Electronic Supplementary Material (ESI) for Physical Chemistry Chemical Physics.

High-resolution resonance-enhanced multiphoton photoelectron circular dichroism

– Supporting Information –

1 Data Evaluation

The C++based pBasex algorithm is operated under ubuntu 18.04 LTS. The algorithm allows the number of angular and radial sampling points to be adjusted, which requires calculation of the inversion matrix. In this work, we kept the angular sampling point number for 180° at the default value of 256 and increased the radial sampling point number to 512. No higher order processes such as above-threshold ionization were observed on fenchone.[1] The camera images for LCP and RCP were therefore cropped to a window size that covers photoelectron energies up to about 1.5 eV, where we typically have more than ten radial sampling points within the FWHM. To reach this number of points, the PAD images need to be up-scaled to a grid size of 1024x1024. The aim is twofold: On the one hand, we try to use the maximum energy resolution provided by the experimental setup. On the other hand, more sampling points within the FWHM make the derivation of the weighted average LPECD values more stable. The C++pBasex runs under typical laptop hardware (Intel Core i5 IvyBridge, 12 GB RAM, SSD), where a single inversion typically takes below half a second.

2 Vibrations of the 3s Rydberg state

Table 1 shows computed vibrational energy levels of the 3s Rydberg state of fenchone up to a wavenumber of 290 cm^{-1}. 2+1 REMPI transitions via these vibrational levels are located near the band origin of the 3s state and are indicated by red arrows in Figure 2 of the main text. The reader should note that only the most intense transitions are indicated by red arrows in the figure. The vibrational energy is counted with respect to the 0-0 transition. The reader is referred to Section 2.2 of the main text for more information on the computational methods. Most levels in the wavenumber range up to 290 cm^{-1} correspond to fundamentals. Video files of animated vibrational modes can also be found in the supporting materials.

Table 1 Selected computed vibrational energy levels of the 3s Rydberg state.

Vibrational Mode	Wavenumber (cm^{-1})	Video File
ν_1	77.7	nu1.mp4
2 ν_1	155.5	
ν_2	175.2	nu2.mp4
ν_3	197.2	nu3.mp4
ν_4	211.3	nu4.mp4
ν_5	228.0	nu5.mp4
ν_6	233.1	nu6.mp4
3 ν_1	233.1	
ν_7	243.4	nu7.mp4
ν_8	248.2	nu8.mp4
$\nu_1 + \nu_2$	252.9	
$\nu_1 + \nu_3$	274.9	
ν_9	288.2	nu9.mp4

3 Rydberg orbitals

Figure 1 shows Rydberg orbitals of fenchone relevant for this study. The s-type and p-type character is evident. More details can be found in Reference 2.

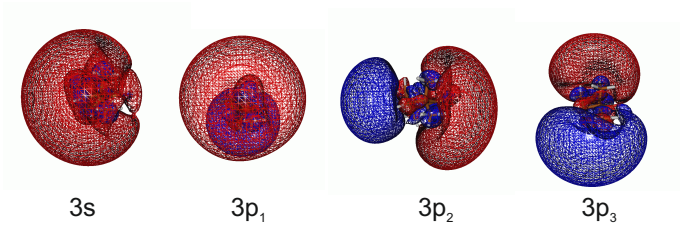

Fig. 1 3s and 3p Rydberg orbitals of fenchone.

4 Coefficients of LPECD Calculation

The LPECD value is calculated using Equation (1) from the main text.

$$\mathrm{LPECD} = \frac{1}{c_0}\left(2c_1 - \frac{1}{2}c_3 + \frac{1}{4}c_5\right). \quad (1)$$

In Figure 2 we show the contribution of each coefficient c_1, c_3, and c_5 to the LPECD value normalized to c_0 . The main contribution originates from c_1.

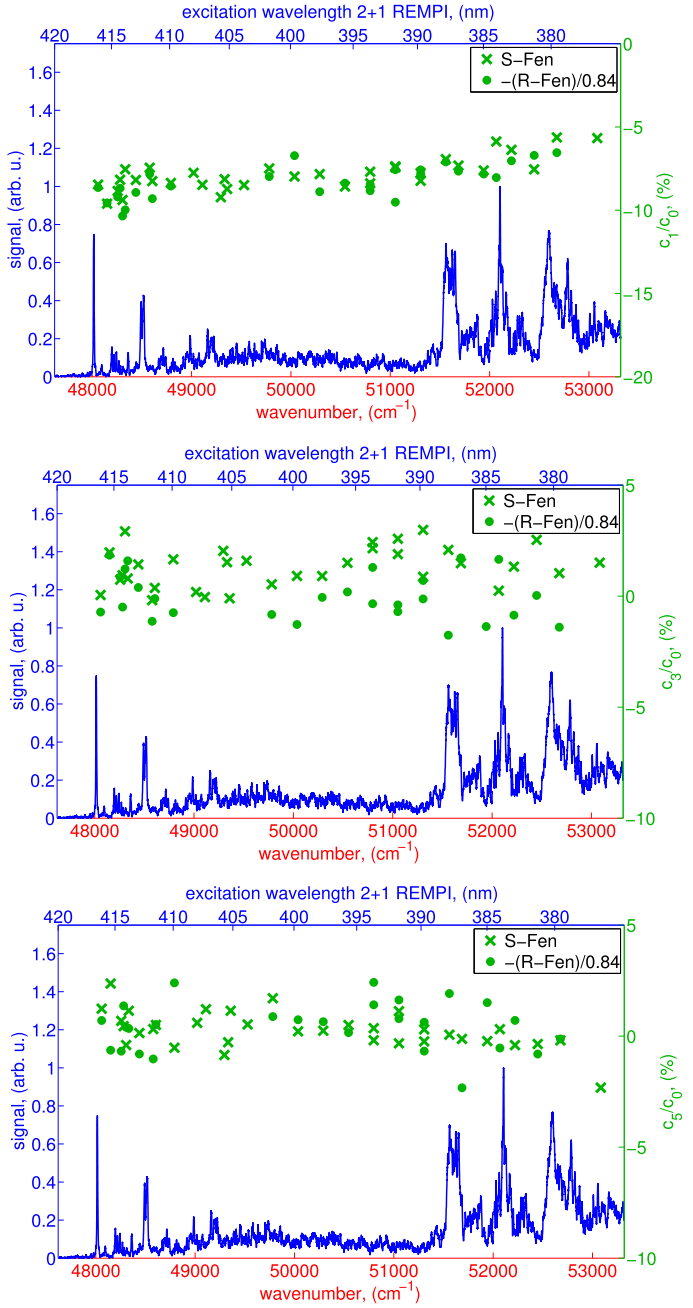

Fig. 2 Contribution of normalized c_1, c_3, and c_5 coefficients to the LPECD value according to Equation 1. The main contribution originates from c_1.

Notes and references

1 C. Lux, A. Senftleben, C. Sarpe, M. Wollenhaupt and T. Baumert, *J. Phys. B At. Mol. Opt. Phys.*, 2016, **49**, 02LT01.

2 R. E. Goetz, T. A. Isaev, B. Nikoobakht, R. Berger and C. P. Koch, *J. Chem. Phys.*, 2017, **146**, 24306.