Chemical Materials Department

Transition state calculations and Intrinsic Reaction Coordinate

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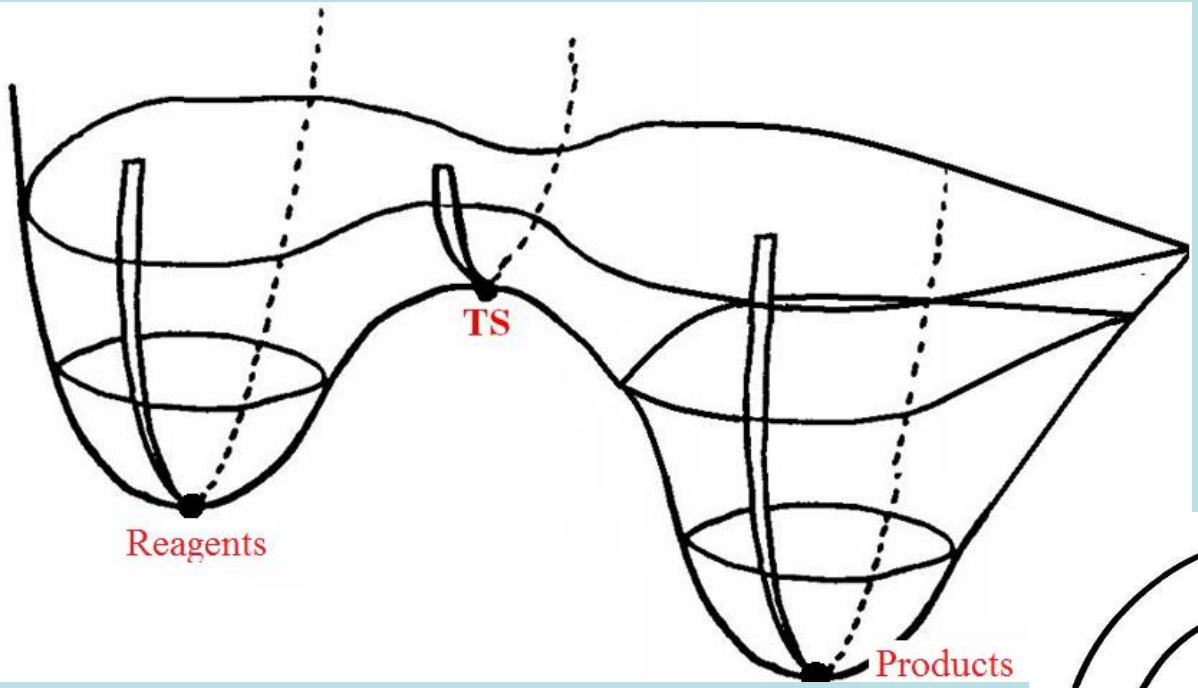
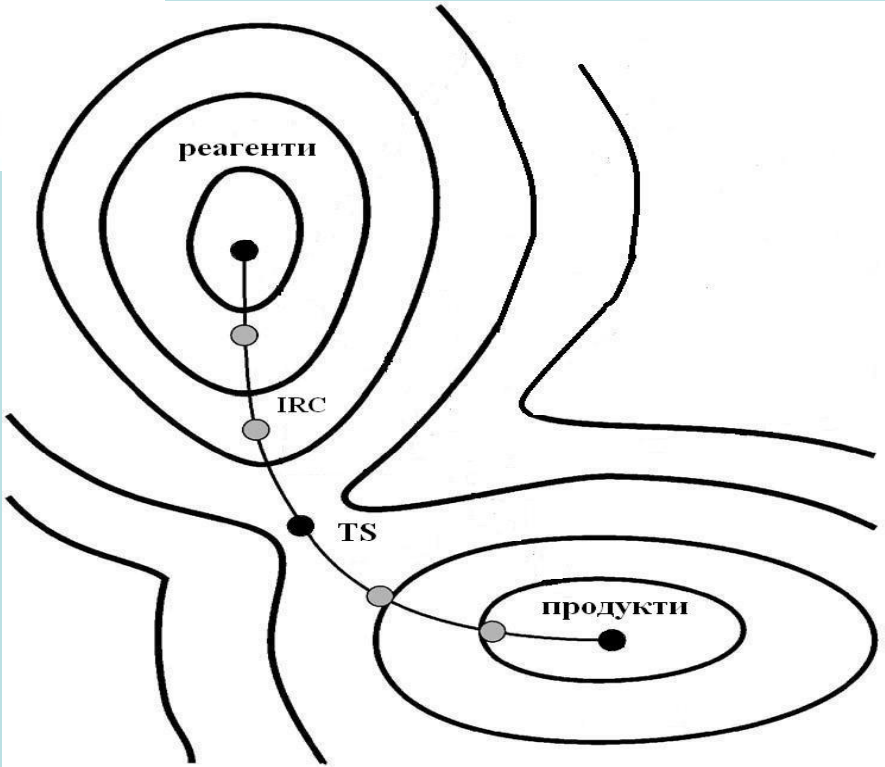
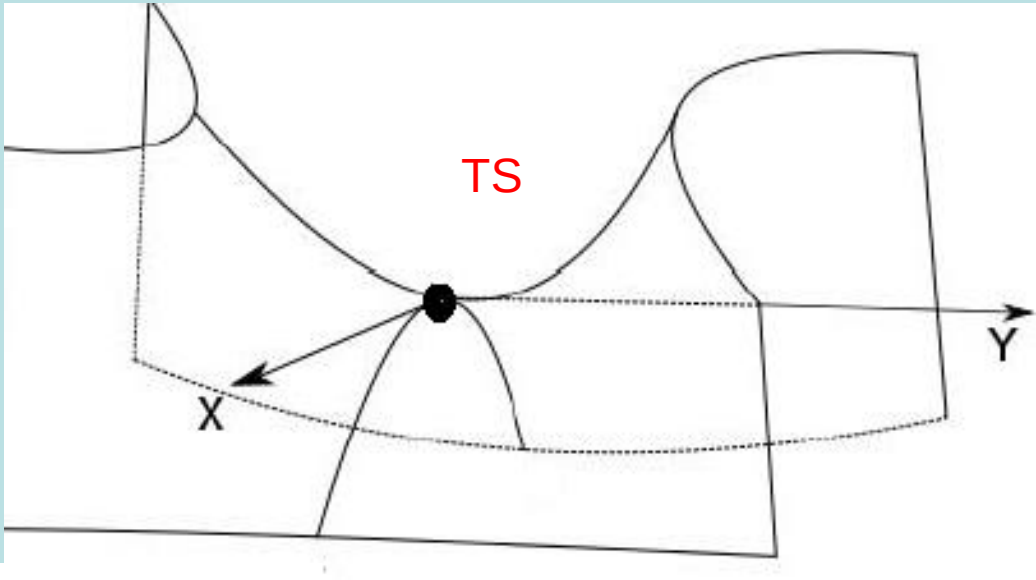
Reagents → **transition state** → Products

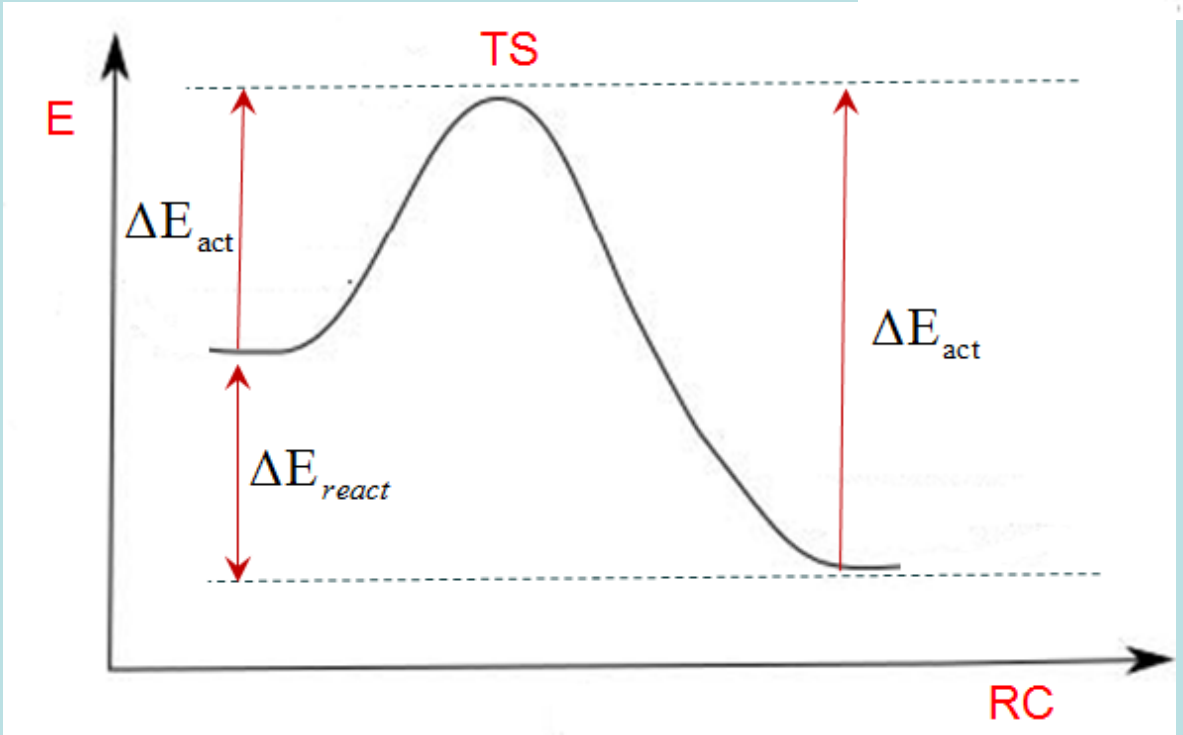


Transition State = Saddle point



Reagents → **transition state** → Products





$$Ha = \omega^2 a$$

$$\begin{pmatrix} \frac{\partial^2 E}{\partial x_1^2} & \frac{\partial^2 E}{\partial x_1 \partial x_2} & \ldots\ldots & \frac{\partial^2 E}{\partial x_1 \partial x_{3N-6}} \\ \frac{\partial^2 E}{\partial x_2 \partial x_1} & \frac{\partial^2 E}{\partial x_2^2} & \ldots\ldots & \ldots\ldots \\ \ldots\ldots & \ldots\ldots & \ldots\ldots & \ldots\ldots \\ \frac{\partial^2 E}{\partial x_{3N-6} \partial x_1} & \ldots\ldots & \ldots\ldots & \frac{\partial^2 E}{\partial x_{3N-6}^2} \end{pmatrix} \begin{pmatrix} a_1 \\ a_2 \\ \ldots \\ a_{3N-6} \end{pmatrix} = \omega^2 \begin{pmatrix} a_1 \\ a_2 \\ \ldots \\ a_{3N-6} \end{pmatrix}$$

$$\begin{pmatrix} \frac{\partial^2 E}{\partial x_1 \partial x_1} & \frac{\partial^2 E}{\partial x_1 \partial x_2} & \ldots & \frac{\partial^2 E}{\partial x_1 \partial x_{3N-6}} \\ \frac{\partial^2 E}{\partial x_2 \partial x_1} & \frac{\partial^2 E}{\partial x_2 \partial x_2} & \ldots & \frac{\partial^2 E}{\partial x_2 \partial x_{3N-6}} \\ \ldots & \ldots & \ldots & \ldots \\ \frac{\partial^2 E}{\partial x_{3N-6} \partial x_1} & \frac{\partial^2 E}{\partial x_{3N-6} \partial x_2} & \ldots & \frac{\partial^2 E}{\partial x_{3N-6} \partial x_{3N\text{-}6}} \end{pmatrix} \rightarrow \begin{pmatrix} \frac{\partial^2 E}{\partial z_1 \partial z_1} & 0 & \ldots & 0 \\ 0 & \frac{\partial^2 E}{\partial z_2 \partial z_2} & \ldots & 0 \\ \ldots & \ldots & \ldots & \ldots \\ 0 & 0 & \ldots & \frac{\partial^2 E}{\partial z_{3N-6} \partial z_{3N\text{-}6}} \end{pmatrix}$$

$$z = \sum_{i=1}^{3N-6} C_i x_i$$

$$\begin{pmatrix} \frac{\partial^2 E}{\partial z_1 \partial z_1} & 0 & \dots & 0 \\ 0 & \frac{\partial^2 E}{\partial z_2 \partial z_2} & \dots & 0 \\ \dots & \dots & \dots & \dots \\ 0 & 0 & \dots & \frac{\partial^2 E}{\partial z_{3N-6} \partial z_{3N-6}} \end{pmatrix} = \begin{pmatrix} \omega_1^2 & 0 & \dots & 0 \\ 0 & \omega_2^2 & \dots & 0 \\ \dots & \dots & \dots & \dots \\ 0 & 0 & \dots & \omega_{3N-6}^2 \end{pmatrix}$$

Optimal Geometry:

$$\frac{\partial^2 E}{\partial z_1 \partial z_1} > 0, \ \frac{\partial^2 E}{\partial z_2 \partial z_2} > 0, \dots, \frac{\partial^2 E}{\partial z_{3N-6} \partial z_{3N-6}} > 0$$

Transition State:

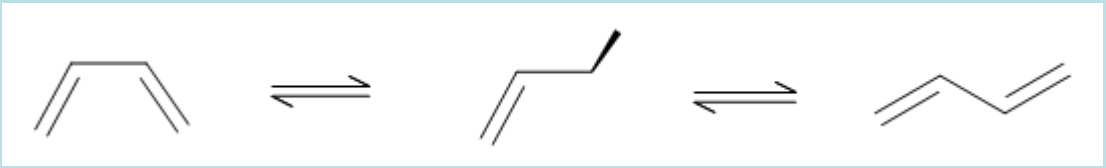
$$\frac{\partial^2 E}{\partial z_1 \partial z_1} > 0, \ \frac{\partial^2 E}{\partial z_2 \partial z_2} > 0, \dots, \frac{\partial^2 E}{\partial z_k \partial z_k} < 0, \dots, \frac{\partial^2 E}{\partial z_{3N-6} \partial z_{3N-6}} > 0$$

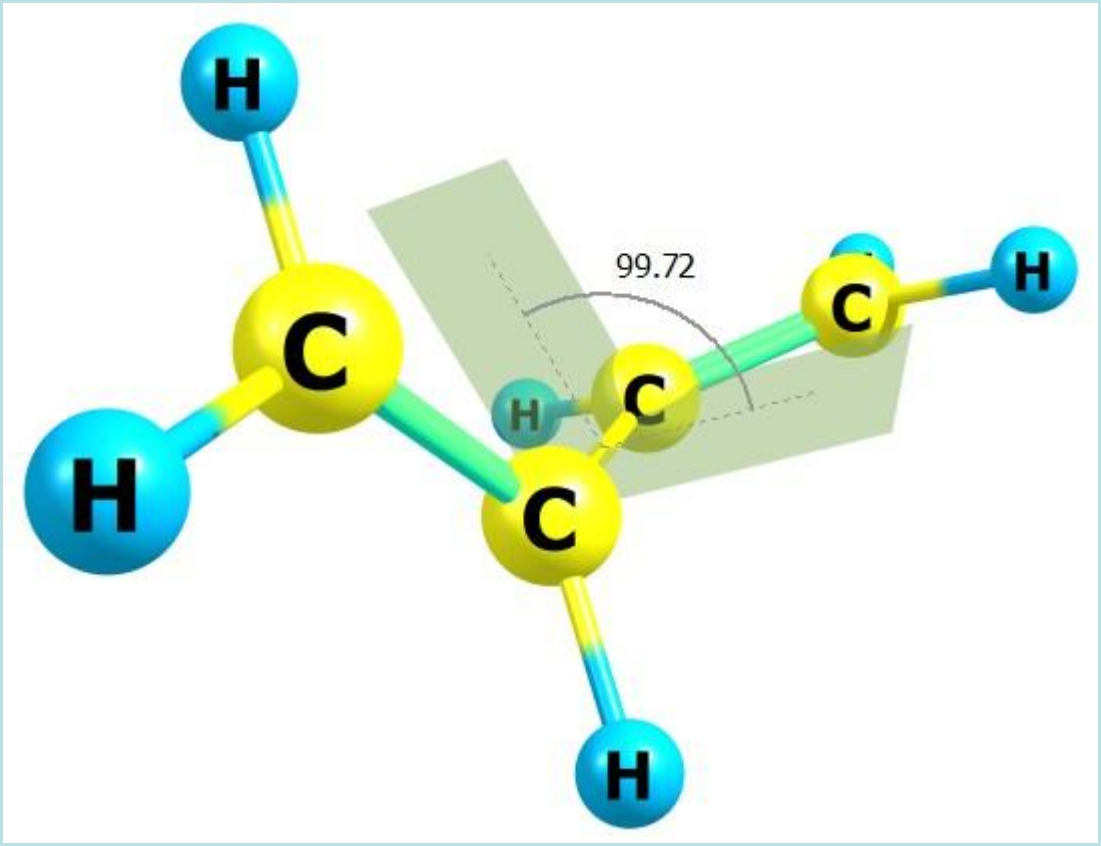
$$\omega_k^2 = \frac{\partial^2 E}{\partial z_k \partial z_k} < 0 \quad \rightarrow \quad \omega = i\sqrt{\left| \frac{\partial^2 E}{\partial z_k \partial z_k} \right|}$$

Algorithm of TS calculation

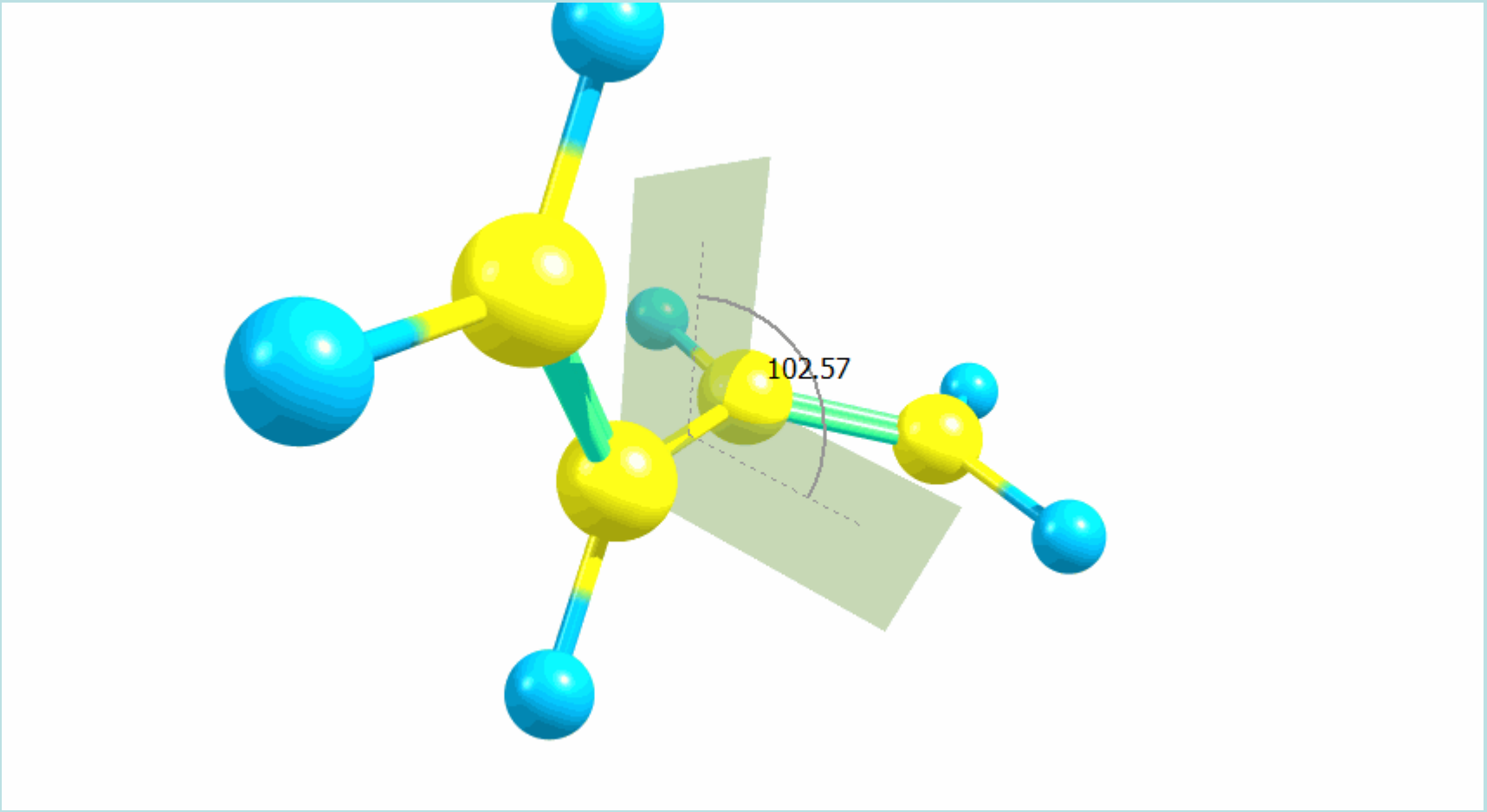
1. Find approximate TS geometry
2. Calculate Frequency of vibrations.
3. Calculate TS
4. Check if only one frequency is imaginary?
5. Calculate Intrinsic reaction path.

Cis-Trans isomerization of butadiene

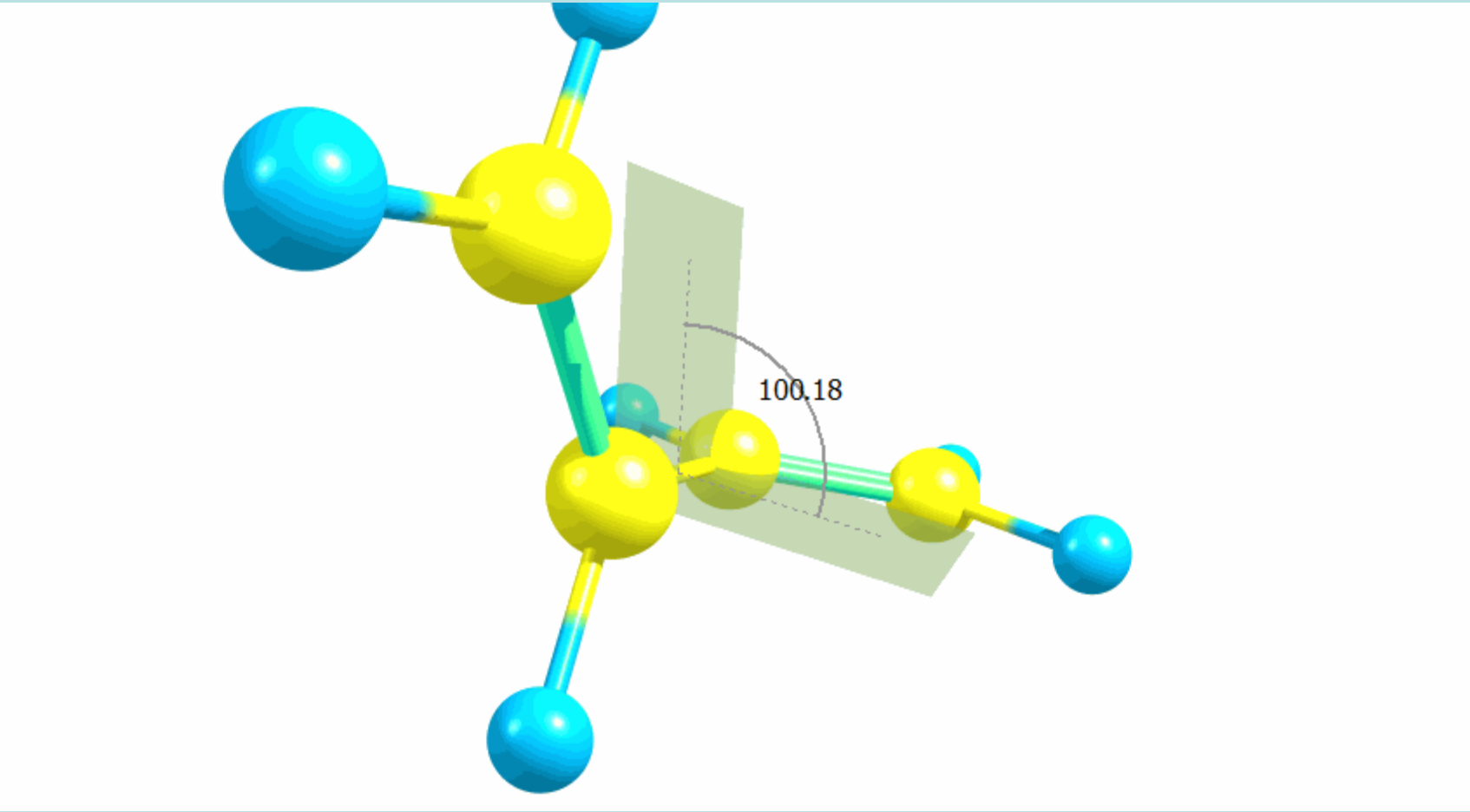




TS-Trans transformation



TS-Cis transformation



Calculated Parameters (6-31G(d,p)

	HF	B3LYP	MP2
$E_{гош}$	-154.925529	-155.886390	-155.466769
$E_{транс}$	-154.930324	-155.891980	-155.470933
E_{TS}	-154.920668	-155.879986	-155.461412
$E_{TS}–E_{транс}$	6.06	7.53	5.97
$\Delta H^{298}_{TS-транс}$	5.28	6.72	5.32
$E_{TS}–E_{гош}$	3.05	4.02	3.36
$\Delta H^{298}_{TS-гош}$	2.29	3.26	2.67
$E_{гош}–E_{транс}$	3.01	3.51	2.61
$\Delta H^{298}_{гош-транс}$	2.99	3.47	2.64

IRC curve of gosh-trans isomerization MP2/6-31G(d,p)