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Subject	Chemistry
Paper No and Title	8/ Physical Spectroscopy
Module No and Title	21/ Comparison with experimental spectra. The potential energy function for a chemical bond, Anharmonicity, Morse potential energy diagram. Modification of selection rules. Overtones and hot bands. Dissociation energies.
Module Tag	CHE_P8_M21

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1. Learning Outcomes

After going through this module, you should be able to:
   (a) Interpret experimental infrared spectra.
   (b) Understand the potential energy function of a real bond.
   (c) Understand the concept of anharmonicity and the modified selection rules.
   (d) Understand the meaning of fundamentals and overtones.
   (e) Calculate dissociation energies of molecules.

2. Introduction

The vibrational spectrum of a heteronuclear diatomic molecule behaving as a harmonic oscillator is expected to consist of a single line, known as the fundamental. However, besides this very intense line, lines decreasing in intensity are observed at slightly less than double, triple of the fundamental transition in real spectra. This means that the spacing does not remain constant and also that the selection rules allow larger changes in the vibrational quantum number than the ±1 allowed by the harmonic oscillator selection rules. This implies that the harmonic oscillator model is not able to satisfactorily explain the observed spectra. In this module, we explore the reason for the same and modify our model.

3. The Potential Energy Function for a Chemical Bond

The harmonic potential is based on Hooke's law, leading to a parabolic potential energy function. According to this potential energy function, the bond can be infinitely stretched or compressed without breaking it. Real bonds, though elastic, are not so homogeneous as to obey Hooke's law (i.e. exactly simple harmonic motion laws), e.g. during stretching there comes a point at which the bond breaks and the molecule will then dissociate into atoms. Thus, although for small compressions and extensions the bond may be taken as perfectly elastic, for larger amplitudes, say more than 10% of the bond length, much more complicated behaviour must be assumed.

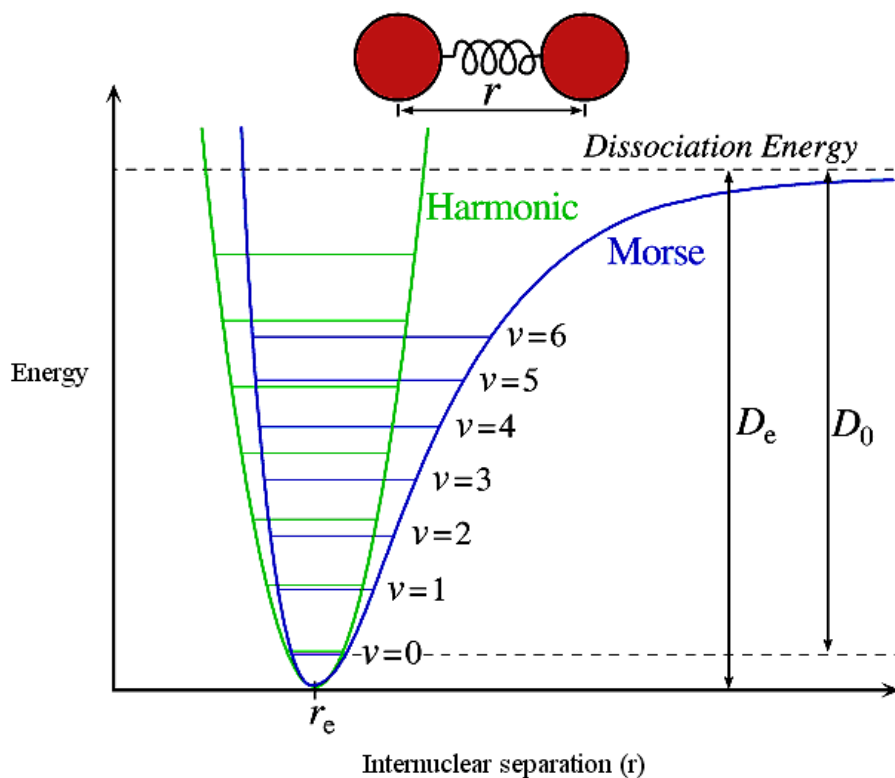Real molecules behave as anharmonic oscillators.

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3.1 The Anharmonic Oscillator

According to the harmonic oscillator model, if a molecule is disturbed from its equilibrium bond length, its energy rises, and this rise is the same whether the bond is compressed or elongated. However, stretching weakens the bond, decreasing the force constant and hence restoring the force. On the other hand, compression of the bond brings the positively charged nuclei closer. This increases the repulsion more than what a harmonic potential would have predicted. The net result is that the potential is more steep to low down the internuclear separations and more shallow at high internuclear separations (Fig. 1).

Figure 1: The Morse potential (blue) and harmonic oscillator potential (green). Unlike the energy levels of the harmonic oscillator potential, which are evenly spaced by hv, the Morse potential level spacing decreases as the energy approaches the dissociation energy. The dissociation energy D_e is larger than the true energy required for dissociation (D_0) due to the zero point energy of the lowest ($v = 0$) vibrational level. (Source: http://en.wikipedia.org/wiki/Image:Morse-potential.png)

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The potential energy of the anharmonic system is given by the following empirical formula (Morse potential):

$$V = D_e[1 - \exp(a(r - r_e))]^2 \qquad (1)$$

where a constant for a particular molecule and D_e is the dissociation energy.

When equation (1) is used for the potential, the Schrödinger equation yields:

$$G(\upsilon) = (\upsilon + \tfrac{1}{2})\omega_e - (\upsilon + \tfrac{1}{2})^2 \omega_e \chi_e \qquad (2)$$

$(\upsilon = 0, 1, 2, \text{í} \ )$

where χ_e is a small constant, known as the anharmonicity constant, and ω is referred to as the equilibrium frequency of the anharmonic system.

3.2 Spectrum of an Anharmonic Oscillator

The selection rules for the anharmonic oscillator are also modified as:

$$\Delta \upsilon = \pm 1, \pm 2, \pm 3, ... \qquad (3)$$

There is a possibility of larger jumps in addition to what is observed in the harmonic oscillator. The larger jumps occur with decreasing probability with only the first three values of ê υ (±1, ±2, ±3), showing observable intensity. These jumps are known as the fundamental, first and second overtone, respectively.

The next aspect to consider is the population. For rotational spectroscopy, several rotational energy levels are occupied, since the spacing between the energy levels is small. Applying the Boltzmann formula at room temperature (300 K) and considering IR radiation of frequency 3×10^{13} s^{-1}, one notes that

$$\frac{N_{\upsilon=1}}{N_{\upsilon=0}} = \exp(-\frac{6.626 \times 10^{-34} \times 3 \times 10^{13}}{1.381 \times 10^{-23} \times 300}) = 0.008$$

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Thus, the population of the $v = 1$ level is less than 1% of the ground state population. Thus, to a very good approximation we may ignore all transitions originating at the $v \times 2$ levels, and restrict ourselves to the following four transitions in absorption spectroscopy:

1. *The fundamental transition*

This refers to the transition $v = 0 \quad 1$, i.e. ê $v = 1$ transition. The wavenumber of the transition is

$$\tilde{\nu} = G(1) - G(0)$$

Substituting equation (2) in the above expression, we find that

$$\begin{aligned}\tilde{\nu} &= [(3/2)\omega_e - (9/4)\omega_e\chi_e] - [(1/2)\omega_e - (1/4)\omega_e\chi_e] \\ &= \omega_e(1 - 2\chi_e)\end{aligned} \tag{4}$$

2. *The first overtone transition*

This refers to the $v = 0 \quad 2$, i.e. ê $v = 2$ transition.

$$\tilde{\nu} = 2\omega_e(1 - 3\chi_e) \tag{5}$$

3. *The second overtone transition*

This refers to the $v = 0 \quad 3$, i.e. ê $v = 3$ transition.

$$\tilde{\nu} = 3\omega_e(1 - 4\chi_e) \tag{6}$$

4. *The hot band transition*

This refers to the $v = 1 \quad 2$, i.e. ê $v = 1$ transition.

$$\tilde{\nu} = \omega_e(1 - 4\chi_e) \tag{7}$$

This transition is so called because increasing the temperature increases its intensity as more molecules go into the $v = 1$ level on raising the temperature. Also, molecules with lower

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vibrational frequencies are more likely to exhibit hot bands, since for them the population of the higher vibrational levels is higher.

Example 1

The spectrum of HCl shows a very intense absorption line at 2886 cm^{-1}, a weaker one at 5668 cm^{-1} and a very weak one at 8347 cm^{-1}. Calculate the equilibrium frequency of the molecule and the anharmonicity constant.

Solution

One has to solve any two of the following equations:

$$\omega_e(1 - 2\chi_e) = 2886$$

$$2\omega_e(1 - 3\chi_e) = 5668$$

$$3\omega_e(1 - 4\chi_e) = 8347$$

Using the first two, it can be shown that $\omega_e = 2990$ cm^{-1} and $\chi_e = 0.0174$.

The force constant is obtained from

$$k = 4\pi^2 \omega_e^2 c^2 \mu = 516 \text{ N m}^{-1}$$

3.3 Dissociation Energies

The decrease in spacing of the energy levels with increasing vibrational quantum number implies that there will come a time when it decreases to zero, the bond breaks and the molecule dissociates.

Equation (2) allows us to compute the spacing between adjacent levels as

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$$\Delta\varepsilon = G(\upsilon+1) - G(\upsilon)$$
$$= \left((\upsilon+\tfrac{3}{2})\omega_e - (\upsilon+\tfrac{3}{2})^2\,\omega_e\chi_e\right) - \left((\upsilon+\tfrac{1}{2})\omega_e - (\upsilon+\tfrac{1}{2})^2\,\omega_e\chi_e\right) \qquad (8)$$
$$= \omega_e - 2(\upsilon+1)\chi_e\omega_e$$

The maximum value of υ is therefore the value at which the spacing becomes zero. Substituting in equation (8), we obtain $\upsilon_{max} = 1/(2_e) -1$. For the HCl spectrum of Example 1, substitution of the values gives $\upsilon_{max} = 27.74$. Since we are looking for the maximum value of υ, 27.74 represents the upper limit and υ_{max} is the next lower whole number, i.e. 27. Using equation (2), we obtain

$$G(27) = \left(27+\frac{1}{2}\right)2990 - 0.0174 \times 2990\left(27+\frac{1}{2}\right)^2 = 42890\ \mathrm{cm}^{-1}$$

which is equal to 513 kJ mol^{-1}, compared to the thermochemical value (427.2 kJ mol^{-1}). Note that the calculated value is D_e, the spectroscopic dissociation energy (Fig. 1) and the experimental value is D_0, the chemical dissociation energy, and $D_e = D_0 + \tfrac{1}{2}\,h\nu$. Therefore, the chemical dissociation energy is 41,395 cm^{-1}, equal to 495 kJ mol^{-1}. The large difference between the theoretical and experimental values is due to the fact that, at higher values of the vibrational quantum number, the energy gap decreases much faster than equation (8) predicts.

4. Summary

- The spectrum of a real molecule does not resemble what is predicted by the harmonic oscillator model.
- The Morse potential is a satisfactory representation of the potential energy function of a real molecule.
- For this oscillator, larger quantum jumps are allowed and one sees the fundamental bands, first and second overtones, as well as hot bands.
- Data from these spectra allow one to get an estimate of the dissociation energy.