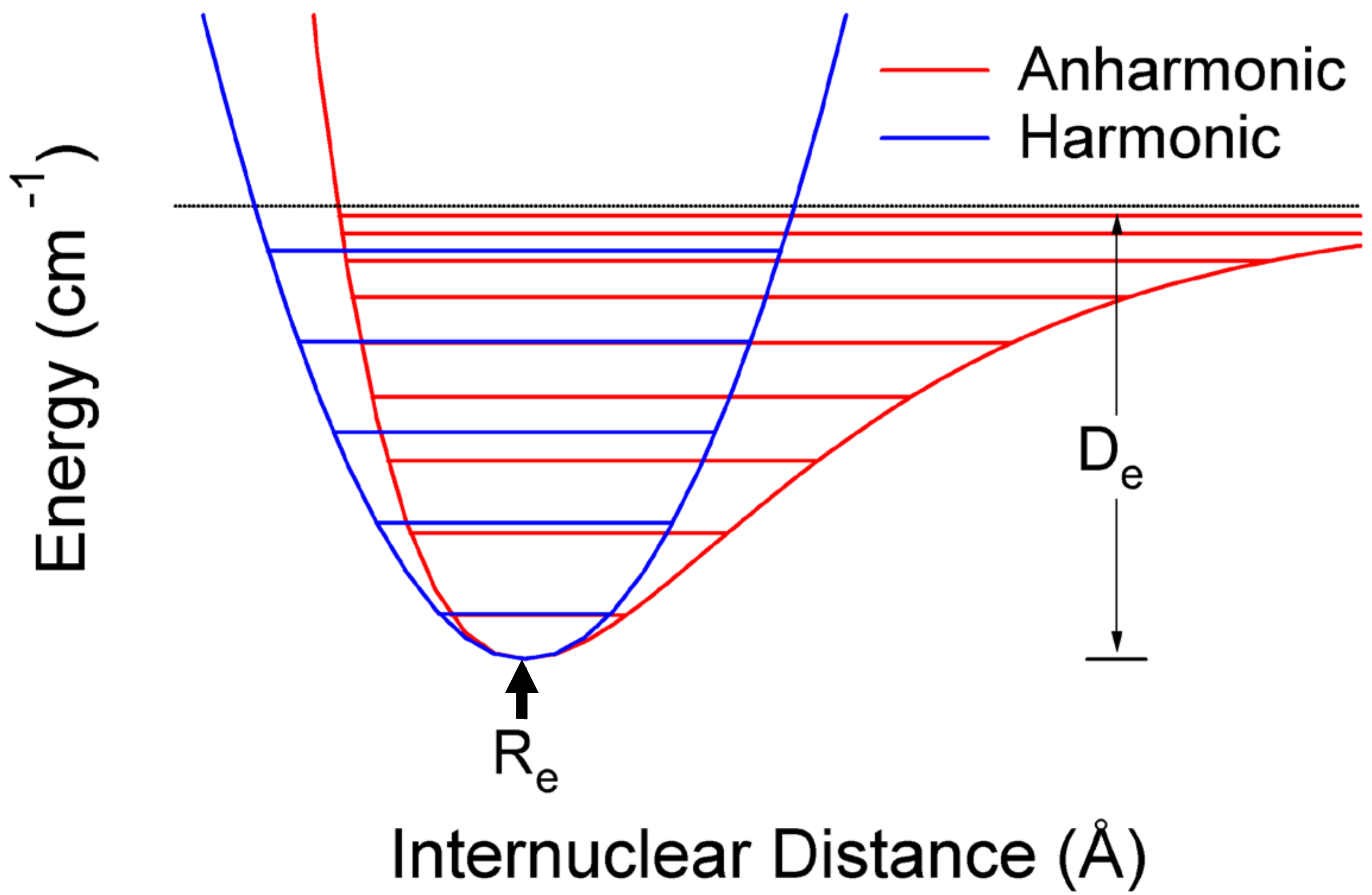
Comparison of harmonic and anharmonic potentials

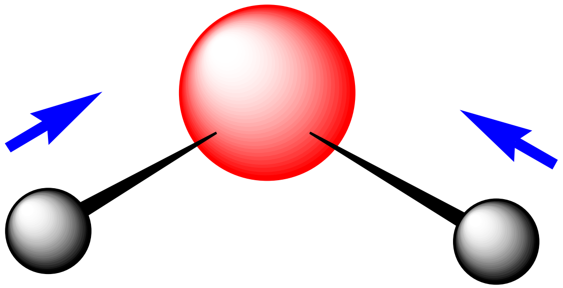


Overtones of water

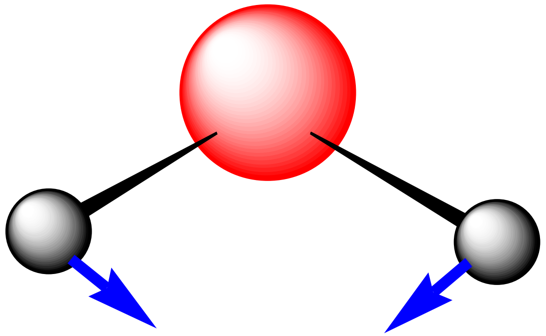
Even in water vapor $\nu_1 \approx \nu_3$, but symmetries are different, $\Gamma_1 \neq \Gamma_3$. However, the third overtone of mode 1 has the same symmetry as the combination band

$\Gamma_1 \Gamma_1 \Gamma_1 = \Gamma_1 \Gamma_3 \Gamma_3$.

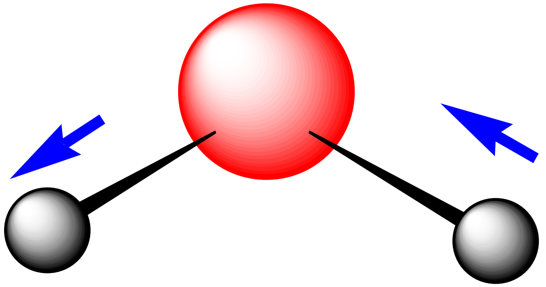
Strong anharmonic coupling leads to strong overtones at 11,032 and 10,613 cm^{-1}. These intense bands give water and ice their blue color.



ν_1 symmetric stretch 3825 cm^{-1}



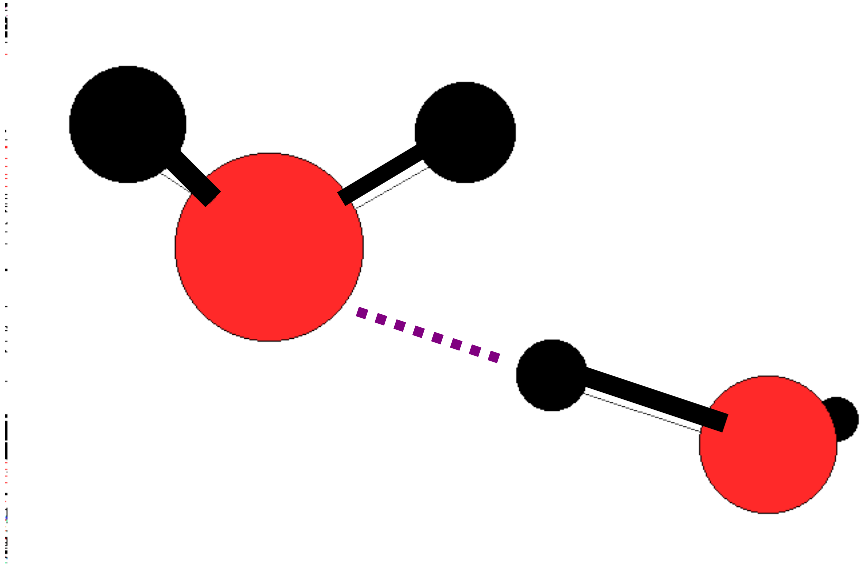
ν_2 bend 1654 cm^{-1}



ν_3 asymmetric stretch 3935 cm^{-1}

Frequency shift due to molecular interactions

Hydrogen bonding lowers O-H force constant and H-O-H bending force constant.



	vapor $\rightarrow$ liquid
ν_1	$3825 \rightarrow 3657$
ν_2	$1654 \rightarrow 1595$
ν_3	$3935 \rightarrow 3756$

Morse potential

The Morse potential function can be used to represent anharmonic surfaces:

$$V(Q) = hc\widetilde{D}_e(1 - e^{-aQ})^2$$

The anharmonic oscillator Schrodinger equation can be solved for the energy, which gives the following transitions:

$$\tilde{E}_v = \left(v + \frac{1}{2}\right)\tilde{\nu}_e + \left(v + \frac{1}{2}\right)^2 x_e\tilde{\nu}_e$$

The value for $\widetilde{D}_e$ is the well depth and x_e is the anharmonicity constant.

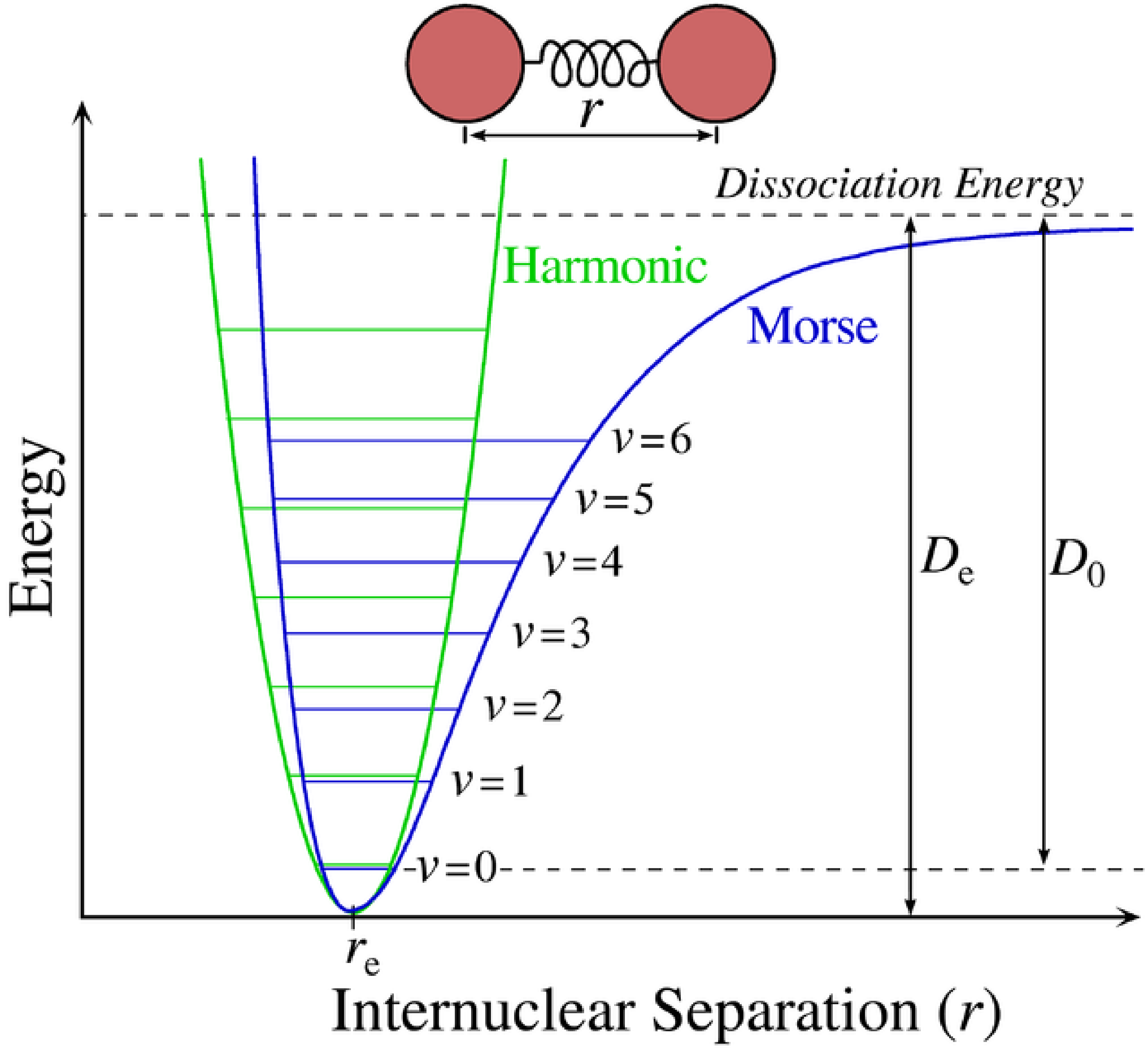
Morse potential

The parameter a in the Morse potential depends on both the vibrational wave number and the well depth.

$$a = 2\pi c\tilde{\nu}_e\sqrt{\frac{\mu}{2\widetilde{D}_e}}$$

From this relationship one can derive the value of the anharmonicity constant in terms of the wave number and the well depth.

$$x_e = \frac{\tilde{\nu}_e}{4\widetilde{D}_e}$$


r
Dissociation Energy
Harmonic
Morse
v=6
v=5
v=4
v=3
v=2
v=1
v=0
D_e
D_0
Energy
r_e
Internuclear Separation (r)