# Stepwise Microhydration of Isoxazole: Infrared Spectroscopy of Isoxazole-(Water)$_{n\leq2}$ Clusters in Helium Nanodroplets

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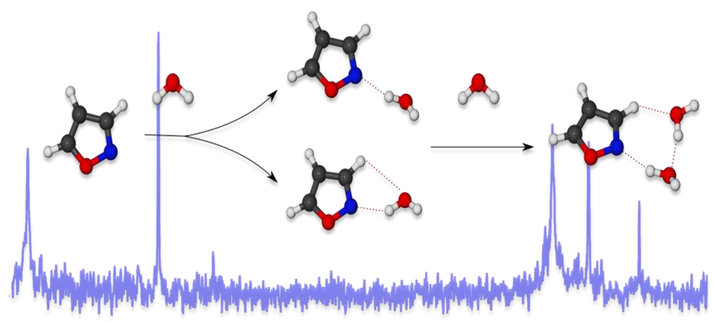
## Abstract

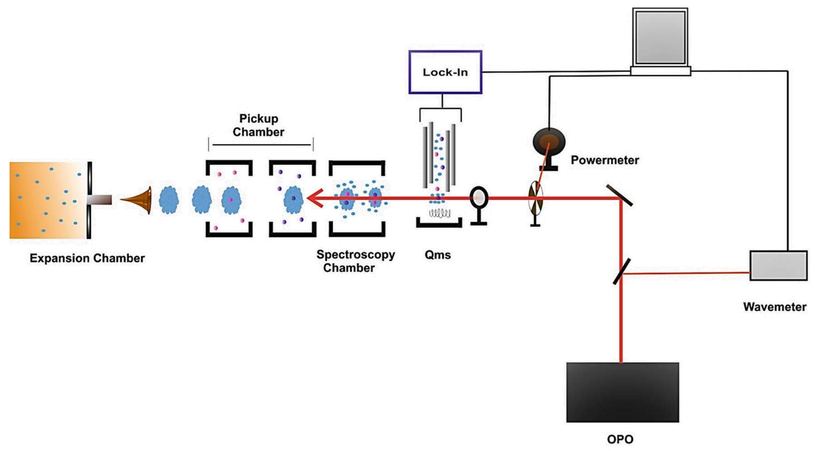
Here, we study microhydration framework around heterocyclic isoxazole obtained by successive addition of water molecules.[1] Isoxazole is a five-membered heterocyclic ring, which features two different neighbouring heteroatoms, nitrogen (N) and oxygen (O). Past microwave investigation of isoxazole-argon (isoxazole-Ar) complex showed that the nonpolar Ar ligand binds to the aromatic p electron cloud and slightly moves to the N-O bond because of the exchange repulsion forces.[2] However, changing the solvent to polar, aprotic CO causes a substantial modification of the solvent-binding motif.[3] The rotational data of isoxazole-CO dimer demonstrated that the solvent CO moves to the aromatic plane and binds to the ring nitrogen. Interestingly, no spectral and computational data are available involving the interaction of isoxazole with the polar, protic solvent, water. Herein, we report the IR spectrum of isoxazole-(water)$_{n\leq2}$ (isotopically substituted water, $D_2O$) recorded inside the helium nanodroplets.



## Spectroscopy in Helium nanodroplets

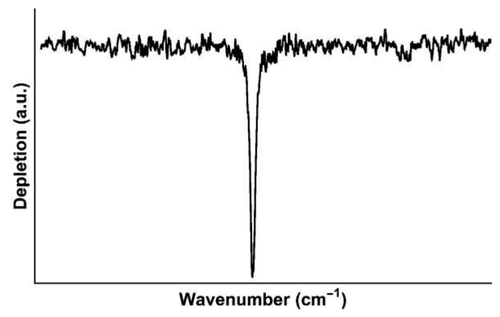
### Helium nanodroplet

- Helium nanodroplets are formed by the supersonic expansion
- Superfluid at their equilibrium temperature (0.37 K)
- IR spectra is close to the gas phase spectra
- Optically transparent to photons below 20eV
- The pickup of molecules in helium nanodroplets follows Poisson statistics




Schematics of the Helium droplet machine at RUB, Bochum.

### Depletion spectroscopy




- Depletion of ion signal at the resonant IR

## Result and Discussion

### Infrared spectra

First pickup chamber- Isoxazole
Second pickup chamber- $D_2O$

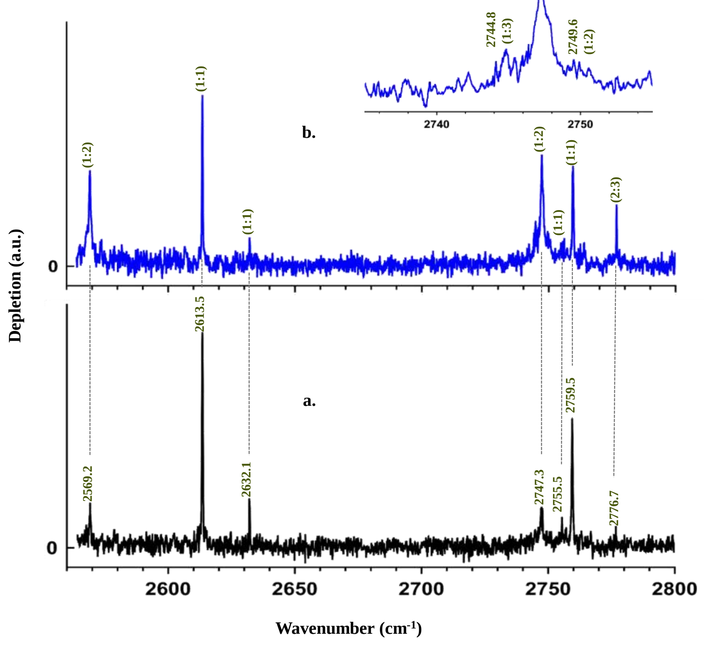
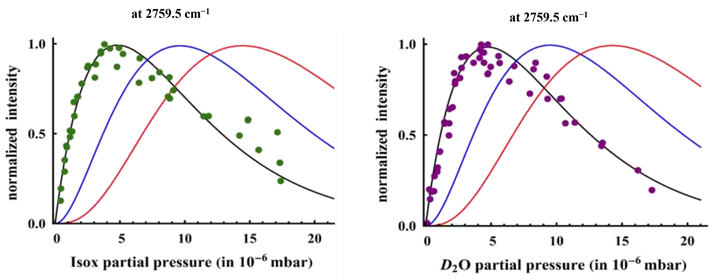



Figure 2 Infrared depletion spectra of isoxazole-$D_2O$ clusters, measured at isoxazole mass channel (m/z =69, $C_3H_3NO^+$). The cluster composition of the observed bands is shown in parentheses.

### Pickup curves

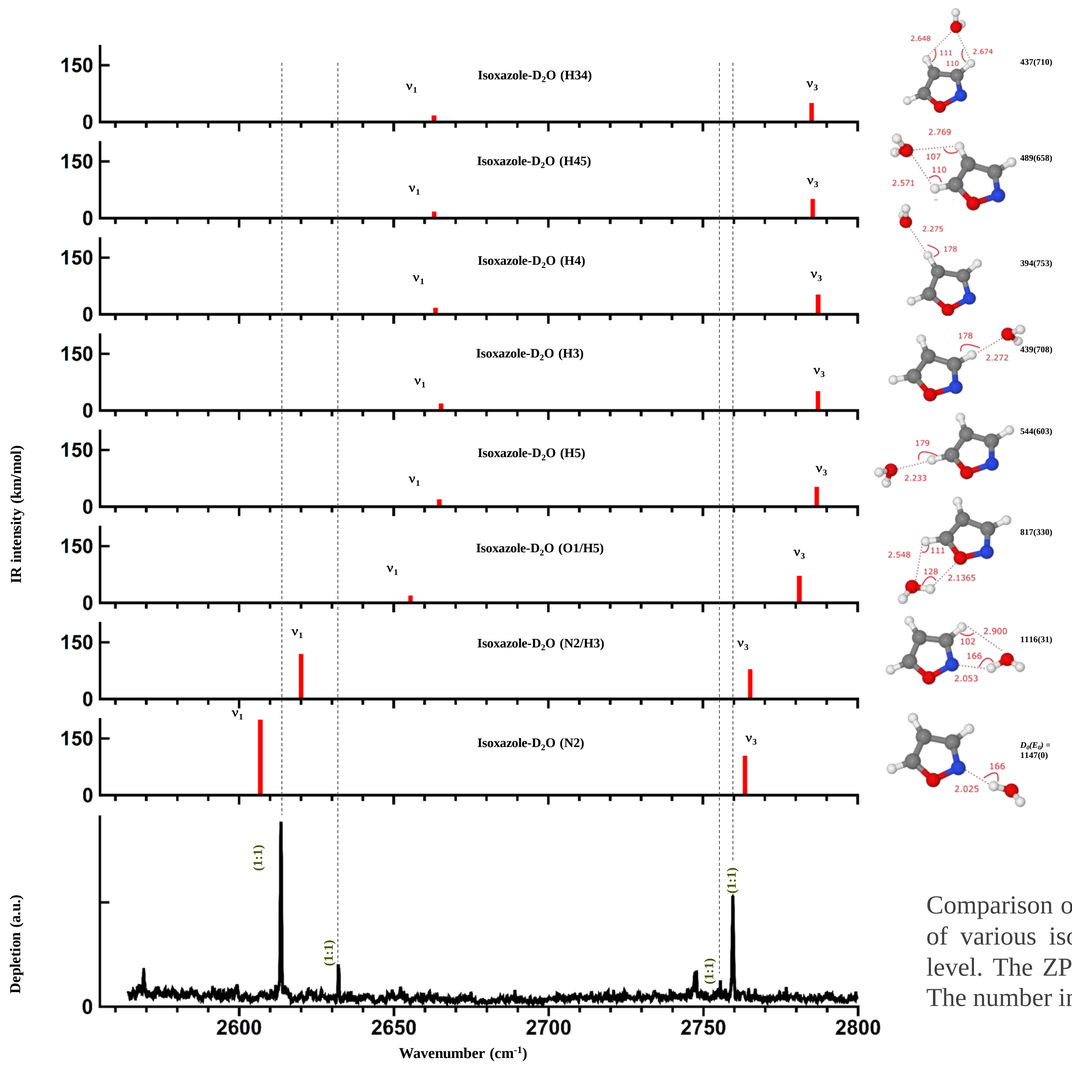
Pick up of molecules by the droplets follows Poisson statistics

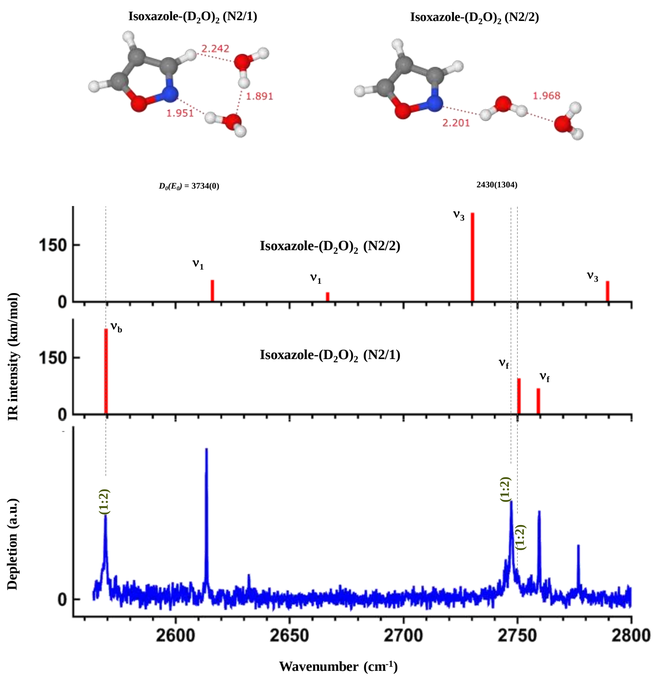
- $P_k = \frac{(\sigma\rho L)^k}{k!}\exp(-\sigma\rho L)$




Pickup curves of isoxazole and $D_2O$ at fixed frequencies, recorded at m/z = 69.

### Quantum chemical calculation and assignment




Comparison of the observed IR bands with the linear IR absorption spectra of various isoxazole-$D_2O$ isomers calculated at the MP2/6-311++G(d,p) level. The ZPE+BSSE corrected binding energy ($D_0$) is provided in cm$^{-1}$. The number in parentheses corresponds to relative energy ($E_0$) in cm$^{-1}$.

## Summary

- **The IR spectra of microhydrated isoxazole clusters in the OD stretch range using helium nanodroplets spectroscopy**
- **In the Isoxazole-$D_2O$ dimer, water molecule exclusively binds to the most basic nitrogen centre via the formation of N···HO**
- **In Isoxazole-$(D_2O)_2$ trimer, a water dimer moiety simultaneously interacts with the heterocyclic isoxazole ring via N···HO and CH···O H-bonds**
- **Understanding the initial hydration network of this important prebiotic molecule is crucial in the context of biochemistry as well as astrochemistry**

## References

1. T.K.Roy et.al *J. Phys. Chem. A*, **2021**, *125*, 4766-4774.
2. U. Spoerel et.al *J. Phys. Chem.* **1996**, *100*, 14298-14309.
3. S. McGlone et.al *J. Chem. Phys.* **1998**, *109*, 5383-5392.

## Acknowledgement

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