Ground State and Excited State Potential Energy Surfaces of Peroxyacetyl Radical

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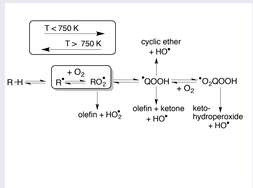
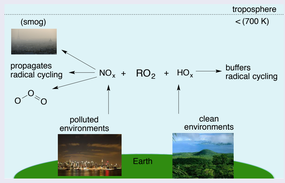
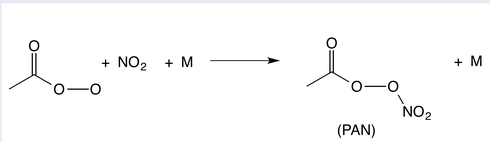
Abstract

Peroxyacetyl radical (PA) is one of the most abundant peroxy radicals in the troposphere. As a precursor of the pollutant peroxyacetyl nitrate (PAN), it contributes to tropospheric ozone and photochemical smog production. Monitoring fleeting species like PA in the laboratory is still a challenge for experimentalists. Consequently, computational work plays an important role in the study of these compounds, providing a means to interpret spectra and model reactivity. Employing coupled cluster theory with single, double, and perturbative triple excitations [CCSD(T)] with an ANO0 atomic natural orbital basis set, we determined the optimized structures of PA's *cis* and *trans* conformers on the ground and excited state surface. Our results resolve a discrepancy in the literature by showing that, upon excitation, the *trans* conformer prefers an asymmetric (C_1) conformation over its original C_s-symmetric structure. All equilibrium and saddle-point structures are identified as such by harmonic vibrational analysis. We found that the *cis* conformer is lower in energy in the ground state by 0.75 kcal $^{-1}$ that the *trans* one, while in the excited state, the *trans* structure is lower in energy by 1.66 kcal $^{-1}$ that *cis*. We determined the barrier to the rotation from *trans* to *cis* to be 5.85 kcal $^{-1}$ in the ground state.

Background Information







The O-N bond in PAN is ~ 7 kcal mol^{-1} stronger than in other peroxy nitrates which yields longer lifetime and allows for the redistribution of ozone in the troposphere.

Preliminary Anharmonic Frequencies

i	Symm.	ω_i	Corr	ν_i Final	Ar Matrix	Gas
1	a'	3185	−152	3033		
2	a'	3075	−122	2953		
3	a'	1884	−31	1853	1842(100)	1851 ± 1(100)
4	a'	1464	−43	1421	1420(4.3)	
5	a'	1401	−35	1367	1367(20)	1372 ± 2(25)
6	a'	1194	−29	1166	1153(47)	1169 ± 6(31)
7	a'	1134	−23	1111	1099(18)	1102 ± 3(29)
8	a'	1000	−29	971	972(16)	
9	a'	765	−18	747	736(22)	
10	a'	564	−12	552	545(4.6)	
11	a'	504	−5	499	500(7.4)	
12	a'	336	−4	332	347	
13	a''	3153	−153	3001		
14	a''	1473	−46	1427	1425(4.1)	
15	a''	1051	−22	1029	1029(10)	
16	a''	540	−6	534		
17	a''	187	−23	165		
18	a''	133	−6	127		

Note: A Fermi resonance exists: $2 * \omega_{17} \approx \omega_{12}$.
Harmonic frequencies computed with CCSD(T)/ANO1.
Anharmonic corrections computed with CCSD(T)/ANO0.

Ground State Harmonic Frequencies

Mode	Symmetry	*cis*-PA	*trans*-PA	Description
ω_1	a'	3201 (1.6)	3200 (1.7)	
ω_2	a'	3084 (0.6)	3073 (0.2)	
ω_3	a'	1887 (202.7)	1904 (183.1)	C=O stretch
ω_4	a'	1469 (11.3)	1475 (11.3)	
ω_5	a'	1403 (23.6)	1402 (26.1)	
ω_6	a'	1191 (152.1)	1175 (159.1)	C−O/C−O antisym.
ω_7	a'	1071 (31.9)	1051 (73.2)	O−O stretch
ω_8	a'	1053 (7.9)	1053 (7.3)	
ω_9	a'	996 (43.4)	994 (8.6)	
ω_{10}	a'	759 (44.0)	778 (71.7)	C−O/O−O sym.
ω_{11}	a'	502 (13.6)	416 (1.4)	
ω_{12}	a'	336 (8.3)	308 (1.6)	
ω_{13}	a''	3173 (0.5)	3158 (1.0)	
ω_{14}	a''	1479 (7.5)	1480 (7.6)	
ω_{15}	a''	558 (4.2)	649 (26.3)	
ω_{16}	a''	545 (7.6)	551 (6.4)	
ω_{17}	a''	191 (0.1)	135 (0.5)	
ω_{18}	a''	128 (1.0)	78 (0.1)	

Harmonic Vibrational Frequencies (ω_e cm^{-1}) and Infrared Intensities (km mol^{-1}, listed in parentheses) of $\tilde{X}^2A''$ PA. Computed at the CCSD(T)/ANO0 Level of Theory

Excited State Harmonic Frequencies

Mode	Sym.	*cis*-PA	Sym.	*trans*-PA	Description
ω_1	a'	3198(1.4)	a	3195(1.7)	
ω_2	a'	3066(0.04)	a	3076(0.8)	
ω_3	a'	1880(278.6)	a	1856(220)	C=O stretch
ω_4	a'	1473(8.7)	a	1479(8.8)	
ω_5	a'	1401(24.2)	a	1403(23.6)	
ω_6	a'	1197(215.2)	a	1204(240)	C−C/C−O-
ω_7	a'	1008(42.3)	a	1006(34.4)	antisym
ω_8	a'	904(69.1)	a	917(47.1)	O−O stretch
ω_9	a'	776(38.9)	a	820(28.7)	C−C/C−O sym.
ω_{10}	a'	541(6.3)	a	634(14)	
ω_{11}	a'	469(6.4)	a	407(1.5)	
ω_{12}	a'	288(4.7)	a	240(0.4)	
ω_{13}	a''	3152(0.4)	a	3166(1.9)	
ω_{14}	a''	1485(9.3)	a	1485(7.4)	
ω_{15}	a''	1065(5.9)	a	1066(7.7)	
ω_{16}	a''	562(5.5)	a	599(6.6)	
ω_{17}	a''	169(0.1)	a	195(1.1)	
ω_{18}	a''	156(0.5)	a	51(0.1)	

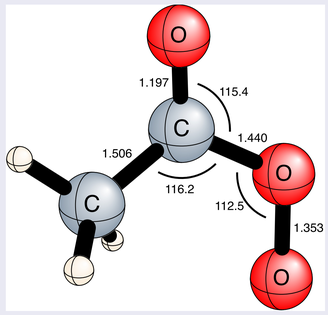
Harmonic Vibrational Frequencies (ω_e cm^{-1}) and Infrared Intensities (km mol^{-1}, listed in parentheses) of $\tilde{A}^2A'$ *cis*- and $\tilde{A}^2A$ *trans*- PA. Computed at the CCSD(T)/ANO0 Level of Theory

Methods

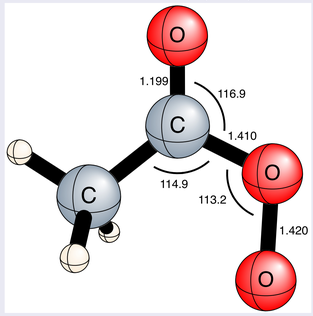
We computed optimized geometries with CFOUR software using coupled cluster theory with single, double, and perturbative triple excitations CCSD(T) with an ANO0 atomic natural orbital basis set. UHF reference was employed for the computations because analytic gradients cannot be easily computed using ROHF reference. In addition, $\langle S^2 \rangle$ was determined to be less than 0.77 $\hbar^2$. We then performed a harmonic frequency analysis which confirmed the optimized structures to correspond to the correct equilibrium geometries on the potential energy surface. We confirmed the transition state to be a a saddle point on the potential energy surface. The transition state was then connected to the *cis* and *trans* equilibrium structures by stepping along the intrinsic reaction coordinate in GAMESS software.

Optimized Geometries

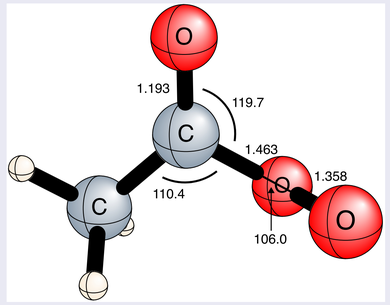
cis $\tilde{X}^2A''$ (C_s)



cis $\tilde{A}^2A'$ (C_s)

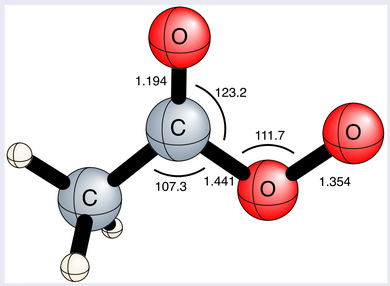


Transition State C_1 symmetry

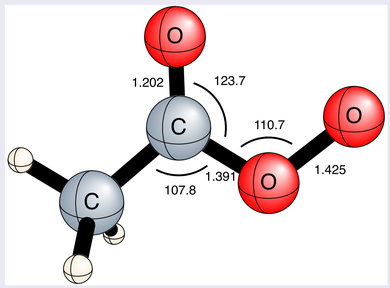


O=C−O−O dihedral angle: -94 degrees

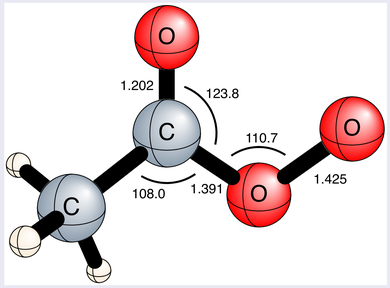
trans $\tilde{X}^2A''$ (C_s)



trans $\tilde{A}^2A'$ (C_s)

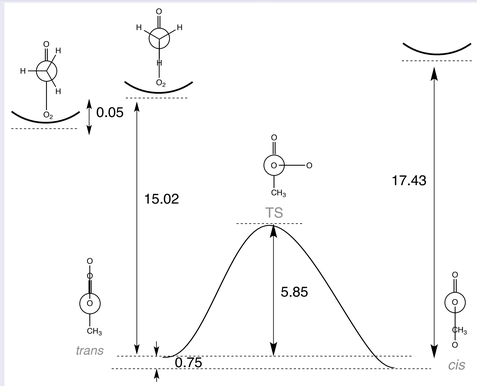


trans $\tilde{A}^2A$ (C_1)



This structure is a saddle point!

Final Potential Energy Surface



Relative energies were determined by focal point analysis, shown here in kcal mol^{-1}.

Focal Point Analysis

Relative Energy *trans* − *cis*

Basis Set	SCF	+δMP2	+δCCSD	+δCCSD(T)	NET
cc-pVDZ	−1.87	+1.72	+0.16	+0.21	[+0.32]
cc-pVTZ	−1.34	+1.74	+0.07	+0.29	[+0.85]
cc-pVQZ	−1.22	+1.77	+0.04	+0.30	[+0.99]
CBS LIMIT	[−1.20]	[+1.75]	[+0.04]	[+0.30]	[+0.98]

Relative Energy *trans* − TS

Basis Set	HF	+δMP2	+δCCSD	+δCCSD(T)	NET
cc-pVDZ	+8.39	−1.48	−1.00	−0.07	[+5.84]
cc-pVTZ	+8.07	−1.55	−0.87	−0.19	[+5.46]
cc-pVQZ	+7.99	−1.53	−0.82	−0.22	[+5.42]
CBS LIMIT	[+7.96]	[−1.51]	[−0.79]	[−0.24]	[+5.42]

Conclusions

C_s symmetry equilibrium structures for $\tilde{X}^2A''$ *cis* and *trans*, and $\tilde{A}^2A'$ *cis*. Equilibrium structure for $\tilde{A}^2A$ *trans* has C_1 symmetry. Methyl rotation of 27 degrees from the C_s symmetry structure. $\tilde{X}^2A''$ *cis* is lower in energy by 0.75 kcal mol^{-1}. Barrier to rotation of the peroxy moiety is 5.85 kcal mol^{-1} from the *trans* conformer. $\tilde{A}^2A'$ *trans* is lower in energy by 1.66 kcal mol^{-1}. Fundamental vibrational frequencies with anharmonic corrections will compare well to experimental values.

References

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Orlando, J. *et al. Chem. Soc. Rev.* **2012**, 41, 6294-6317
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