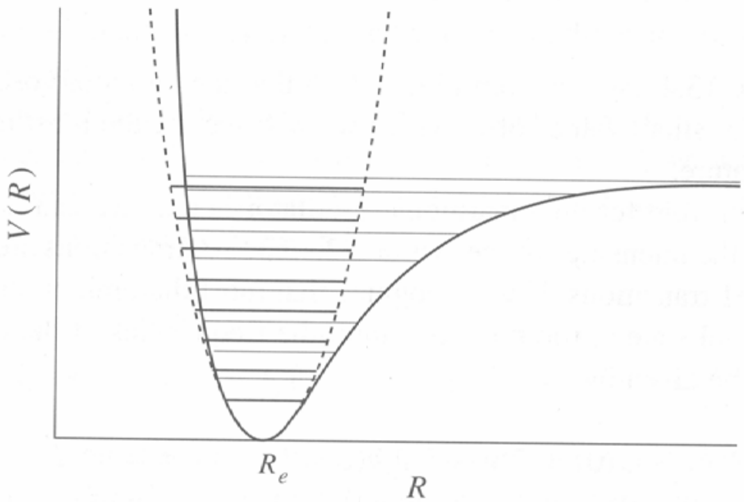
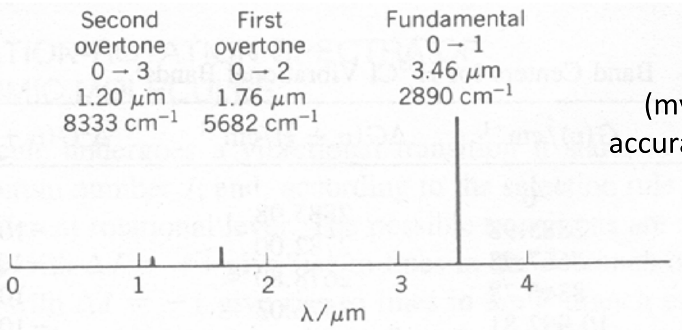


FIGURE 13.4
The energy states of a harmonic oscillator (dashed line) and an anharmonic oscillator superimposed on a harmonic-oscillator potential and a more realistic internuclear potential. (such as the Morse potential)

Donald A. McQuarrie and John D. Simon, *Physical Chemistry*: *A Molecular Approach*; University Science Books: Sausalito, CA; 1997



(my data are more accurate than Alberty's)

Fig. 15.4 Vibrational absorption spectrum of HCl. The relative intensities of the lines fall off five times as fast as indicated.

Robert A. Albert, *Physical Chemistry*, 7th ed.; John Wiley and Sons: New York; 1987

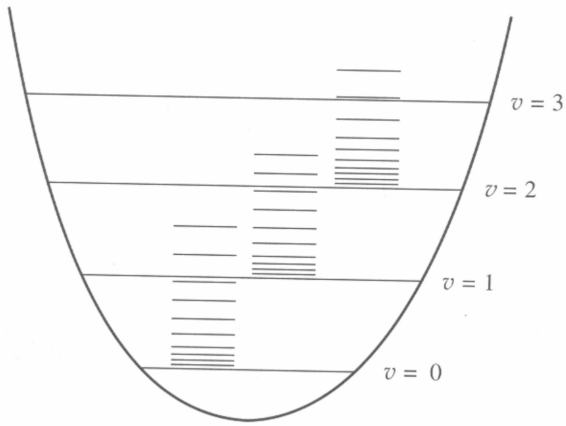


FIGURE 13.1
An energy diagram showing the rotational levels associated with each vibrational state for a diatomic molecule.

Donald A. McQuarrie and John D. Simon, *Physical Chemistry*: *A Molecular Approach*; University Science Books: Sausalito, CA; 1997

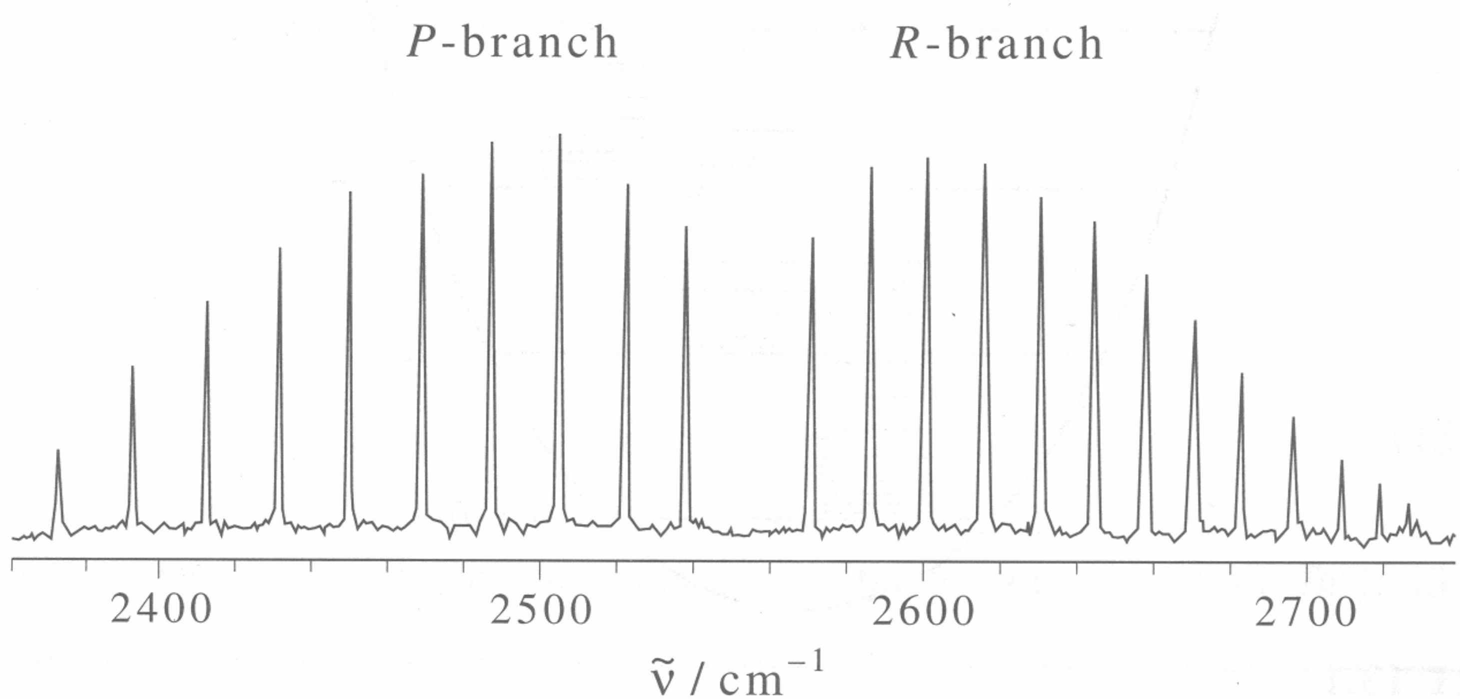


FIGURE 13.2
The rotational-vibrational spectrum of the $0 \rightarrow 1$ vibrational transition of HBr(g). The *R* branch and the *P* branch are indicated in the figure.

Donald A. McQuarrie and John D. Simon, *Physical Chemistry*: *A Molecular Approach*; University Science Books: Sausalito, CA; 1997

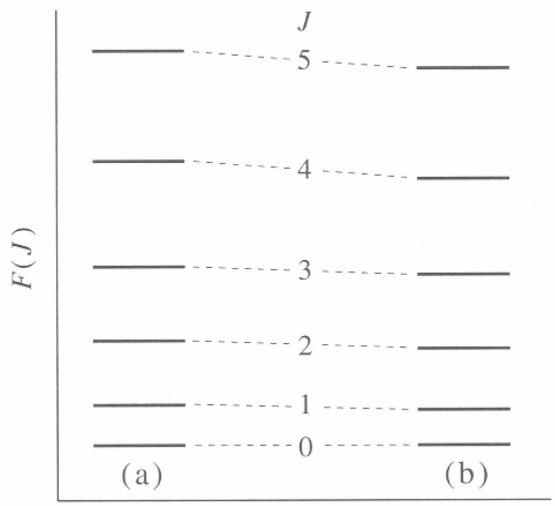


FIGURE 13.3
The rotational energy levels of (a) a rigid rotator and (b) a nonrigid rotator.

Donald A. McQuarrie and John D. Simon, *Physical Chemistry*: *A Molecular Approach*; University Science Books: Sausalito, CA; 1997

From Experiment 3 (FTIR Spectrum of HCl)

If we use Eqns. [1] and [2] to determine the energies of the generic transitions $R(J-1)$ and $P(J)$, we obtain the general expressions

$$R(J-1) = F'(J) - F''(J-1)$$

$$= \tilde{\upsilon}_0 + (B' + B'')J + (B' - B'' - D' + D'')J^2 + (-2D' - 2D'')J^3 + (-D' + D'')J^4$$

$$P(J) = F'(J-1) - F''(J)$$

$$= \tilde{\upsilon}_0 + (-B' - B'')J + (B' - B'' - D' + D'')J^2 + (2D' + 2D'')J^3 + (-D' + D'')J^4$$

From the form of the above two equations, it is possible to fit an identical equation to both branches, namely

$$\tilde{\upsilon} = \tilde{\upsilon}_0 + (B' + B'')m + (B' - B'' - D' + D'')m^2 + (-2D' - 2D'')m^3 + (-D' + D'')m^4 \qquad [3]$$

where m is an integer called the *line number* that takes the values 1, 2, 3, ... for the $R(J)$ branch (that is, $m = J + 1$) and the values –1, –2, –3, ... for the $P(J)$ branch (that is, $m = -J$).