**Supporting Information for:** "Probing the Structure, the Pseudorotational and Radial Vibrations of Cyclopentane by Femtosecond Rotational Raman Coherence Spectroscopy"

## Philipp Kowalewski, Hans-Martin Frey, Daniel Infanger and Samuel Leutwyler

Departement für Chemie und Biochemie, Universität Bern, Freiestrasse 3, CH-3000 Bern 9, Switzerland

## I. FEMTOSECOND LASER SYSTEM AND EXPERIMENTAL SETUPS

The 10 nJ pulses from a Kerr-lens mode-locked Ti:sapphire oscillator (Mai Tai, Spectra-Physics) are amplified in a Ti:sapphire multipass chirped-pulse amplifier system (ODIN DQC, Quantronix), which is pumped by a 14 W pulsed frequency-doubled Nd:YLF laser (Darwin 527-30-M, Quantronix) at a repetition rate of f = 333 Hz. The center wave length of the resulting laser beam is 800 nm with a pulse energy of 360  $\mu$ J. The temporal and bandwidth properties of the fs pulses were characterized as 75 fs FWHM, a time-bandwidth product of 0.45 and a bandwidth of 12.63 nm (corresponding to 196 cm<sup>-1</sup>) bandwidth, using a single-shot second harmonic generation frequency-resolved optical gating device (Grenouille 8-20, Swamp Optics)<sup>1,2</sup>.

The output of the fs laser system is reduced to a laser pulse energy between  $75 - 120 \mu J$  and split into three equally intense pump, dump and probe beams, which are aligned in a forward BOXCARS degenerate four-wave mixing (DFWM) arrangement, and focused by an f = 1000 mm achromatic lens into the center of either a 1.0 m long stainless-steel gas-cell or into the supersonic jet vacuum chamber. The probe beam runs over a retroreflector that is mounted on a high-precision 1000 mm long delay stage, housed in a vacuum tank with 800 nm AR coated windows that is evacuated to  $< 10^{-3}$  mbar. The time-delay of the probe pulse is by measuring the retroreflector displacement with a two-axis He-Ne laser interferometric system (SP2000 D; SIOS GmbH) with an accuracy of  $\pm 30$  nm. After the output window of gas-cell or jet vacuum chamber, the three input beams are blocked by a mask, while the DFWM signal beam is collimated, spatially filtered and detected by a thermoelectrically cooled GaAs photomultiplier (H7422-50, Hamamatsu). The signals are recorded with a 1 GHz/8-bit oscilloscope at a sweep rate of 8 GHz/s. The experiment is controlled and the data acquired by a PC using LabView.

*Molecular beam setup*: The pulsed supersonic jet nozzle is a modified commercial magnetic pulsed valve (SMLD 300D, Gyger AG, Switzerland)<sup>3</sup> running at 333 Hz. The valve is x/y/z aligned within a vacuum chamber that is evacuated by a Roots blower/rotary-vane pump combination to  $10^{-2}$  mbar during the experiment. The pump, dump and probe laser beams are overlapped in the core of the supersonic jet ~ 1.5 mm from the nozzle exit. Helium (purity  $\geq$  99.999%) is bubbled through cyclopentane (Sigma-Aldrich  $\geq$  99%) thermostatted to 22°C (357 mbar). The gas mixture is passed through a 2  $\mu$ m pore size filter into the nozzle to eliminate microdroplets that lead to light scattering. The total backing pressure is 650 mbar, corresponding to a 54% cyclopentane content. *Gas Cell*: Alternatively, the vacuum chamber is filled with cyclopentane at 13.6 mbar at room temperature 295.5 K. We recorded 35 cyclopentane recurrences at the same 26.69 fs step size over a total length of 2.7 ns. The lower delay time range relative to the supersonic-jet experiment is due to the collisional dephasing.<sup>3,4</sup>

- <sup>1</sup> O'Shea, P.; Kimmel, M.; Gu, X.; Trebino, R. Opt. Lett. 2001, 26, 932.
- <sup>2</sup> Akturk, S.; Kimmel, M.; O'Shea, P.; Trebino, R. Opt. Express 2003, 11, 491–501.
- <sup>3</sup> Brügger, G.; Frey, H.-M.; Steinegger, P.; Kowalewski, P.; Leutwyler, S. J. Phys. Chem. A **2011**, 115, 12380–12389.
- <sup>4</sup> Brügger, G.; Frey, H.-M.; Steinegger, P.; Balmer, F.; Leutwyler, S. J. Phys. Chem. A 2011, 115, 9567.
- <sup>5</sup> Ikeda, T.; Lord, R. C.; Malloy, T. B.; Ueda, T. J. Chem. Phys. **1972**, 56, 1434.



FIG. 1. (a)-(c) Shape of the finite central barrier potential  $V = (z_1^2 + z_2^2)^2 + B(z_1^2 + z_2^2)$  as a function of the dimensionless coordinate *B*. (b) Eigenvalues of the finit central barrier potential *V* as a function of *B*, after Ikeda et al.<sup>5</sup>

 

 TABLE I. CCSD(T)/cc-pwCVTZ calculated Cartesian coordinates of C2-symmetric Twist minimum cyclopentane (in Å).

Atom	X	у	у
С	0.0000000000	0.0000000000	1.3010037596
С	-1.2268411756	0.1474147791	0.3674450013
С	1.2268411756	-0.1474147791	0.3674450013
С	-0.7194027540	-0.2582818918	-1.0213449614
С	0.7194027540	0.2582818918	-1.0213449614
Н	1.3275010381	-0.1444380640	-1.8311902800
Н	-1.3275010381	0.1444380640	-1.8311902800
Н	0.7143438837	1.3477089292	-1.1166382155
Н	-0.7143438837	-1.3477089292	-1.1166382155
Н	-2.0779638133	-0.4469820145	0.6978091439
Н	2.0779638133	0.4469820145	0.6978091439
Н	-1.5507082412	1.1897085781	0.3403643775
Н	1.5507082412	-1.1897085781	0.3403643775
Н	-0.0990081863	-0.8696642699	1.9501153344
Н	0.0990081863	0.8696642699	1.9501153344

 TABLE II. CCSD(T)/cc-pwCVTZ calculated Cartesian coordinates of the  $C_s$ -symmetric Bent minimum of cyclopentane (in Å).

Atom	Х	У	У
С	1.2431111243	0.2755030543	0.000000000
С	0.4183921407	-0.2126977325	1.1918393343
С	0.4183921407	-0.2126977325	-1.1918393343
С	-1.0365898023	0.0746912691	-0.7763890307
С	-1.0365898023	0.0746912691	0.7763890307
Η	2.2666615878	-0.0991052679	0.000000000
Η	1.2850233491	1.3686084639	0.000000000
Η	-1.3461086339	1.0506575524	-1.1517048710
Η	-1.3461086339	1.0506575524	1.1517048710
Η	-1.7282861719	-0.6591069997	-1.1883469800
Η	-1.7282861719	-0.6591069997	1.1883469800
Η	0.6901915821	0.2651300418	2.1324189869
Η	0.6901915821	0.2651300418	-2.1324189869
Η	0.5683788088	-1.2883967108	-1.3124355737
Η	0.5683788088	-1.2883967108	1.3124355737