Infrared spectroscopy

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1 Dipole Moment

$$\boldsymbol{\mu} = e \cdot \sum_{i=1}^{n} \boldsymbol{r_i} + \sum_{I=1}^{N} Z_I \boldsymbol{R_I} \tag{1}$$

2 Fermi's golden rule

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

$$\langle\psi_1| \boldsymbol{\mu} |\psi_0\rangle = \int\int \psi_g(\boldsymbol{r};\boldsymbol{Q}) \prod_{i=1}^{3N-6} \chi_0(\boldsymbol{Q_i})(-\sum_{i=1}^{n} \boldsymbol{r_i} + \sum_{I=1}^{N} Z_I \boldsymbol{R_I})\psi_g(\boldsymbol{r};\boldsymbol{Q}) \prod_{i=1}^{3N-7} \chi_0(\boldsymbol{Q_i})\chi_1(\boldsymbol{Q_{3N-6}})d\boldsymbol{r}d\boldsymbol{Q} \tag{2}$$

where, $W_{gg}(\boldsymbol{Q}) = \int \psi_g(\boldsymbol{r};\boldsymbol{Q})(-\sum_{i=1}^{n} \boldsymbol{r_i})\psi_g(\boldsymbol{r};\boldsymbol{Q})d\boldsymbol{r}$

Therefore, Eq.(2) can be simplified to

$$\begin{aligned}
&\int W_{gg}(\boldsymbol{Q}) \prod_{i=1}^{3N-6} \chi_0(\boldsymbol{Q_i}) \prod_{i=1}^{3N-7} \chi_0(\boldsymbol{Q_i})\chi_1(\boldsymbol{Q_{3N-6}})d\boldsymbol{Q} + \int \prod_{i=1}^{3N-6} \chi_0(\boldsymbol{Q_i}) \sum_{I=1}^{N} Z_I \boldsymbol{R_I} \prod_{i=1}^{3N-7} \chi_0(\boldsymbol{Q_i})\chi_1(\boldsymbol{Q_{3N-6}})d\boldsymbol{Q} \\
&= \int (\sum_{I=1}^{N} Z_I \boldsymbol{R_I} + W_{gg}(\boldsymbol{Q})) \prod_{i=1}^{3N-6} \chi_0(\boldsymbol{Q_i}) \prod_{i=1}^{3N-7} \chi_0(\boldsymbol{Q_i})\chi_1(\boldsymbol{Q_{3N-6}})d\boldsymbol{Q}
\end{aligned} \tag{3}$$

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

$$\boldsymbol{\mu_{gg}(Q)} \approx \boldsymbol{\mu_{gg}(Q_0)} + \sum_{i=1}^{3N-6} \left\{ \frac{\partial \boldsymbol{\mu_{gg}}}{\partial \boldsymbol{Q_i}} \right\}_0 (\boldsymbol{Q_i} - \boldsymbol{Q_0^i}) \tag{4}$$

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

$$\begin{aligned}
&\int \boldsymbol{\mu_{gg}}(\boldsymbol{Q_0}) \prod_{i=1}^{3N-6} \chi_0(\boldsymbol{Q_i}) \prod_{i=1}^{3N-7} \chi_0(\boldsymbol{Q_i})\chi_1(\boldsymbol{Q_{3N-6}})d\boldsymbol{Q} \\
&+ \int \sum_{i=1}^{3N-6} \left\{ \frac{\partial \boldsymbol{\mu_{gg}}}{\partial \boldsymbol{Q_i}} \right\}_0 (\boldsymbol{Q_i} - \boldsymbol{Q_0^i}) \prod_{i=1}^{3N-6} \chi_0(\boldsymbol{Q_i}) \prod_{i=1}^{3N-7} \chi_0(\boldsymbol{Q_i})\chi_1(\boldsymbol{Q_{3N-6}})d\boldsymbol{Q} \\
&= \int \boldsymbol{\mu_{gg}}(\boldsymbol{Q_0})\chi_0(\boldsymbol{Q_{3N-6}})\chi_1(\boldsymbol{Q_{3N-6}})d\boldsymbol{Q} \\
&+ \int \left\{ \frac{\partial \boldsymbol{\mu_{gg}}}{\partial \boldsymbol{Q_{3N-6}}} \right\}_0 (\boldsymbol{Q_{3N-6}} - \boldsymbol{Q_0^{3N-6}})\chi_0(\boldsymbol{Q_{3N-6}})\chi_1(\boldsymbol{Q_{3N-6}})d\boldsymbol{Q} \\
&= 0 + \left\{ \frac{\partial \boldsymbol{\mu_{gg}}}{\partial \boldsymbol{Q_{3N-6}}} \right\}_0
\end{aligned} \tag{5}$$

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 $\int (\boldsymbol{Q_{3N-6}} - \boldsymbol{Q_0^{3N-6}})\chi_0(\boldsymbol{Q_{3N-6}})\chi_1(\boldsymbol{Q_{3N-6}})d\boldsymbol{Q} = 1$
Therefore, $I_{IR} \propto \left| \left\{ \frac{\partial \boldsymbol{\mu_{gg}}}{\partial \boldsymbol{Q_{3N-6}}} \right\}_0 \right|^2$