Wednesday, March 25

Last Time:
- QMHO Model
- IR Spectroscopy

Today:
• Anharmonic oscillator model
• Vibrations in polyatomic molecules
• Let's go for a spin: rotations
  • The rigid rotor

Readings:
• Chang & Thoman: 11.1–3

Website: New Homework

Reminders:
Take-home exam coming up soon
The Relationship Between Bond Energy and Force Constant.

Molecule | Fundamental Transition\(a\), \(\varepsilon_1 - \varepsilon_0\) (cm\(^{-1}\)) | Force Constant\(b\) (N m\(^{-1}\)) | Bond Enthalpy\(c\), 25°C (kJ/mole)
---|---|---|---
H\(_2\) | 4159.5 | 514 | 436
D\(_2\) | 2990.3 | 531 | 443

Electromagnetic radiation that increases the vibrational energy of a molecule is usually in the infrared region. Absorption peaks are typically reported with units cm\(^{-1}\), called wavenumbers, which is proportional to energy. The fundamental transition is from \(\nu = 0\) to \(\nu = 1\).

The force constants were calculated from \(\Delta \varepsilon = h - k \mu\).

The bond enthalpy at 25°C is \(\Delta H^\circ\) for the reaction RX(g) \(\rightarrow\) R(g) + X(g).

Critical Thinking Questions

10. Why are the bond enthalpies of H\(_2\) and D\(_2\) almost equal?
Bond energy is determined by the number of protons, number of electrons, and internuclear distances—not by neutrons.

11. Notice that the values of the force constants for H\(_2\) and D\(_2\) are almost equal. Why are the values of the fundamental transitions (\(\nu = 0\) to \(\nu = 1\)) so different?
\(\Delta \varepsilon \propto \frac{1}{\mu}\). \(\mu\)\(_{H_2}\) and \(\mu\)\(_{D_2}\) are different.

12. Based on this analysis, which is the better indicator of bond strength, the fundamental transition energy or the force constant?
Morse Potential

\[ E(R) = D_e \left(1 - e^{-\alpha(R-R_e)}\right)^2 \]
It is beyond the scope of this course, but it can be shown (for the harmonic oscillator model) that the number of vibrational degrees of freedom of a molecule, \( N_{\text{vib}} \), is expressed as the combination of vibrational modes in the molecule. For example, the water molecule has \( N_{\text{vib}} = 3 \) and water has three vibrational modes; each of the modes has an oscillating dipole moment, and all three are infrared active.

Symmetric Stretch
\( \bar{\nu} = 3650 \text{ cm}^{-1} \)

Antiymmetric Stretch
\( \bar{\nu} = 3760 \text{ cm}^{-1} \)

Bend
\( \bar{\nu} = 1600 \text{ cm}^{-1} \)

Problem 1.
\( \text{CO}_2 \) has the four vibrational modes shown below.

Symmetric stretch
\( \bar{\nu} = 1337 \text{ cm}^{-1} \)

Antisymmetric stretch
\( \bar{\nu} = 2349 \text{ cm}^{-1} \)

Bend
\( \bar{\nu} = 667 \text{ cm}^{-1} \)

(a) Which modes are infrared active?

(b) The symmetric stretch, the antisymmetric stretch, and the bending mode on the left in the figure are all within the plane of the paper. The bending mode on the right in the figure is necessary because the molecule does not, of 230 ChemActivity 21 Rotational and Vibrational Spectra of Molecules
Information

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For example, the water molecule has \( N_{\text{vib}} = 3 \) and water has three vibrational modes; each of the modes has an oscillating dipole moment, and all three are infrared active.

\[
\begin{align*}
\text{Symmetric Stretch} & : \quad v = 3650 \text{ cm}^{-1} \\
\text{Antisymmetric Stretch} & : \quad v = 3760 \text{ cm}^{-1} \\
\text{Bend} & : \quad v = 1600 \text{ cm}^{-1}
\end{align*}
\]

**Problem**

1. \( \text{CO}_2 \) has the four vibrational modes shown below.

   - **Symmetric stretch**
     - \( \bar{v} = 1337 \text{ cm}^{-1} \)
   - **Antisymmetric stretch**
     - \( \bar{v} = 2349 \text{ cm}^{-1} \)
   - **Bend**
     - \( \bar{v} = 667 \text{ cm}^{-1} \)
     - **Bend (+ is towards you)**
     - \( \bar{v} = 667 \text{ cm}^{-1} \)

   (a) Which modes are infrared active?

   (b) The symmetric stretch, the antisymmetric stretch, and the bending mode on the left in the figure are all within the plane of the paper. The bending mode on the right in the figure is necessary because the molecule does not, of
Resolution of HCl spectrum

Low

Higher

Highest

Doublets: H$^{37}$Cl and H$^{35}$Cl