Problem V.S ... ethanol or methanol?   10 points; průměr 7,20; řešilo 35 studentů

The binding energy of a fluorine molecule is approximately 37 kcal/mol. Assuming the range of binding interactions to be approximately 3 Å from the optimum distance, what (average) force do we have to exert to break the molecule? Calculate the "stiffness" of the fluorine molecule if such an average force was applied in the middle of this range. What would be the vibrational frequency of this molecule? Compare this with the experimental value of $916.6\,\mathrm{cm}^{-1}$. (4 pts)

Using Psi4, calculate the dissociation curve F_2 and fit a parabola around the minimum. What value will you get for the energy of the vibrational transitions this time? (3 pts)

You are given two bottles of alcohol that you found suspicious, to say the least. After taking them to the lab, you obtain the following Raman spectra from them. Using the Psi4 program, calculate the frequencies at which the vibrational transitions of both the methanol and ethanol molecules occur. Use this to determine which bottle contains methanol and which one contains ethanol. You can use the approximate geometries of ethanol and methanol, which are included in the problem statement on the web. (3 pts)
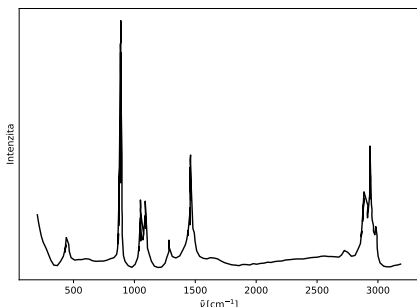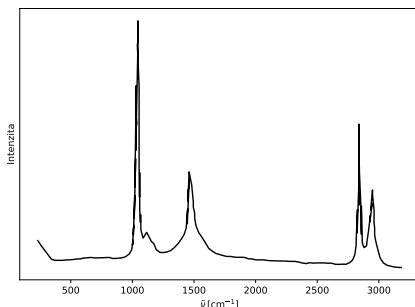

Fig. 1: Raman spectra of bottle A

Fig. 2: Raman spectra of bottle B

Alcohol from Mikuláš?!

To calculate the force, we will use the simplest fundamental equation for calculating work, $E = Fx$. To avoid problems with units, we convert all quantities to SI units. In this case, the force will be $F = \frac{2.57 \cdot 10^{-19}\,\mathrm{J}}{3 \cdot 10^{-10}\,\mathrm{m}} = 8.56 \cdot 10^{-10}\,\mathrm{N}$. Then we can calculate the stiffness from equation $F = kx$ which equals $k = \frac{8.56 - 10\,\mathrm{N}}{1.5 \cdot 10^{-10}\,\mathrm{m}} = 5.7\,\mathrm{N/m}$. Note that we have already reached the common values for macroscopic objects, even though we are talking about molecules!

Finally, we calculate the frequency as $f = \frac{1}{2\pi} \sqrt{\frac{k}{\mu}} = \frac{1}{2\pi} \sqrt{\frac{5.7\,\mathrm{N/m}}{0.5 \cdot 19 \cdot 1.6605 \cdot 10^{-27}\,\mathrm{kg}}} = 3.02 \cdot 10^{12}\,\mathrm{Hz}$, which corresponds to approximately $100\,\mathrm{cm}^{-1}$. That is quite a good match for the rough estimate we made.

If we want a more accurate estimate, we can pick a fluorine molecule and use the Hartree-Fock method in Psi4 in the `cc-pvdz` basis to obtain the full potential curve. We do this by preparing an input that looks like

```
set basis cc-pvdz
molecule F2{
0 1
F 0. 0. 0.
F XXX 0. 0.
}
energy('HF'),
```

and consecutively substituting the specific internuclear distances in `XXX`. Then, we run each file in Psi4, which gives us energy. If we plot the dependence of the energy on the distance, we get the following curve.
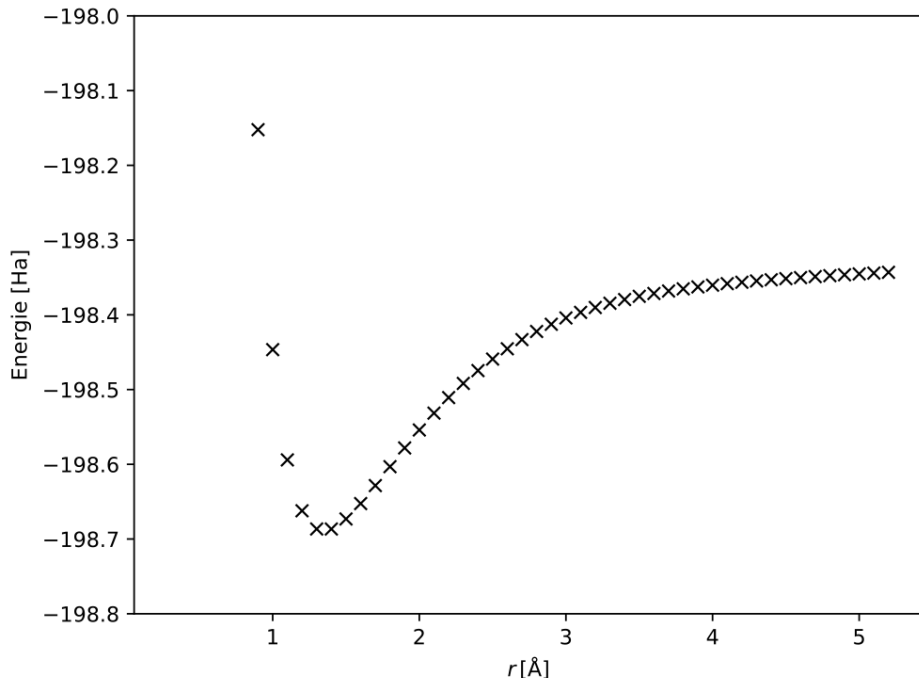

Fig. 3: Potential curve of the fluorine molecule.

For the fitting, we select only the points near the minimum and fit them with the parabolic function $f(x) = \frac{1}{2}k(x - x_{\min})^2 + E_{\min}$. We can see the resulting fit in the following figure, where we have marked in light grey those points, which we have excluded from the fit.

We got the following parameters $k = 1.89\,\text{Ha/Å}^2$, $x_{min} = 1.367\,\text{Å}$ and $E_{min} = -198.689\,\text{Ha}$. Only the parameter k is relevant for us and has a value of $824\,\text{J/m}^2$ in SI units. Substituting into the formula for frequency $f = \frac{1}{2\pi}\sqrt{\frac{k}{\mu}}$ we obtain a value of $36.4\,\text{THz}$, which corresponds to a transition to $1213\,\text{cm}^{-1}$.
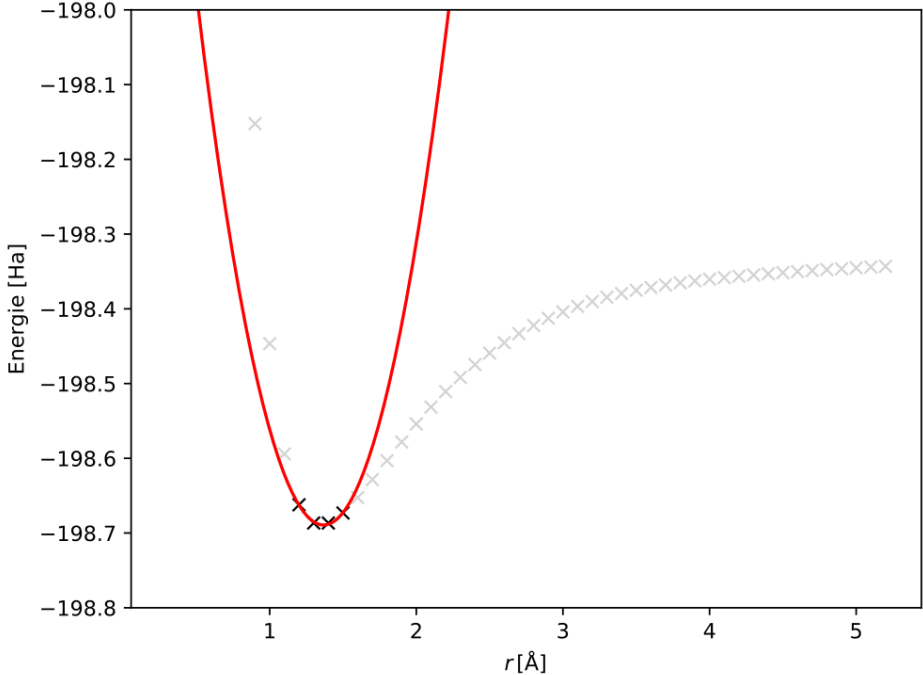

Fig. 4: Potential curve of the fluorine molecule, approximated around the minimum by a parabola.

That is a much better match than before, but if we wanted a more accurate result, we would have to use a significantly better method to calculate the molecule's energy. One of these is calculating the second derivative directly in the Psi4, which gets us $1180\,\text{cm}^{-1}$. The second one is numerically solving the Schrödinger equation for the nuclei, which gets us $1174\,\text{cm}^{-1}$.

In order to solve the last problem, we will use the prepared geometries to create input files for methanol

```
set basis cc-pvdz
molecule Met{
C -3.720857 1.264467 0.014321
H -5.081582 2.621135 0.111960
O -4.091493 2.612354 0.044506
H -4.166693 0.761523 -0.871149
H -4.031107 0.758163 0.954084
H -2.616521 1.197075 -0.068199
}
optimize("HF")
frequency("HF") .
```

After running it, we get the following frequencies (in cm^{-1})

344.7353	1155.1089	1184.1534	1265.1312	1489.7828	1597.6150
1600.4981	1612.5931	3151.1258	3203.9524	3276.1868	4154.4543

Similarly, the frequency for ethanol (in cm^{-1})

273.3196	314.2444	444.6461	877.5750	972.2065	1125.5706
1208.7315	1275.9318	1382.3368	1403.6507	1506.6482	1578.0625
1583.8727	1603.8039	1637.3176	3141.0952	3170.6320	3183.8335
3259.2164	3267.7417	4154.9101			

We get the following figures when plotted with the calculated positions. It shows the calculated
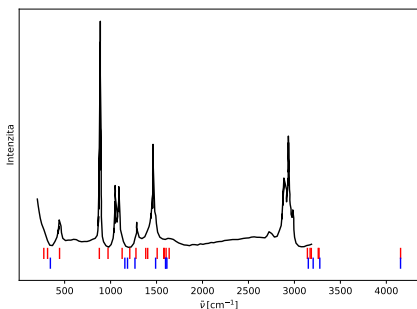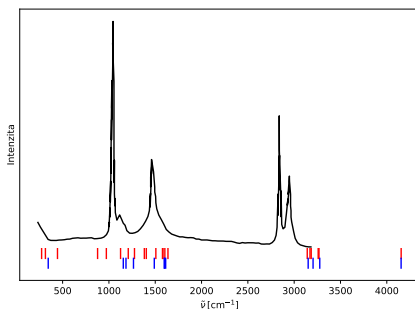

Fig. 5: Raman spectra of bottle A

Fig. 6: Raman spectra of bottle B

ethanol lines in red and the methanol lines below in blue. Although there are discrepancies in the spectra, it is fairly safe to conclude that the left bottle A contains ethanol and the right bottle contains methanol.

There are several clues to this. First, the left spectrum has a line between $400\,\text{cm}^{-1}$ and $500\,\text{cm}^{-1}$ that is missing from the right spectrum. The calculated methanol spectrum has no mode that we would assign to this peak. Next, we have a very intense peak at $900\,\text{cm}^{-1}$ in the left spectrum,

which again has no counterpart in the calculated methanol spectrum, and instead corresponds very closely to one of the ethanol modes. Finally, around $3000\,\mathrm{cm^{-1}}$, we can distinguish at least four peaks in the left spectrum, but the calculation for methanol in this region predicts only three. Conversely for ethanol, we get five peaks here, although they are shifted to slightly higher energies.

All this reinforces our conclusion that there is ethanol in the left bottle. After all, we could have guessed this from the left spectrum having many more peaks, since we expect $3 \cdot 9 - 6 = 21$ vibrational modes for ethanol, while only $3 \cdot 6 - 6 = 12$ for methanol.

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