292(3): Some Examples of Spectra for the Calculation of Evans / Manri Shifts.

In general the shifts are given by:

$$\frac{\omega_1^4}{\left(\exp\left(\frac{\hbar\omega_1}{kT}\right)-1\right)} = \frac{\omega^4}{\left(\exp\left(\frac{\hbar\omega}{kT}\right)-1\right)} \exp(-\alpha r) \quad -(1)$$

If $\hbar\omega_1 \ll kT$ $-(2)$

and $\hbar\omega \ll kT$ $-(3)$

then:

$$\boxed{\left(\frac{\omega_1}{\omega}\right)^3 = \exp(-\alpha r)} \quad -(4)$$

It is seen that the ratio of refracted frequency ω_1 to incident frequency ω depends directly on the power absorption coefficient α. Some types of spectra are given below from Omnic Operation.

Pure Rotational Envelope.

$$\alpha \propto (2J+1)\exp\left(-\frac{E}{RT}\right) \quad -(5)$$

2) Here:

$$E = hcB\,J(J+1) \quad -(6)$$

Here B is the rotational constant in wavenumber and J the rotational quantum number

Dipole Induced Dipole Absorption

$$\alpha(\omega) \propto \left(1 - \exp\left(-\frac{2B(J+1)hc}{kT}\right)\right) 2B(J+1) \exp\left(-\frac{BJ(J+1)hc}{kT}\right) \times \left(4\alpha_0^2 (J+1) + \frac{8}{3}\delta^2 \frac{(J+1)^2(J+2)}{2J+3}\right)$$

Here $\alpha_0 = \frac{1}{3}(\alpha_{\parallel} + 2\alpha_{\perp})$, $\delta = (\alpha_{\parallel} - \alpha_{\perp})$. $-(7)$

Hexadecapole Induced Dipole Absorption

$$\alpha(\omega) \propto 4B(2J+5)\left(1 - \exp\left(-\frac{4B(2J+5)hc}{kT}\right)\right) \cdot \exp\left(-\frac{BJ(J+1)hc}{kT}\right)\left[\frac{175(J+1)(J+2)(J+3)(J+4)}{2(2J+3)(2J+5)(2J+7)}\alpha_0^2 + \frac{875}{12}\delta^2 \left(\frac{(J+1)(J+2)}{(2J+3)}\right)^2 \frac{(J+3)(J+4)}{(2J+5)(2J+7)}\right] \quad -(8)$$

Here:

$$\omega = 2\pi\bar{\nu}c = 2\pi f \quad -(9)$$

and B is expressed in units of wavenumber $\bar{\nu}$ in

cm^{-1}. So:

$$f = \bar{\nu} c \quad -(10)$$

The hexadecapole moment of oxygen has measured in 0011.

The easiest type of spectrum to evaluate is the pure rotational spectrum (5), where:

$$J = 0, 1, 2, \ldots$$

and

$$\Delta J = 1 \quad -(11)$$

The spectrum is a series of lines with an envelope given by the Boltzmann factor $\exp(-E/(kT))$ and the degeneracy $(2J+1)$.

For each absorption line there is an Evans/Maris shift.

Therefore an incident beam of incident frequency ω enters a sample cell filled with gas. The beam is refracted and absorbed, and its frequency is changed by an Evans Maris shift according to eqn. (1), approximated by eqn. (2). For dipole induced dipole absorption the selection rule is again $\Delta J = 1$, but for hexadecapole dipole absorption it is $\Delta J = 4$ (00'11).
