

Chem 30324, Spring 2017, Homework 6

Due March 6, 2017

Quantum mechanics of vibrating NO.

The diatomic nitric oxide (NO) is an unusual and important molecule. It has an odd number of electrons, which is a rarity for stable molecule. It acts as a signaling molecule in the body, helping to regulate blood pressure, is a primary pollutant from combustion, and is a key constituent of smog. It exists in several isotopic forms, but the most common, $^{14}\text{N} = ^{16}\text{O}$, has a bond length of 1.15077 \AA and harmonic vibrational frequency of 1904 cm^{-1} .

1. The ground vibrational wavefunction of N=O can be written

$$\Psi_{v=0}(x) = \left(\frac{1}{\alpha\sqrt{\pi}} \right)^{1/2} e^{-x^2/2\alpha^2}, \quad x = R - R_{eq}, \quad \alpha = \left(\frac{\hbar^2}{\mu k} \right)^{1/4}$$

where $x = R - R_{eq}$. Calculate $\langle x \rangle$ and $\langle x^2 \rangle$ for NO in the $\Psi_{v=0}(x)$ state (you might want to use α as a length unit).

$$\langle x \rangle = \langle \Psi_{v=0}(x) | x | \Psi_{v=0}(x) \rangle, \quad \Psi_{v=0}(x) = \left(\frac{1}{\alpha\sqrt{\pi}} \right)^{1/2} e^{-x^2/2\alpha^2}$$

$\Psi_{v=0}(x)$ is an even function in the domain of $(-\infty, \infty)$. x is an odd function in $(-\infty, \infty)$. So $x\Psi_{v=0}^2(x)$ is an odd function, the integral is zero according to the symmetry of the wavefunctions.

$$\langle x^2 \rangle = \langle \Psi_{v=0}(x) | x^2 | \Psi_{v=0}(x) \rangle = N_0^2 \int_{-\infty}^{\infty} x^2 e^{-x^2/\alpha^2} dx, \quad N_0 = \left(\frac{1}{\alpha\sqrt{\pi}} \right)^{1/2}$$

Use python to calculate $\int_{-\infty}^{\infty} x^2 e^{-x^2/\alpha^2} dx$:

```
In [1]: from sympy import * # import sympy for symbolic mathematics
x = symbols('x')
a = symbols('a', positive=True)
pprint(integrate((x**2*exp(-x**2/a**2)), (x, -oo, oo)))
```

$$\frac{\sqrt{\pi} \cdot a^{\frac{3}{2}}}{2}$$

$$\text{So, } \langle x^2 \rangle = N_0^2 \frac{\sqrt{\pi} \alpha^3}{2} = \frac{1}{\alpha \sqrt{\pi}} \frac{\sqrt{\pi} \alpha^3}{2} = \frac{\alpha^2}{2}$$

2. Calculate the average potential energy, $\langle V(x) \rangle$, in the ground state, in units of $h\nu$. Hint: This is trivial to calculate given the answer to question 1!

$$\langle V(x) \rangle = \frac{1}{2} k \langle x^2 \rangle = \frac{k \alpha^2}{4}, \text{ plug in } \alpha = \left(\frac{\hbar^2}{\mu k} \right)^{1/4}, \text{ we can get } \langle V(x) \rangle = \frac{k \alpha^2}{4} = \frac{k}{4} \left(\frac{\hbar^2}{\mu k} \right)^{1/2} = \frac{\hbar}{4} \sqrt{\frac{k}{\mu}}. \text{ From } \nu = \frac{1}{2\pi} \sqrt{\frac{k}{\mu}}, \text{ we can get } \langle V(x) \rangle = \frac{\hbar}{4} \times 2\pi\nu = \frac{h\nu}{4}.$$

3. Using conservation of energy and your answer to question 11, calculate the average kinetic energy, $\langle T(x) \rangle$, in the ground state, in units of $h\nu$. Comment on the relationship between the kinetic and potential energies. This is a general result for all ν , and is a consequence of the virial theorem for the harmonic potential.

$$E = \langle V(x) \rangle + \langle T(x) \rangle$$

In the ground state, $E = \frac{h\nu}{2}$, $\langle V(x) \rangle = \frac{h\nu}{4}$, so, $\langle T(x) \rangle = E(x) - \langle V(x) \rangle = \frac{h\nu}{4}$, which means $\langle T(x) \rangle = \langle V(x) \rangle$. The relationship $\langle T(x) \rangle = \langle V(x) \rangle$ is also true for classical harmonic oscillator.

4. Calculate the classical minimum and maximum values of the $^{14}\text{N} = ^{16}\text{O}$ bond length for a molecule in the ground vibrational state. Hint: Calculate the classical limits on x , the value of x at which the kinetic energy is 0 and thus the total energy equals the potential energy.

When the kinetic energy is 0, we can get $V(x) = E$, which means $\frac{1}{2} k x^2 = \frac{1}{2} h\nu$. We can get the value of x by solving the equation. From what we got in question 2, $\langle V(x) \rangle = \frac{k \alpha^2}{4} = \frac{h\nu}{4}$, so $k \alpha^2 = h\nu$. So $\frac{1}{2} k x^2 = \frac{1}{2} k \alpha^2$, $x = -\alpha$ or $x = \alpha$.

We can get the value of α from k and ν by $\tilde{\nu} = 1904 \text{ cm}^{-1}$, $\nu = c\tilde{\nu}$ and $\nu = \frac{1}{2\pi} \sqrt{\frac{k}{\mu}}$.

```
In [1]: import numpy as np

wavenumber = 190400 # m^-1
c = 2.998e8 # m/s, the speed of light
N_14 = 14.003 # amu
O_16 = 15.995 # amu
hbar = 1.05457e-34 # J*s

nu = c*wavenumber # s^-1, frequency
mu = N_14*O_16/(N_14+O_16)*1.6605e-27 # kg, reduced mass
k = (2*np.pi*nu)**2*mu # N/m, force constant
alpha = (hbar**2/mu/k)**0.25
print('The value of alpha is {:.5f} angstroms.'.format(alpha*1e10))
```

The value of alpha is 0.04870 angstroms.

$$R_{\max} = R_{eq} + \alpha, R_{\min} = R_{eq} - \alpha$$

```
In [2]: R_eq = 1.15077e-10 # m, bond length
R_max = R_eq + alpha # m, the maximum value of the bond length
R_min = R_eq - alpha # m, the minimum value of the bond length
print('The classical maximum value of the bond length is {0:.5f} angstroms. The classical minimum value of the bond length is {1:.5f} angstroms.'.format(R_max*1e10, R_min*1e10))
```

The classical maximum value of the bond length is 1.19947 angstroms. The classical minimum value of the bond length is 1.10207 angstroms.

5. Calculate the probability for a quantum mechanical $^{14}\text{N} = ^{16}\text{O}$ molecule to have a bond length outside the classical limits. This is an example of quantum mechanical tunneling.

$$P_{\text{within-the-limits}} = \int_{x_-}^{x_+} \Psi_{v=0}^2(x) dx = \frac{1}{\alpha\sqrt{\pi}} \int_{-\alpha}^{\alpha} e^{-x^2/\alpha^2} dx \stackrel{x/\alpha=y}{=} \frac{1}{\sqrt{\pi}} \int_{-1}^1 e^{-y^2} dy$$

```
In [3]: from sympy import *
y = symbols('y')
pprint(integrate(1/sqrt(pi)*exp(-y**2), (y, -1, 1)))

erf(1)
```

$$P_{\text{outside-the-limits}} = 1 - \text{erf}(1) = 0.15730$$

Statistical mechanics of vibrating NO

6. Using your knowledge of the harmonic oscillator and the Boltzmann distribution, complete the table below for the first four harmonic vibrational states of $^{14}\text{N}=^{16}\text{O}$.

Quantum number	Energy (kJ/mol)	Relative population at 400 K	Relative population at 410 K
$v = 0$	11.389	1	1
$v = 1$	34.166	1.0608×10^{-3}	1.2536×10^{-3}
$v = 2$	56.944	1.1253×10^{-6}	1.5716×10^{-6}
$v = 3$	79.721	1.1937×10^{-9}	1.9703×10^{-9}

```
In [10]: import numpy as np
h = 6.62607e-34 # J*s
wavenumber = 190400 # m^-1
c = 2.998e8 # m/s, the speed of light
nu = c*wavenumber # s^-1, frequency
NA = 6.02214e23
R = 8.31447 # J/mol/K
T1 = 400 # K
T2 = 410 # K
E = []
P1,P2 = [],[]
for n in [0,1,2,3]:
    E.append((n+0.5)*h*nu*NA) # J/mol, energy
    P1.append(np.exp(-E[n]/R/T1)/np.exp(-E[0]/R/T1)) # relative population at T1
    P2.append(np.exp(-E[n]/R/T2)/np.exp(-E[0]/R/T2)) # relative population at T2
    print('The energy of v={0:.0f} is {1:.3f} kJ/mol, the relative population at 400 K is {2:.4E}, the relative population at 410 K is {3:.4E}.'.format(n,E[n]/1000,P1[n],P2[n]))
```

```
The energy of v=0 is 11.389 kJ/mol, the relative population at 400 K is 1.0000E+00, the relative population at 410 K is 1.0000E+00.
The energy of v=1 is 34.166 kJ/mol, the relative population at 400 K is 1.0608E-03, the relative population at 410 K is 1.2536E-03.
The energy of v=2 is 56.944 kJ/mol, the relative population at 400 K is 1.1253E-06, the relative population at 410 K is 1.5716E-06.
The energy of v=3 is 79.721 kJ/mol, the relative population at 400 K is 1.1937E-09, the relative population at 410 K is 1.9703E-09.
```

7. Use the table to estimate the average vibrational energy of a mole of $^{14}\text{N}=^{16}\text{O}$ at 400 and 410 K.

```
In [11]: P1_total,P2_total = 0,0
          E1,E2 = 0,0
          for n in [0,1,2,3]:
              P1_total += P1[n] # add all the relative probabilities at T1 together
          r
              P2_total += P2[n] # add all the relative probabilities at T2 together
          r
          for n in [0,1,2,3]:
              E1 += E[n]*P1[n]/P1_total # calculate weighted average energy at T1
              E2 += E[n]*P2[n]/P2_total # calculate weighted average energy at T2
          print('The average vibrational energy of a mole of NO is {0:.3f} kJ at 4
          00 K.\n\nThe average vibrational energy of a mole of NO is {1:.3f} kJ at 4
          10 K'.format(E1/1000,E2/1000))
```

The average vibrational energy of a mole of NO is 11.413 kJ at 400 K.
 The average vibrational energy of a mole of NO is 11.417 kJ at 410 K

8. Use your answer to Question 7 to estimate the vibrational heat capacity (dE/dT) of a mole of $^{14}\text{N}=^{16}\text{O}$ in this temperature range. How does your answer compare to the classical estimate, $R = 8.314 \text{ J/mol K}$?

```
In [12]: print('The vibrational heat capacity in this temperature range is {:.5f}
          J/(molK)'.format((E2-E1)/10))
```

The vibrational heat capacity in this temperature range is 0.44030 J/(molK).

9. Predict the harmonic vibrational frequency of the heavier cousin of $^{14}\text{N}=^{16}\text{O}$, $^{15}\text{N}=^{18}\text{O}$, in cm^{-1} . Assume the force constant is independent of isotope. Do you think these two isotopes could be distinguished using infrared spectroscopy?

From $\nu = c\tilde{\nu}$ and $\nu = \frac{1}{2\pi} \sqrt{\frac{k}{\mu}}$, we can get $\tilde{\nu} = \frac{1}{2\pi c} \sqrt{\frac{k}{\mu}}$.

$$\frac{\tilde{\nu}_{^{15}\text{N}^{18}\text{O}}}{\tilde{\nu}_{^{14}\text{N}^{16}\text{O}}} = \sqrt{\frac{\mu_{^{14}\text{N}^{16}\text{O}}}{\mu_{^{15}\text{N}^{18}\text{O}}}}$$

```
In [9]: import numpy as np
wavenumber = 1904 # cm-1
N_14 = 14.003 # amu
O_16 = 15.995 # amu
mu_1 = N_14*O_16/(N_14+O_16) # amu, reduced mass
N_15 = 15.000 # amu
O_18 = 17.999 # amu
mu_2 = N_15*O_18/(N_15+O_18) # amu, reduced mass
print('The harmonic vibrational frequency of the heavier cousin is {:.0f} cm-1.'.format(np.sqrt(mu_1/mu_2)*wavenumber))
```

The harmonic vibrational frequency of the heavier cousin is 1819 cm⁻¹.

These two isotopes could be distinguished using infrared spectroscopy.

In []: