Theoretical Studies of Elementary Hydrocarbon Species and Their Reactions

Final Report

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A. Publications Supported by DOE: 2010-Present

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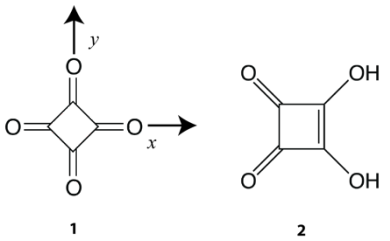
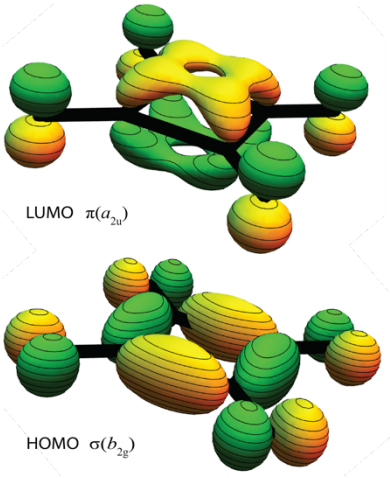
B. Recent Research Highlights

i) Cyclobutanetetraone: An Unusual Cluster of Low-Lying Electronic States

Cyclobutane-1,2,3,4-tetraone (**1**) is a beautifully symmetric, cyclic species that may be regarded as a tetramer of carbon monoxide. Experimental efforts to synthesize and isolate **1** have not been successful heretofore; nonetheless, the molecule was recently probed by low-temperature photoelectron spectroscopy of the $C_4O_4^-$ anion generated in the gas phase by electrospray ionization of **2**. Remarkably, the photoelectron spectrum of $C_4O_4^-$ provided assignments for either two or three low-lying electronic states of the seemingly simple neutral molecule **1**. The theoretical characterization of **1** has proved difficult due to surprising complexities in its electronic structure. Identifying the electronic ground state and quantifying the singlet-triplet gaps of **1** has turned out to be a treacherous task for theory. Not only have different methods predicted different ground states, but computed energetic spacings have also varied by almost 100 kcal mol^{-1}!



1 **2**



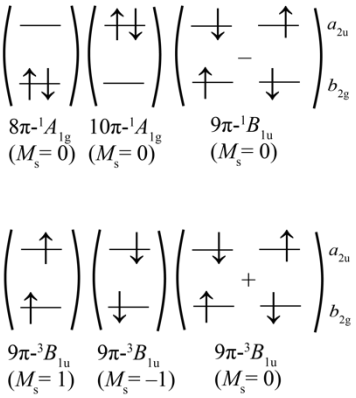


Figure 1. The HOMO and LUMO of **1** and the resulting low-lying electronic states. The 8π and 10π configurations are both of A_{1g} electronic symmetry and can mix to form multiconfigurational states. The M_s=0 components belonging to the triplet ($^3B_{1u}$) and open-shell singlet ($^1B_{1u}$) states contain plus and minus combinations, respectively, of two 9π determinants.

The troublesome electronic structure of cyclobutanetetraone (Figure 1) demands theoretical work using groundbreaking multireference or state-of-the-art high-order single-reference coupled cluster methods. Research in our laboratory over the past several years has developed Mk-MRCC theory into a powerful and practical computational method. This approach is a rigorously size-extensive, state-specific theory that retains the size-consistent property of coupled cluster theory when localized orbitals are used; in addition, Mk-MRCC treats all determinants on an equal footing via the Jeziorski-Monkhurst *ansatz*.

We have optimized the geometric structures of the low-lying states of **1** and computed corresponding vibrational frequencies by means of Mk-MRCCSD/cc-pVQZ, Mk-MRCCSD(T)/cc-pVDZ, and CCSD(T)/cc-pVQZ theory. Systematic focal-point analyses (FPA) were then executed to ascertain final adiabatic electronic excitation energies of **1**, as shown in Table 1. A consistent picture emerges in both the single- and multireference results once the correlation series are pushed to the (T) level. In particular, the ground

state of **1** is actually a triplet (9π-$^3B_{1u}$), while the expected closed-shell singlet candidate (8π-$^1A_{1g}$) lies over 3 kcal mol^{-1} higher. The FPA computations reveal that the quadruples effect (Q) brings the 9π-$^1B_{1u}$ and 10π-$^1A_{1g}$ states within 2 kcal mol^{-1} of 8π-$^1A_{1g}$. The summary conclusion is that **1** has a fascinating cluster of four electronic states lying within a 6 kcal mol^{-1} range.

Table 1. Adiabatic excitation energies (ΔE_0, kcal mol^{-1}) of cyclobutanetetraone[a]

Method	8π-$^1A_{1g}$	9π-$^3B_{1u}$	9π-$^1B_{1u}$	10π-$^1A_{1g}$
Mk-MRCCSD/cc-pVDZ	0	3.74[b]	10.81	21.98
Mk-MRCCSD/cc-pVTZ	0	4.10[b]	10.40	22.98
Mk-MRCCSD/cc-pVQZ	0	4.15[b]	10.17	22.95
Mk-MRCCSD(T)/cc-pVDZ	0	−3.30[b]	3.11	3.03
CCSD/cc-pVDZ	0	3.41	[c]	21.06
CCSD/cc-pVQZ	0	3.82	[c]	22.08
CCSD(T)/cc-pVDZ	0	−3.61	[c]	2.26
CCSD(T)/cc-pVQZ	0	−3.50	[c]	2.69
FPA/CCSDT(Q)[d]	0	−4.34	1.61	1.00

[a] Including ZPVE corrections: CCSD(T)/cc-pVQZ values of (−0.62, −1.08) for (9π-$^3B_{1u}$, 10π-$^1A_{1g}$) in single-reference cases; Mk-MRCCSD/cc-pVQZ values of (−0.54, −0.64, −1.18) for (9π-$^3B_{1u}$, 9π-$^1B_{1u}$, 10π-$^1A_{1g}$) in multireference cases. [b] Results for $M_s = 0$ component of the triplet state; the corresponding $M_s = 1$ values are 3.75, 4.09, 4.15, and −3.33 kcal mol^{-1}, from top to bottom. [c] Not accessible by single-reference coupled-cluster method. [d] Focal-point analysis targeting the complete basis set (CBS) limit of CCSDT(Q) with auxiliary core correlation, relativistic, and DBOC corrections.

ii) Peroxyacetyl Radical: Electronic Excitation Energies, Fundamental Vibrational Frequencies, and Symmetry Breaking in the First Excited State

Fundamental understanding of peroxy radicals (RO_2), key components in the oxidation of organic compounds at low temperatures, is limited by the transient nature of these compounds. Experimental monitoring of peroxy radicals often relies on either the strong, but broad and uninformative, $\tilde{B} \leftarrow \tilde{X}$ transition, or the sharp and weak $\tilde{A} \leftarrow \tilde{X}$ transition. Miller has advanced the use of the latter excitation though cavity ringdown techniques [*Phys. Chem. Chem. Phys.* **2008**, 10, 3955].

The peroxyacetyl radical [$CH_3C(O)O_2$] is a model compound that is among the most abundant peroxy radicals in the atmosphere. To support spectroscopic studies on this species, we have undertaken a high-level *ab initio* study of the ground ($\tilde{X}$) and first ($\tilde{A}$) excited state surfaces of $CH_3C(O)O_2$. The energetics (Figure 2) have been determined using coupled-cluster theory through full triple excitations (CCSDT), extrapolated to the complete basis set (CBS) limit via the focal-point scheme and corrected for vibrational, diagonal Born-Oppenheimer, and relativistic effects. On the ground-state surface, internal rotation of the peroxy terminus yields *cis* and *trans* conformers lying 0.87 kcal mol^{-1} apart (*cis* < *trans*) with an intervening barrier of 5.14 kcal mol^{-1} (relative to *trans*). Adiabatic $\tilde{A} \leftarrow \tilde{X}$ electronic excitation energies of 13.96 and 16.04 kcal mol^{-1} are predicted for the *trans* and *cis* conformers, respectively. The observed *cis* $\tilde{A} \leftarrow \tilde{X}$ excitation energy is within 0.08 kcal mol^{-1} of our computed value. Interestingly, excitation of the *trans*

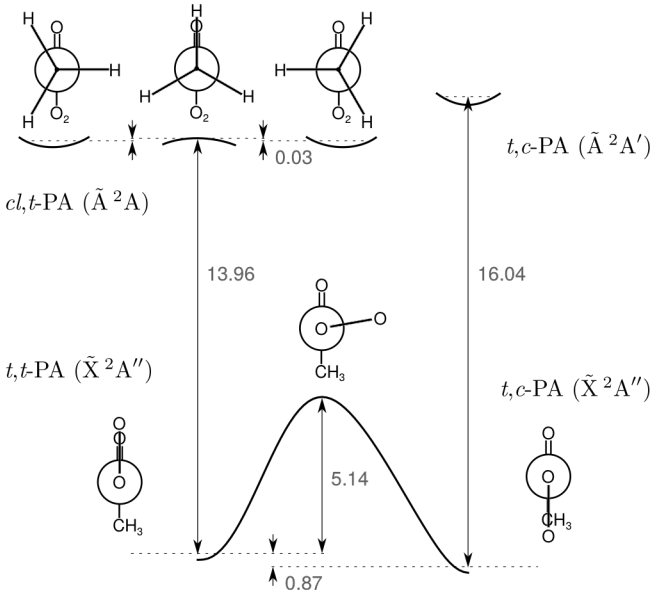


Figure 2. Key energetic relationships (in kcal mol^{-1}) between conformers on the ground and first excited state surfaces of peroxyacetyl radical.

conformer induces a symmetry-lowering conformational change caused by second-order Jahn-Teller interactions with higher-lying excited states, which we verify using multireference configuration interaction (MRCI) and equation-of-motion coupled-cluster (EOM-CC) computations. This finding resolves the curious absence of an observable $\tilde{A} \leftarrow \tilde{X}$ transition from the *trans* conformer in experimental studies, despite the fact that both conformers have been observed in ground-state vibrational spectra. Also determined in our study are anharmonic vibrational frequencies for the two ground-state minima, computed using CCSD(T) theory with second-order vibrational perturbation theory (VPT2). The available gas-phase and matrix-isolation IR data are in excellent agreement with our predictions.

iii) Reaction profiles for radical-radical abstraction via multireference coupled cluster theory

Radical-radical hydrogen abstractions in combustion chemistry are disproportionation reactions that are generally exothermic with little or no barrier, yet are underappreciated and poorly studied. Prototypically these reactions begin with two open-shell reactants and end with two closed-shell products, and thus the electronic transformation is intrinsically multireference in nature. Such challenging electronic structure problems have been tackled using our recently developed state-specific multireference coupled cluster methods Mk-MRCCSD and Mk-MRCCSD(T), as well as the companion perturbation theory Mk-MRPT2 and the popular MRCISD, MRCISD+Q, and CASPT2 approaches.[13] Reaction paths were investigated for five prototypes involving radical-radical hydrogen abstraction: H + BeH → H_2 + Be, H + NH_2 → H_2 + NH, CH_3 + C_2H_5 → CH_4 + C_2H_4, H + C_2H_5 → H_2 + C_2H_4, and H + HCO → H_2 + CO. Selected results are plotted in Figures 3 and 4. Full configuration interaction (FCI) benchmark computations for the H + BeH, H + NH_2, and H + HCO reactions prove that the Mk-MRCCSD(T) potential energy curves display superior accuracy, with mean absolute errors of only 0.2 kcal mol^{-1}. To facilitate studies of combustion kinetics in collaboration with Stephen Klippenstein and Larry Harding at Argonne, energetics for the CH_3 + C_2H_5, H + C_2H_5, and H + HCO reactions were computed at each level of theory with correlation-consistent basis sets (cc-pV*X*Z, *X* = T, Q, 5) and extrapolated to the complete basis set (CBS) limit. The rigorous Mk-MRCCSD(T)/CBS results demonstrate unequivocally that these three reactions proceed with no barrier in the entrance channel, contrary to some earlier predictions. Mk-MRCCSD(T) also reveals that the economical CASPT2 method performs well for large interfragment separations but may deteriorate substantially at shorter distances.

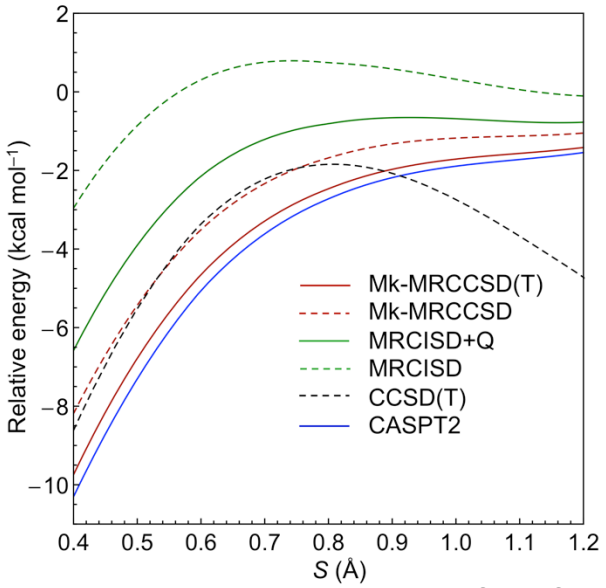


Figure 3. Potential energy curves for the CH_3 + C_2H_5 entrance channel computed at numerous levels and extrapolated to the CBS limit. The reaction coordinate *S* is the difference between C–H distances of the forming and breaking bonds.

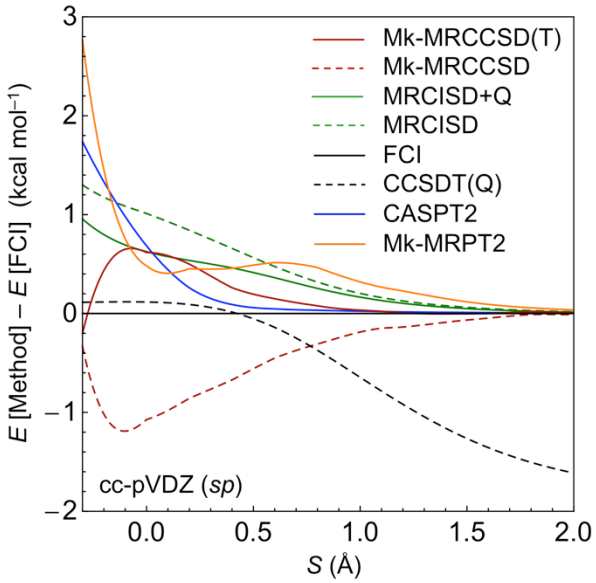


Figure 4. For the entrance channel of H + HCO, energy deviations are plotted with respect to FCI for different levels of theory with the cc-pVDZ(*sp*) basis set.

iv) The Intricate Internal Rotation Surface and Fundamental Vibrations of the n-Propyl Radical

Although the *n*-propyl radical is an archetypical intermediate in combustion chemistry, only four of its vibrational modes have been observed via infrared spectroscopy. Three of these modes are C–H stretches, while the fourth near 530 cm^{-1} has been assigned to pyramidal bending of the easily distorted radical center. Both ESR spectroscopy and electronic structure theory have been used to study large-amplitude internal rotation in the *n*-propyl radical, but there is disagreement over the key features of the underlying potential energy surface.

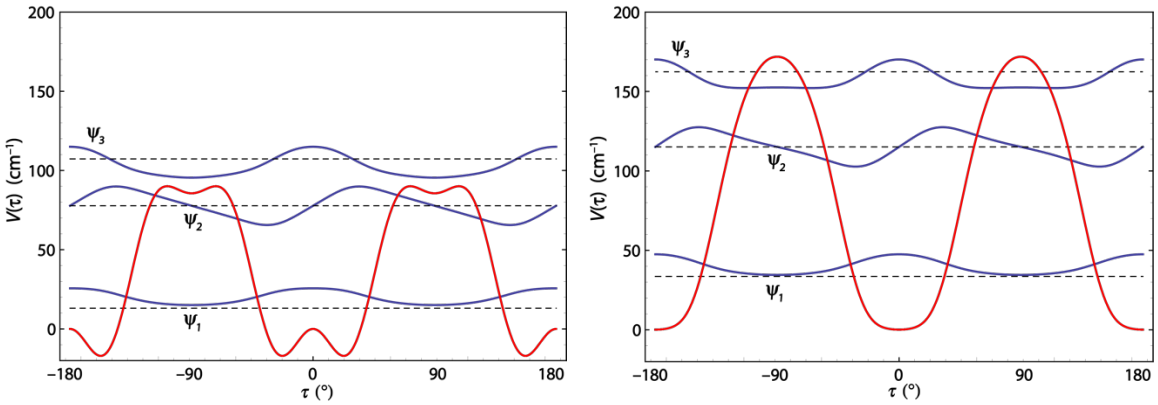


Figure 2. Potential energy (V) and converged vibrational wave functions (ψ) vs. H_2C–C–C torsion angle (τ) for internal rotation in *n*-propyl radical. Left panel: bare CCSD(T)/cc-pVQZ; right panel: final FPA potential with zero-point vibrational corrections.

To promote its definitive spectroscopic characterization, all stationary points of *n*-propyl were optimized with CCSD(T)/cc-pVTZ theory, and focal point analyses (FPA) targeting the CBS limit of CCSDT(Q) were executed to pinpoint the relative energetics. Anharmonic vibrational frequencies were then computed by applying second-order vibrational perturbation theory (VPT2) to a force field assembled from CCSD(T)/ANO1 quadratic and CCSD(T)/ANO0 cubic and quartic terms. As shown in Figure 2 (left panel), the bare internal rotation surface exhibits multiple local minima, owing to the coupling between CH_2 out-of-plane bending at the radical center and the H_2C–C–C torsional motion. However, when the zero-point vibrational energy of the complementary modes is included, a striking transformation takes place (right panel, Figure 2). In particular, $V(\tau)$ collapses to a single minimum every 180°, and the barrier height increases by about 70%! Far-infrared measurements of transitions between the highly anharmonic torsional states of *n*-propyl would not only have diagnostic merit but would also provide fundamental tests of vibrational adiabaticity for a multimode system.