The depletion of the ozone layer by a series of reactions with other atmospheric molecules in the upper atmosphere is today an important and interesting problem. The ozone-water interaction could be a key to understand reactions responsible for ozone depletion and changes in the global climate. We studied the structure and electronic states of ozone-water complexes and $O_3$-Ice. In the case of the dimer $O_3$-(H$_2$O) our results indicate that the underlying intermolecular interactions induce small but measurable vibrational frequency shifts. The origin of these spectroscopic changes is investigated in terms of an NBO analysis of charge transfer and repulsion interactions between the $O_3$ and water.
The overall aim of the project is to advance our understanding of the fundamental interactions responsible for stabilization of weakly bounded van der Waals complexes, with emphasis on studying the effect of water molecules on the electronic properties of ozone (O$_3$). It has been observed that the hole in the ozone layer over Antarctica is created at the end of the polar night, when both clouds and light are present in the lower stratosphere. This observation has motivated researchers to propose that water ice microcrystals might be responsible for catalyzing heterogeneous photochemical reactions with pollutants. Surprisingly, however, the direct effect of water itself on the ozone electronic structure (even in the absence of pollutants) has yet to be understood. This poster investigates the fundamental interactions responsible for stabilizing the 1:1 ozone-water complex which is the most abundant in the earth atmosphere. It is expected, however, that the dominant interactions in this complex will be common to many other hydrated ozone complexes that are relevant to atmospheric chemistry and changes in the global climate. The extent to which these weakly bound van der Waals complexes affect the atmospheric chemistry and the global climate is ultimately determined by their abundance, with water being a major player in the absorption of solar radiation.
All calculations were performed with the Gaussian 03 suite of programs. Geometry optimizations and all calculations relevant to the NBO analysis of stereoelectronic interactions were performed at the MP2/6-31G+(2d,p) level of theory.
Contributions of Delocalization and Steric interactions

Canonical orbitals $\rightarrow$ NBO localized set

Substitution of $F$ elements

Delocalization
Deletion of $F_{\sigma,\sigma^*}$

Steric
Replace of $F_{\sigma,\sigma}^{NBO}$ with $F_{\sigma,\sigma}^{PNBO}$

Calculation of the density matrix in the AO basis with the mentioned substitutions

Use of the modified matrix in the calculation of molecular properties ($P'$)

$\Delta P = P - P'$
Charge is delocalized from O₃ to H₂O, mainly due the $\pi$(O₁-O₂) $\rightarrow$ $\sigma^*$(O₅-H₆) interaction illustrated in panel (a.1). Such delocalization process decreases the electronic charge density between the two monomers as illustrated by the brown iso-surface density in panel (a.2). The overall charge redistribution, shown in panel (a.2), indicates that the O₃ - H₂O charge transfer forms a hydrogen bond with water and stabilizes a “diradical” substructure relative to other resonance structures of ozone.
$\text{O}_3 \rightarrow \text{H}_2\text{O}$ Charge Transfer

$\pi(\text{O}_1-\text{O}_2)$

$\sigma^*(\text{O}_5-\text{H}_6)$

(a.1) (a.2)
Interactions that delocalize charge form H$_2$O to O$_3$ are of smaller intensity than $\pi$(O$_1$-O$_2$) $\rightarrow$ $\sigma^*$($O_5$-H$_6$) interactions. One of the most important H$_2$O - O$_3$ charge transfer interactions is the $\eta_p$(O$_5$) $\rightarrow$ $\sigma^*$(O$_1$-O$_2$) interaction represented in panel (b.1). The effect of these interactions is the decrease of charge density in regions that correspond to the $\eta_p$(O5) orbital. The overall response of the electronic structure to this interactions is an increase of charge near the O and the stabilization of the “dianion” substructure relative to other resonance structures.
$\text{H}_2\text{O} \rightarrow \text{O}_3$ Charge Transfer

$\sigma^* (O_1-H_2)$  $n_\pi (O_5)$

(b.1)  (b.2)
This figure shows the quantitative analysis of NBO occupancies. It is shown that ozone bond orbitals reduce their occupancy, showing the effect of stabilization produced by delocalization interactions, which strength the O-O bonds due to formation of the hydrated complex.
Depletion of electronic charge

Accumulation of electronic charge
Iso-density surfaces showing the difference between the electron density of the complex O$_3$-H$_2$O and the sum of the electronic density in the isolated monomers O$_3$ and H$_2$O. The underlying charge redistribution shows a decrease of charge density between the two monomers (brown iso-surface), responsible for stabilizing the complex by reducing the electrostatic repulsion between both molecules. The observed reduction in charge density is correlated with the delocalization interactions from O$_3$ to H$_2$O as indicated by the NBO analysis. The increase of electronic density next to the H$_2$O-oxygen atom indicates an inductive effect.
Effect of Complex Formation over Vibrational Frequencies

Bending
Symmetric stretch
Antisymmetric stretch
### Calculated Values B3LYP/6-311+G(2p,d)

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### Experimental Values

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All frequencies shift due to formation of the hydrated complex. The computed spectroscopic changes are of the same order of magnitude as those observed experimentally. Calculated frequencies increase after the formation of the complex. These changes are consistent with stabilizing interactions between the ozone and the water molecule. A direct comparison to experimental shifts is difficult since the absolute error of the calculations are comparable to the magnitude of the spectroscopic shifts. However, tendencies are very similar.
We have shown how to analyze the effect of intermolecular interactions on the electronic structure of $O_3$-$H_2O$ complexes according to an NBO stereoelectronic analysis. To the best of our knowledge, this is the first study where an NBO based methodology has been implemented to investigate the effects of delocalization and steric interactions on the molecular properties of this weakly bound hydrated complex. It has been found that the formation of the complex reduces the electronic charge density between the two monomers and therefore the electrostatic repulsion between $O_3$ and $H_2O$. Consistently, electron transfer from NBOs of $O_3$ to $H_2O$ cause a reduction of charge between $O_3$ and $H_2O$. 

Conclusions
The charge delocalization increases the electronic density between $O_1$ of ozone and $H_4$ of water, and between $O_3$ of ozone and $H_6$ of water, giving rise to an overall charge distribution similar to typical electronic distributions in H-bonded systems. The NBO analysis provides a theoretical framework to interpret changes in vibrational frequencies, due to formation of the hydrated complex. The increase of stabilization interactions in monomer due to the influence of the other, is consistent with an increase of the vibrational frequencies. It has been shown that the calculated vibrational frequencies changes agree with the experimental values within the experimental and computational errors. Work in progress involves studying the effect of orbital interactions between monomers on other molecular properties, such as electronic transitions and the appearance of new spectroscopic bands due to formation of hydrated ozone complex.
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