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Formation of Benzonitrile Anions in Low Temperature Matrices and their Microsolvation in Water

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Abstract

The discovery of benzonitrile (PhCN) molecule in Taurus Molecular Cloud - 1 in 2018, has led to a pursuit of research for neutral and protonated benzonitrile molecules, aggregates and their interaction with water molecules. However, literature reports on PhCN anion (PhCN-), a probable candidate yet to be identified in space, are scarce. Here we report the novel synthesis and spectroscopic characterization of PhCN- in LDA water ices and inert gas matrices at 4K using matrix isolation FTIR spectroscopy. PhCN- is a curious case because preparing an anion out of PhCN is challenging owing to the negative electron affinity (~ -4.5 kcal mol^{-1}) of the molecule!

Experimental Results and Calculations

Formation of Benzonitrile Anion

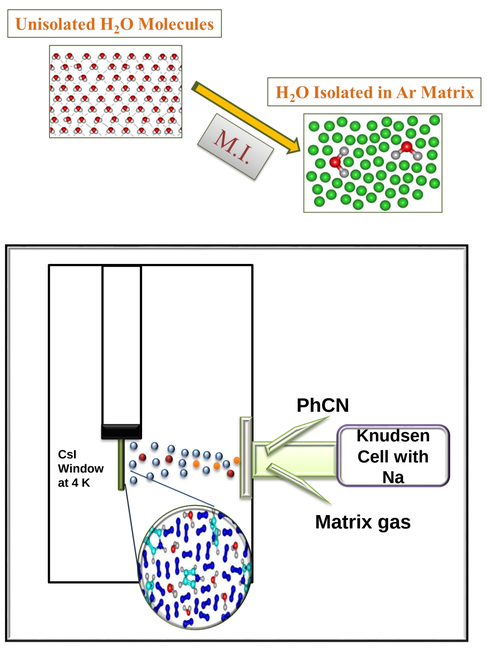
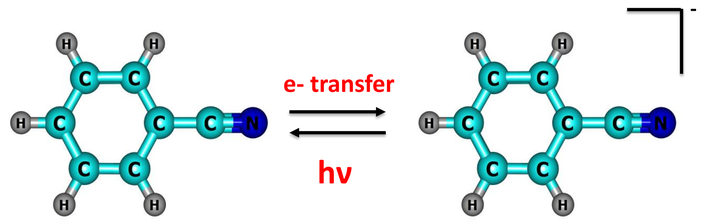


Figure1. Schematic representation of the Matrix isolation set-up and the procedure of Na deposition along with sample and matrix gases.

PhCN- is thermally stable, but photo labile and gets converted to the neutral molecule during photolysis.



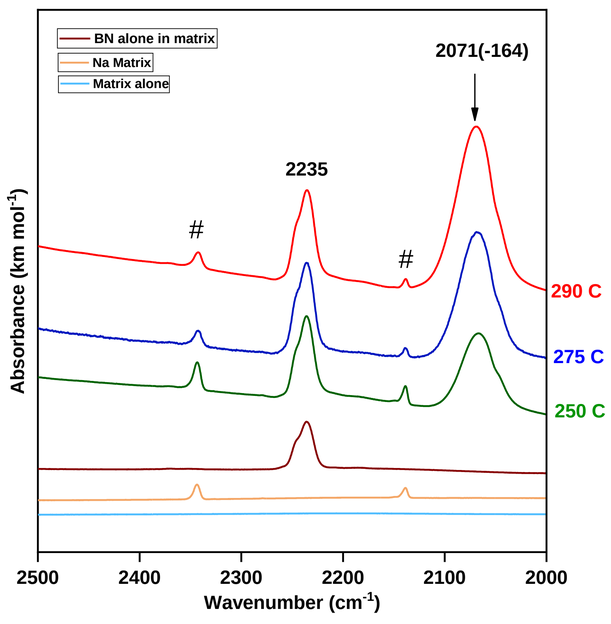


Figure2. IR spectra of the C≡N stretching mode of PhCN in LDA water ice matrix before and after Na deposition.

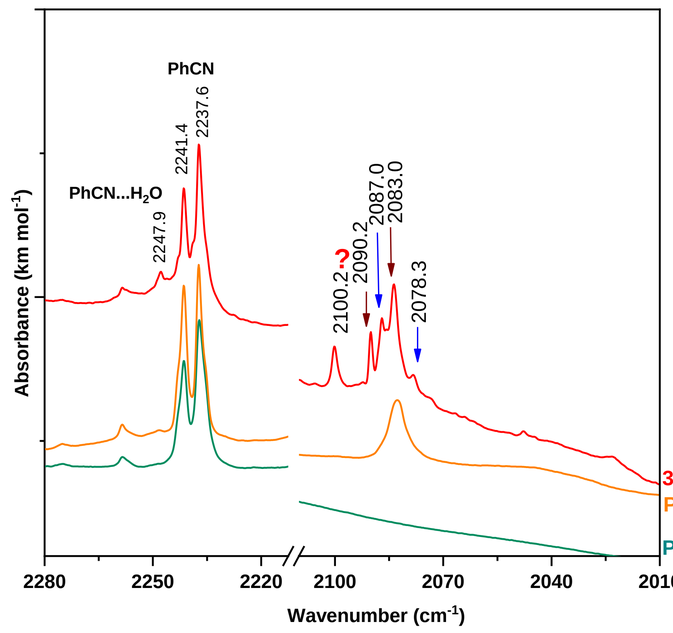


Figure3. IR spectra of the C≡N stretching mode of PhCN in Ar matrix before and after Na deposition.

Microsolvation of Benzonitrile Anion in Water

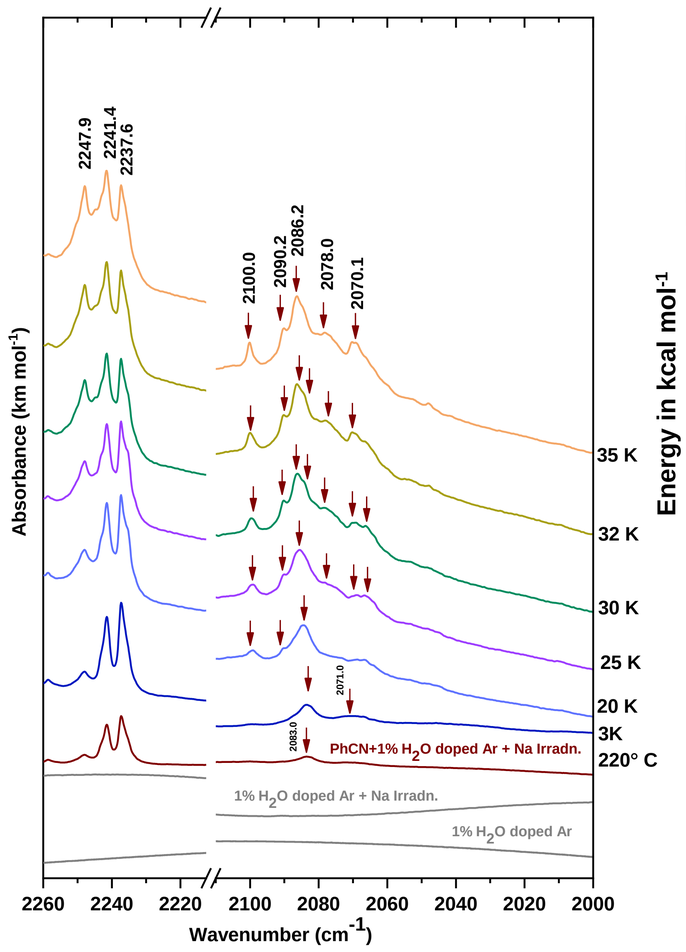
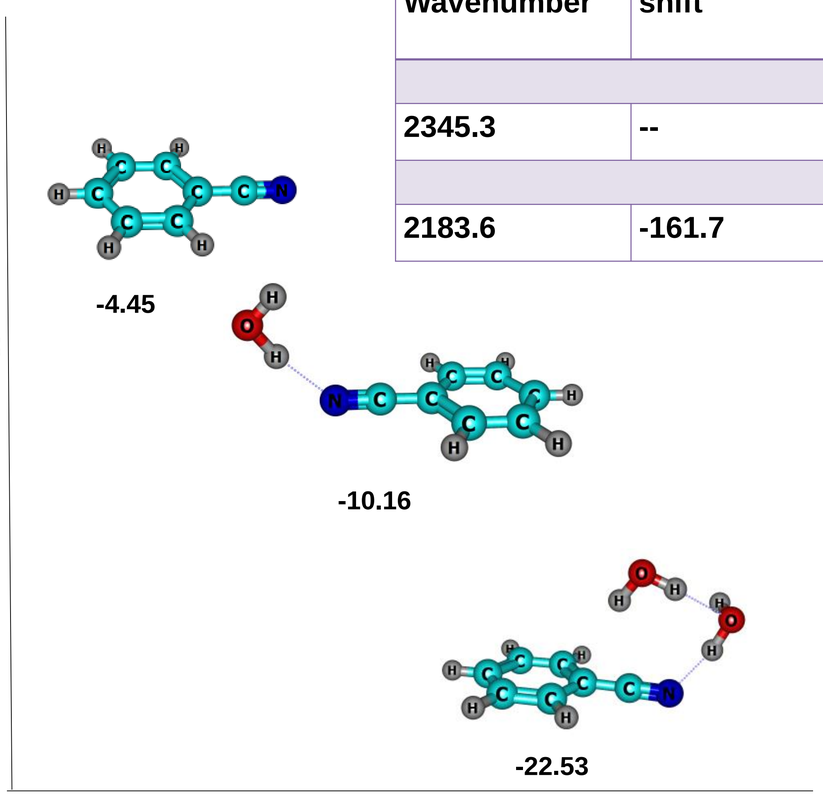


Figure4. IR spectra of the C≡N stretching mode of PhCN in 1% water doped Ar matrix before and after Na deposition.



Computed Wavenumber	Wavenumber shift	Experimental wavenumber in LDA water ice	Wavenumber shift	Experimental wavenumber in Ar Matrix	Wavenumber shift
PhCN					
2345.3	--	2235.0	--	2241.4; 2237.6	--
PhCN-					
2183.6	-161.7	2071.0	-164.0	2090.2; 2083.0	-152.9

Computed Wavenumber	Wavenumber shift	Experimental wavenumber in Ar Matrix	Wavenumber shift
PhCN-… Water			
2179.8	-165.2	2086.2; 2078.0	-157.4
PhCN- … Water Dimer			
2166.0	-179.0	2070.1	-169.4

Conclusion

- The synthesis of PhCN- involved the use of sodium as a source of electrons.
- Hydrated electrons are produced after co-deposition of water with sodium. These electrons are easily transferred to a PhCN molecule to produce PhCN-.
- PhCN- is thermally stable, but photolabile and gets converted to the neutral molecule during photolysis.
- The thermal stability of PhCN- anion in the low temperature matrix aided the study of the microsolvation of PhCN- with water.

Reference

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Acknowledgement

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