Vibrations and waves: exercise sheet 1

Vibrations of diatomic molecules of single elements

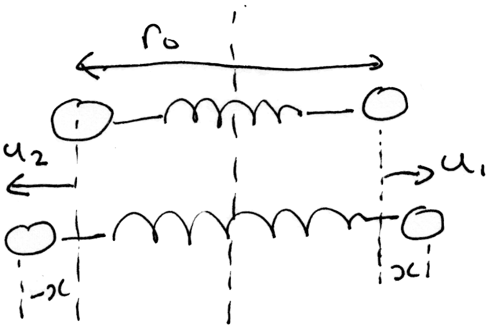
The purpose of this exercise is to put some data into the analysis of the vibrations of diatomic molecule developed in Lecture week 1, and to analyse the validity of a simple model for the interatomic interactions. Data are provided in the following table

Molecule	Mass (g/mol)	Bond length (Å)	Frequency (THz)	Dissociation energy (kJ/mol)
H_2	1	0.74	132	436
D_2	2	0.74	93.5	436
N_2	14	1.10	71	945
O_2	16	1.21	47	498
F_2	19	1.42	27	159
Cl_2	35.5	1.99	17	243
Br_2	79.9	2.28	9.5	193
I_2	126.9	2.67	6.2	151

1. Show from the mass and frequency values provided in the table that the force constants for stretching the bonds in the hydrogen and deuterium molecules are virtually identical. Check your numerical answers with the class demonstrator.

The relevant extract from the lectures is …

Picture of molecule showing the vibration



Energy

$$E = \frac{1}{2} k \left(u_1 - u_2\right)^2$$

Let's look at each atom

$$f_1 = -\frac{\partial E}{\partial u_1} = -k(u_1 - u_2) = m\ddot{u}_1$$
$$f_2 = -\frac{\partial E}{\partial u_2} = +k(u_1 - u_2) = m\ddot{u}_2$$

But we know the solutions. One is atoms move together, and one is they move exactly in opposite directions. The first doesn't involve

$$\begin{aligned}
f_1 &= -\frac{\partial E}{\partial u_1} = -k(u_1 - u_2) = m\ddot{u}_1 \\
f_2 &= -\frac{\partial E}{\partial u_2} = +k(u_1 - u_2) = m\ddot{u}_2 \\
u_1 &= a\cos\omega t \\
u_2 &= -a\cos\omega t \\
m\omega^2 a\cos\omega t &= k2a\cos\omega t \\
\omega^2 &= 2k/m
\end{aligned}$$

So we can evaluate the force constants from rearranging the last equation

$k = m\omega^2/2 = 2\pi^2 m\nu^2$

We need to be careful with units and powers of 10. For the H_2 and D_2 molecules we have

$k(\mathrm{H}_2) = 2\pi^2 \times (1\times10^{-3}/6.022\times10^{23}) \times (132\times10^{12}) = 571\ \mathrm{J/m^2/bond}$

$k(\mathrm{D}_2) = 2\pi^2 \times (2\times10^{-3}/6.022\times10^{23}) \times (93.5\times10^{12}) = 573\ \mathrm{J/m^2/bond}$

2. Show that the frequency change on increased mass of the halogens is not simply due to the increased mass, and that there is a gradual decrease in the bond stretching force constant with increasing atomic number.

No need to calculate everything here; it is enough to show that mass × frequency^2 is not constant, and decreases with element. Values using the raw numbers are

F_2 = 19 × 27^2 = 13,851

Cl_2 = 35.5 × 17^2 = 10,259.5

Br_2 = 79.9 × 9.5^2 = 7,211

I_2 = 126.9 × 6.2^2 = 4,878

3. From the dissociation energies and the bond lengths, calculate the parameters in the Lennard-Jones energy function for N_2 and O_2, using the following form of the potential energy function:

$$E(r) = -4\varepsilon\left[\left(\frac{\sigma}{r}\right)^6 - \left(\frac{\sigma}{r}\right)^{12}\right]$$

$$\frac{\mathrm{d}E}{\mathrm{d}r} = \frac{4\varepsilon}{\sigma}\left(6\left(\frac{\sigma}{r}\right)^7 - 12\left(\frac{\sigma}{r}\right)^{13}\right)$$

$$\frac{\mathrm{d}E}{\mathrm{d}r} = 0 \Rightarrow 6\left(\frac{\sigma}{r}\right)^7 - 12\left(\frac{\sigma}{r}\right)^{13} = 0 \Rightarrow \frac{\sigma}{r} = 2^{-1/6}$$

$$E(r = 2^{1/2}\sigma) = -4\varepsilon\left(\frac{1}{2} - \frac{1}{4}\right) = -\varepsilon$$

$$\frac{\mathrm{d}^2E}{\mathrm{d}r^2} = -\frac{4\varepsilon}{\sigma^2}\left(42\left(\frac{\sigma}{r}\right)^8 - 156\left(\frac{\sigma}{r}\right)^{14}\right) = -\frac{4\varepsilon}{\sigma^2}\left(\frac{42}{2\times 2^{1/3}} - \frac{156}{4\times 2^{1/3}}\right) = \frac{72\varepsilon}{2^{1/3}\sigma^2}$$

For N_2 and O_2 we have

$$\mathrm{N}_2: \quad \sigma = 1.10/2^{1/6} = 0.98\ \text{Å} \quad ; \quad \varepsilon = 945\ \text{kJ/mol}$$

$$\mathrm{O}_2: \quad \sigma = 1.21/2^{1/6} = 1.08\ \text{Å} \quad ; \quad \varepsilon = 498\ \text{kJ/mol}$$

4. Evaluate the quality of the Lennard-Jones potential for the calculation of vibrational frequencies of N_2 and O_2.

Calculation of experimental force constants, now being very careful about units

$$k(\mathrm{N}_2) = 2\pi^2 \times (14\times 10^{-3}/6.022\times 10^{23}) \times (71\times 10^{12}) = 2313\ \text{J/m}^2\text{/bond}$$

$$k(\mathrm{O}_2) = 2\pi^2 \times (16\times 10^{-3}/6.022\times 10^{23}) \times (47\times 10^{12}) = 1158\ \text{J/m}^2\text{/bond}$$

Calculation of force constants from Lennard-Jones model

$$k = \frac{72\varepsilon}{2^{1/3}\sigma^2}$$

$$k(\mathrm{N}_2) = 72 \times (945\times 10^3/6.022\times 10^{23})/2^{1/3}/(0.98\times 10^{-10})^2 = 9337\ \text{J/m}^2\text{/bond}$$

$$k(\mathrm{O}_2) = 72 \times (498\times 10^3/6.022\times 10^{23})/2^{1/3}/(1.08\times 10^{-10})^2 = 4051\ \text{J/m}^2\text{/bond}$$

These values are too large by a factor of 3–4. No-one should be surprised that the model doesn’t work – it is really designed to work for weak interactions between closed-shell atoms, not to describe a covalent bond. Using any 2-parameter model to describe three independent quantities might be thought to be over-optimistic.