General formalism for vibronic Hamiltonians in tetragonal symmetry and beyond Supporting Information

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Section S1 Acting A-, B- and E_{+1}-projection operators on $f(w,\rho,\phi)$.

Acting the A-irrep projection operator on f gives a $\hat{C}_4$-eigenfunction with eigenvalue 1:

$$\begin{aligned}
f^{(1)}(w,\rho,\phi) &= f(w,\rho,\phi)+\hat{C}_4 f(w,\rho,\phi)+\hat{C}_4^2 f(w,\rho,\phi)+\hat{C}_4^3 f(w,\rho,\phi) \\
&= a_{m,n,K}\Big(w^m\rho^{|n|+2K}e^{in\phi}+(-w)^m\rho^{|n|+2K}e^{in\left(\phi-\frac{\pi}{2}\right)} \\
&\quad +w^m\rho^{|n|+2K}e^{in(\phi-\pi)}+(-w)^m\rho^{|n|+2K}e^{in\left(\phi-\frac{3\pi}{2}\right)}\Big) \\
&= a_{m,n,K}w^m\rho^{|n|+2K}e^{in\phi}\left(1+(-1)^m(-i)^n+(-1)^n+(-1)^m i^n\right) \\
&= a_{m,n,K}w^m\rho^{|n|+2K}e^{in\phi}\left(1+(-1)^n\right)\left(1+(-1)^m i^n\right) \\
&\quad [n \text{ needs to be even; } n\to 2n] \\
&= 2a_{m,2n,K}w^m\rho^{|2n|+2K}e^{i2n\phi}\left(1+(-1)^{(m+n)}\right) \\
&\quad [m+n \text{ needs to be even; } m\to \mathit{mod}(n,2)+2I] \\
&= a_{I,2n,K}w^{\mathit{mod}(n,2)+2I}\rho^{|2n|+2K}e^{i2n\phi}. \qquad \text{(S1)}
\end{aligned}$$

Acting the B-irrep projection operator on f gives an eigenfunction with eigenvalue -1:

$$\begin{aligned}
f^{(-1)}(w,\rho,\phi) &= f(w,\rho,\phi)-\hat{C}_4 f(w,\rho,\phi)+\hat{C}_4^2 f(w,\rho,\phi)-\hat{C}_4^3 f(w,\rho,\phi) \\
&= a_{m,n,K}w^m\rho^{|n|+2K}e^{in\phi}\left(1-(-1)^m(-i)^n+(-1)^n-(-1)^m i^n\right) \\
&= a_{m,n,K}w^m\rho^{|n|+2K}e^{in\phi}\left(1+(-1)^n\right)\left(1-(-1)^m i^n\right)\ [n \text{ needs to be even; } n\to 2n] \\
&= 2a_{m,2n,K}w^m\rho^{|2n|+2K}e^{i2n\phi}\left(1-(-1)^{(m+n)}\right) \\
&\quad [m+n \text{ needs to be odd; } m\to \mathit{mod}(n,2)+2I+1] \\
&= a_{I,2n,K}w^{\mathit{mod}(n,2)+2I+1}\rho^{|2n|+2K}e^{i2n\phi}. \qquad \text{(S2)}
\end{aligned}$$

Acting the E_{+1}-irrep projection operator generates an eigenfunction with eigenvalue i:

$$\begin{aligned}
f^{(i)}(w,\rho,\phi) &= f(w,\rho,\phi) - i\hat{C}_4 f(w,\rho,\phi) - \hat{C}_4^2 f(w,\rho,\phi) + i\hat{C}_4^3 f(w,\rho,\phi) \\
&= a_{m,n,K} w^m \rho^{|n|+2K} e^{in\phi} \left(1 - i(-1)^m (-i)^n - (-1)^n + i(-1)^m i^n\right) \\
&= a_{m,n,K} w^m \rho^{|n|+2K} e^{in\phi} \left(1 - (-1)^n\right)\left(1 + (-1)^m i^{n+1}\right) \;\; [n \text{ needs to be odd; } n \to 2n-1] \\
&= 2a_{m,2n-1,K} w^m \rho^{|2n-1|+2K} e^{i(2n-1)\phi} \left(1 + (-1)^{m+n}\right) \\
&\quad [m+n \text{ needs to be even; } m \to mod(n,2) + 2I] \\
&= a_{I,2n-1,K} w^{mod(n,2)+2I} \rho^{|2n-1|+2K} e^{i(2n-1)\phi}. \qquad \text{(S3)}
\end{aligned}$$

Section S2 Obtaining the $(e+b_2)$ expansions with $\left(\chi^{C_4},(\chi^{\sigma_v}_{Re},\chi^{\sigma_v}_{Im})\right)=(-1,(1,-1))$

Now the w in the $(e+b)$ expansion in Table 3 in the main text is for a b_2 mode, and the real and imaginary parts are

$$\begin{aligned} Re &= w^{mod(m,2)+2I+1}\left[b^{r,2m}_{2I,2K}\cos 2m\phi - b^{i,2m}_{2I,2K}\sin 2m\phi\right]; \\ Im &= w^{mod(m,2)+2I+1}\left[b^{r,2m}_{2I,2K}\sin 2m\phi + b^{i,2m}_{2I,2K}\cos 2m\phi\right]. \end{aligned} \tag{S4}$$

The $\rho^{|2m|+2K}$ factor is ignored as it does not transform under $\hat{\sigma}_v$. Acting $\hat{P}_{\sigma_v,e}$ and $\hat{P}_{\sigma_v,d}$ on Re and Im respectively,

$$\begin{aligned} \hat{P}_{\sigma_v,e}Re &= w^{mod(m,2)+2I+1}\left[b^{r,2m}_{2I,2K}\cos 2m\phi\left(1-(-1)^{mod(m,2)}\right) - b^{i,2m}_{2I,2K}\sin 2m\phi\left(1+(-1)^{mod(m,2)}\right)\right]; \\ \hat{P}_{\sigma_v,o}Im &= w^{mod(m,2)+2I+1}\left[b^{r,2m}_{2I,2K}\sin 2m\phi\left(1-(-1)^{mod(m,2)}\right) + b^{i,2m}_{2I,2K}\cos 2m\phi\left(1+(-1)^{mod(m,2)}\right)\right]. \end{aligned} \tag{S5}$$

Obviously, when m is even only the b^i terms survive and when m is odd only the b^r terms survive. Therefore, keeping only the b^r terms with odd m and the b^i terms with even m in the the $(e+b)$ formula in Eq. 3 gives the $(e+b_2)$ formula with $\left(\chi^{C_4},(\chi^{\sigma_v}_{Re},\chi^{\sigma_v}_{Im})\right)=(-1,(1,-1))$:

$$\begin{aligned} & b^{r,4k}_{2I,2K}w^{2I+1}\rho^{|4k|+2K}\left(\cos 4k\phi + i\sin 4k\phi\right) + ib^{i,4k+2}_{2I,2K}w^{2I}\rho^{|4k+2|+2K}\left(\cos\left(4k+2\right)\phi + i\sin\left(4k+2\right)\phi\right) \\ &\qquad = b^{r,4k}_{2I,2K}w^{2I+1}\rho^{|4k|+2K}e^{i4k\phi} + ib^{i,4k+2}_{2I,2K}w^{2I}\rho^{|4k+2|+2K}e^{i(4k+2)\phi}. \end{aligned} \tag{S6}$$

Here, m has been replaced by $2k$ and $2k+1$ to differentiate its being odd and even. Dropping the imaginary part gives the $(e+b_2)$ formula with $\left(\chi^{C_4},(\chi^{\sigma_v}_{Re},\chi^{\sigma_v}_{Im})\right)=(-1,(1,0))$:

$$b^{r,4k}_{2I,2K}w^{2I+1}\rho^{|4k|+2K}\cos 4k\phi - b^{i,4k+2}_{2I,2K}w^{2I}\rho^{|4k+2|+2K}\sin\left(4k+2\right)\phi. \tag{S7}$$

Section S3 Constraints on root expansions to obtain I-adapted expansions in C_{4h} symmetry

Table S1: Constraints on expansions in Table 2 in the main text to give the appropriate $\left(\chi^{C_4} = 1, \chi^I\right)$.

Vibrational Modes	$(1, 1)$	$(1, -1)$
$(a_g + a_g)$	nr	na
$(a_g + a_u)^\dagger$	I_2 even	I_2 odd
$(a_u + a_u)$	I_1, I_2 ee or oo	I_1, I_2 eo or oe
$(a_g + b_g)$, $(a_g + b_u)$	nr	na
$(a_u + b_g)$, $(a_u + b_u)$	I_1, I_2 even	I_1, I_2 odd
$(b_g + b_g)$, $(b_u + b_u)$	nr	na
$(b_g + b_u)$	a_{ee} nz	a_{oo} nz
$(e_g + a_g)$, $(e_u + a_g)$	nr	na
$(e_g + a_u)$, $(e_u + a_u)$	I even	I odd
$(e_g + b_g)$, $(e_u + b_g)$	nr	na
$(e_g + b_u)$, $(e_u + b_u)$	m even	m odd
$(e_g + e_g)$, $(e_u + e_u)$	nr	na
$(e_g + e_u)$	m_1 even	m_1 odd

† For two modes whose irreps only differ in subscripts, α-subscripted coordinates in Table 2 in the main text are for the first (a_g here) and β- for the second (a_u here) mode. This rule applies in all constraints tables in ESI and the main text.

Table S2: Constraints on expansions in Table 3 in the main text to give the appropriate $(\chi^{C_4} = -1, \chi^I)$.

Vibrational Modes	$(-1, 1)$	$(-1, -1)$
$(a_g + b_g)$	nr	na
$(a_g + b_u)$	na	nr
$(a_u + b_g)$	I_1 even	I_1 odd
$(a_u + b_u)$	I_1 odd	I_1 even
$(b_g + b_g)$	nr	na
$(b_g + b_u)$	b_{oe} nz	b_{eo} nz
$(b_u + b_u)$	na	nr
$(e_u + a_g)$, $(e_g + a_g)$	nr	na
$(e_u + a_u)$, $(e_g + a_u)$	I even	I odd
$(e_u + b_g)$, $(e_g + b_g)$	nr	na
$(e_u + b_u)$, $(e_g + b_u)$	m odd	m even
$(e_u + e_u)$	nr	na
$(e_u + e_g)$	m_1 even	m_1 odd
$(e_g + e_g)$	nr	na

Table S3: Constraints on expansions in Table 4 in the main text to give the appropriate $(\chi^{C_4} = i, \chi^I)$.

Vibrational Modes	$(i, 1)$	$(i, -1)$
$(e_g + a_g)$	nr	na
$(e_g + a_u)$	I even	I odd
$(e_u + a_g)$	na	nr
$(e_u + a_u)$	I odd	I even
$(e_g + b_g)$	nr	na
$(e_g + b_u)$	n even	n odd
$(e_u + b_g)$	na	nr
$(e_u + b_u)$	n odd	n even
$(e_g + e_g)$	nr	na
$(e_g + e_u)$	m_1 odd	m_1 even
$(e_u + e_u)$	na	nr