Supporting Information
First and Second Order Expansions for Origin Independent Vibronic Calculations of Electronic Chiroptical Spectra Beyond the Franck-Condon Approximation

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A Convergence of TDM with basis set size

As expected, both length and velocity gauge get closer as the size of the basis size increases, with the values in the length gauge convergin slightly more quickly. Still, the relative change from the smaller to the larger basis size remains moderate, decreasing by 16% (velocity gauge) or 9% (length gauge) at the ES equilibrium geometry (similar changes are observed at the ES minimum). Contrarily, the magnetic TDM changes more significantly upon increasing the basis size from cc-pVTZ to aug-cc-pVQZ, nearly doubling the value computed at the CoM, i.e. m^{ref}, as the basis size increases.

Table S1: Modulus of TDMs (in atomic units) computed at CAM-B3LYP level with different basis sets for molecule **1**, **2** and **3**. The values are evaluated at the excited state (minES) or ground state (minGS) equilibrium geometries computed at CAM-B3LYP/TZVP level.

	minES				minGS			
Basis	$\|\boldsymbol{\mu}^v\|$	$\|\boldsymbol{\mu}^l\|$	$\|\mathbf{m}^{\text{CoM}}\|$	$\|\mathbf{m}^{\text{Shift}}\|$	$\|\boldsymbol{\mu}^v\|$	$\|\boldsymbol{\mu}^l\|$	$\|\mathbf{m}^{\text{CoM}}\|$	$\|\mathbf{m}^{\text{Shift}}\|$
Molecule **1**								
TZVP	0.154	0.155	0.165	0.356	0.113	0.115	0.145	0.279
cc-pVTZ	0.165	0.162	0.175	0.394	0.125	0.122	0.156	0.321
cc-pVQZ	0.161	0.161	0.174	0.381	0.120	0.120	0.155	0.306
aug-cc-pVTZ	0.155	0.155	0.171	0.366	0.112	0.112	0.150	0.284
aug-cc-pVQZ	0.155	0.155	0.171	0.366	0.112	0.112	0.150	0.285
Molecule **2**								
TZVP	0.310	0.296	0.035	1.875	0.213	0.200	0.034	1.376
cc-pVTZ	0.317	0.299	0.028	1.919	0.221	0.204	0.027	1.432
cc-pVQZ	0.295	0.288	0.042	1.787	0.199	0.192	0.041	1.291
aug-cc-pVTZ	0.268	0.272	0.061	1.638	0.169	0.172	0.061	1.111
aug-cc-pVQZ	0.267	0.271	0.062	1.634	0.168	0.170	0.062	1.104
Molecule **3**								
TZVP	1.354	1.234	0.024	2.044	1.235	1.130	0.046	1.981
cc-pVTZ	1.237	1.193	0.024	1.839	1.123	1.086	0.044	1.777
cc-pVQZ	1.202	1.188	0.025	0.025	1.092	1.080	0.044	0.044
aug-cc-pVTZ	1.181	1.185	0.025	1.738	1.070	1.074	0.044	1.680
aug-cc-pVQZ	1.184	1.185	0.025	1.742	1.073	1.073	0.044	1.684

Table S2: Angle between TDMs (in degrees) computed with CAM-B3LYP level with different basis sets for molecules **1**, **2** and **3**. The values are evaluated at the excited state (minES) or ground state (minGS) equilibrium geometries computed at CAM-B3LYP/TZVP level.

	minES					minGS				
Basis	$\widehat{\boldsymbol{\mu}^v\boldsymbol{\mu}^l}$	$\widehat{\boldsymbol{\mu}^l\mathbf{m}}^{\text{CoM}}$	$\widehat{\boldsymbol{\mu}^v\mathbf{m}}^{\text{CoM}}$	$\widehat{\boldsymbol{\mu}^l\mathbf{m}}^{\text{Shift}}$	$\widehat{\boldsymbol{\mu}^v\mathbf{m}}^{\text{Shift}}$	$\widehat{\boldsymbol{\mu}^v\boldsymbol{\mu}^l}$	$\widehat{\boldsymbol{\mu}^l\mathbf{m}}^{\text{CoM}}$	$\widehat{\boldsymbol{\mu}^v\mathbf{m}}^{\text{CoM}}$	$\widehat{\boldsymbol{\mu}^l\mathbf{m}}^{\text{Shift}}$	$\widehat{\boldsymbol{\mu}^v\mathbf{m}}^{\text{Shift}}$
Molecule **1**										
TZVP	0.77	89.52	89.45	90.01	89.74	1.04	89.67	89.61	90.12	89.80
cc-pVTZ	0.36	89.58	89.73	89.66	89.88	0.51	89.86	90.06	89.73	90.03
cc-pVQZ	0.06	89.58	89.57	89.83	89.80	0.06	89.77	89.73	89.92	89.86
aug-cc-pVTZ	0.22	89.20	88.98	89.73	89.52	0.04	89.37	89.37	89.66	89.67
aug-cc-pVQZ	0.23	89.18	88.95	89.73	89.51	0.09	89.32	89.39	89.60	89.68
Molecule **2**										
TZVP	0.42	86.93	86.91	89.54	89.94	0.69	85.46	85.68	89.21	89.89
cc-pVTZ	0.56	84.47	84.51	89.36	89.92	0.92	83.74	84.04	88.97	89.89
cc-pVQZ	0.22	85.34	85.40	89.67	89.89	0.41	84.17	84.37	89.42	89.82
aug-cc-pVTZ	0.20	86.66	86.69	90.04	89.88	0.09	85.25	85.23	89.82	89.74
aug-cc-pVQZ	0.19	86.90	86.96	90.01	89.89	0.10	85.27	85.24	89.83	89.73
Molecule **3**										
TZVP	0.09	80.34	80.26	89.81	89.89	0.18	92.94	92.77	90.03	90.06
cc-pVTZ	0.06	81.21	81.18	89.83	89.89	0.12	93.36	93.29	89.98	90.08
cc-pVQZ	0.07	82.03	81.96	82.03	81.96	0.09	93.65	93.58	93.65	93.58
aug-cc-pVTZ	0.02	83.02	83.03	89.91	89.90	0.02	94.11	94.11	90.13	90.11
aug-cc-pVQZ	0.01	82.96	82.97	89.91	89.90	0.02	94.08	94.07	90.12	90.11

B Additional simulated spectra

B.1 Molecule 1

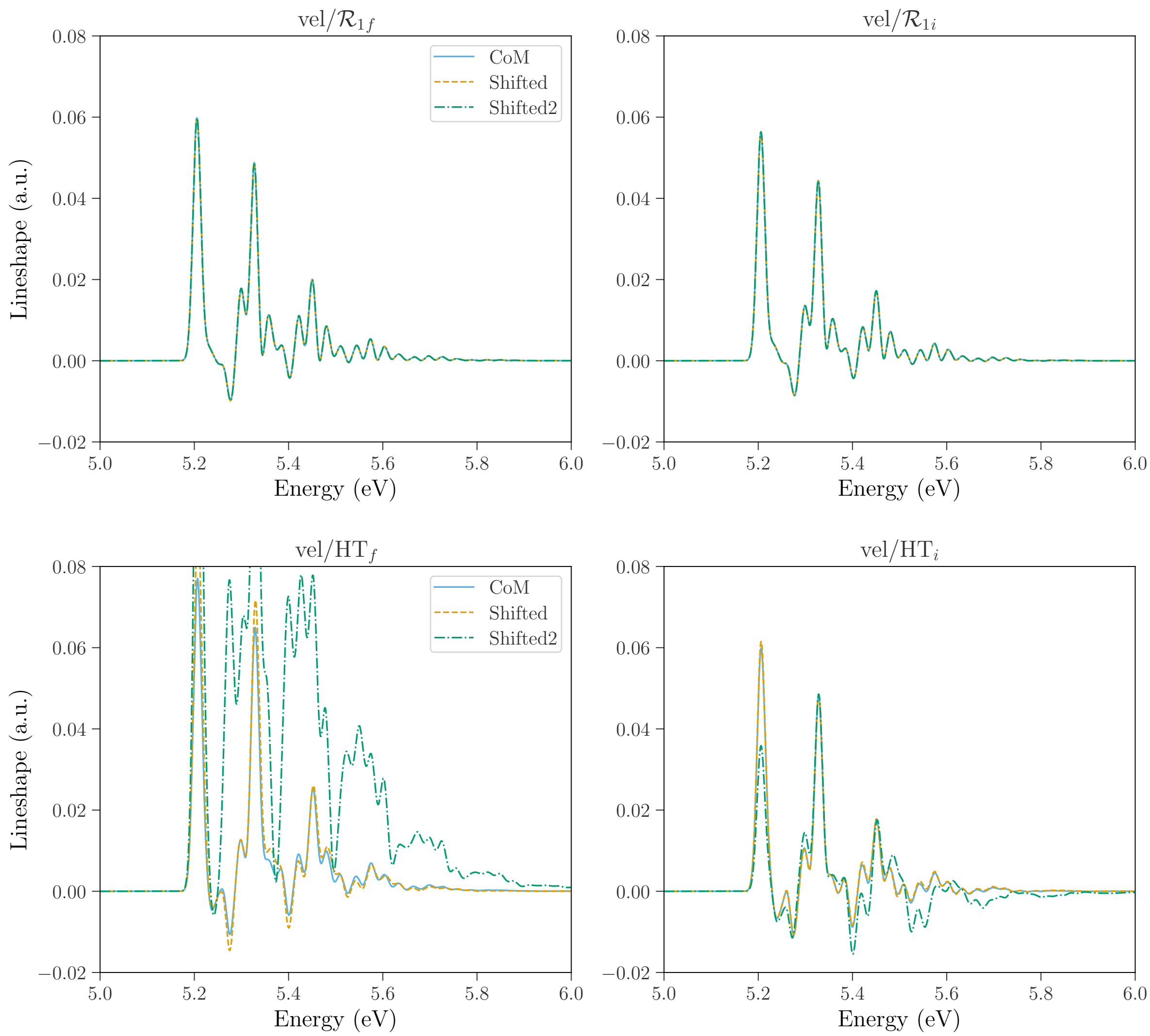

Figure S1: ECD spectra of molecule **1** adopting the velocity gauge at HT_f (left panel) or HT_i (right panel) levels including $\mathcal{R}_1$ terms (top panels) or all HT terms (bottom panels) using both Q_f and Q_i frames. The spectra are computed locating the molecule either at the center of mass (CoM) or shifted by an arbitrary vector.

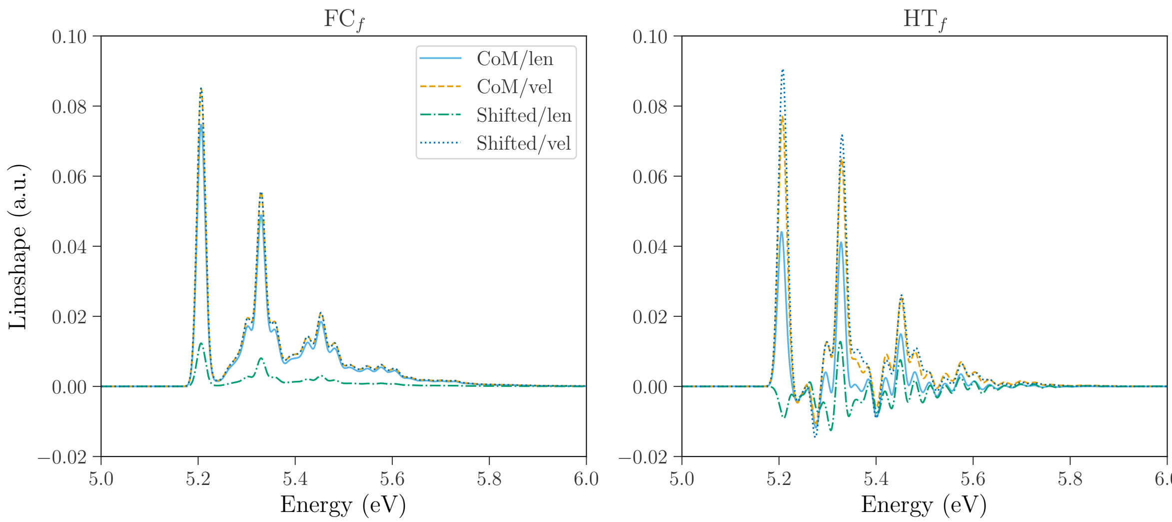

Figure S2: ECD spectra of molecule **1** using TDM$_f$ data including the standar FC (left panel) or HT (right panel), computed locating the molecule either at the center of mass (CoM) or shifted by an arbitrary vector.

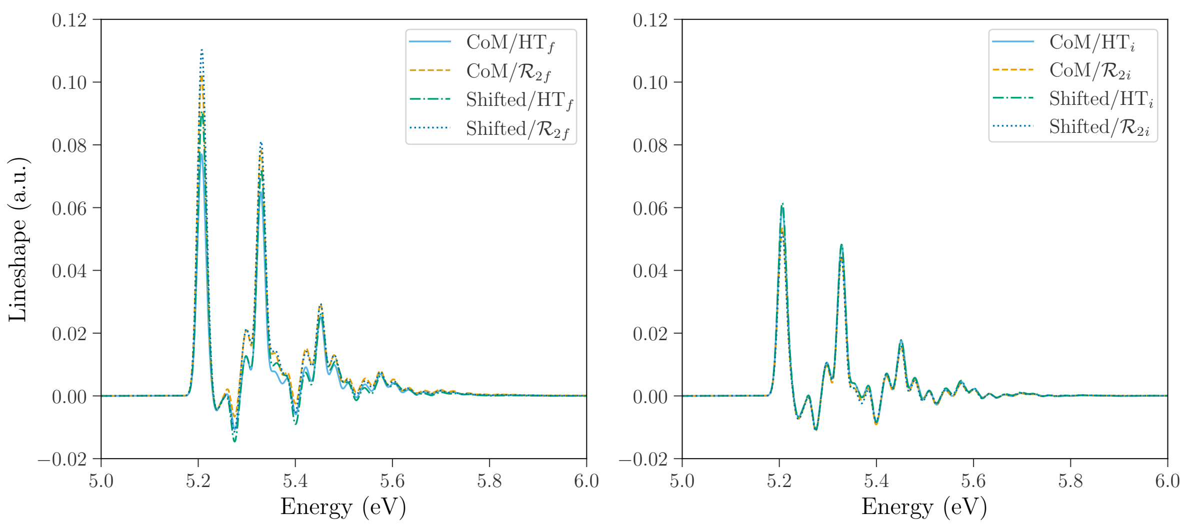

Figure S3: ECD spectra of molecule **1** adopting the velocity gauge at HT$_f$ or HT$_i$ levels including all HT terms additionally retaining up to $\mathcal{R}_2$. The calculations are performed at HT$_f$ level in the Q_f frame (left) or at HT$_i$ level in the Q_i frame (right), locating the molecule either at the center of mass (CoM) or shifted by an arbitrary vector.

B.2 Molecule 2

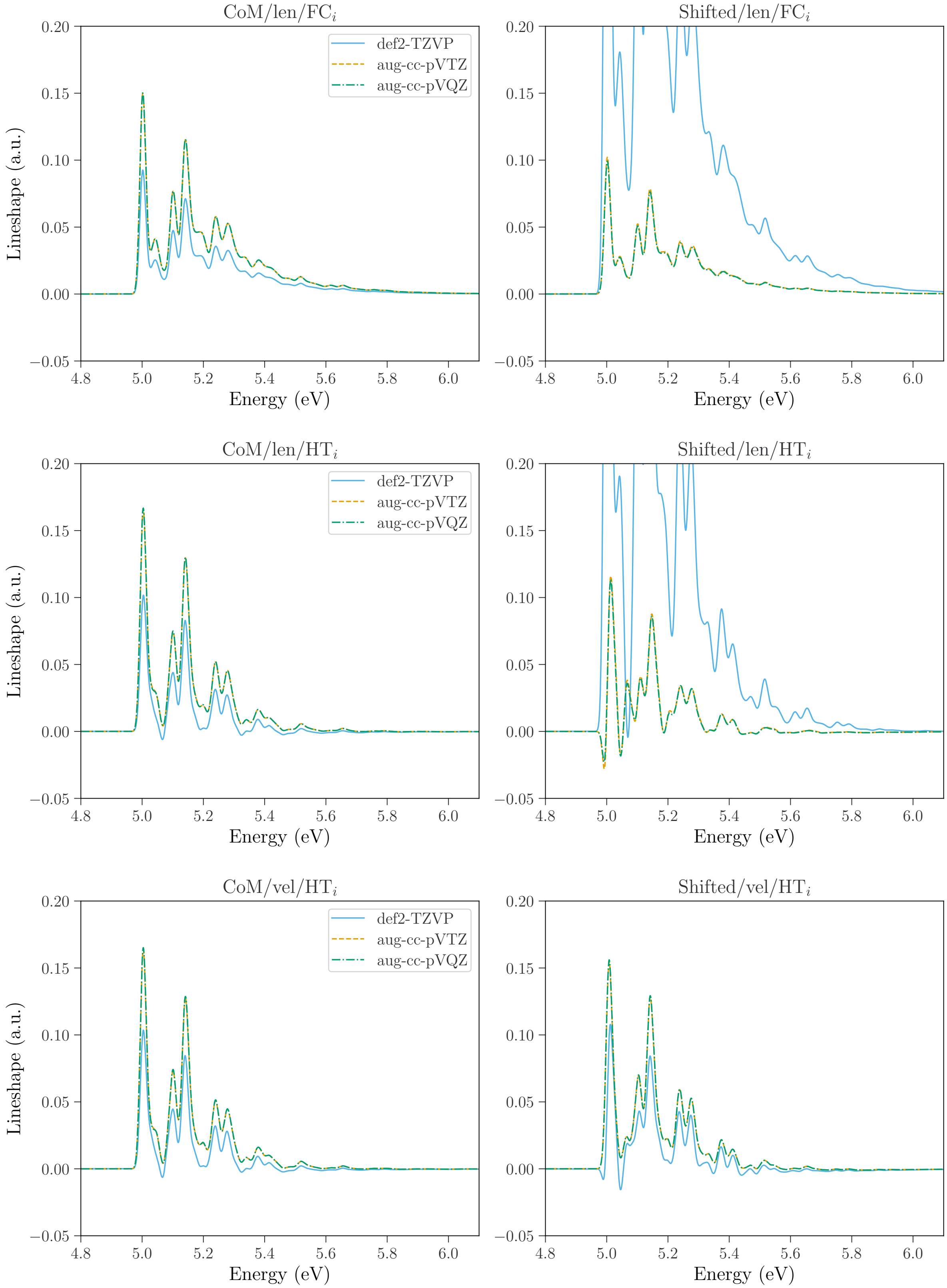

Figure S4: ECD spectra of molecule **2** with TDM$_i$ data, including standard FC (top) and HT (middle) contributions in the length gauge and HT (bottom) in the velocity gauge, computed with the molecule located either at the center of mass (CoM) or shifted by an arbitrary vector. The calculations are carried out with def2-TZVP, aug-cc-pVTZ and aug-cc-pVQZ basis sets.

B.3 Molecule 3

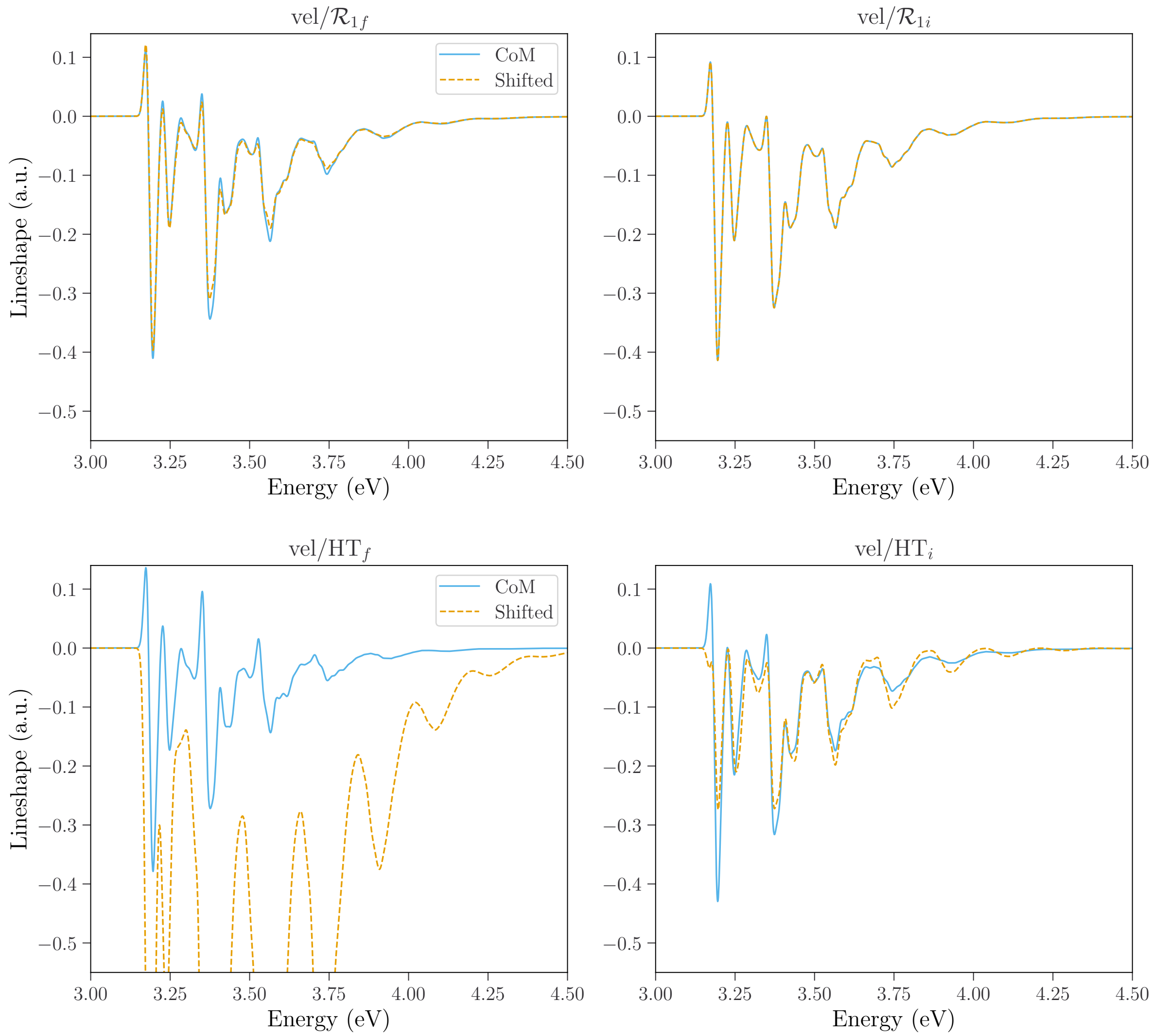

Figure S5: ECD spectra of molecule **3** adopting the velocity gauge at HT_f (left panel) or HT_i (right panel) levels including $\mathcal{R}_1$ terms (top panels) or all HT terms (bottom panels) using both Q_f and Q_i frames. The spectra are computed locating the molecule either at the center of mass (CoM) or shifted by an arbitrary vector.

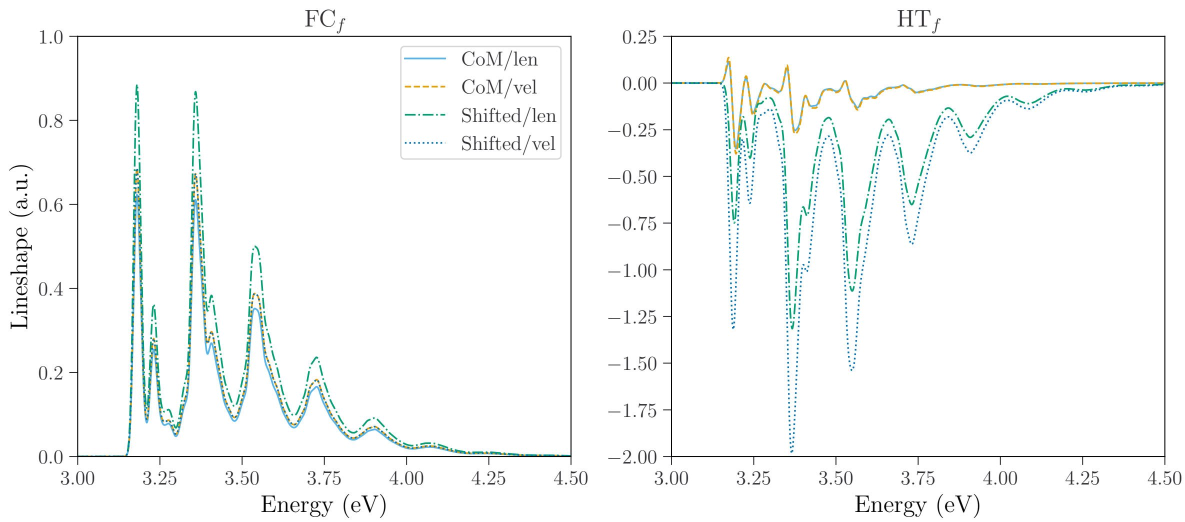

Figure S6: ECD spectra of molecule **3** at HT$_f$/Qf including the standar FC (left panel) or HT (right panel), computed locating the molecule either at the center of mass (CoM) or shifted by an arbitrary vector.

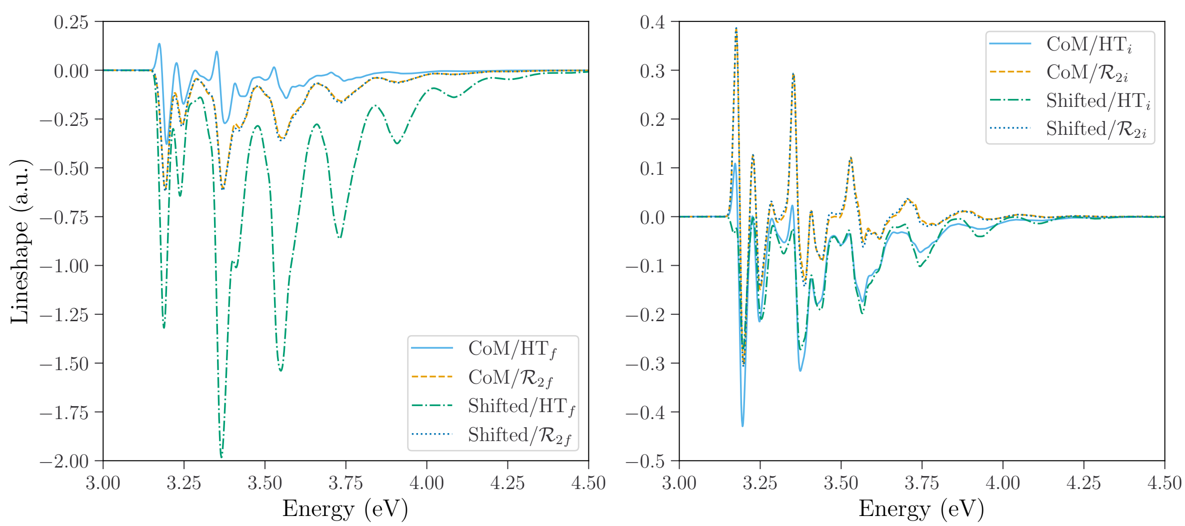

Figure S7: ECD spectra of molecule **3** adopting the velocity gauge at HT$_f$ or HT$_i$ levels including all HT terms additionally retaining up to $\mathcal{R}_2$. The calculations are performed at HT$_f$ level in the Q_f frame (left) or at HT$_i$ level in the Q_i frame (right), locating the molecule either at the center of mass (CoM) or shifted by an arbitrary vector.

B.4 Summary of all systems

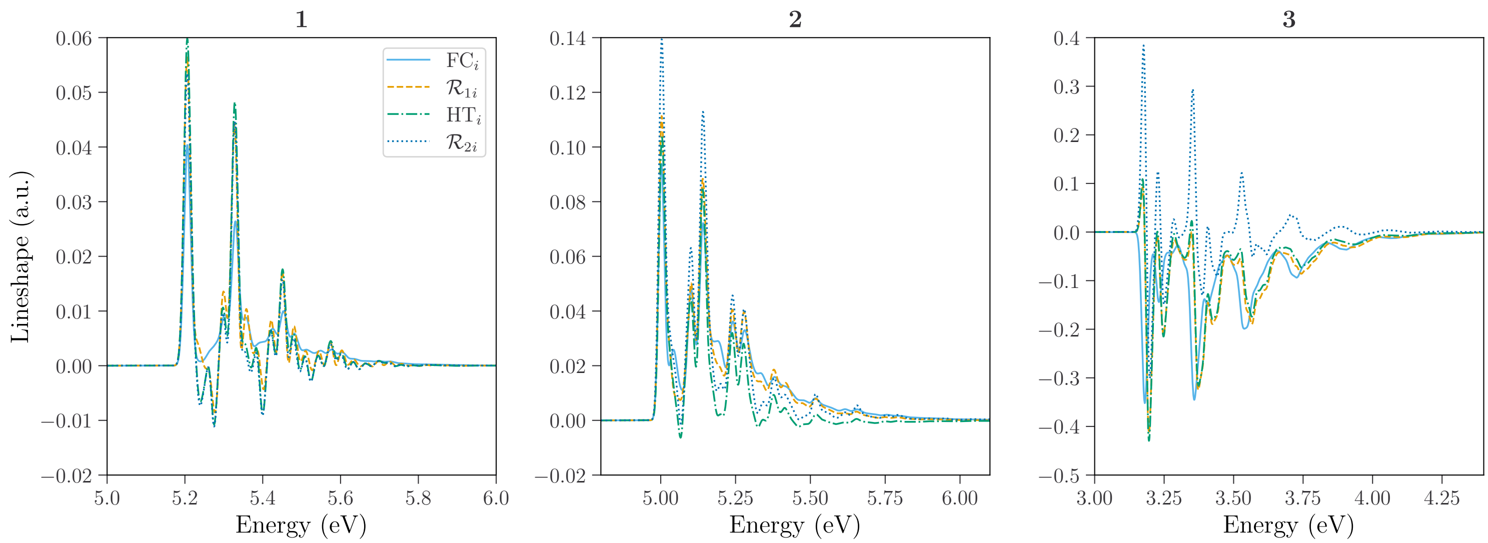

Figure S8: ECD spectra of molecules **1**, **2** and **3**, computed in the velocity gauge at the center of mass with TDM$_i$ data.

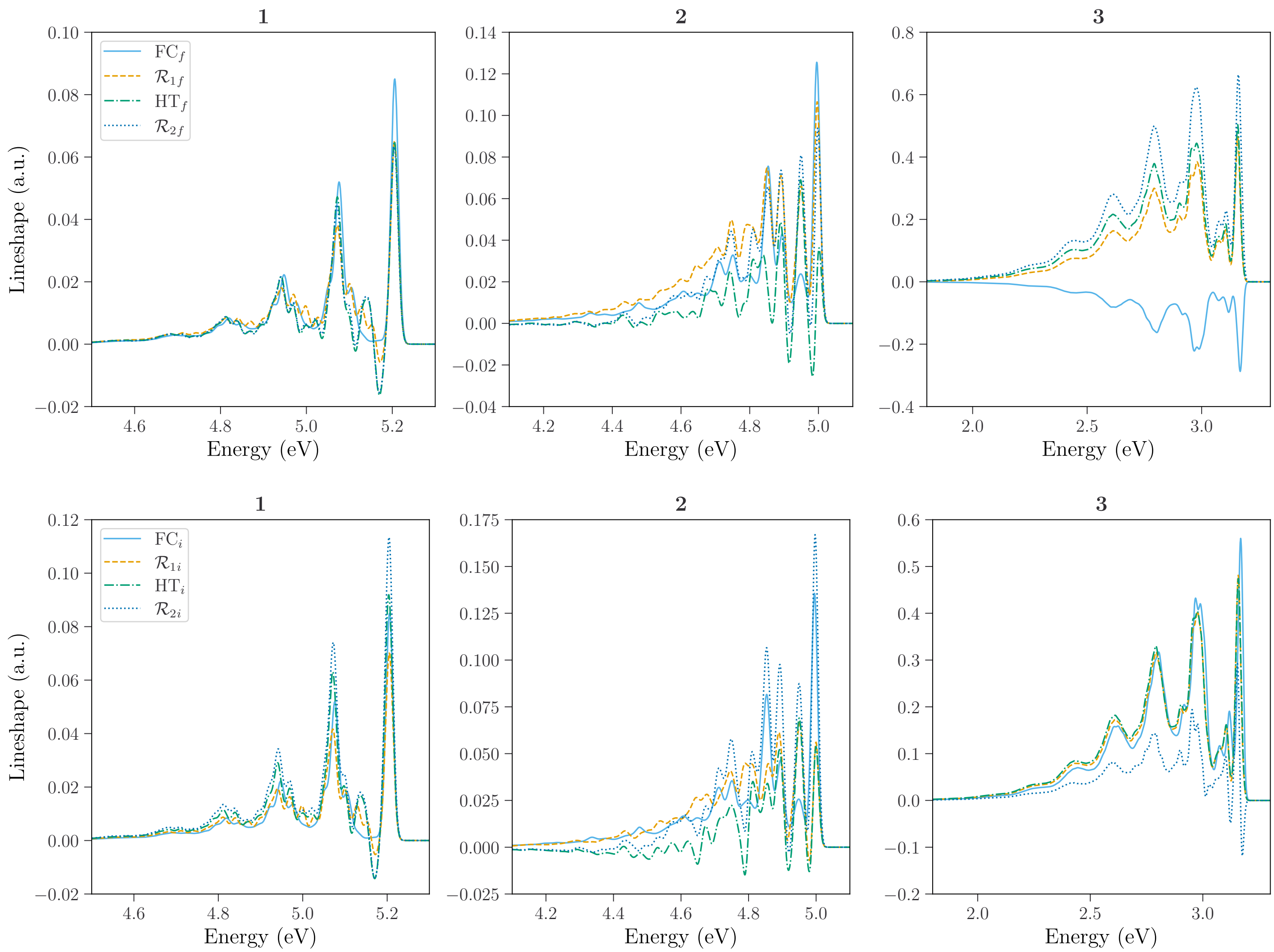

Figure S9: CPL spectra of molecules **1**, **2** and **3**, computed in the velocity gauge at the center of mass with TDM evaluated either at the initial (i) of final (f) stage geometry.

C Additional derivations

C.1 Invariance of Rotatory Strength in the vel gauge

Let us assume we have a system placed in the center of mass (CoM) and we compute its magnetic TDM ($\mathbf{m}_{if}^{\text{ref}}$). If we apply a translation of the origin (by $\mathbf{R}$), the magnetic TDM becomes

$$\mathbf{m}_{f0} = \mathbf{m}_{f0}^{\text{ref}} - \frac{E_{if}}{2\hbar}\mathbf{R} \times \boldsymbol{\mu}_{if}^{v}, \tag{1}$$

$$\mathbf{m}'_{f0} = \mathbf{m}_{f0}^{\text{ref}\prime} - \frac{E_{if}}{2\hbar}\mathbf{R} \times \boldsymbol{\mu}_{if}^{v\,\prime} - \frac{E'_{if}}{2\hbar}\mathbf{R} \times \boldsymbol{\mu}_{if}^{v}. \tag{2}$$

The above expression for $\mathbf{m}$ arises from relation with the angular momentum operator. In practice, when the angular momentum of the system is not computed at the reference position (in this work, the CoM), an additional term arises. Therefore, $\mathbf{R}$ refers to the position of the system CoM with respect to the origin. In the following, we will omit the if subscript and, to simplify the notation, we assume a 1D system (with coordinate ξ). Therefore, $\boldsymbol{\mu}^{v\prime}$ is a 3D vector: $(\partial\mu_x^v/\partial\xi, \partial\mu_y^v/\partial\xi, \partial\mu_z^v/\partial\xi)$ (and the same for $\boldsymbol{m}'$), and the gradient and Hessian of the transition energy are scalars. The extensions to the general N-dimensional case reported in the main text is straightforward.

We can now analyse the behavior of the FC/FC FC/HT and HT/HT terms after a translation of the origin

- FC term:

$$(\boldsymbol{\mu}_0^v)^T \cdot \mathbf{m}_0 = (\boldsymbol{\mu}_0^v)^T \cdot \mathbf{m}_0^{\mathrm{ref}} - \frac{E}{2\hbar} \underbrace{(\boldsymbol{\mu}_0^v)^T \cdot \mathbf{R} \times \boldsymbol{\mu}_0^v}_{=0} = (\boldsymbol{\mu}_0^v)^T \cdot \mathbf{m}_0^{\mathrm{ref}}. \tag{3}$$

where we recognized that the mixed product involving two colinear vectors is zero.

- FC/HT term:

$$\begin{aligned}(\boldsymbol{\mu}^{v\prime})^T \cdot \mathbf{m}_0 + (\boldsymbol{\mu}_0^v)^T \cdot \mathbf{m}' &= (\boldsymbol{\mu}^{v\prime})^T \cdot \mathbf{m}_0^{\mathrm{ref}} + (\boldsymbol{\mu}_0^v)^T \cdot \mathbf{m}^{\mathrm{ref}\prime} - \\ &\frac{E}{2\hbar} \underbrace{\left((\boldsymbol{\mu}^{v\prime})^T \cdot \mathbf{R} \times \boldsymbol{\mu}_0^v + (\boldsymbol{\mu}_0^v)^T \cdot \mathbf{R} \times \boldsymbol{\mu}^{v\prime}\right)}_{=0} - \frac{E'}{2\hbar} \underbrace{(\boldsymbol{\mu}_0^v)^T \cdot \mathbf{R} \times \boldsymbol{\mu}_0^v}_{=0} = \\ &= (\boldsymbol{\mu}^{v\prime})^T \cdot \mathbf{m}_0^{\mathrm{ref}} + (\boldsymbol{\mu}_0^v)^T \cdot \mathbf{m}^{\mathrm{ref}\prime}.\end{aligned} \tag{4}$$

where we recognized that the mixed product changes sign when swapping two of the vectors involved.

- HT/HT term:

$$\begin{aligned}(\boldsymbol{\mu}^{v\prime})^T \cdot \mathbf{m}' &= (\boldsymbol{\mu}^{v\prime})^T \cdot \mathbf{m}^{\mathrm{ref}\prime} - \frac{E}{2\hbar} \underbrace{\left((\boldsymbol{\mu}^{v\prime})^T \cdot \mathbf{R} \times \boldsymbol{\mu}^{v\prime}\right)}_{=0} - \frac{E'}{2\hbar} \left((\boldsymbol{\mu}^{v\prime})^T \cdot \mathbf{R} \times \boldsymbol{\mu}_0^v\right) = \\ &= (\boldsymbol{\mu}^{v\prime})^T \cdot \mathbf{m}^{\mathrm{ref}\prime} - \frac{E'}{2\hbar} \left((\boldsymbol{\mu}^{v\prime})^T \cdot \mathbf{R} \times \boldsymbol{\mu}_0^v\right).\end{aligned} \tag{5}$$

According to the above derivation, the FC and FC/HT ontributions are actually origin independent. On the contrary, it turns that the HT/HT term is not origin independent in the velocity gauge (because it characterized by a non-vanishing term that depends explicitly on $\mathbf{R}$).

C.1.1 Exact quadratic expansion of RS

The HT/HT contribution reports, partly, the second order term of a Taylor expansion of the RS $= \boldsymbol{\mu}^T \mathbf{m}$ (note we drop the v superindex). In order to have the complete second order term of the Taylor expansion, we need a second order expansion of $\mathbf{m}$ and $\boldsymbol{\mu}$. The second order term (for one dimensional system) will be

$$
\begin{aligned}
&\left(\boldsymbol{\mu}_0+\boldsymbol{\mu}'Q+\tfrac{1}{2}\boldsymbol{\mu}''Q^2\right)^T\left(\mathbf{m}_0+\mathbf{m}'Q+\tfrac{1}{2}\mathbf{m}''Q^2\right)= \\
&=\boldsymbol{\mu}_0^T\mathbf{m}_0+ \\
&\quad\left(\boldsymbol{\mu}_0^T\mathbf{m}'+(\boldsymbol{\mu}')^T\mathbf{m}_0\right)Q+ \\
&\quad\left(\tfrac{1}{2}\boldsymbol{\mu}_0^T\mathbf{m}''+\tfrac{1}{2}(\boldsymbol{\mu}'')^T\mathbf{m}_0+(\boldsymbol{\mu}')^T\mathbf{m}'\right)Q^2+\mathcal{O}\left(Q^3\right).
\end{aligned}
\tag{6}
$$

The second order term can be evaluated taking into account that

$$
\mathbf{m}''=\mathbf{m}^{\text{ref}\prime\prime}-\frac{E}{2\hbar}\mathbf{R}\times\boldsymbol{\mu}''-\frac{E''}{2\hbar}\mathbf{R}\times\boldsymbol{\mu}-\frac{E'}{\hbar}\mathbf{R}\times\boldsymbol{\mu}'. \tag{7}
$$

Therefore,

$$
\begin{aligned}
(\underbrace{(\boldsymbol{\mu}')^T\mathbf{m}'}_{=\text{HT/HT}}+\quad&\tfrac{1}{2}\boldsymbol{\mu}_0^T\mathbf{m}''+\tfrac{1}{2}(\boldsymbol{\mu}'')^T\mathbf{m}_0)=(\boldsymbol{\mu}')^T\cdot\mathbf{m}^{\text{ref}\prime}-\tfrac{E'}{2\hbar}\left((\boldsymbol{\mu}')^T\cdot\mathbf{R}\times\boldsymbol{\mu}_0\right)+ \\
&\tfrac{1}{2}\left(\boldsymbol{\mu}_0^T\mathbf{m}^{\text{ref}\prime\prime}-\tfrac{E}{2\hbar}\boldsymbol{\mu}_0^T\cdot\mathbf{R}\times\boldsymbol{\mu}''-\tfrac{E''}{2\hbar}\boldsymbol{\mu}_0^T\cdot\mathbf{R}\times\boldsymbol{\mu}_0-\tfrac{E'}{\hbar}\boldsymbol{\mu}_0^T\cdot\mathbf{R}\times\boldsymbol{\mu}'\right)+ \\
&\tfrac{1}{2}\left((\boldsymbol{\mu}'')^T\mathbf{m}_0^{\text{ref}}-\tfrac{E}{2\hbar}(\boldsymbol{\mu}'')^T\cdot\mathbf{R}\times\boldsymbol{\mu}_0\right)= \\
&=(\boldsymbol{\mu}')^T\cdot\mathbf{m}^{\text{ref}\prime}+\tfrac{1}{2}\boldsymbol{\mu}_0^T\mathbf{m}^{\text{ref}\prime\prime}+\tfrac{1}{2}(\boldsymbol{\mu}'')^T\mathbf{m}_0^{\text{ref}}.
\end{aligned}
\tag{8}
$$

The complete second order Taylor expansion coeffient is, therefore, origin invariant. Again, the generalization to N-dimensional systems shown in the main text requires to pay some attention to the indices, which also include cross terms, but it is straightforward.

C.1.2 Second order expansion of RS between vibronic states

As indicated in the main text, when dealing with vibronic states, as it is the case when we want to compute the lineshape, we need to consider the vibrational wavefunctions in the vibronic RS:

$$
\mathcal{R}_{\mathbf{v}_i,\mathbf{v}_f}=\langle\mathbf{v}_i|\boldsymbol{\mu}|\mathbf{v}_f\rangle\langle\mathbf{v}_f|\boldsymbol{m}|\mathbf{v}_i\rangle. \tag{9}
$$

For the zeroth- and first order terms, the origin independence is kept as the same terms as in the purely electronic version appear (cancelling out the origin dependent terms), multiplied by common matrix elements, as shown in the main text. The zeroth order term is immediate, while for the first order term we have,

$$\boldsymbol{\mu}_0^T \langle \mathbf{v}_i | \mathbf{v}_f \rangle \boldsymbol{m}' \langle \mathbf{v}_f | Q | \mathbf{v}_i \rangle + (\boldsymbol{\mu}')^T \langle \mathbf{v}_i | Q | \mathbf{v}_f \rangle \boldsymbol{m} \langle \mathbf{v}_f | \mathbf{v}_i \rangle. \tag{10}$$

Taking into account the following equality,

$$\langle \mathbf{v}_i | \mathbf{v}_f \rangle \langle \mathbf{v}_f | Q | \mathbf{v}_i \rangle = \langle \mathbf{v}_i | Q | \mathbf{v}_f \rangle \langle \mathbf{v}_f | \mathbf{v}_i \rangle, \tag{11}$$

which holds assuming that the product is real. Now, the terms can be effectively grouped as,

$$\left((\boldsymbol{\mu}')^T \cdot \mathbf{m}_0^{\mathrm{ref}} + \boldsymbol{\mu}_0^T \cdot \mathbf{m}^{\mathrm{ref}\prime} \right) \langle \mathbf{v}_i | \mathbf{v}_f \rangle \langle \mathbf{v}_f | Q | \mathbf{v}_i \rangle, \tag{12}$$

where we have already taken into account the derivations shown in Eq. 4.

In this case, it can be shown the second order term is separated into two parts, each multiplied by different matrix elements in the nuclear coordinates, which can no longer be grouped together,

$$(\boldsymbol{\mu}')^T \mathbf{m}' \langle \mathbf{v}_i | Q | \mathbf{v}_f \rangle \langle \mathbf{v}_f | Q | \mathbf{v}_i \rangle + \quad \frac{1}{2} \left(\boldsymbol{\mu}_0^T \mathbf{m}'' + (\boldsymbol{\mu}'')^T \mathbf{m}_0 \right) \langle \mathbf{v}_i | Q^2 | \mathbf{v}_f \rangle \langle \mathbf{v}_f | \mathbf{v}_i \rangle, \tag{13}$$

where we have applied a generalized version of equality in Eq. 11 to group the second term. We note that the first term corresponds to the HT/HT term in the purely electric RS, Eq. 5. In both terms, the same origin dependent term survives which, in this case, cannot be cacelled,

$$\left[(\boldsymbol{\mu}')^T \cdot \mathbf{m}^{\mathrm{ref}\prime} - \frac{E'}{2\hbar}\left((\boldsymbol{\mu}')^T \cdot \mathbf{R} \times \boldsymbol{\mu}_0\right)\right] \langle \mathbf{v}_i|Q|\mathbf{v}_f\rangle\langle \mathbf{v}_f|Q|\mathbf{v}_i\rangle +$$

$$\left[\tfrac{1}{2}\left(\boldsymbol{\mu}_0^T \mathbf{m}^{\mathrm{ref}\prime\prime} + (\boldsymbol{\mu}'')^T \mathbf{m}_0\right) + \frac{E'}{2\hbar}\left((\boldsymbol{\mu}')^T \cdot \mathbf{R} \times \boldsymbol{\mu}_0\right)\right] \langle \mathbf{v}_i|Q^2|\mathbf{v}_f\rangle\langle \mathbf{v}_f|\mathbf{v}_i\rangle =$$

$$\left[(\boldsymbol{\mu}')^T \cdot \mathbf{m}^{\mathrm{ref}\prime}\right] \langle \mathbf{v}_i|Q|\mathbf{v}_f\rangle\langle \mathbf{v}_f|Q|\mathbf{v}_i\rangle + \left[\frac{1}{2}\left(\boldsymbol{\mu}_0^T \mathbf{m}^{\mathrm{ref}\prime\prime} + (\boldsymbol{\mu}'')^T \mathbf{m}_0\right)\right] \langle \mathbf{v}_i|Q^2|\mathbf{v}_f\rangle\langle \mathbf{v}_f|\mathbf{v}_i\rangle -$$

$$\frac{E'}{2\hbar}\left((\boldsymbol{\mu}')^T \cdot \mathbf{R} \times \boldsymbol{\mu}_0\right) \left[\langle \mathbf{v}_i|Q|\mathbf{v}_f\rangle\langle \mathbf{v}_f|Q|\mathbf{v}_i\rangle - \langle \mathbf{v}_i|Q^2|\mathbf{v}_f\rangle\langle \mathbf{v}_f|\mathbf{v}_i\rangle\right], \tag{14}$$

The generalizatio to the N-dimensional case shown in the main text requires some attention to the indices, but follows the same reasoning.

C.2 Consistency of $\mathbf{HT}_x/Q_x$ schemes

The geometry at which the TDMs and their derivatives are computed are usually the equilibrium geometry of either the initial or final states, leading to the so-called HT_i or HT_f approaches, respectively [**?**]. As indicated in the main text, the apparently more consistent choice is to adopt HT_i with Q_i norma modes (HT_i/Q_i) and, similarly, HT_f/Q_f. However, in principle, it is possible to adopt *mixed* HT_f/Q_i or HT_i/Q_f schemes, resorting to the Duschinsky transformation and extrapolating the zero-order values and ther gradients from the point the TDM are evaluated to the origin set by the selected normal modes [**?**]. Such extrapolation, however, while valid for HT, generally results in rotatory strengths that are not origin invariant for $\mathcal{R}_1$ or $\mathcal{R}_2$ approaches.

The linear extrapolation of the values computed at the minimum of the initial state to the minimum of the final state, required when combining HT_i with the Q_f reference, takes the form:

$$\boldsymbol{\mu}_0^f = \boldsymbol{\mu}_0^i + (\boldsymbol{\mu}')^T \mathbf{K}^{Q_i}, \tag{15a}$$

$$\mathbf{m}_0^f = \mathbf{m}_0^i + (\mathbf{m}')^T \mathbf{K}^{Q_i}, \tag{15b}$$

where we assume that the derivatives of the TDMs are taken with respect to coordinates in the Q_i frame. The constant term of the rotatory strength in this frame, for HT_i with the Q_f reference, is thus given by:

$$
\begin{aligned}
(\boldsymbol{\mu}_0^f)^T \cdot \mathbf{m}_0^f &= \left((\boldsymbol{\mu}_0^i)^T + (\boldsymbol{\mu}')^T\mathbf{K}^{Q_i}\right) \cdot \left((\mathbf{m}_0^i)^T + (\mathbf{m}')^T\mathbf{K}^{Q_i}\right) = \\
&= (\boldsymbol{\mu}_0^i)^T \cdot \mathbf{m}_0^i + \left((\boldsymbol{\mu}_0^i)^T \cdot \mathbf{m}' + (\mathbf{m}_0^i)^T \cdot \boldsymbol{\mu}'\right)\mathbf{K}^{Q_i} + \left(\mathbf{K}^{Q_i}\right)^T (\boldsymbol{\mu}')^T\mathbf{m}'\mathbf{K}^{Q_i}.
\end{aligned}
\tag{16}
$$

Comparing with the derviations in Section C.1., it can be shown that the first two terms (analogous to the FC and FC/HT terms) are origin independent, while the last term, $\left(\mathbf{K}^{Q_i}\right)^T \boldsymbol{\mu}'\mathbf{m}'\mathbf{K}^{Q_i}$ (analogous to the HT/HT term), is origin dependent. A similar origin-dependent contribution appears in the linear term. Therefore, performing extrapolations renders the resulting rotatory strength origin dependent and, in more general grounds, lead to different results with Q_i and Q_f modes.

In general, $\mathcal{R}_1$ and $\mathcal{R}_2$ approaches require consistent, HT_f/Q_f or HT_i/Q_i, to avoid artifacts that broke the origin invariance (in the velocity gauge), while adopting all HT terms gives the same results regardless the frame, e.g. HT_f/Q_f or HT_f/Q_i yield identical spectra.

The above statements are verified with the calculation of the ECD for molecule **2**, shown in Figure **??**. In this Figure, we present the ECD spectra computed using the $\mathcal{R}_1$ approximation at both the CoM and the arbitrarily shifted origin, combining different choices of HT_i or HT_f with Q_i or Q_f frames. These results confirm that origin invariance is achieved at $\mathcal{R}_1$ level only when the geometry where derivatives are evaluated and reference frames are treated consistently (i.e., HT_i/Q_i or HT_f/Q_f). Indeed, we also verify that the $\mathcal{R}_1$ spectra depend on the choice of reference frame, and this sensitivity becomes particularly pronounced when the origin is shifted. In contrast, when all HT terms are retained, the spectra become frame-independent but are no longer origin-invariant.

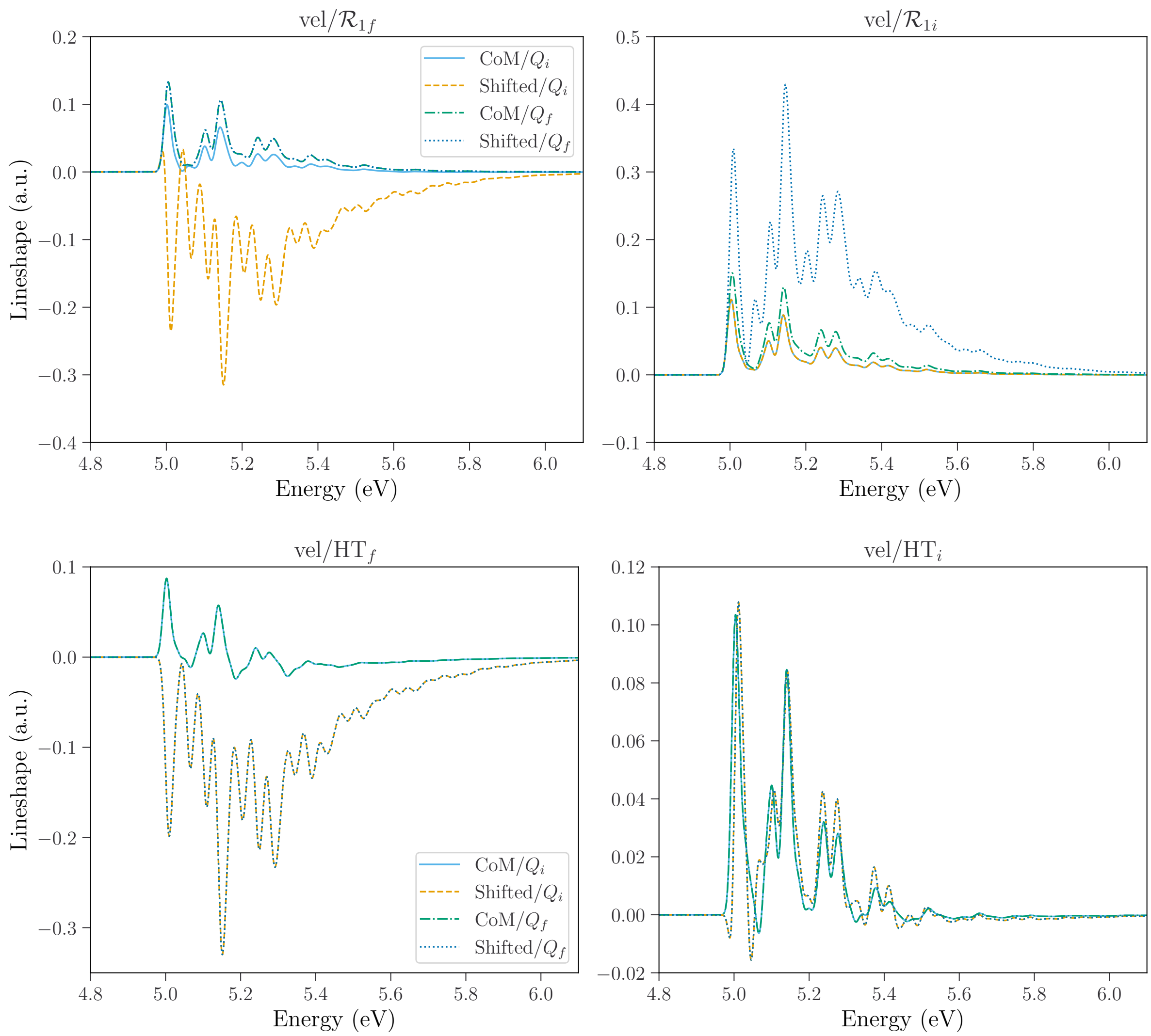

Figure S10: ECD spectra of molecule **2** computed in the velocity gauge at HT$_f$ (left panels) and HT$_i$ (right panels) levels. Top panels: $\mathcal{R}_1$ approximation; bottom panels: full HT model. Spectra are shown for both Q_f and Q_i frames, with the origin of coordinates placed at the center of mass (CoM) or arbitrarily shifted.

C.3 Derivation of FC/HT2 correlation function

The correlation function for the FC/HT2 term is given by

$$\chi_{\mathrm{FC/HT2}}(t,T) = \sum_{kl}\left[\boldsymbol{\mu}_{kl}^{(2)}\boldsymbol{m}^{(0)}\right]\int \mathrm{d}\mathbf{Q}\left\langle \mathbf{Q}\,\middle|\, Q_kQ_l e^{-itH_f/\hbar}e^{-(\beta-it)/\hbar}\,\middle|\,\mathbf{Q}\right\rangle + \sum_{kl}\left[\boldsymbol{\mu}^{(0)}\boldsymbol{m}_{kl}^{(2)}\right]\int \mathrm{d}\mathbf{Q}\left\langle \mathbf{Q}\,\middle|\, e^{-itH_f/\hbar}Q_kQ_l e^{-(\beta-it)/\hbar}\,\middle|\,\mathbf{Q}\right\rangle. \tag{17}$$

Each contribution is treated separately, such that

$$\begin{aligned}\chi_{\mathrm{FC/HT2}}(\tau_i,\tau_f) &= \chi^{\mathrm{QU1}}(\tau_i,\tau_f) + \chi^{\mathrm{QU2}}(\tau_i,\tau_f)\\ &= \sum_{kl}\left[\boldsymbol{\mu}_{kl}^{(2)}\boldsymbol{m}^{(0)}\right]\chi_{kl}^{\mathrm{QU1}}(\tau_i,\tau_f) + \sum_{kl}\left[\boldsymbol{\mu}^{(0)}\boldsymbol{m}_{kl}^{(2)}\right]\chi_{kl}^{\mathrm{QU2}}(\tau_i,\tau_f),\end{aligned} \tag{18}$$

where $\tau_i = -(i\beta+t)/\hbar$ and $\tau_f = t/\hbar$, and $\beta = (k_BT)^{-1}$. The indices k,l run over the N_{vib} normal coordinates.

The QU1 contribution, in the $\mathbf{Q}_i$ reference, reads

$$\chi_{kl}^{\mathrm{QU1}}(\tau_i,\tau_f) = \int_{-\infty}^{\infty}\mathrm{d}\mathbf{Q}_i\left\langle \mathbf{Q}_i\,\middle|\, Q_{fk}Q_{fl}e^{-iH_f\tau_f}e^{-iH_i\tau_i}\,\middle|\,\mathbf{Q}_i\right\rangle, \tag{19}$$

where $\mathbf{Q}_i$ and $\mathbf{Q}_f$ are the normal coordinates of the initial and final states of size N_{vib} (number of vibrational degrees of freedom).

By adding a new set for the initial state: $\left|\bar{\mathbf{Q}}_i\right\rangle\left\langle\bar{\mathbf{Q}}_i\right|$ to the left of $e^{-iH_i\tau_i}$

$$\chi_{kl}^{\mathrm{QU1}}(\tau_i,\tau_f) = \iint_{-\infty}^{\infty}\mathrm{d}\bar{\mathbf{Q}}_i\,\mathrm{d}\mathbf{Q}_i\left\langle \mathbf{Q}_i\,\middle|\, Q_{fk}Q_{fl}e^{-iH_f\tau_f}\,\middle|\,\bar{\mathbf{Q}}_i\right\rangle\left\langle\bar{\mathbf{Q}}_i\,\middle|\, e^{-iH_i\tau_i}\,\middle|\,\mathbf{Q}_i\right\rangle, \tag{20}$$

and two new sets for the final state: $\left|\mathbf{Q}_f\right\rangle\left\langle\mathbf{Q}_f\right|$ to the left of $e^{-iH_f\tau_f}$ and $\left|\bar{\mathbf{Q}}_f\right\rangle\left\langle\bar{\mathbf{Q}}_f\right|$ to the right of $e^{-iH_f\tau_f}$

$$\begin{aligned}\chi_{kl}^{\mathrm{QU1}}(\tau_i,\tau_f) = \iiiint_{-\infty}^{\infty}&\mathrm{d}\bar{\mathbf{Q}}_f\,\mathrm{d}\mathbf{Q}_f\,\mathrm{d}\bar{\mathbf{Q}}_i\,\mathrm{d}\mathbf{Q}_i\left\langle \mathbf{Q}_i\,\middle|\, Q_{fk}Q_{fl}\,\middle|\,\mathbf{Q}_f\right\rangle\left\langle\mathbf{Q}_f\,\middle|\, e^{-iH_f\tau_f}\,\middle|\,\bar{\mathbf{Q}}_f\right\rangle\\ &\left\langle\bar{\mathbf{Q}}_f\,\middle|\,\bar{\mathbf{Q}}_i\right\rangle\left\langle\bar{\mathbf{Q}}_i\,\middle|\, e^{-iH_i\tau_i}\,\middle|\,\mathbf{Q}_i\right\rangle,\end{aligned} \tag{21}$$

the Feynman's result for path integrals

$$\begin{aligned}\left\langle\mathbf{Q}_x\,\middle|\, e^{-iH_x\tau_x}\,\middle|\,\bar{\mathbf{Q}}_x\right\rangle = &\sqrt{\frac{\det[\mathbf{a}_x(\tau_x)]}{2\pi i\hbar}}\\ &\exp\left\{\frac{i}{\hbar}\left[\frac{1}{2}\mathbf{Q}_x^T\mathbf{b}_x(\tau_x)\,\mathbf{Q}_x + \frac{1}{2}\bar{\mathbf{Q}}_x^T\mathbf{b}_x(\tau_x)\,\bar{\mathbf{Q}}_x - \mathbf{Q}_x^T\mathbf{a}_x(\tau_x)\,\bar{\mathbf{Q}}_x\right]\right\},\end{aligned} \tag{22}$$

can be used for the propagators $\left\langle \mathbf{Q}_f \,\middle|\, e^{-iH_f\tau_f} \,\middle|\, \bar{\mathbf{Q}}_f \,\middle|\, \right\rangle$ and $\left\langle \bar{\mathbf{Q}}_i \,\middle|\, e^{-iH_i\tau_i} \,\middle|\, \mathbf{Q}_i \,\middle|\, \right\rangle$, taking into account that $\left\langle \bar{\mathbf{Q}}_i \,\middle|\, e^{-iH_i\tau_i} \,\middle|\, \mathbf{Q}_i \right\rangle = \left\langle \mathbf{Q}_i \,\middle|\, e^{-iH_i\tau_i} \,\middle|\, \bar{\mathbf{Q}}_i \right\rangle^T$, such that

$$\begin{aligned}\chi_{kl}^{\mathrm{QU1}}(\tau_i,\tau_f) =& \sqrt{\frac{\det(\mathbf{a}_f)\det(\mathbf{a}_i)}{(2\pi i\hbar)^{2N}}} \iiiint_{-\infty}^{\infty} \mathrm{d}\bar{\mathbf{Q}}_f \, \mathrm{d}\mathbf{Q}_f \, \mathrm{d}\bar{\mathbf{Q}}_i \, \mathrm{d}\mathbf{Q}_i \, \langle \mathbf{Q}_i \,|\, Q_{fk}Q_{fl} \,|\, \mathbf{Q}_f \rangle \\ & \exp\left\{ \frac{i}{\hbar} \left[\frac{1}{2}\mathbf{Q}_f^T \mathbf{b}_f \mathbf{Q}_f + \frac{1}{2}\bar{\mathbf{Q}}_f^T \mathbf{b}_f \bar{\mathbf{Q}}_f - \mathbf{Q}_f^T \mathbf{a}_f \bar{\mathbf{Q}}_f \right] \right\} \langle \bar{\mathbf{Q}}_f \,|\, \bar{\mathbf{Q}}_i \rangle \\ & \exp\left\{ \frac{i}{\hbar} \left[\frac{1}{2}\mathbf{Q}_i^T \mathbf{b}_i \mathbf{Q}_i + \frac{1}{2}\bar{\mathbf{Q}}_i^T \mathbf{b}_i \bar{\mathbf{Q}}_i - \mathbf{Q}_i^T \mathbf{a}_i \bar{\mathbf{Q}}_i \right] \right\}, \end{aligned} \tag{23}$$

where $\mathbf{a}_x \equiv \mathbf{a}_x(\tau_x)$ and $\mathbf{b}_x \equiv \mathbf{b}_x(\tau_x)$ are diagonal $(N_{\mathrm{vib}} \times N_{\mathrm{vib}})$ matrices dependent of the vibrational frequencies, of the form

$$(\mathbf{a}_x(\tau_x))_k = \frac{\omega_{xk}}{\sin(\hbar\omega_{xk}\tau_x)}, \tag{24}$$

$$(\mathbf{b}_x(\tau_x))_k = \frac{\omega_{xk}}{\tan(\hbar\omega_{xk}\tau_x)}, \tag{25}$$

where ω_{xk} is the frequency of the k-th harmonic oscillator in the state x.

Recalling the Duschinsky relation

$$\mathbf{Q}_i = \mathbf{J}\mathbf{Q}_f + \mathbf{K}, \tag{26}$$

where $\mathbf{J}$ is the Duschinsky matrix $(N_{\mathrm{vib}} \times N_{\mathrm{vib}})$ and $\mathbf{K}$ is the displacement vector (N_{vib}). With the orthonormalization condition

$$\langle \mathbf{Q}_f \,|\, \mathbf{Q}_i \rangle = \delta(\mathbf{Q}_f - \mathbf{Q}_i) = \delta(\mathbf{Q}_f - \mathbf{J}\mathbf{Q}_f - \mathbf{K}) = \prod_k \delta\left(Q_{ik} - \sum_i J_{kj} Q_{fj} - K_k \right), \tag{27}$$

and the following property for the Dirac delta

$$\int_{-\infty}^{\infty} f(t)\,\delta(t-T)\,\mathrm{d}t = f(T), \tag{28}$$

we can integrate over $\mathbf{Q}_i$ and $\bar{\mathbf{Q}}_i$ in eq. (23), noting that $\langle \mathbf{Q}_i \,|\, Q_{fk}Q_{fl} \,|\, \mathbf{Q}_f \rangle = Q_{fk}Q_{fl} \langle \mathbf{Q}_i \,|\, \mathbf{Q}_f \rangle$

$$\begin{aligned}\int_{-\infty}^{\infty} \mathrm{d}\mathbf{Q}_i \exp\left\{ \frac{i}{\hbar} \left[\frac{1}{2}\mathbf{Q}_i^T \mathbf{b}_i \mathbf{Q}_i + \frac{1}{2}\bar{\mathbf{Q}}_i^T \mathbf{b}_i \bar{\mathbf{Q}}_i - \mathbf{Q}_i^T \mathbf{a}_i \bar{\mathbf{Q}}_i \right] \right\} \delta(\mathbf{Q}_i - \mathbf{Q}_f) = \\ = \exp\left\{ \frac{i}{\hbar} \left[\frac{1}{2}\mathbf{Q}_f^T \mathbf{b}_f \mathbf{Q}_f + \frac{1}{2}\bar{\mathbf{Q}}_f^T \mathbf{b}_f \bar{\mathbf{Q}}_f - \mathbf{Q}_f^T \mathbf{a}_f \bar{\mathbf{Q}}_f \right] \right\}, \end{aligned} \tag{29}$$

$$\begin{aligned}\int_{-\infty}^{\infty} \mathrm{d}\bar{\mathbf{Q}}_i \exp\left\{ \frac{i}{\hbar} \left[\frac{1}{2}\mathbf{Q}_f^T \mathbf{b}_f \mathbf{Q}_f + \frac{1}{2}\bar{\mathbf{Q}}_f^T \mathbf{b}_f \bar{\mathbf{Q}}_f - \mathbf{Q}_f^T \mathbf{a}_f \bar{\mathbf{Q}}_f \right] \right\} \delta(\bar{\mathbf{Q}}_f - \bar{\mathbf{Q}}_i) = \\ = \exp\left\{ \frac{i}{\hbar} \left[\frac{1}{2}\mathbf{Q}_i^T \mathbf{b}_i \mathbf{Q}_i + \frac{1}{2}\bar{\mathbf{Q}}_i^T \mathbf{b}_i \bar{\mathbf{Q}}_i - \mathbf{Q}_i^T \mathbf{a}_i \bar{\mathbf{Q}}_i \right] \right\}. \end{aligned} \tag{30}$$

In eq. (23)

$$\chi_{kl}^{\mathrm{QU1}}\left(\tau_i,\tau_f\right) = \sqrt{\frac{\det(\mathbf{a}_f)\det(\mathbf{a}_i)}{(2\pi i\hbar)^{2N}}} \int_{-\infty}^{\infty} \mathrm{d}\bar{\mathbf{Q}}_f \int_{-\infty}^{\infty} \mathrm{d}\mathbf{Q}_f\, Q_{fk} Q_{fl}$$
$$\exp\left\{\frac{i}{\hbar}\left[\frac{1}{2}\mathbf{Q}_f^T\mathbf{b}_f\mathbf{Q}_f + \frac{1}{2}\bar{\mathbf{Q}}_f^T\mathbf{b}_f\bar{\mathbf{Q}}_f - \mathbf{Q}_f^T\mathbf{a}_f\bar{\mathbf{Q}}_f\right]\right\}$$
$$\exp\left\{\frac{i}{\hbar}\left[\frac{1}{2}\mathbf{Q}_i^T\mathbf{b}_i\mathbf{Q}_i + \frac{1}{2}\bar{\mathbf{Q}}_i^T\mathbf{b}_i\bar{\mathbf{Q}}_i - \mathbf{Q}_i^T\mathbf{a}_i\bar{\mathbf{Q}}_i\right]\right\}, \tag{31}$$

using the Duschinsky relation (eq. (26)) and noting that $(\mathbf{K}-\mathbf{J}\mathbf{Q}_f)^T = \mathbf{K}^T + \mathbf{Q}_f^T\mathbf{J}^T$

$$\chi_{kl}^{\mathrm{QU1}}\left(\tau_i,\tau_f\right) = \sqrt{\frac{\det[\mathbf{a}_f]\det[\mathbf{a}_i]}{(2\pi i\hbar)^{2N}}} \int_{-\infty}^{\infty} \mathrm{d}\bar{\mathbf{Q}}_f \int_{-\infty}^{\infty} \mathrm{d}\mathbf{Q}_f\, Q_{fk} Q_{fl}$$
$$\exp\left\{\frac{i}{\hbar}\left[\frac{1}{2}\mathbf{Q}_f^T\mathbf{b}_f\mathbf{Q}_f + \frac{1}{2}\bar{\mathbf{Q}}_f^T\mathbf{b}_f\bar{\mathbf{Q}}_f - \mathbf{Q}_f^T\mathbf{a}_f\bar{\mathbf{Q}}_f\right]\right\}$$
$$\exp\left\{\frac{i}{\hbar}\left[\frac{1}{2}\left(\mathbf{K}^T + \mathbf{Q}_f^T\mathbf{J}^T\right)\mathbf{b}_i\left(\mathbf{J}\mathbf{Q}_f + \mathbf{K}\right)\right.\right.$$
$$+\frac{1}{2}\left(\mathbf{K}^T + \bar{\mathbf{Q}}_f^T\mathbf{J}^T\right)\mathbf{b}_i\left(\mathbf{J}\bar{\mathbf{Q}}_f + \mathbf{K}\right)$$
$$\left.\left.-\left(\mathbf{K}^T + \mathbf{Q}_f^T\mathbf{J}^T\right)\mathbf{a}_i\left(\mathbf{J}\bar{\mathbf{Q}}_f + \mathbf{K}\right)\right]\right\}, \tag{32}$$

and factorizing for $\mathbf{Q}_f$ and $\bar{\mathbf{Q}}_f$

$$\chi_{kl}^{\mathrm{QU1}}\left(\tau_i,\tau_f\right) = \sqrt{\frac{\det(\mathbf{a}_f)\det(\mathbf{a}_i)}{(2\pi i\hbar)^{2N}}} \exp\left[\frac{i}{\hbar}\mathbf{K}^T\mathbf{E}\mathbf{K}\right] \int_{-\infty}^{\infty} \mathrm{d}\bar{\mathbf{Q}}_f \int_{-\infty}^{\infty} \mathrm{d}\mathbf{Q}_f\, Q_{fk} Q_{fl}$$
$$\exp\left\{\frac{i}{\hbar}\left[\frac{1}{2}\mathbf{Q}_f^T\mathbf{B}\mathbf{Q}_f + \frac{1}{2}\bar{\mathbf{Q}}_f^T\mathbf{B}\bar{\mathbf{Q}}_f - \mathbf{Q}_f^T\mathbf{A}\bar{\mathbf{Q}}_f + \mathbf{K}^T\mathbf{E}\mathbf{J}\left(\mathbf{Q}_f + \bar{\mathbf{Q}}_f\right)\right]\right\}, \tag{33}$$

where the following matrices have been defined

$$\mathbf{E} = \mathbf{b}_i - \mathbf{a}_i, \tag{34}$$

$$\mathbf{B} = \mathbf{b}_f + \mathbf{J}^T\mathbf{b}_i\mathbf{J}, \tag{35}$$

$$\mathbf{A} = \mathbf{a}_f + \mathbf{J}^T\mathbf{a}_i\mathbf{J}. \tag{36}$$

A change of variables is made by forming linear combinations of $\mathbf{Q}_f$ and $\bar{\mathbf{Q}}_f$ with the following orthognoal transformation

$$\mathbf{Z} = 2^{-1/2}\left(\mathbf{Q}_f + \bar{\mathbf{Q}}_f\right), \tag{37}$$

$$\mathbf{U} = 2^{-1/2}\left(\mathbf{Q}_f - \bar{\mathbf{Q}}_f\right), \tag{38}$$

so that in eq. (33)

$$\chi_{kl}^{\mathrm{QU1}}\left(\tau_i,\tau_f\right) = \sqrt{\frac{\det(\mathbf{a}_f)\det(\mathbf{a}_i)}{\left(2\pi i\hbar\right)^{2N}}}\exp\left[\frac{i}{\hbar}\mathbf{K}^T\mathbf{E}\mathbf{K}\right]\int_{-\infty}^{\infty}\mathrm{d}\mathbf{Z}\int_{-\infty}^{\infty}\mathrm{d}\mathbf{U}\,Q_{fk}Q_{fl}$$
$$\exp\left\{\frac{i}{\hbar}\left[\frac{1}{2}\mathbf{Z}^T\left(\mathbf{B}-\mathbf{A}\right)\mathbf{Z}+\frac{1}{2}\mathbf{U}^T\left(\mathbf{B}+\mathbf{A}\right)\mathbf{U}+\sqrt{2}\mathbf{K}^T\mathbf{E}\mathbf{J}\mathbf{Z}\right]\right\}. \tag{39}$$

Two new matrices, $\mathbf{C}$ and $\mathbf{D}$, are defined to relate $\mathbf{A}$ and $\mathbf{B}$. Recalling the following trigonometric relations for the hyperbolic cotangent and tangent, and its relation with $\mathbf{a}_x$ and $\mathbf{b}_x$ (eqs. (24) and (25))

$$-\coth\left(\frac{i\hbar\omega_{kx}\tau_x}{2}\right) = \frac{i}{\tan(\hbar\omega_{kx}\tau_x)}+\frac{i}{\sin(\hbar\omega_{kx}\tau_x)} = \frac{i}{\omega_{kx}}\left[\mathbf{b}_x+\mathbf{a}_x\right], \tag{40}$$
$$-\tanh\left(\frac{i\hbar\omega_{kx}\tau_x}{2}\right) = \frac{i}{\tan(\hbar\omega_{kx}\tau_x)}-\frac{i}{\sin(\hbar\omega_{kx}\tau_x)} = \frac{i}{\omega_{kx}}\left[\mathbf{b}_x-\mathbf{a}_x\right], \tag{41}$$

the elements of $\mathbf{C}$ and $\mathbf{D}$ are defined as

$$\mathbf{c}_x\left(\frac{\tau_x}{2}\right) = \frac{\omega_{kx}}{\hbar}\coth\left(\frac{i\omega_{kx}\hbar\tau_x}{2}\right) = -\frac{i}{\hbar}\left[\mathbf{a}_x+\mathbf{b}_x\right], \tag{42}$$
$$\mathbf{d}_x\left(\frac{\tau_x}{2}\right) = \frac{\omega_{kx}}{\hbar}\tanh\left(\frac{i\omega_{kx}\hbar\tau_x}{2}\right) = -\frac{i}{\hbar}\left[\mathbf{b}_x-\mathbf{a}_x\right], \tag{43}$$

such that

$$\mathbf{C}\left(\tau_i,\tau_f\right) = \mathbf{c}_f\left(\tau_f\right)+\mathbf{J}^T\mathbf{c}_i\left(\tau_i\right)\mathbf{J}, \tag{44}$$
$$\mathbf{D}\left(\tau_i,\tau_f\right) = \mathbf{d}_f\left(\tau_f\right)+\mathbf{J}^T\mathbf{d}_i\left(\tau_i\right)\mathbf{J}, \tag{45}$$

so the following relations between $\mathbf{A}$ and $\mathbf{B}$ can be stablished

$$\frac{i}{\hbar}\left[\mathbf{B}\left(\tau_i,\tau_f\right)+\mathbf{A}\left(\tau_i,\tau_f\right)\right] = -\mathbf{C}\left(\tau_i,\tau_f\right), \tag{46}$$
$$\frac{i}{\hbar}\left[\mathbf{B}\left(\tau_i,\tau_f\right)-\mathbf{A}\left(\tau_i,\tau_f\right)\right] = -\mathbf{D}\left(\tau_i,\tau_f\right), \tag{47}$$

and also, from eq. (34)

$$\frac{i}{\hbar}\mathbf{E} = -\mathbf{d}_i\left(\tau_i\right). \tag{48}$$

In eq. (39)

$$\chi_{kl}^{\mathrm{QU1}}\left(\tau_i,\tau_f\right) = \sqrt{\frac{\det(\mathbf{a}_f)\det(\mathbf{a}_i)}{\left(2\pi i\hbar\right)^{2N}}}\exp\left[\frac{i}{\hbar}\mathbf{K}^T\mathbf{E}\mathbf{K}\right]\int_{-\infty}^{\infty}\mathrm{d}\mathbf{Z}\int_{-\infty}^{\infty}\mathrm{d}\mathbf{U}\,Q_{fk}Q_{fl}$$
$$\exp\left[-\frac{1}{2}\mathbf{Z}^T\mathbf{D}\mathbf{Z}-\frac{1}{2}\mathbf{U}^T\mathbf{C}\mathbf{U}-\sqrt{2}\boldsymbol{\lambda}^T\mathbf{Z}\right], \tag{49}$$

where

$$\boldsymbol{\lambda} = \mathbf{J}^T \mathbf{d}_i \mathbf{K}. \tag{50}$$

The goal is to transform this integrals to gaussian integrals. To do so, new integration variables to uncouple the dependence between $\mathbf{Z}$ and $\mathbf{U}$ are defined.

First, the $\mathbf{Z}$-dependent term

$$-\frac{1}{2}\mathbf{Z}^T\mathbf{D}\mathbf{Z} - \sqrt{2}\boldsymbol{\lambda}^T\mathbf{Z} = -\frac{1}{2}\left(\mathbf{Z}^T\mathbf{D}\mathbf{Z} + 2\sqrt{2}\boldsymbol{\lambda}^T\mathbf{Z}\right), \tag{51}$$

consists of a quadratic component plus a linear component on $\mathbf{Z}$. To make the integral simpler, we seek to eliminate this linear component. To do so, we seek to *complete the square*, adding and substracting a term that allow us to complete the perfect square. Bearing in mind that we can arrive at the above equation by means of an expansion of the type

$$\left(\mathbf{Z} + \sqrt{2}\mathbf{D}^{-1}\boldsymbol{\lambda}\right)^T \mathbf{D}\left(\mathbf{Z} + \sqrt{2}\mathbf{D}^{-1}\boldsymbol{\lambda}\right) - 2\boldsymbol{\lambda}^T\mathbf{D}^{-1}\boldsymbol{\lambda} = \mathbf{Z}^T\mathbf{D}\mathbf{Z} + 2\sqrt{2}\boldsymbol{\lambda}^T\mathbf{Z}, \tag{52}$$

noting that $\mathbf{Z}^T\boldsymbol{\lambda}$ is a scalar, so that $\mathbf{Z}^T\boldsymbol{\lambda} = \boldsymbol{\lambda}^T\mathbf{Z}$.

This way, since the $\boldsymbol{\lambda}^T\mathbf{D}^{-1}\boldsymbol{\lambda}$ term is a constant, the linear term on $\mathbf{Z}$ is eliminated.

In order to obtain the simple gaussian-type integral, $\mathbf{D}$ is splitted as $\mathbf{D} = \mathbf{D}^{1/2}\mathbf{D}^{1/2}$ and a new integration variable is defined as

$$\mathbf{Z}_1 = \left(\mathbf{Z} + \sqrt{2}\mathbf{D}^{-1}\boldsymbol{\lambda}\right)\mathbf{D}^{1/2} = \mathbf{D}^{1/2}\mathbf{Z} + \sqrt{2}\mathbf{D}^{-1/2}\boldsymbol{\lambda}, \tag{53}$$

so that in eq. (52)

$$\mathbf{Z}_1^T\mathbf{Z}_1 - 2\boldsymbol{\lambda}^T\mathbf{D}^{-1}\boldsymbol{\lambda} = \mathbf{Z}^T\mathbf{D}\mathbf{Z} + 2\sqrt{2}\boldsymbol{\lambda}^T\mathbf{Z}. \tag{54}$$

Similarly, the other new integration variable is defined as

$$\mathbf{U}_1 = \mathbf{C}^{1/2}\mathbf{U}, \tag{55}$$

such that

$$-\frac{1}{2}\mathbf{U}^T\mathbf{C}\mathbf{U} = -\frac{1}{2}\mathbf{U}_1^T\mathbf{U}_1. \tag{56}$$

Then, making this change of variables to eq. (39) noting that $\mathrm{d}\mathbf{Z} = \det\left(\mathbf{D}^{-1/2}\right) \mathrm{d}\mathbf{Z}_1$ and $\mathrm{d}\mathbf{U} = \det\left(\mathbf{C}^{-1/2}\right) \mathrm{d}\mathbf{U}_1$

$$\chi_{kl}^{\mathrm{QU1}}(\tau_i, \tau_f) = \sqrt{\frac{\det(\mathbf{a}_f)\det(\mathbf{a}_i)}{(2\pi i\hbar)^{2N}}} \exp\left[-\mathbf{K}^T \mathbf{d}_i \mathbf{K}\right] \int_{-\infty}^{\infty} \det\left(\mathbf{D}^{-1/2}\right) \mathrm{d}\mathbf{Z}_1 \int_{-\infty}^{\infty} \det\left(\mathbf{C}^{-1/2}\right) \mathrm{d}\mathbf{U}_1$$
$$Q_{fk} Q_{fl} \exp\left[-\frac{1}{2}\mathbf{Z}_1^T \mathbf{Z}_1 + \boldsymbol{\lambda}^T \mathbf{D}^{-1} \boldsymbol{\lambda}\right] \exp\left[-\frac{1}{2}\mathbf{U}_1^T \mathbf{U}_1\right], \tag{57}$$

which can be rewritten by taking the constant terms out of the integral as

$$\chi_{kl}^{\mathrm{QU1}}(\tau_i, \tau_f) = \sqrt{\frac{\det(\mathbf{a}_f)\det(\mathbf{a}_i)}{(2\pi i\hbar)^{2N}\det(\mathbf{CD})}} \exp\left[-\mathbf{K}^T \mathbf{d}_i \mathbf{K}\right] \exp\left[\boldsymbol{\lambda}^T \mathbf{D}^{-1} \boldsymbol{\lambda}\right]$$
$$\int_{-\infty}^{\infty} \mathrm{d}\mathbf{Z}_1 \int_{-\infty}^{\infty} \mathrm{d}\mathbf{U}_1 \, Q_{fk} Q_{fl} \exp\left[-\frac{1}{2}\mathbf{Z}_1^T \mathbf{Z}_1\right] \exp\left[-\frac{1}{2}\mathbf{U}_1^T \mathbf{U}_1\right]. \tag{58}$$

Now, from the definition of $\mathbf{Z}$ and $\mathbf{U}$ in eqs. (37) and (38), the dependence of the factor $Q_{fk}Q_{fl}$ on $\mathbf{Z}$ and $\mathbf{U}$ is recovered as

$$Q_{fk} = 2^{-1/2}\left(\mathbf{Z_k} + \mathbf{U_k}\right), \tag{59}$$

$$Q_{fl} = 2^{-1/2}\left(\mathbf{Z_l} + \mathbf{U_l}\right), \tag{60}$$

substituting in eq. (58) and separating the integrals

$$\chi_{kl}^{\mathrm{QU1}}(\tau_i, \tau_f) = \frac{1}{2}\sqrt{\frac{\det(\mathbf{a}_f)\det(\mathbf{a}_i)}{(2\pi i\hbar)^{2N}\det(\mathbf{CD})}} \exp\left[-\mathbf{K}^T \mathbf{d}_i \mathbf{K}\right] \exp\left[\boldsymbol{\lambda}^T \mathbf{D}^{-1} \boldsymbol{\lambda}\right]$$
$$\left\{\int_{-\infty}^{\infty} \mathrm{d}\mathbf{Z}_1 \, \mathbf{Z_k}\mathbf{Z_l} \exp\left[-\frac{1}{2}\mathbf{Z}_1^T \mathbf{Z}_1\right] \int_{-\infty}^{\infty} \mathrm{d}\mathbf{U}_1 \exp\left[-\frac{1}{2}\mathbf{U}_1^T \mathbf{U}_1\right]\right.$$
$$+ \int_{-\infty}^{\infty} \mathrm{d}\mathbf{Z}_1 \, \mathbf{Z_k} \exp\left[-\frac{1}{2}\mathbf{Z}_1^T \mathbf{Z}_1\right] \int_{-\infty}^{\infty} \mathrm{d}\mathbf{U}_1 \, \mathbf{U_l} \exp\left[-\frac{1}{2}\mathbf{U}_1^T \mathbf{U}_1\right]$$
$$+ \int_{-\infty}^{\infty} \mathrm{d}\mathbf{Z}_1 \, \mathbf{Z_l} \exp\left[-\frac{1}{2}\mathbf{Z}_1^T \mathbf{Z}_1\right] \int_{-\infty}^{\infty} \mathrm{d}\mathbf{U}_1 \, \mathbf{U_k} \exp\left[-\frac{1}{2}\mathbf{U}_1^T \mathbf{U}_1\right]$$
$$\left.+ \int_{-\infty}^{\infty} \mathrm{d}\mathbf{Z}_1 \exp\left[-\frac{1}{2}\mathbf{Z}_1^T \mathbf{Z}_1\right] \int_{-\infty}^{\infty} \mathrm{d}\mathbf{U}_1 \, \mathbf{U_k}\mathbf{U_l} \exp\left[-\frac{1}{2}\mathbf{U}_1^T \mathbf{U}_1\right]\right\}. \tag{61}$$

Recalling eq. (18), the full QU1 contribution is obtained by summing over all k, l. Inserting the $\boldsymbol{\mu}_{kl}^{(2)}\boldsymbol{m}^{(0)}$ factor and summing over k, l noting that $\sum_k \mathbf{Z_k} = \mathbf{Z}$, $\sum_k \mathbf{U_k} = \mathbf{U}$ and defining

$$\boldsymbol{\gamma} = \sum_{kl} \boldsymbol{\mu}_{kl}^{(2)}\boldsymbol{m}^{(0)} = \boldsymbol{\mu}^{(2)}\boldsymbol{m}^{(0)}, \tag{62}$$

in eq. (61), then

$$\chi^{\mathrm{QU1}}(\tau_i,\tau_f) = \sum_{kl}\chi_{kl}^{\mathrm{QU1}}(\tau_i,\tau_f)$$
$$= \frac{1}{2}\sqrt{\frac{\det(\mathbf{a}_f)\det(\mathbf{a}_i)}{(2\pi i\hbar)^{2N}\det(\mathbf{CD})}}\exp\left[-\mathbf{K}^T\mathbf{d}_i\mathbf{K}\right]\exp\left[\boldsymbol{\lambda}^T\mathbf{D}^{-1}\boldsymbol{\lambda}\right]$$
$$\left\{\int_{-\infty}^{\infty}\mathrm{d}\mathbf{Z}_1\,\mathbf{Z}^T\boldsymbol{\gamma}\mathbf{Z}\exp\left[-\frac{1}{2}\mathbf{Z}_1^T\mathbf{Z}_1\right]\int_{-\infty}^{\infty}\mathrm{d}\mathbf{U}_1\exp\left[-\frac{1}{2}\mathbf{U}_1^T\mathbf{U}_1\right]\right.$$
$$+2\int_{-\infty}^{\infty}\mathrm{d}\mathbf{Z}_1\,\boldsymbol{\gamma}^T\mathbf{Z}\exp\left[-\frac{1}{2}\mathbf{Z}_1^T\mathbf{Z}_1\right]\int_{-\infty}^{\infty}\mathrm{d}\mathbf{U}_1\,\mathbf{U}\exp\left[-\frac{1}{2}\mathbf{U}_1^T\mathbf{U}_1\right]$$
$$\left.+\int_{-\infty}^{\infty}\mathrm{d}\mathbf{Z}_1\exp\left[-\frac{1}{2}\mathbf{Z}_1^T\mathbf{Z}_1\right]\int_{-\infty}^{\infty}\mathrm{d}\mathbf{U}_1\,\mathbf{U}^T\boldsymbol{\gamma}\mathbf{U}\exp\left[-\frac{1}{2}\mathbf{U}_1^T\mathbf{U}_1\right]\right\}. \tag{63}$$

Now, the $\boldsymbol{\gamma}^T\mathbf{Z}$ and $\mathbf{Z}^T\boldsymbol{\gamma}\mathbf{Z}$ term have to be rewritten in terms of $\mathbf{Z}_1$. From eq. (53)

$$\mathbf{Z} = \mathbf{D}^{-1/2}\mathbf{Z}_1 - \sqrt{2}\mathbf{D}^{-1}\boldsymbol{\lambda}, \tag{64}$$

then

$$\boldsymbol{\gamma}^T\mathbf{Z} = \boldsymbol{\gamma}^T\left(\mathbf{D}^{-1/2}\mathbf{Z}_1 - \sqrt{2}\mathbf{D}^{-1}\boldsymbol{\lambda}\right), \tag{65}$$

and

$$\mathbf{Z}^T\boldsymbol{\gamma}\mathbf{Z} = \mathbf{D}^{-1/2}\mathbf{Z}_1^T\boldsymbol{\gamma}\mathbf{Z}_1\mathbf{D}^{-1/2} - 2\sqrt{2}\mathbf{D}^{-1/2}\mathbf{Z}_1\boldsymbol{\gamma}\boldsymbol{\lambda}^T\mathbf{D}^{-1} + 2\mathbf{D}^{-1}\boldsymbol{\lambda}^T\boldsymbol{\gamma}\boldsymbol{\lambda}\mathbf{D}^{-1}. \tag{66}$$

Also, the $\mathbf{U}^T\boldsymbol{\gamma}\mathbf{U}$ term has to be rewritten in terms of $\mathbf{U}_1$. From eq. (55)

$$\mathbf{U} = \mathbf{U}_1^T\mathbf{C}^{-1/2}, \tag{67}$$

and

$$\mathbf{U}^T\boldsymbol{\gamma}\mathbf{U} = \mathbf{C}^{-1/2}\mathbf{U}_1^T\boldsymbol{\gamma}\mathbf{U}_1\mathbf{C}^{-1/2}. \tag{68}$$

Now, substituting eqs. (65) to (68) in eq. (63) and only preserving the even integrands

$$\chi^{\mathrm{QU1}}(\tau_i,\tau_f) = \frac{1}{2}\sqrt{\frac{\det(\mathbf{a}_f)\det(\mathbf{a}_i)}{(2\pi i\hbar)^{2N}\det(\mathbf{CD})}}\exp\left[-\mathbf{K}^T\mathbf{d}_i\mathbf{K}\right]\exp\left[\boldsymbol{\lambda}^T\mathbf{D}^{-1}\boldsymbol{\lambda}\right]$$
$$\left\{\int_{-\infty}^{\infty}\mathrm{d}\mathbf{Z}_1\,\mathbf{D}^{-1/2}\mathbf{Z}_1^T\boldsymbol{\gamma}\mathbf{Z}_1\mathbf{D}^{-1/2}\exp\left[-\frac{1}{2}\mathbf{Z}_1^T\mathbf{Z}_1\right]\int_{-\infty}^{\infty}\mathrm{d}\mathbf{U}_1\exp\left[-\frac{1}{2}\mathbf{U}_1^T\mathbf{U}_1\right]\right.$$
$$+2\mathbf{D}^{-1}\boldsymbol{\lambda}^T\boldsymbol{\gamma}\boldsymbol{\lambda}\mathbf{D}^{-1}\int_{-\infty}^{\infty}\mathrm{d}\mathbf{Z}_1\exp\left[-\frac{1}{2}\mathbf{Z}_1^T\mathbf{Z}_1\right]\int_{-\infty}^{\infty}\mathrm{d}\mathbf{U}_1\exp\left[-\frac{1}{2}\mathbf{U}_1^T\mathbf{U}_1\right]$$
$$\left.+\int_{-\infty}^{\infty}\mathrm{d}\mathbf{Z}_1\exp\left[-\frac{1}{2}\mathbf{Z}_1^T\mathbf{Z}_1\right]\int_{-\infty}^{\infty}\mathrm{d}\mathbf{U}_1\,\mathbf{C}^{-1/2}\mathbf{U}_1^T\boldsymbol{\gamma}\mathbf{U}_1\mathbf{C}^{-1/2}\exp\left[-\frac{1}{2}\mathbf{U}_1^T\mathbf{U}_1\right]\right\}, \tag{69}$$

we end with standard Gaussian integrals, with solution

$$\int_{-\infty}^{\infty} \mathrm{d}\mathbf{Z}_1 \exp\left[-\frac{1}{2}\mathbf{Z}_1^T\mathbf{Z}_1\right] = \int_{-\infty}^{\infty} \mathrm{d}\mathbf{U}_1 \exp\left[-\frac{1}{2}\mathbf{U}_1^T\mathbf{U}_1\right] = (2\pi)^{N/2}\,, \tag{70}$$

$$\int_{-\infty}^{\infty} \mathrm{d}\mathbf{Z}_1\, \mathbf{D}^{-1/2}\mathbf{Z}_1^T\boldsymbol{\gamma}\mathbf{Z}_1\mathbf{D}^{-1/2} \exp\left[-\frac{1}{2}\mathbf{Z}_1^T\mathbf{Z}_1\right] = (2\pi)^{N/2}\,\mathrm{tr}\big[\mathbf{D}^{-1/2}\boldsymbol{\gamma}\mathbf{D}^{-1/2}\big], \tag{71}$$

$$\int_{-\infty}^{\infty} \mathrm{d}\mathbf{U}_1\, \mathbf{C}^{-1/2}\mathbf{U}_1^T\boldsymbol{\gamma}\mathbf{U}_1\mathbf{C}^{-1/2} \exp\left[-\frac{1}{2}\mathbf{U}_1^T\mathbf{U}_1\right] = (2\pi)^{N/2}\,\mathrm{tr}\big[\mathbf{C}^{-1/2}\boldsymbol{\gamma}\mathbf{C}^{-1/2}\big]. \tag{72}$$

Therefore, substituting eqs. (70) to (72) in eq. (69) and simplifying, the following result is obtained for the QU1 contribution

$$\begin{aligned}\therefore \chi^{\mathrm{QU1}}(\tau_i,\tau_f) = \frac{1}{2}\sqrt{\frac{\det(\mathbf{a}_f)\det(\mathbf{a}_i)}{(i\hbar)^{2N}\det(\mathbf{CD})}}\exp\big[-\mathbf{K}^T\mathbf{d}_i\mathbf{K}\big]\exp\big[\boldsymbol{\lambda}^T\mathbf{D}^{-1}\boldsymbol{\lambda}\big]\\ \big\{2\mathbf{D}^{-1}\boldsymbol{\lambda}^T\boldsymbol{\gamma}\boldsymbol{\lambda}\mathbf{D}^{-1} + \mathrm{tr}\big[\mathbf{D}^{-1/2}\boldsymbol{\gamma}\mathbf{D}^{-1/2} + \mathbf{C}^{-1/2}\boldsymbol{\gamma}\mathbf{C}^{-1/2}\big]\big\}\,.\end{aligned} \tag{73}$$

The second contribution

$$\chi_{kl}^{\mathrm{QU2}}(\tau_i,\tau_f) = \int_{-\infty}^{\infty} \mathrm{d}\mathbf{Q}_i \left\langle \mathbf{Q}_i \,\middle|\, e^{-iH_f\tau_f}Q_{fk}Q_{fl}e^{-iH_i\tau_i} \,\middle|\, \mathbf{Q}_i\right\rangle, \tag{74}$$

is treated similarly to the QU1 contribution. Adding a new set for the initial state, $\left|\bar{\mathbf{Q}}_i\right\rangle\left\langle\bar{\mathbf{Q}}_i\right|$ to the left of $e^{-iH_i\tau_i}$, and two for the final state, $\left|\mathbf{Q}_f\right\rangle\left\langle\mathbf{Q}_f\right|$ to the left of $e^{-iH_f\tau_f}$ and $\left|\bar{\mathbf{Q}}_f\right\rangle\left\langle\bar{\mathbf{Q}}_f\right|$ to the left of Q_{fk}, we get to

$$\begin{aligned}\chi_{kl}^{\mathrm{QU2}}(\tau_i,\tau_f) = \iiiint_{-\infty}^{\infty} \mathrm{d}\bar{\mathbf{Q}}_f\,\mathrm{d}\mathbf{Q}_f\,\mathrm{d}\bar{\mathbf{Q}}_i\,\mathrm{d}\mathbf{Q}_i \left\langle \mathbf{Q}_i \,\middle|\, \mathbf{Q}_f\right\rangle \left\langle \mathbf{Q}_f \,\middle|\, e^{-iH_f\tau_f} \,\middle|\, \bar{\mathbf{Q}}_f\right\rangle\\ \left\langle \bar{\mathbf{Q}}_f \,\middle|\, Q_{fk}Q_{fl} \,\middle|\, \bar{\mathbf{Q}}_i\right\rangle \left\langle \bar{\mathbf{Q}}_i \,\middle|\, e^{-iH_i\tau_i} \,\middle|\, \mathbf{Q}_i\right\rangle,\end{aligned} \tag{75}$$

where the only difference with the QU1 term is in the propagator $\left\langle \bar{\mathbf{Q}}_f \,\middle|\, Q_{fk}Q_{fl} \,\middle|\, \bar{\mathbf{Q}}_i\right\rangle = \bar{Q}_{fk}\bar{Q}_{fl}\left\langle \bar{\mathbf{Q}}_f \,\middle|\, \bar{\mathbf{Q}}_i\right\rangle$. Therefore, the same steps from eq. (21) to eq. (58) are followed, leading to

$$\begin{aligned}\chi_{kl}^{\mathrm{QU2}}(\tau_i,\tau_f) = \sqrt{\frac{\det(\mathbf{a}_f)\det(\mathbf{a}_i)}{(2\pi i\hbar)^{2N}\det(\mathbf{CD})}}\exp\big[-\mathbf{K}^T\mathbf{d}_i\mathbf{K}\big]\exp\big[\boldsymbol{\lambda}^T\mathbf{D}^{-1}\boldsymbol{\lambda}\big]\\ \int_{-\infty}^{\infty}\mathrm{d}\mathbf{Z}_1\int_{-\infty}^{\infty}\mathrm{d}\mathbf{U}_1\,\bar{Q}_{fk}\bar{Q}_{fl}\exp\left[-\frac{1}{2}\mathbf{Z}_1^T\mathbf{Z}_1\right]\exp\left[-\frac{1}{2}\mathbf{U}_1^T\mathbf{U}_1\right],\end{aligned} \tag{76}$$

where, from eqs. (37) and (38)

$$Q_{fk} = 2^{-1/2}\left(\mathbf{Z}_{\mathbf{k}} - \mathbf{U}_{\mathbf{k}}\right), \tag{77}$$

$$Q_{fl} = 2^{-1/2}\left(\mathbf{Z}_{\mathbf{l}} - \mathbf{U}_{\mathbf{l}}\right), \tag{78}$$

and

$$
\begin{aligned}
\chi_{kl}^{\mathrm{QU2}}\left(\tau_i,\tau_f\right)=&\frac{1}{2}\sqrt{\frac{\det\left(\mathbf{a}_f\right)\det\left(\mathbf{a}_i\right)}{\left(2\pi i\hbar\right)^{2N}\det\left(\mathbf{CD}\right)}}\exp\left[-\mathbf{K}^T\mathbf{d}_i\mathbf{K}\right]\exp\left[\boldsymbol{\lambda}^T\mathbf{D}^{-1}\boldsymbol{\lambda}\right]\\
&\left\{\int_{-\infty}^{\infty}\mathrm{d}\mathbf{Z}_1\,\mathbf{Z_k}\mathbf{Z_l}\exp\left[-\frac{1}{2}\mathbf{Z}_1^T\mathbf{Z}_1\right]\int_{-\infty}^{\infty}\mathrm{d}\mathbf{U}_1\exp\left[-\frac{1}{2}\mathbf{U}_1^T\mathbf{U}_1\right]\right.\\
&-\int_{-\infty}^{\infty}\mathrm{d}\mathbf{Z}_1\,\mathbf{Z_k}\exp\left[-\frac{1}{2}\mathbf{Z}_1^T\mathbf{Z}_1\right]\int_{-\infty}^{\infty}\mathrm{d}\mathbf{U}_1\,\mathbf{U_l}\exp\left[-\frac{1}{2}\mathbf{U}_1^T\mathbf{U}_1\right]\\
&-\int_{-\infty}^{\infty}\mathrm{d}\mathbf{Z}_1\,\mathbf{Z_l}\exp\left[-\frac{1}{2}\mathbf{Z}_1^T\mathbf{Z}_1\right]\int_{-\infty}^{\infty}\mathrm{d}\mathbf{U}_1\,\mathbf{U_k}\exp\left[-\frac{1}{2}\mathbf{U}_1^T\mathbf{U}_1\right]\\
&\left.+\int_{-\infty}^{\infty}\mathrm{d}\mathbf{Z}_1\exp\left[-\frac{1}{2}\mathbf{Z}_1^T\mathbf{Z}_1\right]\int_{-\infty}^{\infty}\mathrm{d}\mathbf{U}_1\,\mathbf{U_k}\mathbf{U_l}\exp\left[-\frac{1}{2}\mathbf{U}_1^T\mathbf{U}_1\right]\right\},
\end{aligned}
\tag{79}
$$

that, summing over k,l and defining

$$
\bar{\boldsymbol{\gamma}}=\sum_{kl}\boldsymbol{\mu}^{(0)}\boldsymbol{m}_{kl}^{(2)}=\boldsymbol{\mu}^{(0)}\boldsymbol{m}^{(2)},
\tag{80}
$$

then

$$
\begin{aligned}
\chi^{\mathrm{QU2}}\left(\tau_i,\tau_f\right)=&\sum_{kl}\chi_{kl}^{\mathrm{QU2}}\left(\tau_i,\tau_f\right)\\
=&\frac{1}{2}\sqrt{\frac{\det\left(\mathbf{a}_f\right)\det\left(\mathbf{a}_i\right)}{\left(2\pi i\hbar\right)^{2N}\det\left(\mathbf{CD}\right)}}\exp\left[-\mathbf{K}^T\mathbf{d}_i\mathbf{K}\right]\exp\left[\boldsymbol{\lambda}^T\mathbf{D}^{-1}\boldsymbol{\lambda}\right]\\
&\left\{\int_{-\infty}^{\infty}\mathrm{d}\mathbf{Z}_1\,\mathbf{Z}^T\bar{\boldsymbol{\gamma}}\mathbf{Z}\exp\left[-\frac{1}{2}\mathbf{Z}_1^T\mathbf{Z}_1\right]\int_{-\infty}^{\infty}\mathrm{d}\mathbf{U}_1\exp\left[-\frac{1}{2}\mathbf{U}_1^T\mathbf{U}_1\right]\right.\\
&-2\int_{-\infty}^{\infty}\mathrm{d}\mathbf{Z}_1\,\bar{\boldsymbol{\gamma}}^T\mathbf{Z}\exp\left[-\frac{1}{2}\mathbf{Z}_1^T\mathbf{Z}_1\right]\int_{-\infty}^{\infty}\mathrm{d}\mathbf{U}_1\,\mathbf{U}\exp\left[-\frac{1}{2}\mathbf{U}_1^T\mathbf{U}_1\right]\\
&\left.+\int_{-\infty}^{\infty}\mathrm{d}\mathbf{Z}_1\exp\left[-\frac{1}{2}\mathbf{Z}_1^T\mathbf{Z}_1\right]\int_{-\infty}^{\infty}\mathrm{d}\mathbf{U}_1\,\mathbf{U}^T\bar{\boldsymbol{\gamma}}\mathbf{U}\exp\left[-\frac{1}{2}\mathbf{U}_1^T\mathbf{U}_1\right]\right\}.
\end{aligned}
\tag{81}
$$

The only difference with the QU1 contribution is the change of sign of the second summand see (eq. (63)). Since, as it was shown for QU1, this term is cancelled because of the odd integrand over $\mathbf{U}_1$, the same result is obtained for QU2 but considering $\bar{\boldsymbol{\gamma}}$ instead of $\boldsymbol{\gamma}$.

Therefore

$$
\begin{aligned}
\therefore\chi^{\mathrm{QU2}}\left(\tau_i,\tau_f\right)=&\frac{1}{2}\sqrt{\frac{\det\left(\mathbf{a}_f\right)\det\left(\mathbf{a}_i\right)}{\left(i\hbar\right)^{2N}\det\left(\mathbf{CD}\right)}}\exp\left[-\mathbf{K}^T\mathbf{d}_i\mathbf{K}\right]\exp\left[\boldsymbol{\lambda}^T\mathbf{D}^{-1}\boldsymbol{\lambda}\right]\\
&\left\{2\mathbf{D}^{-1}\boldsymbol{\lambda}^T\bar{\boldsymbol{\gamma}}\boldsymbol{\lambda}\mathbf{D}^{-1}+\mathrm{tr}\left[\mathbf{D}^{-1/2}\bar{\boldsymbol{\gamma}}\mathbf{D}^{-1/2}+\mathbf{C}^{-1/2}\bar{\boldsymbol{\gamma}}\mathbf{C}^{-1/2}\right]\right\}.
\end{aligned}
\tag{82}
$$

Substituting eqs. (73) and (82) into eq. (17), the correlation function for the FC/HT2 term is given by

$$\begin{aligned}\chi_{\mathrm{FC/HT2}}(\tau_i,\tau_f) &= \chi^{\mathrm{QU1}}(\tau_i,\tau_f)+\chi^{\mathrm{QU2}}(\tau_i,\tau_f) = \\ &\frac{1}{2}\sqrt{\frac{\det(\mathbf{a}_f)\det(\mathbf{a}_i)}{(i\hbar)^{2N}\det(\mathbf{CD})}}\exp\left[-\mathbf{K}^T\mathbf{d}_i\mathbf{K}\right]\exp\left[\boldsymbol{\lambda}^T\mathbf{D}^{-1}\boldsymbol{\lambda}\right] \\ &\left\{2\mathbf{D}^{-1}\boldsymbol{\lambda}^T\boldsymbol{\gamma}\boldsymbol{\lambda}\mathbf{D}^{-1}+\mathbf{D}^{-1}\boldsymbol{\lambda}^T\bar{\boldsymbol{\gamma}}\boldsymbol{\lambda}\mathbf{D}^{-1}\right. \\ &\left.+\,\mathrm{tr}\left[\mathbf{D}^{-1/2}\boldsymbol{\gamma}\mathbf{D}^{-1/2}+\mathbf{C}^{-1/2}\boldsymbol{\gamma}\mathbf{C}^{-1/2}+\mathbf{D}^{-1/2}\bar{\boldsymbol{\gamma}}\mathbf{D}^{-1/2}+\mathbf{C}^{-1/2}\bar{\boldsymbol{\gamma}}\mathbf{C}^{-1/2}\right]\right\},\end{aligned} \tag{83}$$

or, recovering the definition of $\boldsymbol{\lambda}$ (eq. (50)), $\boldsymbol{\gamma}$ (eq. (62)) and $\bar{\boldsymbol{\gamma}}$ (eq. (80))

$$\begin{aligned}\chi_{\mathrm{FC/HT2}}(\tau_i,\tau_f) &= \sqrt{\frac{\det(\mathbf{a}_f)\det(\mathbf{a}_i)}{(i\hbar)^{2N}\det(\mathbf{CD})}}\exp\left[-\mathbf{K}^T\mathbf{d}_i\mathbf{K}\right]\exp\left[\mathbf{K}^T\mathbf{d}_i\mathbf{J}\mathbf{D}^{-1}\mathbf{J}^T\mathbf{d}_i\mathbf{K}\right] \\ &\frac{1}{2}\left\{2\mathbf{D}^{-1}\mathbf{K}^T\mathbf{d}_i\mathbf{J}\boldsymbol{\mu}^{(2)}\boldsymbol{m}^{(0)}\mathbf{J}^T\mathbf{d}_i\mathbf{K}\mathbf{D}^{-1}+\mathbf{D}^{-1}\mathbf{K}^T\mathbf{d}_i\mathbf{J}\boldsymbol{\mu}^{(0)}\boldsymbol{m}^{(2)}\mathbf{J}^T\mathbf{d}_i\mathbf{K}\mathbf{D}^{-1}\right. \\ &+\,\mathrm{tr}\left[\mathbf{D}^{-1/2}\boldsymbol{\mu}^{(2)}\boldsymbol{m}^{(0)}\mathbf{D}^{-1/2}+\mathbf{C}^{-1/2}\boldsymbol{\mu}^{(2)}\boldsymbol{m}^{(0)}\mathbf{C}^{-1/2}\right] \\ &\left.+\,\mathrm{tr}\left[\mathbf{D}^{-1/2}\boldsymbol{\mu}^{(0)}\boldsymbol{m}^{(2)}\mathbf{D}^{-1/2}+\mathbf{C}^{-1/2}\boldsymbol{\mu}^{(0)}\boldsymbol{m}^{(2)}\mathbf{C}^{-1/2}\right]\right\}.\end{aligned} \tag{84}$$

Now, identifying the FC term as the term in the first line after the equal sign [?], and further reorganizing terms, we arrive to

$$\begin{aligned}\chi_{\mathrm{FC/HT2}}(\tau_i,\tau_f) &= \chi_{\mathrm{FC}}(\tau_i,\tau_f) \\ &\left\{\mathbf{D}^{-1}\mathbf{K}^T\mathbf{d}_i\mathbf{J}\left(\boldsymbol{\mu}^{(2)}\boldsymbol{m}^{(0)}+\boldsymbol{\mu}^{(0)}\boldsymbol{m}^{(2)}\right)\mathbf{J}^T\mathbf{d}_i\mathbf{K}\mathbf{D}^{-1}\right. \\ &\left.+\,\frac{1}{2}\,\mathrm{tr}\left[\left(\boldsymbol{\mu}^{(2)}\boldsymbol{m}^{(0)}+\boldsymbol{\mu}^{(0)}\boldsymbol{m}^{(2)}\right)(\mathbf{D}+\mathbf{C})\right]\right\}.\end{aligned} \tag{85}$$

Finally, we can give a more compact expression as

$$\begin{aligned}\therefore\ \chi_{\mathrm{FC/HT2}}(\tau_i,\tau_f) &= \chi_{\mathrm{FC}}(\tau_i,\tau_f) \\ &\mathrm{tr}\left[(\boldsymbol{\mu}^{(2)}\boldsymbol{m}^{(0)}+\boldsymbol{\mu}^{(0)}\boldsymbol{m}^{(2)})\left\{(\mathbf{D}^{-1}\mathbf{K}^T\mathbf{d}_i\mathbf{J})(\mathbf{D}^{-1}\mathbf{K}^T\mathbf{d}_i\mathbf{J})^T+\frac{1}{2}(\mathbf{D}+\mathbf{C})\right\}\right].\end{aligned} \tag{86}$$

C.4 Derivation of the total intensity for OPA and ECD

Let us consider an electronic transition between two electronic states, 1 and 2, and a second order expansion of the corresponding electric and magnetic transition dipoles (1 and 2 are omitted for clarity)

$$\mu^\alpha(\mathbf{Q}) = \mu_0^\alpha + \sum_i \mu_i^\alpha Q_i + \frac{1}{2}\sum_{i,j} \mu_{ij}^\alpha Q_i Q_j, \tag{87}$$

$$m^\alpha(\mathbf{Q}) = m_0^\alpha + \sum_i m_i^\alpha Q_i + \frac{1}{2}\sum_{i,j} m_{ij}^\alpha Q_i Q_j. \tag{88}$$

The sum of the intensities of the associated vibronic transitions from initial states $|v_1\rangle$, with Boltzmann population $p_{v1} = \exp(-\beta E_{v1})/Z$, to final states $|v_2\rangle$ for absorption and ECD are, respectively

$$\begin{aligned} I_{\text{abs}}^{\text{tot}} = & \sum_{v_1,v_2\alpha} p_{v1}\langle v_1|\mu_0^\alpha + \sum_i \mu_i^\alpha Q_i + \frac{1}{2}\sum_{i,j}\mu_{ij}^\alpha Q_i Q_j|v_2\rangle \\ & \langle v_2|\mu_0^\alpha + \sum_k \mu_k^\alpha Q_k + \frac{1}{2}\sum_{k,l}\mu_{kl}^\alpha Q_k Q_l|v_1\rangle, \end{aligned} \tag{89}$$

$$\begin{aligned} I_{\text{ECD}}^{\text{tot}} = & \sum_{v_1,v_2\alpha} p_{v1}\langle v_1|\mu_0^\alpha + \sum_i \mu_i^\alpha Q_i + \frac{1}{2}\sum_{i,j}\mu_{ij}^\alpha Q_i Q_j|v_2\rangle \\ & \langle v_2|m_0^\alpha + \sum_k m_k^\alpha Q_k + \frac{1}{2}\sum_{k,l} m_{kl}^\alpha Q_k Q_l|v_1\rangle. \end{aligned} \tag{90}$$

C.4.1 Total intensity for absorption

Let us focus on $I_{\text{abs}}^{\text{tot}}$ first. Exploiting the identity $\sum_{v_2} |v_2\rangle\langle v_2| = 1$ we get

$$\begin{aligned} I_{\text{abs}}^{\text{tot}} = & \sum_{v_1,\alpha} p_{v1}\langle v_1|\big(\mu_0^\alpha\big)^2|v_1\rangle + \\ & 2\sum_{v_1,\alpha,i} p_{v1}\langle v_1|\mu_0^\alpha \mu_i^\alpha Q_i|v_1\rangle + \\ & \sum_{v_1,\alpha,i,k} p_{v1}\langle v_1|\mu_i^\alpha \mu_k^\alpha Q_i Q_k|v_1\rangle + \\ & \sum_{v_1,\alpha,i,j} p_{v1}\langle v_1|\mu_0^\alpha \mu_{ij}^\alpha Q_i Q_j|v_1\rangle + \\ & \sum_{v_1,\alpha,i,j,k} p_{v1}\langle v_1|\mu_i^\alpha \mu_{kl}^\alpha Q_i Q_k Q_l|v_1\rangle + \\ & \frac{1}{4}\sum_{v_1,\alpha,i,j,k,l} p_{v1}\langle v_1|\mu_{ij}^\alpha \mu_{kl}^\alpha Q_i Q_j Q_k Q_l|v_1\rangle. \end{aligned} \tag{91}$$

Since the only non-vanishing matrix elements are those involving operators with even exponents for each normal coordinate, we have

$$\begin{aligned}
I_{\text{abs}}^{\text{tot}} &= \sum_{\alpha} \left(\mu_0^\alpha\right)^2 + \\
& \sum_{v_1,\alpha,i} p_{v1} \left(\mu_i^\alpha\right)^2 \langle v_1|Q_i^2|v_1\rangle + \\
& \sum_{v_1,\alpha,i} p_{v1} \mu_0^\alpha \mu_{ii}^\alpha \langle v_1|Q_i^2|v_1\rangle + \\
& \frac{1}{4} \sum_{v_1,\alpha,i} p_{v1} \left(\mu_{ii}^\alpha\right)^2 \langle v_1|Q_i^4|v_1\rangle + \\
& \frac{1}{4} \sum_{v_1,\alpha,i,k\neq i} p_{v1} \mu_{ii}^\alpha \mu_{kk}^\alpha \langle v_1|Q_i^2 Q_k^2|v_1\rangle + \\
& \sum_{v_1,\alpha,i,j>i} p_{v1} \left(\mu_{ij}^\alpha\right)^2 \langle v_1|Q_i^2 Q_j^2|v_1\rangle. \qquad (92)
\end{aligned}$$

Now, remembering that

$$\langle v|Q_i^2|v\rangle = \frac{\hbar}{2\omega_i}\left(2n_i + 1\right), \qquad (93)$$

$$\langle v|Q_i^4|v\rangle = \frac{\hbar^2}{4\omega_i^2}\left(6n_i^2 + 6n_i + 3\right), \qquad (94)$$

and that their thermal average is (Markham 1959)

$$\sum_v \frac{e^{-\beta H}}{Z} \langle v|Q_i^2|v\rangle = \frac{\hbar}{2\omega_i} \coth\left(\frac{\beta\hbar\omega_i}{2}\right), \qquad (95)$$

$$\sum_v \frac{e^{-\beta H}}{Z} \langle v|Q_i^4|v\rangle = 3\left(\frac{\hbar}{2\omega_i}\right)^2 \coth^2\left(\frac{\beta\hbar\omega_i}{2}\right), \qquad (96)$$

we have

$$\begin{aligned}
I_{\text{abs}}^{\text{tot}} &= \sum_{\alpha} \left(\mu_0^\alpha\right)^2 + \sum_{\alpha,i} \left(\mu_i^\alpha\right)^2 \frac{\hbar}{2\omega_i} \coth\left(\frac{\beta\hbar\omega_i}{2}\right) + \\
& \sum_{\alpha,i} \mu_0^\alpha \mu_{ii}^\alpha \frac{\hbar}{2\omega_i} \coth\left(\frac{\beta\hbar\omega_i}{2}\right) + \\
& \frac{3}{4} \sum_{\alpha,i} \left(\mu_{ii}^\alpha\right)^2 \left(\frac{\hbar}{2\omega_i}\right)^2 \coth^2\left(\frac{\beta\hbar\omega_i}{2}\right) + \\
& \frac{1}{4} \sum_{\alpha,i,k\neq i} \mu_{ii}^\alpha \mu_{kk}^\alpha \frac{\hbar^2}{4\omega_i\omega_k} \coth\left(\frac{\beta\hbar\omega_i}{2}\right) \coth\left(\frac{\beta\hbar\omega_k}{2}\right) + \\
& \sum_{\alpha,i,j\neq i} \left(\mu_{ij}^\alpha\right)^2 \frac{\hbar^2}{4\omega_i\omega_j} \coth\left(\frac{\beta\hbar\omega_i}{2}\right) \coth\left(\frac{\beta\hbar\omega_j}{2}\right). \qquad (97)
\end{aligned}$$

It is worth noticing that in the last equation the first term of the rhs corresponds to the total intensity in the FC approximation, and it is also the only term standing in the $\mathcal{R}_1$ approach. The second term of the first line is the contribution to the total density from a first-order expansion of the transition dipole (i.e., the HT/HT term). However, this correction does arise from a quadratic term and therefore it actually belongs to a second-order expansion of the dipole strength. The term in the second line is actually what is missing for a complete second-order expansion of the dipole strength, i.e. the $\mathcal{R}_2$ approach, and it does have an impact on the total intensity. All the further terms arise from a second-order expansion of the electric transition dipole. They correspond to only some of the terms necessary to expand the dipole strength to third order (these third-order terms are not influential on the total intensity, but this does not mean that they do not have an impact on the spectral shape) and to the fourth order (on the contrary, fourth-order terms do have an impact on the total intensity).

C.4.2 Total intensity for ECD

In order to obtain the total ECD intensity we can follow the same lines

$$
\begin{aligned}
I_{\mathrm{ECD}}^{\mathrm{tot}} = & \sum_{v_1,\alpha} p_{v1}\langle v_1|\mu_0^\alpha m_0^\alpha|v_1\rangle + \\
& \sum_{v_1,\alpha,i} p_{v1}\langle v_1|\mu_0^\alpha m_i^\alpha Q_i|v_1\rangle + \\
& \sum_{v_1,\alpha,k} p_{v1}\langle v_1|\mu_i^\alpha m_0^\alpha Q_k|v_1\rangle + \\
& \sum_{v_1,\alpha,i,k} p_{v1}\langle v_1|\mu_i^\alpha m_k^\alpha Q_i Q_k|v_1\rangle + \\
& \frac{1}{2}\sum_{v_1,\alpha,k,l} p_{v1}\langle v_1|\mu_0^\alpha m_{kl}^\alpha Q_k Q_l|v_1\rangle + \\
& \frac{1}{2}\sum_{v_1,\alpha,i,j} p_{v1}\langle v_1|\mu_{ij}^\alpha m_0^\alpha Q_i Q_j|v_1\rangle + \\
& \frac{1}{2}\sum_{v_1,\alpha,i,k,l} p_{v1}\langle v_1|\mu_i^\alpha m_{kl}^\alpha Q_i Q_k Q_l|v_1\rangle + \\
& \frac{1}{2}\sum_{v_1,\alpha,i,j,k} p_{v1}\langle v_1|\mu_{ij}^\alpha m_k^\alpha Q_i Q_j Q_l|v_1\rangle + \\
& \frac{1}{4}\sum_{v_1,\alpha,i,j,k,l} p_{v1}\langle v_1|\mu_{ij}^\alpha m_{kl}^\alpha Q_i Q_j Q_k Q_l|v_1\rangle. \qquad (98)
\end{aligned}
$$

Considering only the non-vanishing elements we have

$$
\begin{aligned}
I_{\mathrm{ECD}}^{\mathrm{tot}} = & \sum_{\alpha} \mu_0^\alpha m_0^\alpha + \\
& \sum_{v_1,\alpha,i} p_{v1}\mu_i^\alpha m_i^\alpha \langle v_1|Q_i^2|v_1\rangle + \\
& \frac{1}{2}\sum_{v_1,\alpha,i} p_{v1}(\mu_0^\alpha m_{ii}^\alpha + \mu_{ii}^\alpha m_0^\alpha)\langle v_1|Q_i^2|v_1\rangle + \\
& \frac{1}{4}\sum_{v_1,\alpha,i} p_{v1}\mu_{ii}^\alpha m_{ii}^\alpha \langle v_1|Q_i^4|v_1\rangle + \\
& \frac{1}{4}\sum_{v_1,\alpha,i,k\neq i} p_{v1}\mu_{ii}^\alpha m_{kk}^\alpha \langle v_1|Q_i^2 Q_k^2|v_1\rangle + \\
& \sum_{v_1,\alpha,i,j>i} p_{v1}\mu_{ij}^\alpha m_{ij}^\alpha \langle v_1|Q_i^2 Q_j^2|v_1\rangle. \qquad (99)
\end{aligned}
$$

Taking into account Eq. 96 we finally get

$$\begin{aligned}
I_{\text{ECD}}^{\text{tot}} &= \sum_{\alpha}\mu_0^\alpha m_0^\alpha + \sum_{\alpha,i}\mu_i^\alpha m_i^\alpha \frac{\hbar}{2\omega_i}\coth\left(\frac{\beta\hbar\omega_i}{2}\right) + \\
&\frac{1}{2}\sum_{\alpha,i}(\mu_0^\alpha m_{ii}^\alpha + \mu_{ii}^\alpha m_0^\alpha)\frac{\hbar}{2\omega_i}\coth\left(\frac{\beta\hbar\omega_i}{2}\right) + \\
&\frac{3}{4}\sum_{\alpha,i}\mu_{ii}^\alpha m_{ii}^\alpha\left(\frac{\hbar}{2\omega_i}\right)^2\coth^2\left(\frac{\beta\hbar\omega_i}{2}\right) + \\
&\frac{1}{4}\sum_{\alpha,i,k\neq i}\mu_{ii}^\alpha m_{kk}^\alpha\frac{\hbar^2}{4\omega_i\omega_k}\coth\left(\frac{\beta\hbar\omega_i}{2}\right)\coth\left(\frac{\beta\hbar\omega_k}{2}\right) + \\
&\sum_{\alpha,i,j>i}\mu_{ij}^\alpha m_{ij}^\alpha\frac{\hbar^2}{4\omega_i\omega_j}\coth\left(\frac{\beta\hbar\omega_i}{2}\right)\coth\left(\frac{\beta\hbar\omega_j}{2}\right). \qquad (100)
\end{aligned}$$

Analogously to the final expression of $I_{\text{abs}}^{\text{tot}}$ the first term of the RHS corresponds to the total intensity in the FC approximation, as well as for $\mathcal{R}_1$. The second term of the first line is the additional contribution to the total density for a first-order expansion of both the electric and magnetic transition dipoles. Interestingly, such "first-order" correction to the FC total intensity arises from the HT-HT term and, therefore, in the current formulation of first-order HT, it breaks the origin invariance. It is noteworthy that the HT-HT term does actually belong to the quadratic terms of the expansion of the rotatory strength and the term in the second line is what is missing for a complete second-order expansion of the rotatory strength, i.e. the $\mathcal{R}_2$ approach, and it restores the origin invariance. It should also be noticed that the second term on the first line and the term on the second line do depend on different parameters and therefore they do not cancel out in general. We conclude that the sum of these terms is both non-vanishing and origin-invariant. All further terms in the following lines arise from a second-order expansion of the electric and magnetic transition dipoles but they correspond only to some of the terms necessary to expand the rotatory strength to third order (however third-order terms are not influential on the total intensity) and to fourth order (fourth-order terms on the contrary do have an impact on the total intensity).

C.4.3 Total intensity with TDM computed at the final state geometry

In the previous equations, the integration is taken over Q_i normal modes, whihc is imposed by the presence of the Boltzmann population, which naturally refers to the initial state. This means, that if we use TDM computed at the equilibrium geometry of the final state, where the Taylor exansions is given in terms of Q_f, we need to resort to the Duschinsky transformation and extrapolate the TDM data to the initial geometry, as discussed in Section C.2. This strategy works properly for FC, HT or HT2 approaches, but, again as discussed in that section, will fail for $\mathcal{R}_1$ and $\mathcal{R}_2$ methods, as in this case there is a conflict between the extrapolation and the selection of specific cross terms between TDM expansions to ensure a complete rotatory strength uo to first ($\mathcal{R}_1$) or second ($\mathcal{R}_2$) order.

This issue can be solved by cherry-picking the terms of the extrapolation that are retained. Sice we need to go from Q_f to Q_i normal modes,

$$\mathbf{Q_f} = \mathbf{J}^{-1}\mathbf{Q_i} - \mathbf{J}^{-1}\mathbf{K}, \tag{101}$$

We then take the expansion of the TDMs in terms of Q_f modes (see Eqs.7a an d7b in the main text), and apply the above Duschinsky relation to yield,

$$\boldsymbol{\mu} = \boldsymbol{\mu}_0^f + \boldsymbol{\mu}^{f\prime}(\mathbf{J}^{-1}\mathbf{Q_i} - \mathbf{J}^{-1}\mathbf{K}) + \cdots\ , \tag{102a}$$

$$\mathbf{m} = \mathbf{m}_0^f + \mathbf{m}^{f\prime}(\mathbf{J}^{-1}\mathbf{Q_i} - \mathbf{J}^{-1}\mathbf{K}) + \cdots\ , \tag{102b}$$

At this point, we can take the linear extrapolation, i.e., for the constant term,

$$\boldsymbol{\mu}_0^i = \boldsymbol{\mu}_0^f - \boldsymbol{\mu}^{f\prime}\mathbf{J}^{-1}\mathbf{K}, \tag{103a}$$

$$\mathbf{m}_0^i = \mathbf{m}_0^f - \mathbf{m}^{f\prime}\mathbf{J}^{-1}\mathbf{K} \tag{103b}$$

and similarly for the gradient. With these extrapolated values, we can then apply the expressions in Eqs. 97 and 100 to compute the total intensity. Such strategy will work for HT and HT2 (using a quadraic extrapolation). For $\mathcal{R}_1$, instead, we need to retain only the terms:

$$
\begin{aligned}
\mathcal{R}_{1f}(\mathbf{Q_i}) =& \boldsymbol{\mu}_0^f \mathbf{m}_0^f + \\
& (\boldsymbol{\mu}_0^f \mathbf{m}^{f\prime} + \mathbf{m}_0^f \boldsymbol{\mu}^{f\prime})\mathbf{J}^{-1}\mathbf{Q_i} - \\
& (\boldsymbol{\mu}_0^f \mathbf{m}^{f\prime} + \mathbf{m}_0^f \boldsymbol{\mu}^{f\prime})\mathbf{J}^{-1}\mathbf{K},
\end{aligned} \tag{104}
$$

the term in the first line correspond to the FC_f spectrum, while the complete expression corresponds to the total $\mathcal{R}_{1f}$. From this point we define the rotated derivatives of the TDM as,

$$
\begin{aligned}
\boldsymbol{\mu}^{i\prime} &= \boldsymbol{\mu}^{f\prime}\mathbf{J}^{-1}, \\
\mathbf{m}^{i\prime} &= \mathbf{m}^{f\prime}\mathbf{J}^{-1},
\end{aligned} \tag{105}
$$

which contains the derivatives of the TDM with respect Q_i modes (even if evaluated at the geometry of the final state).

If we take the integral for this spectrum, following Eq. 100, only the first (FC) and the last terms are non-zero. Interestingly, the total intensity of the $\mathcal{R}_{1f}$ would be different than the FC one, namely

$$
\begin{aligned}
I^{tot}_{\mathcal{R}_{1f}} &= \sum_{\alpha} \mu_0^{f\alpha} m_0^{f\alpha} - \\
& \sum_{\alpha,i} (\mu_0^{f\alpha} m_i^{i\alpha} + m_0^{f\alpha} \mu_i^{i\alpha}) K_i,
\end{aligned} \tag{106}
$$

The intensity of the HT_f spectrum can be formulated similarly,

$$
\begin{aligned}
I^{tot}_{\mathrm{HT}_f} &= I^{tot}_{\mathcal{R}_{1f}} + \\
& \sum_{\alpha,j} \mu_j^{i\alpha} m_j^{i\alpha} \frac{\hbar}{2\omega_j^i} \coth\left(\frac{\beta\hbar\omega_j^i}{2}\right) + \\
& \sum_{\alpha,j,k} K_j \mu_j^{i\alpha} m_k^{i\alpha} K_k
\end{aligned} \tag{107}
$$

where we here note that the frequencies, ω^i, correspond to the initial state normal modes. The above expression is equivalent to the one that would be obtained using the extrapolated values.

Finally, the total intentisity for $\mathcal{R}_{2f}$ spectra reads,

$$\begin{aligned} I^{tot}_{\mathcal{R}_{2f}} &= I^{tot}_{\mathrm{HT}_f} + \\ &\frac{1}{2}\sum_{\alpha,j}(\mu_0^{f\alpha}m_{jj}^{i\alpha} + \mu_{jj}^{i\alpha}m_0^{f\alpha})\frac{\hbar}{2\omega_j^i}\coth\left(\frac{\beta\hbar\omega_j^i}{2}\right) + \\ &\frac{1}{2}\sum_{\alpha,j,k}K_j(\mu_0^{f\alpha}m_{jk}^{i\alpha} + m_0^{f\alpha}\mu_{jk}^{i\alpha})K_k \end{aligned} \tag{108}$$

where we have introduced the rotated second derivatives,

$$\begin{aligned} \boldsymbol{\mu}^{i\prime\prime} &= \mathbf{J}\boldsymbol{\mu}^{f\prime}\mathbf{J}^T, \\ \mathbf{m}^{i\prime\prime} &= \mathbf{J}\mathbf{m}^{f\prime}\mathbf{J}^T, \end{aligned} \tag{109}$$

where we have exploited the orthognoality of $\mathbf{J}$, i.e., $\mathbf{J}^{-1} = \mathbf{J}^T$, and assume that the matrix multiplication affects the dimensions with size N_{vib}.

The previous expressions have been adopted to compute the total intensity with TDM_f. The analytical total intensities , which are practically identical to those obtained by numerical integration of the computed spectra, are shown in Table S3.

Table S3: Total intensities (a.u.) of OPA and ECD lineshapes computed for molecule **2** with TMD evaluated at the equilibrium geometry of the final (TDM_f) state. The electric TDMs are evaluated in the velocity gauge.

	OPA$\times 10^2$		ECD$\times 10^4$	
	CoM	Shifted	CoM	Shifted
FC	9.629	9.629	5.883	5.882
$\mathcal{R}_1$	3.713	3.713	6.923	6.922
HT	7.640	7.640	-0.220	-28.88
$\mathcal{R}_2$	8.474	8.474	7.783	7.784
HT2	9.100	9.100	8.412	22.20

$$\chi(t,T) = \chi_{FC} \tag{110}$$

$$\Bigg[\boldsymbol{\mu}^T\mathbf{m} + \sum_i (\boldsymbol{\mu}_0^T\mathbf{m}'_i + (\boldsymbol{\mu}'_i)^T\mathbf{m}_0)(\mathbf{D_{HT}})_i \tag{111}$$

$$+ \sum_{ij} (\boldsymbol{\mu}'_i)^T\mathbf{m}'_j(\mathbf{A_{HT}})_{ij} \tag{112}$$

$$+ \sum_{ij} (\boldsymbol{\mu}_0^T\mathbf{m}''_{ij} + (\boldsymbol{\mu}''_{ij})^T\mathbf{m}_0)(\mathbf{B_{HT}})_{ij}\Bigg] \tag{113}$$

where:

$$\mathbf{A}_{HT} = \mathbf{D}_{HT}\mathbf{D}_{HT}^t + \frac{1}{2}(\mathbf{D}^{-1} - \mathbf{C}^{-1}) \tag{114}$$

$$\mathbf{B}_{HT} = \mathbf{D}_{HT}\mathbf{D}_{HT}^t + \frac{1}{2}(\mathbf{D}^{-1} + \mathbf{C}^{-1}) \tag{115}$$