

# Infrared spectroscopy

Zhu xiaotong

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## 1 Dipole Moment

$$\boldsymbol{\mu} = e \cdot \sum_{i=1}^n \mathbf{r}_i + \sum_{I=1}^N Z_I \mathbf{R}_I \quad (1)$$

## 2 Fermi's golden rule

The probability for the transition from state  $|\psi_0\rangle$  to state  $|\psi_1\rangle$  is proportional to  $|\langle\psi_1|\mathbf{V}|\psi_0\rangle|^2$

$$\langle\psi_1|\boldsymbol{\mu}|\psi_0\rangle = \int \int \psi_g(\mathbf{r}; \mathbf{Q}) \prod_{i=1}^{3N-6} \chi_0(\mathbf{Q}_i) \left(-\sum_{i=1}^n \mathbf{r}_i + \sum_{I=1}^N Z_I \mathbf{R}_I\right) \psi_g(\mathbf{r}; \mathbf{Q}) \prod_{i=1}^{3N-7} \chi_0(\mathbf{Q}_i) \chi_1(\mathbf{Q}_{3N-6}) d\mathbf{r} d\mathbf{Q} \quad (2)$$

where,  $W_{gg}(\mathbf{Q}) = \int \psi_g(\mathbf{r}; \mathbf{Q}) \left(-\sum_{i=1}^n \mathbf{r}_i\right) \psi_g(\mathbf{r}; \mathbf{Q}) d\mathbf{r}$

Therefore, Eq.(2) can be simplified to

$$\begin{aligned} & \int W_{gg}(\mathbf{Q}) \prod_{i=1}^{3N-6} \chi_0(\mathbf{Q}_i) \prod_{i=1}^{3N-7} \chi_0(\mathbf{Q}_i) \chi_1(\mathbf{Q}_{3N-6}) d\mathbf{Q} + \int \prod_{i=1}^{3N-6} \chi_0(\mathbf{Q}_i) \sum_{I=1}^N Z_I \mathbf{R}_I \prod_{i=1}^{3N-7} \chi_0(\mathbf{Q}_i) \chi_1(\mathbf{Q}_{3N-6}) d\mathbf{Q} \\ &= \int \left(\sum_{I=1}^N Z_I \mathbf{R}_I + W_{gg}(\mathbf{Q})\right) \prod_{i=1}^{3N-6} \chi_0(\mathbf{Q}_i) \prod_{i=1}^{3N-7} \chi_0(\mathbf{Q}_i) \chi_1(\mathbf{Q}_{3N-6}) d\mathbf{Q} \end{aligned} \quad (3)$$

where, permanent dipole moment  $\boldsymbol{\mu}_{gg}(\mathbf{Q}) = \sum_{I=1}^N Z_I \mathbf{R}_I + W_{gg}(\mathbf{Q})$ . Next, for the permanent dipole moment, Taylor expansion is performed in the equilibrium configuration.

$$\boldsymbol{\mu}_{gg}(\mathbf{Q}) \approx \boldsymbol{\mu}_{gg}(\mathbf{Q}_0) + \sum_{i=1}^{3N-6} \left\{ \frac{\partial \boldsymbol{\mu}_{gg}}{\partial \mathbf{Q}_i} \right\}_0 (\mathbf{Q}_i - \mathbf{Q}_0^i) \quad (4)$$

Put Eq.(4) into Eq.(3) to get

$$\begin{aligned} & \int \boldsymbol{\mu}_{gg}(\mathbf{Q}_0) \prod_{i=1}^{3N-6} \chi_0(\mathbf{Q}_i) \prod_{i=1}^{3N-7} \chi_0(\mathbf{Q}_i) \chi_1(\mathbf{Q}_{3N-6}) d\mathbf{Q} \\ &+ \int \sum_{i=1}^{3N-6} \left\{ \frac{\partial \boldsymbol{\mu}_{gg}}{\partial \mathbf{Q}_i} \right\}_0 (\mathbf{Q}_i - \mathbf{Q}_0^i) \prod_{i=1}^{3N-6} \chi_0(\mathbf{Q}_i) \prod_{i=1}^{3N-7} \chi_0(\mathbf{Q}_i) \chi_1(\mathbf{Q}_{3N-6}) d\mathbf{Q} \\ &= \int \boldsymbol{\mu}_{gg}(\mathbf{Q}_0) \chi_0(\mathbf{Q}_{3N-6}) \chi_1(\mathbf{Q}_{3N-6}) d\mathbf{Q} \\ &+ \int \left\{ \frac{\partial \boldsymbol{\mu}_{gg}}{\partial \mathbf{Q}_{3N-6}} \right\}_0 (\mathbf{Q}_{3N-6} - \mathbf{Q}_0^{3N-6}) \chi_0(\mathbf{Q}_{3N-6}) \chi_1(\mathbf{Q}_{3N-6}) d\mathbf{Q} \\ &= 0 + \left\{ \frac{\partial \boldsymbol{\mu}_{gg}}{\partial \mathbf{Q}_{3N-6}} \right\}_0 \end{aligned} \quad (5)$$

where,  $\chi_0(x) = \sqrt{\frac{\alpha}{\sqrt{\pi}}} e^{-\frac{1}{2}\alpha^2 x^2}$ ,  $\chi_1(x) = \sqrt{\frac{\alpha}{\sqrt{\pi}}} e^{-\frac{1}{2}\alpha^2 x^2} \times 2\alpha x$ ,

and  $\int (\mathbf{Q}_{3N-6} - \mathbf{Q}_0^{3N-6}) \chi_0(\mathbf{Q}_{3N-6}) \chi_1(\mathbf{Q}_{3N-6}) d\mathbf{Q} = 1$

Therefore,  $I_{IR} \propto \left| \left\{ \frac{\partial \boldsymbol{\mu}_{gg}}{\partial \mathbf{Q}_{3N-6}} \right\}_0 \right|^2$