Supplementary information for
"Aiming at an Accurate Prediction of Vibrational and Electronic Spectra for Medium-to-Large Molecules: An Overview"

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1 DARLING-DENNISON RESONANCES

1.1 1-1 Terms: $\langle\, \boldsymbol{v}+1_i \mid \mathcal{H}' \mid \boldsymbol{v}+1_j \,\rangle$

$$\langle\, \boldsymbol{v}+1_i \mid \mathcal{H}' \mid \boldsymbol{v}+1_j \,\rangle = \frac{\sqrt{(v_i+1)(v_j+1)}}{2}\left\{\frac{3}{2}(v_i+1)\mathcal{K}_{ii;ij} + \frac{3}{2}(v_j+1)\mathcal{K}_{ij;jj} + \sum_{k=1 k\neq i,j}^{N}\left(v_k+\frac{1}{2}\right)\mathcal{K}_{ik;jk}\right\} \tag{1}$$

with

$$\begin{aligned}\mathcal{K}_{ii;ij} =& \frac{1}{6}k_{iiij} \\ & - \frac{1}{24}\sum_{l=1}^{N} k_{ijl}k_{iil}\left[\frac{1}{2\omega_i+\omega_l} + \frac{1}{\omega_l-2\omega_i} + \frac{4}{\omega_l}\right. \\ & \left. - \frac{2}{\omega_i-\omega_j-\omega_l} - \frac{2}{\omega_j-\omega_i-\omega_l} + \frac{1}{\omega_i+\omega_j+\omega_l} + \frac{1}{\omega_l-\omega_i-\omega_j}\right]\end{aligned} \tag{2}$$

$$\begin{aligned}\mathcal{K}_{ij;jj} =& \frac{1}{6}k_{ijjj} \\ & - \frac{1}{24}\sum_{l=1}^{N} k_{ijl}k_{jjl}\left[\frac{1}{2\omega_j+\omega_l} + \frac{1}{\omega_l-2\omega_j} + \frac{4}{\omega_l}\right. \\ & \left. - \frac{2}{\omega_j-\omega_i-\omega_l} - \frac{2}{\omega_i-\omega_j-\omega_l} + \frac{1}{\omega_i+\omega_j+\omega_l} + \frac{1}{\omega_l-\omega_i-\omega_j}\right]\end{aligned} \tag{3}$$

$$\begin{aligned}\mathcal{K}_{ik;jk} =& \frac{1}{2}k_{ijkk} + 2\sum_{\tau} B_{\tau}^{\mathrm{eq}}\frac{\zeta_{ik,\tau}\zeta_{jk,\tau}({\omega_k}^2+\omega_i\omega_j)}{\omega_k\sqrt{\omega_i\omega_j}} \\ & - \frac{1}{8}\sum_{l=1}^{N} k_{ikl}k_{jkl}\left[\frac{1}{\omega_i+\omega_k+\omega_l} + \frac{1}{\omega_l-\omega_i-\omega_k} + \frac{1}{\omega_j+\omega_k+\omega_l} + \frac{1}{\omega_l-\omega_j-\omega_k}\right. \\ & \left. - \frac{1}{\omega_i-\omega_k-\omega_l} - \frac{1}{\omega_k-\omega_i-\omega_l} - \frac{1}{\omega_j-\omega_k-\omega_l} - \frac{1}{\omega_k-\omega_j-\omega_l}\right] \\ & - \frac{1}{8}\sum_{l=1}^{N} k_{ijl}k_{kkl}\left[-\frac{1}{\omega_j-\omega_i-\omega_l} - \frac{1}{\omega_i-\omega_j-\omega_l} + \frac{2}{\omega_l}\right]\end{aligned} \tag{4}$$

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1.2 2-2 Terms: $\langle\, \boldsymbol{v} + 1_i + 1_j \mid \mathcal{H}' \mid \boldsymbol{v} + 1_k + 1_l \,\rangle$

1.2.1 2-2 Terms

$$\langle\, \boldsymbol{v} + 2_i \mid \mathcal{H}' \mid \boldsymbol{v} + 2_k \,\rangle = \frac{\sqrt{(v_i+1)(v_i+2)(v_k+1)(v_k+2)}}{4}\mathcal{K}_{ii;kk} \tag{5}$$

with

$$\begin{aligned}\mathcal{K}_{ii;kk} =& \frac{k_{iikk}}{4} - \sum_{\tau} B^{\text{eq}}_{\tau} \frac{{\zeta_{ik,\tau}}^2(\omega_i+\omega_k)^2}{\omega_i\omega_k} - \frac{1}{16}\sum_{m=1}^{N} k_{iim}k_{kkm}\left[\frac{1}{2\omega_i+\omega_m} + \frac{1}{\omega_m-2\omega_i} + \frac{1}{2\omega_k+\omega_m} + \frac{1}{\omega_m-2\omega_k}\right] \\ & - \frac{1}{4}\sum_{m=1}^{N} {k_{ijm}}^2\left[-\frac{1}{\omega_k-\omega_i-\omega_m} - \frac{1}{\omega_i-\omega_k-\omega_m}\right]\end{aligned} \tag{6}$$

1.2.2 2-11 Terms

$$\langle\, \boldsymbol{v} + 2_i \mid \mathcal{H}' \mid \boldsymbol{v} + 1_k + 1_l \,\rangle = \frac{\sqrt{(v_i+1)(v_i+2)(v_k+1)(v_l+1)}}{4}\mathcal{K}_{ii;kl} \tag{7}$$

with

$$\begin{aligned}\mathcal{K}_{ii;kl} =& \frac{k_{iikl}}{2} - 2\sum_{\tau} B^{\text{eq}}_{\tau} \frac{\zeta_{ik,\tau}\zeta_{il,\tau}(\omega_i+\omega_k)(\omega_i+\omega_l)}{\omega_i\sqrt{\omega_k\omega_l}} \\ & + \frac{1}{4}\sum_{m=1}^{N} k_{ikm}k_{ilm}\left[\frac{1}{\omega_k-\omega_i-\omega_m} + \frac{1}{\omega_i-\omega_k-\omega_m} + \frac{1}{\omega_l-\omega_i-\omega_m} + \frac{1}{\omega_i-\omega_l-\omega_m}\right] \\ & - \frac{1}{8}\sum_{m=1}^{N} k_{iim}k_{klm}\left[\frac{1}{2\omega_i+\omega_m} + \frac{1}{\omega_m-2\omega_i} + \frac{1}{\omega_k+\omega_l+\omega_m} + \frac{1}{\omega_m-\omega_k-\omega_l}\right]\end{aligned} \tag{8}$$

1.2.3 11-11 Terms

$$\langle\, \boldsymbol{v} + 1_i + 1_j \mid \mathcal{H}' \mid \boldsymbol{v} + 1_k + 1_l \,\rangle = \frac{\sqrt{(v_i+1)(v_j+1)(v_k+1)(v_l+1)}}{4}\mathcal{K}_{ij;kl} \tag{9}$$

with

$$\begin{aligned}\mathcal{K}_{ij;kl} =& k_{ijkl} + 2\sum_{\tau} B^{\text{eq}}_{\tau} \frac{\zeta_{ij,\tau}\zeta_{kl,\tau}(\omega_i-\omega_j)(\omega_l-\omega_k) - \zeta_{ik,\tau}\zeta_{jl,\tau}(\omega_i+\omega_k)(\omega_l+\omega_j) - \zeta_{il,\tau}\zeta_{jk,\tau}(\omega_i+\omega_l)(\omega_k+\omega_j)}{\sqrt{\omega_i\omega_j\omega_k\omega_l}} \\ & - \frac{1}{4}\sum_{m=1}^{N} k_{ijm}k_{klm}\left[\frac{1}{\omega_k+\omega_l+\omega_m} + \frac{1}{\omega_m-\omega_k-\omega_l} - \frac{1}{\omega_i+\omega_j+\omega_m} - \frac{1}{\omega_m-\omega_i-\omega_j}\right] \\ & + \frac{1}{4}\sum_{m=1}^{N} k_{ikm}k_{jlm}\left[\frac{1}{\omega_k-\omega_i-\omega_m} + \frac{1}{\omega_i-\omega_k-\omega_m} + \frac{1}{\omega_j-\omega_l-\omega_m} + \frac{1}{\omega_l-\omega_j-\omega_m}\right] \\ & + \frac{1}{4}\sum_{m=1}^{N} k_{ilm}k_{jkm}\left[\frac{1}{\omega_l-\omega_i-\omega_m} + \frac{1}{\omega_i-\omega_l-\omega_m} + \frac{1}{\omega_k-\omega_j-\omega_m} + \frac{1}{\omega_j-\omega_k-\omega_m}\right]\end{aligned} \tag{10}$$

Note that if the quartic force constants are obtained by numerical differentiation of analytic second derivatives of the energy, then k_{ijkl} is unknown.

2 TRANSITION MOMENTS

2.1 1-quantum Transition

$$
\begin{aligned}
\langle \boldsymbol{P} \rangle_{0,1_i} = & \frac{1}{\sqrt{2}}\boldsymbol{P}_i + \frac{1}{4\sqrt{2}}\sum_{j=1}^{N}\boldsymbol{P}_{ijj} - \frac{1}{8\sqrt{2}}\sum_{j,k=1}^{N} k_{ijkk}\boldsymbol{P}_j\left[\frac{1}{\omega_i+\omega_j} - \frac{1-\delta_{ij}}{\omega_i-\omega_j}\right] \\
& - \frac{1}{8\sqrt{2}}\sum_{j=1}^{N}\sum_{k=1}^{N}\left\{k_{ijk}\boldsymbol{P}_{jk}\left(\frac{1}{\omega_i+\omega_j+\omega_k} - \frac{1}{\omega_i-\omega_j-\omega_k}\right) + \frac{2k_{jkk}}{\omega_j}\boldsymbol{P}_{ij}\right\} \\
& + \frac{1}{2\sqrt{2}}\sum_{j,k=1}^{N}\left(\sum_{\tau=x,y,z} B_\tau^{\mathrm{eq}}\zeta_{ik,\tau}\zeta_{jk,\tau}\right)\boldsymbol{P}_j\left\{\frac{\sqrt{\omega_i\omega_j}}{\omega_k}\left(\frac{1}{\omega_i+\omega_j} + \frac{1-\delta_{ij}}{\omega_i-\omega_j}\right) - \frac{\omega_k}{\sqrt{\omega_i\omega_j}}\left(\frac{1}{\omega_i+\omega_j} - \frac{1-\delta_{ij}}{\omega_i-\omega_j}\right)\right\} \\
& + \frac{1}{16\sqrt{2}}\sum_{j,k,l=1}^{N} k_{ikl}k_{jkl}\boldsymbol{P}_j\left\{\frac{4\omega_j(\omega_k+\omega_l)(1-\delta_{ij})(1-\delta_{ik})(1-\delta_{il})}{({\omega_j}^2-{\omega_i}^2)\left[(\omega_k+\omega_l)^2-{\omega_i}^2\right]}\right. \\
& \quad + \frac{(\omega_k+\omega_l)\left[(\omega_k+\omega_l)^2-3{\omega_i}^2\right]\delta_{ij}(1+\delta_{ik})(1-\delta_{il})}{\omega_i\left[(\omega_k+\omega_l)^2-{\omega_i}^2\right]^2} \\
& \quad \left. + \frac{4\omega_j(3\omega_k+4\omega_i)(1-\delta_{ij})(1-\delta_{ik})\delta_{il}}{\omega_k({\omega_j}^2-{\omega_i}^2)(\omega_k+2\omega_i)}\right\} \\
& \quad + k_{ijk}k_{llk}\boldsymbol{P}_j\left\{\frac{\delta_{ij}}{\omega_i\omega_k}\left(1+\frac{2\delta_{ik}\delta_{il}}{9}\right) + \frac{4\omega_j(1-\delta_{ij})(1-\delta_{ik})(1-\delta_{il})}{\omega_k\left({\omega_j}^2-{\omega_i}^2\right)}\right. \\
& \quad \left. + \frac{4\omega_j\delta_{ik}(1-\delta_{ij})}{\omega_i({\omega_j}^2-{\omega_i}^2)}\left(1+\frac{2\delta_{ij}}{3}\right)\right\}
\end{aligned}
\tag{11}
$$

2.2 2-quanta Transition

$$
\langle \boldsymbol{P} \rangle_{0,(1+\delta_{ij})_i(1-\delta_{ij})_j} = \frac{1}{2(1+\delta_{ij})}\left[\boldsymbol{P}_{ij} + \frac{1}{2}\sum_{k=1}^{N} k_{ijk}\boldsymbol{P}_k\left(\frac{1}{\omega_i+\omega_j-\omega_k} - \frac{1}{\omega_i+\omega_j+\omega_k}\right)\right] \tag{12}
$$

3 FRANCK-CONDON INTEGRALS

3.1 0-0 transition integral

$$
\begin{aligned}
\langle \bar{\mathbf{0}} \mid \bar{\bar{\mathbf{0}}} \rangle = & 2^{N/2}\det\left(\bar{\boldsymbol{\Gamma}}\bar{\bar{\boldsymbol{\Gamma}}}\right)^{1/4}\left[\det(\boldsymbol{J})\det(\boldsymbol{Y})\right]^{1/2} \\
& \times\exp\left(-\frac{1}{2}\boldsymbol{K}^T\bar{\boldsymbol{\Gamma}}\boldsymbol{K} + \frac{1}{2}\boldsymbol{K}^T\bar{\boldsymbol{\Gamma}}\boldsymbol{J}\boldsymbol{T}\boldsymbol{J}^T\bar{\bar{\boldsymbol{\Gamma}}}\boldsymbol{K}\right)
\end{aligned}
\tag{13}
$$

with

$$
\boldsymbol{Y} = (\boldsymbol{J}^T\bar{\boldsymbol{\Gamma}}\boldsymbol{J} + \bar{\bar{\boldsymbol{\Gamma}}})^{-1}
$$

3.2 Recursion relations

$$
\langle \bar{\boldsymbol{v}} \mid \bar{\bar{\boldsymbol{v}}} \rangle = \frac{1}{\sqrt{2\bar{\bar{v}}_i}}\left[\mathrm{D}_i\langle \bar{\boldsymbol{v}} \mid \bar{\bar{\boldsymbol{v}}}-1_i \rangle + \sum_{j=1}^{N}\sqrt{2(\bar{\bar{v}}_j-\delta_{ij})}\mathrm{C}_{ij}\langle \bar{\boldsymbol{v}} \mid \bar{\bar{\boldsymbol{v}}}-1_i-1_j \rangle + \sum_{j=1}^{N}\sqrt{\bar{v}_j}\mathrm{E}_{ij}\langle \bar{\boldsymbol{v}}-1_j \mid \bar{\bar{\boldsymbol{v}}}-1_i \rangle\right] \tag{14}
$$

$$
\langle \bar{\boldsymbol{v}} \mid \bar{\bar{\boldsymbol{v}}} \rangle = \frac{1}{\sqrt{2\bar{v}_i}}\left[\mathrm{B}_i\langle \bar{\boldsymbol{v}}-1_i \mid \bar{\bar{\boldsymbol{v}}} \rangle + \sum_{j=1}^{N}\sqrt{2(\bar{v}_j-\delta_{ij})}\mathrm{A}_{ij}\langle \bar{\boldsymbol{v}}-1_i-1_j \mid \bar{\bar{\boldsymbol{v}}} \rangle + \sum_{j=1}^{N}\sqrt{\bar{\bar{v}}_j}\mathrm{E}_{ji}\langle \bar{\boldsymbol{v}}-1_i \mid \bar{\bar{\boldsymbol{v}}}-1_j \rangle\right] \tag{15}
$$

with

$$
\begin{aligned}
\boldsymbol{A} &= 2\bar{\boldsymbol{\Gamma}}^{1/2}\boldsymbol{J}\boldsymbol{Y}\boldsymbol{J}^T\bar{\boldsymbol{\Gamma}}^{1/2} - \boldsymbol{I} \\
\boldsymbol{B} &= -2\bar{\boldsymbol{\Gamma}}^{1/2}\big(\boldsymbol{J}\boldsymbol{Y}\boldsymbol{J}^T\bar{\boldsymbol{\Gamma}} - \boldsymbol{I}\big)\boldsymbol{K} \\
\boldsymbol{C} &= 2\bar{\bar{\boldsymbol{\Gamma}}}^{1/2}\boldsymbol{Y}\bar{\bar{\boldsymbol{\Gamma}}}^{1/2} - \boldsymbol{I} \\
\boldsymbol{D} &= -2\bar{\bar{\boldsymbol{\Gamma}}}^{1/2}\boldsymbol{Y}\boldsymbol{J}^T\bar{\boldsymbol{\Gamma}}\boldsymbol{K} \\
\boldsymbol{E} &= 4\bar{\bar{\boldsymbol{\Gamma}}}^{1/2}\boldsymbol{Y}\boldsymbol{J}^T\bar{\boldsymbol{\Gamma}}^{1/2}
\end{aligned}
$$