1 Advanced Physical Chemistry – Exercizes

1.1 For $H^{35}Cl$ the wavenumber of the rotation transition $J = 0 \rightarrow 1$ is 20.8784 cm^{-1}, while it amounts to 10.7840 cm^{-1} for $D^{35}Cl$. Do the molecules have the same bond length?

M(H) = 1.007985 g/mol, M(D) = 2.0140 g/mol, M(Cl) = 34.96885 g/mol

1.2 The intensity of spectral lines resulting from the transition between vibrational states of a molecule is proportional to the square of the integral $\int \psi_{v'} x \psi_v \, \mathrm{d}x$. The unnormalized wave functions of an harmonic oscillator having the potential $V(x) = \frac{1}{2}Kx^2$are

$$\psi_v = H_v(y)e^{-\frac{y^2}{2}}, \quad y = x/\alpha, \quad \alpha^2 = \frac{\hbar}{\sqrt{\mu K}} \; ,$$

where $H_v(y)$ denotes a Hermitian polynomial. Prove that only transitions with $v' = v \pm 1$ are allowed!

Hints: Hermitian polynomials can be obtained from the recursion relation

$$H_{v+1} = 2yH_v - 2vH_{v-1} \; .$$

Furthermore, there exists an orthogonality relation,

$$\int_{-\infty}^{\infty} H_{v'} H_v e^{-y^2} \, \mathrm{d}y = \begin{cases} 0 & \text{if } v \neq v' \\ \sqrt{\pi}\, 2^v v! & \text{if } v = v' \end{cases}$$

1.3 The infrared spectrum of N_2O consists of 3 fundamental bands.

a) Can one deduce from this—assuming that N_2O is linear—whether the molecule has the structure NNO or NON?

b) Sketch the motions of the atoms for the fundamental vibrations of both structures!

1.4 The infrared spectrum of HCl shows absorption lines at 2885.65, 5667.18, 8344.62, and 10917.94 cm^{-1}. Calculate the dissociation energy D_0, the zero point energy, and the depth of the vibration potential minimum D_e!

1.5 The chlorine molecule can be regarded as an anharmonic oscillator having the wavenumber $\tilde{\nu}$ = 564.9 cm^{-1} and the anharmonicity constant $x_\mathrm{e}\tilde{\nu}$ = 4 cm^{-1}. Calculate

a) the zero-point energy

b) the dissociation energy

c) the number of vibration levels

Hint: Look for the maximum of the vibration energy.