C6-31*O6-31* H6-31) it has been demonstrated that there is charge on the proton as reported previously by other scientists. The following graph has Mulliken Population with respect to Impact Parameter.

Mulliken Population for Orientation [90-00] in all the basis sets

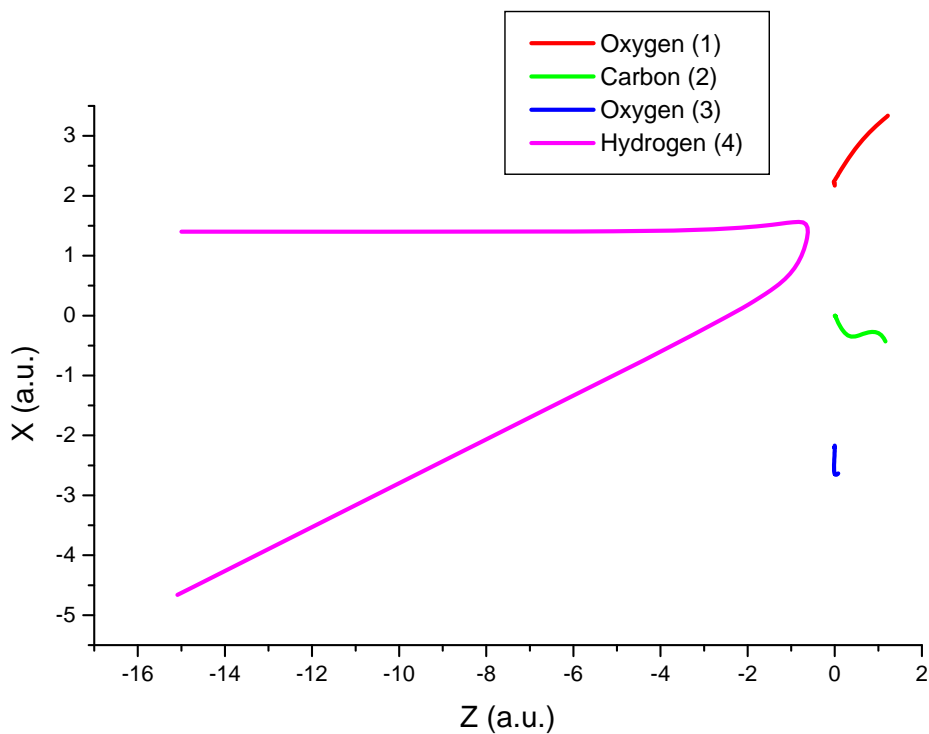


Finally, we illustrate the scattering and reactive processes by plotting the relative distances between atoms at different simulation times. On the reactivity table, we found vibrational behavior on the target molecule carbon dioxide on orientation [90, 00]. Also, the proton showed deflection behavior. The relative motion of the atoms is different at different impact parameter. There are some impact parameter ranges where the vibrations are strong as shown below in the table below:

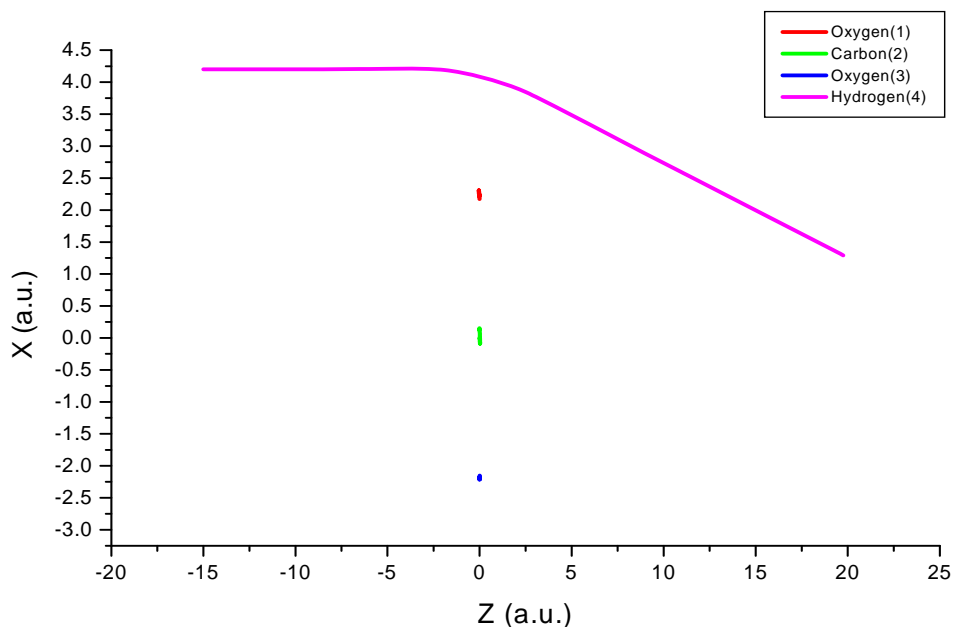
[90,0]	0.4-2.0	O1---O2 Vibration
	1.0-1.6	C2---O3 Vibration
	0.0-2.0	C2---O1 Vibration
	0.5-2.0	O1---H4 Deflection
	0.0-0.4	C2---H4 Deflection
	0.0-2.0 (O3 & H away from each other)	O3---H4 Deflection

A detail of those processes is shown on the graph below with orientation 90 and impact parameter 1.4. The following graph is showing that a repulsive force on the incoming proton by the target molecule is involved in orientation 90 and impact parameter 4.2. This behavior happens in the middle of low and high impact parameters.

Orientation 90, Impact Parameter 1.4



Orientation 90, Impact Parameter 4.2



CONCLUSION

The study of the selected chemical system is crucial to understand current atmospheric changes that can influence climate and weather. Carbon dioxide is one of the green gases that exists in the atmosphere, and which is required for many chemical function pathways that exist in the Earth planet. Our simulations show that no modification on the atmosphere may take place as a result of the interaction between carbon dioxide molecules and solar wind protons. The present study for this particular system showed theoretically that no reactivity of a proton and carbon dioxide occurred. According to our results, sometime the protons induce the carbon dioxide's vibration. In a few cases, the double bonds of carbon dioxide were almost broken by the incoming proton. In our research approach electron nuclear dynamics played an important role to understand reactivity in terms of quantum mechanics theory. Our results lead to the

conclusion that there is not appreciable reactivity in the selected chemical system ($\text{H}^+ + \text{CO}_2$).

REFERENCES

Acknowledgments:

I would like to thank Dr. Jorge A. Morales for being my faculty mentor in this McNair/URP research project. Also, I would like to thank Mr. Patrick McLaurin for teaching me all the computational tools during my research times and for his patience. Then, I would like to thank the High Performance Computational Center. Finally, I would like to thank the McNair/URP program for letting me to accomplish one of my dreams in doing this research project.

1. G. Niedner, M Noll, J.P. Toennies; **Journal of Chemical Physics**, Volume 87, Year 1987, pages 2067-2083, "Selective Vibrational Excitation and mode conservation in $H^+ + CO_2$ inelastic and charge transfer collisions."
2. Jorge A. Morales, Buddhadev Maiti, Yunan Yan, Kakha Tsereteli, Jennifer Laraque, Srirangm Addepalli; **Chemical Physics Letters**, Volume 414, Year 2005, Pages 405-411, "Coherent-states dynamics of the $H^+ + C_2H_2$ reaction at $E_{lab}=30eV$: A complete electron nuclear dynamics Investigation."