Trends in the calculated geometries of the lowest two electronic states of 12 valence electron triatomic HAB molecules

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Introduction

The most accurate way to determine empirical geometries of a molecule is by analyzing spectroscopic constants, but due to practical constraints such as budget and safety, sometimes it is not feasible to use this method. Quantum mechanical calculation is often cost effective and safe while still accurate enough to determine a theoretical geometry for a molecule that can predict some empirical results.

HAB is the form of prototypical triatomic molecule with one hydrogen and two heavy atoms A and B. Our interest in this work is with 12 valence electron HAB molecules, such as HNO and HCF. In the 1950s, the angular correlation diagram for HAB molecules¹ was developed by Walsh, which proves useful to predict the geometries of these small molecules. A reproduction of the so-called Walsh diagram is shown below for a 12-valence electron HAB molecule. The Walsh diagram can use to make the prediction that the ground state geometry of HNO should bent due to the correlation of the HOMO. Because of the correlation of the LUMO, the excited state which should be less bent than ground state.

Fig. 1 - HAB Walsh diagram showing electron configuration for the ground state of a molecule containing 12 valence electrons.

Table 1 – Geometry changes calculated from spectroscopically derived molecular geometries for three HNO analogs.

Molecule	Δr_{AB} (Å)	Δr_{AH} (Å)	$\Delta \angle HAB$ (°)
HNO ^a	-0.017	0.029	6.9
HPO ^a	0.015	0.079	-7.0
HAso ^a	-0.007	0.117	-8.4

^a Based on geometry information collected in Ref. 4.

The geometry changes upon electronic excitation have been observed for some HNO analogs through analysis of spectra. HNO is an example that follows the Walsh diagram², and it is also part of data that Walsh diagram is derived from. But, when phosphorous³ or arsenic⁴ becomes the central atom, the analysis of spectroscopic constants show that the HAB angle decreases upon the electron excitation.

Examples of molecules where the central atom is in group 14 instead of group 15, such as HSiCl, follow the Walsh diagram. The molecules that thus far have been experimentally reported upon lead to a trend that if a central atom is P or As, the molecule will tend to behave opposite to prediction, but the molecules with group 14 and element Nitrogen will follow the prediction by Walsh diagram (reference¹).

Fig. 2 - Frontier orbitals of a 12 valence HAB molecule. These particular orbitals are plotted from a B3LYP density functional calculation using the aug-cc-pvtz basis set for the molecule HNO. a) shows the HOMO, an orbital of A' symmetry. b) shows the LUMO, an A'' symmetry orbital. The two orbitals correlate to the two components of a degenerate Π pair at linearity.

Computational Details

Density functional quantum mechanical calculations were completed using the B3LYP combined functional.^{6,7} Basis sets were selected based on atoms availabilities: Dunning's correlation consistent triple zeta basis sets including diffuse functions⁸ were used when available, and Weigend and Ahlrich's split valence quadruple zeta basis sets⁹ for calculations involving elements beyond Kr. All calculations were performed using the Gaussian 09 suite of programs.¹⁰ The method and basis sets were picked to be computationally inexpensive since the combination produces qualitatively correct results for the experimentally known molecules while allowing for a survey of molecules to be computed relatively easily.

Calculated Orbital Angular Correlation Diagrams

Fig. 3 - Plot of HNO angle change versus the energy change for the HNO geometries.

Fig. 4 - Plot of HPO angle change versus the energy change for the HPO geometries.

Fig. 5 - Plot of HASO angle change versus the energy change for the HASO geometries.

Fig. 6 - Plot of HSiF angle versus the energy for the HSiF geometries.

Figures 3-6 above show four angular orbital correlation diagrams constructed for HAB molecules made by fixing the bond lengths at their equilibrium values and recording orbital energies at various angles. Each of these diagrams shows orbitals that have local minima between 90 and 180 degrees, behavior that is not predicted by the idea underlying the Walsh diagram. Some orbitals show trends that are different from the Walsh diagram as well. For example, the LUMO orbitals for HPO, HASO, and HSiF each show a trend toward lower energy at linearity.

One feature of note is a difference in the lower energy occupied molecular orbitals for molecules that follow the original Walsh diagrams prediction (HNO and HSiF) in comparison to molecules that do not follow the prediction (HPO and HASO). Both HNO and HSiF have low energy orbitals that favor a linear geometry quite strongly, whereas HPO and HASO do not. This difference is possibly interesting as a cause or secondary result of the difference in behavior.

No single factor from its orbital angular correlation diagram seems to indicate whether a particular molecule will follow the prediction based on the HAB Walsh diagram or not. The most remarkable feature of these diagrams is that HPO and HASO show different (but similar to each other) behavior for the lower orbitals than HNO and HSiF.

Ground and Excited State Geometries

Fig. 7 - Plot of angle change versus bond length change for the *ab initio* geometries.

Figure 7 shows a plot of angle change versus AB bond length change upon electronic excitation for 36 HAB molecules and ions (charge limited to +1 or -1). All molecules were variationally calculated with an A' ground state and an A'' excited state. A general trend is observed that molecules with a large increase in AB bond length have a HAB angle decrease. If the AB bond length decreases or remains similar upon excitation, the HAB angle tends to increase.

Partial Optimization Results

Partial optimizations on the ground state were conducted with bond lengths fixed and angles allowed to vary. The HA bond lengths were held at their optimized values, and each calculation optimized the HAB angle at a fixed AB bond length. Figure 8 shows the results for HSiF and HPO. Similar behavior observed for the two molecules (and several not pictured), showing that the even when just the ground state is considered, an increase in bond length results in a decrease in angle. This trend holds for molecules that follow and break Walsh's rules.

Fig. 8 - Plot of optimized angle versus AB bond length change for HSiF (blue) and HPO (orange).

Conclusion and Future Work

A survey of *ab initio* geometries for the ground and first excited electronic states of various HNO analogs was conducted using density functional theory. Our calculations qualitatively agree with spectroscopically derived geometries for the experimentally observed molecules.

Although the current work has more fully explored the problem, it has not provided any more in-depth explanation of what causes the anomalous behavior – it appears that there is a general trend for N, O and group 14 central atoms and a different trend for group 15 and 16 central atoms. Additional exploration of the calculated orbital angular correlation diagram is needed, and it also needs more experimental data to support and test the truth of this result. Further calculations such as natural bond analysis may be required in order to determine the fundamental differences in molecules that do not follow orbital angular correlation diagram. A possible course of inquiry would be to construct full multi-dimensional potential energy surfaces for prototypical example molecules to search for differences in their potential energy landscapes.

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