Chirped-Pulse Fourier Transform Microwave Spectroscopy Coupled with a Flash Pyrolysis Micro-Reactor: Structural Determination of the Reactive Intermediate Cyclopentadienone

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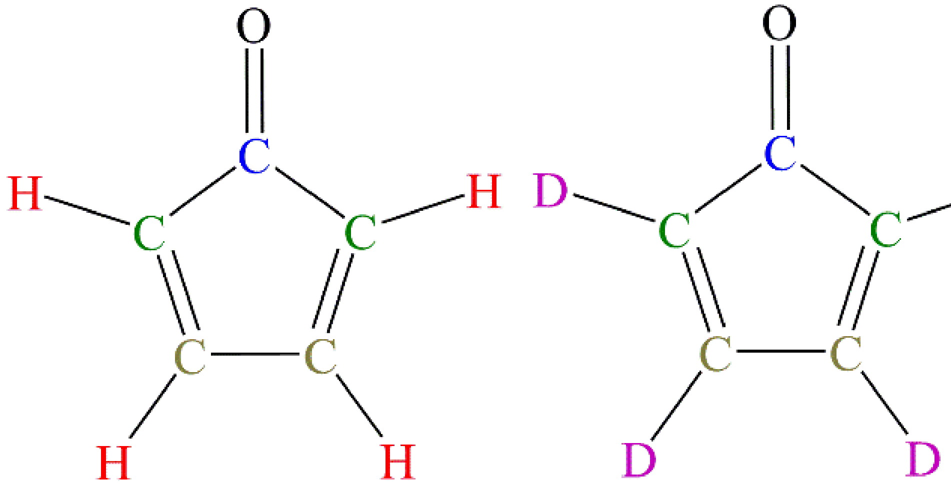

Supporting Information: Measured Frequencies of Isotopic C_5H_4=O

Observed Frequency (MHz)	Simulated Frequency (MHz)	Isotopomer	Assignment ($J'_{Ka'Kc'}$-$J''_{Ka''Kc''}$)	OMC^a (MHz)
6595.320	6595.338	C_5H_4=O	1_{01}-0_{00}	-0.018
7646.404	7646.362	C_5D_4=O	3_{12}-3_{13}	0.042
7670.970	7670.977	C_5H_4=O	3_{12}-3_{13}	-0.007
10713.557	10713.600	C_5D_4=O	2_{12}-1_{11}	-0.043
11669.482	11669.485	C_5D_4=O	2_{02}-1_{01}	-0.003
11744.842	11744.836	^{13}C C_5H_4=O	2_{12}-1_{11}	0.006
11846.294	11846.304	^{13}C C_5H_4=O	2_{12}-1_{11}	-0.010
11864.814	11864.807	^{13}C C_5H_4=O	2_{12}-1_{11}	0.007
11906.919	11906.919	C_5H_4=O	2_{12}-1_{11}	0.000
12469.273	12469.255	C_5D_4=O	4_{13}-4_{14}	0.018
12622.042	12622.046	C_5H_4=O	4_{13}-4_{14}	-0.004
12760.811	12760.809	^{13}C C_5H_4=O	2_{02}-1_{01}	0.002
12881.318	12881.322	^{13}C C_5H_4=O	2_{02}-1_{01}	-0.004
12891.865	12891.862	^{13}C C_5H_4=O	2_{02}-1_{01}	0.003
12939.311	12939.322	C_5H_4=O	2_{02}-1_{01}	-0.011
13280.488	13280.505	C_5D_4=O	2_{11}-1_{10}	-0.017
14262.85	14262.851	^{13}C C_5H_4=O	2_{11}-1_{10}	-0.001
14412.682	14412.683	^{13}C C_5H_4=O	2_{11}-1_{10}	-0.001

14453.051	14453.048	$^{13}C\ C_5H_4=O$	$2_{11}-1_{10}$	0.003
14474.413	14474.407	$C_5H_4=O$	$2_{11}-1_{10}$	0.006
15705.589	15705.589	$^{13}C\ C_5D_4=O$	$3_{13}-2_{12}$	0.001
15805.972	15805.972	$^{13}C\ C_5D_4=O$	$3_{13}-2_{12}$	0.000
15831.092	15831.092	$^{13}C\ C_5D_4=O$	$3_{13}-2_{12}$	0.000
15886.301	15886.282	$C_5D_4=O$	$3_{13}-2_{12}$	0.019
16276.44	16276.415	$C_5D_4=O$	$3_{22}-3_{03}$	0.025
16619.686	16619.686	$^{13}C\ C_5D_4=O$	$3_{03}-2_{02}$	0.000
16700.625	16700.625	$^{13}C\ C_5D_4=O$	$3_{03}-2_{02}$	0.000
16751.456	16751.456	$^{13}C\ C_5D_4=O$	$3_{03}-2_{02}$	0.000
16805.1	16805.082	$C_5D_4=O$	$3_{03}-2_{02}$	0.018
17477.584	17477.588	$^{13}C\ C_5H_4=O$	$3_{13}-2_{12}$	-0.004
17615.981	17615.973	$^{13}C\ C_5H_4=O$	$3_{13}-2_{12}$	0.008
17655.368	17655.374	$^{13}C\ C_5H_4=O$	$3_{13}-2_{12}$	-0.006
17716.108	17716.088	$C_5H_4=O$	$3_{13}-2_{12}$	0.020
17777.429	17777.429	$^{13}C\ C_5D_4=O$	$3_{22}-2_{21}$	0.000
17906.986	17907.011	$C_5D_4=O$	$5_{14}-5_{15}$	-0.025
17922.025	17922.015	$^{13}C\ C_5D_4=O$	$3_{22}-2_{21}$	0.010
17948.194	17948.194	$^{13}C\ C_5D_4=O$	$3_{22}-2_{21}$	0.000
17995.554	17995.548	$C_5D_4=O$	$3_{22}-2_{21}$	0.006
18433.758	18433.751	$C_5H_4=O$	$5_{14}-5_{15}$	0.007
18491.589	18491.614	$C_5D_4=O$	$4_{23}-4_{04}$	-0.025
18838.354	18838.364	$C_5H_4=O$	$3_{03}-2_{02}$	-0.010

[a] "OMC" = Observed Minus Calculated

Methods

The micro-reactor assembly was modeled after the Boulder design, consisting of a 2 mm inner diameter, 2.8 cm long silicon carbide (SiC) tube through which the *o*-phenylene sulfite sample flows. The sample, entrained as a dilute mixture in high pressure argon, is pulsed into the micro-reactor assembly (Figure 1a) which is heated to 1000 K to initiate decomposition. Specifically, the SiC tube may be resistively heated to well-defined temperatures when applying current to two molybdenum spring clips, which fasten two carbon ring electrodes onto the SiC tube surface. An alumina tube concentrically surrounds the SiC tube in order to prevent radiative heat loss, and the entire assembly is mounted onto a copper heat sink that interfaces with the pulsed valve (1 mm orifice diameter). A type C thermocouple lies on the SiC tube surface to provide real-time temperature monitoring.

A chirped microwave pulse (1 μs duration) from 7.5 – 18.5 GHz is then broadcast from a microwave horn to interact with the effluent from the micro-reactor, producing a net polarization in the sample that consequently undergoes free induction decay (FID). The FID emission signal from the sample is collected by the receiving microwave horn, amplified, heterodyned down to the 0.4-11.4 GHz range with a phase locked oscillator and directly digitized by a 12 GHz digital oscilloscope (40 GS/s) using the experimental scheme shown in Figure 1b. Fourier transformation of the FID emission produces the microwave spectrum over the entire 11 GHz bandwidth in a single shot.

Footnote 1

It is often equated with the zero-point vibrationally averaged structure, but this is not correct. While a few more subtle considerations further undermine an equivalence, the most important issue is that the zero-point structures of isotopic species are not the same (because of vibrational effects, which are mass-dependent) and the process of fitting the constants to a single structure leads to obvious ambiguities. Among these is that the r_0 structure depends on which isotopic species are used in the fit. Nevertheless, r_0 structures are undoubtedly useful and differ only slightly from any other notion of structure (or order 0.01 Å at most) for all but the most pathological molecules.

Footnote 2

It should be noted that inclusion of the electronic contribution to the moment of inertia (which is due to the difference between subsuming the electronic masses into the nuclear mass and properly accounting for the electronic contributions) is reasonably significant in this example. Although the effect of this correction on the structural parameters documented below is negligible, the inertial defect is significantly lowered when these terms are added into the correction for the rotational constants. This is the third such system that we are aware of; the other two molecules are also cyclic species with π systems; pyridazine[1] and SiC_3.[2]

Full Citation for Reference 44

Coupled-Cluster techniques for Computational Chemistry, A Quantum-Chemical Program Package by J.F. Stanton, J. Gauss, M.E. Harding, P.G. Szalay with contributions from A.A. Auer, R.J. Bartlett, U. Benedikt, C. Berger, D.E. Bernholdt, Y.J. Bomble, L. Cheng, O. Christiansen, M. Heckert, O. Heun, C. Huber, T.-C. Jagau, D. Jonsson, J. Jusélius, K. Klein, W.J. Lauderdale, D.A. Matthews, T. Metzroth, L.A. Mück, D.P. O'Neill, D.R. Price, E. Prochnow, C. Puzzarini, K. Ruud, F. Schiffmann, W. Schwalbach, C. Simmons, S. Stopkowicz, A. Tajti, J. Vázquez, F. Wang, J.D. Watts and the integral packages MOLECULE (J. Almlöf and P.R. Taylor), PROPS (P.R. Taylor), ABACUS (T. Helgaker, H.J. Aa. Jensen, P. Jørgensen, and J. Olsen), and ECP routines by A. V. Mitin and C. van Wüllen. For the current version, see http://www.cfour.de

References for Figure 5

The literature structures for are for the following compounds: ethane(r_e),[3] ethylene(r_e),[4] benzene(r_e),[5] cyclopentadiene(r_s),[6] cyclopentadienyl cation(r_e),[3] acetone(r_s),[7] cyclopentanone(r_s),[8] cyclopent-2-en-1-one (r_s),[9] and fulvene(r_s).[10]

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