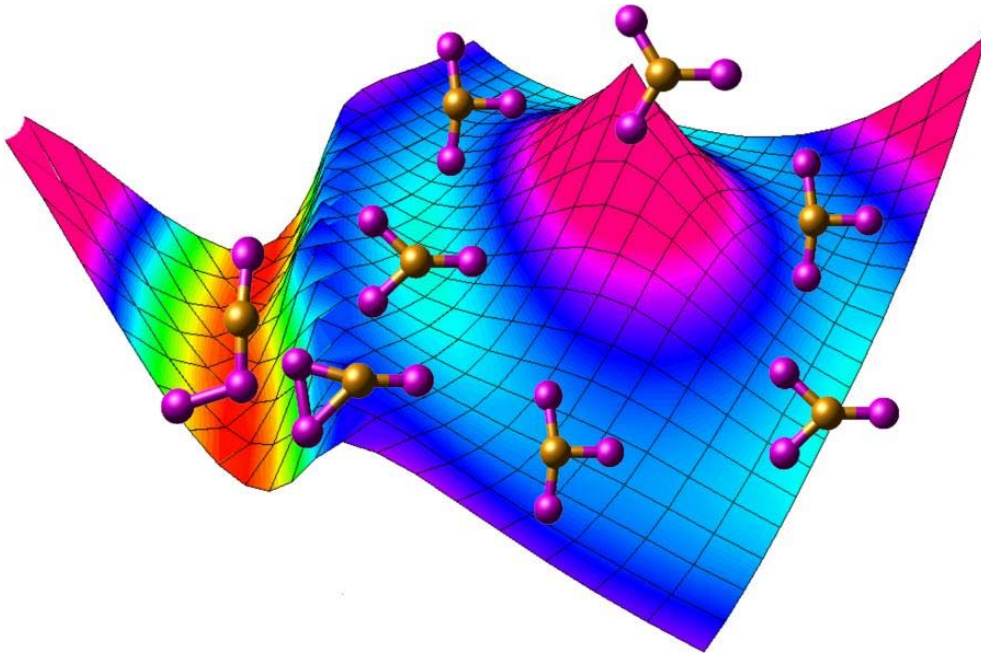


Frequency-Analysis

Potential Energy Surface of AuI₃



The PES of AuI₃ displays different types of stationary points: minima, transition states (NIMAG = 1) and a saddle points 2nd order (NIMAG = 2). Each point can be unequivocally be characterized by a frequency analysis.

Frequency-analysis deals

- characterization of stationary points
- normal coordinate analysis (assignment of vibrations, intensity)
- comparison with experimental data

Theory

The Born-Oppenheimer-approximation results in an electronic Schrödinger-Gleichung and an equation which describes the movement of nuclei.

Schrödinger-equation

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

Born-Oppenheimer-approximation

$$\underline{H}^{\text{el}}\Psi^{\text{el}} = E^{\text{el}}\Psi^{\text{el}} \text{ and}$$

$$\underline{H}^{\text{nuc}}\Theta^{\text{nuc}} = E^{\text{nuc}}\Theta^{\text{nuc}}$$

Calculation of the Harmonic Vibrational Frequencies

Once a stationary point has been found on the Born-Oppenheimer hypersurface, this point has to be characterized as minimum, transition state or saddle point of n^{th} order. In practice, this characterization is done by a frequency analysis.

To describe the individual energetic states of a molecule, different approximations are introduced. Firstly, there is the already-mentioned Born-Oppenheimer approach, which allows the separation of the electron motion from the motion of the nuclei. Secondly, translation of the nuclei is separated out by applying internal coordinates. The interaction between rotation and vibration is also neglected at the beginning and both problems are considered separately, using the model of the harmonic oscillator for the vibration and the rigid rotator for the rotation. From these models, spectroscopic constants are derived which can be used within the applied model.

To solve the above-mentioned problem, the motion of nuclei has to be investigated in detail. The equation for the **nuclear motion** can be written within the Born Oppenheimer picture (with space-fixed Cartesian coordinates, $\mathbf{R}_j, j = 1, 2, 3$ for $\mathbf{R}_1 = R_x, \mathbf{R}_2 = R_y, \mathbf{R}_3 = R_z$):

$$\left\{ -\hbar^2 \sum_{\alpha=1}^M \sum_{j=1}^3 \frac{1}{2m_{\alpha}} \frac{\partial^2}{\partial R_{\alpha j}^2} + U(\mathbf{R}_1 \dots \mathbf{R}_M) \right\} \Theta(\mathbf{R}_1 \dots \mathbf{R}_M) = E \Theta(\mathbf{R}_1 \dots \mathbf{R}_M)$$

Of special interest is the behavior of the nuclear configuration close to a stationary point. For this reason, the potential, U , which describes the molecule, will be expanded in a Taylor series around the **equilibrium structure** (stationary point) $\mathbf{R}_{\text{eq}} = (\mathbf{R}_1^{\text{eq}}, \dots, \mathbf{R}_M^{\text{eq}})$:

$$\begin{aligned}
U(\mathbf{R}_1, \dots, \mathbf{R}_M) &= U(\mathbf{R}_1^{\text{eq}}, \dots, \mathbf{R}_M^{\text{eq}}) + \sum_{\alpha=1}^M \sum_{j=1}^3 \left(\frac{\partial U(\mathbf{R}_1, \dots, \mathbf{R}_M)}{\partial R_{\alpha j}} \right)_{\mathbf{R}=\mathbf{R}^{\text{eq}}} (\mathbf{R}_{\alpha j} - \mathbf{R}_{\alpha j}^{\text{eq}}) \\
&+ \frac{1}{2} \sum_{\alpha, \beta=1}^M \sum_{j, k=1}^3 \left(\frac{\partial^2 U(\mathbf{R}_1, \dots, \mathbf{R}_M)}{\partial R_{\alpha j} \partial R_{\beta k}} \right)_{\mathbf{R}=\mathbf{R}^{\text{eq}}} (\mathbf{R}_{\alpha j} - \mathbf{R}_{\alpha j}^{\text{eq}})(\mathbf{R}_{\beta k} - \mathbf{R}_{\beta k}^{\text{eq}}) + \dots
\end{aligned}$$

Within the **harmonic approximation**, the Taylor series is truncated after the quadratic term. Moreover, at a stationary point the gradient (first derivatives) becomes zero:

$$\left(\frac{\partial U(\mathbf{R}_1, \dots, \mathbf{R}_M)}{\partial R_{\alpha j}} \right)_{\mathbf{R}=\mathbf{R}^{\text{eq}}} = 0$$

By introducing a **coordinate transformation**, the solution of the motion of the nuclei can be simplified. Starting with space-fixed Cartesian coordinates, **mass-weighted Cartesian coordinates** can be introduced. For each atom (nucleus), the equilibrium structure is described by the vector $\mathbf{R}_{\text{eq}} = (\mathbf{R}_1^{\text{eq}}, \dots, \mathbf{R}_M^{\text{eq}})$. Around this equilibrium position, all atoms are vibrating and these small displacements can be expressed by the $(\mathbf{R}_{\alpha j} - \mathbf{R}_{\alpha j}^{\text{eq}})$. The motion of the atoms using mass-weighted coordinates can be expressed as:

$$\mathbf{X}_{3\alpha+j-3} := \sqrt{m_{\alpha}} (\mathbf{R}_{\alpha j} - \mathbf{R}_{\alpha j}^{\text{eq}}) \quad \text{with } \alpha = 1, \dots, M; j = 1, 2, 3.$$

Substituting the Cartesian coordinates by mass-weighted coordinates in the Schrödinger equation for the motion of the nuclei within the harmonic approximation leads to:

$$\left\{ -\frac{\hbar^2}{2} \sum_{j=1}^M \frac{\partial^2}{\partial X_j^2} + \frac{1}{2} \sum_{j=1}^{3M} \sum_{k=1}^{3M} u_{jk} X_j X_k \right\} \phi(X_1, \dots, X_M) = E^{\text{vib}} \phi(X_1, \dots, X_M)$$

with the **mass-weighted force constant matrix**, $\mathbf{U} = (u_{jk})$:

$$u_{3\alpha+j-3, 3\beta+k-3} = (m_\alpha m_\beta)^{-1/2} \left(\frac{\partial^2 U(\mathbf{R}_1, \dots, \mathbf{R}_M)}{\partial R_{\alpha j} \partial R_{\beta k}} \right) \Big|_{\mathbf{R}=\mathbf{R}^{\text{eq}}}$$

and

$$E^{\text{vib}} = E - U(\mathbf{R}_1^{\text{eq}}, \dots, \mathbf{R}_M^{\text{eq}}).$$

The mass-weighted force constant, $\mathbf{U} = (u_{jk})$, is a real, symmetric matrix and can be diagonalized by a transformation matrix, \mathbf{M} ,*:

$$\mathbf{M}^T \mathbf{U} \mathbf{M} = \text{diag}(\lambda_1, \dots, \lambda_{3M})$$

By this transformation, the mass-weighted coordinates are also transformed and are now called **normal coordinates** (modes). They are defined as follows:

$$Q_j = \sum_{k=1}^{3M} u_{jk}^T \cdot X_k$$

By means of the normal coordinates, Q_j , the displacements corresponding to the harmonic vibrations (normal modes) can be illustrated graphically.

The **eigenvalues, λ_j , of the mass-weighted-force-constant matrix are directly correlated with the harmonic vibrations, f_j** , which again correspond to the normal coordinates, Q_j :

$$f_j = \frac{\sqrt{\lambda_j}}{2\pi}$$

Hence, $F = 3M - 5(6)$ *genuine frequencies* (F = vibrational degrees of freedom) are obtained.

The normal modes, Q_j , describe the motion of the atoms while vibrating with frequency, f_j . During a normal vibration, all nuclei move in *phase*, which means that each frequency (normal mode) can be excited independently from the others.

The eigenvalues, λ_j , or the frequencies, f_j , are used to characterize stationary points on a F -dimensional Born-Oppenheimer-energy surface.

F positive frequencies	\Rightarrow local minimum	\Rightarrow stable molecule
n imaginary frequencies	\Rightarrow saddle point	\Rightarrow transition state
$(n = 1, 2, \dots, F-1)$	n^{th} order	
F imaginary frequencies	\Rightarrow local maximum	\Rightarrow no molecular interpretation

Often in literature, a transition structure for a chemical reaction is a stationary point on an energy surface that is a local minimum along one and only one direction while being a local maximum in all other orthogonal directions. This unique direction is termed the transition vector and is the eigenvector associated with the negative eigenvalue of the force constant

matrix. In general, the orientation of the transition vector is not known a priori, and hence must be determined in the course of a transition structure optimization.

To summarize: Once a stationary point has been identified on the PES with the necessary condition:

$$\nabla U(\mathbf{R}) = 0, \quad \text{i.e.} \quad \frac{\partial U(\mathbf{R})}{\partial x_i} = 0,$$

that stationary point must be characterized via its force constant matrix, where a (local or global) minimum must fulfill the condition:

$$\frac{\partial^2 U(\mathbf{R})}{\partial x_i \partial x_j} \geq 0.$$

In an *ab initio* calculation, the force constants are either numerically or analytically

$$\frac{\Delta(\Delta U)}{\Delta x_i \Delta x_j} \cong \frac{\partial^2 U}{\partial x_i \partial x_j}$$

determined. The mass weighted force constants matrix is then generated, transformed and the normal coordinates and frequencies (wave numbers) determined. Using the normal modes and eigenvalues of the mass weighted force constant matrix, the Hamiltonian is given by:

$$\underline{H}^{\text{vib}} = \sum_{j=1}^{3M-5(6)} \underline{h}_j = \sum_{j=1}^{3M-5(6)} \left(-\frac{\hbar^2}{2} \frac{\partial^2}{\partial Q_j^2} + \frac{1}{2} \lambda_j Q_j^2 \right)$$

The Hamiltonian, $\underline{H}^{\text{vib}}$, describes a system of F decoupled harmonic vibrations, so that the vibrational energy is given by the sum over all vibrational energy contributions (with ν_j as the vibrational quantum number):

$$E_{\nu_j}^{\text{vib}} = \sum_{j=1}^{3M-5(6)} \varepsilon_j = \sum_{j=1}^{3M-5(6)} \left(\nu_j + \frac{1}{2} \right) \hbar \sqrt{\lambda_j} \quad (\text{with } \nu_j = 0, 1, 2 \dots).$$

If the absolute values of the frequencies are of interest, e.g. in order to compare with the experiment, then a scaling factor (0.9 to 1.0) must be introduced, as the harmonic approximation gives frequencies which are up to 10% too large. This is due to anharmonicities. Furthermore, the calculated wave number depends on the method (HF, MPn, CI ...) applied, so that absolute values have to be considered very carefully, especially if no experimental data is available for comparison.

However, considering one specific normal mode, we should always remember that in a molecule all atoms will move, so that assignments such as stretching mode, deformation mode etc. are approximations! *The best way of assignment is to use the symmetry according to group theory, or a graphical representation of the considered normal mode.*

* The transformation matrix, M, is generated by (3M) linear, independent, orthonormal, real eigenvectors, \mathbf{v} , of U which are written as column vectors for an orthogonal matrix. Thus, $\lambda_1 \dots \lambda_{3M}$ are the eigenvalues of U. If e.g. the potential $U(\mathbf{R}_{\alpha j} - \mathbf{R}_{\alpha j}^{\text{eq}})$ is known, the normal coordinates can be determined as follows:

1. Determination of the force constant matrix
2. Transformation into mass-weighted force constant matrix
3. Determination of the eigenvalues and eigenvectors:

$$Uv = \lambda v \rightarrow \det[U - \lambda E] = 0 \rightarrow [(U_{jk}) - \lambda_j E] v_j = 0$$

4. Construction of the orthogonal transformation matrix, M , from the eigenvectors
5. Calculation of the normal coordinates

Since translation and rotation were not separately considered in this approach, there are 5(6) eigenvalues which are zero, corresponding to 3 translational and 2(3) rotational degrees of freedom .

Example: triatomic molecule

$$U(\xi_1, \xi_2, \xi_3) = 1/2 k (\xi_1 - \xi_2)^2 + 1/2 k (\xi_2 - \xi_3)^2$$

$$\begin{array}{ccccccc} & \xi_1 & & \xi_2 & & \xi_3 & \\ \otimes & \rightarrow & \otimes & \rightarrow & \otimes & \rightarrow & \rightarrow x\text{-Richtung} \\ m_A & & m_B & & m_A & & \end{array}$$

$\xi_i \equiv$ Auslenkungscoordinate, $\xi_i := (x_i - x_i^0)$

$q_i \equiv$ massegewichtete Auslenkungscoordinate, $q_i := m_i^{1/2} \xi_i = m_i^{1/2} (x_i - x_i^0)$

1. Bestimmung der Matrix der Kraftkonstanten

$$k_{ij} = \frac{\partial^2 U(\vec{x})}{\partial x_i \partial x_j} \Big|_{\vec{x} = \vec{x}^0} \text{ lokales Minimum}$$

$$U(\vec{x}) = \bar{U}(\vec{\xi}(\vec{x})) = \frac{\partial^2 \bar{U}(\vec{\xi})}{\partial \xi_i \partial \xi_j} \Big|_{\vec{\xi} = 0}$$

$$(k_{ij}) = \begin{pmatrix} k & -k & 0 \\ -k & 2k & -k \\ 0 & -k & k \end{pmatrix}$$

2. Übergang zur Matrix der massegewichteten Kraftkonstanten

$$K_{ij} = \frac{k_{ij}}{m_i^{1/2} m_j^{1/2}} \Rightarrow (K_{ij}) = \begin{pmatrix} \frac{k}{m_B} & -\frac{k}{\sqrt{m_A} \sqrt{m_B}} & 0 \\ -\frac{k}{\sqrt{m_A} \sqrt{m_B}} & \frac{2k}{\sqrt{m_A^2}} & -\frac{k}{\sqrt{m_A} \sqrt{m_B}} \\ 0 & -\frac{k}{\sqrt{m_A} \sqrt{m_B}} & \frac{k}{m_B} \end{pmatrix}$$

3. Bestimmen der Eigenwerte und Eigenvektoren

$$0 = \det(k - \lambda E)$$

Vereinfachung: $\frac{k}{m_B} = a, \frac{k}{\sqrt{m_A}\sqrt{m_B}} = b, \frac{k}{m_A} = c$

$$\begin{vmatrix} a-\lambda & -b & 0 \\ -b & 2c-\lambda & -b \\ 0 & -b & a-\lambda \end{vmatrix} \Rightarrow 0 = (a-\lambda)[(a-\lambda)(2c-\lambda) - 2b^2]$$

$$\Rightarrow \lambda_1 = \frac{k}{m_B}, \lambda_2 = \frac{k(m_A + 2m_B)}{m_A m_B}, \lambda_3 = 0$$

Eigenvektoren: $[(K_{ij}) - (\lambda_i E)] \vec{v}_i = \vec{0}$

z.B. für λ_1

$$\begin{pmatrix} a-a & -b & 0 \\ -b & 2c-a & -b \\ 0 & -b & a-a \end{pmatrix} \begin{pmatrix} v_1 \\ v_2 \\ v_3 \end{pmatrix}$$

$$\Rightarrow \vec{v}^i = t \begin{pmatrix} 1 \\ 0 \\ -1 \end{pmatrix} \text{ Normierung: } \vec{v}_1 = \frac{1}{\sqrt{2}} \begin{pmatrix} 1 \\ 0 \\ -1 \end{pmatrix}$$

die anderen analog

$$\lambda_1 = \frac{k}{m_B} \quad \Rightarrow \vec{v}_1 = \frac{1}{\sqrt{2}} \begin{pmatrix} 1 \\ 0 \\ -1 \end{pmatrix}$$

$$\lambda_2 = \frac{k(m_A + 2m_B)}{m_A m_B} \quad \Rightarrow \vec{v}_2 = \frac{1}{\sqrt{2M}} \begin{pmatrix} m_A^{1/2} \\ 2m_B^{1/2} \\ m_A^{1/2} \end{pmatrix}$$

$$\lambda_3 = 0 \quad \Rightarrow \vec{v}_3 = \frac{1}{\sqrt{M}} \begin{pmatrix} m_B^{1/2} \\ m_A^{1/2} \\ m_B^{1/2} \end{pmatrix}$$

4. Konstruktion der Modalmatrix : $M^T K M = \text{diag}(\lambda_1, \lambda_2, \lambda_3)$

$$M = \begin{pmatrix} \frac{1}{\sqrt{2}} & \frac{m_A^{1/2}}{\sqrt{2M}} & \frac{m_B^{1/2}}{\sqrt{M}} \\ 0 & \frac{2m_B^{1/2}}{\sqrt{2M}} & \frac{m_A^{1/2}}{\sqrt{M}} \\ \frac{1}{\sqrt{2}} & \frac{m_A^{1/2}}{\sqrt{2M}} & \frac{m_B^{1/2}}{\sqrt{M}} \end{pmatrix}$$

Normalkoordinaten : $\Rightarrow \vec{Q} := M^T \vec{q}$

$$\text{a) } \vec{q} = \begin{pmatrix} \sqrt{m_B} \xi_1 \\ \sqrt{m_A} \xi_2 \\ \sqrt{m_B} \xi_3 \end{pmatrix}$$

b) Darstellung der Auslenkung durch Normalkoordinaten $\vec{Q} = \begin{pmatrix} Q_1 \\ Q_2 \\ Q_3 \end{pmatrix}$

$$\vec{Q} = M^T \vec{q} \quad | \bullet M$$

$$\Rightarrow E \vec{q} = M \vec{Q}$$

$$\xi_1 = \frac{1}{\sqrt{2}} \frac{1}{\sqrt{m_B}} Q_1 + \frac{1}{\sqrt{2M}} \left(\frac{m_A}{m_B}\right)^{1/2} Q_2 + \frac{1}{\sqrt{M}} Q_3$$

$$\xi_2 = 0 Q_1 - \frac{2}{\sqrt{2M}} \frac{1}{\sqrt{m_A m_B}} Q_2 + \frac{1}{\sqrt{M}} Q_3$$

$$\xi_3 = -\frac{1}{\sqrt{2}} \frac{1}{\sqrt{m_B}} Q_1 + \frac{1}{\sqrt{2M}} \frac{\sqrt{m_A}}{\sqrt{m_B}} Q_2 + \frac{1}{\sqrt{M}} Q_3$$

5. Übergang zur harmonischen Lösung

a) $Q_1 = Q_2 = 0; Q_3 \neq 0, \lambda_3 = 0$

$$\xi_1 = \frac{1}{\sqrt{M}} Q_3$$

$$\xi_2 = \frac{1}{\sqrt{M}} Q_3$$

$$\xi_3 = \frac{1}{\sqrt{M}} Q_3$$

$\Rightarrow f = 0 / 2\pi = 0 \Rightarrow$ Translation

b) $Q_2 = Q_3 = 0; Q_1 \neq 0, \lambda_1 = \frac{k}{m_B}$

$$\begin{aligned}\xi_1 &= \frac{1}{\sqrt{2}} \frac{1}{m_B} Q_1 \\ \xi_2 &= 0 Q_1 \\ \xi_3 &= -\frac{1}{\sqrt{2}} \frac{1}{m_B} Q_1\end{aligned} \quad \Rightarrow f = \frac{\sqrt{k}}{2\pi} \quad \Rightarrow \text{symmetrische Streckschwingung}$$

$$\text{b) } Q_1 = Q_3 = 0; Q_2 \neq 0, \lambda_2 = \frac{k(m_A + 2m_B)}{m_A m_B}$$

$$\begin{aligned}\xi_1 &= \frac{1}{\sqrt{2M}} \sqrt{\frac{m_A}{m_B}} Q_2 \\ \xi_2 &= -2 \frac{1}{\sqrt{2M}} \frac{m_A}{\sqrt{m_B}} Q_2 \\ \xi_3 &= \frac{1}{\sqrt{2M}} \sqrt{\frac{m_A}{m_B}} Q_2\end{aligned} \quad \Rightarrow f = \frac{\sqrt{k(m_A + 2m_B)}}{2\pi} \quad \Rightarrow \text{asymmetrische Streckschwingung}$$