Supporting Information

Fluorescence-detected Circular Dichroism Spectroscopy of
Jet-cooled Ephedrine

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Equation estimating the asymmetry factor $g_i$:

The numbers of the excited molecules by LCP and RCP pulses are given by

$$N_{exc}^L = N_0\sigma_{exc}^L$$  \hspace{1cm} (1)

$$N_{exc}^R = N_0\sigma_{exc}^R$$  \hspace{1cm} (2)

, where $N_0$ is the number of molecules in the irradiated volume and $\sigma_{exc}$ is the cross section for excitation of molecules. With the assumption that the fluorescence quantum yield parallels its absorbance, the asymmetry factor $g_f$ is given by

$$g_f = \frac{2(N_{exc}^L - N_{exc}^R)}{(N_{exc}^L + N_{exc}^R)} = \frac{2(\sigma_{exc}^L - \sigma_{exc}^R)}{(\sigma_{exc}^L + \sigma_{exc}^R)}$$  \hspace{1cm} (3)

Then, the numbers of ions produced by LCP and RCP pulses using R2PI are given by

$$N_{ion}^L = N_{exc}^L \sigma_{ion}^L = N_0\sigma_{exc}^L\sigma_{ion}^L$$  \hspace{1cm} (4)

$$N_{ion}^R = N_{exc}^R \sigma_{ion}^R = N_0\sigma_{exc}^R\sigma_{ion}^R$$  \hspace{1cm} (5)

, where $\sigma_{ion}$ is the cross section for photoionization of molecules from the excited state. The asymmetry factor $g_{r2pi}$ is given by
\[ g_{r2p} = \frac{2(N_{\text{ion}}^L - N_{\text{ion}}^R)}{(N_{\text{ion}}^L + N_{\text{ion}}^R)} = \frac{2(\sigma_{\text{exc}}^L \sigma_{\text{ion}}^L - \sigma_{\text{exc}}^R \sigma_{\text{ion}}^R)}{(\sigma_{\text{exc}}^L \sigma_{\text{ion}}^L + \sigma_{\text{exc}}^R \sigma_{\text{ion}}^R)} \]  

Then, the asymmetry factor for one-photon ionization of the excited molecules, \( g_i \), is given by

\[ g_i = \frac{2(N_{\text{exc}} \sigma_{\text{ion}}^L - N_{\text{exc}} \sigma_{\text{ion}}^R)}{(N_{\text{exc}} \sigma_{\text{ion}}^L + N_{\text{exc}} \sigma_{\text{ion}}^R)} = \frac{2(\sigma_{\text{ion}}^L - \sigma_{\text{ion}}^R)}{(\sigma_{\text{ion}}^L + \sigma_{\text{ion}}^R)} \]  

By introducing the parameters of \( \alpha \) and \( \beta \), \( \sigma_{\text{exc}}^L \) and \( \sigma_{\text{ion}}^R \) are given by

\[
\sigma_{\text{exc}}^R = \alpha \sigma_{\text{exc}}^L \\
\sigma_{\text{ion}}^R = \beta \sigma_{\text{ion}}^L
\]

The \( \alpha \) and \( \beta \) represent the differences in the cross-sections for LCP and RCP pulses.

The replacement of \( \sigma_{\text{exc}}^L \) and \( \sigma_{\text{ion}}^R \) with Eqns. (8-9) gives

\[
g_f = \frac{2(\sigma_{\text{exc}}^L - \alpha \sigma_{\text{exc}}^L)}{(\sigma_{\text{exc}}^L + \alpha \sigma_{\text{exc}}^L)} = \frac{2(1 - \alpha)}{(1 + \alpha)} \]  

\[
g_{r2p} = \frac{2(\sigma_{\text{exc}}^L \sigma_{\text{ion}}^L - \alpha \beta \sigma_{\text{exc}}^L \sigma_{\text{ion}}^L)}{(\sigma_{\text{exc}}^L \sigma_{\text{ion}}^L + \alpha \beta \sigma_{\text{exc}}^L \sigma_{\text{ion}}^L)} = \frac{2(1 - \alpha \beta)}{(1 + \alpha \beta)} \]  

\[
g_i = \frac{2(\sigma_{\text{ion}}^L - \beta \sigma_{\text{ion}}^L)}{(\sigma_{\text{ion}}^L + \beta \sigma_{\text{ion}}^L)} = \frac{2(1 - \beta)}{(1 + \beta)} \]  

Rearrangement of Eqns. (10-11) gives

\[
\alpha = \frac{2 - g_f}{2 + g_f} \]  

\[
\beta = \frac{1}{\alpha} \left( \frac{2 - g_{r2p}}{2 + g_{r2p}} \right) \]  

\( \alpha \) and \( \beta \) values are determined from the experimental \( g_f \) and \( g_{r2p} \) values. Then, the \( g_i \) value can be estimated using the Eqn. (12).
Table S1. Relative energies and Gibbs free energies, and rotatory strengths of −EPD conformers calculated at the M06-2X/6-311++G(d,p) level.

<table>
<thead>
<tr>
<th></th>
<th>$\Delta E_{rel}^a$</th>
<th>$\Delta G_{rel}^a$</th>
<th>$R^b$</th>
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</thead>
<tbody>
<tr>
<td>AG(a)</td>
<td>0</td>
<td>0</td>
<td>0.91</td>
</tr>
<tr>
<td>AG(b)</td>
<td>1.10</td>
<td>1.22</td>
<td>1.16</td>
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<td>GG(a)</td>
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<td>0.17</td>
<td>0.68</td>
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<tr>
<td>GG(b)</td>
<td>3.12</td>
<td>3.74</td>
<td>0.47</td>
</tr>
</tbody>
</table>

$^a$Units in kcal/mol. Relative energies were calculated with zero-point energy corrections. The Gibbs free energies were calculated at 298 K. $^b$Units in cgs (10$^{-40}$ erg esu cm/Gauss).
**Figure S1.** Plots of log $I_{ion}$ versus log $P$ obtained by fixing the laser wavenumber at (a) the A and (b) B bands. $I_{ion}$ and $P$ are the ion signal of the fragment at m/z=58 and the laser intensity, respectively.
**Figure S2.** (a) FE spectrum and (b) electronic spectrum of +EPD simulated using TDDFT at the M06-2X/6-311++G(d,p) level in consideration of Franck-Condon factors.