

CH₃CN complex with water as a precursor for radiation induced synthesis of acetamide in low-temperature matrix



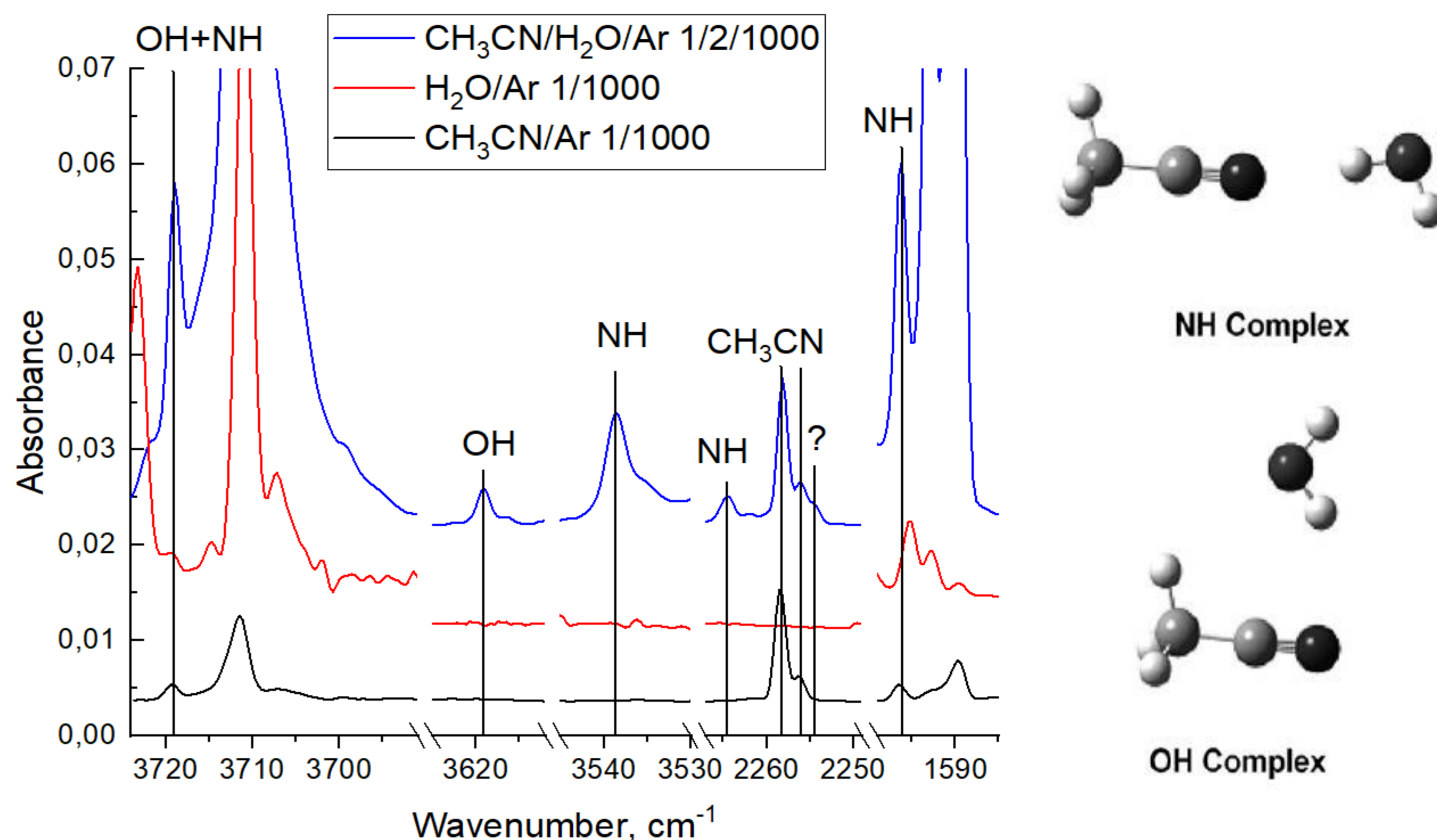
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Introduction

Small nitrogen-containing molecules play an important role in extraterrestrial prebiotic chemistry. In particular, acetonitrile (CH₃CN) was found in different space objects. It is supposed to be a precursor of a variety of biologically relevant molecules, including amides. Considering the solid-phase chemistry driven by ionizing radiation, one may come to an idea that the intermolecular complexes of acetonitrile with oxygen-bearing molecules can serve as "building blocks" for complex organic molecules (COMs) containing both N and O atoms. However, little is known on the mechanisms of such processes. The strategy to investigation of the radiation-chemical transformations occurring within isolated complexes frozen in rigid environment was recently developed in our laboratory. In this work we have examined for the first time the radiation-induced transformations of acetonitrile complexes with water occurring under X-ray irradiation in solid argon matrices at 5 – 6 K using FTIR spectroscopy.

Deposition



Fragments of FTIR spectra of deposited CH₃CN/H₂O/Ar 1/2/1000, H₂O/Ar 1/1000 and CH₃CN/Ar 1/1000 samples

Calculated and observed wavenumbers of two forms of acetonitrile-water complex in argon matrix, cm⁻¹

Modes	NH complex		OH complex	
	Calculated	Experimental	Calculated	Experimental
vOH _{as}	3897 ¹ ; 3893 ²	3719	3905 ¹ ; 3907 ²	3719
vOH _s	3735 ¹ ; 3738 ²	3538	3785 ¹ ; 3789 ²	3619
vCN	2365 ¹ ; 2374 ²	2264	2347 ¹ ; 2356 ²	2254
δOH	1667 ¹ ; 1632 ²	-	1643 ¹ ; 1612 ²	1596

Experiment

Sample preparation*

CH₃CN/H₂O/Ar (1:2:1000)
 CD₃CN/H₂O/Ar (1:2:1000)
 CH₃CN/Ar (1:1000)

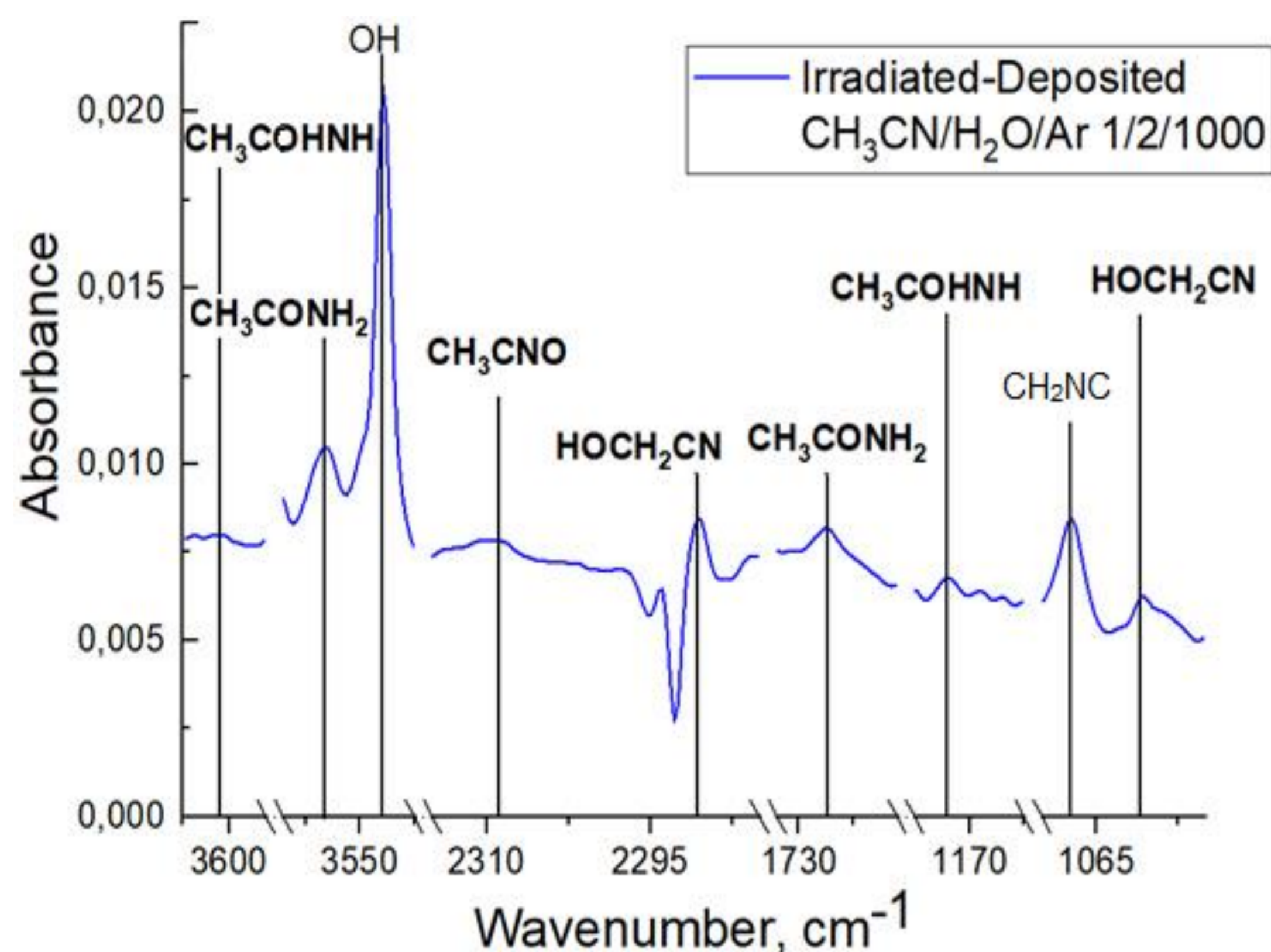
IR spectroscopy (6 K)

Deposition (18K)

Irradiation with X-rays (45 kVp, 6 K)

*Irina V. Tyulpina

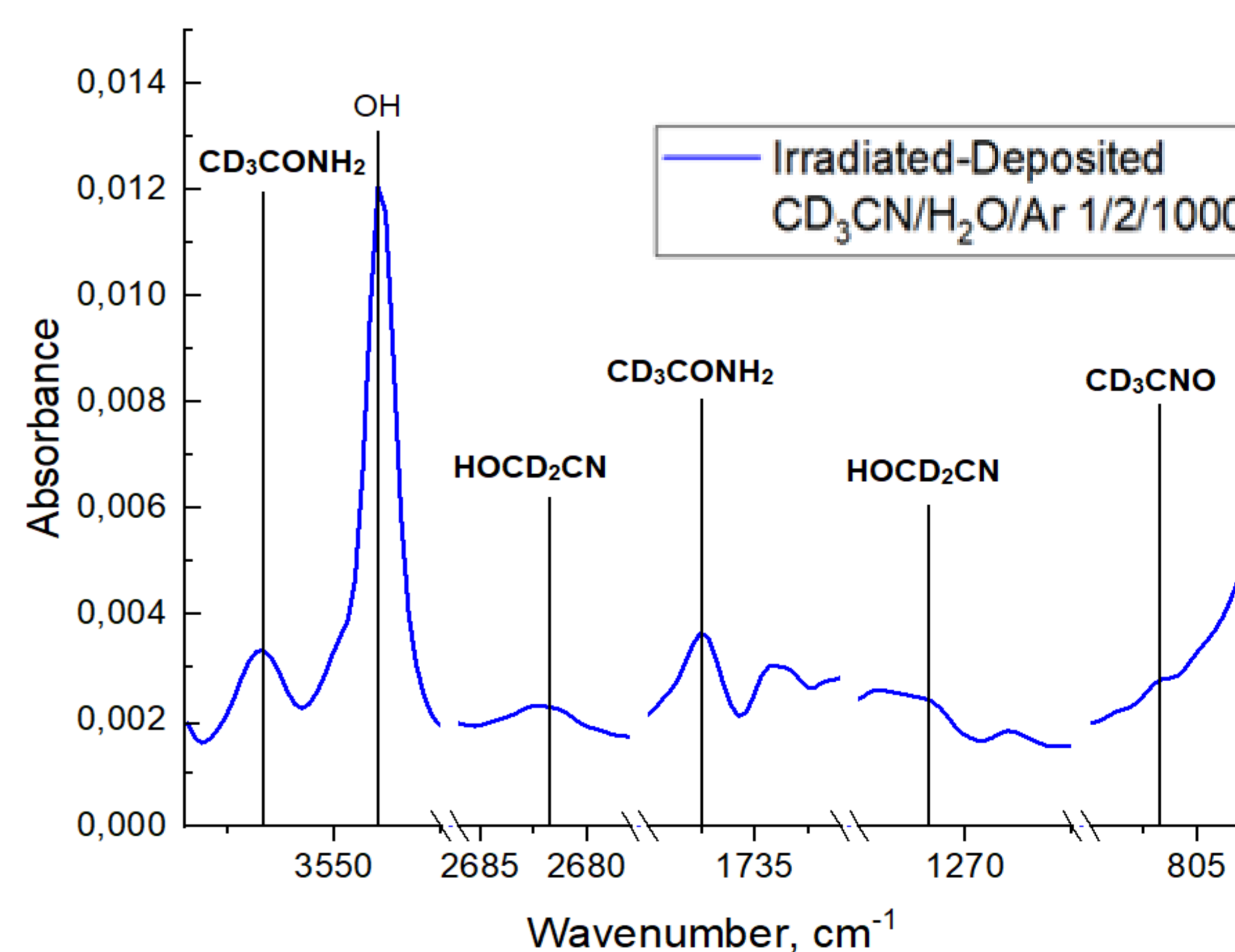
Irradiation



Difference spectrum of irradiated and deposited CH₃CN/H₂O/Ar 1/2/1000 sample

Observed wavenumbers of main radiolysis products of CH₃CN/H₂O/Ar sample, cm⁻¹

Acetamide CH ₃ CONH ₂	Acetimidic acid CH ₃ COHNH	Acetonitrile N-oxide CH ₃ CNO	Hydroxyacetonitrile HOCH ₂ CN
1588; 1727; 3435; 3553	3603; 1680; 1169; 1094; 843	857; 1332; 2309	1061; 1274; 2291

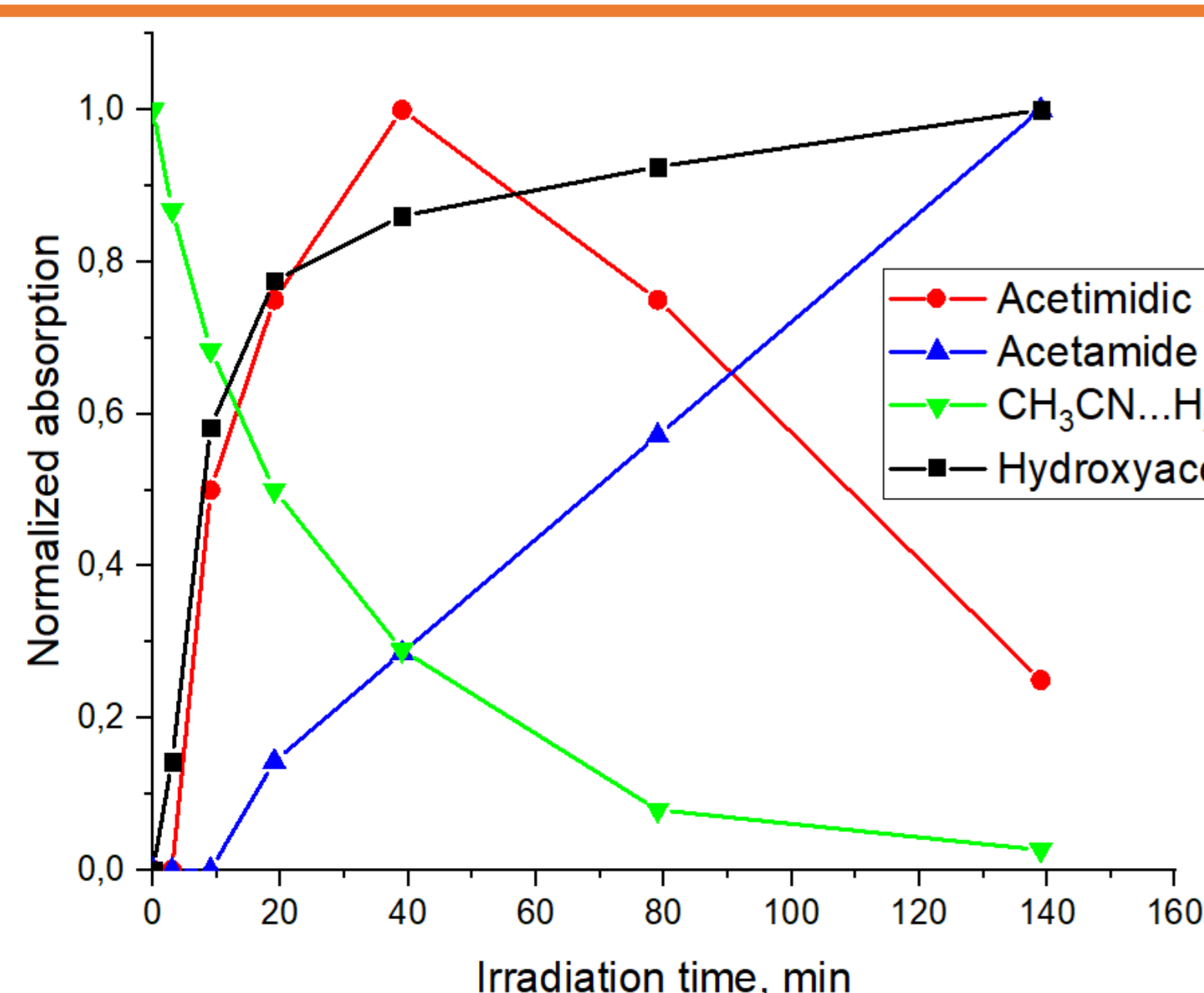


Difference spectrum of irradiated and deposited CD₃CN/H₂O/Ar 1/2/1000 sample

Observed wavenumbers of main radiolysis products of CD₃CN/H₂O/Ar sample, cm⁻¹

Acetamide CD ₃ CONH ₂	Acetonitrile N-oxide CD ₃ CNO	Hydroxyacetonitrile HOCD ₂ CN
1587; 1737; 3436; 3553	578; 807; 2297	979; 1133; 1273; 2682

Results



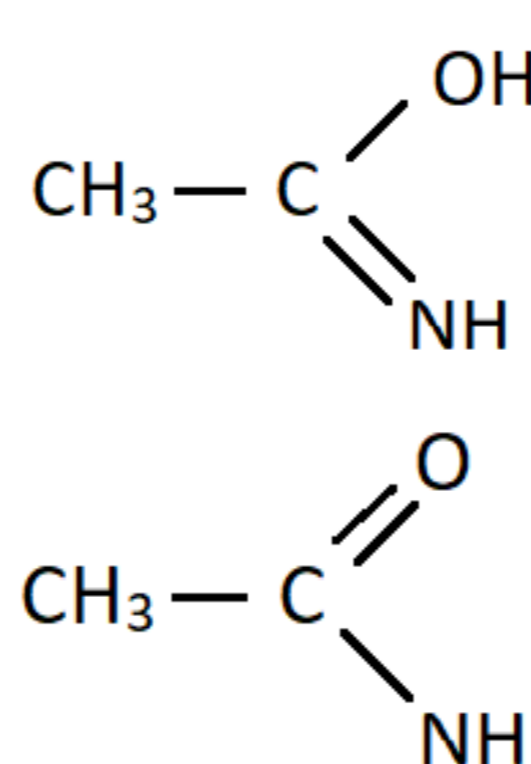
The kinetic behavior of initial CH₃CN...H₂O complex and products of its radiolysis in an argon matrix



X-ray



X-ray



Conclusion

- Complex of acetonitrile with water was obtained in two forms in argon matrix;
- Acetimidic acid was observed as a primary radiolysis product of acetonitrile complex with water;
- Acetamide was observed as a secondary radiolysis product resulting from radiation-induced intermolecular H-transfer.

¹F. Duvernay, P. Chatron-Michaud, F. Borget, D. M. Birney, and T. Chiavassa, *Phys. Chem. Chem. Phys.*, vol. 9, no. 9, pp. 1099–1106, 2007

²R. Gopi, N. Ramanathan, and K. Sundararajan, *J. Mol. Struct.*, vol. 1094, pp. 118–129, 2015

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