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

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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 μJ. 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^{-1}) bandwidth, using a single-shot second harmonic generation frequency-resolved optical gating device (Grenouille 8-20, Swamp Optics)[1,2].

The output of the fs laser system is reduced to a laser pulse energy between $75 - 120$ μJ 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)[3] 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 μm 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.[3,4]

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[1] O'Shea, P.; Kimmel, M.; Gu, X.; Trebino, R. *Opt. Lett.* **2001**, *26*, 932.

[2] Akturk, S.; Kimmel, M.; O'Shea, P.; Trebino, R. *Opt. Express* **2003**, *11*, 491–501.

[3] Brügger, G.; Frey, H.-M.; Steinegger, P.; Kowalewski, P.; Leutwyler, S. *J. Phys. Chem. A* **2011**, *115*, 12380–12389.

[4] Brügger, G.; Frey, H.-M.; Steinegger, P.; Balmer, F.; Leutwyler, S. *J. Phys. Chem. A* **2011**, *115*, 9567.

[5] Ikeda, T.; Lord, R. C.; Malloy, T. B.; Ueda, T. *J. Chem. Phys.* **1972**, *56*, 1434.

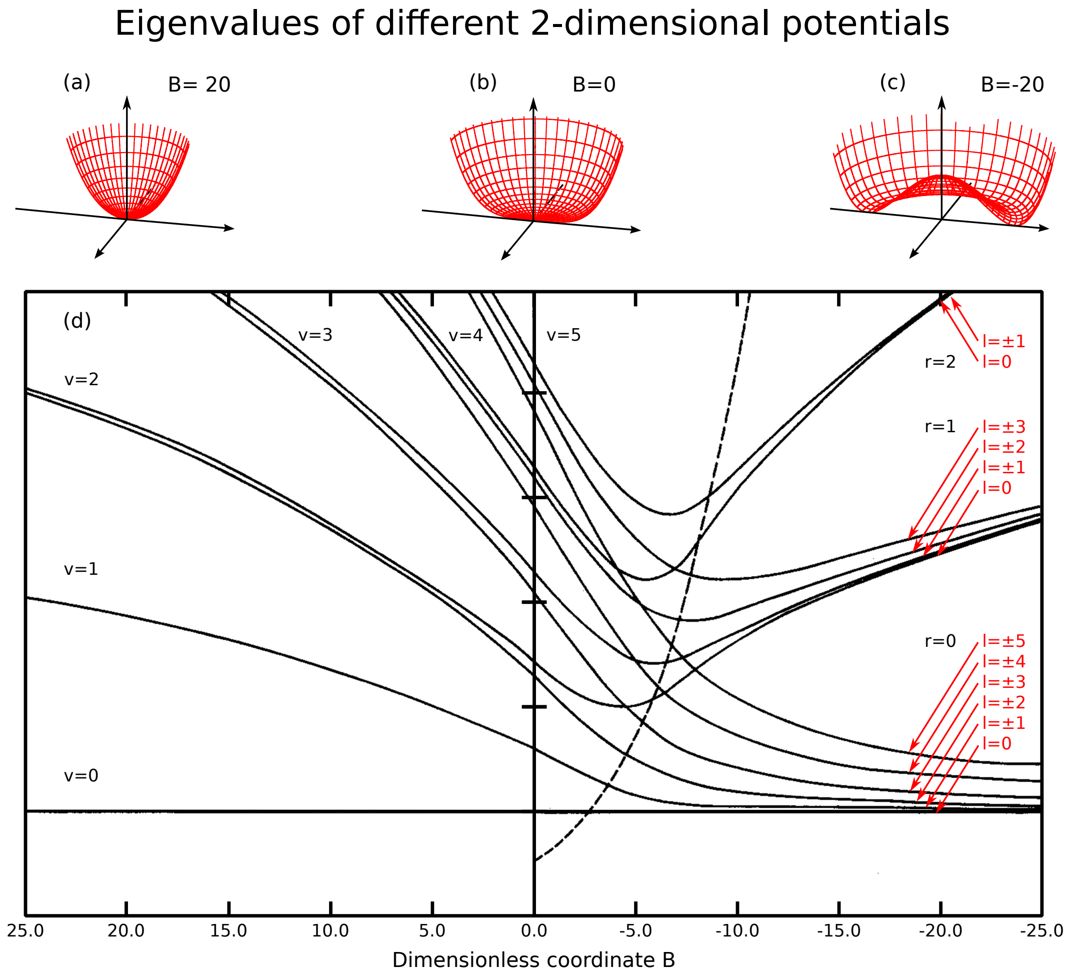

FIG. 1. (a)-(c) Shape of the finite central barrier potential $V = \left(z_1^2 + z_2^2\right)^2 + B\left(z_1^2 + z_2^2\right)$ as a function of the dimensionless coordinate B. (b) Eigenvalues of the finit central barrier potential V as a function of B, after Ikeda et al.[5]

TABLE I. CCSD(T)/cc-pwCVTZ calculated Cartesian coordinates of C_2-symmetric *Twist* minimum cyclopentane (in Å).

Atom	x	y	y
C	0.0000000000	0.0000000000	1.3010037596
C	-1.2268411756	0.1474147791	0.3674450013
C	1.2268411756	-0.1474147791	0.3674450013
C	-0.7194027540	-0.2582818918	-1.0213449614
C	0.7194027540	0.2582818918	-1.0213449614
H	1.3275010381	-0.1444380640	-1.8311902800
H	-1.3275010381	0.1444380640	-1.8311902800
H	0.7143438837	1.3477089292	-1.1166382155
H	-0.7143438837	-1.3477089292	-1.1166382155
H	-2.0779638133	-0.4469820145	0.6978091439
H	2.0779638133	0.4469820145	0.6978091439
H	-1.5507082412	1.1897085781	0.3403643775
H	1.5507082412	-1.1897085781	0.3403643775
H	-0.0990081863	-0.8696642699	1.9501153344
H	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	x	y	y
C	1.2431111243	0.2755030543	0.0000000000
C	0.4183921407	-0.2126977325	1.1918393343
C	0.4183921407	-0.2126977325	-1.1918393343
C	-1.0365898023	0.0746912691	-0.7763890307
C	-1.0365898023	0.0746912691	0.7763890307
H	2.2666615878	-0.0991052679	0.0000000000
H	1.2850233491	1.3686084639	0.0000000000
H	-1.3461086339	1.0506575524	-1.1517048710
H	-1.3461086339	1.0506575524	1.1517048710
H	-1.7282861719	-0.6591069997	-1.1883469800
H	-1.7282861719	-0.6591069997	1.1883469800
H	0.6901915821	0.2651300418	2.1324189869
H	0.6901915821	0.2651300418	-2.1324189869
H	0.5683788088	-1.2883967108	-1.3124355737
H	0.5683788088	-1.2883967108	1.3124355737