

Supporting Information

1 Polarity of the E state of C_3 molecules based on group theory

Hochstrasser [1] stated that molecules with symmetry C_3 , C_{3v} , S_3 , D_3 , and D_{3h} , etc., show a first-order Stark effect, or a polar excited state. We will show that based on group theory, this is indeed the case.

Following general conventions, the molecule lies in the X-Y plane, and the Z axis is the rotational axis. The doubly degenerate excited state has E symmetry. Take C_3 molecules as an example, the C_3 group table is as follows,

C_3	E	C_3	C_3^2
A	1	1	1
E	1	$-\frac{1}{2} + i\frac{\sqrt{3}}{2}$	$-\frac{1}{2} - i\frac{\sqrt{3}}{2}$
	1	$-\frac{1}{2} - i\frac{\sqrt{3}}{2}$	$-\frac{1}{2} + i\frac{\sqrt{3}}{2}$

It can be simplified by combining the two columns of C_3 and C_3^2 rotation operations and adding the values of the two E rows,

C_3	E	$2C_3$	
A	1	1	z
E	2	-1	(x,y)

The direct product between two E states is $E \otimes E = E + 2A$. The dipole moment of the E state is expressed as $\langle E | e\hat{r} | E \rangle$. As the molecule lies in the X-Y plane, the transition moment of the excitation is typically also in the X-Y plane. Therefore, the dipole moment of the E state can be reduced to $\langle E | E \rangle$, which is non-zero, indicating that the E state of C_3 molecules contain dipole moment vectors in the X-Y plane.

2 Electroabsorption spectrum of C_3 symmetric dendrimer

2.1 Ponder's derivation in molecular coordinates

Following Ponder's [2] derivation, the essential equations are listed below. The extinction coefficient ε is,

$$\varepsilon(\nu) = K\nu \langle (\hat{e} \cdot \underline{TM})^2 S(\nu) \rangle \quad (1)$$

where K is a constant, ν is the transition frequency, \hat{e} is a unit vector in the direction of the light polarization, \underline{TM} is the transition moment of the molecule, $S(\nu)$ is the absorption band shape function, and $\langle \rangle$ denotes an average over all possible molecular orientations.

When an electric field is applied to the solid sample, several molecular properties are changed, including the molecular orientation, the excited state energy levels, and the transition moment. These properties are examined below.

First, to consider the alignment of the polar molecules in a field, we assume a Boltzmann average, therefore

$$\langle (\hat{e} \cdot \underline{TM})^2 S(\nu) \rangle = \frac{\int (\hat{e} \cdot \underline{TM})^2 S(\nu) e^{-\beta U} d\tau}{\int e^{-\beta U} d\tau} \quad (2)$$

where $\beta = (k_B T)^{-1}$, and

$$U = -\underline{\mu}_g \cdot \underline{F} - \frac{1}{2} \underline{F} \cdot \underline{\underline{\alpha}}_g \cdot \underline{F} \quad (3)$$

where \underline{F} is the electric field, and $\underline{\mu}_g$ and $\underline{\underline{\alpha}}_g$ are the ground state dipole moment and polarizability, respectively. The exponential term is thus,

$$e^{-\beta U} = 1 + \beta \underline{\mu}_g \cdot \underline{F} + \frac{1}{2} \beta \underline{F} \cdot \underline{\underline{\alpha}}_g \cdot \underline{F} + \frac{1}{2} \beta^2 (\underline{\mu}_g \cdot \underline{F})^2 \quad (4)$$

Second, to consider the excited state energy level changes, the change in absorption frequency is

$$h\Delta\nu = -\underline{\underline{\Delta\mu}} \cdot \underline{F} - \frac{1}{2} \underline{F} \cdot \underline{\underline{\Delta\alpha}} \cdot \underline{F} \quad (5)$$

where $\underline{\underline{\Delta\mu}}$ and $\underline{\underline{\Delta\alpha}}$ are the changes in dipole moment and in polarizability upon excitation, respectively. Correspondingly, the shape function is changed and can be represented by a Taylor series,

$$\begin{aligned} S^F(\nu) &= S^0(\nu - \Delta\nu) \\ &= S^0(\nu) - \frac{\partial S^0(\nu)}{\partial \nu} \Delta\nu + \frac{\partial^2 S^0(\nu)}{2\partial \nu^2} \Delta\nu^2 \end{aligned} \quad (6)$$

Inserting Eqn. 5 into Eqn. 6 leads to

$$\begin{aligned} S^F(\nu) &= S^0(\nu) - \frac{1}{h} \frac{\partial S^0(\nu)}{\partial \nu} \left(-\underline{\underline{\Delta\mu}} \cdot \underline{F} - \frac{1}{2} \underline{F} \cdot \underline{\underline{\Delta\alpha}} \cdot \underline{F} \right) \\ &\quad + \frac{1}{2h^2} \frac{\partial^2 S^0(\nu)}{2\partial \nu^2} \left(-\underline{\underline{\Delta\mu}} \cdot \underline{F} - \frac{1}{2} \underline{F} \cdot \underline{\underline{\Delta\alpha}} \cdot \underline{F} \right)^2 \end{aligned} \quad (7)$$

To connect the shape function to the extinction coefficient, an isotropic distribution in the absence of an external electric field obeys

$$\langle (\hat{e} \cdot \underline{TM})^2 S^0(\nu) \rangle = \frac{1}{3} S^0(\nu) |\underline{TM}|^2. \quad (8)$$

where $\frac{1}{3}$ results from averaging the angle x between the light vector and the transition moment vector, as in

$$\begin{aligned} \langle \cos^2 x \rangle &= \frac{\int_0^\pi \sin x \cos^2 x dx}{\int_0^\pi \sin x dx} \\ &= \frac{1}{3} \end{aligned} \quad (9)$$

Therefore,

$$\begin{aligned} S^0(\nu) &= \frac{3\varepsilon^0(\nu)}{K\nu |\underline{TM}|^2} \\ \frac{\partial S^0(\nu)}{\partial \nu} &= \frac{3}{K |\underline{TM}|^2} \frac{\partial (\varepsilon/\nu)}{\partial \nu} \\ \frac{\partial^2 S^0(\nu)}{\partial \nu^2} &= \frac{3}{K |\underline{TM}|^2} \frac{\partial^2 (\varepsilon/\nu)}{\partial \nu^2} \end{aligned} \quad (10)$$

Third, the electric field also cause changes in the transition moment, expressed as,

$$\underline{TM}(\underline{F}) = \underline{TM} + \underline{A} \cdot \underline{F} + \underline{B} : \underline{F}^2 \quad (11)$$

Putting all the above effects of the field together, we have,

$$\begin{aligned} \varepsilon^F(\nu) &= K\nu \langle [\hat{e} \cdot \underline{TM}(\underline{F})]^2 S^F(\nu) \rangle \\ &= \frac{3}{|\underline{TM}|^2} \left\{ \int \left[1 + \beta \underline{\mu}_g \cdot \underline{F} + \frac{1}{2} \beta \underline{F} \cdot \underline{\alpha}_g \cdot \underline{F} + \frac{1}{2} \beta^2 (\underline{\mu}_g \cdot \underline{F})^2 \right] d\tau \right\}^{-1} \\ &\quad \times \int \left\{ \left[1 + \beta \underline{\mu}_g \cdot \underline{F} + \frac{1}{2} \beta \underline{F} \cdot \underline{\alpha}_g \cdot \underline{F} + \frac{1}{2} \beta^2 (\underline{\mu}_g \cdot \underline{F})^2 \right] \right. \\ &\quad \times [\hat{e} \cdot \underline{TM} + \hat{e} \cdot \underline{A} \cdot \underline{F} + \hat{e} \cdot \underline{B} : \underline{F}^2] \\ &\quad \times \left[\varepsilon^0(\nu) - \frac{\nu}{h} \frac{\partial (\varepsilon/\nu)}{\partial \nu} \left(-\underline{\Delta\mu} \cdot \underline{F} - \frac{1}{2} \underline{F} \cdot \underline{\Delta\alpha} \cdot \underline{F} \right) \right. \\ &\quad \left. \left. + \frac{\nu}{2h^2} \frac{\partial^2 (\varepsilon/\nu)}{\partial \nu^2} \left(-\underline{\Delta\mu} \cdot \underline{F} - \frac{1}{2} \underline{F} \cdot \underline{\Delta\alpha} \cdot \underline{F} \right)^2 \right] \right\} d\tau \end{aligned} \quad (12)$$

Ponder [2] worked in the laboratory fixed coordinate system denoted as x, y, and z axes in which the applied field lies along the z axis. It is more convenient here to work in the molecule fixed coordinate system, labeled as X, Y, and Z axes, with the molecule in the X-Y

plane. All variables with subscript M indicates coordinates in the molecular frame, and the subscript L indicates coordinates in the laboratory frame.

In the molecular coordinate system, the applied field \underline{F}_M is positioned at angle θ from the Z axis, and its projection onto the X-Y plane is at angle ϕ from the X axis. Therefore, in the molecular coordinate system,

$$\underline{F}_M = F \begin{pmatrix} \sin \theta \cos \phi \\ \sin \theta \sin \phi \\ \cos \theta \end{pmatrix} \quad (13)$$

where F is the magnitude of the applied field.

When an isotropic sample is considered, an integration is done over all orientations of the applied field, i.e., integrating over theta and phi in Eqn. 13. In electroabsorption experiments, the light polarization is usually applied at a fixed angle χ from the electric field. Therefore, an integration over all orientations of the light field is also needed. In order to express the light vector in terms of θ and ϕ for the purpose of the integration, the light vector is decomposed into one component that is parallel to the electric field and the other component that is perpendicular to the electric field, as the following.

$$\hat{e} = \cos \chi \hat{e}^{F_{\parallel}} + \sin \chi \hat{e}^{F_{\perp}}, \quad \chi \in [0, \pi] \quad (14)$$

where $\hat{e}^{F_{\parallel}}$ is the unit vector that is parallel to the applied field, and $\hat{e}^{F_{\perp}}$ is the unit vector that is perpendicular to the applied field.

In the molecular coordinate system, from Eqn. 13, the light vector parallel to the applied field $\hat{e}_M^{F_{\parallel}}$ is defined as

$$\hat{e}_M^{F_{\parallel}} = \begin{pmatrix} \sin \theta \cos \phi \\ \sin \theta \sin \phi \\ \cos \theta \end{pmatrix} \quad (15)$$

To find the expression of $\hat{e}_M^{F_{\perp}}$, the light vector perpendicular to the applied field in the molecular frame, in terms of θ and ϕ , we work in the laboratory fixed coordinate system first, and then transform all expressions to the molecular fixed coordinate system. In the laboratory fixed frame, the applied electric field is along the z axis, and therefore the unit vector that is parallel to the applied field $\hat{e}_L^{F_{\parallel}}$ can be expressed as

$$\hat{e}_L^{F_{\parallel}} = \begin{pmatrix} 0 \\ 0 \\ 1 \end{pmatrix}, \quad (16)$$

thus

$$\begin{aligned} \underline{F}_M &= F \hat{e}_L^{F_{\parallel}} \\ &= F \begin{pmatrix} 0 \\ 0 \\ 1 \end{pmatrix} \end{aligned} \quad (17)$$

Any unit vector that is perpendicular to the applied field $\hat{e}_L^{F_\perp}$ can be expressed as

$$\hat{e}_L^{F_\perp} = \begin{pmatrix} \cos \psi \\ \sin \psi \\ 0 \end{pmatrix} \quad (18)$$

where ψ is the rotational angle of the unit vector $\hat{e}_L^{F_\perp}$ from the x axis.

Now to transform the expression of the light vectors parallel or perpendicular to the applied field from the laboratory fixed frame to the molecular fixed frame, we need to rotate the laboratory coordinate system about the y axis by $-\theta$, giving rise to an intermediate coordinate system labeled as x' , y , z' . Then we rotate the intermediate coordinate system about the z' axis by $-\phi$. These rotations transform the expression of the electric field from the expression in Eqn. 17 to that in Eqn. 13. The total rotational matrix that represents these two rotations is

$$\begin{aligned} \underline{\underline{R}} &= \begin{pmatrix} \cos \phi & -\sin \phi & 0 \\ \sin \phi & \cos \phi & 0 \\ 0 & 0 & 1 \end{pmatrix} \times \begin{pmatrix} \cos \theta & 0 & \sin \theta \\ 0 & 1 & 0 \\ -\sin \theta & 0 & \cos \theta \end{pmatrix} \\ &= \begin{pmatrix} \cos \theta \cos \phi & -\sin \phi & \sin \theta \cos \phi \\ \cos \theta \sin \phi & \cos \phi & \sin \theta \sin \phi \\ -\sin \theta & 0 & \cos \theta \end{pmatrix}. \end{aligned} \quad (19)$$

It can be shown that Eqn. 19 fulfills

$$\underline{\underline{R}} \begin{pmatrix} 0 \\ 0 \\ 1 \end{pmatrix} = \begin{pmatrix} \sin \theta \cos \phi \\ \sin \theta \sin \phi \\ \cos \theta \end{pmatrix} \quad (20)$$

It should be noted that the rotational matrix that satisfies Eqn. 20 is not unique, due to a third undefined rotational angle (not present in Eqn. 19). Since in this study, this third angle corresponds to the rotational angle ψ of the light vector perpendicular to the applied field which needs to be integrated over, the rotational matrix in Eqn. 19 that uses only θ and ϕ is thus correct.

The light vector that is perpendicular to the applied field in the laboratory fixed frame expressed in Eqn. 18 can also be transformed to the molecular fixed frame by the following,

$$\begin{aligned} \hat{e}_M^{F_\perp} &= \underline{\underline{R}} \begin{pmatrix} \cos \psi \\ \sin \psi \\ 0 \end{pmatrix} \\ &= \begin{pmatrix} \cos \theta \cos \phi \cos \psi - \sin \phi \sin \psi \\ \cos \theta \sin \phi \cos \psi + \cos \phi \sin \psi \\ -\sin \theta \cos \psi \end{pmatrix} \end{aligned} \quad (21)$$

Finally, in the molecular coordinate system, the light field vector in Eqn. 14 is expressed in terms of θ and ϕ (the orientation of the applied field in the molecular frame), ψ (the

rotational freedom of the light vector around the applied field), and χ (the angle between the light vector and the applied field).

$$\begin{aligned}\hat{e} &= \cos \chi \begin{pmatrix} \sin \theta \cos \phi \\ \sin \theta \sin \phi \\ \cos \theta \end{pmatrix} + \sin \chi \begin{pmatrix} \cos \theta \cos \phi \cos \psi - \sin \phi \sin \psi \\ \cos \theta \sin \phi \cos \psi + \cos \phi \sin \psi \\ -\sin \theta \cos \psi \end{pmatrix} \\ &= \begin{pmatrix} \cos \chi \sin \theta \cos \phi + \sin \chi \cos \theta \cos \phi \cos \psi - \sin \chi \sin \phi \sin \psi \\ \cos \chi \sin \theta \sin \phi + \sin \chi \cos \theta \sin \phi \cos \psi + \sin \chi \cos \phi \sin \psi \\ \cos \chi \cos \theta - \sin \chi \sin \theta \cos \psi \end{pmatrix}\end{aligned}\quad (22)$$

Using Eqn. 22, the dot product of the light vector and the transition moment $\hat{e} \cdot \underline{TM}$ can be easily derived for any orientation of the transition moment. This is important for studying the C_3 symmetric molecules, as the transition moments of the E states are orthogonal to each other and lie in the X-Y plane.

2.2 Simple molecules with a dominant non-degenerate excited state

Take the monomer as an example, we know that the dipole moment, transition moment and the polarizability of the monomer are all along the X axis. If we ignore the change to the molecular orientation (the thermal term in Eqn. 3), and the change to the transition moment, Eqn. 12 can be simplified to be

$$\varepsilon^F(\nu) = \frac{3 \int \{(\hat{e} \cdot \underline{TM})^2 (A - B\Delta E + C\Delta E^2)\} d\tau}{|\underline{TM}|^2 \int d\tau}\quad (23)$$

where the constants are defined as

$$\begin{aligned}A &= \varepsilon^0(\nu) \\ B &= \frac{\nu}{h} \frac{\partial(\varepsilon/\nu)}{\partial \nu} \\ C &= \frac{\nu}{2h^2} \frac{\partial^2(\varepsilon/\nu)}{\partial \nu^2}.\end{aligned}\quad (24)$$

and the excitation energy shift in field defined in Eqn. 5 $\Delta E = h\Delta\nu$ is

$$\Delta E = -\underline{\Delta\mu} \cdot \underline{F} - \frac{1}{2} \underline{F} \cdot \underline{\underline{\Delta\alpha}} \cdot \underline{F}\quad (25)$$

From Eqn. 13, we take out the X element of the applied field,

$$F_x = F \sin \theta \cos \phi\quad (26)$$

Therefore, the right hand side of Eqn. 5 becomes

$$-\underline{\Delta\mu} \cdot \underline{F} - \frac{1}{2} \underline{F} \cdot \underline{\underline{\Delta\alpha}} \cdot \underline{F} = -\Delta\mu_x F \sin \theta \cos \phi - \frac{1}{2} \Delta\alpha_{xx} F^2 \sin^2 \theta \cos^2 \phi\quad (27)$$

$\hat{e} \cdot \underline{TM}$ becomes

$$TM (\cos \chi \sin \theta \cos \phi + \sin \chi \cos \theta \cos \phi \cos \psi - \sin \chi \sin \phi \sin \psi) \quad (28)$$

Since electroabsorption experiment is usually carried out such that the angle between the applied field and the light field is at the magic angle, $3 \cos^2 \chi = 1$ or $\chi = 54.7^\circ$ is assumed. Take the above equations to Eqn. 23 and substituting the derivative terms of $\varepsilon^0(\nu)$ by Eqn. 24, we obtain

$$\begin{aligned} \Delta \varepsilon^F(\nu) &= B \frac{\Delta \alpha_{xx} F^2}{6} + C \frac{\Delta \mu_x^2 F^2}{3} \\ &= \frac{\nu \Delta \alpha_{xx} F^2}{6h} \frac{\partial(\varepsilon/\nu)}{\partial \nu} + \frac{\nu \Delta \mu_x^2 F^2}{6h^2} \frac{\partial^2(\varepsilon/\nu)}{\partial \nu^2} \end{aligned} \quad (29)$$

where we have ignored all terms of F with an order of greater than 2.

Maple9 [3] is used for the integrations. In summary, the coefficient for the first-derivative term of the absorption function is

$$\frac{\nu \Delta \alpha_{xx} F^2}{6h} \quad (30)$$

and the coefficient for the second-derivative term of the absorption function is

$$\frac{\nu \Delta \mu_x^2 F^2}{6h^2} \quad (31)$$

2.3 Extension to doubly degenerate excited states in C_3 symmetric dendrimers

2.3.1 Expressing the properties of the trimer in terms of those of the monomer

Now let us consider the case for C_3 symmetric molecules. For the molecule we are interested in (the trimer in Ref. [4]), which is an assembly of three identical monomer units, we express the monomer's properties as the following,

$$\underline{\Delta \mu^m} = \begin{pmatrix} \mu_x \\ \mu_y \\ \mu_z \end{pmatrix} \quad (32)$$

$$\underline{TM^m} = \begin{pmatrix} TM_x \\ TM_y \\ TM_z \end{pmatrix} \quad (33)$$

where $\underline{\Delta \mu^m}$ and $\underline{TM^m}$ are the dipole moment change and the transition moment of the monomer, respectively.

Let us define the excited states of the trimer as $|0\rangle$ for the ground state, $|E_1\rangle$ and $|E_2\rangle$ for the two E states, and $|A\rangle$ for the A state.

The dipole operator of the symmetric trimer in the monomer basis is

$$\underline{\underline{\vec{\mu}^t}} = \begin{pmatrix} 0 & \underline{TM^m} & \underline{R TM^m} & \underline{R^2 TM^m} \\ \underline{TM^m} & \underline{\Delta\mu^m} & 0 & 0 \\ \underline{R TM^m} & 0 & \underline{R \Delta\mu^m} & 0 \\ \underline{R^2 TM^m} & 0 & 0 & \underline{R^2 \Delta\mu^m} \end{pmatrix} \quad (34)$$

where \underline{R} corresponds to rotation about the Z axis by 120° . The excited states of the trimer are obtained by diagonalizing the Hamiltonian and transforming the dipole operator, which becomes,

$$\underline{\underline{\vec{\mu}^t}} = \begin{pmatrix} \begin{pmatrix} 0 \\ 0 \\ 0 \end{pmatrix} \begin{pmatrix} \sqrt{\frac{3}{2}}TM_y \\ -\sqrt{\frac{3}{2}}TM_x \\ 0 \end{pmatrix} \begin{pmatrix} \sqrt{\frac{3}{2}}TM_x \\ \sqrt{\frac{3}{2}}TM_y \\ 0 \end{pmatrix} \begin{pmatrix} 0 \\ 0 \\ \sqrt{3}TM_z \end{pmatrix} \\ \begin{pmatrix} \sqrt{\frac{3}{2}}TM_y \\ -\sqrt{\frac{3}{2}}TM_x \\ 0 \end{pmatrix} \begin{pmatrix} -\frac{1}{2}\mu_x \\ -\frac{1}{2}\mu_y \\ \mu_z \end{pmatrix} \begin{pmatrix} -\frac{1}{2}\mu_y \\ \frac{1}{2}\mu_x \\ 0 \end{pmatrix} \begin{pmatrix} \frac{1}{\sqrt{2}}\mu_y \\ -\frac{1}{\sqrt{2}}\mu_x \\ 0 \end{pmatrix} \\ \begin{pmatrix} \sqrt{\frac{3}{2}}TM_x \\ \sqrt{\frac{3}{2}}TM_y \\ 0 \end{pmatrix} \begin{pmatrix} -\frac{1}{2}\mu_y \\ \frac{1}{2}\mu_x \\ 0 \end{pmatrix} \begin{pmatrix} \frac{1}{2}\mu_x \\ \frac{1}{2}\mu_y \\ \mu_z \end{pmatrix} \begin{pmatrix} \frac{1}{\sqrt{2}}\mu_x \\ \frac{1}{\sqrt{2}}\mu_y \\ 0 \end{pmatrix} \\ \begin{pmatrix} 0 \\ 0 \\ \sqrt{3}TM_z \end{pmatrix} \begin{pmatrix} \frac{1}{\sqrt{2}}\mu_y \\ -\frac{1}{\sqrt{2}}\mu_x \\ 0 \end{pmatrix} \begin{pmatrix} \frac{1}{\sqrt{2}}\mu_x \\ \frac{1}{\sqrt{2}}\mu_y \\ 0 \end{pmatrix} \begin{pmatrix} 0 \\ 0 \\ \mu_z \end{pmatrix} \end{pmatrix} \quad (35)$$

where the dipole moment changes of the two E states are

$$\begin{aligned} \underline{\underline{\Delta\mu_1^t}} &= \begin{pmatrix} -\frac{1}{2}\mu_x \\ -\frac{1}{2}\mu_y \\ \mu_z \end{pmatrix} \\ \underline{\underline{\Delta\mu_2^t}} &= \begin{pmatrix} \frac{1}{2}\mu_x \\ \frac{1}{2}\mu_y \\ \mu_z \end{pmatrix} \end{aligned} \quad (36)$$

and the dipole coupling term between the two E states $\underline{\underline{\mu_{12}^t}}$ is

$$\underline{\underline{\mu_{12}^t}} = \begin{pmatrix} -\frac{1}{2}\mu_y \\ \frac{1}{2}\mu_x \\ 0 \end{pmatrix} \quad (37)$$

The transition moment from the ground state $|0\rangle$ to the two E states are

$$\begin{aligned} \langle 0 | \hat{\mu} | E_1 \rangle &= \begin{pmatrix} \sqrt{\frac{3}{2}}TM_y \\ -\sqrt{\frac{3}{2}}TM_x \\ 0 \end{pmatrix} \\ \langle 0 | \hat{\mu} | E_2 \rangle &= \begin{pmatrix} \sqrt{\frac{3}{2}}TM_x \\ \sqrt{\frac{3}{2}}TM_y \\ 0 \end{pmatrix} \end{aligned} \quad (38)$$

where $\hat{\mu}$ is the transition dipole operator.

If we make the approximation that the monomer's dipole moment change and the transition moment is along the X axis (this is a good approximation for most of the monomer geometries), the above expressions for the dipole moment changes and transition moments for the two E states and the dipole coupling between them are therefore as follows,

$$\begin{aligned}
\underline{\Delta\mu_1^t} &= \begin{pmatrix} -\frac{1}{2}\mu \\ 0 \\ 0 \end{pmatrix} \\
\underline{\Delta\mu_2^t} &= \begin{pmatrix} \frac{1}{2}\mu \\ 0 \\ 0 \end{pmatrix} \\
\langle 0 | \hat{\mu} | E_1 \rangle &= \begin{pmatrix} 0 \\ -\sqrt{\frac{3}{2}}TM \\ 0 \end{pmatrix} \\
\langle 0 | \hat{\mu} | E_2 \rangle &= \begin{pmatrix} \sqrt{\frac{3}{2}}TM \\ 0 \\ 0 \end{pmatrix} \\
\underline{\mu_{12}^t} &= \begin{pmatrix} 0 \\ \frac{1}{2}\mu \\ 0 \end{pmatrix}
\end{aligned} \tag{39}$$

where TM and μ are the magnitude of the transition moment and the dipole moment change of the monomer,

$$\begin{aligned}
\mu_x &= \mu \\
TM_x &= TM.
\end{aligned} \tag{40}$$

2.3.2 Perturbation of the trimer by light and the electric field

Now we only need to examine the first two excited states (E symmetry states; the A state is dark). We can see that the first excited state of the trimer is only polarized by light along the Y direction; whereas the other excited state is excited by X-polarized light. When one of these excited state is reached, depending on the direction of the applied field, we will be observing either a blue-shift or red-shift of the energy level, due to two effects: the first one is when the applied field is along the X axis, thus is parallel to the dipole moment of the excited state; the second one is when the field is along Y axis, causing the dipole coupling term between the two E states to split in an external field, resulting in essentially the same amount of blue-shift or red-shift. Let us examine this more closely.

First, let us consider X-polarized light. Such light will excite only the second E state. If the applied field is along +X, we will see a red-shift of the energy level of the excitation. If the applied field is along -X, we will see a blue-shift of the energy level. If the field is along Y, the coupling of the two E states will cause the two states to be split by an energy separation

of $\mu_x F$. Then depending on if the field is along $+Y$ or $-Y$, we could see either a blue-shift or red-shift from the original degenerate energy level by $\frac{1}{2}\mu_x F$.

Similarly, we consider the case in which the light is polarized along the Y axis. In this case, the first E state is excited. When the field is along X , we see a shift in energy in analogy to the previous case; when the field is along Y , the coupling between the two states will also cause a splitting of the energy level. Therefore, we can see that no matter if the applied field is along the light vector, or perpendicular to it, we will see a splitting.

To capture the above arguments, let us express these ideas into mathematical forms. Focusing on the two E states, we express the change in the Hamiltonian of the trimer in the field as,

$$\underline{\underline{H'}} = \begin{pmatrix} \underline{\Delta\mu_1^t} \cdot \underline{F} & \underline{\mu_{12}^t} \cdot \underline{F} \\ \underline{\mu_{12}^t} \cdot \underline{F} & \underline{\Delta\mu_2^t} \cdot \underline{F} \end{pmatrix} \quad (41)$$

Utilizing the expression of \underline{F} as in Eqn. 13, and the vector representations of $\underline{\Delta\mu_1^t}$, $\underline{\Delta\mu_2^t}$, and $\underline{\mu_{12}^t}$ in Eqns. 39, the Hamiltonian in basis $|E_1\rangle$ and $|E_2\rangle$ is found to be

$$\begin{aligned} \underline{\underline{H'}} &= \begin{pmatrix} -\frac{1}{2}\mu F \sin \theta \cos \phi & \frac{1}{2}\mu F \sin \theta \sin \phi \\ \frac{1}{2}\mu F \sin \theta \sin \phi & \frac{1}{2}\mu F \sin \theta \cos \phi \end{pmatrix} \\ &= \frac{1}{2}\mu F \sin \theta \begin{pmatrix} -\cos \phi & \sin \phi \\ \sin \phi & \cos \phi \end{pmatrix} \end{aligned} \quad (42)$$

To find out the energy level shifts, we find the unitary matrix $\underline{\underline{U}}$ that diagonalizes the Hamiltonian. The results are as follows,

$$\underline{\underline{U^T H' U}} = \frac{1}{2}\mu F \sin \theta \begin{pmatrix} 1 & 0 \\ 0 & -1 \end{pmatrix} \quad (43)$$

$$\begin{aligned} \underline{\underline{U}} &= \begin{pmatrix} \frac{\sin \phi}{\sqrt{2+2\cos \phi}} & \frac{\sin \phi}{\sqrt{2-2\cos \phi}} \\ \sqrt{\frac{1+\cos \phi}{2}} & \sqrt{\frac{1-\cos \phi}{2}} \end{pmatrix} \\ &= \begin{pmatrix} \sin \frac{\phi}{2} & -\cos \frac{\phi}{2} \\ \cos \frac{\phi}{2} & \sin \frac{\phi}{2} \end{pmatrix} \end{aligned} \quad (44)$$

The excited states with the energy shifts of $\frac{1}{2}\mu_x F \sin \theta$ are denoted as $|1\rangle$, and $|2\rangle$. They can be represented in the old basis $|E_1\rangle$ and $|E_2\rangle$ as the following,

$$\begin{aligned} |1\rangle &= \sin \frac{\phi}{2} |E_1\rangle + \cos \frac{\phi}{2} |E_2\rangle \\ |2\rangle &= -\cos \frac{\phi}{2} |E_1\rangle + \sin \frac{\phi}{2} |E_2\rangle \end{aligned} \quad (45)$$

Now the transition moments from the ground states to states $|1\rangle$ and $|2\rangle$ can be found by the following equations.

$$\begin{aligned}
\langle 0 | \hat{\mu} | 1 \rangle &= \sin \frac{\phi}{2} \langle 0 | \hat{\mu} | E_1 \rangle + \cos \frac{\phi}{2} \langle 0 | \hat{\mu} | E_2 \rangle \\
&= \sin \frac{\phi}{2} \begin{pmatrix} 0 \\ -\sqrt{\frac{3}{2}} TM \\ 0 \end{pmatrix} + \cos \frac{\phi}{2} \begin{pmatrix} \sqrt{\frac{3}{2}} TM \\ 0 \\ 0 \end{pmatrix} \\
&= \begin{pmatrix} \sqrt{\frac{3}{2}} \cos \frac{\phi}{2} TM \\ -\sqrt{\frac{3}{2}} \sin \frac{\phi}{2} TM \\ 0 \end{pmatrix} \\
\langle 0 | \hat{\mu} | 2 \rangle &= -\cos \frac{\phi}{2} \langle 0 | \hat{\mu} | E_1 \rangle + \sin \frac{\phi}{2} \langle 0 | \hat{\mu} | E_2 \rangle \\
&= -\cos \frac{\phi}{2} \begin{pmatrix} 0 \\ -\sqrt{\frac{3}{2}} TM \\ 0 \end{pmatrix} + \sin \frac{\phi}{2} \begin{pmatrix} \sqrt{\frac{3}{2}} TM \\ 0 \\ 0 \end{pmatrix} \\
&= \begin{pmatrix} \sqrt{\frac{3}{2}} \sin \frac{\phi}{2} TM \\ \sqrt{\frac{3}{2}} \cos \frac{\phi}{2} TM \\ 0 \end{pmatrix} \tag{46}
\end{aligned}$$

2.3.3 Ponder's formalism for symmetric C_3 molecules

Now for C_3 symmetric molecules, Eqn. 12 needs to be modified to reflect the above changes to the dipole moment and transition moment of the trimer molecule. First, Eqn. 8 needs to be modified as there are two equally bright excited state contributing to the total absorption,

$$\begin{aligned}
\varepsilon^0(\nu) &= 2K\nu \left\langle (\hat{e} \cdot \underline{TM}_1)^2 S(\nu) \right\rangle \\
&= 2K\nu \left\langle (\hat{e} \cdot \underline{TM}_2)^2 S(\nu) \right\rangle \\
&= 2K\nu S^0(\nu) \int_0^{2\pi} d\psi \int_0^{2\pi} d\phi \int_0^\pi d\theta \sin \theta \left(-\sqrt{\frac{3}{2}} TM (\cos \chi \sin \theta \sin \phi \right. \\
&\quad \left. + \sin \chi \cos \theta \sin \phi \cos \psi + \sin \chi \cos \phi \sin \psi) \right)^2 \\
&= 2K\nu \frac{1}{2} TM^2 S^0(\nu) \\
&= K\nu TM^2 S^0(\nu) \tag{47}
\end{aligned}$$

where $|\underline{TM}|^2$ is $\frac{3}{2} TM^2$ according to Eqn. 46. The shape function $S^0(\nu)$ arises from absorption signals for both excited states. TM_1 and TM_2 are from Eqn. 39. Therefore, Eqn. 10 becomes

$$\begin{aligned}
S^0(\nu) &= \frac{\varepsilon^0(\nu)}{K\nu TM^2} \\
\frac{\partial S^0(\nu)}{\partial \nu} &= \frac{1}{K TM^2} \frac{\partial (\varepsilon/\nu)}{\partial \nu}
\end{aligned}$$

$$\frac{\partial^2 S^0(\nu)}{\partial \nu^2} = \frac{1}{K T M^2} \frac{\partial^2 (\varepsilon/\nu)}{\partial \nu^2} \quad (48)$$

We will consider the two excited states separately, and add their responses to the field later. To make things simpler, we will ignore the thermal distribution term (Eqn. 4), the change in the transition moments (Eqn. 11), and polarizability terms in Eqn. 5. This way, Eqn. 12 becomes the following,

$$\varepsilon_i^F(\nu) = \frac{\int \left\{ (\hat{e} \cdot \underline{TM})^2 \left[\varepsilon^0(\nu) - \frac{\nu}{h} \frac{\partial(\varepsilon/\nu)}{\partial \nu} \left(-\underline{\Delta\mu}_i \cdot \underline{F} \right) + \frac{\nu}{2h^2} \frac{\partial^2(\varepsilon/\nu)}{\partial \nu^2} \left(-\underline{\Delta\mu}_i \cdot \underline{F} \right)^2 \right] \right\} d\tau}{T M^2 \{ \int d\tau \}} \quad (49)$$

where $i = 1, 2$ for each of the two excited states. The electroabsorption can be obtained by the following equation,

$$\Delta \varepsilon^F(\nu) = \varepsilon_1^F(\nu) + \varepsilon_2^F(\nu) - \varepsilon_1^0(\nu) - \varepsilon_2^0(\nu) \quad (50)$$

$-\underline{\Delta\mu}_i \cdot \underline{F}$ for the two excited states $|1\rangle$ and $|2\rangle$ are $(-\frac{1}{2}\mu F \sin \theta)$ and $(\frac{1}{2}\mu F \sin \theta)$, respectively. The term of $\hat{e} \cdot \underline{TM}$ becomes

$$\begin{aligned} \hat{e} \cdot \underline{TM}_1 &= \sqrt{\frac{3}{2}} T M \cos \frac{\phi}{2} (\cos \chi \sin \theta \cos \phi + \sin \chi \cos \theta \cos \phi \cos \psi - \sin \chi \sin \phi \sin \psi) \\ &- \sqrt{\frac{3}{2}} T M \sin \frac{\phi}{2} (\cos \chi \sin \theta \sin \phi + \sin \chi \cos \theta \sin \phi \cos \psi + \sin \chi \cos \phi \sin \psi) \end{aligned} \quad (51)$$

for state $|1\rangle$, and

$$\begin{aligned} \hat{e} \cdot \underline{TM}_2 &= \sqrt{\frac{3}{2}} T M \sin \frac{\phi}{2} (\cos \chi \sin \theta \cos \phi + \sin \chi \cos \theta \cos \phi \cos \psi - \sin \chi \sin \phi \sin \psi) \\ &+ \sqrt{\frac{3}{2}} T M \cos \frac{\phi}{2} (\cos \chi \sin \theta \sin \phi + \sin \chi \cos \theta \sin \phi \cos \psi + \sin \chi \cos \phi \sin \psi) \end{aligned} \quad (52)$$

for state $|2\rangle$.

Therefore Eqn. 49 becomes

$$\varepsilon_i^F(\nu) = \frac{\int_0^{2\pi} d\psi \int_0^{2\pi} d\phi \int_0^\pi \sin \theta d\theta \left\{ (\hat{e} \cdot \underline{TM}_i)^2 \left[A \pm \frac{1}{2} B \mu F \sin \theta + C \left(\frac{1}{2} \mu F \sin \theta \right)^2 \right] \right\}}{T M^2 \int_0^{2\pi} d\psi \int_0^{2\pi} d\phi \int_0^\pi \sin \theta d\theta} \quad (53)$$

where $i = 1, 2$ for the two excited states. And the sign before the term $\frac{1}{2} B \mu F \sin \theta$ is $+$ for the first excited state, and $-$ for the second state. The constants A , B , and C are defined in Eqn. 24.

Take Eqn. 53 into Maple, and solve for the integration. The denominator is

$$\int_0^{2\pi} d\psi \int_0^{2\pi} d\phi \int_0^\pi \sin \theta d\theta = 8\pi^2 \quad (54)$$

The above equations can be verified by calculating $\varepsilon_i^0(\nu)$ ($i = 1, 2$),

$$\varepsilon_1^0(\nu) = \varepsilon_2^0(\nu) = \frac{1}{2}\varepsilon^0(\nu) \quad (55)$$

Assuming that the applied field and the light field are at the magic angle, Eqn. 50 is calculated to be

$$\begin{aligned} \Delta\varepsilon^F(\nu) &= \frac{\nu}{2h^2} \frac{\partial^2(\varepsilon/\nu)}{\partial\nu^2} \frac{\mu^2 F^2}{6} \\ &= \frac{\nu\mu^2 F^2}{12h^2} \frac{\partial^2(\varepsilon/\nu)}{\partial\nu^2} \end{aligned} \quad (56)$$

Since we ignored the polarizability of the molecule, the first derivative term of the absorption function is zero.

In summary, if the polarizability signal is ignored, the second derivative shape of the absorption function of the C_3 symmetric molecule has a coefficient of

$$\frac{\nu\mu^2 F^2}{12h^2} \quad (57)$$

Since μ is the monomer's dipole moment change, this factor is exactly one half of the value of the non-degenerate case in Eqn. 31. This suggests that for C_3 symmetric molecules, the Stark second derivative signal of the excited state is one half that of the constituent arm, therefore, the trimer's dipole moment change of the E state is $\sqrt{1/2}$ that of the monomer.

2.3.4 Ignoring coupling between the two E states

The previous section deals with ideal situations in which the degeneracy of the C_3 molecules is maintained. In realistic situations, however, a small perturbation in the experimental sample could lift the degeneracy of the E states. In these cases, the excited state wavefunctions are still largely delocalized, and the C_3 molecular symmetry is more or less preserved. But the energy separation between the two E states could be larger than the dipole coupling between them, making this coupling effect insignificant. Ignoring the dipole coupling, Eqn. 42 becomes

$$\underline{\underline{H'}} = \frac{1}{2}\mu F \sin\theta \cos\phi \begin{pmatrix} -1 & 0 \\ 0 & 1 \end{pmatrix}; \quad (58)$$

and the unitary matrix becomes the unit matrix. Therefore,

$$\begin{aligned} \hat{e} \cdot \underline{TM_1} &= -\sqrt{\frac{3}{2}}TM \sin\frac{\phi}{2} (\cos\chi \sin\theta \sin\phi + \sin\chi \cos\theta \sin\phi \cos\psi + \sin\chi \cos\phi \sin\psi) \\ \hat{e} \cdot \underline{TM_2} &= \sqrt{\frac{3}{2}}TM \sin\frac{\phi}{2} (\cos\chi \sin\theta \cos\phi + \sin\chi \cos\theta \cos\phi \cos\psi - \sin\chi \sin\phi \sin\psi) \end{aligned} \quad (59)$$

$-\underline{\Delta\mu_i} \cdot \underline{F}$ for the two excited states $|1\rangle$ and $|2\rangle$ are $(-\frac{1}{2}\mu F \sin\theta \cos\phi)$ and $(\frac{1}{2}\mu F \sin\theta \cos\phi)$, respectively. Eqn. 49 is used to calculate the four terms in Eqn. 50.

Eqn. 55 is found to be true, and assuming that the applied field and the light field are at the magic angle,

$$\begin{aligned}\Delta\varepsilon^F(\nu) &= \frac{\nu}{2h^2} \frac{\partial^2(\varepsilon/\nu)}{\partial\nu^2} \frac{\mu^2 F^2}{12} \\ &= \frac{\nu\mu^2 F^2}{24h^2} \frac{\partial^2(\varepsilon/\nu)}{\partial\nu^2}\end{aligned}\tag{60}$$

This result shows that when the coupling term between the two E states is ignored, the coefficient for the second derivative shape of the absorption spectrum of the trimer is one quarter of that of the monomer in the applied field with the same magnitude. Therefore, the trimer’s dipole moment change should be one half that of the monomer. This result agrees with the approach in Ref. [4] in which the transition moment weighted average dipole moment norm of the two E states is one half that of the monomer at small disorder.

3 Symmetry-broken molecules

From the previous sections, we see that for symmetric C_3 molecules, the dipole moment change is $\frac{1}{\sqrt{2}}$ that of the constituent branch if the dipole coupling between the two E states is considered, and $\frac{1}{2}$ that of the constituent branch if the coupling is ignored.

When the symmetry of the trimer is broken, we expect the energy separation among the trimer’s excited states to be much larger than the coupling (J in Ref. [4]) between them. In essence, the trimer becomes a simple collection of three non-interacting monomers. Therefore, for molecules in which the C_3 symmetry is broken, we can obtain the dipole moment change of the trimer by summing the dipole moment changes of the excited states weighted by the corresponding transition intensities, as in Ref. [4].

References

- [1] Hochstrasser, R. M. “*Electric Field Effects on Oriented Molecules and Molecular Crystals*”, *Acc. Chem. Res.* **6**, 263 (1973).
- [2] Ponder, M. C. Ph.D. Thesis. “*Electric Field Spectroscopy of Diphenylpolyenes, all-trans retinal, and bacteriorhodopsin*”, University of California, Berkeley, **1983**.
- [3] <http://www.maplesoft.com/products/maple/>.
- [4] Liu, L. A.; Peteanu, L. A.; Yaron, D. J. “*Effects of Disorder-Induced Symmetry Breaking on the Electroabsorption Properties of a Model Dendrimer*”, the main paper of this Supporting Information.