

A DEEPER LOOK 6 Vibrational selection rules

As explained in *A deeper look 5*, the starting point for the calculation of selection rules is the expression for the transition dipole moment between the initial state i and the final state f is (Topic 11A)

$$\mu_{fi} = \int \psi_f^* \hat{\mu} \psi_i d\tau$$

where $\hat{\mu} = -e\mathbf{r}$ is the electric dipole moment operator.

(a) Pure vibrational spectra

In this case, the calculation depends on noting how the dipole moment changes with displacement from equilibrium.

Step 1 Express how the dipole moment varies with the displacement

The electric dipole moment operator depends on the location of all the electrons and all the nuclei in the molecule, so it varies as the internuclear separation changes. The variation can be written as

$$\hat{\mu} = \hat{\mu}_0 + \left(\frac{d\hat{\mu}}{dx} \right)_0 x + \dots$$

where $\hat{\mu}_0$ is the electric dipole moment operator when the nuclei have their equilibrium separation.

Step 2 Express the transition dipole moment in terms of the displacement

It then follows that, with $f \neq i$ and keeping only the term linear in the small displacement x ,

$$\mu_{fi} = \int_{-\infty}^{\infty} \psi_f^* \hat{\mu} \psi_i dx = \mu_0 \int_{-\infty}^{\infty} \psi_f^* \psi_i dx + \left(\frac{d\mu}{dx} \right)_0 \int_{-\infty}^{\infty} \psi_f^* x \psi_i dx$$

The term multiplying μ_0 is zero because the states with different values of ν are orthogonal. It follows that the transition dipole moment is

$$\mu_{fi} = \left(\frac{d\mu}{dx} \right)_0 \int_{-\infty}^{\infty} \psi_f^* x \psi_i dx$$

The term $(d\mu/dx)_0$ is zero unless the dipole moment varies with displacement: this is the gross selection rule for infrared spectroscopy.

Step 3 Analyse the integral

The integral is evaluated by writing the wavefunctions in terms of the Hermite polynomials given in Topic 7E and then using their properties listed in Table 7E.1. The polynomials are written in terms of the variable y , where

$x = \alpha y$ and $\alpha = (\hbar^2/m_{\text{eff}}k_f)^{1/4}$ (this is eqn 7E.7 of Topic 7E), to give

$$\begin{aligned} \int_{-\infty}^{\infty} \psi_{v_f}^* \psi_{v_i} dx &= N_{v_f} N_{v_i} \int_{-\infty}^{\infty} H_{v_f} x H_{v_i} e^{-y^2} dy \\ &= \alpha^2 N_{v_f} N_{v_i} \int_{-\infty}^{\infty} H_{v_f} y H_{v_i} e^{-y^2} dy \end{aligned}$$

Now use the recursion relation

$$yH_\nu = \nu H_{\nu-1} + \frac{1}{2}H_{\nu+1}$$

and obtain

$$\begin{aligned} \int_{-\infty}^{\infty} \psi_{v_f}^* x \psi_{v_i} dx &= \alpha^2 N_{v_f} N_{v_i} \left\{ v_i \int_{-\infty}^{\infty} H_{v_f} H_{v_i-1} e^{-y^2} dy + \frac{1}{2} \int_{-\infty}^{\infty} H_{v_f} H_{v_i+1} e^{-y^2} dy \right\} \end{aligned}$$

The first integral is zero unless $v_f = v_i - 1$ and the second is zero unless $v_f = v_i + 1$ (Table 7E.1 of the text). It follows that the transition dipole moment is zero unless $\Delta\nu = \pm 1$, which is the specific selection rule for infrared transitions.

(b) Vibrational Raman spectra

The oscillating electric field, $\mathcal{E}(t)$, of the incident electromagnetic radiation induces an electric dipole moment that is proportional to the strength of the field. This induced moment is written $\hat{\mu} = \alpha(x)\mathcal{E}(t)$, where $\alpha(x)$ is the polarizability of the molecule (Topic 11B). The calculation then proceeds as above.

Step 1 Relate the dipole moment of the molecule to its polarizability

The transition dipole moment is

$$\begin{aligned} \mu_{fi} &= \int \psi_f^* \hat{\mu} \psi_i d\tau = \int_{-\infty}^{\infty} \psi_f^* \alpha(x) \mathcal{E}(t) \psi_i dx \\ &= \mathcal{E}(t) \int_{-\infty}^{\infty} \psi_f^* \alpha(x) \psi_i dx \end{aligned}$$

Step 2 Identify how the polarizability depends on the length of the bond

The polarizability varies with the length of the bond because the control of the nuclei over the electrons varies as their position changes, so $\alpha(x) = \alpha_0 + (d\alpha/dx)_0 x + \dots$. The calculation now proceeds as above with $(d\mu/dx)_0$ replaced by $\mathcal{E}(t)(d\alpha/dx)_0$ in the expression for μ_{fi} . For $f \neq i$,

$$\mu_{fi} = \mathcal{E}(t) \left(\frac{d\alpha}{dx} \right)_0 \int_{-\infty}^{\infty} \psi_f^* x \psi_i dx$$

Therefore, the vibration is Raman active only if $(d\alpha/dx)_0 \neq 0$; that is, only if the polarizability varies with displacement, and, as in Part (a), if $v_f - v_i = \pm 1$.