# Computational Study of the Dissociation of Cyclohexanol Using Natural Bond Orbital Analysis

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## Introduction

We are interested in using natural bond orbital (NBO) methods to predict the dissociation pathways that are responsible for the distribution of radical cation fragments and intensities in mass spectra. In this project we use high-level computational chemistry methods to examine the fragmentation of cyclohexanol, $C_6H_5OH$. Features of the reaction energy profile, including numerous equilibrium structures and several transition states, are reported. Natural resonance theory (NRT) analysis of the equilibrium structures reveals significantly diminished bond orders for the bonds that homolytically cleave during fragmentation. These bonds are compromised when beta (spin-down electron) bonding density delocalizes into a vicinal "hole" that is left when an electron is ejected from the parent molecule.

## $C_6H_5OH$ Mass Spectrum



Cyclohexanol MASS SPECTRUM

Nist Chemistry WebBook
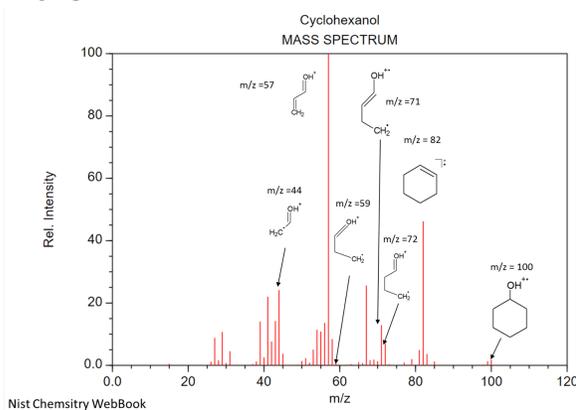
## Methods

- **B3LYP/cc-pVTZ**

Possible fragments were optimized using density functional theory (the B3LYP functional) with triple-zeta basis sets. The energies of each fragment at its equilibrium geometry are reported. Frequencies calculations were used to characterize each optimized geometry. All calculations were performed using Gaussian-16.

- **Transition State Calculations**

Several transition states were identified using Gaussian's TS search algorithms, include opt=qst2, qst3, and ts. These searches are rather challenging, and effort to identify additional transition states is ongoing.

- **Natural Resonance Theory**

The NRT method expands the total density operator as a linear combinations of localized density operators, one operator for each resonance structure. The weights of the resonance expansion are optimized to best represent the total density.
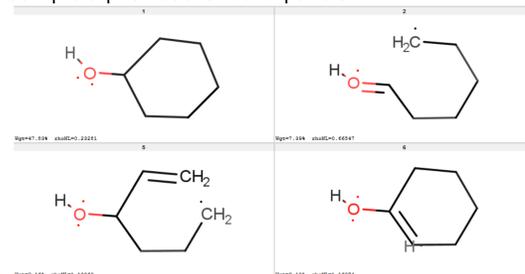
1) $\Gamma_{B3LYP} \cong \Gamma_{NRT} = \sum_\alpha w_\alpha \Gamma_\alpha \quad ; \quad w_\alpha \geq 0, \ \sum_\alpha w_\alpha = 1$

2) $D(w) = \min \left(\frac{1}{n_b}\right)^{\frac{1}{2}} \cdot \left\| \Gamma_{QC} - \sum_\alpha w_\alpha \Gamma_\alpha \right\|$
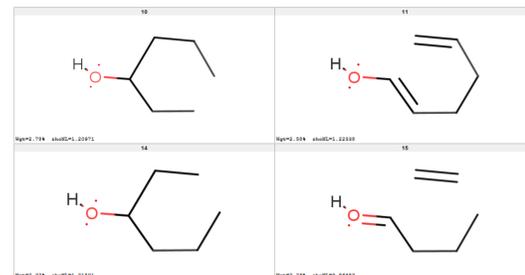
For open-shell systems, like radicals, there are separate one-electron resonance expansions for the different alpha (spin-up) and beta (spin-down) electron densities.
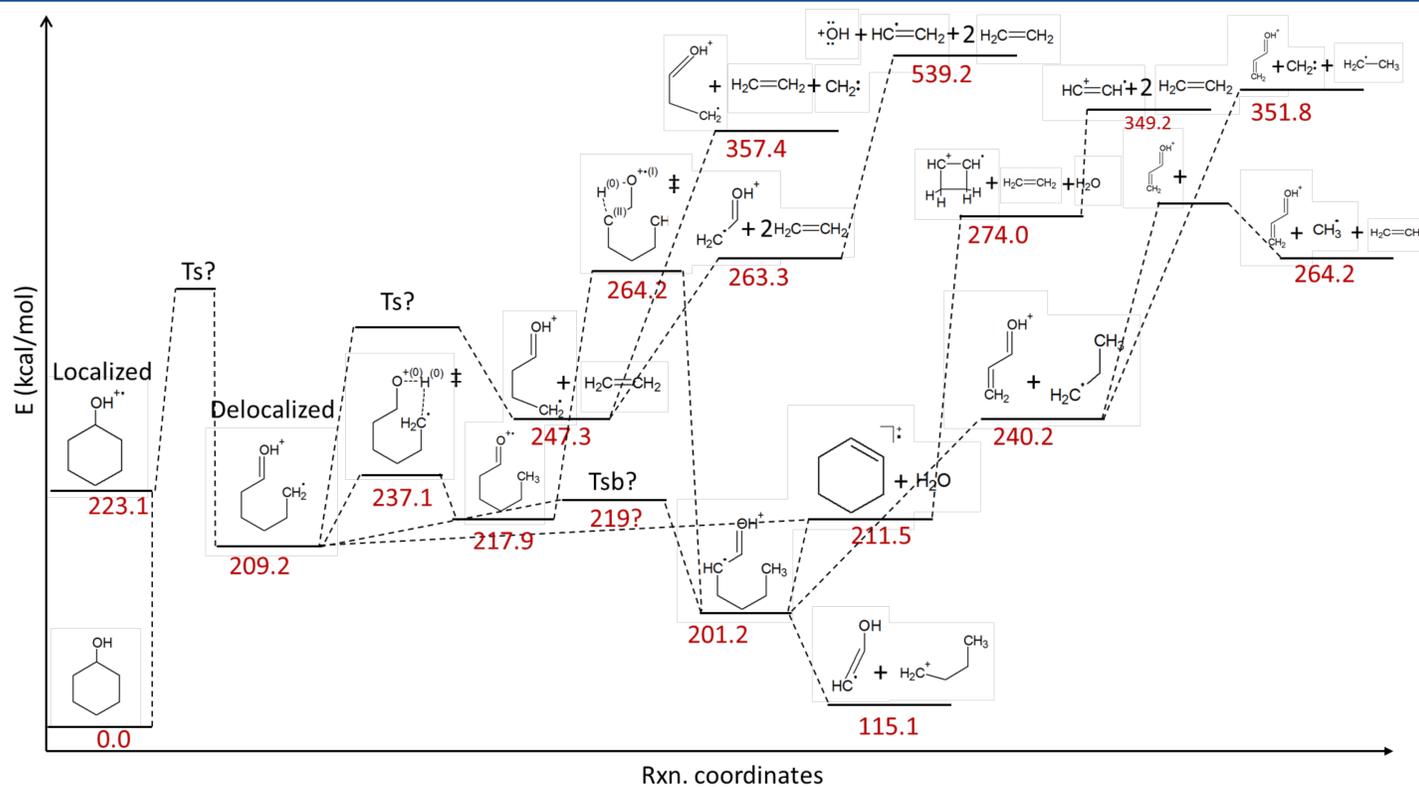


- Sample alpha resonance expansion
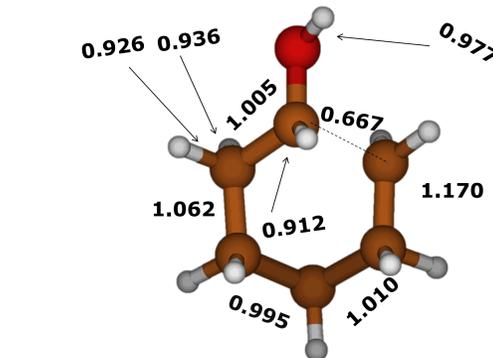


- Sample beta resonance expansion



- **Natural Bond Order**

The bond order is evaluated as the resonance-weighted average of the integer number of bonds between a pair of atoms A,B in each structure of the NRT resonance hybrid.

3) $b_{AB} = \sum_\alpha w_\alpha b_{AB}$

The value of the natural bond order can be used to determine whether a bond is compromised and likely to cleave.



- **Natural Spin Density (NSD)**

For an open-shell system, one obtains different NBOs for different spins, one for alpha-spin and one for beta. These correspond to the different Lewis structures for different spins description. NRT analysis is applied to the separate alpha- and beta-spin manifolds which results in different resonance hybrids for different spins. The alpha-spin analysis resembles that of the closed-shell system, whereas the beta-spin analysis usually resembles that of an electron-deficient cation. The natural spin density at each atom can be expressed as the difference of the alpha and beta electron populations at that atom, a positive spin density reflecting the excess alpha electron density at the atom, and a negative spin density reflecting any excess beta density.

4) $NSD \ on \ atom \ A = \sum_\mu^{on \ A} \left(P_{\mu\mu}^{(\alpha)} - P_{\mu\mu}^{(\beta)}\right)$

NSD is generally used to determine the location of any unpaired electrons in the radical. The location of these electrons is often associated with bond breaking and forming processes.
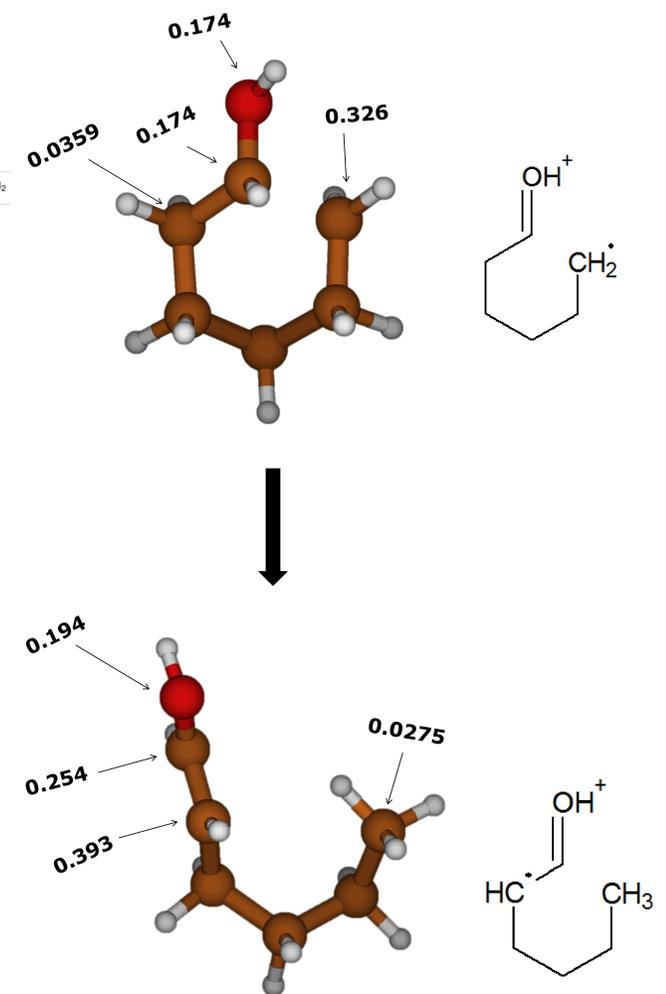
## Conclusions

1. NRT analysis shows that bond orders in equilibrium structures are significantly diminished for bonds that break during fragmentation.

2. Diminished bond orders arise as beta electron density delocalizes into "holes" in the valence shell that arise as a beta electron is ejected during ionization.

3. This work is ongoing. We have yet to correlate bond orders with the probability that a molecule undergoes fragmentation.

## Acknowledgements