On the Electronic Structure of the Ground State of Cyclopentoxy. The Case for a Two Coupled State Description

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Abstract

Previous descriptions of the cyclopentoxy radical have considered the ground state as an isolated electronic state; however, the doublet ground and first excited states of the cyclopentoxy radical arise from three electrons in the oxygen $2p\pi$ orbitals, yielding states that may not be adequately described by a single state model. In this work, a prelude to the determination of the photoelectron spectrum of cyclopentoxide, the electronic structure of the ground and first excited state of cyclopentoxy is studied. Both axial and equatorial structures are considered. The ground state is found to have an axial configuration. Conical intersections on the ground and excited state potential energy surfaces in both axial and equatorial nuclear configurations are found, with the minimum energy axial (equatorial) conical intersection lying within ~ 515 (260) cm^{-1} of the axial (equatorial) ground state minimum. The barriers to axial-equatorial interconversion and to ring opening are estimated. The implications for the simulation of the cyclopentoxide photoelectron spectrum are discussed.

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I. Introduction

Alkoxy radicals, R-O, are important participants in atmospheric^{1,2} and combustion processes.³ In atmospheric chemistry alkoxy radicals are intermediates in the production of tropospheric ozone. In combustion processes alkoxy radicals are produced from the reaction of alkyl radicals with O or O₂.² The prevalence of cyclic hydrocarbons in nontraditional fuel sources such as oil shales and oil sands has stimulated interest in cyclic alkoxy radicals, here denoted cyc-R-O. In combustion processes cyclic alkoxy radicals can ring open or further react to form soots. Cyc-R-O have been the subject of both experimental and computational studies.^{1,2,4-8} The stability of cyc-R-O depends on the size of the ring R and reflects the degree of ring strain.⁶ For example as first pointed out in Ref. ⁹ added ring strain in the five member ring cyclopentoxy lowers the enthalpy for ring-opening resulting in a ~100 fold increase in the rate of ring opening when compared with cyclohexoxy C₆H₁₁O.

In this work we consider the cyc-R-O, cyclopentoxy, which has been the subject of previous experimental^{1,10} and computational^{6,7,10} studies. For cyclopentoxy the cyclic structure is calculated to be thermodynamically unstable by ~1500 cm⁻¹ with respect to the ring open structure 5-oxo-pentan-1-yl.⁶ These ring and ring open structures are separated by a barrier inferred from kinetic measurements to be <3500 cm⁻¹, with respect to the cyclic isomer.¹ This ring opening barrier for cyclopentoxy is not that dissimilar from the ring opening barrier inferred from kinetic measurements for cyclohexoxy of 11.5±2.2kcal/mol.¹

All computational studies reported to date have treated the ground electronic state of cyclopentoxy as a single isolated state, which is not unreasonable given its low symmetry. However the single state representation may be lacking. The ground and first excited state arise, as is the case in methoxy, CH₃O, from three electrons in the oxygen 2p π orbitals, yielding two doublet states, degenerate by symmetry in methoxy. Cyclopentoxy can be

viewed as a substitutional isomer of methoxy with two of the methoxy hydrogens replaced by equivalent groups, the two ends of the $(\text{CH}_2)_{N-1}$ opened ring, where, we have denoted cyclopentoxo as cyclo- $(\text{CH}_2)_{N-1}\text{CHO}$ with $N = 5$. See Fig. 1.

From our previous work on substitutional isomers of methoxy¹¹⁻¹³ two possible situations may arise. Methoxy has a 2E ground state which is split by the Jahn-Teller interaction¹⁴ into $\tilde{X}^2A$ and $\tilde{A}^2A$ states. One would expect that the replacement of hydrogens, which removes the high symmetry, would produce an even greater lifting of the 2E degeneracy in the $\tilde{X}^2A$ and $\tilde{A}^2A$ states. This indeed occurs in ethoxy, which substitutes a methyl for 1 hydrogen.¹¹ and has a measured $\tilde{A}(0) - \tilde{X}(0)$ splitting of 364 (355) cm^{-1} from dispersed fluorescence¹⁵ (photoelectron)¹⁶ spectroscopy. In ethoxy the ground electronic state potential energy surface has three minima and three saddle points, as in methoxy, but the arrangement of these critical points is qualitative different from that of methoxy. See Ref. ¹¹, Fig. 2b. A different situation arises in isopropoxy where two hydrogens are replaced by methyl groups. Here the $\tilde{A}(0) - \tilde{X}(0)$ splitting is small, $\sim 62 \text{ cm}^{-1}$.^{12,17} In this case the ground potential energy surface also has three distinct minima and saddle points, but their arrangement qualitatively resembles that of methoxy, see Ref. ¹² Fig. 2b. Since in this latter case, the nominal $\tilde{A}(0) - \tilde{X}(0)$ splitting is small it is necessary to consider the possibility of the spin-orbit interaction making a non-negligible contribution to the level splitting, as it does in methoxy¹⁴ and isopropoxy. We refer to this later situation, an unexpectedly small nonrelativistic $\tilde{A}(0) - \tilde{X}(0)$ splitting and a non-negligible spin-orbit contribution, as the isopropoxy paradigm where it was first explained.¹²

A third alternative occurs in pyrrolyl, $(\text{CH})_4\text{N}$ where one $-\text{CH}$ group in cyclopentadienyl, C_5H_5 , is replaced by a nitrogen reducing C_{5v} symmetry to C_{2v} symmetry and lifting the symmetry required 2E_1 degeneracy.¹⁸ In this case however, where the π system of the ring, which is responsible to the degeneracy, is strongly perturbed, the multiple ground state minima and saddle points in C_5H_5 are reduced to a single minimum

and saddle point which together with the minimum energy conical intersection lie approximately along a single internal coordinate. See Fig. 2 in Ref. ¹⁸.

In this work the electronic structure of cyclopentoxo will be characterized in the context of the above described possibilities. These calculations represent a key first step in the determination of the electron photodetachment spectrum of cyclopentoxo's anion, cyclopentoxide, which has been previously measured¹⁰ but not well assigned. We will also consider ring opening to produce 5-oxo-pentan-1-yl. See Fig. 1. The barrier to ring-opening places a practical limit on the portion of the electron photodetachment spectrum of cyclopentoxide which can be simulated using the KDC vibronic coupling model.¹⁹

Section II reports the electronic structure description of cyclopentoxo and its ring open form. The electronic structure results obtained from these representations are reported and discussed in Sec. III. Sec. IV summarizes and discusses prospects for spectroscopic studies.

II Electronic Structure Descriptions

The regions of cyclic nuclear configurations and those corresponding to ring opening are described by distinct multireference configuration interaction (MRCI) expansions. In the cyclic region the 47 electrons are partitioned among 6 frozen core orbitals, 15 doubly occupied orbitals and a five electron three orbital (5,3) active space. The (5,3) active space is comprised of the two oxygen $2p\pi$ orbitals (contributing three electrons) and the oxygen lone pair (contributing two electrons). In this case cc-p-VTZ bases were used on oxygen and carbon and on the hydrogens cc-p-VDZ bases were used. With this active space and basis set the multireference single and double excitation CI (MRCISD) expansion, denoted CIA, is comprised of 19,302,445 configuration state functions (CSFs).

The description of the transition between the cyclic and opened ring regions requires a more flexible active space. In this case an additional orbital from the doubly occupied space and an orbital from the virtual space were included in the active space to

describe bond breaking, giving a seven electron five orbital (7,5) active space. In these calculations the larger active space necessitated use cc-p-VDZ bases. The resulting MRCISD expansion is comprised of 58,404,754 CSFs and denoted CIB .

All calculations using CIA or CIB were carried out using the COLUMBUS electronic structure codes.²⁰⁻²²

The spin-orbit coupling was computed using a MRCISD expansion with the (5,3) active space and cc-p-VDZ bases on all atoms and the restriction of only single excitations from the doubly occupied space. The resulting MRCISD expansion is comprised of 2,057,740 CSFs. These calculations were out carried out using a direct method based on the symbolic matrix method.²³

III. Results

The above described wave functions were used to look for key extrema involving the ground and first excited states. Cyclopentoxo exists in both axial and equatorial forms which complicates the description of the ground state potential energy surfaces. In view of the discussion in the Introduction, minimum energy conical intersections descendant from the 2E state of methoxy were sought in both the axial and equatorial regions, using CIA. Minima and saddle points separating those minima in this cyclic, also called the Jahn-Teller region, on the ground state potential energy surface were also sought, using CIA. A saddle point connecting the ring open and cyclic regions, was determined, using CIB. In addition the barrier separating the axial and equatorial minima in the cyclic region was estimated. Since, as noted above, cyclopentoxo can be viewed as a substitutional isomer of methoxy we anticipated finding three minima and corresponding saddle points on the ground state potential energy surface in the cyclic regions. Significantly, only a single minimum and a single saddle point were found. Both the extrema we located and those not found enable us to paint a much clearer picture of the complex electronic structure of this molecule than was previously available.

The level of agreement of CIA and CIB based energetics presented below supports the reliability of the energetics reported in this work.

A. The Cyclic or Jahn-Teller region

Figures (2a) and (2b) and Tables I and IIA describe the minima $\min_1^w$ and saddle points sp_1^w on the 1^2A potential energy surface and conical intersections $mex_{1,2}^w$ of the 1^2A - 2^2A states where $w = ax$ for axial structures and $w = eq$ for equatorial structures, determined in the cyclic or Jahn-Teller regions using CIA. Below, for simplicity of notation, we will use labels such as $\min_1^w$ to denote both the name of a structure and its geometry. Figs. (2a) and (2b) depict the key bond distances and angles of the $\min_1^w$, $w = ax, eq$, the saddle point sp_1^w $w = ax$ and the minimum energy conical intersection $mex_{1,2}^w$ $w = ax, eq$. As explained below sp_1^{eq} is very slowly convergent so only the partially converged energy is reported here. Table IIA provides a more complete characterization of these structures. The energies at these points are reported in Table I. Cartesian coordinates for all tabulated structures are found in the Supplemental Data. The energy difference between $mex_{1,2}^w$ and $\min_1^w$, the Jahn-Teller stabilization energy, is only 515 (260) cm^{-1} for $w = ax$ (eq) clearly demonstrating the importance of a two state description.

At each of $\min_1^w$ $w = ax, eq$ and sp_1^w $w = ax, eq$ there is a single low frequency mode $\nu = 60.7, 34.7, 30.2$ and ~ 23 cm^{-1} , respectively involving principally the ring deformation dihedral angle C2C6C5C4. Such low frequency modes have been reported previously in other work on this molecule.⁷ The particularly small (but positive) frequency for sp_1^{eq} makes precise determination of this point tedious. The remaining frequencies are between 220 and 3200 cm^{-1} . The zero point energies are given in Table IIA.

The spin orbit coupling matrix element,²⁴ computed at the CIA determined $mex_{1,2}^w$ is found to be 60.7 (60.4) cm^{-1} for $w = ax$ (eq). This value for the the spin-orbit coupling is similar to its value of 67 cm^{-1} in methoxy.²⁵

The **g** and **h** vectors at $mex_{1,2}^w$ 1^2A $w = ax$ and eq are reported in mass weighted coordinates in Figs. (3a,3b) and (4a,4b), respectively. For comparison Figs. (5a) and (5b)

report the **g** and **h** vectors at the minimum energy conical intersection for isopropoxy.¹² Although the similarities are evident in these figures it is important to note the increased participation of the ring carbons for cyclopentoxy when compared with isopropoxy.

In view of the discussion in the Introduction what is unexpected in the above findings is the fact that no other extrema were found in this region, that is the topography in the Jahn-Teller region is pyrrole-like rather than ethoxy or isopropoxy-like. This may possibly be attributed to the contributions to the **g** and **h** vectors from the ring degrees of freedom, the substituents replacing the methoxy hydrogens in the cyclopentoxy. Significant substituent contributions to **g** and **h** were not found in isopropoxy or ethoxy.

B. Axial-Equatorial Interconversion

When simulating cyclopentoxy spectra it is essential to know under what circumstances, if any, the axial and equatorial structures can be treated as distinct species. To that end the saddle point sp_1^{ax-eq} for the interconversion of $\min_1^{ax}$ and $\min_1^{eq}$ is required. This interconversion was studied using CIB. The CIB determined $\min_1^{ax}$ and $\min_1^{eq}$ structures are reported in Table IIB. Note from Table I that the energies of CIA and CIB are in satisfactory accord supporting the reliability of the reported energetics. However from Tables IIA and IIB it is seen that smaller basis used in CIB yields carbon – carbon and carbon –hydrogen bond lengths that differ somewhat from those obtained from CIA.

While the precise structure of sp_1^{ax-eq} remains to be determined, the linear synchronous transit paths obtained with CIB, connecting $\min_1^{ax}$ and to $\min_1^{eq}$, provides an upper bound of $\sim 800\text{ cm}^{-1}$ for the barrier height. However preliminary calculations suggest the barrier may be as low as 500 cm^{-1} . Since neither of these barriers include the zero point energy (ZPE) contribution these initial results suggest that equatorial and axial structures will be coupled except for the lowest vibronic levels.

C. Ring opening

The ring opening saddle points, sp_1^{ro} determines when the ring opened structures must be considered in the simulation of a spectrum of $\text{C}_5\text{H}_9\text{O}$. The computational

complexities introduced by this channel are considerable, when compared with sp_1^{ax-eq} discussed above. The ring opened structures require a different set of internal coordinates for their compact description. While this situation can be readily handled by modern surfaced fitting techniques,²⁶ the solution of the vibrational Schrödinger equation becomes quite complicated. In addition the possibility of the ring open structure dissociating becomes an issue.¹⁰

The determined structure of sp_1^{ro} and the ZPE obtained from CIB are reported in Table IIB. Fig. (6) reports the energy along a linear synchronous transit path connecting sp_1^{ro} to $\min_1^{ax}$ and sp_1^{ro} to a ring open structure confirming the role of sp_1^{ro} . The computed barrier height of 4265 (<3500) cm^{-1} including the zero point energy is somewhat larger than but still in reasonable accord with the experimental determination given parenthetically. In future studies the basis set dependence of this result will be assessed.

IV. Summary and Conclusions

The electronic structure of the two lowest states of cyclopentoxo, the 1^2A and 2^2A states, are determined using MRCISD wave functions. It is found that these states are coupled by a conical intersection seam beginning only 550 cm^{-1} , above the ground state minimum, a feature which has not been addressed in previous studies of this system. Conical intersections are found with the oxygen located both axial and equatorial with respect to the ring. The conical intersection seam is attributed to the fact that cyclopentoxo can be viewed as a substitutional isomer of the methoxy radical which has symmetry required and Jahn-Teller distorted 2E ground state. The spin-orbit coupling computed for points on this seam is found to be 60 cm^{-1} in good accord with the 67 cm^{-1} reported for methoxy. However unlike, ethoxy and isopropoxy, substitutional isomers of methoxy previously investigated which have three minima and three saddle points approximately in the $g-h$ plane, cyclopentoxo has only one such pair.

The barriers to axial-equatorial interconversion and to ring opening were estimated. The implications for the simulation of the cyclopentoxide photoelectron spectrum were discussed.

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Table I Energies (in cm^{-1}) from indicated CI expansions

		Axial ^a		Equatorial ^b		
	$\min_1^x$	sp_1^x	$mex_{1,2}^x$	$\min_1^x$	sp_1^x	$mex_{1,2}^x$
CIA						
E ₁	0	485.5	515.21	401.2	588	660.9
E ₂	1508.3	760.3	515.21	1442.9		660.9
CIB						
E ₁	0		600.07	454.9		
E ₂	1650.5		600.07			

^a $||H^{so}|| = 60.7 \text{ cm}^{-1}$ at axial $mex1^2A-2^2A$

^b $||H^{so}|| = 60.4 \text{ cm}^{-1}$ at equatorial $mex1^2A-2^2A$

Table IIA. Energies (in cm⁻¹) and Structures of extrema in the Cyclic region from CIA

	Axial 12MEX	Axial JT Min	Axial JT Sad	Eqtrl 12MEX	Eqtrl JT Min
E1	515.2	0	485.5	660.9	401.2
ZPE		30235.1	29738.9		30189.5
<i>Bond Distances</i>					
R(C2-C3)	1.52966	1.52315	1.53556	1.53093	1.54061
R(C3-C4)	1.51991	1.51869	1.52022	1.53922	1.53967
R(C4-C5)	1.52340	1.52224	1.52219	1.53470	1.53121
R(C5-C6)	1.53466	1.53342	1.53139	1.51871	1.51879
R(C6-C2)	1.53904	1.54815	1.53817	1.52276	1.51856
R(C2-O1)	1.38274	1.37946	1.38027	1.37571	1.37160
R(C2-H7)	1.09137	1.08983	1.09183	1.09417	1.09360
<i>COH Angles</i>					
A(O1,C2,H7)	105.596	110.011	104.875	107.394	109.656
A(O1,C2,C6)	112.195	105.428	113.568	113.393	115.831
A(O1,C2,C3)	109.816	111.058	109.564	113.153	108.143
<i>Ring Angles</i>					
A(C2,C3,C4)	103.243	103.593	103.664	105.395	105.164
A(C3,C4,C5)	102.549	102.504	102.487	105.811	105.879
A(C4,C5,C6)	104.618	104.720	104.125	104.255	103.626
A(C5,C6,C2)	106.092	105.901	106.138	102.053	102.078
A(C6,C2,C3)	105.152	104.986	105.389	103.930	103.885
A(O1,C2,C5)	120.011	113.716	124.734	150.059	150.682
<i>Ring Dihedral Angles</i>					
D(C2,C3,C4,C5)	-42.957	-42.985	-41.768	2.357	-0.837
D(C3,C4,C5,C6)	37.645	37.645	39.943	23.613	26.665
D(C4,C5,C6,C2)	-17.971	-18.117	-22.809	-40.462	-42.422
D(C5,C6,C2,C3)	-8.454	-8.253	-2.901	42.015	41.949
D(C6,C2,C3,C4)	31.730	31.587	27.547	-27.380	-25.323

Table II.B Energies (in cm⁻¹) and Structures from CIB

	SadPoint (RingOpen)	Axial 12MEX	Axial JT Min	Equtrl Min
E1	5055.6	600.1	0.0	454.4
ZPE	29422.8		30212.4	
<i>Bond Distances</i>				
R(C(2)-C(3))	1.5250	1.5380	1.5319	1.5303
R(C(3)-C(4))	1.5248	1.5298	1.5280	1.5275
R(C(4)-C(5))	1.5315	1.5338	1.5324	1.5345
R(C(5)-C(6))	1.5119	1.5445	1.5430	1.5443
R(C(6)-C(2))	2.0711	1.5641	1.5758	1.5785
R(C(2)-O(1))	1.2545	1.3872	1.3820	1.3740
R(C(2)-H(7))	1.1024	1.0997	1.0986	1.1013
<i>COH Angles</i>				
A(O(1),C(2),H(7))	118.40	105.95	110.67	110.16
A(O(1),C(2),C(6))	101.15	112.59	105.15	107.65
A(O(1),C(2),C(3))	119.79	109.59	110.96	115.58
<i>Ring Angles</i>				
A(C(2),C(3),C(4))	107.95	102.97	103.34	102.97
A(C(3),C(4),C(5))	105.55	102.77	102.69	102.88
A(C(4),C(5),C(6))	107.93	104.88	105.00	105.42
A(C(5),C(6),C(2))	98.97	105.83	105.64	105.33
A(C(6),C(2),C(3))	94.47	104.73	104.40	104.31
<i>Ring Dihedral Angles</i>				
D(C(2),C(3),C(4),C(5))	-54.02	-43.81	-44.07	-44.28
D(C(3),C(4),C(5),C(6))	46.55	36.83	36.87	35.03
D(C(4),C(5),C(6),C(2))	-21.62	-15.77	-15.80	-12.56
D(C(5),C(6),C(2),C(3))	-7.44	-11.07	-11.09	-14.48
D(C(6),C(2),C(3),C(4))	34.10	33.74	33.87	36.13

Figure Captions

1. Cyclopentoxy and its ring open form with the atom numbering used in this work.
2. Key geometric parameters for $mex_{1,2}^x$ top, min_1^x middle sp_1^x bottom, for $x = ax$, plate a and $x = eq$, plate b .
3. $mex_{1,2}^{ax}$ for cyclopentoxy with **g** plate a and **h** plate b in mass weighted coordinates.
4. $mex_{1,2}^{eq}$ for cyclopentoxy with **g** plate a and **h** plate b in mass weighted coordinates
5. Minimum energy conical intersection for isopropoxy with **g** plate a and **h** plate b vectors in mass weighted coordinates. From Ref. ¹².
6. Linear synchronous transit path connecting sp_1^{ro} to min_1^{ax} and sp_1^{ro} to a local minimum ring opened structure. Blue line is E_1 . Yellow line is E_2

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Figure 1: Cyclopentoxo and its ring open form with the atom numbering used in this work.

2. Key geometric parameters for $mex_{1,2}^x$ top, min_1^x middle, sp_1^x bottom and for $x = ax$, plate a and $x = eq$, plate b .

3. $mex_{1,2}^{ax}$ for cyclopentoxy with **g** plate a and **h** plate b in mass weighted coordinates.

a

b

4. $mex_{1,2}^{eq}$ for cyclopentoxy with **g** plate a and **h** plate b in mass weighted coordinates

a

b

5. Minimum energy conical intersection for isopropoxy with **g** plate a and **h** plate b vectors in mass weighted coordinates. From Ref. ¹².

a

b

6 Linear synchronous transit path connecting sp_1^{ro} to $\min_1^{ax}$ and sp_1^{ro} to a local minimum ring opened structure. Blue line is E_1 . Yellow line is E_2

Graphical Abstract