Phenolic Resin Surface Restructurings Upon Exposure to Humid Air: A Sum Frequency Generation Vibrational Spectroscopic Study

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1. Bond additivity approach to para-substituted phenyl ring

We used the bond additivity approach to evaluate the hyperpolarizability components for ν_2 and ν_{7b} modes[S1]. The molecule-fixed coordinate is defined as an (a, b, c) system. The "c" axis is parallel to the C-O main axis; the "a" axis is perpendicular to the "c" axis and is in the phenyl plane; the "b" axis is orthogonal to the phenyl plane (Fig. S1). Using the single C-H bond "r1" as an example, "//"is defined as the direction along the single bond; "⊥in" is the direction perpendicular to the single bond r1 and is in the phenyl plane; "⊥out" is perpendicular to the phenyl plane (Fig. S1).

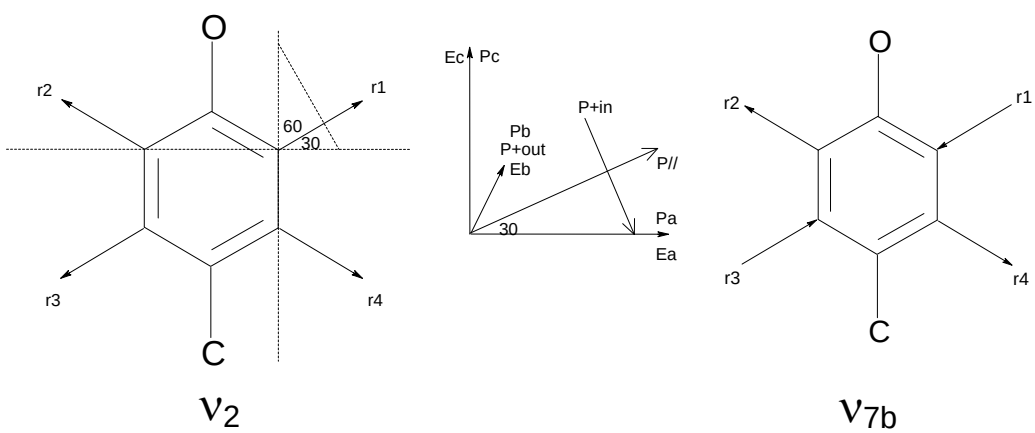


FIG. S1 A schematic picture of ν_2 mode (left) and ν_{7b} mode (right). The middle plot is the coordinate system, (a, b, c). ($P_{//}$, $P_{\perp in}$, $P_{\perp out}$) is the induced dipole transition moment because of the polarizability of a single C-H bond r1. (P_a, P_b, P_c) is the corresponding dipole transition moment projected onto the (a, b, c) coordinate system. (E_a, E_b, E_c) is the external field. a, b, c axis are in the same directions as E_a, E_b, E_c, respectively.

Whiffen deduced the Raman tensor components of an aromatic C-H stretching along the single bond direction, perpendicular to the single bond and in the ac plane, and perpendicular to both the single bond and the phenyl plane are 2.6 Å^2, 1.2 Å^2, and 0.1 Å^2,

respectively[S2]. Therefore $\alpha'_{//} = 2.6$ Å^2, $\alpha'_{\perp in} = 1.2$ Å^2, and $\alpha'_{\perp out} = 0.1$ Å^2.

Supposing there is an external field $\vec{E}$ (E_a, E_b, E_c) acting on all four C-H bonds in the phenol group, a polarization $\vec{P}$ ($P_{\parallel}$, $P_{\perp in}$, $P_{\perp out}$) is induced because of the single bond polarizability. We have

For C-H bond r1,

$$P^1_{//} = \left(E_a \cos\frac{\pi}{6} + E_c \sin\frac{\pi}{6} \right) \cdot \alpha_{//}$$

$$P^1_{\perp in} = \left(E_a \sin\frac{\pi}{6} - E_c \cos\frac{\pi}{6} \right) \cdot \alpha_{\perp in}$$

$$P^1_{\perp out} = E_b \cdot \alpha_{\perp out}$$

Projecting ($P_{\parallel}$, $P_{\perp in}$, $P_{\perp out}$) to (P_a, P_b, P_c), we have

$$P^1_a = P^1_{//} \cos\frac{\pi}{6} + P^1_{\perp in} \sin\frac{\pi}{6} = E_a \left(\alpha_{//} \cos^2\frac{\pi}{6} + \alpha_{\perp in} \sin^2\frac{\pi}{6} \right) + E_c \sin\frac{\pi}{6} \cos\frac{\pi}{6} \left(\alpha_{//} - \alpha_{\perp in} \right)$$

$$P^1_b = P^1_{\perp out} = E_b \cdot \alpha_{\perp out}$$

$$P^1_c = P^1_{//} \sin\frac{\pi}{6} + P^1_{\perp in} \cos\frac{\pi}{6} = E_a \sin\frac{\pi}{6} \cos\frac{\pi}{6} \left(\alpha_{//} - \alpha_{\perp in} \right) + E_c \left(\alpha_{//} \sin^2\frac{\pi}{6} + \alpha_{\perp in} \cos^2\frac{\pi}{6} \right)$$

For C-H bond r2,

$$P^2_{//} = \left(-E_a \cos\frac{\pi}{6} + E_c \sin\frac{\pi}{6} \right) \cdot \alpha_{//}$$

$$P_{\perp in}^{2} = \left(-E_a \sin\frac{\pi}{6} - E_c \cos\frac{\pi}{6} \right) \cdot \alpha_{\perp in}$$

$$P_{\perp out}^{2} = -E_b \cdot \alpha_{\perp out}$$

Projecting ($P_{\parallel}$, $P_{\perp in}$, $P_{\perp out}$) to (P_a, P_b, P_c), we have

$$P_a^2 = -P_{//}^2 \cos\frac{\pi}{6} - P_{\perp in}^2 \sin\frac{\pi}{6} = E_a \left(\alpha_{//} \cos^2\frac{\pi}{6} + \alpha_{\perp in} \sin^2\frac{\pi}{6} \right) + E_c \sin\frac{\pi}{6} \cos\frac{\pi}{6} \left(\alpha_{\perp in} - \alpha_{//} \right)$$

$$P_b^2 = P_{\perp out}^2 = -E_b \cdot \alpha_{\perp out}$$

$$P_c^2 = P_{//}^2 \sin\frac{\pi}{6} - P_{\perp in}^2 \cos\frac{\pi}{6} = E_a \sin\frac{\pi}{6} \cos\frac{\pi}{6} \left(\alpha_{\perp in} - \alpha_{//} \right) + E_c \left(\alpha_{//} \sin^2\frac{\pi}{6} + \alpha_{\perp in} \cos^2\frac{\pi}{6} \right)$$

For C-H bond r3,

$$P_{//}^3 = \left(-E_a \cos\frac{\pi}{6} - E_c \sin\frac{\pi}{6} \right) \cdot \alpha_{//}$$

$$P_{\perp in}^3 = \left(E_a \sin\frac{\pi}{6} - E_c \cos\frac{\pi}{6} \right) \cdot \alpha_{\perp in}$$

$$P_{\perp out}^3 = -E_b \cdot \alpha_{\perp out}$$

Projecting ($P_{\parallel}$, $P_{\perp in}$, $P_{\perp out}$) to (P_a, P_b, P_c), we have

$$P_a^3 = -P_{//}^3 \cos\frac{\pi}{6} + P_{\perp in}^2 \sin\frac{\pi}{6} = E_a \left(\alpha_{//} \cos^2\frac{\pi}{6} + \alpha_{\perp in} \sin^2\frac{\pi}{6} \right) + E_c \sin\frac{\pi}{6} \cos\frac{\pi}{6} \left(\alpha_{//} - \alpha_{\perp in} \right)$$

$$P_b^3 = P_{\perp out}^3 = -E_b \cdot \alpha_{\perp out}$$

$$P_c^3 = -P_{//}^3 \sin\frac{\pi}{6} - P_{\perp in}^3 \cos\frac{\pi}{6} = E_a \sin\frac{\pi}{6}\cos\frac{\pi}{6}\left(\alpha_{//} - \alpha_{\perp in}\right) + E_c\left(\alpha_{//}\sin^2\frac{\pi}{6} + \alpha_{\perp in}\cos^2\frac{\pi}{6}\right)$$

For C-H bond r4,

$$P_{//}^4 = \left(E_a \cos\frac{\pi}{6} - E_c \sin\frac{\pi}{6}\right) \cdot \alpha_{//}$$

$$P_{\perp in}^4 = \left(-E_a \sin\frac{\pi}{6} - E_c \cos\frac{\pi}{6}\right) \cdot \alpha_{\perp in}$$

$$P_{\perp out}^4 = E_b \cdot \alpha_{\perp out}$$

Projecting ($P_{\parallel}$, $P_{\perp in}$, $P_{\perp out}$) to (P_a, P_b, P_c), we have

$$P_a^4 = P_{//}^4 \cos\frac{\pi}{6} - P_{\perp in}^4 \sin\frac{\pi}{6} = E_a\left(\alpha_{//}\cos^2\frac{\pi}{6} + \alpha_{\perp in}\sin^2\frac{\pi}{6}\right) + E_c \sin\frac{\pi}{6}\cos\frac{\pi}{6}\left(\alpha_{\perp in} - \alpha_{//}\right)$$

$$P_b^4 = P_{\perp out}^4 = E_b \cdot \alpha_{\perp out}$$

$$P_c^4 = -P_{//}^4 \sin\frac{\pi}{6} - P_{\perp in}^4 \cos\frac{\pi}{6} = E_a \sin\frac{\pi}{6}\cos\frac{\pi}{6}\left(\alpha_{\perp in} - \alpha_{//}\right) + E_c\left(\alpha_{//}\sin^2\frac{\pi}{6} + \alpha_{\perp in}\cos^2\frac{\pi}{6}\right)$$

Therefore,

$$P_a = P_a^1 + P_a^2 + P_a^3 + P_a^4 = 4E_a\left(\alpha_{//}\cos^2\frac{\pi}{6} + \alpha_{\perp in}\sin^2\frac{\pi}{6}\right)$$

$$P_b = 0$$

$$P_c = P_c^1 + P_c^2 + P_c^3 + P_c^4 = 4E_c\left(\alpha_{//}\sin^2\frac{\pi}{6} + \alpha_{\perp in}\cos^2\frac{\pi}{6}\right)$$

Based on the relation $P_A = \sum_B \alpha_{AB} E_B (A, B = a, b, c)$, we have

$$\alpha_{aa} = 4\left(\alpha_{//}\cos^2\frac{\pi}{6} + \alpha_{\perp in}\sin^2\frac{\pi}{6}\right)$$

$$\alpha_{cc} = 4\left(\alpha_{//}\sin^2\frac{\pi}{6} + \alpha_{\perp in}\cos^2\frac{\pi}{6}\right)$$

$$\alpha_{ab} = \alpha_{ac} = \alpha_{ba} = \alpha_{bb} = \alpha_{bc} = \alpha_{ca} = \alpha_{cb} = 0$$

So for the ν_2 mode, only α_{aa} and α_{cc} are nonzero. Assuming that the dipole transition moments of C-H bonds in the ortho and meta positions are different (μ_{ortho} corresponds to r1 and r2, and μ_{meta} corresponds to r3 and r4), for ν_2 mode, only $\mu_{c,\nu 2} = 2(\mu_{ortho} - \mu_{meta})\sin\frac{\pi}{6}$ is nonzero. Therefore, only two hyperpolarizability tensor components $\beta_{aac,\nu 2}$ and $\beta_{ccc,\nu 2}$ are nonzero and their ratio can be obtained:

$$\frac{\beta_{ccc,\nu 2}}{\beta_{aac,\nu 2}} = \frac{\alpha'_{//}\sin^2\frac{\pi}{6} + \alpha'_{\perp in}\cos^2\frac{\pi}{6}}{\alpha'_{//}\cos^2\frac{\pi}{6} + \alpha'_{\perp in}\sin^2\frac{\pi}{6}} = \frac{2.6\sin^2\frac{\pi}{6} + 1.2\cos^2\frac{\pi}{6}}{2.6\cos^2\frac{\pi}{6} + 1.2\sin^2\frac{\pi}{6}} = 0.69$$

Similar treatment can be performed for the ν_{7b} mode. For C-H bonds r2 and r4, the projection is the same as that of the ν_2 mode. For C-H bonds r1 and r3, the diagonal single bond polariability tensors of ($\alpha_{\parallel}$, $\alpha_{\perp in}$, $\alpha_{\perp out}$) should be replaced by ($-\alpha_{\parallel}$, $-\alpha_{\perp in}$, $-\alpha_{\perp out}$)

in the projection. Therefore for the ν_{7b} mode

$$P_a = P_a^1 + P_a^2 + P_a^3 + P_a^4 = 4E_c \sin\frac{\pi}{6}\cos\frac{\pi}{6}\left(\alpha_{//} - \alpha_{\perp in}\right)$$

$$P_b = 0$$

$$P_c = P_c^1 + P_c^2 + P_c^3 + P_c^4 = 4E_a \sin\frac{\pi}{6}\cos\frac{\pi}{6}\left(\alpha_{//} - \alpha_{\perp in}\right)$$

So we have $\alpha_{ac} = \alpha_{ca} = 4\sin\frac{\pi}{6}\cos\frac{\pi}{6}\left(\alpha_{\perp in} - \alpha_{//}\right)$. For the ν_{7b} mode, only $\mu_{a,\nu 7b} = -2\left(\mu_{ortho} - \mu_{meta}\right)\cos\frac{\pi}{6}$ is nonzero. So we have only two nonzero hyperpolarizability components, $\beta_{aca,\nu 7b} = \beta_{caa,\nu 7b}$.

Now we can determine the relationship between the ν_2 and ν_{7b} modes:

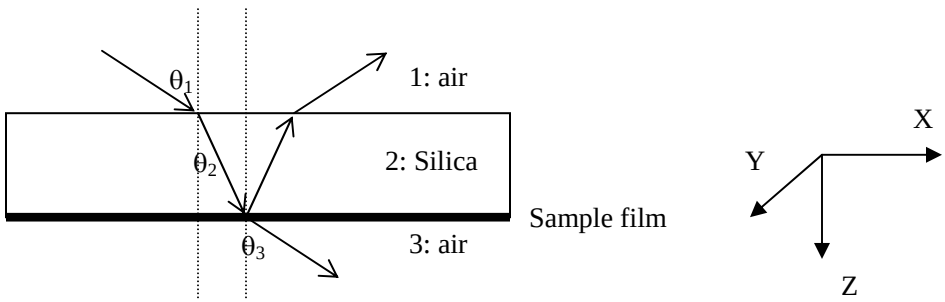
$$\frac{\beta_{aca,\nu 7b}}{\beta_{aac,\nu 2}} = \frac{\alpha'_{ac,\nu 7b}}{\alpha'_{aa,\nu 2}} \cdot \frac{\mu'_{c,\nu 7b}}{\mu'_{c,\nu 2}} = \frac{\sin\frac{\pi}{6}\cos\frac{\pi}{6}\left(\alpha'_{\perp in} - \alpha'_{//}\right)}{\left(\alpha'_{//}\cos^2\frac{\pi}{6} + \alpha'_{\perp in}\sin^2\frac{\pi}{6}\right)} \cdot \frac{-\left(\mu'_{ortho} - \mu'_{meta}\right)\cos\frac{\pi}{6}}{\left(\mu'_{ortho} - \mu'_{meta}\right)\sin\frac{\pi}{6}}$$

$$= \frac{\cos^2\frac{\pi}{6}\left(1.2 - 2.6\right)}{-\left(2.6\cos^2\frac{\pi}{6} + 1.2\sin^2\frac{\pi}{6}\right)} = \frac{4.2}{9} = 0.47$$

This value is similar to that reported by Duffy et. al[S3].

2. Fresnel coefficients

Considering the experimental geometry of the air/silica window/sample film/air (face-down geometry) system[S4], as shown in Fig. S2, Fresnel coefficients can be deduced.



S2. Face-down geometry for the SFG experiment.

Here we ignore the frequency dependence of refractive indices for the sum frequency, visible, and infrared beams for simplification. For the incidence beams (visible and infrared) at the interface between the media 1 and 2:

$$t_{12}^{s} = \frac{E_{i2}^{s}}{E_{i1}^{s}} = \frac{E_{i2}^{y}}{E_{i1}^{y}} = \frac{2n_1 \cos\theta_1}{n_1 \cos\theta_1 + n_2 \cos\theta_2}$$

$$t_{12}^{p} = \frac{E_{i2}^{p}}{E_{i1}^{p}} = \frac{E_{i2}^{x} / \cos\theta_2}{E_{i1}^{x} / \cos\theta_1} = \frac{E_{i2}^{z} / \sin\theta_2}{E_{i1}^{z} / \sin\theta_1} = \frac{2n_1 \cos\theta_1}{n_2 \cos\theta_1 + n_1 \cos\theta_2}$$

For the output beam (SF) at the interface between the media 2 and 1:

$$t_{21}^{s} = \frac{E_{o1}^{s}}{E_{o2}^{s}} = \frac{E_{o1}^{y}}{E_{o2}^{y}} = \frac{2n_2 \cos\theta_2}{n_2 \cos\theta_2 + n_1 \cos\theta_1}$$

$$t_{21}^{p} = \frac{E_{o1}^{p}}{E_{o2}^{p}} = \frac{E_{o1}^{x} / \cos\theta_1}{E_{o2}^{x} / \cos\theta_2} = \frac{E_{o1}^{z} / \sin\theta_1}{E_{o2}^{z} / \sin\theta_2} = \frac{2n_2 \cos\theta_2}{n_1 \cos\theta_2 + n_2 \cos\theta_1}$$

At the interface between the media 2 and 3, the sum frequency beam is generated. The Fresnel coefficients for this interface in the reflection geometry for both input and output beams can be calculated as:

$$l_{xx}^{in}(\omega)=\frac{E_{\text{int}}^{x}}{E_{i2}^{x}}=\frac{2n_2\cos\theta_3}{n_2\cos\theta_3+n_3\cos\theta_2}$$

$$l_{yy}^{in}(\omega)=\frac{E_{\text{int}}^{y}}{E_{i2}^{y}}=\frac{2n_2\cos\theta_2}{n_2\cos\theta_2+n_3\cos\theta_3}$$

$$l_{zz}^{in}(\omega)=\frac{E_{\text{int}}^{z}}{E_{i2}^{z}}=\frac{2n_3\cos\theta_2}{n_2\cos\theta_3+n_3\cos\theta_2}\left[\frac{n_2(\omega)}{n_{\text{int}}(\omega)}\right]^2$$

$$l_{xx}^{out}(\omega)=\frac{2n_2\cos\theta_3}{n_2\cos\theta_3+n_3\cos\theta_2}$$

$$l_{yy}^{out}(\omega)=\frac{2n_2\cos\theta_2}{n_2\cos\theta_2+n_3\cos\theta_3}$$

$$l_{zz}^{out}(\omega)=\frac{2n_3\cos\theta_2}{n_2\cos\theta_3+n_3\cos\theta_2}\left[\frac{n_2(\omega)}{n_{\text{int}}(\omega)}\right]^2$$

So we can derive the overall Fresnel coefficients for both the input and output beams by projection of the transmission of input beams at the interface between media 1 and 2 and output beam at same interface.

Input:

$$L_{xx}^{in}(\omega)=\frac{E_{\text{int}}^{x}}{E_{i1}^{x}}=l_{xx}(\omega)t_{12}^{p}\cos\theta_2$$

$$L_{yy}^{in}(\omega)=\frac{E_{\text{int}}^{y}}{E_{i1}^{y}}=l_{yy}(\omega)t_{12}^{s}$$

$$L_{zz}^{in}(\omega) = \frac{E_{\text{int}}^{z}}{E_{i1}^{z}} = l_{zz}(\omega) t_{12}^{p} \sin\theta_2$$

Output:

$$L_{xx}^{out}(\omega) = l_{xx}(\omega) t_{21}^{p} \cos\theta_2$$

$$L_{yy}^{out}(\omega) = l_{yy}(\omega) t_{21}^{s}$$

$$L_{zz}^{out}(\omega) = l_{zz}(\omega) t_{21}^{p} \sin\theta_2$$

So, we can obtain all the overall Fresnel coefficients.

$$F_{yyz} = L_{yy}^{out}(\omega) L_{yy}^{in}(\omega_1) L_{zz}^{in}(\omega_2)$$

$$F_{yzy} = L_{yy}^{out}(\omega) L_{zz}^{in}(\omega_1) L_{yy}^{in}(\omega_2)$$

$$F_{xxz} = -L_{xx}^{out}(\omega) L_{xx}^{in}(\omega_1) L_{zz}^{in}(\omega_2)$$

$$F_{xzx} = -L_{xx}^{out}(\omega) L_{zz}^{in}(\omega_1) L_{xx}^{in}(\omega_2)$$

$$F_{zxx} = L_{zz}^{out}(\omega) L_{xx}^{in}(\omega_1) L_{xx}^{in}(\omega_2)$$

$$F_{zzz} = L_{zz}^{out}(\omega) L_{zz}^{in}(\omega_1) L_{zz}^{in}(\omega_2)$$

3. Evaluation of the surface free energy

We used the geometric mean method to evaluate the surface free energies of DCPD, BPP, and their blend[S5]. This method divides the surface free energy into two parts, dispersive and polar, as shown in the following equation. Nonpolar diiodomethane and

polar water were used in our measurement.

$$\gamma_L(1+\cos\theta) = 2\left[\left(\gamma_L^p\right)^{1/2}\left(\gamma_S^p\right)^{1/2} + \left(\gamma_L^d\right)^{1/2}\left(\gamma_S^d\right)^{1/2}\right]$$

The surface free energies of the dispersive and polar contributions deduced using Fowkes' values[S5].

γH_2O, (mN·m^{-1})		γCH_2I_2, (mN·m^{-1})	
γ^d	γ^p	γ^d	γ^p
21.80	51.00	49.5	1.3

References:

S1. Hirose, C. K.; Akamatsu, N.; Domen, K. *J. Chem. Phys.* **1992**, 96, 997-1004. Wei, X.; Hong, S.-C.; Zhuang, X.; Goto, T.; Shen, Y. R. *Phys. Rev. E.* **2000**, 62, 5160-5172.

S2. Whiffen, D. H. Proc. Phys. Soc. 1956, 69A, 375-380.

S3. Duffy, D. C.; Davies, P. B.; Bain, C. D. *J. Phys. Chem.* **1995**, 99, 15241-15246.

S4. Wang, J.; Woodcock, S. E.; Buck, S. M.; Chen, C.; Chen, C. *J. Am. Chem. Soc.* **2001**, 123, 9470-9471.

S5. Owens, D. K.; Wendt, R. C. *J. Appl. Polym. Sci.* **1969**, 13, 1741-1747.