# Studies Aimed at Determining the Importance of Molecular Complexes in Atmospheric Chemistry

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# Molecular Complexes

- Formation of molecular complexes can significantly impact the chemistry of atmospheres.
- Reactant molecules can be “tied up” and prevented from participation in certain chemical reactions, leading to a net loss in some compound.
- Alternatively, some reactions may be enhanced, leading to a net gain in a specific molecule.
- This latter process can occur when one molecule from a complex photodissociates and immediately reacts with the second monomer molecule.

# Molecular Complexes: Earth

- Over the last few years, there has been considerable interest in the impact of molecular complexes on the chemistry of Earth's atmosphere.
- Complexes that have attracted attention usually involve a chemically reactive component, such as $O_3$ or $O_2$, complexing with a more inert component such as $N_2$ or $H_2O$.
- Even small binding energies can lead to complex concentrations large enough to impact the chemistry significantly, depending on conditions.

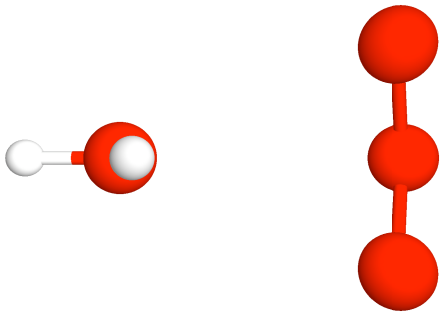
# $O_3 \cdot H_2O$

- One example of an important complex is $O_3 \cdot H_2O$.
- Laboratory experiments have established that photodissociation of $O_3 \cdot H_2O$ can lead to significant production of OH in the troposphere.
- OH is the most important scavenger molecule in the atmosphere; an unknown source is very important.
- The only remaining uncertainty in the assessment of $O_3 \cdot H_2O$ is the atmospheric abundance.
- More accurate physical data (thermochemical functions) for $O_3 \cdot H_2O$ are needed -- computational chemistry is ideal approach for obtaining the needed data.

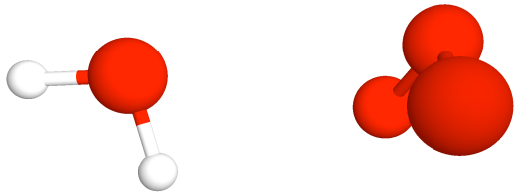
# Computational Approach

- For the types of highly accurate physical data that are needed for $O_3 \cdot H_2O$, computational chemistry is ideal.
- CCSD(T) used for electronic structure calculations -- mentioned by David Schwenke in rovibrational studies.
- Accurate potential energy surface (PES) that includes anharmonic effects in intra- and inter-molecular modes will be computed.
- This PES can be used to calculate highly accurate, temperature dependent thermodynamic functions for $O_3 \cdot H_2O$.

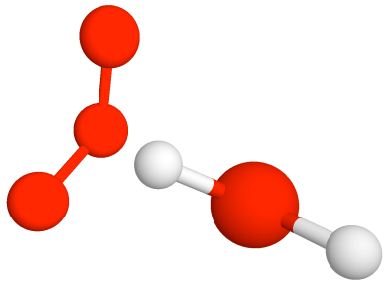
# Three Views of $O_3 \cdot H_2O$



Photodissociation of $O_3 \cdot H_2O$ can lead to formation of two OH molecules.



The complex has $C_s$ symmetry, with the $H_2O$ molecule and the central O of $O_3$ occupying a plane.



One of the H atoms is closest to the $O_3$ molecule, making it available for abstraction once $O_3$ photodissociates.

# Atmospheric Simulations

- The highly accurate thermodynamic functions for $O_3 \cdot H_2O$ will be used to determine atmospheric concentrations for different conditions.
- These concentrations will be used in atmospheric simulations to assess the impact of the $O_3 \cdot H_2O$ complex on formation rates for OH radical.
- Once these steps have been completed, we will be able to assess the importance of the $O_3 \cdot H_2O$ complex to atmospheric chemistry under all possible conditions.

# Summary

- Molecular complexes can significantly impact the chemistry of atmospheres -- Earth as well as other planets, and potentially the ISM as well.
- The Earth sciences program from the ROSES 2005 announcement of interest is A.14 Atmospheric Composition.
- Several Space science programs may be of interest, the most obvious being B.10 Planetary Atmospheres -- suggestions welcome.

# Other Projects

- Collaboration on the Evolutionary Chemistry of Protoplanetary Disks, with S. Davis and D. Richard
- Collaboration on the study of the electronic spectra of PAHs and PAH derivative compounds, with M. Head-Gordon and the Ames Astrochemistry group.

- Computation of highly accurate rovibrational spectra of small molecules.
- Search for possible stratospheric bromine reservoir species.
- Radiation biology countermeasures: investigation of reaction mechanisms for melatonin and other physiological radical scavengers.