

all values in atomic units and radians, internal coord. ordered as: R(ClO), r(OH), and Theta

**near HOCl**

$$\text{Hess1} := \begin{bmatrix} 0.29043 & -0.01008 & 0.06094 \\ -0.01008 & 0.55820 & -0.00339 \\ 0.06094 & -0.00339 & 0.21614 \end{bmatrix} \quad \text{grad1} := \begin{bmatrix} 0.00470 \\ 0.01291 \\ -0.00397 \end{bmatrix}$$

near TS

$$\text{Hess2} := \begin{bmatrix} 0.14903 & 0.09973 & 0.33109 \\ 0.09973 & 0.01345 & 0.44075 \\ 0.33109 & 0.44075 & 2.55826 \end{bmatrix} \quad \text{grad2} := \begin{bmatrix} -0.03916 \\ -0.01312 \\ 0.01662 \end{bmatrix}$$

near HCIO

$$\text{Hess3} := \begin{bmatrix} 0.26198 & -0.05918 & -0.09524 \\ -0.05918 & 0.18855 & 0.57516 \\ -0.09524 & 0.57516 & 2.90916 \end{bmatrix} \quad \text{grad3} := \begin{bmatrix} -0.04921 \\ 0.00603 \\ 0.01375 \end{bmatrix}$$

**Eigenvalues of Hessian ordered by size**

Column of eigenvector matrix ass. with  
**nth eigenvalue**

$$\text{eigenvals}(\text{Hess1}) = \begin{bmatrix} 0.559 \\ 0.324 \\ 0.182 \end{bmatrix} \quad \text{eigenvecs}(\text{Hess1}) = \begin{bmatrix} -0.041 & 0.871 & -0.49 \\ 0.999 & 0.045 & -5.272 \cdot 10^{-3} \\ -0.017 & 0.49 & 0.872 \end{bmatrix}$$

$$\text{eigenvals}(\text{Hess2}) = \begin{bmatrix} -0.071 \\ 0.113 \\ 2.679 \end{bmatrix} \quad \text{eigenvecs}(\text{Hess2}) = \begin{bmatrix} -0.238 & 0.962 & 0.134 \\ 0.962 & 0.215 & 0.167 \\ -0.131 & -0.169 & 0.977 \end{bmatrix}$$

$$\text{eigenvals}(\text{Hess3}) = \begin{bmatrix} 0.266 \\ 0.064 \\ 3.03 \end{bmatrix} \quad \text{eigenvecs}(\text{Hess3}) = \begin{bmatrix} 0.98 & 0.197 & -0.038 \\ -0.186 & 0.962 & 0.199 \\ 0.076 & -0.188 & 0.979 \end{bmatrix}$$

**Newton - Raphson step for:**

**HOCl**

**TS**

**HCIO**

$$-\text{Hess1}^{-1} \cdot \text{grad1} = \begin{bmatrix} -0.022 \\ -0.023 \\ 0.024 \end{bmatrix} \quad -\text{Hess2}^{-1} \cdot \text{grad2} = \begin{bmatrix} 0.386 \\ 7.848 \cdot 10^{-3} \\ -0.058 \end{bmatrix} \quad -\text{Hess3}^{-1} \cdot \text{grad3} = \begin{bmatrix} 0.198 \\ 0.063 \\ -0.011 \end{bmatrix}$$

at HOCl

$$\text{Hess1} := \begin{bmatrix} 0.30565 & -0.01073 & 0.06009 \\ -0.01073 & 0.60530 & -0.003391 \\ 0.06009 & -0.003391 & 0.21462 \end{bmatrix} \quad \text{grad1} := \begin{bmatrix} 0.0 \\ 0.0 \\ 0.0 \end{bmatrix}$$

at TS

$$\text{Hess2} := \begin{bmatrix} 0.17566 & -0.00366 & 0.53963 \\ -0.00366 & -0.02079 & 0.06654 \\ 0.53963 & 0.06654 & 2.00028 \end{bmatrix} \quad \text{grad2} := \begin{bmatrix} 0.0 \\ 0.0 \\ 0.0 \end{bmatrix}$$

at HClO

$$\text{Hess3} := \begin{bmatrix} 0.04173 & -0.04808 & -0.17655 \\ -0.04808 & 0.16877 & 0.77474 \\ -0.17655 & 0.77474 & 4.3661 \end{bmatrix} \quad \text{grad3} := \begin{bmatrix} 0.0 \\ 0.0 \\ 0.0 \end{bmatrix}$$

$$\text{eigenvals}(\text{Hess1}) = \begin{bmatrix} 0.606 \\ 0.335 \\ 0.185 \end{bmatrix} \quad \text{eigenvecs}(\text{Hess1}) = \begin{bmatrix} -0.039 & 0.895 & -0.445 \\ 0.999 & 0.041 & -4.144 \cdot 10^{-3} \\ -0.015 & 0.445 & 0.895 \end{bmatrix}$$

$$\text{eigenvals}(\text{Hess2}) = \begin{bmatrix} -0.03 \\ 0.036 \\ 2.15 \end{bmatrix} \quad \text{eigenvecs}(\text{Hess2}) = \begin{bmatrix} 0.321 & 0.91 & 0.264 \\ 0.94 & -0.34 & 0.029 \\ -0.116 & -0.238 & 0.964 \end{bmatrix}$$

$$\text{eigenvals}(\text{Hess3}) = \begin{bmatrix} 0.016 \\ 0.049 \\ 4.512 \end{bmatrix} \quad \text{eigenvecs}(\text{Hess3}) = \begin{bmatrix} 0.662 & 0.748 & -0.041 \\ 0.742 & -0.647 & 0.176 \\ -0.105 & 0.147 & 0.984 \end{bmatrix}$$

**HCIO in HCIO internal coordinates, R(CIO), r(HCI), Theta(HCIO):**

$$\text{Hess3} := \begin{bmatrix} 0.02921 & 0.00578 & 0.0185 \\ 0.00578 & 0.3567 & -0.0057 \\ 0.0185 & -0.0057 & 0.1075 \end{bmatrix}$$

$$\text{eigenvals}(\text{Hess3}) = \begin{bmatrix} 0.357 \\ 0.025 \\ 0.112 \end{bmatrix}$$

$$\text{eigenvecs}(\text{Hess3}) = \begin{bmatrix} 0.016 & 0.975 & 0.22 \\ 1 & -0.021 & 0.017 \\ -0.022 & -0.22 & 0.975 \end{bmatrix}$$