Global Warming Lecture
3-31-08
Dr. Steven Davis

Department of Chemistry and Biochemistry
University of Mississippi

Calculation of Potential Energy Surfaces using ab initio Quantum Chemistry Techniques

Potential Energy Surfaces

Plots of Energy vs Nuclear Coordinates

Cartesian Coordinates = 3N
Internal Coordinates = 3N-6 or 3N-5
3 translations
2-3 rotations

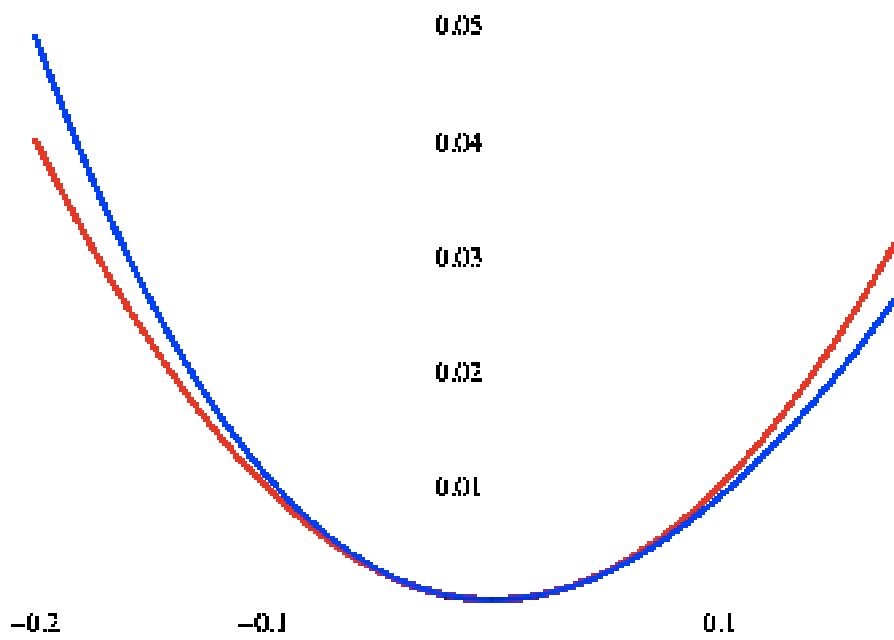
ernal Coordinates are bond lengths and ang

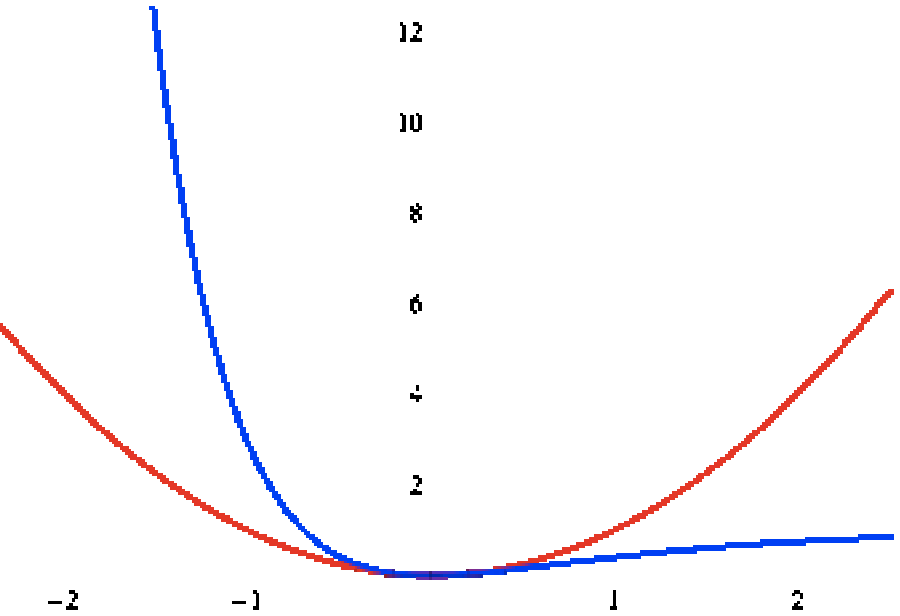
rmal Vibrational Modes Expressed in Terms
Internal Coordinates

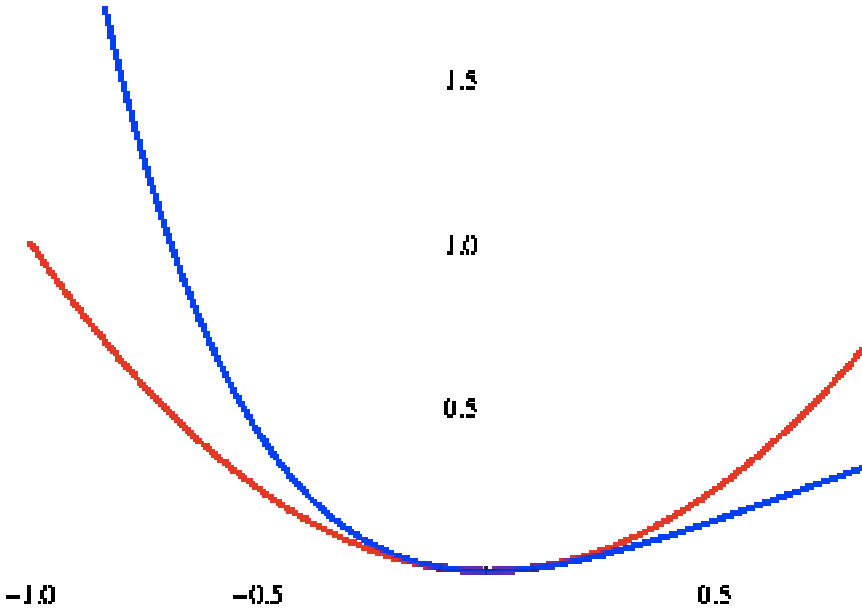
[{x^2, (1 - e^-x)^2}, {x, -0.2, 0.2}

- quadratic (harmonic oscillator)

ed - Morse potential (atomic interactions)







Schrödinger Equation

$$\mathcal{H}\Psi = E\Psi$$

$$\mathcal{H} = T + V = \sum_{i=1}^{n} \frac{p_i^2}{2m_e} - \sum_N \sum_i \frac{Z_N e^2}{r_{iN}} + \sum_{M>N} \frac{Z_M Z_N e^2}{R_{MN}} + \sum_{i>j} \frac{e^2}{r_{ij}}$$

$$\Psi = \begin{vmatrix} \chi_1(1) & \chi_2(1) & \cdots & \chi_n(1) \\ \chi_1(2) & \chi_2(2) & \cdots & \chi_n(2) \\ & & \vdots & \\ \chi_1(n) & \chi_2(n) & \cdots & \chi_n(n) \end{vmatrix}$$

The Variation Theorem States:

$$E' = \frac{\int \Phi^* \mathcal{H} \Phi d\tau}{\int \Phi^* \Phi d\tau} > E \qquad \text{where } \Phi \text{ is a trial wavefunction and } \Phi_k = \sum_i c_{ki}\phi_i$$

$$\frac{\partial E'}{\partial c_{ki}} = 0 \text{ leads to the Roothan-Hall equations}$$

$$\sum_{v=1}^{n} (F_{uv} - \epsilon_i S_{uv}) c_{vi} = 0 \qquad u = 1, 2, \ldots n$$

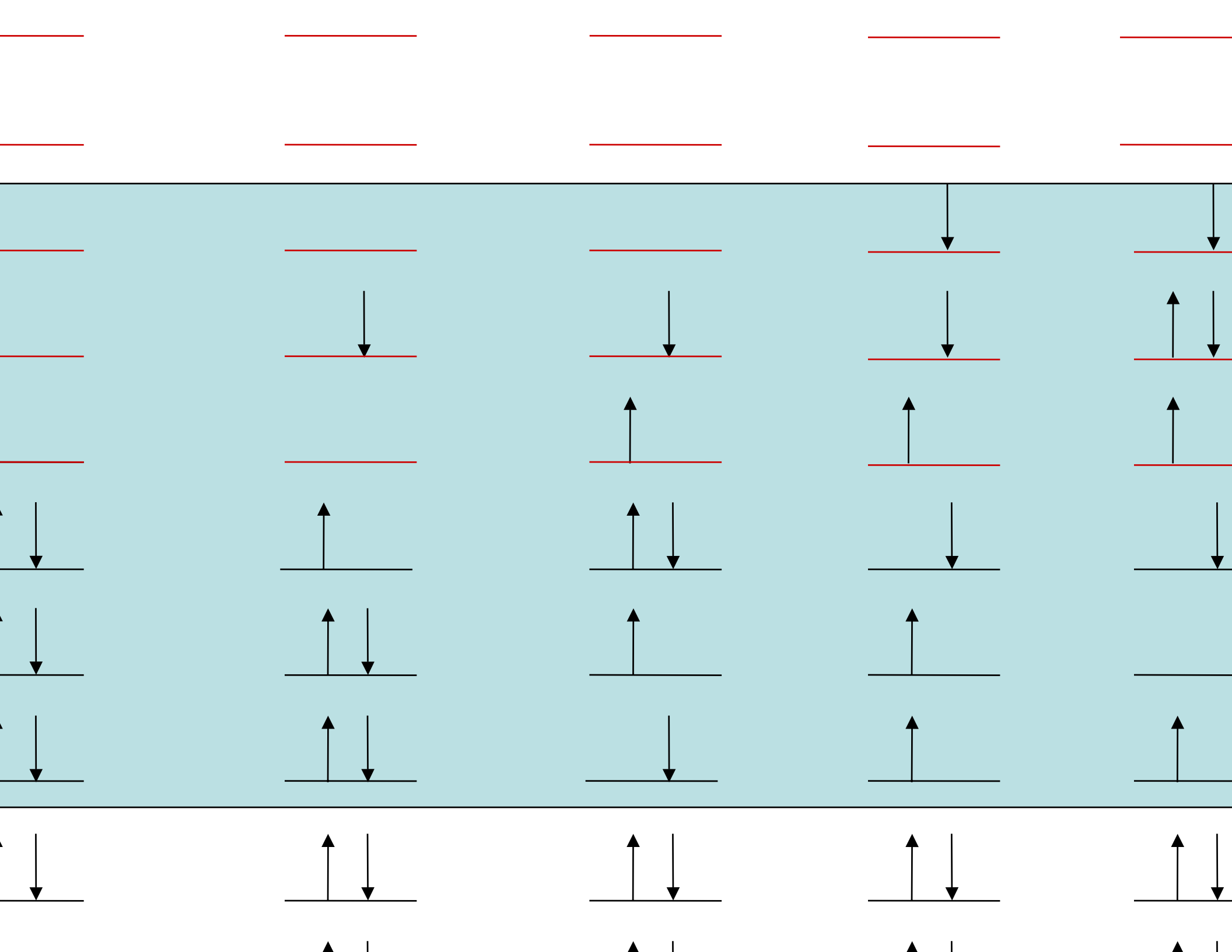
Configuration Interaction

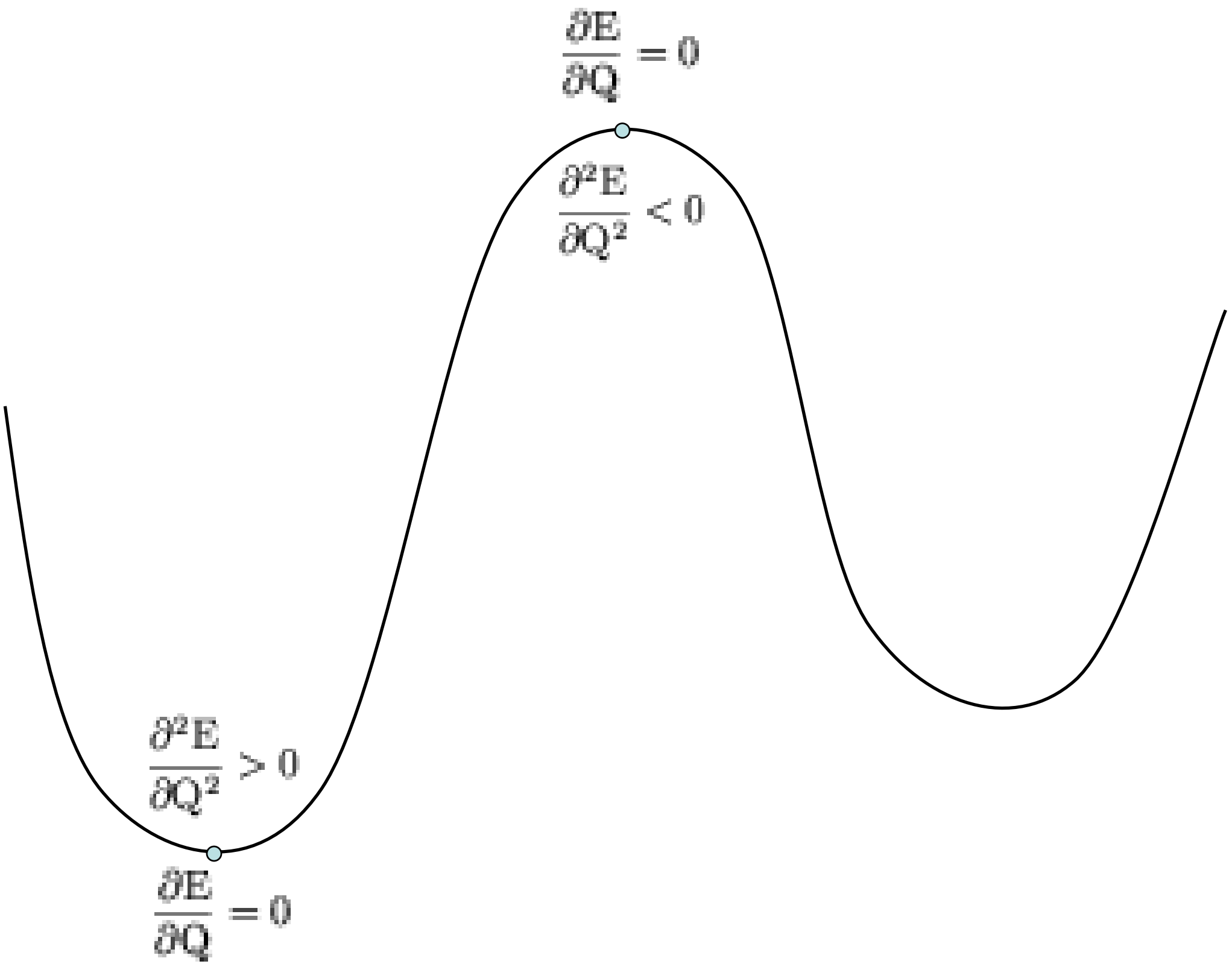
$$\Psi >= c_0|\Psi_0 > + \left(\frac{1}{1!}\right)^2 \sum_{ar} c_a^r|\Psi_a^r > + \left(\frac{1}{2!}\right)^2 \sum_{abrs} c_{ab}^{rs}|\Psi_{ab}^{rs} > + \left(\frac{1}{3!}\right)^2 \sum_{abcrst} c_{abc}^{rst}|\Psi_{abc}^{rst} > + \cdots$$

Moller-Plessett Perturbation Theory

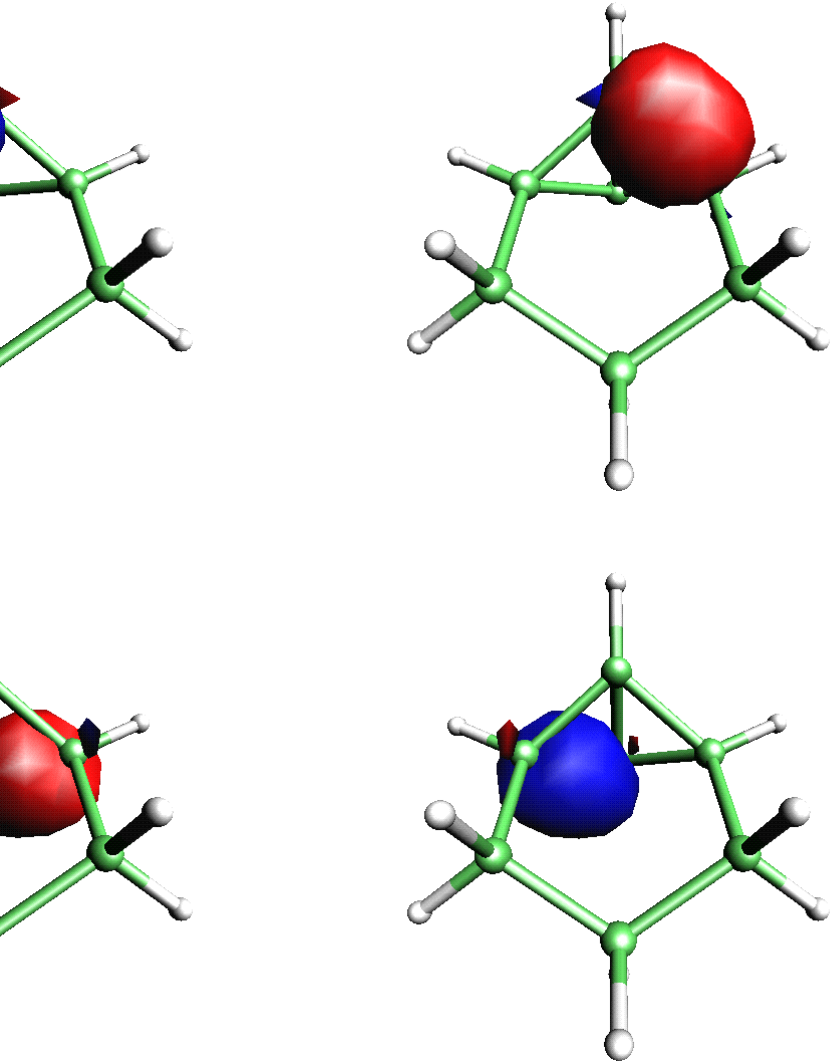
$$E_0^{(0)} = \sum_a \epsilon_a \qquad E_0^{(1)} = < \Psi_0|V|\Psi_0 > \qquad E_0^{(0)} + E_0^{(1)} = \text{HF Energy}$$

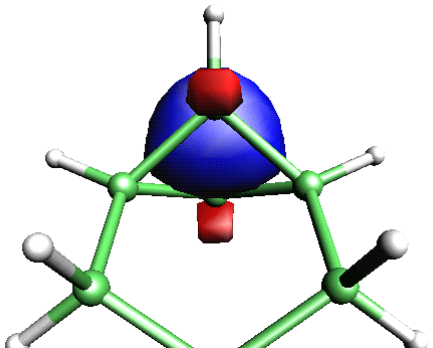
$$E_0^{(2)} = \sum_{a<b} \frac{\left| < \Psi_0| \sum_{i<j} \frac{1}{r_{ij}} |\Psi_{ab}^{rs}| \right|^2}{\epsilon_a + \epsilon_b + \epsilon_r + \epsilon_s}$$



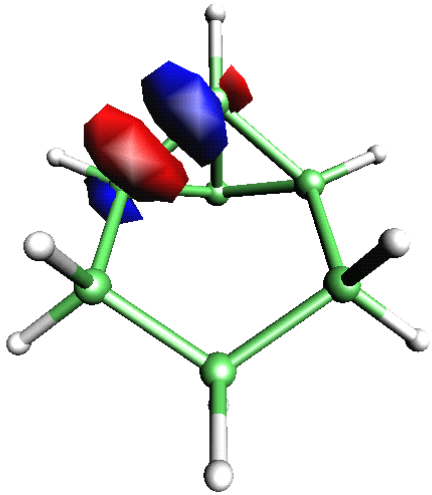

$\frac{\partial E}{\partial Q} = 0$
$\frac{\partial^2 E}{\partial Q^2} < 0$
$\frac{\partial^2 E}{\partial Q^2} > 0$
$\frac{\partial E}{\partial Q} = 0$

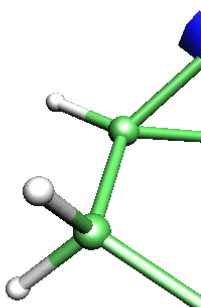
Occupied orbitals

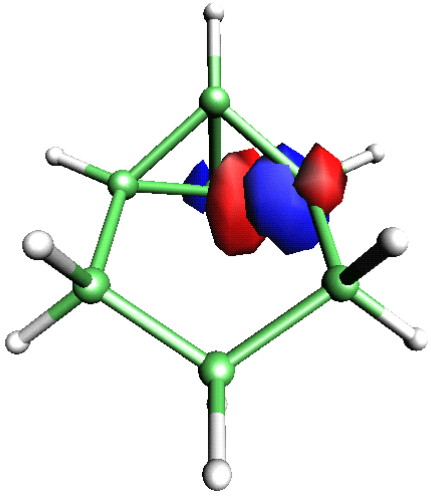


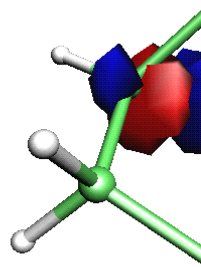


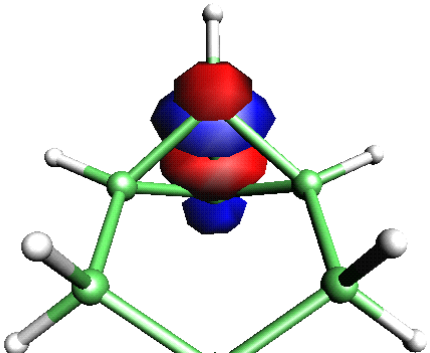
Virtual orbitals





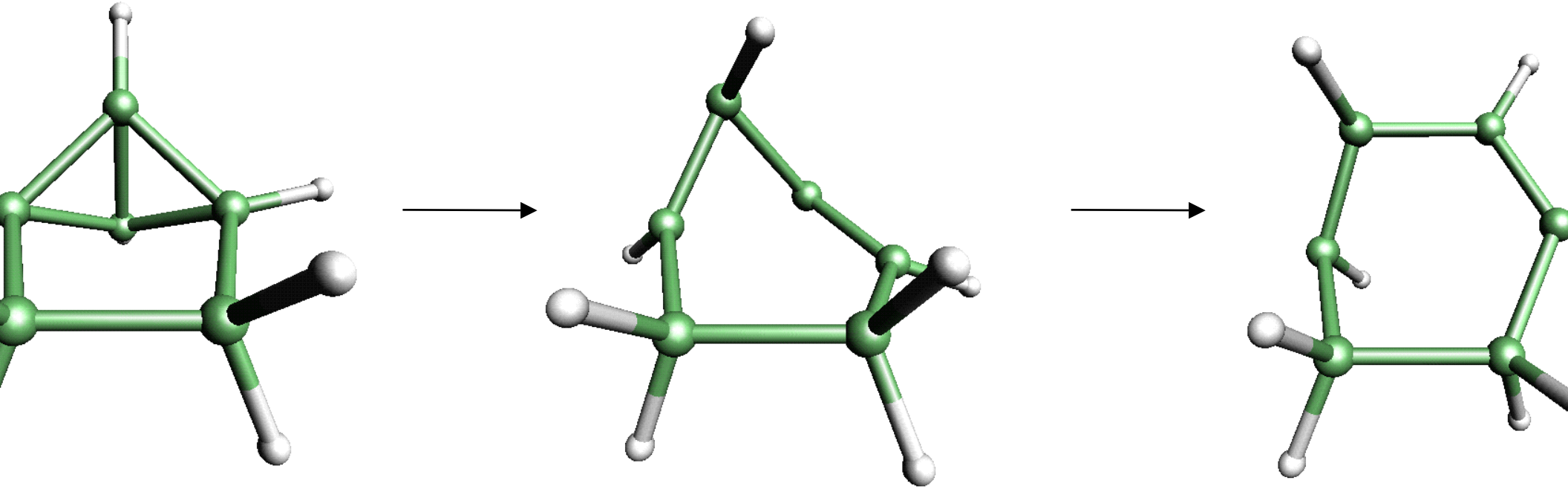






Tricyclo[3.1.0.0^{2,6}]hexane (TC6) Isomerization

Allowed Pathway

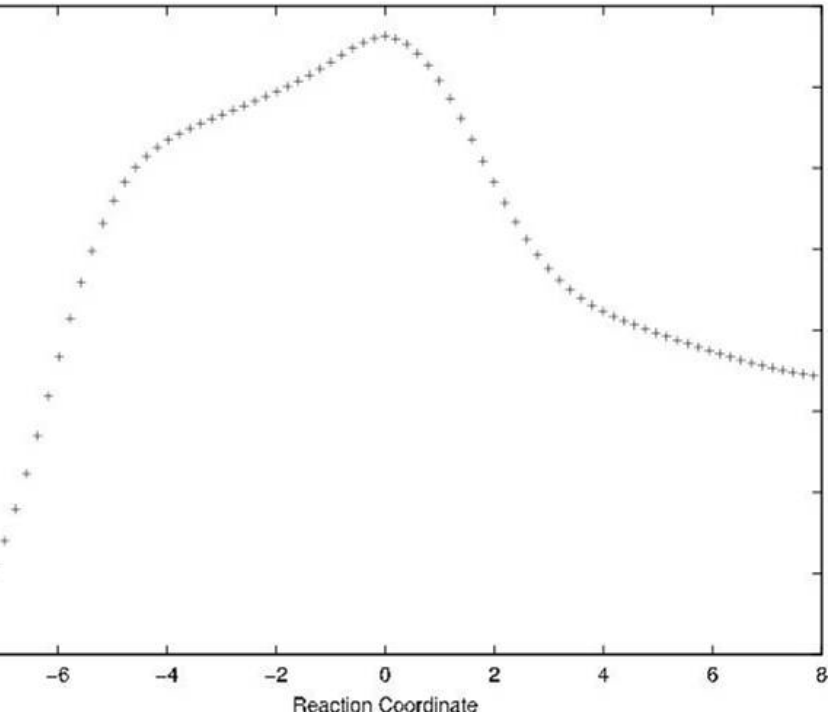


TC6 TS (E,Z)-C6D

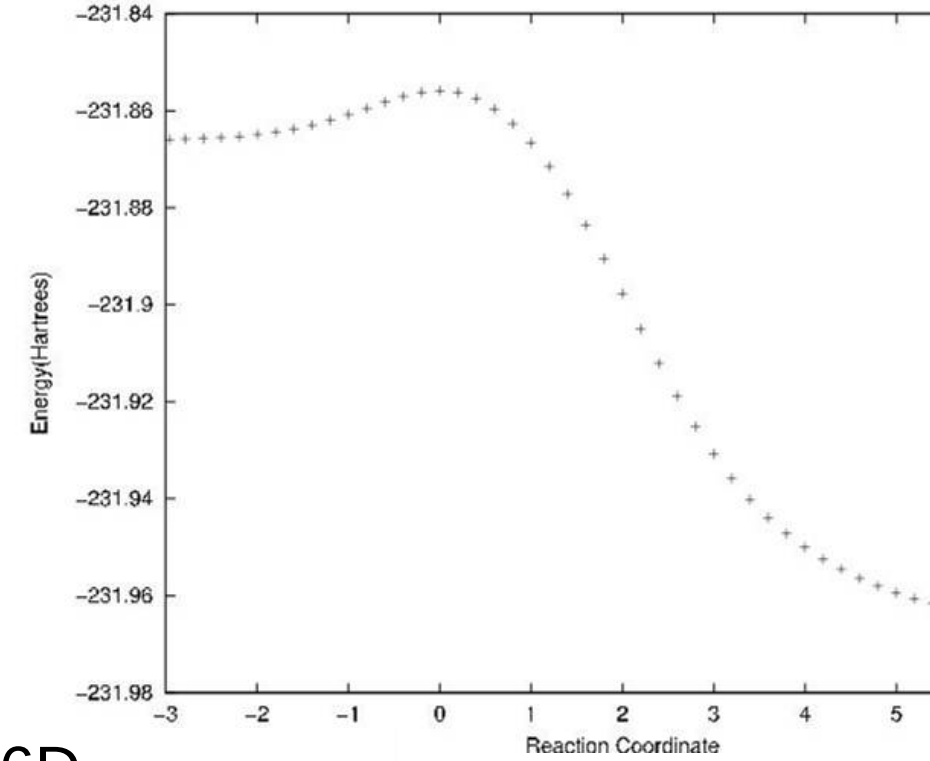
Activation Energies in kcal/mol (including ZPE)

MCSCF	MCQDPT2	CCSD(T)	MP2	B3LYP

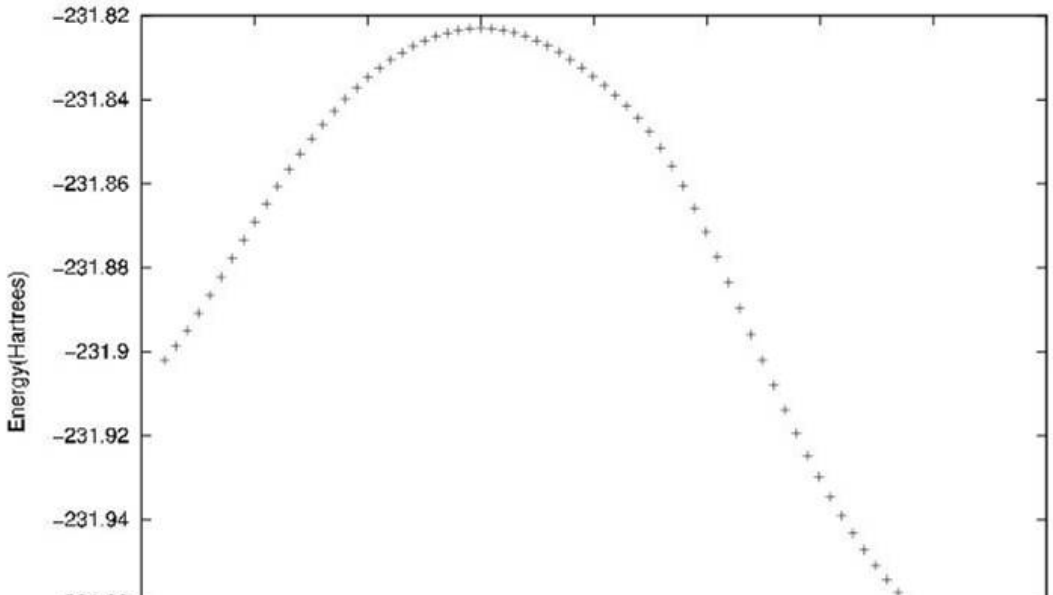
TC6 → (E,Z)-C6D



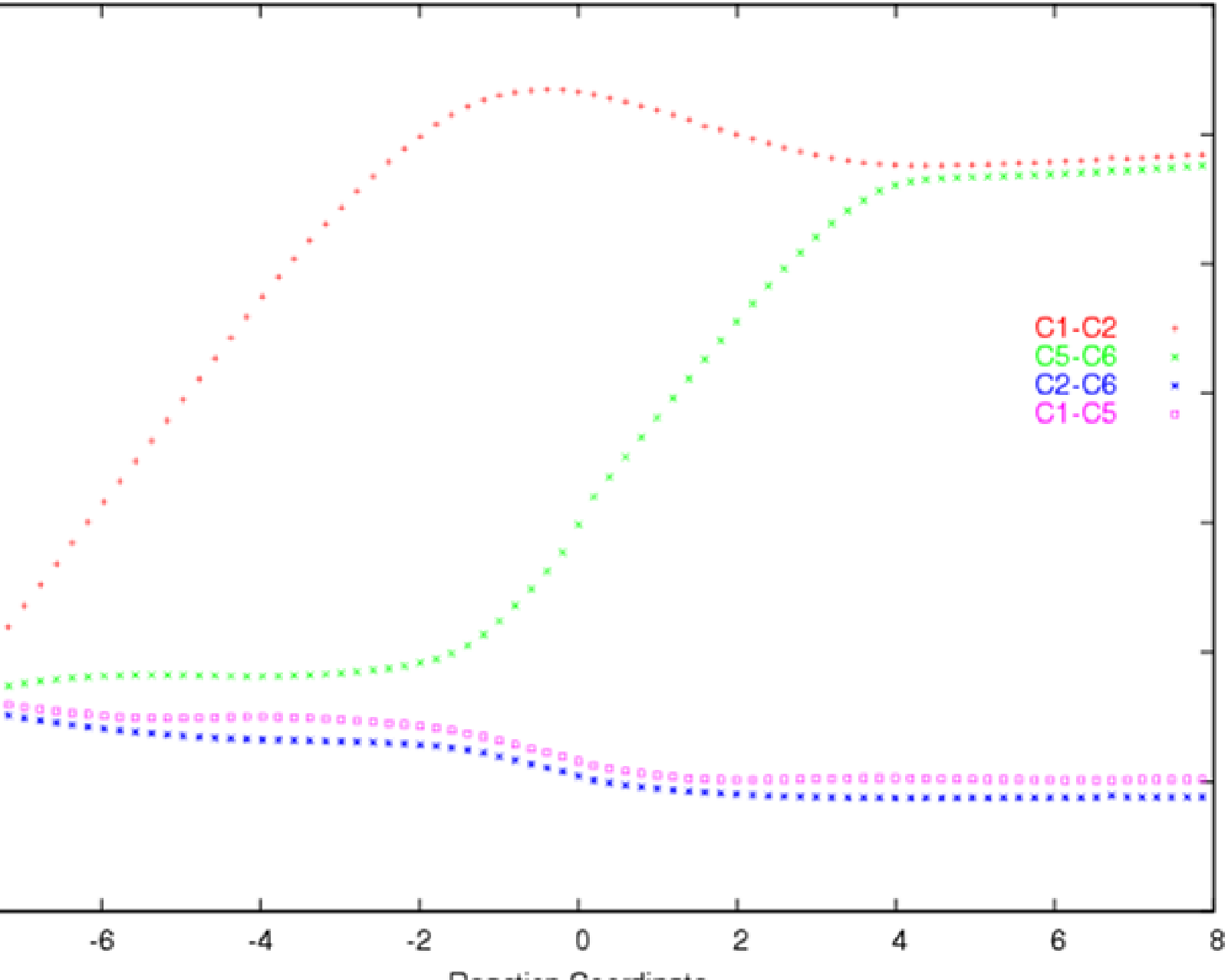
(E,Z)-C6D → (Z,Z)-C6D

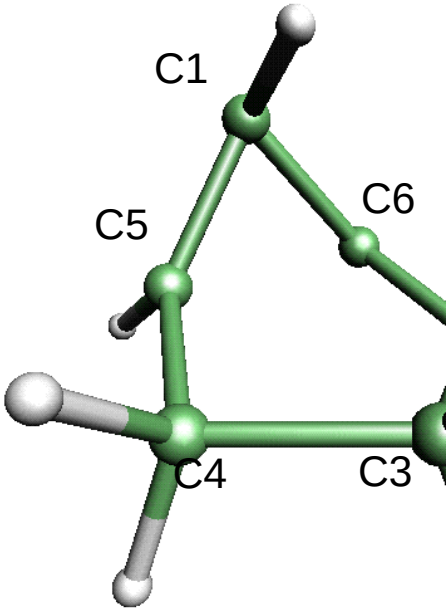


TC6 → C6D



Plot of Bond Distance vs. Reaction Coordinate

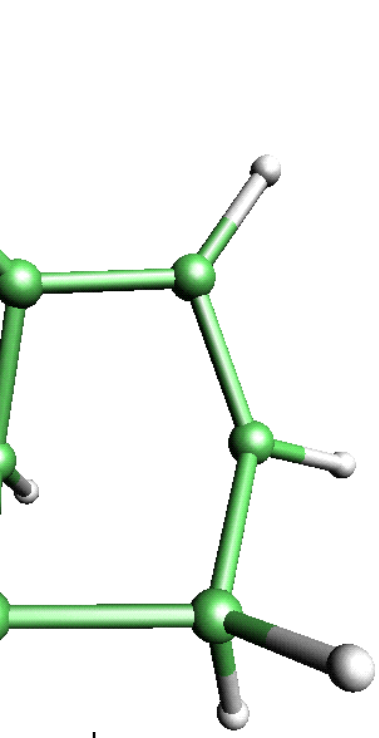


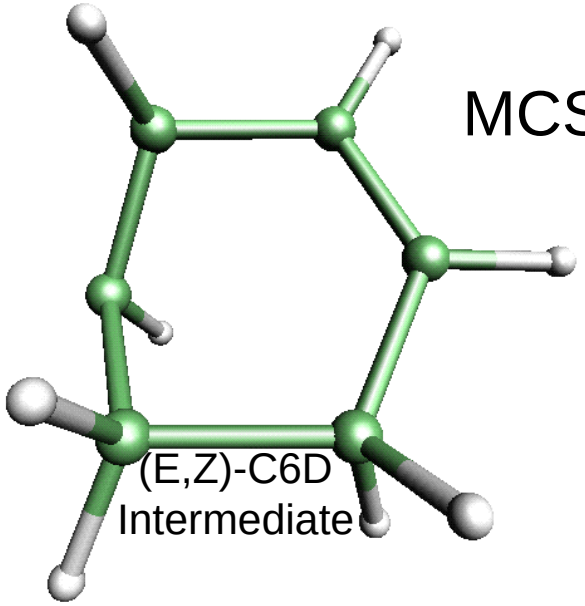


at the MP2 and MCSCF Levels

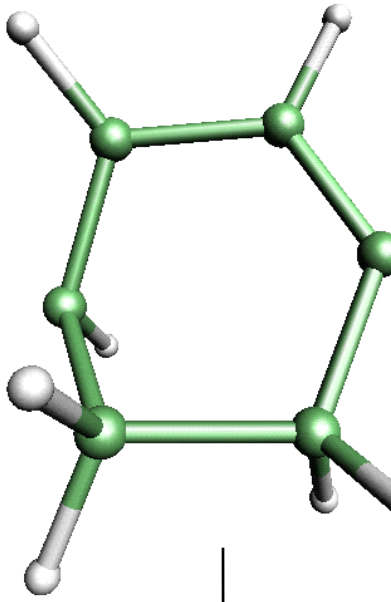
MP2 Level

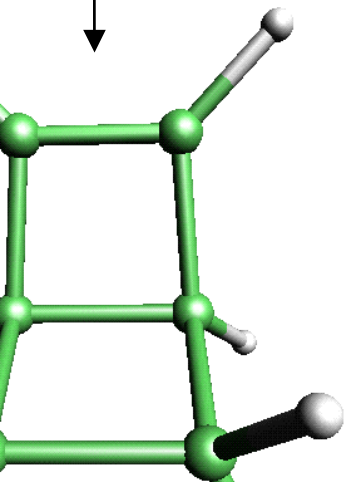
MCSCF Level





(E,Z)-C6D
Intermediate

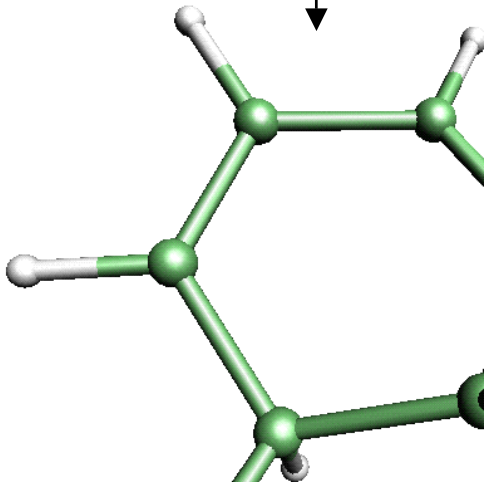




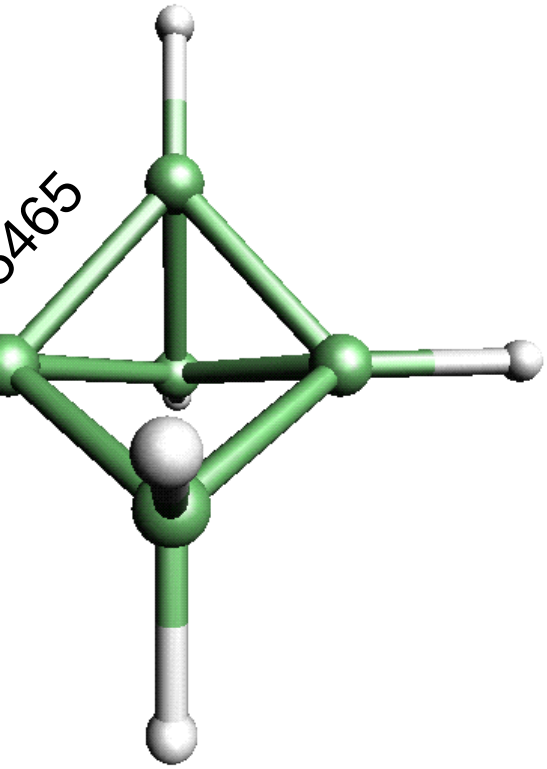
Natural Orbital Occupation Numbers

for TS at MCSCF Level

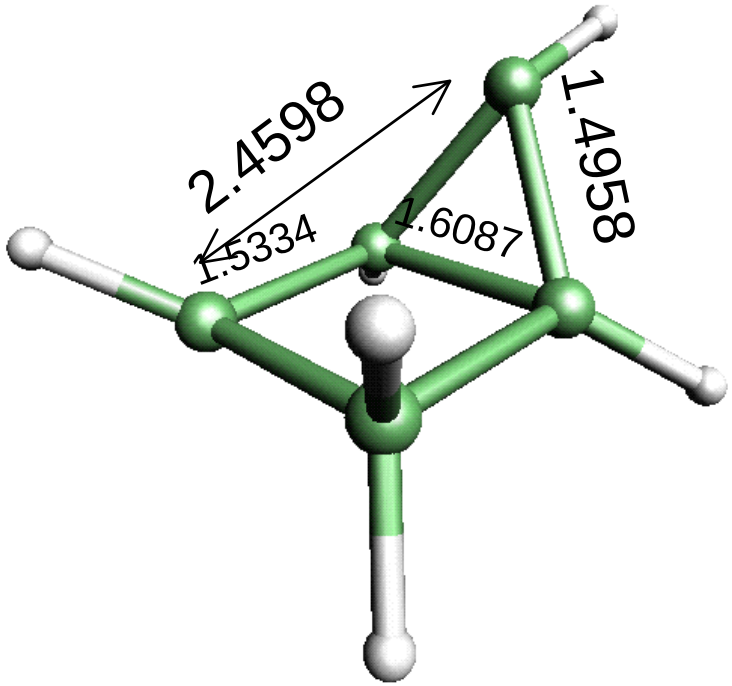
Occupied	Virtual
1.9834	0.0179
1.9783	0.0213
1.9756	0.0225
1.9110	0.0887



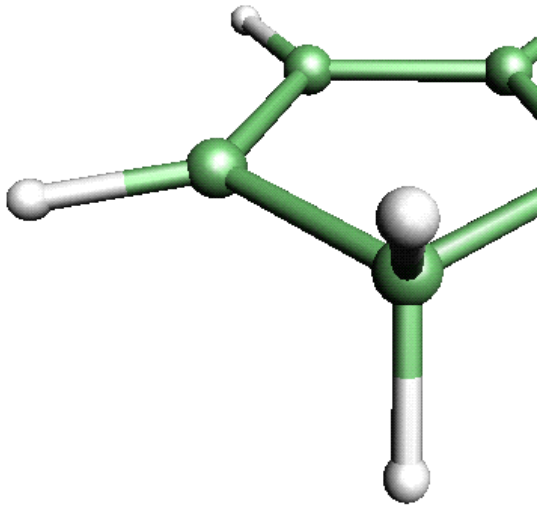
Forbidden Pathway



TC5

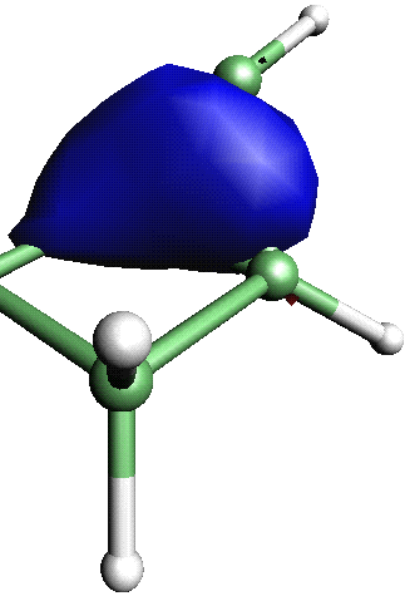


TS

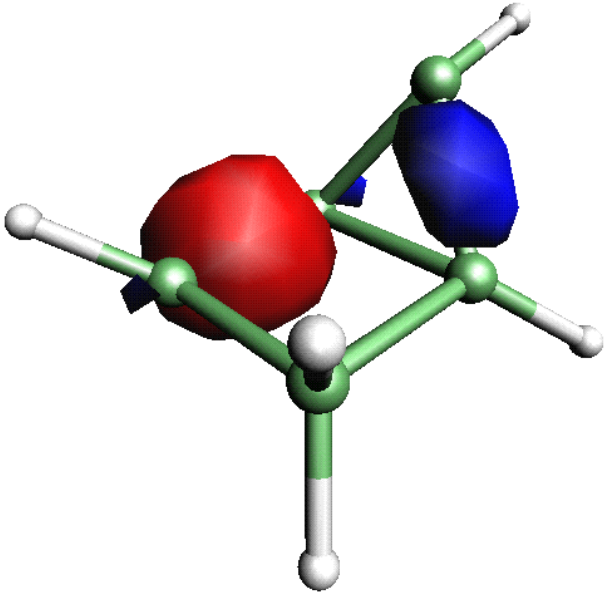


C5D

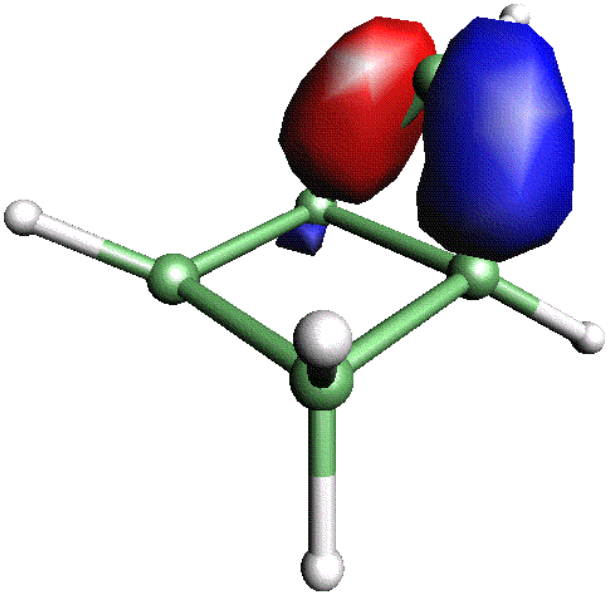
ccupied Molecular Orbitals and Natural Orbital Occupation Numbers



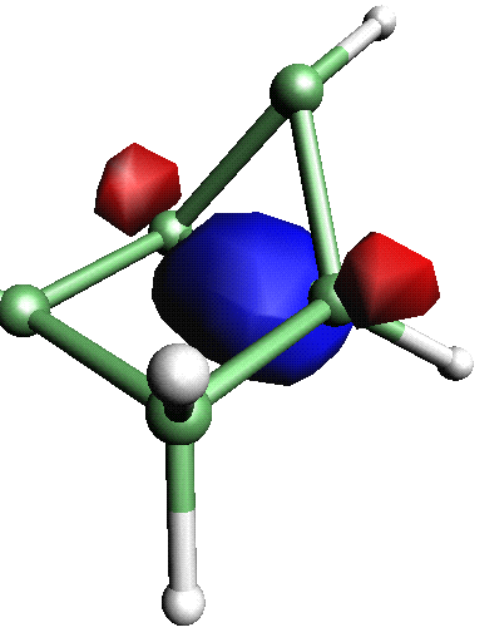
1.9832

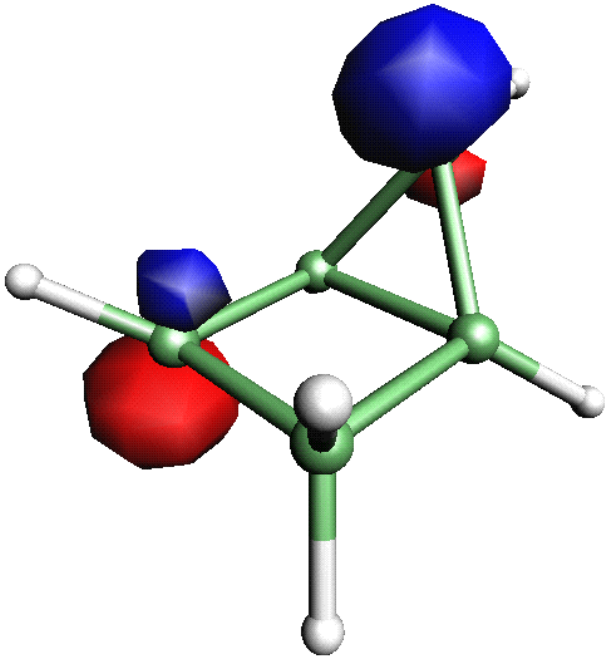


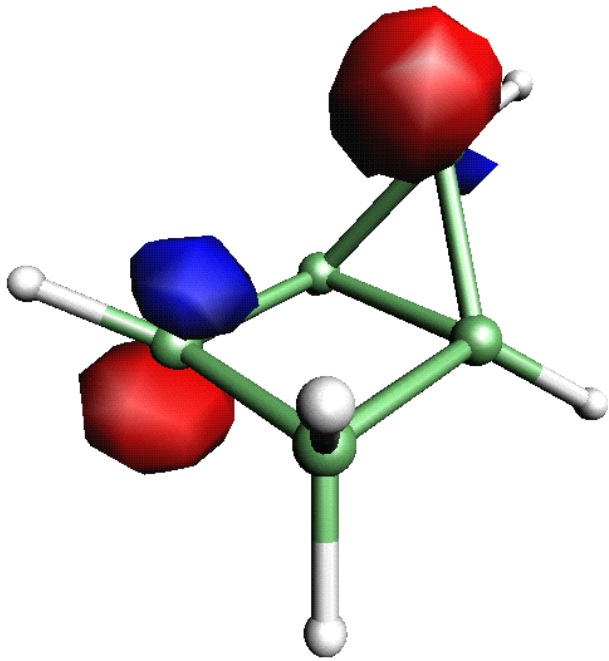
1.9765



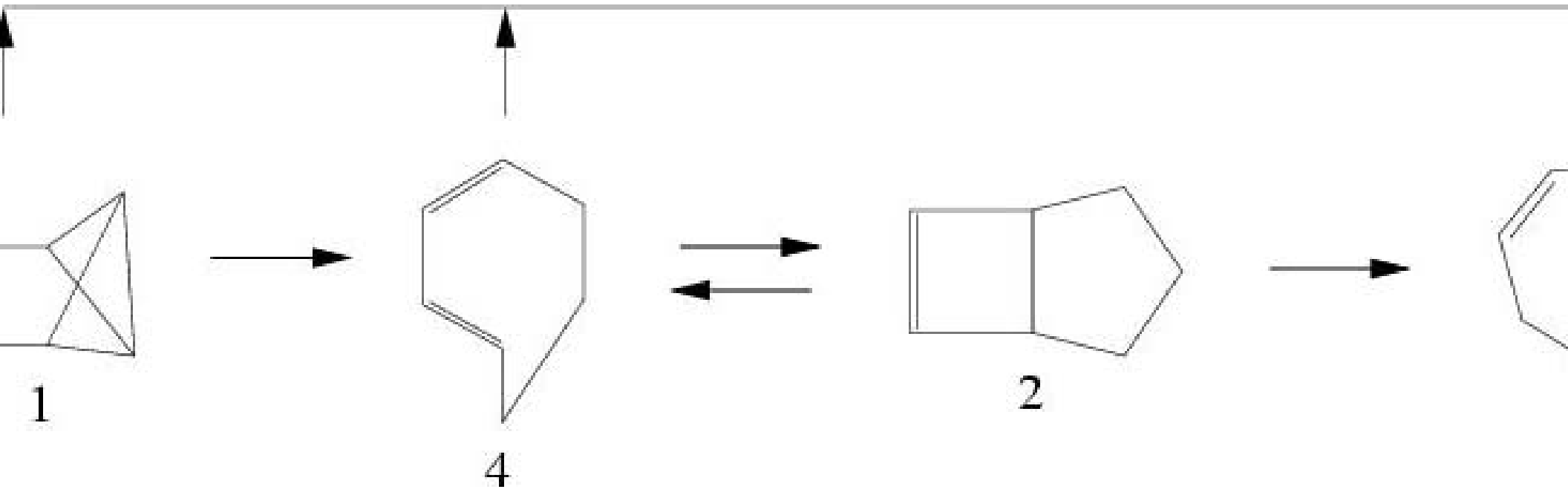
1.9681





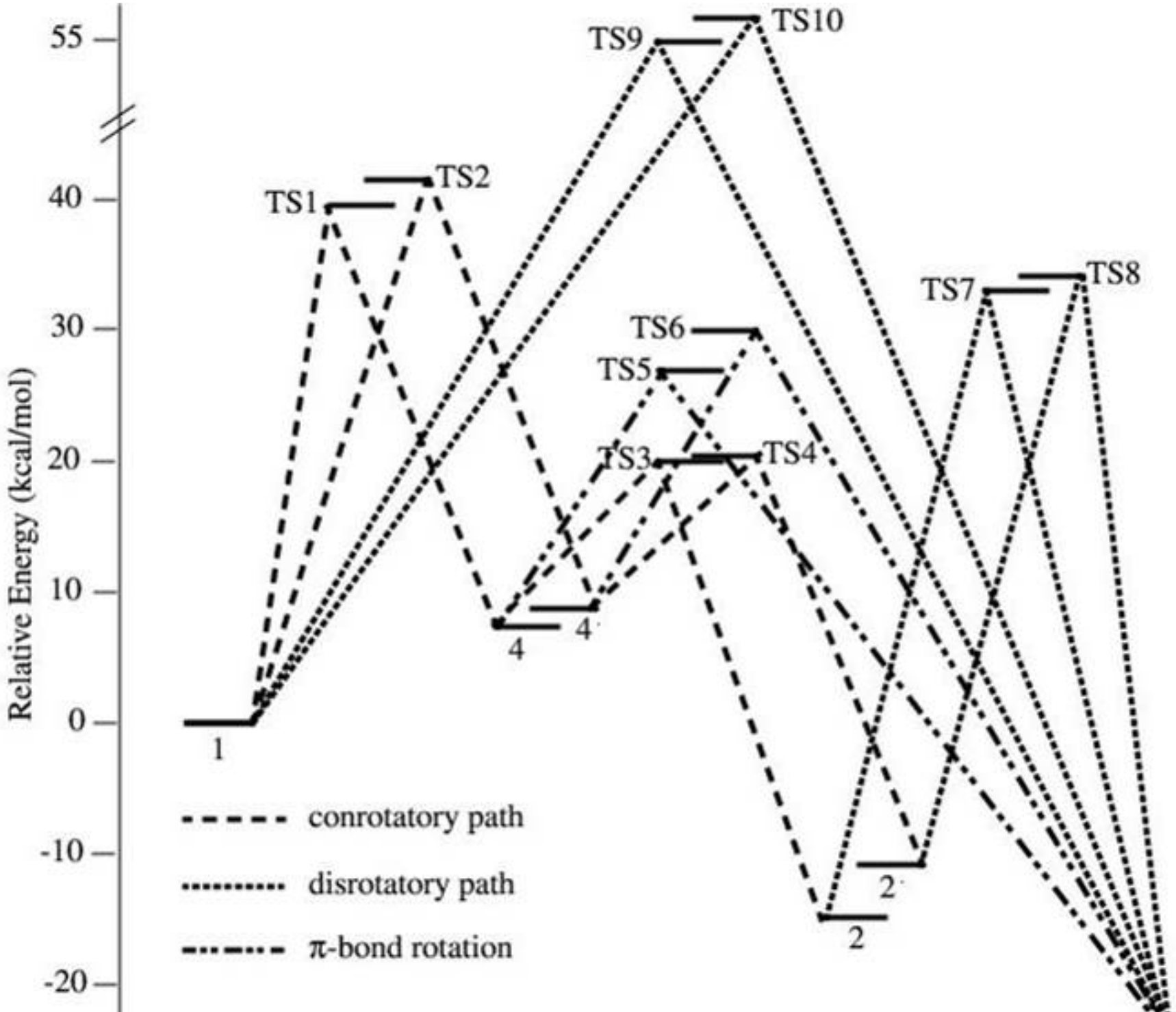


Tricyclo[4.1.0.0^{2,7}]heptane Isomerization



Qin, C. and Davis, S. R. *J. Org. Chem*. **2003,** *68*, 9081

Reaction Summary



Two Opposing Nineteenth Century Views of Chemistry

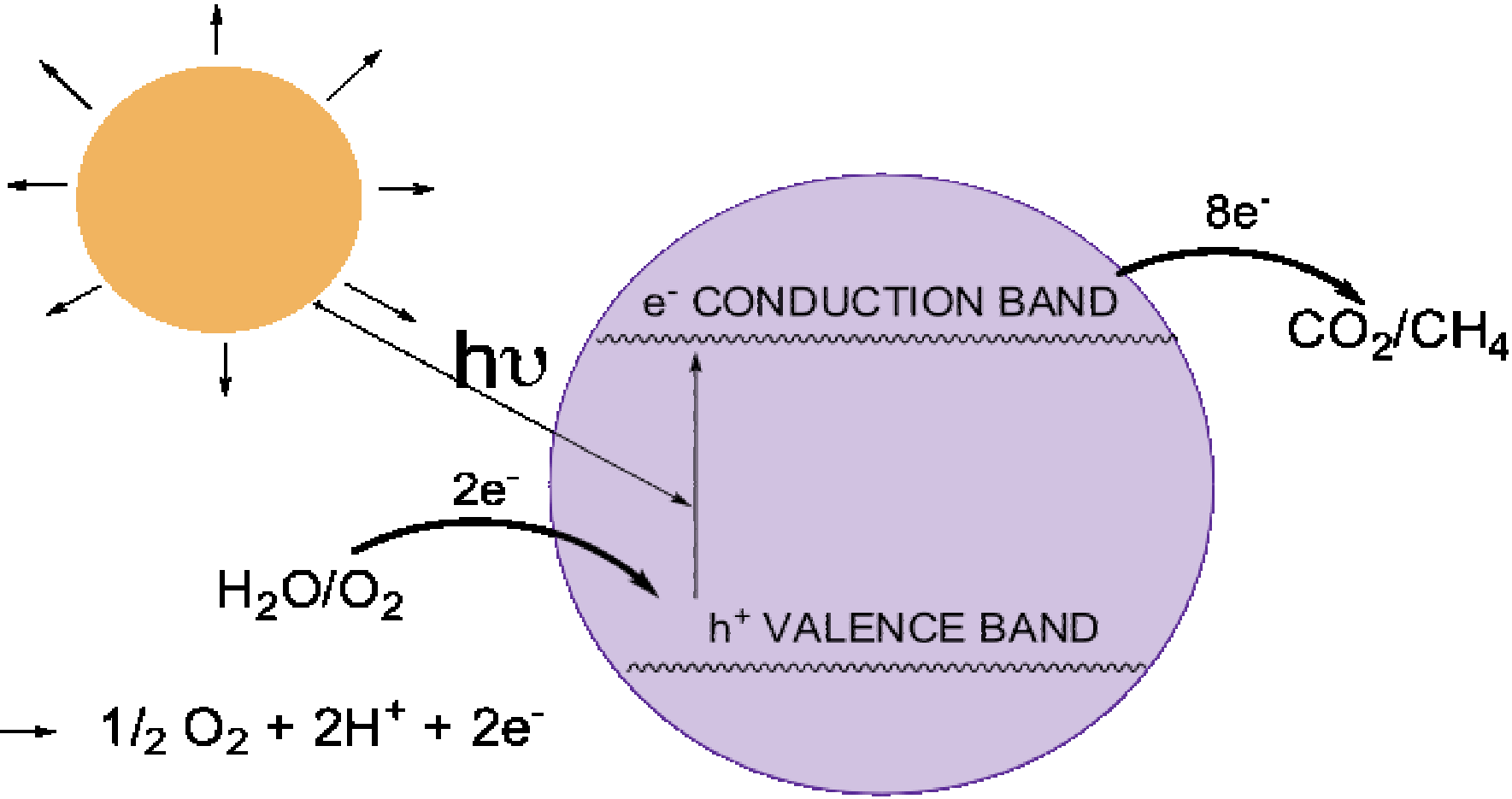
Every attempt to employ
mathematical methods in the
study of chemical questions
must be considered profoundly
irrational and contrary to the
spirit of chemistry. If
mathematical analysis should
ever hold a prominent place in
chemistry – an aberration
which is happily almost
impossible – it would occasion
a rapid and widespread
degeneration of that science."

Compte *Philosophie Positive* **1830**.

"The more progress physica
sciences make, the more th
tend to enter the domain of
mathematics, which is a kin
center to which they all
converge. We may even ju
the degree of perfection to
which a science has arrived
the facility with which it may
submitted to calculation."

A. Quetelet, *Instructions Populaires sur le C*
des Probabilites, Tarlier, Brussels, **1828**.

CO_2 photocatalytic reduction



$$H_2O \longrightarrow 1/_2\, O_2 + 2H^+ + 2e^-$$

$$CO_2 + 8H^+ + 8e^- \longrightarrow CH_4 + 2H_2O \quad E^o = -0.24 \text{ V vs NHE @ pH=7}$$

$$CO_2 + 2H_2O \xrightarrow{h\upsilon} CH_4 + 2O_2$$

Venkata Pradeep Indrakanti, J.D.Kubicki, M.M. Maroto-Valer, H.H. Schobert

July 11, 2007

CHEMRAWN-XVII and ICCDU-IX conference on greenhouse gases

Objectives

entify the intermediate species formed during CO_2 photoreductio

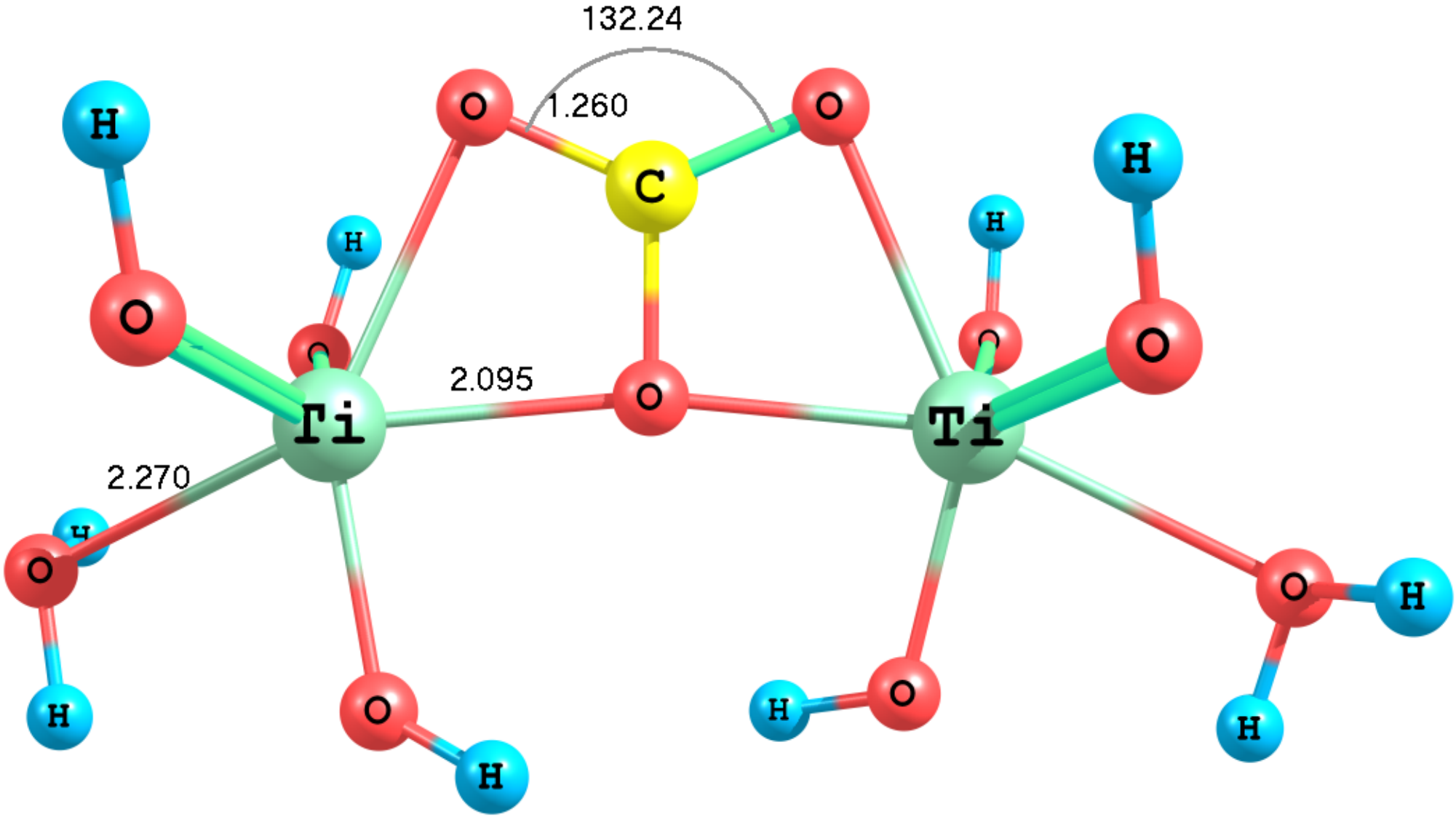
odeling the excited-state chemistry of CO_2 species adsorbed on rious low index surface planes of TiO_2 .

st the hypothesis of dopant-induced charge carrier trapping fecting photoactivity by performing photoreactions with various ncentrations of La, Sm and Gd-doped TiO_2 as photocatalysts.

udy the intermediates of this photoreduction through spectrosco aracterizations and use computational methods to rroborate/complement spectroscopic data.

singlet

B3LYP/6-31+G(d), C_2 symmetry



Bond lengths in Å, angles in degrees

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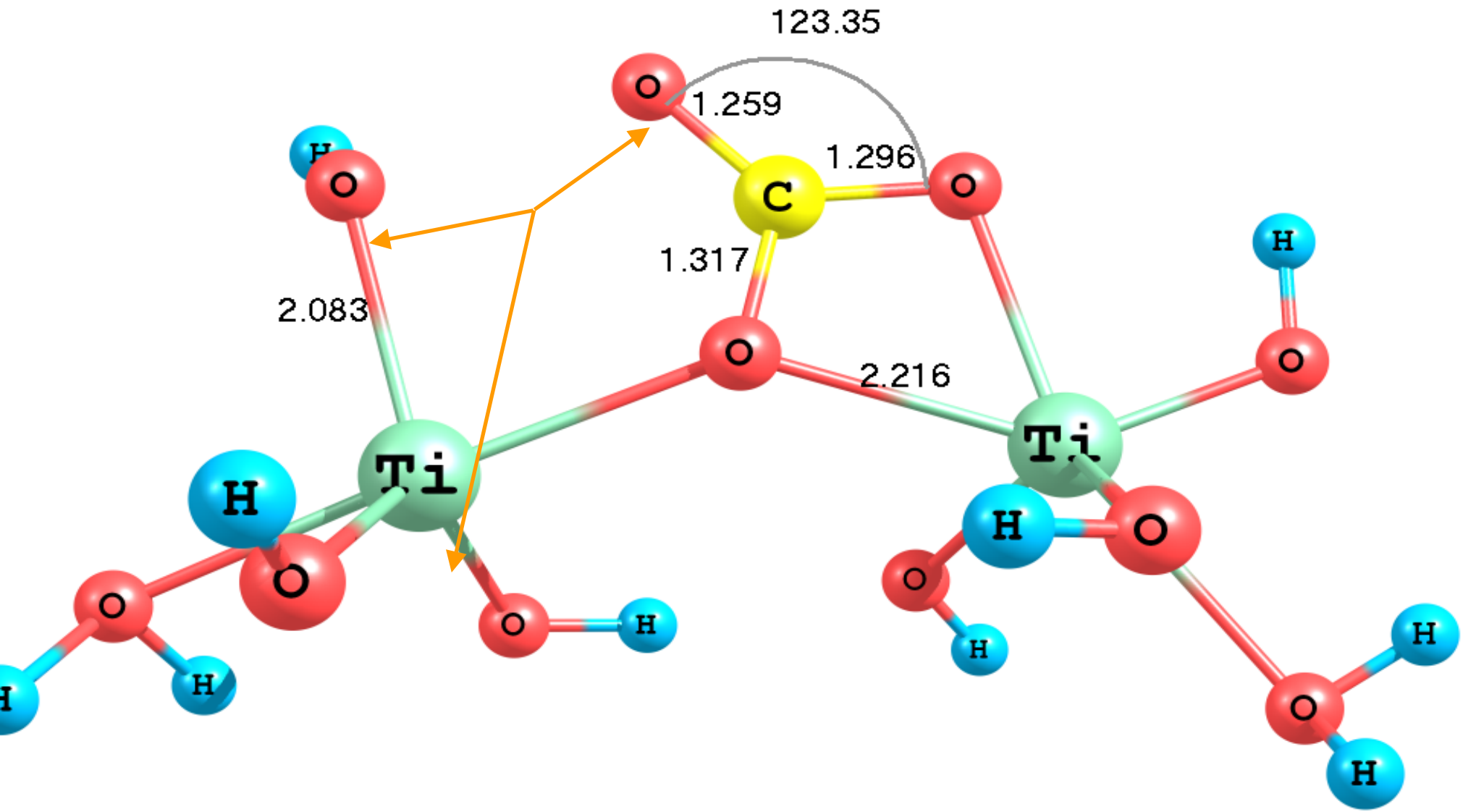
July 11, 2007

triplet B3LYP/6-31+G(d)



CO_3 species (triplet-singlet ^{TM}q) = -0.29 e^-

Bond lengths in Å, angles in degrees

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