

Practical Exercises in Physical Chemistry

Advanced Level

Institute of Physical and Theoretical Chemistry, Freie Universität Berlin

14: Absorption spectroscopy of diatomic molecules

I Electron-vibrational excitation

1 Introduction

In the experiment Vibrational Spectra, it was shown that molecules vibrate and that the vibrational energy is quantized. When a diatomic molecule is illuminated with light of suitable wavelength, a transition takes place into an electronically excited state. The molecule vibrates in the electronically excited state, and the vibrational energy is quantized. Accordingly, the transition from the electronic ground state to the electronically excited state may be made into various vibrational states.

Whereas sharp spectral lines are observed in absorption spectra of atoms, the spectra of molecules contain broad absorption bands.

If only vibrational transitions from the vibrational ground state to the next higher vibrational level are considered, the linear harmonic oscillator may be used as a model for the molecule. In this model, the potential energy V obeys Hooke's law. However, if higher vibrational states are included, this law is not valid anymore. If the bonding distance r is reduced to $r < r_0$, the slope of $V(r)$ is steeper than expected according to Hooke's law; if r is increased to $r > r_0$, the slope of $V(r)$ is smaller than predicted by Hooke's law; and, for very large values of r , V is even independent of r (cf. figure 1).

In this case the potential energy function can be described approximately by the Morse-function:

$$V = E_D [1 - e^{-k(r-r_0)}]^2 \quad (1)$$

The constant k is given by:

$$k = \nu_0 \sqrt{\frac{2\pi^2 \mu}{E_D}} \quad (2)$$

E_D is, as shown in Figure 1, the difference between the potential energy at $r = r_0$ and the potential energy of the atoms after dissociation. $\nu_0 = \frac{1}{2\pi} \sqrt{\frac{D}{\mu}}$ is the classical vibrational frequency of a harmonic oscillator with force constant D and reduced mass μ . In the case of small amplitudes ($r - r_0$) is rather small and equation (1) becomes

$$V = \frac{1}{2} D (r - r_0)^2 \quad (3)$$

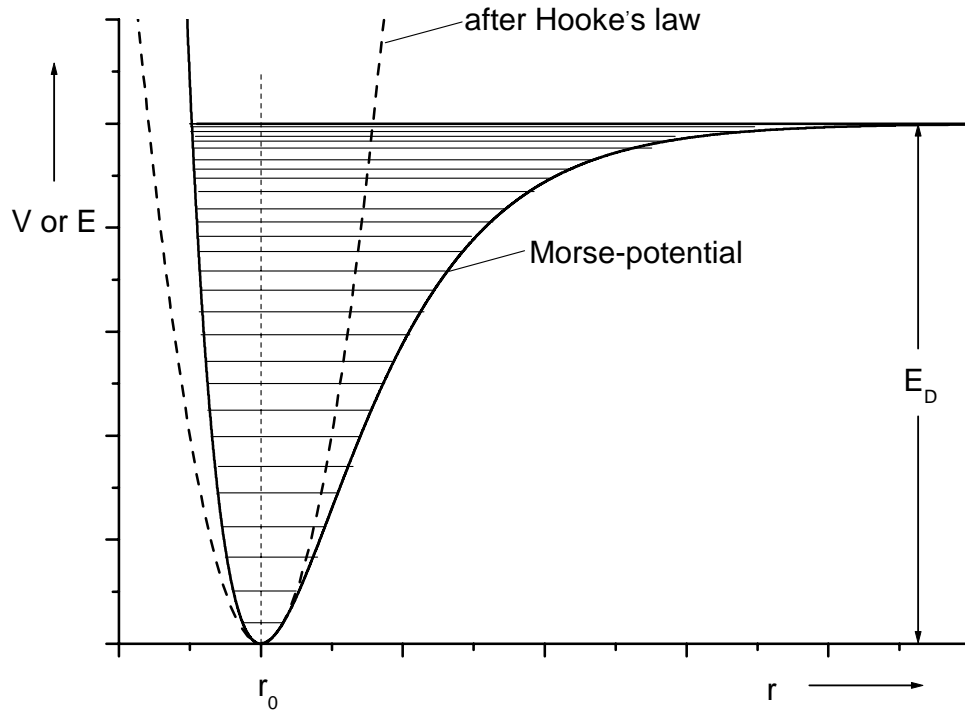


Figure 1: Electronic ground state and electronically excited state of a diatomic molecule

Equation (3) is the parabolic potential curve for the harmonic oscillator.

For the energy values E_n of an anharmonic oscillator in quantum state n , whose potential energy is given by eq. (1), the following expression is obtained by solving the Schrödinger equation:

$$E = h\nu_0 \left[\left(n + \frac{1}{2} \right) - \frac{h\nu_0}{4E_D} \left(n + \frac{1}{2} \right)^2 \right] \quad n = 0, 1, 2, \dots \quad (4)$$

As a result, the difference between two energy levels may be written as:

$$\Delta E = E_{n+1} - E_n = h\nu_0 - \frac{(h\nu_0)^2}{2E_D} - \frac{(h\nu_0)^2}{2E_D}n \quad n = 0, 1, 2, \dots \quad (5)$$

With increasing quantum number n , ΔE_n decreases, and the energy levels move together (figure 2). At a certain quantum number, the molecule splits into atomic components (normal or excited atoms, positive or negative ions) - it dissociates. At first it is assumed that only the lowest vibrational level of the electronic ground state is occupied ($n = 0$). If the molecule is excited with light, the transition can occur into different vibrational states of the electronically excited state (figure 2).

For the vibrational energies E_n^* of the electronically excited state, the following equation is valid:

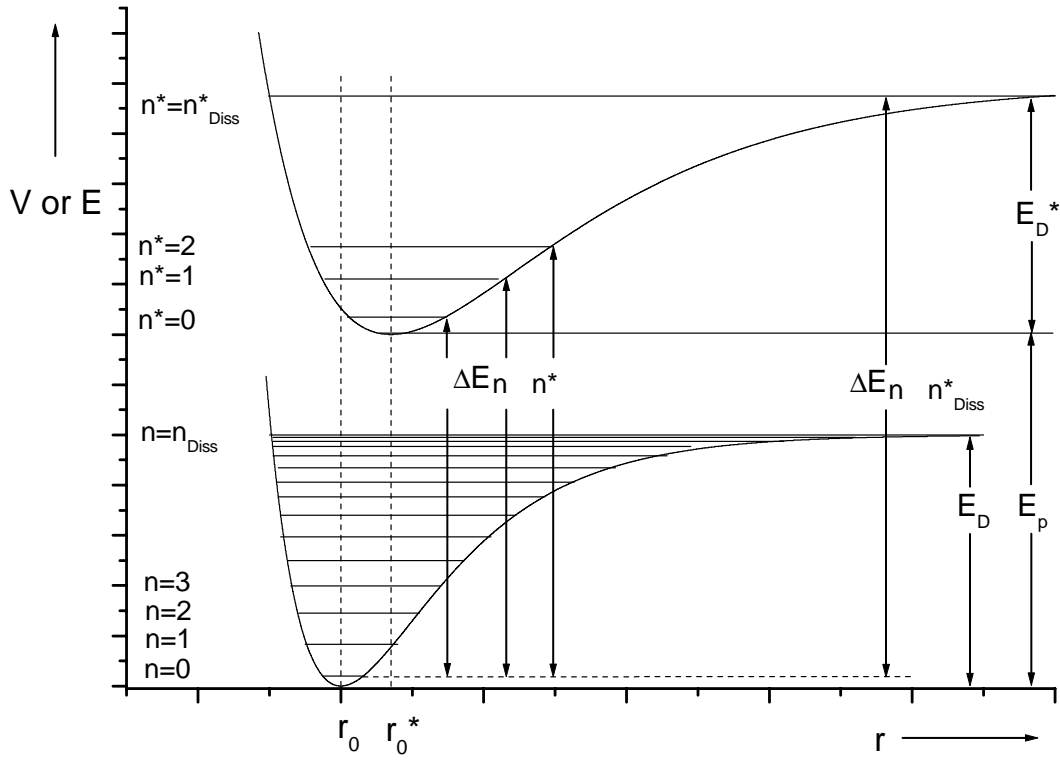


Figure 2: Potential energy V or total energy E of a diatomic molecule.
 r_0 : equilibrium distance, E_D : dissociation energy

$$E_{n^*} = h\nu_0^* \left[\left(n^* + \frac{1}{2} \right) - \frac{h\nu_0^*}{4E_D^*} \left(n^* + \frac{1}{2} \right)^2 \right] \quad (6)$$

If E_p is the energy difference between the minima of the potential energy functions of the electronic ground state and the electronically excited state, the excitation energy ΔE_{0-n^*} from the lowest vibrational level ($n = 0$) of the electronic ground state into vibrational levels ($n^* = 0, 1, 2, \dots$) of the electronically excited state can be written referring to eq. (4) and (6) as:

$$\begin{aligned} \Delta E_{\sigma-n^*} &= E_p + E_{n^*} - E_{n=0} = \\ &= E_p + h\nu_0^* \left[\left(n^* + \frac{1}{2} \right) - \frac{h\nu_0^*}{4E_D^*} \left(n^* + \frac{1}{2} \right)^2 \right] - h\nu_0 \left[\frac{1}{2} - \frac{h\nu_0}{16E_D} \right] \end{aligned} \quad (7)$$

$n^* = 0, 1, 2, \dots$
 $n = 0$

Other excitation energies ($\Delta E_{1-n^*}, \Delta E_{2-n^*}, \dots$) must also be considered, if higher vibrational levels are occupied in the electronic ground state.

2 Exercises

1. You are asked to show that equation 1 corresponds to the graph in figure 1 and that, for small amplitudes, equation 3 is valid.
2. Give reasons why r_0^* is generally greater than r_0 . Are you familiar with any cases in which $r_0^* < r_0$?
3. Record the absorption spectra (400 nm – 800 nm) of I₂-vapor (obtained by heating solid iodine to 50 °C).
4. Identify the band systems (same lower state n , various upper states n^*) associated with transitions starting from $n = 0$ and $n = 1$, and calculate the corresponding values of ΔE_{0-n^*} and ΔE_{1-n^*} (cf. figure 2).
5. Calculate approximately the resultant values of ν_0 , D and E_D , and draw the graph for the potential energy function (equations 1 and 2, figure 1) of I₂.
6. Using the Maxwell-Boltzmann distribution law, calculate the population number for $n = 0$ and $n = 1$, and compare with the intensities of the spectral bands in the absorption spectra.
7. Compare the obtained values for ν_0 , D and E_D with data from the literature. Explain deviations.

The assignment of the absorption bands to the different band systems can be done by choosing the absorption band at the highest wavelength in the spectra and measuring the distance between adjacent maxima. If the bands belong to the same band system, the distance must decrease continuously with progression towards smaller wavelengths.

3 Implementation

To exercise 4

The energy difference A_{n^*} of two neighboring energy levels may be obtained by using equation 7:

$$A_{n^*} = \Delta E_{n-(n^*+1)} - \Delta E_{n-n^*} = h\nu_0^* - \frac{(h\nu_0^*)^2}{2E_D^*} - \frac{(h\nu_0^*)^2}{2E_D^*}n^* \quad n^* = 0, 1, 2, \dots \quad (8)$$

A_{n^*} may be taken from the experimental spectra (distance of two adjacent maxima). If A_{n^*} is plotted as a function of n^* , a straight line with the slope $\frac{(h\nu_0^*)^2}{2E_D^*}$ is expected. The point of intersection of this line with the abscissa corresponds to n_{Diss}^* .

The excitation energy, $\Delta E_{0-n_{Diss}^*}$, which is necessary for dissociation from the electronic ground state (cf. figure 2) should be found from the experimental spectra. For this purpose the energy

$\Delta E_{0-n_a^*}$ for an arbitrary quantum number n_a^* is taken from the spectra. $\Delta E_{0-n_{Diss}^*}$ may now be expressed as:

$$\Delta E_{0-n_{Diss}^*} = \Delta E_{0-n_a^*} + \sum_{n_a^*}^{n_{Diss}^*} A_{n^*} \quad (9)$$

According to eq. 8 the sum members A_{n^*} get smaller relative to n^* and so the sum in equation 9 is as big as the $(n_{Diss}^* - n_a^*)$ fold of the average distance \bar{A}_{n^*} of two bands. \bar{A}_{n^*} is given by:

$$\bar{A}_{n^*} = \frac{1}{2} (A_{n_a^*} + A_{n_{Diss}^*}) = \frac{1}{2} A_{n^*} \quad (10)$$

Respectively equation 9 becomes:

$$\Delta E_{0-n_{Diss}^*} = \Delta E_{0-n_a^*} + \frac{1}{2} (n_{Diss}^* - n_a^*) A_{n^*} \quad (11)$$

To solve equation 11 only the difference $(n_{Diss}^* - n_a^*)$ is required. Therefore, it is not necessary to know the absolute values of the quantum numbers of the single bands. This is very convenient since, according to the Frank- Condon Principle for transitions, different probabilities exist and so often the bands associated with transitions to lower vibrational levels of the electronically excited state (e.g. $n^* = 0, n^* = 1$) are missing.

To exercise 5

In case of heavy molecules (e.g. I_2) higher vibrational states than $n = 0$ (e.g. $n = 1, n = 2$) are noticeably occupied at room temperature. As a result, additional band systems are expected. For these band systems, the energies $\Delta E_{1-n_{Diss}^*}, \Delta E_{2-n_{Diss}^*}, \dots$ may also be calculated referring to the procedure described above. Because these energies differ in the vibrational level the transition starts from, the distances of the vibrational states and therefore ν_0, D and E_D can be obtained. According to equation 5 the difference of these energies may be expressed as:

$$\Delta E_{0-n_{Diss}^*} - \Delta E_{1-n_{Diss}^*} = h\nu_0 \left[1 - \frac{h\nu_0}{2E_D} \right] \quad (12)$$

...

With the approximation $h\nu_0/E_D \ll 1$, the vibrational frequency ν_0 and the force constant D of the bonding may be determined on basis of equation 12. In principal, it is also possible to obtain the dissociation energy E_D through a combination of both equations in eq. 12. For that purpose, it would be essential to measure the differences in eq. 12 very precisely. In order to achieve such precision, a spectrometer with an extraordinarily good resolution (better than 0.2 nm) would be advisable. In determining E_D for a molecule consisting of two atoms, it is assumed that after dissociation of an excited-state molecule, one of the two atoms is in the electronically excited

state the other atom is in its electronic ground state. Instead of excitation of the molecule it is also possible that the molecule dissociates from the electronic ground state and subsequently one atom is electronically excited (excitation energy ΔE_{atom}). It follows:

$$E_D = \Delta E_{0-n_{Diss}^*} + h\nu_0 \left[\frac{1}{2} - \frac{h\nu_0}{16E_D} \right] - \Delta E_{atom} \quad (13)$$

For an iodine-atom, $\Delta E_{atom} = 1.52 \cdot 10^{-12}$ erg is obtained from the atomic absorption spectra. Provided $h\nu_0/E_D \ll 1$, E_D may be calculated with equation 13. Further, it may be examined whether the assumption that $h\nu_0/E_D \ll 1$ is justified.

References

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- [3] HOLLENBERG, J. L.: Energy States of Molecules. *Journal of Chemical Education* 47 (1970), S. 2–14