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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

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

$$N_{exc}^{R} = N_0 \sigma_{exc}^{R} \quad (2)$$

, where N_0 is the number of molecules in the irradiated volume and σ_{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

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

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

$$N_{ion}^{L} = N_{exc}^{L} \sigma_{ion}^{L} = N_0 \sigma_{exc}^{L} \sigma_{ion}^{L} \quad (4)$$

$$N_{ion}^{R} = N_{exc}^{R} \sigma_{ion}^{R} = N_0 \sigma_{exc}^{R} \sigma_{ion}^{R} \quad (5)$$

, where σ_{ion} is the cross section for photoionization of molecules from the excited state. The asymmetry factor g_{r2pi} is given by

$$g_{r2pi} = \frac{2(N_{ion}^L - N_{ion}^R)}{(N_{ion}^L + N_{ion}^R)} = \frac{2(\sigma_{exc}^L \sigma_{ion}^L - \sigma_{exc}^R \sigma_{ion}^R)}{(\sigma_{exc}^L \sigma_{ion}^L + \sigma_{exc}^R \sigma_{ion}^R)} \tag{6}$$

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

$$g_i = \frac{2(N_{exc}\sigma_{ion}^L - N_{exc}\sigma_{ion}^R)}{(N_{exc}\sigma_{ion}^L + N_{exc}\sigma_{ion}^R)} = \frac{2(\sigma_{ion}^L - \sigma_{ion}^R)}{(\sigma_{ion}^L + \sigma_{ion}^R)} \tag{7}$$

By introducing the parameters of α and β, σ_{exc}^R and σ_{ion}^R are given by

$$\sigma_{exc}^R = \alpha \sigma_{exc}^L \tag{8}$$

$$\sigma_{ion}^R = \beta \sigma_{ion}^L \tag{9}$$

The α and β represent the differences in the cross-sections for LCP and RCP pulses.
The replacement of σ_{exc}^R and σ_{ion}^R with Eqns. (8-9) gives

$$g_f = \frac{2(\sigma_{exc}^L - \alpha\sigma_{exc}^L)}{(\sigma_{exc}^L + \alpha\sigma_{exc}^L)} = \frac{2(1-\alpha)}{(1+\alpha)} \tag{10}$$

$$g_{r2pi} = \frac{2(\sigma_{exc}^L \sigma_{ion}^L - \alpha\beta\sigma_{exc}^L \sigma_{ion}^L)}{(\sigma_{exc}^L \sigma_{ion}^L + \alpha\beta\sigma_{exc}^L \sigma_{ion}^L)} = \frac{2(1-\alpha\beta)}{(1+\alpha\beta)} \tag{11}$$

$$g_i = \frac{2(\sigma_{ion}^L - \beta\sigma_{ion}^L)}{(\sigma_{ion}^L + \beta\sigma_{ion}^L)} = \frac{2(1-\beta)}{(1+\beta)} \tag{12}$$

Rearrangement of Eqns. (10-11) gives

$$\alpha = \frac{2 - g_f}{2 + g_f} \tag{13}$$

$$\beta = \frac{1}{\alpha}\left(\frac{2 - g_{r2pi}}{2 + g_{r2pi}}\right) \tag{14}$$

α and β values are determined from the experimental g_f and g_{r2pi} 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.

	$\Delta E_{rel}{}^{a}$	$\Delta G_{rel}{}^{a}$	R^{b}
AG(a)	0	0	0.91
AG(b)	1.10	1.22	1.16
GG(a)	0.49	0.17	0.68
GG(b)	3.12	3.74	0.47

[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).

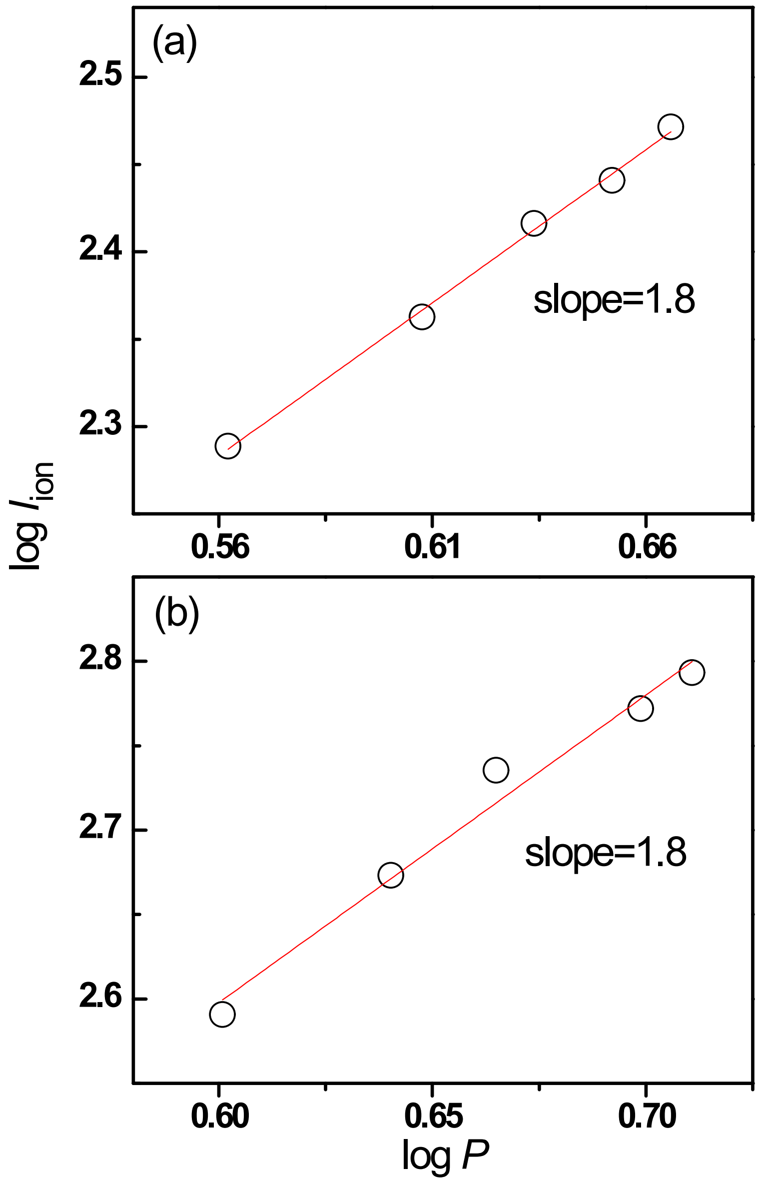

Figure S1. Plots of log I_{ion} versus log P obtained by fixing the laser wavenumber at (a) the A and (b) B bands. I_{ion} and P are the ion signal of the fragment at m/z=58 and the laser intensity, respectively.

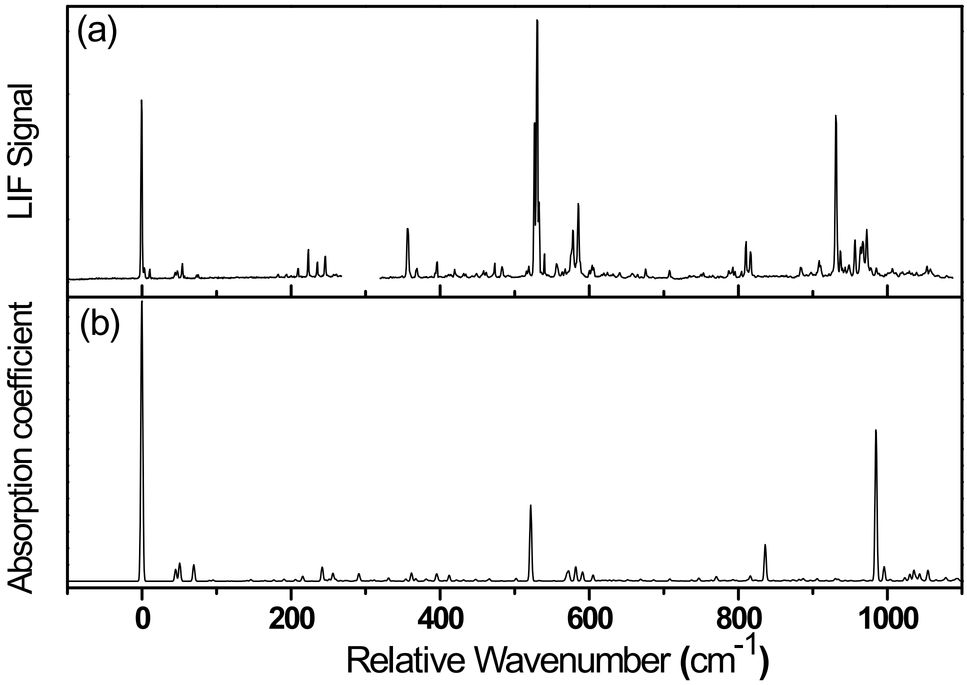

Figure S2. (a) FE spectrum and (b) electronic spectrum of +EPD simulated using TDDFT at the M06-2X/6-311++G(d,p) level in consideration of Franck-Condon factors.