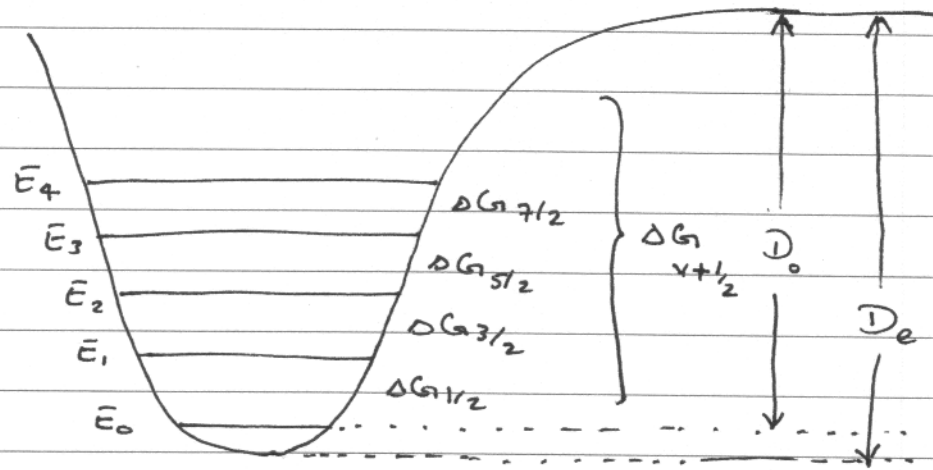


Dissociation Energies from Spectroscopic Data



For diatomic molecules, D_0 is given by:

$$D_0 = \sum_v \Delta G_{v+1/2}$$

A plot of $\Delta G_{v+1/2}$ vs. v (or $v+1/2$) is known as

Birge-Sponer plot, and the area under the curve is the dissociation energy (D_0).

Two possibilities:

- ① All the vibrational levels are known, the application of the above equation gives an accurate value of dissociation energy.
- ② Not all vibrational levels are observed experimentally. An extrapolation from the last few observed levels up to the unobserved dissociation limit (v_D) is needed.

Some uncertainty in D_0 results here.

v_D is known also as the effective vibrational quantum number and can be non-integer. It corresponds to the intercept of the Birge-Sponer curve with the x-axis.

If the anharmonicity is considered here:

$$G(v) = \omega_e(v + 1/2) - \omega_e x_e(v + 1/2)^2$$

Then

$$\Delta G_{v+1/2} = \omega_e - 2\omega_e x_e - 2\omega_e x_e v$$

Here, the Birge-Sponer plot becomes linear ($\Delta G_{v+1/2}$ vs. v) over the entire range of v . D_e value for the Morse potential can be deduced here as:

$$D_e = \frac{\omega_e^2}{4\omega_e x_e}$$

D_e : equilibrium dissociation energy.

ω_e : harmonic frequency

$\omega_e x_e$: anharmonicity constant.

Vibration-Rotation Spectra (Diatomic)

Molecules vibrate and rotate at the same time.

Both rotational and vibrational levels are excited simultaneously.

$$\bar{E}_{\text{tot}} = \bar{E}_{\text{vib}} + \bar{E}_{\text{rot}}$$

$$\bar{E}_{\text{vJ}} = G(v) + F(J)$$

$$= \omega_e \left(v + \frac{1}{2}\right) - \omega_e x_e \left(v + \frac{1}{2}\right)^2 + \dots$$

$$+ B_v J(J+1) - D_v J^2(J+1)^2 + \dots$$

In vibration-rotation spectroscopy, a transition takes place between the stacks of rotational energy levels associated with two different vibrational energy levels.

Vibration-rotation transitions can be seen only in gaseous phase at low pressures.

Selection Rules

	<u>vibrational</u>	<u>Rotational</u>
Infrared	$\Delta v = 1$	$\Delta J = \pm 1$
Raman	$\Delta v = 1$	$\Delta J = 0, \pm 2$

Band Labels :

$$\Delta J = -3 \quad -2 \quad -1 \quad 0 \quad +1 \quad +2 \quad +3$$

"Branch" N O P Q R S T

N and T branches are too rare.

Q branch corresponds to $\Delta J = 0$ which is not allowed always.

The first line of the Q-branch (the $J' = 0 - J'' = 0$ transition) is known as the band center.

Most of the linear molecules follow the selection rule $\Delta J \neq 0$ for the infrared spectra

For the Raman spectra $\Delta J = 0$ transitions are allowed and thus can be observed as Q branch at the band center.

Ignoring the effect of centrifugal distortion, the line positions for R and P branches are given by:

$$\nu_R(\nu', J+1 \leftarrow \nu'', J) = \nu_0 + (B' + B'')J + 1 + (B' - B'')(J+1)^2$$

$$\nu_P(\nu', J-1 \leftarrow \nu'', J) = \nu_0 - (B' + B'')J + 1 + (B' - B'')(J+1)^2$$

where $\nu_0 = G(\nu') - G(\nu'')$

↑

band origin.

ν_R and ν_P expressions can be combined:

$$\nu = \nu_0 + (B' + B'')m + (B' - B'')m^2$$

$m = J+1$ for the R-branch.

$m = -J$ for the P-branch.

Note that when $B' = B''$, the separation between bands is $2B$.

IN INFRARED SPECTRA (IGNORING CENTRIFUGAL DISTORTION AND DIFFERENCE BETWEEN ROTATIONAL CONSTANTS B_0 AND B_1) THE SEPARATION BETWEEN BANDS IS $2\bar{B}$, THE CENTER GAP IS $4\bar{B}$.

$R \} \Delta J = +1$
 $P \} \Delta J = -1$

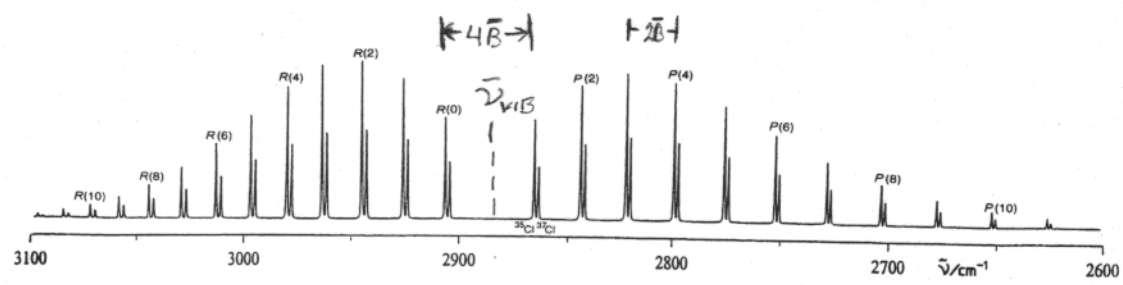


Figure 5.9 The $\nu = 1 - 0$ infrared spectrum of the $^1\text{H}^{35}\text{Cl}$ and $^1\text{H}^{37}\text{Cl}$ molecules showing the P- and R-branch rotational structure

$\bar{\nu}_{\text{vib}}$ IS DIFFERENT FOR H^{35}Cl (MORE INTENSE) ^{75%} AND H^{37}Cl ^(25%) DUE TO SLIGHT DIFFERENCE IN μ .

$$\mu_{\text{H}^{35}\text{Cl}} = \frac{35}{36} = 0.972 \text{ au} \quad \mu_{\text{H}^{37}\text{Cl}} = \frac{37}{38} = 0.974$$

For CO molecule:

$S \} \Delta J = +2$
 $O \} \Delta J = 0$
 $Q \} \Delta J = 0$

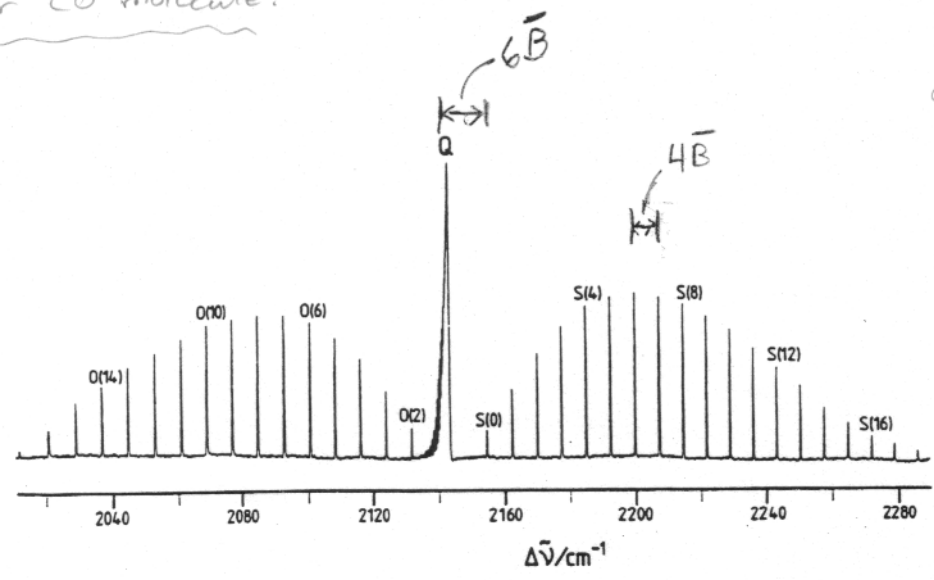


Figure 5.10 The $\nu = 1-0$ Stokes Raman spectrum of the CO molecule showing the O-, Q- and S-branch rotational structure