

Introduction

Vibrational frequencies obtained through the **harmonic oscillator framework** provide only quantitative, but no qualitative explanation of observed spectra. Anharmonicity of molecular vibration is responsible for the finer features observed in spectra of molecules, for example the uneven spacings of overtone levels [1].

In this part of the practical course, we apply the **Numerov's method** to numerically solve the **nuclear Schrödinger** equation. For the systems F<sub>2</sub> and trans-CH<sub>3</sub>COOH we perform a geometry optimization, harmonic frequency calculation and a bond scan of F-F, O-H, and O-D to obtain discrete points on the potential energy surface (PES). By comparison of the results of the **harmonic approximation** and **Numerov's method** we can gain insight of the interplay of anharmonicity and mode coupling to molecular vibrations

Starting Structures / Calculation Parameters

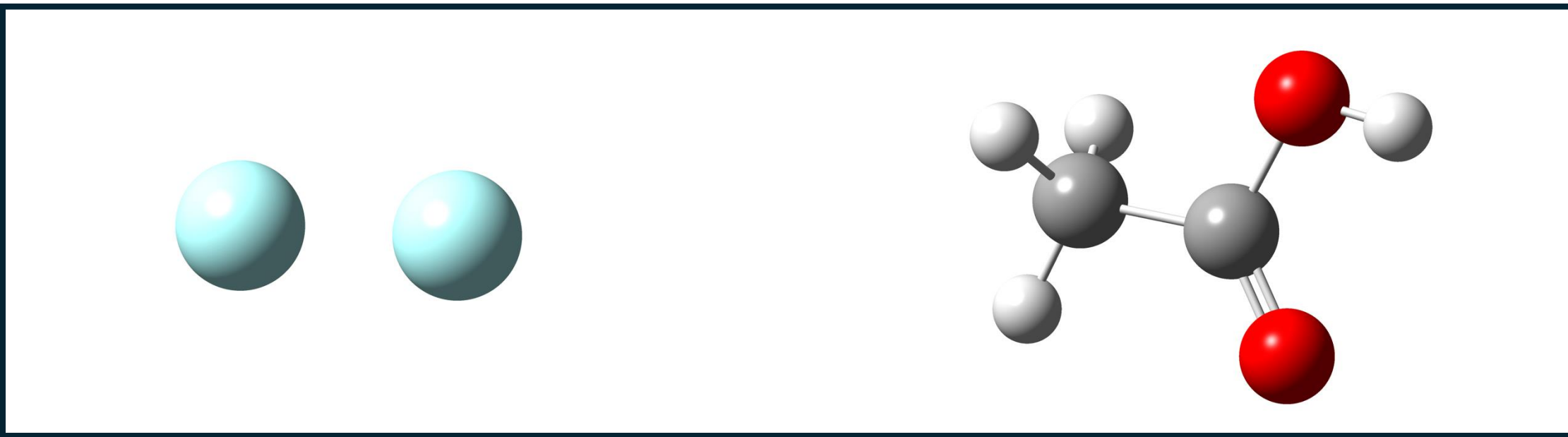


Fig 1: F<sub>2</sub> and CH<sub>3</sub>COOH optimized with B3LYP/6-311++G(3df,3pd).

The geometry optimization and frequency calculation of both structures were carried out with the B3LYP functional using the 6-311++G(3df,3pd) basis set and additional convergence criteria.

Calculation of force constants and reduced masses

The force constant can be calculated using **finite differences method** from the potential energy curve of the bond scan:

$$k \approx \frac{E_{min-1} + 2E_{min} + E_{min+1}}{\Delta x^2}$$

The harmonic ossscillator framework gives us the frequencies  $\bar{\nu}$ , for the calculation one needs to further determine the reduced mass  $\mu$ :

$$\mu = \frac{m_1 m_2}{m_1 + m_2} \qquad \bar{\nu} = \frac{1}{c} \frac{1}{2\pi} \sqrt{\frac{k}{\mu}}$$

- $\mu$ ... reduced mass in (g mol<sup>-1</sup>)
- $c$ ... speed of light (m s<sup>-1</sup>)
- $m_1, m_2$ ... mass of first and second atom (g mol<sup>-1</sup>)
- $\bar{\nu}$ ... frequency in (cm<sup>-1</sup>)
- $k$ ... force constant in (kcal mol<sup>-1</sup> Å<sup>-1</sup>)

The table below shows the atomic masses and the reduced masses  $\mu$  calculated for the atoms involved in the bond stretch vibration.

**Tab 1:** Atomic and reduced masses for the atoms used in the analysis

	F <sub>2</sub>	trans-CH <sub>3</sub> COOH		trans-CH <sub>2</sub> COOD	
Atoms	F	O	H	O	D
Amu (g mol <sup>-1</sup> )	18.9984	15.9949	1.0078	15.9949	2.0141
Reduced mass (g mol <sup>-1</sup> )	9.4992	0.9481		2.228800	

With potential energies of the bond scan the following force constants were determined:

- F<sub>2</sub>:  $k = 874.943$  kcal mol<sup>-1</sup> Å<sup>-1</sup>
- Trans-CH<sub>3</sub>COOH:  $k = 1136.401$  kcal mol<sup>-1</sup> Å<sup>-1</sup>
- Trans-CH<sub>3</sub>COOD:  $k = 1137.198$  kcal mol<sup>-1</sup> Å<sup>-1</sup>

Numerov Procedure

**Numerov's method** is a numerical algorithm to solve differential equations. This method can be used to obtain the energy eigenvalues  $E_n$  and the wave functions  $\psi$ :

$$\frac{\partial^2 \Psi}{\partial x^2} = \frac{2m}{\hbar} (V - E) \Psi \Rightarrow \frac{\partial^2 \Psi}{\partial x^2} \approx \frac{\Delta g}{\Delta x}$$

With the energy eigenvalues, the vibrational frequencies of both the fundamental and overtones can be calculated:

$$\nu_{n0} = \frac{E_n - E_0}{h}$$

The following table displays the Overlap matrix:

$$S_{ij} = \int_{-\infty}^{\infty} \psi_i(x) \psi_j(x) dx$$

```
# Extract potential energy from scan_data
V = [scan_data.loc[i, "Energy"] - np.min(scan_data.loc[:, "Energy"]) + 6.275095E2
# Build diagonal matrix
V_diag = np.diag(V)
# Initialize stencil
stencil = np.zeros((np.shape(V_diag)[0], np.shape(V_diag)[0]))
i,j = np.indices(stencil)
# Fill up stencil with finite difference coefficients
stencil[i==j] = -2
stencil[i==j-1] = 1
stencil[i==j+1] = 1
#Scaling factor
scaling_fact = ((const.hbar**2 / (2*reduced_mass)) * 1E20 * const.Avogadro**2 ) / 4.184
T = stencil * scaling_fact + (1/(0.81**2))
eigenvalues, eigenvectors = np.linalg.eigh(-T + V_diag)
```

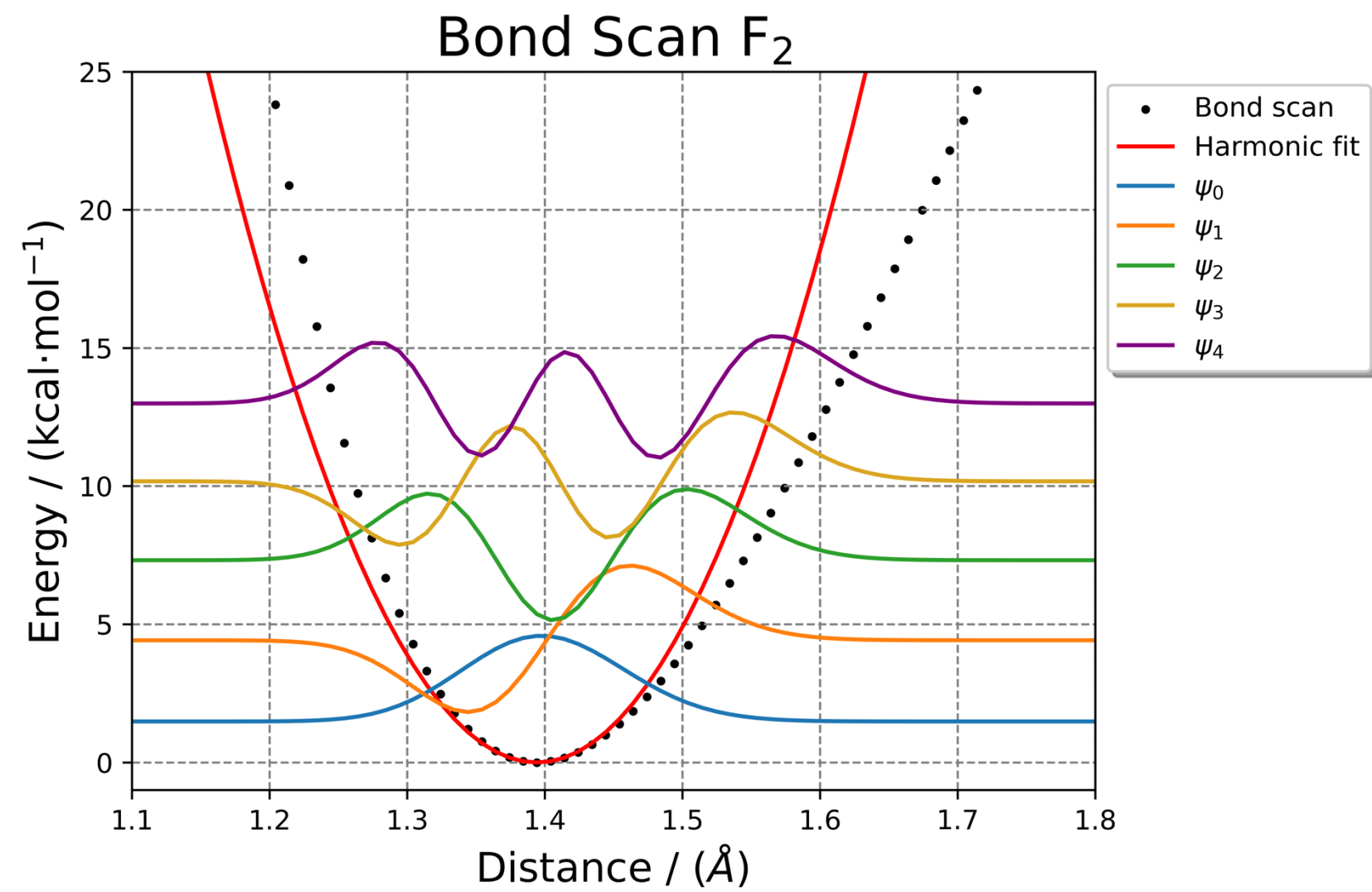
Fig 2: Python implementation for Numerov's method.

**Tab 2/3:** Overlap Matrix for  $\psi_0 - \psi_4$ , obtained by **Numerov's method** for trans-CH<sub>3</sub>COOH (right) and trans-CH<sub>3</sub>COOD (left).

	$\psi_0$	$\psi_1$	$\psi_2$	$\psi_3$	$\psi_4$		$\psi_0$	$\psi_1$	$\psi_2$	$\psi_3$	$\psi_4$
$\psi_0$	1.0	3.15E-14	1.11E-14	2.24E-14	-1.19E-14	$\psi_0$	1.0	3.69E-14	1.75E-14	-2.28E-14	2.26E-14
$\psi_1$	-3.17E-14	1.0	-1.70E-14	9.93E-15	-8.65E-16	$\psi_1$	3.59E-14	1.0	-8.89E-15	2.43E-14	5.34E-15
$\psi_2$	2.25E-14	9.35E-15	1.0	-3.29E-14	2.03E-14	$\psi_2$	-2.89E-14	2.32E-14	1.0	3.19E-14	8.91E-15
$\psi_3$	2.25E-14	9.35E-15	-3.29E-14	1.0	-4.45E-14	$\psi_3$	1.745E-14	-8.80E-15	3.29E-14	1.0	5.83E-15
$\psi_4$	-1.88E-14	-8.65E-15	2.03E-14	-4.45E-14	1.0	$\psi_4$	2.26E-14	5.34E-15	8.91E-15	5.83E-15	1.0

Bond Scan along F-F

The figure below shows the potential energy against the bond distance. The red curve shows the harmonic fit, the wave functions  $\psi_0 - \psi_4$  are the eigenstates obtained by **Numerov's method**.



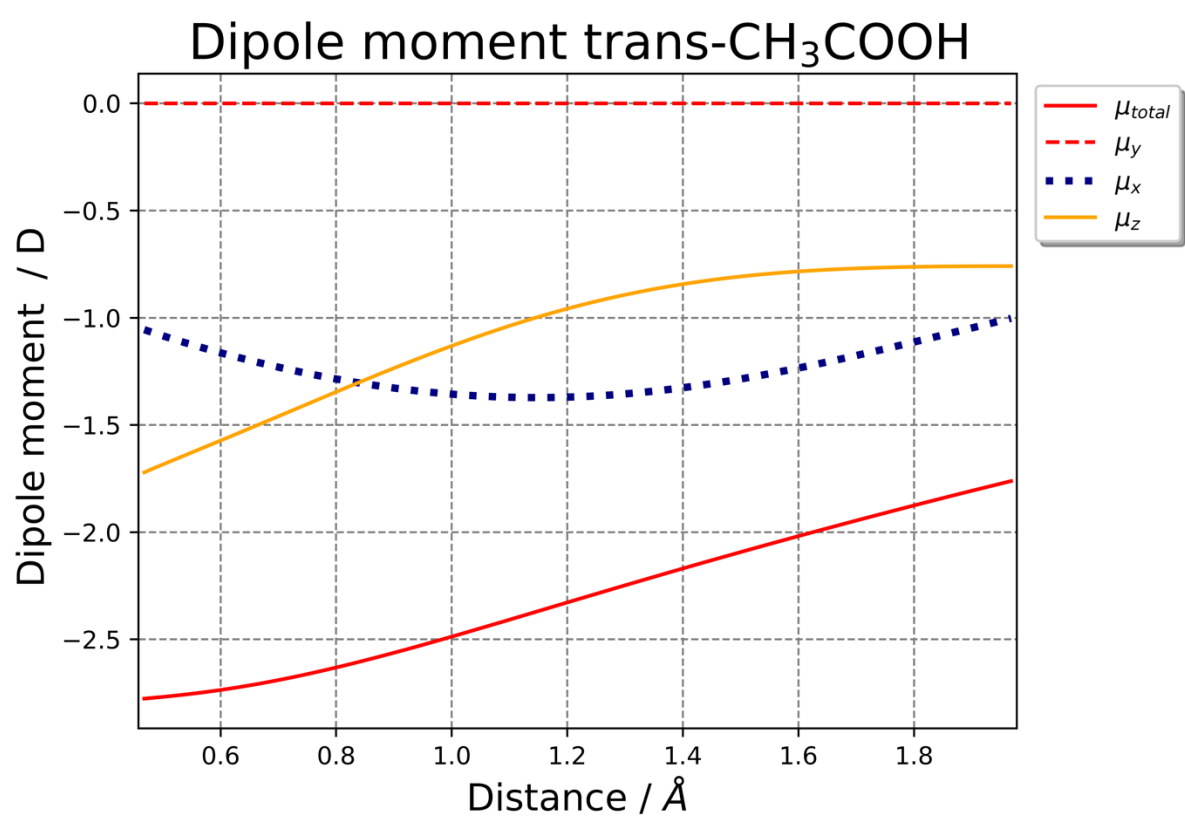
**Fig 3:** Potential energy surface of the bond scan of F<sub>2</sub>(black dots), the harmonic fit (red) and the first five wave functions shifted by their respective eigenenergies.

**Tab 4:** Comparison of the frequencies obtained by Gaussian, the harmonic fit, and the **Numerov's method** with literature calculations (CCSD/cc-pVXZ).

	base (cm <sup>-1</sup> )	1st overtone (cm <sup>-1</sup> )	2nd overtone (cm <sup>-1</sup> )	3rd overtone (cm <sup>-1</sup> )
Gaussian	1042.04	2084.35	3126.53	4168.71
Harmonic	1042.18	2084.35	3126.53	4168.71
Numerov	1027.70	2041.15	3040.47	4025.77
Literature [2]	1012.5	--	--	--

With 14.5 cm<sup>-1</sup> (1,43 %) **Numerov's method** has the smallest deviation compared to the literature. The PES along a bond stretch is best described by a Morse-Potential, Fig 3. clearly displays the deviation of the harmonic approximation. Here, anharmonic methods like VSFC, VCI or Numerov lead to more precise results.

Dipole Moment / Oscillator strenght



**Fig 6:** The total dipole moment as well the components along x,y,z plotted against the distance between O-H.

In order for a vibration to be IR active the dipole moment must change. The plot on the left side displays the change in the dipole moment components  $\mu_x, \mu_y, \mu_z$ . The component  $\mu_y$  is zero, this is a result of the orientation of the molecule in the coordinate system.

$\mu_{total}$  shows an overall change in the dipole moment which is expected as the change in the bond length alters the distribution of electron density.

The oscillator strength [3] provides insights into the probability and intensity of transitions between vibrational energy levels. The selection rules are determined by the transition moment integral:

$$\mu_{n \rightarrow n+1} = \int_{-\infty}^{\infty} \psi_n^* \hat{\mu} \psi_{n+1}$$

**Tab 7:** Comparison of the osscillator strength  $f$  in the harmonic oscillator framework and the Numerov' Method.

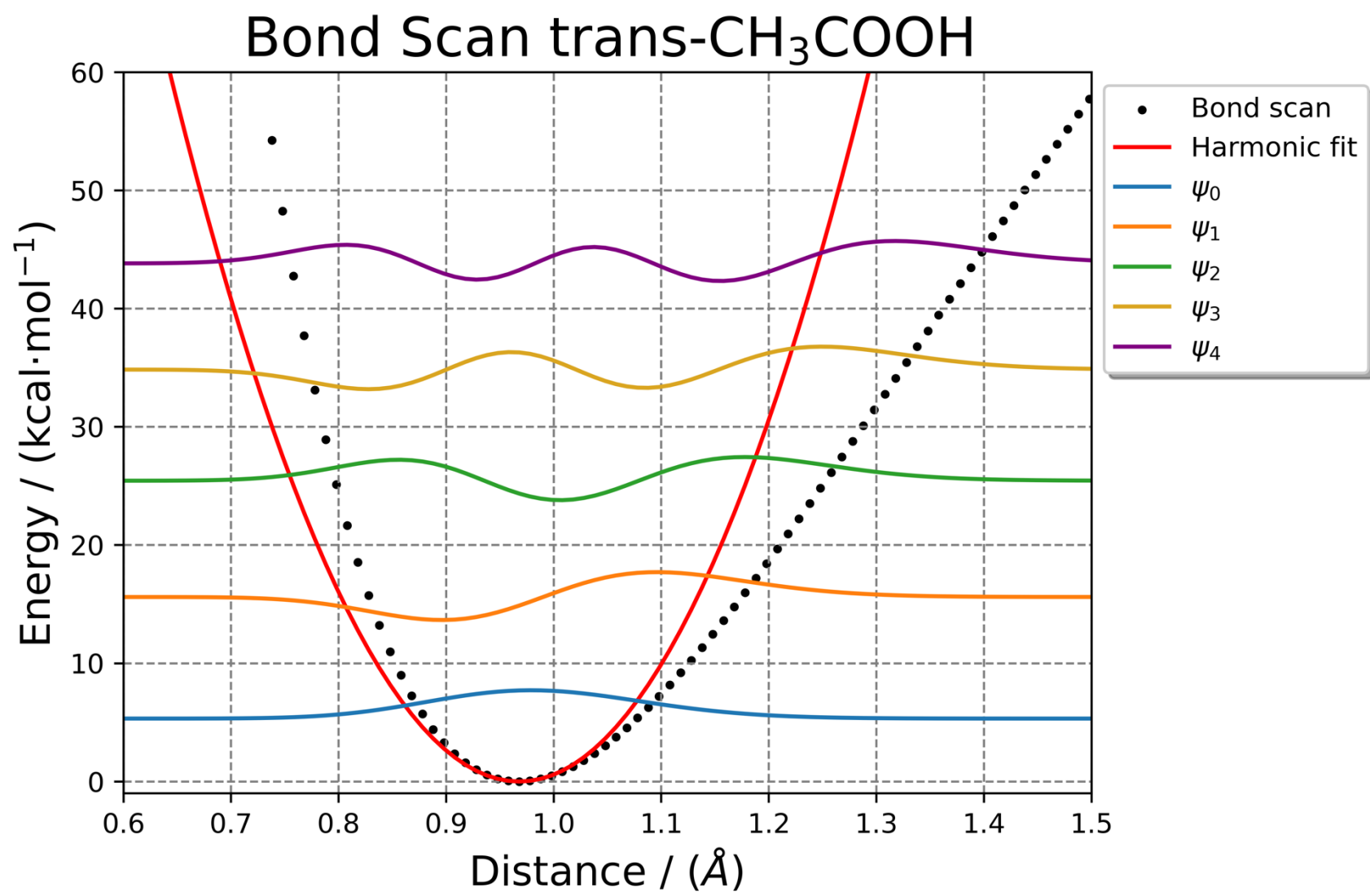
Excitation	$\bar{\nu}$ Harmonic / cm <sup>-1</sup>	$f$ Harmonic / ( )	$\bar{\nu}$ Numerov / cm <sup>-1</sup>	$f$ Numerov / ( )
0 → 1	3548.54	1	3596.88	8.337E-06
0 → 2	7097.08	0	7036.90	5.591E-07

The harmonic oscillator allows only transitions with  $\Delta n \pm 1$ , in reality, anharmonicity introduces non-zero oscillator strength also for higher transitions.

Potential Energy Curves

Determination of the effect of deuteration of trans-acetic-acid

The figures below show the effect of deuteration to the bond scan between O-H and O-D. For trans-CH<sub>3</sub>COOD the substitution was carried out in Gaussian using the **iso** keyword in the Z-matrix coordinates. One thing to note here is the anharmonicity of the PES. For more complicated chemical systems, effect like mode coupling become more dominant, making the harmonic approximation less precise.

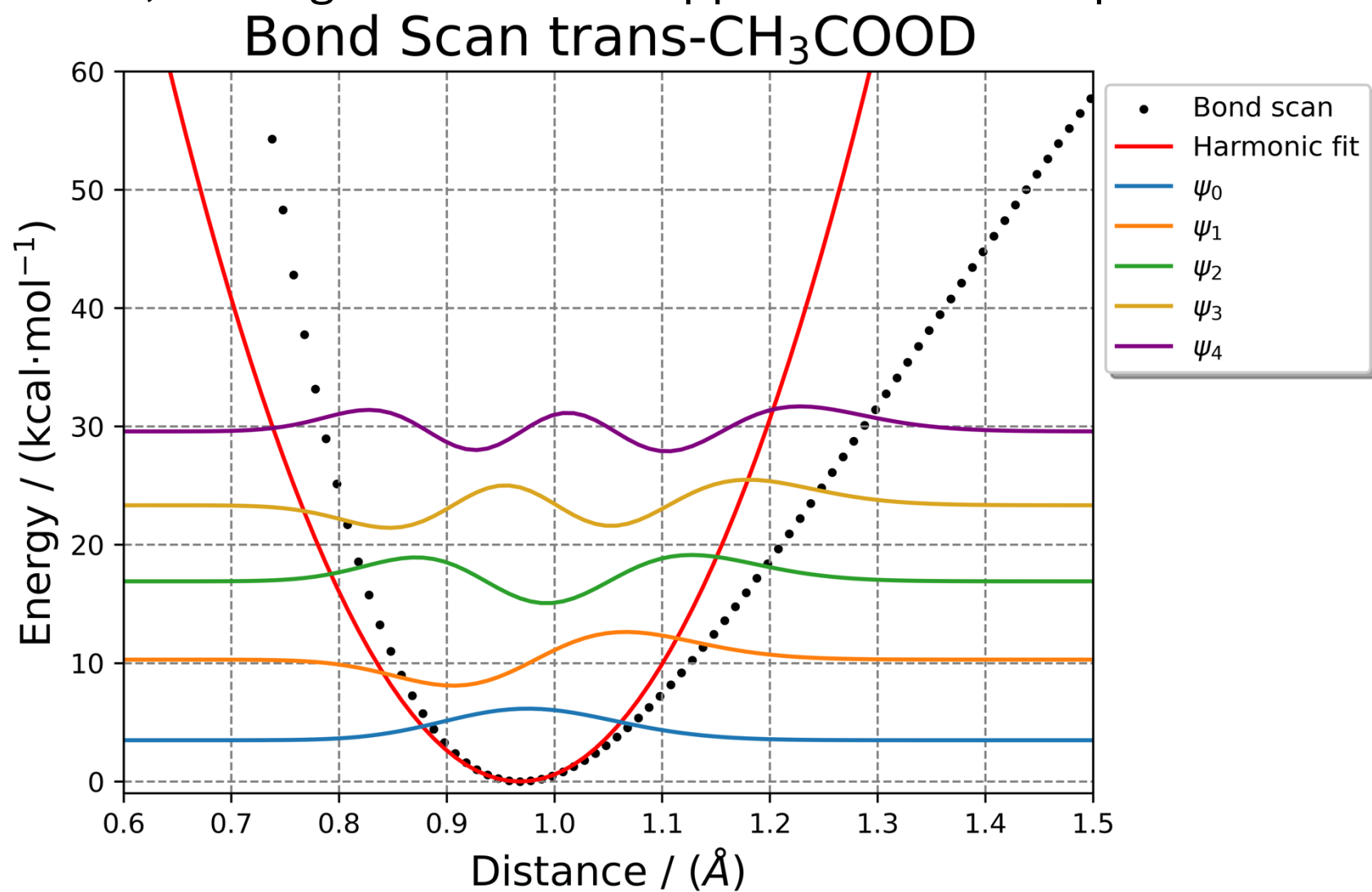


**Fig 4:** Potential energy surface of the bond scan of trans-CH<sub>3</sub>COOH (black dots), the harmonic fit (red) and the first five wave functions shifted by their respective eigenenergies.

**Tab 5:** Comparison of the frequencies obtained by Gaussian, the harmonic fit, and the **Numerov's method** with experimental data (FTIR) for trans-CH<sub>3</sub>COOH.

	base (cm <sup>-1</sup> )	1st overtone (cm <sup>-1</sup> )	2nd overtone (cm <sup>-1</sup> )	3rd overtone (cm <sup>-1</sup> )
Gaussian	3753.12	7506.24	11259.36	15012.48
Harmonic	3548.54	7097.08	10645.61	14194.15
Numerov	3596.88	7036.90	10325.04	13466.99
Literature [3]	3581(8)	6991(30)	10246(32)	--

Regarding the fundamental frequency, again the **Numerov method** with 15.88 cm<sup>-1</sup> (0,44 %) shows the smallest derivation to the literature data. In reality the overtones are not equally spaced due to anharmonicity of molecular vibration. Tab 5. shows clearly that **Numerov's method** shows the best fit to the literature data.



**Fig 5:** Potential energy surface of the bond scan of trans-CH<sub>3</sub>COOD (black dots), the harmonic fit (red) and the first five wave functions shifted by their respective eigenenergies.

**Tab 6:** Comparison of the frequencies obtained by Gaussian, the harmonic fit, and the **Numerov's method** with experimental data (\*FTIR, trans-CD<sub>3</sub>COOD) for trans-CH<sub>3</sub>COOD.

	base (cm <sup>-1</sup> )	1st overtone (cm <sup>-1</sup> )	2nd overtone (cm <sup>-1</sup> )	3rd overtone (cm <sup>-1</sup> )
Gaussian	2729.98	5459.96	8189.95	10919.93
Harmonic	2452.89	4905.78	7358.66	9811.55
Numerov	2382.38	4696.81	6944.72	9127.60
Literature* [4]	2630.4	-	-	--

Here with a deviation of 99.58 cm<sup>-1</sup> (3.79 %) the frequencies obtained from Gaussian perform the best in respect to the experimental data. The experimental data comes from a FTIR measurement in an Ar matrix at 8K. The smaller deviation of the harmonic Gaussian result could be an error cancellation of error compensation.

References:

- [1] ANHARMONICITY OF VIBRATION IN MOLECULES, K. S. VISWANATHAN (1957), <https://doi.org/10.1007/BF03052565>
- [2] Accuracy of spectroscopic constants of diatomic molecules from ab initio calculations (2003); Pawloski et al. <https://doi.org/10.1063/1.1533032>
- [3] Integrated Intensities of O-H Stretching Bands: Fundamentals and Overtones in Vapor-Phase Alcohols and Acids (2001), Lange et.al; DOI: <https://doi.org/10.1021/jp003277u>
- [4] Photochemistry and Vibrational Spectroscopy of the Trans and Cis Conformers of Acetic Acid in Solid Ar (2004), Macoas et al, doi: <https://doi.org/10.1021/jp037840v>