Structure and Spectra of Diatomic Molecules

Spectrophysics Ch 5 and 6. Exercises: 41, 42 and H43. Focus on the vibration and rotation, that is unique to molecules.

- **Energy** = electronic + vibrational + rotational

- Bonding and anti-bonding electronic states
- Photodissociation (Ozon)

- Vibration: \( E_{\text{vib}} = \hbar \omega_0 (\nu + \frac{1}{2}) \)

- Rotation: \( E_{\text{rot}} = \frac{\hbar^2}{2\mu r^2} \cdot \ell (\ell + 1) \)

- Roto-vibrational transitions:

- Basic physics regarding the green house effect
Potential in a diatomic molecule with $N$ electrons

$$V(R, \bar{r}_1, \bar{r}_2, \ldots, \bar{r}_N) = -\sum_{i=1}^{N} \frac{Z_A e^2}{4\pi \varepsilon_0 |\bar{r}_i - \bar{R}_A|} - \sum_{i=1}^{N} \frac{Z_B e^2}{4\pi \varepsilon_0 |\bar{r}_i - \bar{R}_B|} + \sum_{\substack{i,j=1 \atop i > j}}^{N} \frac{\varepsilon^2}{4\pi \varepsilon_0 |\bar{r}_i - \bar{r}_j|} + \frac{Z_A Z_B e^2}{4\pi \varepsilon_0 R}$$
Ionic bond in NaCl:
Energy to remove 3s electron from Na: -5.14 eV
Energy gain in Cl to fill the 3p-orbital: +3.62 eV

\[ \Delta E = 1.52 \text{ eV} \]

Dissociation energy \( E_d \) = 4.27 eV

\( r_0 = 0.236 \text{ nm} \)
$\psi_g$  

$\psi_u$  

1s state in molecular hydrogen ion  

$|\psi_g|^2$  

$|\psi_u|^2$  

Bonding  

Anti-bonding

https://chem.libretexts.org/LibreTexts/New_York_University/CHEM-UA_127%3A_Advanced_General_Chemistry_I/14%3A_Linear_combination_of_atomic_orbitals
Potential curves in OH

$E / \text{eV}$

$0$

$1$

$2$

$3$

$4$

$r (\text{Å})$

$A^2\Sigma^*$

$O(^1\text{D}) + H(^2\text{S})$

$O(^3\text{P}) + H(^2\text{S})$

$X^2\Pi$

$\Sigma^-$

$\Sigma^-$
160-240 nm

\[ \text{u} \text{v} \rightarrow \text{O}_2 \rightarrow 2\text{O} + 2\text{O}_2 \rightarrow 2\text{O}_3 \]

240-360 nm

\[ \text{u} \text{v} \rightarrow \text{O}_3 \rightarrow 2\text{O} + 2\text{O}_2 \rightarrow 3\text{O}_2 \]
Absorption of Sunlight in the Atmosphere

- Solar window
- Atmospheric window

Absorption (%)

Wavelength (μm)

- UV
- Vis
- Near IR
- Far IR (longwave, thermal)

Gases:
- O₂
- O₃
- H₂O
- CO₂
- O₃
<table>
<thead>
<tr>
<th>Atoms</th>
<th>Molecules</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Energy levels</strong></td>
<td><strong>Energy curves</strong> (function of $R$)</td>
</tr>
<tr>
<td>Infinite number, converging to ionization limit</td>
<td>Limited number</td>
</tr>
<tr>
<td>$E \sim \text{eV}, \lambda \sim \text{UV, Visible}$</td>
<td>$E \sim \text{eV}, \lambda \sim \text{UV, Visible}$</td>
</tr>
<tr>
<td>Ionized up to $Z$</td>
<td>1, 2 times</td>
</tr>
<tr>
<td>-</td>
<td>Photo dissociation (ozone)</td>
</tr>
<tr>
<td>-</td>
<td>Vibration</td>
</tr>
<tr>
<td>-</td>
<td>Rotation</td>
</tr>
</tbody>
</table>
Vibrational Energy in a Diatomic Molecule

HO approximation (red) of the exact potential (blue) in CO
Quantized harmonic oscillator

\[ U(x) = \frac{1}{2} k x^2 = \frac{1}{2} m \omega_0^2 x^2 \]

\[ E_0 = \frac{1}{2} \hbar \omega_0 \]
\[ E_1 = (1 + \frac{1}{2}) \hbar \omega_0 \]
\[ E_2 = (2 + \frac{1}{2}) \hbar \omega_0 \]
\[ E_3 = (3 + \frac{1}{2}) \hbar \omega_0 \]
\[ E_4 = (4 + \frac{1}{2}) \hbar \omega_0 \]
\[ E_5 = (5 + \frac{1}{2}) \hbar \omega_0 \]

\[ E = (n + \frac{1}{2}) \hbar \omega_0, \quad n = 0, 1, 2 \ldots \]

\[ \Delta E = \hbar \omega_0 \]
Comparison of vibrational energies in the HO approximation and in the real potential

Selection rules:
- HO: $\Delta \nu = 1$
- Real: $\Delta \nu = 1, 2, 3 (>1$ weak)
CO-spektrum med FTS

$\nu = 0 - 2$

$\nu = 0 - 3$
Energies in a Diatomic Molecule - Summary.

\[ E = E_{\text{elektron}} + E_{\text{vib}} + E_{\text{rot}} = E_{\text{elektron}} + \hbar \alpha_0 (\nu + \frac{1}{2}) + \frac{\hbar^2}{2\mu r^2} \cdot \ell (\ell + 1) \]

Orders of magnitude

<table>
<thead>
<tr>
<th></th>
<th>Electron</th>
<th>Vibration</th>
<th>Rotation</th>
</tr>
</thead>
<tbody>
<tr>
<td>(E/\text{cm}^{-1})</td>
<td>40000</td>
<td>1500</td>
<td>10</td>
</tr>
<tr>
<td>(E/\text{eV})</td>
<td>5</td>
<td>0.2</td>
<td>0.001</td>
</tr>
<tr>
<td>(\lambda/\mu\text{m})</td>
<td>0.3</td>
<td>6</td>
<td>1000</td>
</tr>
<tr>
<td>(T/\text{K})</td>
<td>40000</td>
<td>1500</td>
<td>10</td>
</tr>
</tbody>
</table>

(Note the coincidence that energies expressed in cm\(^{-1}\) and as a temperature in K has almost the same numerical value, i.e. \(1/(100 \cdot \hbar \cdot c) = 5.035 \cdot 10^{22} \approx 2/(3 \cdot k) = 4.83 \cdot 10^{22}\).)
Rotational Fine Structure in the 0 – 2 Vibrational Transition in CO
Rotational fine structure in a vibrational transition.

\[ E_{rot} = \frac{\hbar^2}{2\mu R_0^2} \cdot \ell \cdot (\ell + 1) \equiv B \cdot \ell \cdot (\ell + 1) \]

Selection rule for rotation: \( \Delta \ell = \pm 1 \).

\( \Delta \ell = +1 \) is called R-branch \( \Delta \ell = -1 \) is called P-branch
The figure shows part of an absorption spectrum for CO, in the
$0 - 2$ vibrational transition, registered using a Fourier-Transform
spectrometer (in the figure the absorption spectrum is inverted so that it looks like
an emission spectrum).
Using a Gaussian line profile we obtain the wavenumbers:

$P_1$, i.e. $\ell = 1 \rightarrow \ell = 0$: $4256.1248 \text{ cm}^{-1}$

$R_1$, i.e. $\ell = 0 \rightarrow \ell = 1$: $4263.7566 \text{ cm}^{-1}$.

Use this to determine the equilibrium distance between the C and
O atoms assuming the moment of inertia is the same in the 2
vibrational levels.
Molecular spectra – selection rules. (SP Ch.6)

For light to be emitted or absorbed the total angular momentum of the molecule has to change since the photon that is emitted/absorbed in a transition carries one unit of angular momentum. Since the vibrational states are not associated with any angular momentum, this implies that the rotational state and/or the electronic state must change. To state selection rules we therefore have to separate three cases.

**Pure rotational transitions, i.e. within a vibrational level in a given electronic state. Wavelengths in the microwave range.**

a. Homonuclear molecules (e.g. O₂, N₂), that lack permanent dipole moment, do not have rotational spectra since their rotation cannot interact with electromagnetic radiation.
b. \( \Delta \ell = \pm 1 \)

**Rotational-vibrational transitions, i.e. within a given electronic state. Wavelengths in IR.**

a. Homonuclear molecules, that lack a permanent dipole moment, do not have rotational-vibrational spectra since their vibration cannot interact with the light.
b. \( \Delta v = \pm 1 \) (harmonic-oscillator approximation), \( \pm 2, \pm 3, ... \)
c. \( \Delta \ell = \pm 1 \) (\( \pm 1 \) yield R-branch, -1 yield P-branch)

**Transitions between electronic states. Wavelengths in visible or UV.**

a. Analogous with the situation in atoms, selection rules can be stated for electronic transitions in molecules, utilizing the total electron angular momentum and spin.
b. \( \Delta v = 0, \pm 1, \pm 2, \pm 3, ... \)
c. \( \Delta \ell = 0, \pm 1 \) (\( \Delta \ell = 0 \) is called the Q-branch)

\( \Delta \ell = 0 \) is forbidden in a pure rotational-vibrational transition, i.e. within an electronic state but permitted in conjunction with electronic transitions since the total angular momentum of the molecule might be different in the lower and upper electronic state respectively.
Planck's radiation

\[ \rho(f) \, df = \frac{8 \pi hf^3}{c^3} \cdot \frac{1}{e^{hf/kT} - 1} \, df \]

Wien's displacement

\[ \lambda_{\text{max}} T = 2.898 \cdot 10^{-3} \text{K} \cdot \text{m} \]

Stefan–Boltzmann's

\[ P = A \sigma (T^4 - T_0^4), \quad \sigma = 5.67 \cdot 10^{-8} \text{ W/m}^2\text{K}^4 \]
The Greenhouse Effect.

The black-body radiation from the Sun (5500 °C) and the Earth (18 °C) and the absorption in the atmosphere in different wavelength regions.

- Carbon Dioxide: 76%
- Methane: 16%
- Nitrous Oxide: 6%
- HFC, PFC, SF6: 2%

NOTES

CO2 accounts for about 76 percent of total greenhouse gas emissions. Methane, primarily from agriculture, contributes 16 percent of greenhouse gas emissions and nitrous oxide, mostly from industry and agriculture, contributes 6 percent to global emissions. All figures here are expressed in CO2-equivalents.

SOURCE

Global Average Temperature and Carbon Dioxide Concentrations, 1880 - 2006

Data Source CO2 (Siple Ice Cores): http://cdiac.esd.ornl.gov/ftp/trends/co2/siple2.013

Graphic Design: Michael Ernst, The Woods Hole Research Center
Global Greenhouse Gas Emissions by Economic Sector

Source: IPCC (2014); based on global emissions from 2010. Details about the sources included in these estimates can be found in the Contribution of Working Group III to the Fifth Assessment Report of the Intergovernmental Panel on Climate Change.