Revisiting the $(E+A)\otimes(e+a)$ problems of molecules with trigonal symmetry: general expansions of their vibronic Hamiltonians

Supporting Information

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Section S.1 Constraints on summing indices for the expansions of D_{3h} and D_{3d} $(E+A)\otimes(e+a)$ vibronic Hamiltonians

The C_3 $(E+A)\otimes(e+a)$ vibronic Hamiltonian has its general expansion shown in Eq. S.1. The Einstein's convention of summing duplicate indices is used. Compared to Eq. 25 in the main text, I_7, I_8, and $3m'$ in the H_{ZZ} expansion have been replaced by I_1, I_2, and $3m$. This is because the two sets of indices take the same values. The 64 D_{3h} $(E+A)\otimes(e+a)$ vibronic Hamiltonians can be obtained from Eq. S.1 with the extra constraints summarized in Table S.1. Some of the "not applicable"s (na) in the table arise from the incompatibility of the D_3 and C_{3h} constraints. For instance, for the $(E''+A_1'')\otimes(e'+a_2'')$ and $(E'+A_1')\otimes(e'+a_2'')$ cases, I_4 and I_6 needs to be even according to Table 2 in the main text but odd according to Table 1 in the main text. The incompatibility leads to the "na"s of the two indices for the two cases. Similarly, for the $(E''+A_2'')\otimes(e'+a_2'')$ and $(E'+A_2')\otimes(e'+a_2'')$ cases, I_4 and I_5 need to be even according to Table 2 but odd according to Table 1. The incompatibility again leads to the "na"s of the two indices for the two cases. Due to the isomorphism of the D_{3h} and D_{3d} groups, the D_{3d} $(E+A)\otimes(e+a)$ vibronic Hamiltonians share the same constraint table with D_{3h}, simply with the prime and double-prime of the irreducible representations being replaced by the subscripts g and u. The D_{3d} constraints are given in Table S.2.

$$
\begin{aligned}
\hat{H} \;=\; & \left(|X\rangle\,|Y\rangle\,|Z\rangle\right) \\
& \begin{pmatrix}
\begin{gathered} a^{r,3m}_{I_1,2K} z^{I_1} \rho^{3m+2K} \cos(3m\phi) \\ -a^{i,3m}_{I_2,2K} z^{I_2} \rho^{3m+2K} \sin(3m\phi) \\ +b^{r,3n+1}_{I_3,2K} z^{I_3} \rho^{|3n+1|+2K} \cos((3n+1)\phi) \\ -b^{i,3n+1}_{I_4,2K} z^{I_4} \rho^{|3n+1|+2K} \sin((3n+1)\phi) \end{gathered} & \begin{gathered} -b^{r,3n+1}_{I_3,2K} z^{I_3} \rho^{|3n+1|+2K} \sin((3n+1)\phi) \\ -b^{i,3n+1}_{I_4,2K} z^{I_4} \rho^{|3n+1|+2K} \cos((3n+1)\phi) \end{gathered} & \begin{gathered} d^{r,3n'+1}_{I_5,2K} z^{I_5} \rho^{|3n'+1|+2K} \cos((3n'+1)\phi) \\ +d^{i,3n'+1}_{I_6,2K} z^{I_6} \rho^{|3n'+1|+2K} \sin((3n'+1)\phi) \end{gathered} \\
 & \begin{gathered} a^{3m}_{I_1,2K} z^{I_1} \rho^{3m+2K} \cos(3m\phi) \\ -a^{i,3m}_{I_2,2K} z^{I_2} \rho^{3m+2K} \sin(3m\phi) \\ -b^{r,3n+1}_{I_3,2K} z^{I_3} \rho^{|3n+1|+2K} \cos((3n+1)\phi) \\ +b^{i,3n+1}_{I_4,2K} z^{I_4} \rho^{|3n+1|+2K} \sin((3n+1)\phi) \end{gathered} & \begin{gathered} d^{r,3n'+1}_{I_5,2K} z^{I_5} \rho^{|3n'+1|+2K} \sin((3n'+1)\phi) \\ -d^{i,3n'+1}_{I_6,2K} z^{I_6} \rho^{|3n'+1|+2K} \cos((3n'+1)\phi) \end{gathered} \\
 & & \begin{gathered} c^{3m'}_{I_7,2K} z^{I_7} \rho^{3m'+2K} \cos(3m'\phi) \\ -c^{i,3m'}_{I_8,2K} z^{I_8} \rho^{3m'+2K} \sin(3m'\phi) \end{gathered}
\end{pmatrix} \\
& \begin{pmatrix} \langle X| \\ \langle Y| \\ \langle Z| \end{pmatrix}, m, m', K, I_{1-8} = 0, 1, 2, \cdots; 3n+1, 3n'+1 = \cdots, -2, -1, 0, 1, 2, \cdots
\end{aligned}
\tag{S.1}
$$

Table S.1: Constraints on the summing indices for the $(E+A)\otimes(e+a)$ vibronic Hamiltonian expansions for D_{3h} molecules.[a]

	$I_{1,3,7}$	$I_{2,4,8}$	$3m, 3n+1, 3m'$	I_5	I_6	$3n'+1$
$(E''+A_1'')\otimes(e'+a_1')$, $(E'+A_1')\otimes(e'+a_1')$	nr	na	nr	nr	na	nr
$(E''+A_1'')\otimes(e'+a_2')$, $(E'+A_1')\otimes(e'+a_2')$	even	odd	nr	even	odd	nr
$(E''+A_2'')\otimes(e'+a_1')$, $(E'+A_2')\otimes(e'+a_1')$	nr	na	nr	na	nr	nr
$(E''+A_2'')\otimes(e'+a_2')$, $(E'+A_2')\otimes(e'+a_2')$	even	odd	nr	odd	even	nr
$(E''+A_1'')\otimes(e''+a_1')$, $(E'+A_1')\otimes(e''+a_1')$	nr	na	even	nr	na	even
$(E''+A_1'')\otimes(e''+a_2')$, $(E'+A_1')\otimes(e''+a_2')$	even	odd	even	even	odd	even
$(E''+A_2'')\otimes(e''+a_1')$, $(E'+A_2')\otimes(e''+a_1')$	nr	na	even	na	nr	even
$(E''+A_2'')\otimes(e''+a_2')$, $(E'+A_2')\otimes(e''+a_2')$	even	odd	even	odd	even	even
$(E''+A_1'')\otimes(e'+a_1'')$, $(E'+A_1')\otimes(e'+a_1'')$	even	na	nr	even	na	nr
$(E''+A_1'')\otimes(e'+a_2'')$, $(E'+A_1')\otimes(e'+a_2'')$	even	na	nr	even	na	nr
$(E''+A_2'')\otimes(e'+a_1'')$, $(E'+A_2')\otimes(e'+a_1'')$	even	na	nr	na	even	nr
$(E''+A_2'')\otimes(e'+a_2'')$, $(E'+A_2')\otimes(e'+a_2'')$	even	na	nr	na	even	nr
$(E''+A_1'')\otimes(e''+a_1'')$, $(E'+A_1')\otimes(e''+a_1'')$	(even odd	na	even odd)	(even odd	na	even odd)
$(E''+A_1'')\otimes(e''+a_2'')$, $(E'+A_1')\otimes(e''+a_2'')$	(even na	na odd	even odd)	(even na	na odd	even odd)
$(E''+A_2'')\otimes(e''+a_1'')$, $(E'+A_2')\otimes(e''+a_1'')$	(even odd	na	even odd)	na	(even odd	even odd)
$(E''+A_2'')\otimes(e''+a_2'')$, $(E'+A_2')\otimes(e''+a_2'')$	(even na	na odd	even odd)	(na odd	even na	even odd)
$(E''+A_1')\otimes(e'+a_1')$, $(E'+A_1'')\otimes(e'+a_1')$	nr	na	nr	na	na	na
$(E''+A_1')\otimes(e'+a_2')$, $(E'+A_1'')\otimes(e'+a_2')$	even	odd	nr	na	na	na
$(E''+A_2')\otimes(e'+a_1')$, $(E'+A_2'')\otimes(e'+a_1')$	nr	na	nr	na	na	na
$(E''+A_2')\otimes(e'+a_2')$, $(E'+A_2'')\otimes(e'+a_2')$	even	odd	nr	na	na	na
$(E''+A_1')\otimes(e''+a_1')$, $(E'+A_1'')\otimes(e''+a_1')$	nr	na	even	nr	na	odd
$(E''+A_1')\otimes(e''+a_2')$, $(E'+A_1'')\otimes(e''+a_2')$	even	odd	even	even	odd	odd
$(E''+A_2')\otimes(e''+a_1')$, $(E'+A_2'')\otimes(e''+a_1')$	nr	na	even	na	nr	odd
$(E''+A_2')\otimes(e''+a_2')$, $(E'+A_2'')\otimes(e''+a_2')$	even	odd	even	odd	even	odd
$(E''+A_1')\otimes(e'+a_1'')$, $(E'+A_1'')\otimes(e'+a_1'')$	even	na	nr	odd	na	nr
$(E''+A_1')\otimes(e'+a_2'')$, $(E'+A_1'')\otimes(e'+a_2'')$	even	na	nr	na	odd	nr
$(E''+A_2')\otimes(e'+a_1'')$, $(E'+A_2'')\otimes(e'+a_1'')$	even	na	nr	na	odd	nr
$(E''+A_2')\otimes(e'+a_2'')$, $(E'+A_2'')\otimes(e'+a_2'')$	even	na	nr	odd	na	nr

table continues

	$I_{1,3,7}$	$I_{2,4,8}$	$3m, 3m', 3n+1$	I_5	I_6	$3n'+1$
$(E''+A'_1)\otimes(e''+a''_1)$, $(E'+A''_1)\otimes(e''+a''_1)$	(even	na	even)	(even	na	odd)
	(odd		odd)	(odd		even)
$(E''+A'_1)\otimes(e''+a''_2)$, $(E'+A''_1)\otimes(e''+a''_2)$	(even	na	even)	(even	na	odd)
	(na	odd	odd)	(na	odd	even)
$(E''+A'_2)\otimes(e''+a''_1)$, $(E'+A''_2)\otimes(e''+a''_1)$	(even	na	even)	na	(even	odd)
	(odd		odd)		(odd	even)
$(E''+A'_2)\otimes(e''+a''_2)$, $(E'+A''_2)\otimes(e''+a''_2)$	(even	na	even)	(na	even	odd)
	(na	odd	odd)	(odd	na	even)

[a] "nr" and "na" stand for "no further restriction" other than indicated in Eq. S.1 and "not applicable", respectively. Terms with the "na" indices should be zeroed. Some rows are split to accommodate possible combinations of constraints within each pairs of parentheses.

Table S.2: Constraints on the summing indices for the $(E + A) \otimes (e + a)$ vibronic Hamiltonian expansions for D_{3d} molecules.[a]

	$I_{1,3,7}$	$I_{2,4,8}$	$3m, 3n+1, 3m'$	I_5	I_6	$3n'+1$
$(E_u + A_{1u}) \otimes (e_g + a_{1g})$, $(E_g + A_{1g}) \otimes (e_g + a_{1g})$	nr	na	nr	nr	na	nr
$(E_u + A_{1u}) \otimes (e_g + a_{2g})$, $(E_g + A_{1g}) \otimes (e_g + a_{2g})$	even	odd	nr	even	odd	nr
$(E_u + A_{2u}) \otimes (e_g + a_{1g})$, $(E_g + A_{2g}) \otimes (e_g + a_{1g})$	nr	na	nr	na	nr	nr
$(E_u + A_{2u}) \otimes (e_g + a_{2g})$, $(E_g + A_{2g}) \otimes (e_g + a_{2g})$	even	odd	nr	odd	even	nr
$(E_u + A_{1u}) \otimes (e_u + a_{1g})$, $(E_g + A_{1g}) \otimes (e_u + a_{1g})$	nr	na	even	nr	na	even
$(E_u + A_{1u}) \otimes (e_u + a_{2g})$, $(E_g + A_{1g}) \otimes (e_u + a_{2g})$	even	odd	even	even	odd	even
$(E_u + A_{2u}) \otimes (e_u + a_{1g})$, $(E_g + A_{2g}) \otimes (e_u + a_{1g})$	nr	na	even	na	nr	even
$(E_u + A_{2u}) \otimes (e_u + a_{2g})$, $(E_g + A_{2g}) \otimes (e_u + a_{2g})$	even	odd	even	odd	even	even
$(E_u + A_{1u}) \otimes (e_g + a_{1u})$, $(E_g + A_{1g}) \otimes (e_g + a_{1u})$	even	na	nr	even	na	nr
$(E_u + A_{1u}) \otimes (e_g + a_{2u})$, $(E_g + A_{1g}) \otimes (e_g + a_{2u})$	even	na	nr	even	na	nr
$(E_u + A_{2u}) \otimes (e_g + a_{1u})$, $(E_g + A_{2g}) \otimes (e_g + a_{1u})$	even	na	nr	na	even	nr
$(E_u + A_{2u}) \otimes (e_g + a_{2u})$, $(E_g + A_{2g}) \otimes (e_g + a_{2u})$	even	na	nr	na	even	nr
$(E_u + A_{1u}) \otimes (e_u + a_{1u})$, $(E_g + A_{1g}) \otimes (e_u + a_{1u})$	(even odd	na	even odd)	(even odd	na	even odd)
$(E_u + A_{1u}) \otimes (e_u + a_{2u})$, $(E_g + A_{1g}) \otimes (e_u + a_{2u})$	(even na	na odd	even odd)	(even na	na odd	even odd)
$(E_u + A_{2u}) \otimes (e_u + a_{1u})$, $(E_g + A_{2g}) \otimes (e_u + a_{1u})$	(even odd	na	even odd)	na	(even odd	even odd)
$(E_u + A_{2u}) \otimes (e_u + a_{2u})$, $(E_g + A_{2g}) \otimes (e_u + a_{2u})$	(even na	na odd	even odd)	(na odd	even na	even odd)
$(E_u + A_{1g}) \otimes (e_g + a_{1g})$, $(E_g + A_{1u}) \otimes (e_g + a_{1g})$	nr	na	nr	na	na	na
$(E_u + A_{1g}) \otimes (e_g + a_{2g})$, $(E_g + A_{1u}) \otimes (e_g + a_{2g})$	even	odd	nr	na	na	na
$(E_u + A_{2g}) \otimes (e_g + a_{1g})$, $(E_g + A_{2u}) \otimes (e_g + a_{1g})$	nr	na	nr	na	na	na
$(E_u + A_{2g}) \otimes (e_g + a_{2g})$, $(E_g + A_{2u}) \otimes (e_g + a_{2g})$	even	odd	nr	na	na	na
$(E_u + A_{1g}) \otimes (e_u + a_{1g})$, $(E_g + A_{1u}) \otimes (e_u + a_{1g})$	nr	na	even	nr	na	odd
$(E_u + A_{1g}) \otimes (e_u + a_{2g})$, $(E_g + A_{1u}) \otimes (e_u + a_{2g})$	even	odd	even	even	odd	odd
$(E_u + A_{2g}) \otimes (e_u + a_{1g})$, $(E_g + A_{2u}) \otimes (e_u + a_{1g})$	nr	na	even	na	nr	odd
$(E_u + A_{2g}) \otimes (e_u + a_{2g})$, $(E_g + A_{2u}) \otimes (e_u + a_{2g})$	even	odd	even	odd	even	odd
$(E_u + A_{1g}) \otimes (e_g + a_{1u})$, $(E_g + A_{1u}) \otimes (e_g + a_{1u})$	even	na	nr	odd	na	nr
$(E_u + A_{1g}) \otimes (e_g + a_{2u})$, $(E_g + A_{1u}) \otimes (e_g + a_{2u})$	even	na	nr	na	odd	nr
$(E_u + A_{2g}) \otimes (e_g + a_{1u})$, $(E_g + A_{2u}) \otimes (e_g + a_{1u})$	even	na	nr	na	odd	nr
$(E_u + A_{2g}) \otimes (e_g + a_{2u})$, $(E_g + A_{2u}) \otimes (e_g + a_{2u})$	even	na	nr	odd	na	nr

table continue						
	$I_{1,3,7}$	$I_{2,4,8}$	$3m, 3m', 3n+1$	I_5	I_6	$3n'+1$
$(E_u + A_{1g}) \otimes (e_u + a_{1u})$, $(E_g + A_{1u}) \otimes (e_u + a_{1u})$	even odd	na	even odd	even odd	na	odd even
$(E_u + A_{1g}) \otimes (e_u + a_{2u})$, $(E_g + A_{1u}) \otimes (e_u + a_{2u})$	even na	na odd	even odd	even na	na odd	odd even
$(E_u + A_{2g}) \otimes (e_u + a_{1u})$, $(E_g + A_{2u}) \otimes (e_u + a_{1u})$	even odd	na	even odd	na	even odd	odd even
$(E_u + A_{2g}) \otimes (e_u + a_{2u})$, $(E_g + A_{2u}) \otimes (e_u + a_{2u})$	even na	na odd	even odd	na odd	even na	odd even

[a] "nr" and "na" stand for "no further restriction" other than indicated in Eq. S.1 and "not applicable", respectively. Terms with the "na" indices should be zeroed. Some rows are split to accommodate possible combinations of constraints within each pairs of parentheses.

Section S.2 The 9-th and 10-th order expansions of the D_{3h} $(E' + A_2'') \otimes (e' + a_2'')$ vibronic Hamiltonian

Table S.3: Allowed summing indices in constructing the D_{3h} $(E' + A_2'') \otimes (e' + a_2'')$ vibronic Hamiltonian expansion at the 9-th and 10-th orders.

Order	I_1	$3m$	$2K$	I_3	$3n+1$	$2K$	I_5	$3n'+1$	$2K$	Order	I_1	$3m$	$2K$	I_3	$3n+1$	$2K$	I_5	$3n'+1$	$2K$
9	6	3	0	8	1	0	7	-2	0	10	10	0	0	8	-2	0	9	1	0
	4	3	2	6	1	2	5	-2	2		8	0	2	6	-2	2	7	1	2
	2	3	4	4	1	4	3	-2	4		6	0	4	4	-2	4	5	1	4
	0	3	6	2	1	6	1	-2	6		4	0	6	2	-2	6	3	1	6
	0	9	0	0	1	8	5	4	0		2	0	8	0	-2	8	1	1	8
				4	-5	0	3	4	2		0	0	10	6	4	0	5	-5	0
				2	-5	2	1	4	4		4	6	0	4	4	2	3	-5	2
				0	-5	4	1	-8	0		2	6	2	2	4	4	1	-5	4
				2	7	0					0	6	4	0	4	6	3	7	0
				0	7	2								2	-8	0	1	7	2
														0	-8	2			
														0	10	0			

The allowed summing indices for 9-th and 10-th order expansions of the D_{3h} $(E' + A_2'') \otimes (e' + a_2'')$ vibronic Hamiltonian are summarized in Table S.3. Using the table and Eq. S.1, we obtain the following 9-th order expansions:

$$
\begin{aligned}
H_{XX}^{(9)} &= a_{0,0}^{9}\rho^9\cos 9\phi + a_{0,6}^{3}\rho^9\cos 3\phi + a_{2,4}^{3}z^2\rho^7\cos 3\phi + a_{4,2}^{3}z^4\rho^5\cos 3\phi + a_{6,0}^{3}z^6\rho^3\cos 3\phi \\
&+b_{0,2}^{r,7}\rho^9\cos 7\phi + b_{2,0}^{r,7}z^2\rho^7\cos 7\phi + b_{0,4}^{r,-5}\rho^9\cos(-5\phi) + b_{2,2}^{r,-5}z^2\rho^7\cos(-5\phi) + b_{4,0}^{r,-5}z^4\rho^5\cos(-5\phi) \\
&+b_{0,8}^{r,1}\rho^9\cos\phi + b_{2,6}^{r,1}z^2\rho^7\cos\phi + b_{4,4}^{r,7}z^4\rho^5\cos\phi + b_{6,2}^{r,1}z^6\rho^3\cos\phi + b_{8,0}^{r,1}z^8\rho\cos\phi \\
&= a_{0,0}^{9}\left(x^9 - 36x^7y^2 + 126x^5y^4 - 84x^3y^6 + 9xy^8\right) + a_{0,6}^{3}\left(x^2+y^2\right)^3\left(x^3-3xy^2\right) \\
&+a_{2,4}^{3}z^2\left(x^2+y^2\right)^2\left(x^3-3xy^2\right) + a_{4,2}^{3}z^4\left(x^2+y^2\right)\left(x^3-3xy^2\right) + a_{6,0}^{3}z^6\left(x^3-3xy^2\right) \\
&+b_{0,2}^{r,7}\left(x^2+y^2\right)\left(x^7-21x^5y^2+35x^3y^4-7xy^6\right) + b_{2,0}^{r,7}z^2\left(x^7-21x^5y^2+35x^3y^4-7xy^6\right) \\
&+b_{0,4}^{r,-5}\left(x^2+y^2\right)^2\left(x^5-10x^3y^2+5xy^4\right) + b_{2,2}^{r,-5}z^2\left(x^2+y^2\right)\left(x^5-10x^3y^2+5xy^4\right) \\
&+b_{4,0}^{r,-5}z^4\left(x^5-10x^3y^2+5xy^4\right) + b_{0,8}^{r,1}\left(x^2+y^2\right)^4x + b_{2,6}^{r,1}z^2\left(x^2+y^2\right)^3x + b_{4,4}^{r,1}z^4\left(x^2+y^2\right)^2x \\
&+b_{6,2}^{r,1}z^6\left(x^2+y^2\right)x + b_{8,0}^{r,1}z^8x; \qquad \text{(S.2)}
\end{aligned}
$$

$$
\begin{aligned}
H_{XY}^{(9)} &= -b_{0,2}^{r,7}\rho^9\sin 7\phi - b_{2,0}^{r,7}z^2\rho^7\sin 7\phi - b_{0,4}^{r,-5}\rho^9\sin(-5\phi) - b_{2,2}^{r,-5}z^2\rho^7\sin(-5\phi) - b_{4,0}^{r,-5}z^4\rho^5\sin(-5\phi)\\
&\quad -b_{0,8}^{r,1}\rho^9\sin\phi - b_{2,6}^{r,1}z^2\rho^7\sin\phi - b_{4,4}^{r,7}z^4\rho^5\sin\phi - b_{6,2}^{r,1}z^6\rho^3\sin\phi - b_{8,0}^{r,1}z^8\rho\sin\phi\\
&= -b_{0,2}^{r,7}\left(x^2+y^2\right)\left(-y^7+21x^2y^5-35x^4y^3+7x^6y\right) - b_{2,0}^{r,7}z^2\left(-y^7+21x^2y^5-35x^4y^3+7x^6y\right)\\
&\quad -b_{0,4}^{r,-5}\left(x^2+y^2\right)^2\left(-y^5+10x^2y^3-5x^4y\right) - b_{2,2}^{r,-5}z^2\left(x^2+y^2\right)\left(-y^5+10x^2y^3-5x^4y\right)\\
&\quad -b_{4,0}^{r,-5}z^4\left(-y^5+10x^2y^3-5x^4y\right) - b_{0,8}^{r,1}\left(x^2+y^2\right)^4 y - b_{2,6}^{r,1}z^2\left(x^2+y^2\right)^3 y - b_{4,4}^{r,1}z^4\left(x^2+y^2\right)^2 y\\
&\quad -b_{6,2}^{r,1}z^6\left(x^2+y^2\right)y - b_{8,0}^{r,1}z^8 y; \qquad \text{(S.3)}
\end{aligned}
$$

$$
\begin{aligned}
H_{XZ}^{(9)} &= d_{1,0}^{r,-8}z\rho^8\cos(-8\phi) + d_{1,4}^{r,4}z\rho^8\cos 4\phi + d_{3,2}^{r,4}z^3\rho^6\cos 4\phi + d_{5,0}^{r,4}z^5\rho^4\cos 4\phi + d_{1,6}^{r,-2}z\rho^8\cos(-2\phi)\\
&\quad +d_{3,4}^{r,-2}z^3\rho^6\cos(-2\phi) + d_{5,2}^{r,-2}z^5\rho^4\cos(-2\phi) + d_{7,0}^{r,-2}z^7\rho^2\cos(-2\phi)\\
&= d_{1,0}^{r,-8}z\left(x^8-28x^6y^2+70x^4y^4-28x^2y^6+y^8\right) + d_{1,4}^{r,4}z\left(x^2+y^2\right)^2\left(x^4+y^4-6x^2y^2\right)\\
&\quad +d_{3,2}^{r,4}z^3\left(x^2+y^2\right)\left(x^4+y^4-6x^2y^2\right) + d_{5,0}^{r,4}z^5\left(x^4+y^4-6x^2y^2\right) + d_{1,6}^{r,-2}z\left(x^2+y^2\right)^3\left(x^2-y^2\right)\\
&\quad +d_{3,4}^{r,-2}z^3\left(x^2+y^2\right)^2\left(x^2-y^2\right) + d_{5,2}^{r,-2}z^5\left(x^2+y^2\right)\left(x^2-y^2\right) + d_{7,0}^{r,-2}z^7\left(x^2-y^2\right); \qquad \text{(S.4)}
\end{aligned}
$$

$$
\begin{aligned}
H_{YZ}^{(9)} &= d_{1,0}^{r,-8}z\rho^8\sin(-8\phi) + d_{1,4}^{r,4}z\rho^8\sin 4\phi + d_{3,2}^{r,4}z^3\rho^6\sin 4\phi + d_{5,0}^{r,4}z^5\rho^4\sin 4\phi + d_{1,6}^{r,-2}z\rho^8\sin(-2\phi)\\
&\quad +d_{3,4}^{r,-2}z^3\rho^6\sin(-2\phi) + d_{5,2}^{r,-2}z^5\rho^4\sin(-2\phi) + d_{7,0}^{r,-2}z^7\rho^2\sin(-2\phi)\\
&= d_{1,0}^{r,-8}z\left(-8x^7y+56x^5y^3-56x^3y^5+8xy^7\right) + d_{1,4}^{r,4}z\left(x^2+y^2\right)^2 4xy\left(x^2-y^2\right)\\
&\quad +d_{3,2}^{r,4}z^3\left(x^2+y^2\right)4xy\left(x^2-y^2\right) + d_{5,0}^{r,4}z^5 4xy\left(x^2-y^2\right) + d_{1,6}^{r,-2}z\left(x^2+y^2\right)^3(-2xy)\\
&\quad +d_{3,4}^{r,-2}z^3\left(x^2+y^2\right)^2(-2xy) + d_{5,2}^{r,-2}z^5\left(x^2+y^2\right)(-2xy) + d_{7,0}^{r,-2}z^7(-2xy). \qquad \text{(S.5)}
\end{aligned}
$$

Flipping the signs of all the $b_{I_3,2K}^{r,3n+1}$ terms in $H_{XX}^{(9)}$ gives $H_{YY}^{(9)}$. Taking all $a_{I1,2K}^{3m}$ terms in $H_{XX}^{(9)}$ and replacing the coefficients $a_{I_1,2K}^{3m}$ by $c_{I_1,2K}^{3m}$ gives $H_{ZZ}^{(9)}$.

The 10-th order expansions are:

$$
\begin{aligned}
H_{XX}^{(10)} &= a_{0,4}^{6}\rho^{10}\cos 6\phi + a_{2,2}^{6}z^{2}\rho^{8}\cos 6\phi + a_{4,0}^{6}z^{4}\rho^{6}\cos 6\phi + a_{0,10}^{0}\rho^{10} + a_{2,8}^{0}z^{2}\rho^{8} + a_{4,6}^{0}z^{4}\rho^{6} + a_{6,4}^{0}z^{6}\rho^{4} \\
&\quad + a_{8,2}^{0}z^{8}\rho^{2} + a_{10,0}^{0}z^{10} + b_{0,0}^{r,10}\rho^{10}\cos 10\phi + b_{0,2}^{r,-8}\rho^{10}\cos(-8\phi) + b_{2,0}^{r,-8}z^{2}\rho^{8}\cos(-8\phi) \qquad \text{(S.6)} \\
&\quad + b_{0,6}^{r,4}\rho^{10}\cos 4\phi + b_{2,4}^{r,4}z^{2}\rho^{8}\cos 4\phi + b_{4,2}^{r,4}z^{4}\rho^{6}\cos 4\phi + b_{6,0}^{r,4}z^{6}\rho^{4}\cos 4\phi + b_{0,8}^{r,-2}\rho^{10}\cos(-2\phi) \\
&\quad + b_{2,6}^{r,-2}z^{2}\rho^{8}\cos(-2\phi) + b_{4,4}^{r,-2}z^{4}\rho^{6}\cos(-2\phi) + b_{6,2}^{r,-2}z^{6}\rho^{4}\cos(-2\phi) + b_{8,0}^{r,-2}z^{8}\rho^{2}\cos(-2\phi) \\
&= a_{0,4}^{6}\left(x^2+y^2\right)^2\left(x^6-15x^4y^2+15x^2y^4-y^6\right) + a_{2,2}^{6}z^2\left(x^2+y^2\right)\left(x^6-15x^4y^2+15x^2y^4-y^6\right) \\
&\quad + a_{4,0}^{6}z^4\left(x^6-15x^4y^2+15x^2y^4-y^6\right) + a_{0,10}^{0}\left(x^2+y^2\right)^5 + a_{2,8}^{0}z^2\left(x^2+y^2\right)^4 + a_{4,6}^{0}z^4\left(x^2+y^2\right)^3 \\
&\quad + a_{6,4}^{0}z^6\left(x^2+y^2\right)^2 + a_{8,2}^{0}z^8\left(x^2+y^2\right) + a_{10,0}^{0}z^{10} \\
&\quad + b_{0,0}^{r,10}\left(x^{10}-45x^8y^2+210x^6y^4-210x^4y^6+45x^2y^8-y^{10}\right) \\
&\quad + b_{0,2}^{r,-8}\left(x^2+y^2\right)\left(x^8-28x^6y^2+70x^4y^4-28x^2y^6+y^8\right) \\
&\quad + b_{2,0}^{r,-8}z^2\left(x^8-28x^6y^2+70x^4y^4-28x^2y^6+y^8\right) + b_{0,6}^{r,4}\left(x^2+y^2\right)^3\left(x^4+y^4-6x^2y^2\right) \\
&\quad + b_{2,4}^{r,4}z^2\left(x^2+y^2\right)^2\left(x^4+y^4-6x^2y^2\right) + b_{4,2}^{r,4}z^4\left(x^2+y^2\right)\left(x^4+y^4-6x^2y^2\right) \\
&\quad + b_{6,0}^{r,4}z^6\left(x^4+y^4-6x^2y^2\right) + b_{0,8}^{r,-2}\left(x^2+y^2\right)^4\left(x^2-y^2\right) + b_{2,6}^{r,-2}z^2\left(x^2+y^2\right)^3\left(x^2-y^2\right) \\
&\quad + b_{4,4}^{r,-2}z^4\left(x^2+y^2\right)^2\left(x^2-y^2\right) + b_{6,2}^{r,-2}z^6\left(x^2+y^2\right)\left(x^2-y^2\right) + b_{8,0}^{r,-2}z^8\left(x^2-y^2\right); \qquad \text{(S.7)}
\end{aligned}
$$

$$
\begin{aligned}
H_{XY}^{(10)} &= -b_{0,0}^{r,10}\rho^{10}\sin 10\phi - b_{0,2}^{r,-8}\rho^{10}\sin(-8\phi) - b_{2,0}^{r,-8}z^2\rho^8\sin(-8\phi) - b_{0,6}^{r,4}\rho^{10}\sin 4\phi - b_{2,4}^{r,4}z^2\rho^8\sin 4\phi \\
&\quad - b_{4,2}^{r,4}z^4\rho^6\sin 4\phi - b_{6,0}^{r,4}z^6\rho^4\sin 4\phi - b_{0,8}^{r,-2}\rho^{10}\sin(-2\phi) - b_{2,6}^{r,-2}z^2\rho^8\sin(-2\phi) - b_{4,4}^{r,-2}z^4\rho^6\sin(-2\phi) \\
&\quad - b_{6,2}^{r,-2}z^6\rho^4\sin(-2\phi) - b_{8,0}^{r,-2}z^8\rho^2\sin(-2\phi) \\
&= -b_{0,0}^{r,10}\left(10x^9y-120x^7y^3+252x^5y^5-120x^3y^7+10xy^9\right) \\
&\quad - b_{0,2}^{r,-8}\left(x^2+y^2\right)\left(-8x^7y+56x^5y^3-56x^3y^5+8xy^7\right) \\
&\quad - b_{2,0}^{r,-8}z^2\left(-8x^7y+56x^5y^3-56x^3y^5+8xy^7\right) - b_{0,6}^{r,4}\left(x^2+y^2\right)^3 4xy\left(x^2-y^2\right) \\
&\quad - b_{2,4}^{r,4}z^2\left(x^2+y^2\right)^2 4xy\left(x^2-y^2\right) - b_{4,2}^{r,4}z^4\left(x^2+y^2\right)4xy\left(x^2-y^2\right) \\
&\quad - b_{6,0}^{r,4}z^6 4xy\left(x^2-y^2\right) - b_{0,8}^{r,-2}\left(x^2+y^2\right)^4(-2xy) - b_{2,6}^{r,-2}z^2\left(x^2+y^2\right)^3(-2xy) \\
&\quad - b_{4,4}^{r,-2}z^4\left(x^2+y^2\right)^2(-2xy) - b_{6,2}^{r,-2}z^6\left(x^2+y^2\right)(-2xy) - b_{8,0}^{r,-2}z^8(-2xy); \qquad \text{(S.8)}
\end{aligned}
$$

$$
\begin{aligned}
H_{XZ}^{(10)} &= d_{1,2}^{r,7} z\rho^9 \cos 7\phi + d_{3,0}^{r,7} z^3\rho^7 \cos 7\phi + d_{1,4}^{r,-5} z\rho^9 \cos(-5\phi) + d_{3,2}^{r,-5} z^3\rho^7 \cos(-5\phi) + d_{5,0}^{r,-5} z^5\rho^5 \cos(-5\phi) \\
&\quad + d_{1,8}^{r,1} z\rho^9 \cos\phi + d_{3,6}^{r,1} z^3\rho^7 \cos\phi + d_{5,4}^{r,1} z^5\rho^5 \cos\phi + d_{7,2}^{r,1} z^7\rho^3 \cos\phi + d_{9,0}^{r,1} z^9\rho \cos\phi \\
&= d_{1,2}^{r,7} z\left(x^2+y^2\right)\left(x^7 - 21x^5y^2 + 35x^3y^4 - 7xy^6\right) + d_{3,0}^{r,7} z^3\left(x^7 - 21x^5y^2 + 35x^3y^4 - 7xy^6\right) \\
&\quad + d_{1,4}^{r,-5} z\left(x^2+y^2\right)^2\left(x^5 - 10x^3y^2 + 5xy^4\right) + d_{3,2}^{r,-5} z^3\left(x^2+y^2\right)\left(x^5 - 10x^3y^2 + 5xy^4\right) \\
&\quad + d_{5,0}^{r,-5} z^5\left(x^5 - 10x^3y^2 + 5xy^4\right) + d_{1,8}^{r,1} z\left(x^2+y^2\right)^4 x + d_{3,6}^{r,1} z^3\left(x^2+y^2\right)^3 x + d_{5,4}^{r,1} z^5\left(x^2+y^2\right)^2 x \\
&\quad + d_{7,2}^{r,1} z^7\left(x^2+y^2\right) x + d_{9,0}^{r,1} z^9 x; \qquad \text{(S.9)}
\end{aligned}
$$

$$
\begin{aligned}
H_{YZ}^{(10)} &= d_{1,2}^{r,7} z\rho^9 \sin 7\phi + d_{3,0}^{r,7} z^3\rho^7 \sin 7\phi + d_{1,4}^{r,-5} z\rho^9 \sin(-5\phi) + d_{3,2}^{r,-5} z^3\rho^7 \sin(-5\phi) + d_{5,0}^{r,-5} z^5\rho^5 \sin(-5\phi) \\
&\quad + d_{1,8}^{r,1} z\rho^9 \sin\phi + d_{3,6}^{r,1} z^3\rho^7 \sin\phi + d_{5,4}^{r,1} z^5\rho^5 \sin\phi + d_{7,2}^{r,1} z^7\rho^3 \sin\phi + d_{9,0}^{r,1} z^9\rho \sin\phi \\
&= d_{1,2}^{r,7} z\left(x^2+y^2\right)\left(-y^7 + 21x^2y^5 - 35x^4y^3 + 7x^6y\right) + d_{3,0}^{r,7} z^3\left(-y^7 + 21x^2y^5 - 35x^4y^3 + 7x^6y\right) \\
&\quad + d_{1,4}^{r,-5} z\left(x^2+y^2\right)^2\left(-y^5 + 10x^2y^3 - 5x^4y\right) + d_{3,2}^{r,-5} z^3\left(x^2+y^2\right)\left(-y^5 + 10x^2y^3 - 5x^4y\right) \\
&\quad + d_{5,0}^{r,-5} z^5\left(-y^5 + 10x^2y^3 - 5x^4y\right) + d_{1,8}^{r,1} z\left(x^2+y^2\right)^4 y + d_{3,6}^{r,1} z^3\left(x^2+y^2\right)^3 y + d_{5,4}^{r,1} z^5\left(x^2+y^2\right)^2 y \\
&\quad + d_{7,2}^{r,1} z^7\left(x^2+y^2\right) y + d_{9,0}^{r,1} z^9 y. \qquad \text{(S.10)}
\end{aligned}
$$

$H_{YY}^{(10)}$ and $H_{ZZ}^{(10)}$ can be readily obtained in the same manner as $H_{YY}^{(9)}$ and $H_{ZZ}^{(9)}$ above.

Section S.3 Expansion of the C_3 $(E+A)\otimes e$ Hamiltonian up to the 4-th order

Table S.4: Allowed summing indices in constructing the C_3 $(E+A)\otimes e$ vibronic Hamiltonian expansion at the 1-st to 4-th order. $3n'+1$ has the same allowed values as $3n+1$ for this case and is not listed.

Order	$3m$	$2K$	$3n+1$	$2K$	Order	$3m$	$2K$	$3n+1$	$2K$
1			1	0	2	0	2	-2	0
3	3	0	1	2	4	0	4	4	0
								-2	2

Using Eq. S.1 and the allowed indices in Table S.4 and setting $I_{1-8}=0$, we have the following expansions for the C_3 $(E+A)\otimes e$ Hamiltonian matrix elements from the 1-st to 4-th order.

$$
\begin{aligned}
H_{XX}^{(1)} &= b_{0,0}^{r,1}\rho\cos\phi - b_{0,0}^{i,1}\rho\sin\phi = b_{0,0}^{r,1}x - b_{0,0}^{i,1}y; && \text{(S.11)}\\
H_{XX}^{(2)} &= a_{0,2}^{r,0}\rho^2 + b_{0,0}^{r,-2}\rho^2\cos(-2\phi) - b_{0,0}^{i,-2}\rho^2\sin(-2\phi)\\
&= a_{0,2}^{r,0}\left(x^2+y^2\right) + b_{0,0}^{r,-2}\left(x^2-y^2\right) + b_{0,0}^{i,-2}2xy; && \text{(S.12)}\\
H_{XX}^{(3)} &= a_{0,0}^{r,3}\rho^3\cos(3\phi) - a_{0,0}^{i,3}\rho^3\sin(3\phi) + b_{0,2}^{r,1}\rho^3\cos\phi - b_{0,2}^{i,1}\rho^3\sin\phi\\
&= a_{0,0}^{r,3}\left(x^3-3xy^2\right) - a_{0,0}^{i,3}\left(3x^2y-y^3\right) + b_{0,2}^{r,1}\left(x^2+y^2\right)x - b_{0,2}^{i,1}\left(x^2+y^2\right)y; && \text{(S.13)}\\
H_{XX}^{(4)} &= a_{0,4}^{r,0}\rho^4 + b_{0,0}^{r,4}\rho^4\cos(4\phi) - b_{0,0}^{i,4}\rho^4\sin(4\phi) + b_{0,2}^{r,-2}\rho^4\cos(-2\phi) - b_{0,2}^{i,-2}\rho^4\sin(-2\phi)\\
&= a_{0,4}^{r,0}\left(x^2+y^2\right)^2 + b_{0,0}^{r,4}\left(x^4+y^4-6x^2y^2\right) - b_{0,0}^{i,4}4xy\left(x^2-y^2\right)\\
&\quad + b_{0,2}^{r,-2}\left(x^2+y^2\right)\left(x^2-y^2\right) + b_{0,2}^{i,-2}\left(x^2+y^2\right)2xy. && \text{(S.14)}
\end{aligned}
$$

Flipping the signs for the b-coefficient terms gives the expansions for H_{YY}.

$$
\begin{aligned}
H_{XY}^{(1)} &= -b_{0,0}^{r,1}\rho\sin\phi - b_{0,0}^{i,1}\rho\cos\phi = -b_{0,0}^{r,1}y - b_{0,0}^{i,1}x; && \text{(S.15)}\\
H_{XY}^{(2)} &= -b_{0,0}^{r,-2}\rho^2\sin(-2\phi) - b_{0,0}^{i,-2}\rho^2\cos(-2\phi) = b_{0,0}^{r,-2}2xy - b_{0,0}^{i,-2}\left(x^2-y^2\right); && \text{(S.16)}\\
H_{XY}^{(3)} &= -b_{0,2}^{r,1}\rho^3\sin\phi - b_{0,2}^{i,1}\rho^3\cos\phi = -b_{0,2}^{r,1}\left(x^2+y^2\right)y - b_{0,2}^{i,1}\left(x^2+y^2\right)x; && \text{(S.17)}\\
H_{XY}^{(4)} &= -b_{0,0}^{r,4}\rho^4\sin 4\phi - b_{0,2}^{r,-2}\rho^4\sin(-2\phi) - b_{0,0}^{i,4}\rho^4\cos 4\phi - b_{0,2}^{i,-2}\rho^4\cos(-2\phi)\\
&= -b_{0,0}^{r,4}4xy\left(x^2-y^2\right) + b_{0,2}^{r,-2}\left(x^2+y^2\right)2xy - b_{0,0}^{i,4}\left(x^4+y^4-6x^2y^2\right)\\
&\quad - b_{0,2}^{i,-2}\left(x^2+y^2\right)\left(x^2-y^2\right). && \text{(S.18)}
\end{aligned}
$$

$$
\begin{aligned}
H_{XZ}^{(1)} &= d_{0,0}^{r,1}\rho\cos\phi + d_{0,0}^{i,1}\rho\sin\phi = d_{0,0}^{r,1}x + d_{0,0}^{i,1}y; && \text{(S.19)}\\
H_{XZ}^{(2)} &= d_{0,0}^{r,-2}\rho^2\cos(-2\phi) + d_{0,0}^{i,-2}\rho^2\sin(-2\phi) = d_{0,0}^{r,-2}\left(x^2-y^2\right) - d_{0,0}^{i,-2}2xy; && \text{(S.20)}\\
H_{XZ}^{(3)} &= d_{0,2}^{r,1}\rho^3\cos\phi + d_{0,2}^{i,1}\rho^3\sin\phi = d_{0,2}^{r,1}\left(x^2+y^2\right)x + d_{0,2}^{i,1}\left(x^2+y^2\right)y; && \text{(S.21)}\\
H_{XZ}^{(4)} &= d_{0,0}^{r,4}\rho^4\cos(4\phi) + d_{0,0}^{i,4}\rho^4\sin(4\phi) + d_{0,2}^{r,-2}\rho^4\cos(-2\phi) + d_{0,2}^{i,-2}\rho^4\sin(-2\phi)\\
&= d_{0,0}^{r,4}\left(x^4+y^4-6x^2y^2\right) + d_{0,0}^{i,4}4xy\left(x^2-y^2\right)\\
&\quad +d_{0,2}^{r,-2}\left(x^2+y^2\right)\left(x^2-y^2\right) - d_{0,2}^{i,-2}\left(x^2+y^2\right)2xy. && \text{(S.22)}
\end{aligned}
$$

$$
\begin{aligned}
H_{YZ}^{(1)} &= d_{0,0}^{r,1}\rho\sin\phi - d_{0,0}^{i,1}\rho\cos\phi = d_{0,0}^{r,1}y - d_{0,0}^{i,1}x; && \text{(S.23)}\\
H_{YZ}^{(2)} &= d_{0,0}^{r,-2}\rho^2\sin(-2\phi) - d_{0,0}^{i,-2}\rho^2\cos(-2\phi) = d_{0,0}^{r,-2}(-2xy) - d_{0,0}^{i,-2}\left(x^2-y^2\right); && \text{(S.24)}\\
H_{YZ}^{(3)} &= d_{0,2}^{r,1}\rho^3\sin\phi - d_{0,2}^{i,1}\rho^3\cos\phi = d_{0,2}^{r,1}\left(x^2+y^2\right)y - d_{0,2}^{i,1}\left(x^2+y^2\right)x; && \text{(S.25)}\\
H_{YZ}^{(4)} &= d_{0,0}^{r,4}\rho^4\sin(4\phi) - d_{0,0}^{i,4}\rho^4\cos(4\phi) + d_{0,2}^{r,-2}\rho^4\sin(-2\phi) - d_{0,2}^{i,-2}\rho^4\cos(-2\phi)\\
&= d_{0,0}^{r,4}4xy\left(x^2-y^2\right) - d_{0,0}^{i,4}\left(x^4+y^4-6x^2y^2\right)\\
&\quad -d_{0,2}^{r,-2}\left(x^2+y^2\right)2xy - d_{0,2}^{i,-2}\left(x^2+y^2\right)\left(x^2-y^2\right). && \text{(S.26)}
\end{aligned}
$$

$$
\begin{aligned}
H_{ZZ}^{(1)} &= 0; && \text{(S.27)}\\
H_{ZZ}^{(2)} &= c_{0,2}^{r,0}\rho^2 = c_{0,2}^{r,0}\left(x^2+y^2\right); && \text{(S.28)}\\
H_{ZZ}^{(3)} &= c_{0,0}^{r,3}\rho^3\cos(3\phi) - c_{0,0}^{i,3}\rho^3\sin(3\phi) = c_{0,0}^{r,3}\left(x^3-3xy^2\right) - c_{0,0}^{i,3}\left(3x^2y-y^3\right); && \text{(S.29)}\\
H_{ZZ}^{(4)} &= c_{0,4}^{r,0}\rho^4 = c_{0,4}^{r,0}\left(x^2+y^2\right)^2. && \text{(S.30)}
\end{aligned}
$$

Here, we use the formalism (labeled by "EV") in Viel and Eisfeld(2004) and Eisfeld and Viel(2005) to derive the same H_{XX}, H_{YY}, and H_{XY} expansions above. This derivation reveals the origin of the discrepancy between our expansions and those in the two works. Before carrying out the derivation, let us review the symmetry requirements on the matrix elements of the complex electronic states $|+\rangle$ and $|-\rangle$:

1. $H_{++} = H_{--}$ due to the time-reversal symmetry and spin-independence of the Hamiltonian (see below Eq. 6 in the main text);
2. H_{++} is real because it is a diagonal element of a hermitian matrix. It is also an eigenfunction of the $\hat{C}_3$ operator with the eigenvalue 1 (see Eq. 10 in the main text);
3. H_{+-} is an eigenfunction of $\hat{C}_3$ with the eigenvalue $e^{-i2\pi/3}$ (again, see Eq. 10 in the main text).

Those are the only necessary requirements on the matrix elements. Any extra constraints compromise the flexibility of the elements.

The EV derivation employs the complex coordinates:

$$Q_+ = x + iy; Q_- = x - iy. \qquad \text{(S.31)}$$

The $Q_+^p Q_-^q$ monomials that can contribute to the 0-th to 6-th order expansions of H_{++} and H_{+-} are presented in Table I in Viel and Eisfeld(2004). We summarize those that contribute to the 1-st to 4-th order expansions in Table S.5.

Table S.5: Nonvanishing terms of the complex e coordinates in constructing the C_3 $(E+A)\otimes e$ vibronic Hamiltonian expansions at the 1-st to 4-th order. The contents of this table is taken from Table I in Viel and Eisfeld(2004).

Order	Diagonal $H_{++} = H_{--}$	Off-diagonal $H_{++} = H_{-+}^*$
1	-	$Q_+^0 Q_-^1$
2	$Q_+^1 Q_-^1$	$Q_+^2 Q_-^0$
3	$Q_+^3 Q_-^0$ and $Q_+^0 Q_-^3$	$Q_+^1 Q_-^2$
4	$Q_+^2 Q_-^2$	$Q_+^0 Q_-^4$ and $Q_+^3 Q_-^1$

The matrix elements are expanded as

$$H_{kl} = \sum_{p,q} c_{p,q}^{kl} Q_+^p Q_-^q. \tag{S.32}$$

The summation runs over the nonvanishing monomials only. The $(p+q)!$ denominator in Eq. 6 of Viel and Eisfeld(2004) has been absorbed into the coefficient $c_{p,q}^{kl}$. We first obtain the expansions for H_{++} and H_{+-} and transform them to H_{XX}, H_{YY}, and H_{XY} later. With the monomials in Table S.5,

$$H_{++}^{(1-4)} = Re\left(c_{1,1}^{++} Q_+^1 Q_-^1 + c_{3,0}^{++} Q_+^3 Q_-^0 + c_{0,3}^{++} Q_+^0 Q_-^3 + c_{2,2}^{++} Q_+^2 Q_-^2\right); \tag{S.33}$$

$$H_{+-}^{(1-4)} = c_{0,1}^{+-} Q_+^0 Q_-^1 + c_{2,0}^{+-} Q_+^2 Q_-^0 + c_{1,2}^{+-} Q_+^1 Q_-^2 + c_{0,4}^{+-} Q_+^0 Q_-^4 + c_{3,1}^{+-} Q_+^3 Q_-^1. \tag{S.34}$$

We need to take the real part of the expansion for H_{++} because the diagonal element needs to be real. Here is the most essential step in our derivation: we allow the $\{c_{p,q}^{kl}\}$ coefficients to take complex values:

$$c_{p,q}^{kl} = c_{p,q}^{kl,r} + i c_{p,q}^{kl,i}. \tag{S.35}$$

$c_{p,q}^{kl,r}$ and $c_{p,q}^{kl,i}$ are real. Writing all the real and imaginary parts explicitly,

$$\begin{aligned}
H_{++}^{(1-4)} &= Re\left\{\left(c_{1,1}^{++,r} + i c_{1,1}^{++,i}\right)(x+iy)(x-iy) + \left(c_{3,0}^{++,r} + i c_{3,0}^{++,i}\right)\left(x^3 + 3ix^2y - 3xy^2 - iy^3\right)\right. \\
&\quad \left(c_{0,3}^{++,r} + i c_{0,3}^{++,i}\right)\left(x^3 - 3ix^2y - 3xy^2 + iy^3\right) + \left(c_{2,2}^{++,r} + i c_{2,2}^{++,i}\right)\left(x^2+y^2\right)^2 \\
&= Re\left\{c_{1,1}^{++,r}\left(x^2+y^2\right) + i c_{1,1}^{++,i}\left(x^2+y^2\right) + \right. \\
&\quad \left[\left(c_{3,0}^{++,r} + c_{0,3}^{++,r}\right)\left(x^3 - 3xy^2\right) + \left(c_{0,3}^{++,i} - c_{3,0}^{++,i}\right)\left(3x^2y - y^3\right)\right] \\
&\quad + i\left[\left(c_{3,0}^{++,i} + c_{0,3}^{++,i}\right)\left(x^3 - 3xy^2\right) + \left(c_{3,0}^{++,r} - c_{0,3}^{++,r}\right)\left(3x^2y - y^3\right)\right] \\
&\quad \left. + c_{2,2}^{++,r}\left(x^2+y^2\right)^2 + i c_{2,2}^{++,i}\left(x^2+y^2\right)^2\right\}
\end{aligned} \tag{S.36}$$

$$\begin{aligned}
&= c_{1,1}^{++,r}\left(x^2+y^2\right) + \left[\left(c_{3,0}^{++,r} + c_{0,3}^{++,r}\right)\left(x^3 - 3xy^2\right) + \left(c_{0,3}^{++,i} - c_{3,0}^{++,i}\right)\left(3x^2y - y^3\right)\right] \\
&\quad + c_{2,2}^{++,r}\left(x^2+y^2\right)^2;
\end{aligned} \tag{S.37}$$

$$
\begin{aligned}
H_{+-}^{(1-4)} &= \left(c_{0,1}^{+-,r} + ic_{0,1}^{+-,i}\right)(x-iy) + \left(c_{2,0}^{+-,r} + ic_{2,0}^{+-,i}\right)(x+iy)^2 \\
&+ \left(c_{1,2}^{+-,r} + ic_{1,2}^{+-,i}\right)(x+iy)(x-iy)^2 + \left(c_{0,4}^{+-,r} + ic_{0,4}^{+-,i}\right)(x-iy)^4 \\
&+ \left(c_{3,1}^{+-,r} + ic_{3,1}^{+-,i}\right)(x+iy)^3(x-iy) \\
&= \left[c_{0,1}^{+-,r}x + c_{0,1}^{+-,i}y\right] + i\left[c_{0,1}^{+-,i}x - c_{0,1}^{+-,r}y\right] + \left[c_{2,0}^{+-,r}\left(x^2-y^2\right) - c_{2,0}^{+-,i}2xy\right] \\
&+ i\left[c_{2,0}^{+-,i}\left(x^2-y^2\right) + c_{2,0}^{+-,r}2xy\right] + \left[c_{1,2}^{+-,r}x + c_{1,2}^{+-,i}y\right]\left(x^2+y^2\right) \\
&+ i\left[c_{1,2}^{+-,i}x - c_{1,2}^{+-,r}y\right]\left(x^2+y^2\right) \\
&+ \left[c_{0,4}^{+-,r}\left(x^4+y^4-6x^2y^2\right) + c_{0,4}^{+-,i}4xy\left(x^2-y^2\right)\right] \\
&+ i\left[c_{0,4}^{+-,i}\left(x^4+y^4-6x^2y^2\right) - c_{0,4}^{+-,r}4xy\left(x^2-y^2\right)\right] \\
&+ \left[c_{3,1}^{+-,r}\left(x^2-y^2\right) - c_{3,1}^{+-,i}2xy\right]\left(x^2+y^2\right) \\
&+ i\left[c_{3,1}^{+-,i}\left(x^2-y^2\right) + c_{3,1}^{+-,r}2xy\right]\left(x^2+y^2\right). \qquad \text{(S.38)}
\end{aligned}
$$

Note that the H_{++} is real and $\left\{c_{p,q}^{++}\right\}$ do not need to be real to make H_{++} real. And for the generally complex H_{+-}, it is natural to take complex $\left\{c_{p,q}^{+-}\right\}$. The H_{++} and H_{+-}, with a trivial sign flipping for y, are eigenfunctions of the $\hat{C}_3$ operator, with the correct eigenvalues 1 and $e^{-i2\pi/3}$, respectively. They satisfy all the symmetry requirements, yet they have the most flexible expansions, especially with the contributions of the imaginary parts of the $\left\{c_{p,q}^{++}\right\}$ and $\left\{c_{p,q}^{+-}\right\}$ coefficients.

Substituting Eqs. S.37 and S.38 into the following transformation:

$$
\begin{aligned}
\begin{pmatrix} H_{XX} & H_{XY} \\ H_{XY} & H_{YY} \end{pmatrix} &= \frac{1}{2}\begin{pmatrix} 1 & 1 \\ i & -i \end{pmatrix}\begin{pmatrix} H_{++} & H_{+-} \\ H_{+-}^{*} & H_{++} \end{pmatrix}\begin{pmatrix} 1 & -i \\ 1 & i \end{pmatrix} \\
&= \begin{pmatrix} H_{++} + Re\left(H_{+-}\right) & -Im\left(H_{+-}\right) \\ -Im\left(H_{+-}\right) & H_{++} - Re\left(H_{+-}\right) \end{pmatrix}, \qquad \text{(S.39)}
\end{aligned}
$$

we obtain the 1-st to 4-th order expansions of H_{XX} and H_{XY}.

$$
\begin{aligned}
H_{XX}^{(1)} &= c_{0,1}^{+-,r}x + c_{0,1}^{+-,i}y; \qquad \text{(S.40)} \\
H_{XX}^{(2)} &= c_{1,1}^{++,r}\left(x^2+y^2\right) + c_{2,0}^{+-,r}\left(x^2-y^2\right) - c_{2,0}^{+-,i}2xy; \qquad \text{(S.41)} \\
H_{XX}^{(3)} &= \left(c_{3,0}^{++,r} + c_{0,3}^{++,r}\right)\left(x^3-3xy^2\right) + \left(c_{0,3}^{++,i} - c_{3,0}^{++,i}\right)\left(3x^2y-y^3\right) \\
&+ c_{1,2}^{+-,r}x\left(x^2+y^2\right) + c_{1,2}^{+-,i}y\left(x^2+y^2\right); \qquad \text{(S.42)} \\
H_{XX}^{(4)} &= c_{2,2}^{++,r}\left(x^2+y^2\right)^2 + c_{0,4}^{+-,r}\left(x^4+y^4-6x^2y^2\right) + c_{0,4}^{+-,i}4xy\left(x^2-y^2\right) \\
&+ c_{3,1}^{+-,r}\left(x^2+y^2\right)\left(x^2-y^2\right) - c_{3,1}^{+-,i}\left(x^2+y^2\right)2xy. \qquad \text{(S.43)}
\end{aligned}
$$

$$
\begin{aligned}
H_{XY}^{(1)} &= -c_{0,1}^{+-,i}x + c_{0,1}^{+-,r}y; && \text{(S.44)}\\
H_{XY}^{(2)} &= -c_{2,0}^{+-,i}\left(x^2-y^2\right) - c_{2,0}^{+-,r}2xy; && \text{(S.45)}\\
H_{XY}^{(3)} &= -c_{1,2}^{+-,i}\left(x^2+y^2\right)x + c_{1,2}^{+-,r}\left(x^2+y^2\right)y; && \text{(S.46)}\\
H_{XY}^{(4)} &= c_{0,4}^{+-,r}4xy\left(x^2-y^2\right) - c_{0,4}^{+-,i}\left(x^4+y^4-6x^2y^2\right)\\
&\quad -c_{3,1}^{+-,r}\left(x^2+y^2\right)2xy - c_{3,1}^{+-,i}\left(x^2+y^2\right)\left(x^2-y^2\right). && \text{(S.47)}
\end{aligned}
$$

The H_{YY} expansions are readily obtained using the trick introduced between Eqs. S.14 and S.15. With a trivial sign change for y, these eight expressions are identical to our expansions in Eqs. S.11 to S.18.

Clearly, the EV derivation would have led to the same expansions as ours if the $\left\{c_{p,q}^{kl}\right\}$ coefficients had been allowed to take complex values. If all the $c_{p,q}^{kl,i}$s are set to be 0, i.e., if all the $\left\{c_{p,q}^{kl}\right\}$ coefficients are restricted to take real values, the original EV expansions are obtained (see Eqs. 10(b-d), 11(b-d), and 12(b-d) in Viel and Eisfeld(2004)). Evidently, the discrepancy between the EV expansions and ours arises from whether we allow the $\left\{c_{p,q}^{kl}\right\}$ coefficients to be complex. We do not see the necessity of those coefficients to be real. The complex coefficients give the H_{++} in Eq. S.37 that is real and invariant with respect to a $\hat{C}_3$ rotation. These are the only two requirements for H_{++}. They also give the H_{+-} in Eq. S.38 (again, after the sign of y is flipped) that is an eigenfunction of $\hat{C}_3$ with the eigenvalue of $e^{-i2\pi/3}$, which is the only one requirement for H_{+-}. Restricting the $\left\{c_{p,q}^{++}\right\}$ and $\left\{c_{p,q}^{+-}\right\}$ coefficients to be real in Viel and Eisfeld(2004) compromises the flexibilities of H_{++} and H_{+-}, and subsequently the flexibilities of H_{ZZ}, H_{YY}, and H_{XY}, by omitting all terms with the $c_{p,q}^{++,i}$ and $c_{p,q}^{+-,i}$ coefficients in their expansions.

The necessity of flipping the sign of y arises from the different transformation relations of the e_x and e_y components under $\hat{C}_3$ in Viel and Eisfeld(2004) and in this work. In Viel and Eisfeld(2004),

$$
\hat{C}_3 Q_+ = e^{i2\pi/3}Q_+; \hat{C}_3 Q_- = e^{-i2\pi/3}Q_-. \tag{S.48}
$$

Our definition in Eq. 1 in the main text, on the contrary, gives

$$
\hat{C}_3 Q_+ = e^{-i2\pi/3}Q_+; \hat{C}_3 Q_- = e^{i2\pi/3}Q_-. \tag{S.49}
$$

We emphasize again that this difference in sign is trivial.

The discrepancy between the EV expansions and ours cannot be reconciled by coordinate transformation like

$$
\begin{pmatrix} x' \\ y' \end{pmatrix} = \begin{pmatrix} \cos\chi & -\sin\chi \\ \sin\chi & \cos\chi \end{pmatrix} \begin{pmatrix} x \\ y \end{pmatrix}. \tag{S.50}
$$

Such a rotation of x and y is equivalent to multiplying phase factors to Q_+ and Q_- to make the new complex coordinates:

$$
\begin{pmatrix} Q'_+ \\ Q'_- \end{pmatrix} = \begin{pmatrix} x' + iy' \\ x' - iy' \end{pmatrix} = \begin{pmatrix} e^{i\chi}Q_+ \\ e^{-i\chi}Q_- \end{pmatrix}. \tag{S.51}
$$

Expressed in the new complex coordinates, Eqs. S.33 and S.34 become

$$
\begin{aligned}
H_{++}^{(1-4)} &= Re\left(c_{1,1}^{++}Q'^{1}_{+}Q'^{1}_{-} + c_{3,0}^{++}e^{-i3\chi}Q'^{3}_{+} + c_{0,3}^{++}e^{i3\chi}Q'^{3}_{-} + c_{2,2}^{++}Q'^{2}_{+}Q'^{2}_{-}\right); \\
&= Re\left(R_{1,1}^{++}e^{i\phi_{1,1}^{++}}Q'^{1}_{+}Q'^{1}_{-} + R_{3,0}^{++}e^{i\phi_{3,0}^{++}}e^{-i3\chi}Q'^{3}_{+} + R_{0,3}^{++}e^{i\phi_{0,3}^{++}}e^{i3\chi}Q'^{3}_{-}\right. \\
&\quad \left.+R_{2,2}^{++}e^{i\phi_{2,2}^{++}}Q'^{2}_{+}Q'^{2}_{-}\right) \\
&= Re\left(R_{1,1}^{++}e^{i\phi_{1,1}^{++}}Q'^{1}_{+}Q'^{1}_{-} + R_{3,0}^{++}e^{i\left(\phi_{3,0}^{++}-3\chi\right)}Q'^{3}_{+} + R_{0,3}^{++}e^{i\left(\phi_{0,3}^{++}+3\chi\right)}Q'^{3}_{-}\right. \\
&\quad \left.+R_{2,2}^{++}e^{i\phi_{2,2}^{++}}Q'^{2}_{+}Q'^{2}_{-}\right) \\
&= Re\left({c'}_{1,1}^{++}Q'^{1}_{+}Q'^{1}_{-} + {c'}_{3,0}^{++}Q'^{3}_{+} + {c'}_{0,3}^{++}Q'^{3}_{-} + {c'}_{2,2}^{++}Q'^{2}_{+}Q'^{2}_{-}\right); \qquad \text{(S.52)} \\
H_{+-}^{(1-4)} &= c_{0,1}^{+-}e^{i\chi}Q'^{1}_{-} + c_{2,0}^{+-}e^{-i2\chi}Q'^{2}_{+} + c_{1,2}^{+-}e^{i\chi}Q'^{1}_{+}Q'^{2}_{-} + c_{0,4}^{+-}e^{i4\chi}Q'^{4}_{-} \\
&\quad +c_{3,1}^{+-}e^{-i2\chi}Q'^{3}_{+}Q'^{1}_{-} \\
&= R_{0,1}^{+-}e^{i\phi_{0,1}^{+-}}e^{i\chi}Q'^{1}_{-} + R_{2,0}^{+-}e^{i\phi_{2,0}^{+-}}e^{-i2\chi}Q'^{2}_{+} + R_{1,2}^{+-}e^{i\phi_{1,2}^{+-}}e^{i\chi}Q'^{1}_{+}Q'^{2}_{-} \\
&\quad +R_{0,4}^{+-}e^{i\phi_{0,4}^{+-}}e^{i4\chi}Q'^{4}_{-} + R_{3,1}^{+-}e^{i\phi_{3,1}^{+-}}e^{-i2\chi}Q'^{3}_{+}Q'^{1}_{-} \\
&= R_{0,1}^{+-}e^{i\left(\phi_{0,1}^{+-}+\chi\right)}Q'^{1}_{-} + R_{2,0}^{+-}e^{i\left(\phi_{2,0}^{+-}-2\chi\right)}Q'^{2}_{+} + R_{1,2}^{+-}e^{i\left(\phi_{1,2}^{+-}+\chi\right)}Q'^{1}_{+}Q'^{2}_{-} \\
&\quad +R_{0,4}^{+-}e^{i\left(\phi_{0,4}^{+-}+4\chi\right)}Q'^{4}_{-} + R_{3,1}^{+-}e^{i\left(\phi_{3,1}^{+-}-2\chi\right)}Q'^{3}_{+}Q'^{1}_{-} \\
&= {c'}_{0,1}^{+-}Q'^{1}_{-} + {c'}_{2,0}^{+-}Q'^{2}_{+} + {c'}_{1,2}^{+-}Q'^{1}_{+}Q'^{2}_{-} + {c'}_{0,4}^{+-}Q'^{4}_{-} + +{c'}_{3,1}^{+-}Q'^{3}_{+}Q'^{1}_{-}. \qquad \text{(S.53)}
\end{aligned}
$$

In these expressions, the complex $c_{p,q}^{kl}$ has been written as its norm multiplied by its phase factor:

$$c_{p,q}^{kl} = R_{p,q}^{kl}e^{i\phi_{p,q}^{kl}}. \qquad \text{(S.54)}$$

Absorbing the coordinate transformation phase factors, the new complex coefficients are defined as

$${c'}_{p,q}^{kl} = R_{p,q}^{kl}e^{i\left(\phi_{p,q}^{kl}-(p-q)\chi\right)}. \qquad \text{(S.55)}$$

For one specific ${c'}_{p,q}^{kl}$, we may choose $\chi = \phi_{p,q}^{kl}/\left(p-q\right)$ so that ${c'}_{p,q}^{kl}$ becomes real. However, all the other ${c'}_{p,q}^{kl}$ coefficients are still complex because in general, all $\phi_{p,q}^{kl}$s are different and $(p-q)$s are different. We can NOT find one χ (i.e., one coordinate transformation) that satisfy

$$\forall\left(k,l,p,q\right) : \chi = \phi_{p,q}^{kl}/\left(p-q\right). \qquad \text{(S.56)}$$

In short, the coordinate transformation in Eq. S.50 can at most make one ${c'}_{p,q}^{kl}$ real, while the others remain to be complex. Therefore, the discrepancy between the EV expansions and ours cannot be reconciled by such a transformation. The derivation and conclusion above also apply to the H_{XZ}, H_{YZ}, and H_{ZZ} expansions, and are not repeated.

Section S.4 Symmetries of V_{nn} and $|Z\rangle$ state's V_{ne} with respect to e bending and e stretching

The atoms of the boric acid molecule are relabelled as shown in Figure S.1(a) and (b). The O nuclei are labelled as A, B, and C, the H nuclei A', B', and C', and the B nuclei O. There are three points in space a, b, and c, that are connected by $\hat{C}_3$. Momentarily, we assume that a, b, and c are coplanar with the nuclei. The OA, OB, and OC distances are R, the OA', OB', and OC' distances R', and the Oa, Ob, and Oc distances r. $\angle_{aOA} = \angle_{bOB} = \angle_{cOC} = \alpha$. $\angle_{AOA'} = \angle_{BOB'} = \angle_{COC'} = \gamma$. R, R', α, and γ are geometrical parameters for the undistorted structure. The e_x component of the bending is the symmetric scissoring that have the OB and OC arms rotate by δ_x as shown in Figure S.1(a), rigidly followed by B' and C' so that the BB' and CC' distances are still R', and $\angle_{BOB'}$ and $\angle_{COC'}$ are still γ. The e_y component involves rocking of all A, B, and C, with the OA arm rotating by $2\delta_y$ while the OB and OC arms rotating by δ_y in the opposite direction. Again, A', B', and C' rigidly follow the rocking so that the AA', BB', and CC' distances, $\angle_{AOA'}$, $\angle_{BOB'}$ and $\angle_{COC'}$ are unchanged. The e_y bending is shown in Figure S.1(b). The relations between the rotational angles and the bending coordinates are: $x = \sqrt{6}\delta_x$ and $y = \sqrt{18}\delta_y$.

We are interested in how V_{ne} and V_{nn} vary along with the e bending. After the molecule undergoes e_x and e_y distortions, the distance-squares between the spacial points and the nuclei, and between the nuclei themselves are:

$$r_{aA}^2 = R^2 + r^2 - 2Rr\cos(\alpha - 2\delta_y); \quad \text{(S.57)}$$

$$r_{aB}^2 = R^2 + r^2 - 2Rr\cos\left(\frac{2\pi}{3} - \alpha - \delta_y - \delta_x\right); \quad \text{(S.58)}$$

$$r_{aC}^2 = R^2 + r^2 - 2Rr\cos\left(\frac{2\pi}{3} + \alpha + \delta_y - \delta_x\right); \quad \text{(S.59)}$$

$$r_{bA}^2 = R^2 + r^2 - 2Rr\cos\left(\frac{2\pi}{3} + \alpha - 2\delta_y\right); \quad \text{(S.60)}$$

$$r_{bB}^2 = R^2 + r^2 - 2Rr\cos(\alpha + \delta_y + \delta_x); \quad \text{(S.61)}$$

$$r_{bC}^2 = R^2 + r^2 - 2Rr\cos\left(\frac{2\pi}{3} - \alpha - \delta_y + \delta_x\right); \quad \text{(S.62)}$$

$$r_{cA}^2 = R^2 + r^2 - 2Rr\cos\left(\frac{2\pi}{3} - \alpha + 2\delta_y\right); \quad \text{(S.63)}$$

$$r_{cB}^2 = R^2 + r^2 - 2Rr\cos\left(\frac{2\pi}{3} + \alpha + \delta_y + \delta_x\right); \quad \text{(S.64)}$$

$$r_{cC}^2 = R^2 + r^2 - 2Rr\cos(\alpha - \delta_x + \delta_y); \quad \text{(S.65)}$$

$$r_{aA'}^2 = R'^2 + r^2 - 2R'r\cos(\alpha - \gamma - 2\delta_y); \quad \text{(S.66)}$$

$$r_{aB'}^2 = R'^2 + r^2 - 2R'r\cos\left(\frac{2\pi}{3} - \alpha + \gamma - \delta_y - \delta_x\right); \quad \text{(S.67)}$$

$$r_{aC'}^2 = R'^2 + r^2 - 2R'r\cos\left(\frac{2\pi}{3} + \alpha - \gamma + \delta_y - \delta_x\right); \quad \text{(S.68)}$$

$$r_{bA'}^2 = R'^2 + r^2 - 2R'r\cos\left(\frac{2\pi}{3} + \alpha - \gamma - 2\delta_y\right); \quad (S.69)$$

$$r_{bB'}^2 = R'^2 + r^2 - 2R'r\cos(\alpha - \gamma + \delta_y + \delta_x); \quad (S.70)$$

$$r_{bC'}^2 = R'^2 + r^2 - 2R'r\cos\left(\frac{2\pi}{3} - \alpha + \gamma - \delta_y + \delta_x\right); \quad (S.71)$$

$$r_{cA'}^2 = R'^2 + r^2 - 2R'r\cos\left(\frac{2\pi}{3} - \alpha + \gamma + 2\delta_y\right); \quad (S.72)$$

$$r_{cB'}^2 = R'^2 + r^2 - 2R'r\cos\left(\frac{2\pi}{3} + \alpha - \gamma + \delta_y + \delta_x\right); \quad (S.73)$$

$$r_{cC'}^2 = R'^2 + r^2 - 2R'r\cos(\alpha - \gamma - \delta_x + \delta_y); \quad (S.74)$$

$$r_{AB}^2 = 2R^2\left(1 - \cos\left(\frac{2\pi}{3} - 3\delta_y - \delta_x\right)\right); \quad (S.75)$$

$$r_{AC}^2 = 2R^2\left(1 - \cos\left(\frac{2\pi}{3} + 3\delta_y - \delta_x\right)\right); \quad (S.76)$$

$$r_{BC}^2 = 2R^2\left(1 - \cos\left(\frac{2\pi}{3} + 2\delta_x\right)\right); \quad (S.77)$$

$$r_{A'B'}^2 = 2R'^2\left(1 - \cos\left(\frac{2\pi}{3} - 3\delta_y - \delta_x\right)\right); \quad (S.78)$$

$$r_{A'C'}^2 = 2R'^2\left(1 - \cos\left(\frac{2\pi}{3} + 3\delta_y - \delta_x\right)\right); \quad (S.79)$$

$$r_{B'C'}^2 = 2R^2\left(1 - \cos\left(\frac{2\pi}{3} + 2\delta_x\right)\right); \quad (S.80)$$

$$r_{AB'}^2 = R^2 + R'^2 - 2RR'\cos\left(\frac{2\pi}{3} - 3\delta_y - \delta_x + \gamma\right); \quad (S.81)$$

$$r_{AC'}^2 = R^2 + R'^2 - 2RR'\cos\left(\frac{2\pi}{3} + 3\delta_y - \delta_x - \gamma\right); \quad (S.82)$$

$$r_{BA'}^2 = R^2 + R'^2 - 2RR'\cos\left(\frac{2\pi}{3} - 3\delta_y - \delta_x - \gamma\right); \quad (S.83)$$

$$r_{BC'}^2 = R^2 + R'^2 - 2RR'\cos\left(\frac{2\pi}{3} + 2\delta_x + \gamma\right); \quad (S.84)$$

$$r_{CA'}^2 = R^2 + R'^2 - 2RR'\cos\left(\frac{2\pi}{3} + 3\delta_y - \delta_x + \gamma\right); \quad (S.85)$$

$$r_{CB'}^2 = R^2 + R'^2 - 2RR'\cos\left(\frac{2\pi}{3} + 2\delta_x - \gamma\right). \quad (S.86)$$

All distances involving O, as well as $r_{AA'}$, $r_{BB'}$, and $r_{CC'}$ are invariant in the bending and are hence omitted in the discussion. If e_x distorts in the opposite direction, i.e., $\delta_x \to -\delta_x$, the following six pairs of r_{iJ}s are swapped:

$$r_{aB} \leftrightarrow r_{bC}; r_{aC} \leftrightarrow r_{cB}; r_{bB} \leftrightarrow r_{cC}; r_{aB'} \leftrightarrow r_{bC'}; r_{aC'} \leftrightarrow r_{cB'}; r_{bB'} \leftrightarrow r_{cC'}; \quad (S.87)$$

while the other six r_{iJ}s are invariant. Consequently, the accummulated electrostatic potential of the six nuclei on the three spatial points is invariant with respect to $\delta_x \to -\delta_x$. This invariance of electrostatic potential remains if the points a, b, and c are vertically displaced out of the plane of the boric acid molecule. The displacement simply adds a constant to all the r_{iJ}^2s. The $|Z\rangle$, $|+\rangle$, and $|-\rangle$ states give totally symmetric electron densities with respect to $\hat{C}_3$, and therefore, equal electron densities at points a, b, and c. Calculating V_{ne} is integrating all electron-nucleus attraction over electron densities at a set of symmetrically equivalent spatial points like a, b, and c. With the invariance of the electron-nucleus attraction with respect to $x \to -x$, V_{ne} must also be symmetric with respect to this change. There is no invariance or swapping for the internuclear distances r_{IJ}s. V_{nn} is hence in general asymmetric with respect to $x \to -x$ for the e bending.

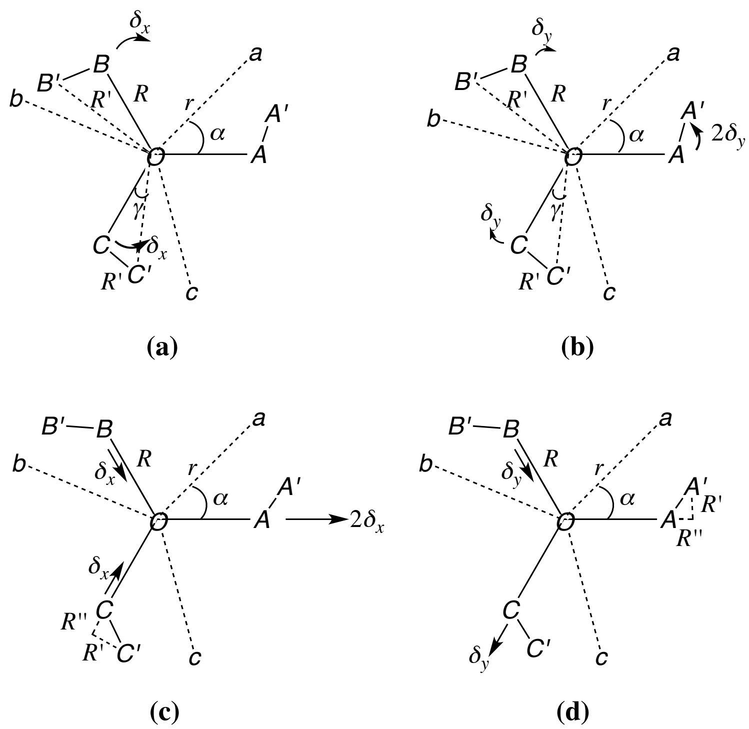

Figure S.1: (a) The setting of a model C_{3h} molecule and the e_x bending; (b) the same setting and the e_y bending; (c) the setting of a model C_{3h} molecule and the e_x stretching; (d) the same setting and the e_y stretching.

If e_y distorts in the opposite direction, $\delta_y \to -\delta_y$, it is readily seen that

$$r_{AB} \leftrightarrow r_{AC}; r_{AB'} \leftrightarrow r_{AC'}; r_{AB'} \leftrightarrow r_{CA'}; r_{AC'} \leftrightarrow r_{BA'}, \tag{S.88}$$

while all the other r_{IJ}s are invariant. Therefore, V_{nn} is symmetric with respect to $y \to -y$. This symmetry is shown in Figure S.2, where the value of the $V_{nn}(x, y) - V_{nn}(x, -y)$ surface of the boric acid molecule along the e bending is essentially 0. There are no swappings or invariances for r_{iJ}s and therefore, V_{ne} is in general asymmetric with respect to $y \to -y$. In the main text, we have used the a'_Z orbital of boric acid as a strict diabatic state to demonstrate these symmetries of the two components (see Figure 2(c) in the main text).

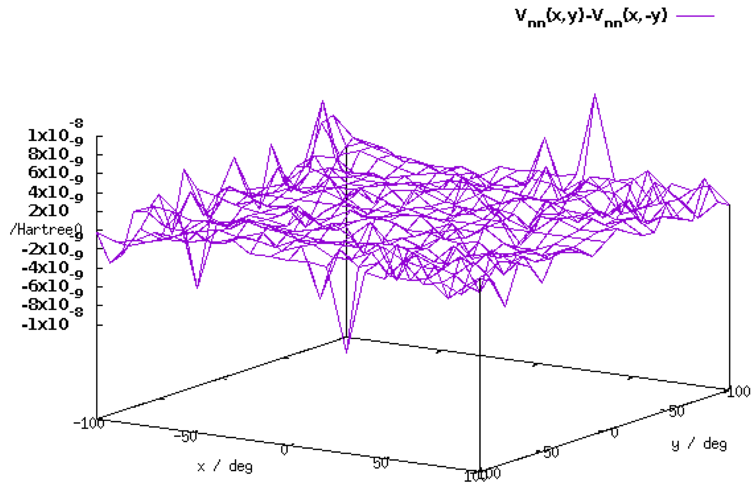

Figure S.2: The $V_{nn}\left(x,y\right)-V_{nn}\left(x,-y\right)$ surface of the boric acid molecule along the e bending.

In the language of the polar angle ϕ, being symmetric with respect to $y\rightarrow -y$ means being symmetric with respect to the line corresponding to $\phi=0$ and $\phi=\pi$. Therefore, V_{nn} can only contain terms with $\cos\left(3m\phi\right)$. Being symmetric with respect to $x\rightarrow -x$ means being symmetric with respect to the line corresponding to $\phi=\frac{\pi}{2}$ and $\phi=\frac{3\pi}{2}$. Therefore, only the $\cos\left(3m\phi\right)$ terms with $m=0,2,4,\cdots$ and the $\sin\left(3m\phi\right)$ terms with $m=1,3,5,\cdots$ can contribute to V_{ne}. The fact that V_{ne} is asymmetric with respect to $y\rightarrow -y$ disallows its expansion exclusively in the $\cos\left(3m\phi\right)$ terms with $m=0,2,4,\cdots$ The $3m$, obviously, arises from the requirement of invariance of V_{nn} and V_{ne} with respect to $\hat{C}_3$.

Adding V_{nn} and V_{ne}, H_{ZZ} in the C_3 $(E+A)\otimes e$ Hamiltonian can be expanded as

$$\begin{aligned}H_{ZZ} &= c^{r,0}_{0,0}+c^{r,0}_{0,2}\rho^2+c^{r,3}_{0,0}\rho^3\cos 3\phi+c^{i,3}_{0,0}\rho^3\sin 3\phi+c^{r,0}_{0,4}\rho^4+c^{r,3}_{0,2}\rho^5\cos 3\phi+c^{r,3}_{0,2}\rho^5\sin 3\phi\\ &\quad +c^{r,0}_{0,6}\rho^6+c^{r,6}_{0,0}\rho^6\cos 6\phi \end{aligned} \tag{S.89}$$

up to the 6-th order. The inclusion of some $\sin\left(3m\phi\right)$ terms but not all makes it a special case for the general expansion in Eq. S.1. This selection of $\sin\left(3m\phi\right)$ terms is specific for the e bending. It does not apply for e stretching.

To examine the symmetries of V_{nn} and V_{ne} along the e stretching, another C_{3h} model is set for the boric acid molecule in Figure S.1(c) and (d), with the stretching motions indicated by the arrows and the magnitudes δ_x and δ_y. The relations between the magnitudes and the stretching coordinates are $x=\sqrt{6}\delta_x$ and $y=\sqrt{2}\delta_y$. R, r, and α have the same meanings as in Figure S.1(a) and (b). R' has been redefined, and a new distance R'' is needed. R' and R'' are the lengths of the right-angle sides for the right triangles shown in Figure S.1(c) and (d). A', B', and C' rigidly follow the motion of A, B, and C in the stretching, respectively, so that the right triangles are not distorted. R' and R'' are constant. The following distance-squares are dependent on the e stretching:

$$\begin{aligned}
r_{aA}^2 &= r^2 + (R+2\delta_x)^2 - 2r\,(R+2\delta_x)\cos\alpha; && \text{(S.90)}\\
r_{aA'}^2 &= r^2 + \left(R+R''+2\delta_x\right)^2 + R'^2 \\
&\quad -2r\sqrt{(R+R''+2\delta_x)^2+R'^2}\cos\left(\alpha - \tan^{-1}\frac{R'}{R+R''+2\delta_x}\right); && \text{(S.91)}\\
r_{aB}^2 &= r^2 + (R-\delta_x-\delta_y)^2 - 2r\,(R-\delta x-\delta_y)\cos\left(\frac{2\pi}{3}-\alpha\right); && \text{(S.92)}\\
r_{aB'}^2 &= r^2 + \left(R+R''-\delta_x-\delta_y\right)^2 + R'^2 \\
&\quad -2r\sqrt{(R+R''-\delta x-\delta_y)^2+R'^2}\cos\left(\frac{2\pi}{3}-\alpha+\tan^{-1}\frac{R'}{R+R''-\delta_x-\delta_y}\right); && \text{(S.93)}\\
r_{aC}^2 &= r^2 + (R-\delta_x+\delta_y)^2 - 2r\,(R-\delta_x+\delta_y)\cos\left(\frac{2\pi}{3}+\alpha\right); && \text{(S.94)}\\
r_{aC'}^2 &= r^2 + \left(R+R''-\delta_x+\delta_y\right)^2 + R'^2 \\
&\quad -2r\sqrt{(R+R''-\delta_x+\delta_y)^2+R'^2}\cos\left(\frac{2\pi}{3}+\alpha-\tan^{-1}\frac{R'}{R+R''-\delta_x+\delta_y}\right); && \text{(S.95)}\\
r_{bA}^2 &= r^2 + (R+2\delta_x)^2 - 2r\,(R+2\delta_x)\cos\left(\frac{2\pi}{3}+\alpha\right); && \text{(S.96)}\\
r_{bA'}^2 &= r^2 + \left(R+R''+2\delta_x\right)^2 + R'^2 \\
&\quad -2r\sqrt{(R+R''+2\delta_x)^2+R'^2}\cos\left(\frac{2\pi}{3}+\alpha-\tan^{-1}\frac{R'}{R+R''+2\delta_x}\right); && \text{(S.97)}\\
r_{bB}^2 &= r^2 + (R-\delta_x-\delta_y)^2 - 2r\,(R-\delta_x-\delta_y)\cos\alpha; && \text{(S.98)}\\
r_{bB'}^2 &= r^2 + \left(R+R''-\delta_x-\delta_y\right)^2 + R'^2 \\
&\quad -2r\sqrt{(R+R''-\delta_x-\delta_y)^2+R'^2}\cos\left(\alpha-\tan^{-1}\frac{R'}{R+R''-\delta_x-\delta_y}\right); && \text{(S.99)}\\
r_{bC}^2 &= r^2 + (R-\delta_x+\delta_y)^2 - 2r\,(R-\delta_x+\delta_y)\cos\left(\frac{2\pi}{3}-\alpha\right); && \text{(S.100)}\\
r_{bC'}^2 &= r^2 + \left(R+R''-\delta_x+\delta_y\right)^2 + R'^2 \\
&\quad -2r\sqrt{(R+R''-\delta_x+\delta_y)^2+R'^2}\cos\left(\frac{2\pi}{3}-\alpha+\tan^{-1}\frac{R'}{R+R''-\delta_x+\delta_y}\right); && \text{(S.101)}\\
r_{cA}^2 &= r^2 + (R+2\delta_x)^2 - 2r\,(R+2\delta_x)\cos\left(\frac{2\pi}{3}-\alpha\right); && \text{(S.102)}\\
r_{cA'}^2 &= r^2 + \left(R+R''+2\delta_x\right)^2 + R'^2 \\
&\quad -2r\sqrt{(R+R''+2\delta_x)+R'^2}\cos\left(\frac{2\pi}{3}-\alpha+\tan^{-1}\frac{R'}{R+R''+2\delta_x}\right); && \text{(S.103)}
\end{aligned}$$

$$r_{cB}^2 = r^2 + (R-\delta_x-\delta_y)^2 - 2r\,(R-\delta_x-\delta_y)\cos\left(\frac{2\pi}{3}+\alpha\right); \tag{S.104}$$

$$\begin{aligned} r_{cB'}^2 &= r^2 + \left(R+R''-\delta_x-\delta_y\right)^2 + R'^2 \\ &\quad -2r\sqrt{(R+R''-\delta_x-\delta_y)^2+R'^2}\cos\left(\frac{2\pi}{3}+\alpha-\tan^{-1}\frac{R'}{R+R''-\delta_x-\delta_y}\right); \end{aligned} \tag{S.105}$$

$$r_{cC}^2 = r^2 + (R-\delta_x+\delta_y)^2 - 2r\,(R-\delta_x+\delta_y)\cos\alpha; \tag{S.106}$$

$$\begin{aligned} r_{cC'}^2 &= r^2 + \left(R+R''-\delta_x+\delta_y\right)^2 + R'^2 \\ &\quad -2r\sqrt{(R+R''-\delta_x+\delta_y)^2+R'^2}\cos\left(\alpha-\tan^{-1}\frac{R'}{R+R''-\delta_x+\delta_y}\right); \end{aligned} \tag{S.107}$$

$$r_{AB}^2 = (R+2\delta_x)^2 + (R-\delta_x-\delta_y)^2 - 2\,(R+2\delta_x)\,(R-\delta_x-\delta_y)\cos\frac{2\pi}{3}; \tag{S.108}$$

$$\begin{aligned} r_{AB'}^2 &= (R+2\delta_x)^2 + \left(R+R''-\delta_x-\delta_y\right)^2 + R'^2 \\ &\quad -2\,(R+2\delta_x)\sqrt{(R+R''-\delta_x-\delta_y)^2+R'^2}\cos\left(\frac{2\pi}{3}+\tan^{-1}\frac{R'}{R+R''-\delta_x-\delta_y}\right); \end{aligned} \tag{S.109}$$

$$r_{AC}^2 = (R+2\delta_x)^2 + (R-\delta_x+\delta_y)^2 - 2\,(R+2\delta_x)\,(R-\delta_x+\delta_y)\cos\frac{2\pi}{3}; \tag{S.110}$$

$$\begin{aligned} r_{AC'}^2 &= (R+2\delta_x)^2 + \left(R+R''-\delta_x+\delta_y\right)^2 + R'^2 \\ &\quad -2\,(R+2\delta_x)\sqrt{(R+R''-\delta_x+\delta_y)^2+R'^2}\cos\left(\frac{2\pi}{3}-\tan^{-1}\frac{R'}{R+R''-\delta_x+\delta_y}\right); \end{aligned}$$

$$\begin{aligned} r_{A'B}^2 &= \left(R+R''+2\delta_x\right)^2 + R'^2 + (R-\delta_x-\delta_y)^2 \\ &\quad -2\sqrt{(R+R''+2\delta_x)^2+R'^2}\,(R-\delta_x-\delta_y)\cos\left(\frac{2\pi}{3}-\tan^{-1}\frac{R'}{R+R''+2\delta_x}\right); \end{aligned} \tag{S.111}$$

$$\begin{aligned} r_{A'B'}^2 &= \left(R+R''+2\delta_x\right)^2 + 2R'^2 + \left(R+R''-\delta_x-\delta_y\right)^2 \\ &\quad -2\sqrt{\left[(R+R''+2\delta_x)^2+R'^2\right]\left[(R+R''-\delta_x-\delta_y)^2+R'^2\right]}\,\cdot \\ &\quad \cos\left(\frac{2\pi}{3}-\tan^{-1}\frac{R'}{R+R''+2\delta_x}+\tan^{-1}\frac{R'}{R+R''-\delta_x-\delta_y}\right); \end{aligned} \tag{S.112}$$

$$\begin{aligned} r_{A'C}^2 &= \left(R+R''+2\delta_x\right)^2 + R'^2 + (R-\delta_x+\delta_y)^2 \\ &\quad -2\sqrt{(R+R''+2\delta_x)^2+R'^2}\,(R-\delta_x+\delta_y)\cos\left(\frac{2\pi}{3}+\tan^{-1}\frac{R'}{R+R''+2\delta_x}\right); \end{aligned} \tag{S.113}$$

$$\begin{aligned} r_{A'C'}^2 &= \left(R+R''+2\delta_x\right)^2 + 2R'^2 + \left(R+R''-\delta_x+\delta_y\right)^2 \\ &\quad -2\sqrt{\left[(R+R''+2\delta_x)^2+R'^2\right]\left[(R+R''-\delta_x+\delta_y)^2+R'^2\right]}\,\cdot \\ &\quad \cos\left(\frac{2\pi}{3}+\tan^{-1}\frac{R'}{R+R''+2\delta_x}-\tan^{-1}\frac{R'}{R+R''-\delta_x+\delta_y}\right); \end{aligned} \tag{S.114}$$

$$r_{BC}^2 = (R-\delta_x-\delta_y)^2 + (R-\delta_x+\delta_y)^2 - 2(R-\delta_x-\delta_y)(R-\delta_x+\delta_y)\cos\frac{2\pi}{3}; \tag{S.115}$$

$$\begin{aligned} r_{BC'}^2 = {} & (R-\delta_x-\delta_y)^2 + \left(R+R''-\delta_x+\delta_y\right)^2 + R'^2 \\ & -2\sqrt{\left[(R+R''-\delta_x+\delta_y)^2+R'^2\right]}(R-\delta_x-\delta_y)\cos\left(\frac{2\pi}{3}+\tan^{-1}\frac{R'}{R+R''-\delta_x+\delta_y}\right); \end{aligned} \tag{S.116}$$

$$\begin{aligned} r_{B'C}^2 = {} & \left(R+R''-\delta_x-\delta_y\right)^2 + R'^2 + (R-\delta_x+\delta_y)^2 \\ & -2\sqrt{\left[(R+R''-\delta_x-\delta_y)^2+R'^2\right]}(R-\delta_x+\delta_y)\cos\left(\frac{2\pi}{3}-\tan^{-1}\frac{R'}{R+R''-\delta_x-\delta_y}\right); \end{aligned} \tag{S.117}$$

$$\begin{aligned} r_{B'C'}^2 = {} & \left(R+R''-\delta_x-\delta_y\right)^2 + 2R'^2 + \left(R+R''-\delta_x+\delta_y\right)^2 \\ & -2\sqrt{\left[(R+R''-\delta_x-\delta_y)^2+R'^2\right]\left[(R+R''-\delta_x+\delta_y)^2+R'^2\right]}\cdot \\ & \cos\left(\frac{2\pi}{3}-\tan^{-1}\frac{R'}{R+R''-\delta_x-\delta_y}+\tan^{-1}\frac{R'}{R+R''-\delta_x+\delta_y}\right); \end{aligned} \tag{S.118}$$

$$r_{OA}^2 = (R+2\delta_x)^2; \tag{S.119}$$

$$r_{OB}^2 = (R-\delta_x-\delta_y)^2; \tag{S.120}$$

$$r_{OC}^2 = (R-\delta_x+\delta_y)^2; \tag{S.121}$$

$$r_{OA'}^2 = \left(R+R''+2\delta_x\right)^2 + R'^2; \tag{S.122}$$

$$r_{OB'}^2 = \left(R+R''-\delta_x-\delta_y\right)^2 + R'^2; \tag{S.123}$$

$$r_{OC'}^2 = \left(R+R''-\delta_x+\delta_y\right)^2 + R'^2. \tag{S.124}$$

Through inspection, we see that on $\delta_y \to -\delta_y$ (i.e., $y \to -y$), the following r_{iJ}s swap:

$$r_{aB} \leftrightarrow r_{aC}; r_{aB'} \leftrightarrow r_{aC'}; r_{bB} \leftrightarrow r_{bC}; r_{bB'} \leftrightarrow r_{bC'}; r_{cB} \leftrightarrow r_{cC}; r_{cB'} \leftrightarrow r_{cC'}, \tag{S.125}$$

and the other r_{iJ}s are invariant. Again, these swappings and invariances maintain if a, b, and c are vertically displaced out of the symmetry plane of the molecule. Threrefore, V_{ne} is symmetric with respect to $y \to -y$. It takes an expansion with the $\cos(3m\phi)$ terms, with no selection of m. For the r_{IJ} distances, on $\delta_y \to -\delta_y$, we have the following swapping:

$$r_{AB} \leftrightarrow r_{AC}; r_{OB} \leftrightarrow r_{OC}; r_{OB'} \leftrightarrow r_{OC'}. \tag{S.126}$$

r_{BC}, $r_{B'C'}$, r_{OA}, and $r_{OA'}$ are invariant. The leftover eight r_{IJ}s can be grouped into four pairs:

$$(r_{A'B'}, r_{A'C'}); (r_{AB'}, r_{AC'}); (r_{A'B}, r_{A'C}); (r_{BC'}, r_{B'C}). \tag{S.127}$$

Each pair is close to swap on $\delta_y \to -\delta_y$ but does not undergo the swapping. For instance, the different signs for the $\tan^{-1}$ terms in Eqs. S.116 and S.117 prevent the $r_{BC'} \leftrightarrow r_{B'C}$ swapping. The other three pairs are not swapped for the same reason: having different signs for the $\tan^{-1}$ terms. The four non-swapped pairs determine that V_{nn} is asymmetric with respect to $y \to -y$, as indicated by the $V_{nn}(x, y) - V_{nn}(x, -y)$ contourplot in Figure 2(d) in the main text.

It is straightforward to see that there is no swapping or invariance for the r_{iJ} and r_{IJ} distances on $\delta_x \to -\delta_x$. Therefore, both V_{ne} and V_{nn} are asymmetric with respect to $x \to -x$. Overall, V_{nn} is asymmetric with respect to $x \to -x$ and $y \to -y$. It takes an expansion with both the $\cos(3m\phi)$ and $\sin(3m\phi)$ terms, with no selection of m. H_{ZZ}, as a summation of V_{ne} and V_{nn}, takes a similar expansion.

References

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