

# A contribution of in situ UV/Vis/NIR spectroscopy to characterize molybdenum oxide catalysts

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## Introduction

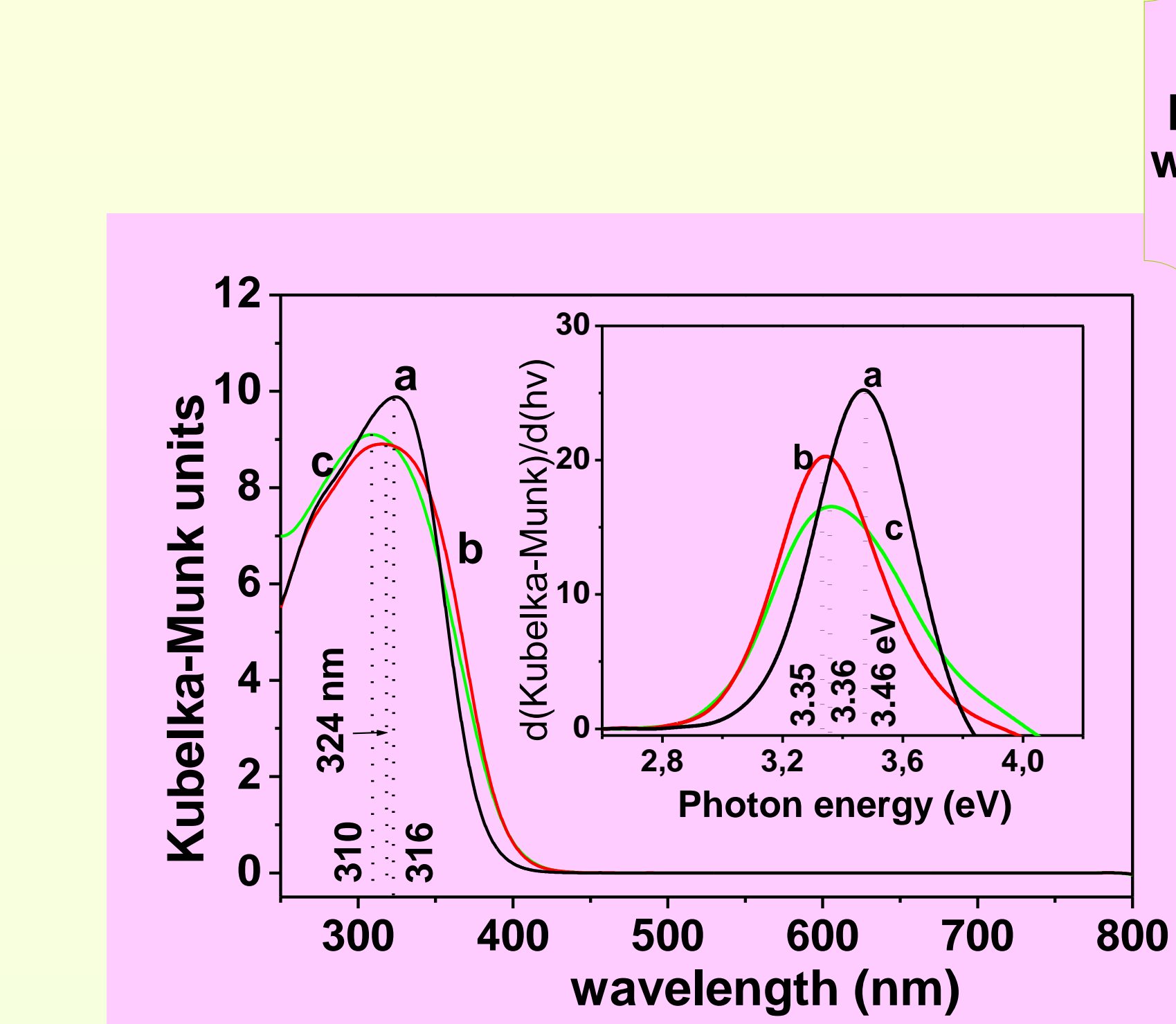
\* Controlled precipitation (different cursor concentration, temperature or nature of counter cation) is used to obtain structural complexity without the need for chemical complexity [1, 2] (**Poster 115**).

\* The obtained materials (orthorhombic, hexagonal MoO<sub>3</sub>, supramolecular Mo<sub>36</sub> and trimolybdate) undergo electronic changes in the presence of certain gas atmospheres.

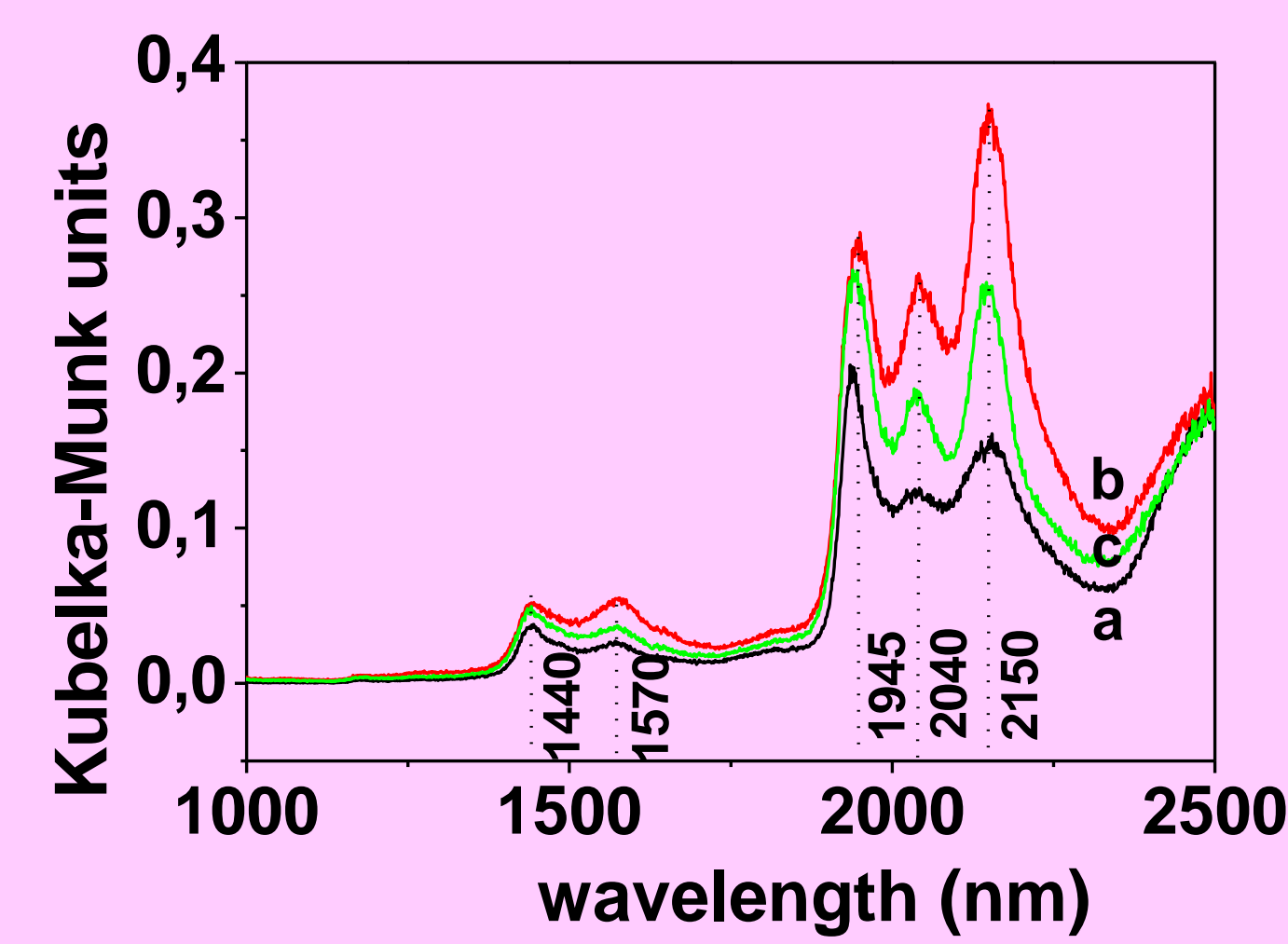
\* Analysis of such materials is carried out by in situ UV/Vis-NIR spectroscopy (**this Poster**).

## References

- [1] S.Knobl, G.A. Zenkovets, G.N. Kryukova, O. Ovsitser, D. Niemeyer, R. Schlögl und G. Mestl, J. Catal., 215, 2003, 177.  
 [2] S. Knobl, O. Timpe, N.D. Orthman, N. Abdullah, Q. Basher, R.E. Jentoft, F. Girgsdies, J. Kröhnert, J. B. Wagner, J. Melsheimer, D. Niemeyer, S.B.A. Hamid and R. Schlögl, in preparation.  
 [3] J. Melsheimer, M. Thiede, R. Ahmad, G. Tzolova-Müller and F.C. Jentoft, PCCP, 2003, 4366.



Molybdenum oxide catalysts prepared from 0.7 mol/L AHM with 1 mol/L HNO<sub>3</sub> at 30°C (a), 50°C (b) and 70°C (c) ;



## Experimental

### Spectroscopic equipment

A commercial UV/Vis/NIR spectrometer (Lambda 9, PerkinElmer) equipped with a BaSO<sub>4</sub> coated integrating sphere was supplemented with a new construction (specially formed light conductor in vertical position) to measure in situ diffuse reflectance spectra of different MoO<sub>x</sub> from room temperature (RT) to 749 K [3].

### Spectroscopic measurements

The spectra were recorded both from 250 to 2500 nm (scan speed of 240 nm·min<sup>-1</sup>, slit 1 nm) and 250 to 800 nm (scan speed 60 nm·min<sup>-1</sup>, slit 0.2 nm) with Spectralon (Labsphere) as a white Standard in the reference position. Powder samples (ca. 0.6 g) were charged in the home-made micro-reactor and fed with a flow of air, pure He or 21 % oxygen in helium.

### Catalyst preparation

s. poster 115

sample number	precursor	conc. (mol/l)	HNO <sub>3</sub> (mol/L)	temp. (°C)	structure
256	AHM	0.7	1	30	supramol.
227				50	hexag.
232				70	hexag.
228	AHM	1.0	1	50	supramol.
225	AHM	0.7	2	50	supramol.
286	K <sub>2</sub> MoO <sub>4</sub>	0.28	5	30	supramol.
247				50	hexag.
233				70	hexag.
253	K <sub>2</sub> MoO <sub>4</sub>	2	5	30	supramol.
246				50	supramol.
243				70	trimolybdate
251	Li <sub>2</sub> MoO <sub>4</sub>	0.28	2	30	orthorhombic
222				50	orthorhombic
230				70	orthorhombic
252	Na <sub>2</sub> MoO <sub>4</sub>	2	2	30	hexag.
226				50	hexag.
231				70	hexag.

sample number	LMCT (nm)	E <sub>g</sub> (eV)
256	324	3.46
227	310	3.36
232	316	3.35
228	308	3.55
225	330	3.36
286	305	3.46
247	305	3.30
233	319	3.30
253	329	3.43
246	308	3.43
243	284	3.77
251	288	3.48
222	295	3.37
230	306	3.37
252	320	3.27
226	328	3.27
231	332	3.27

sample number	group	NIR (nm)		
		hexag. MoO <sub>3</sub>	supram. Mo <sub>36</sub>	trimolybdate
256, 227, 232, 228, 225	-OH(H <sub>2</sub> O) <sub>ads</sub>	1440	1440	-
	(H <sub>2</sub> O) <sub>ads</sub>	1570	1570	-
	-OH(H <sub>2</sub> O) <sub>ads</sub>	1945	1940	-
	-OH(H <sub>2</sub> O) <sub>ads</sub>	2040	2030	-
	NH <sub>4</sub> <sup>+</sup>	2150	2150	-
286, 247, 233, 253, 246, 243	-OH(H <sub>2</sub> O) <sub>ads</sub>	1430	1435	1435
	-OH(H <sub>2</sub> O) <sub>ads</sub>	1940	1930	1930
	NO <sub>3</sub> <sup>-</sup>	-	1790/1810	1790
	?	-	-	2000
	?	2090	2075	2095
252, 226, 231	NO <sub>3</sub> <sup>-</sup>	2230	2250	2250
	?	-	-	970
	-OH(H <sub>2</sub> O) <sub>ads</sub>	1430	251, 222, 230	1430
	NO <sub>3</sub> <sup>-</sup>	1820	251, 222, 230	1790
	-OH(H <sub>2</sub> O) <sub>ads</sub>	1955	251, 222, 230	1930
	NO <sub>3</sub> <sup>-</sup>	2280	251, 222, 230	2280

## Summary (RT spectroscopy)

The following average LMCT bands (nm) (I) and E<sub>g</sub>'s (eV) (II) at RT are attributed to certain MoO<sub>x</sub> families:

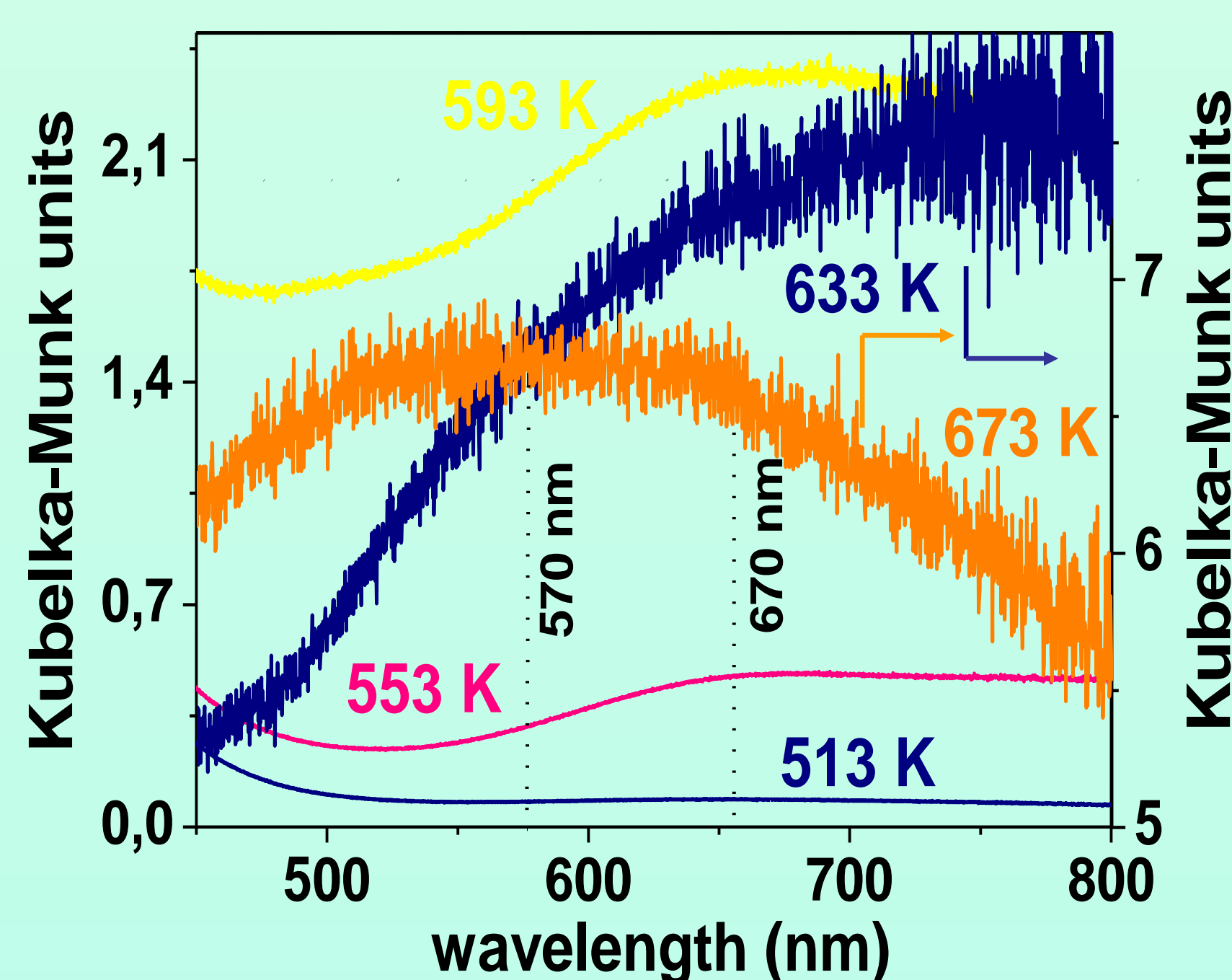
- (I) 322 (NH<sub>4</sub><sup>+</sup>), 314 (K<sup>+</sup>); (II) 3.48 (NH<sub>4</sub><sup>+</sup>), 3.44 (K<sup>+</sup>) to supramolecular Mo<sub>36</sub>;
- (I) 313 (NH<sub>4</sub><sup>+</sup>), 319 (K<sup>+</sup>), 327 (Na<sup>+</sup>); (II) 3.35 (NH<sub>4</sub><sup>+</sup>); 3.30 (K<sup>+</sup>), 3.27 (Na<sup>+</sup>) to hexagonal MoO<sub>3</sub>;
- (I) (296 (Li<sup>+</sup>)); (II) 3.44 (Li<sup>+</sup>) to orthorhombic MoO<sub>3</sub> and
- (I) 284 (K<sup>+</sup>); (II) 3.77 (K<sup>+</sup>) to trimolybdate MoO<sub>x</sub>.

From a blue shift of the LMCT band in the series supramolecular/hexagonal → orthorhombic → trimolybdate and a decreasing broadening of this band it may be concluded that the cluster size decreases.

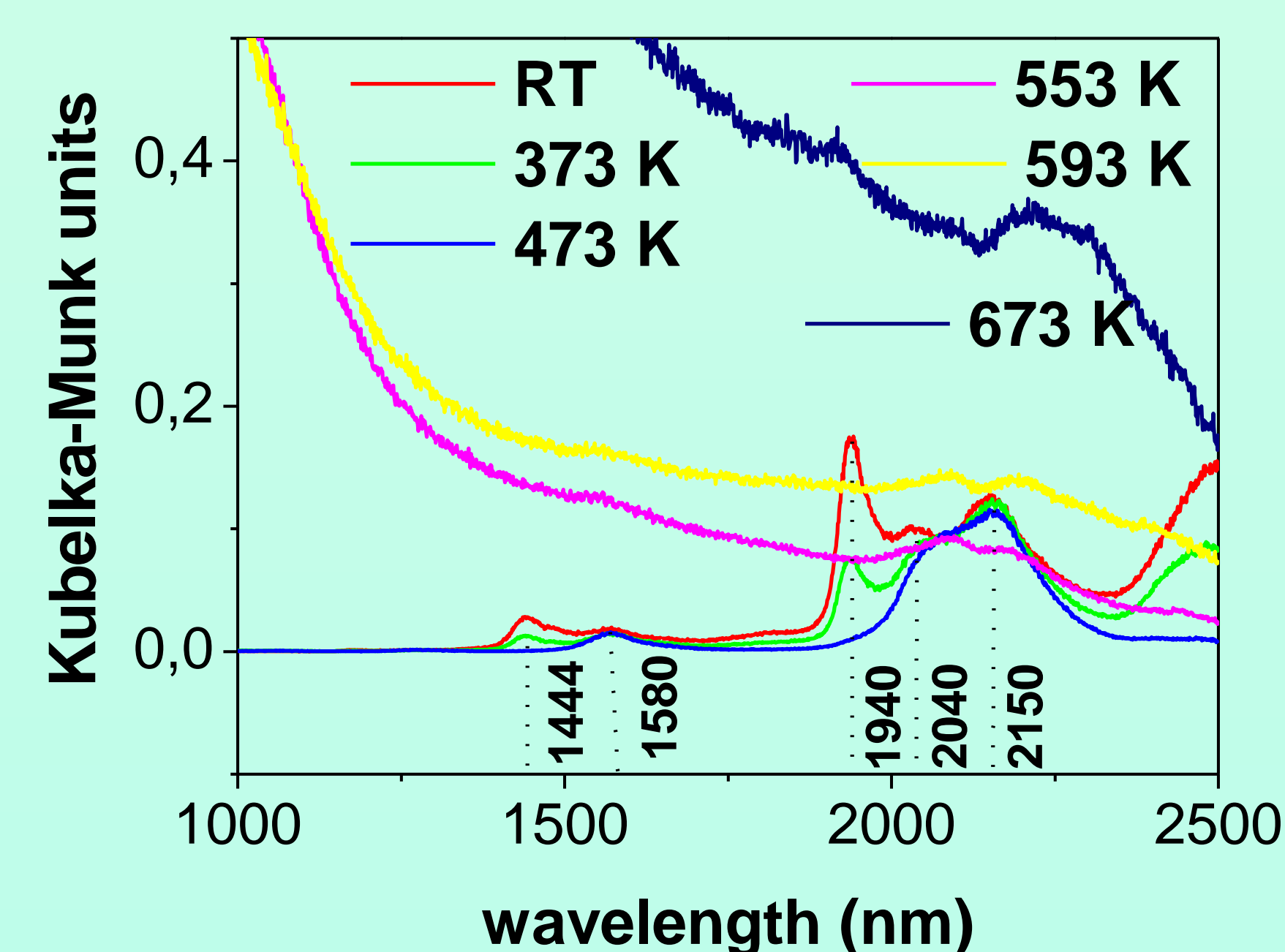
## Summary (high temperature spectroscopy)

- By increasing the temperature the band at 2150 nm begins to disappear at 553 K and the band at 1570 nm diminished around 633 K.
- In Vis range a new band at 660/670 nm develops at 553 K which decreases in the presence of He and increases in the presence of O<sub>2</sub> in He with increasing temperature. This band is assigned to a d-d transition.
- In He this band suffers a blue shift to about 570 nm at 673 K. The appearance of the new Vis band is in line with TG/DSC data. At 553 K ammonia as counter ion decomposes to NO<sub>x</sub> and reduces the Mo matrix; ammonia is completely removed from the sample at around 693 K (**Poster 76**).

Spectra recorded from room temperature up to 673 K under flow of Helium

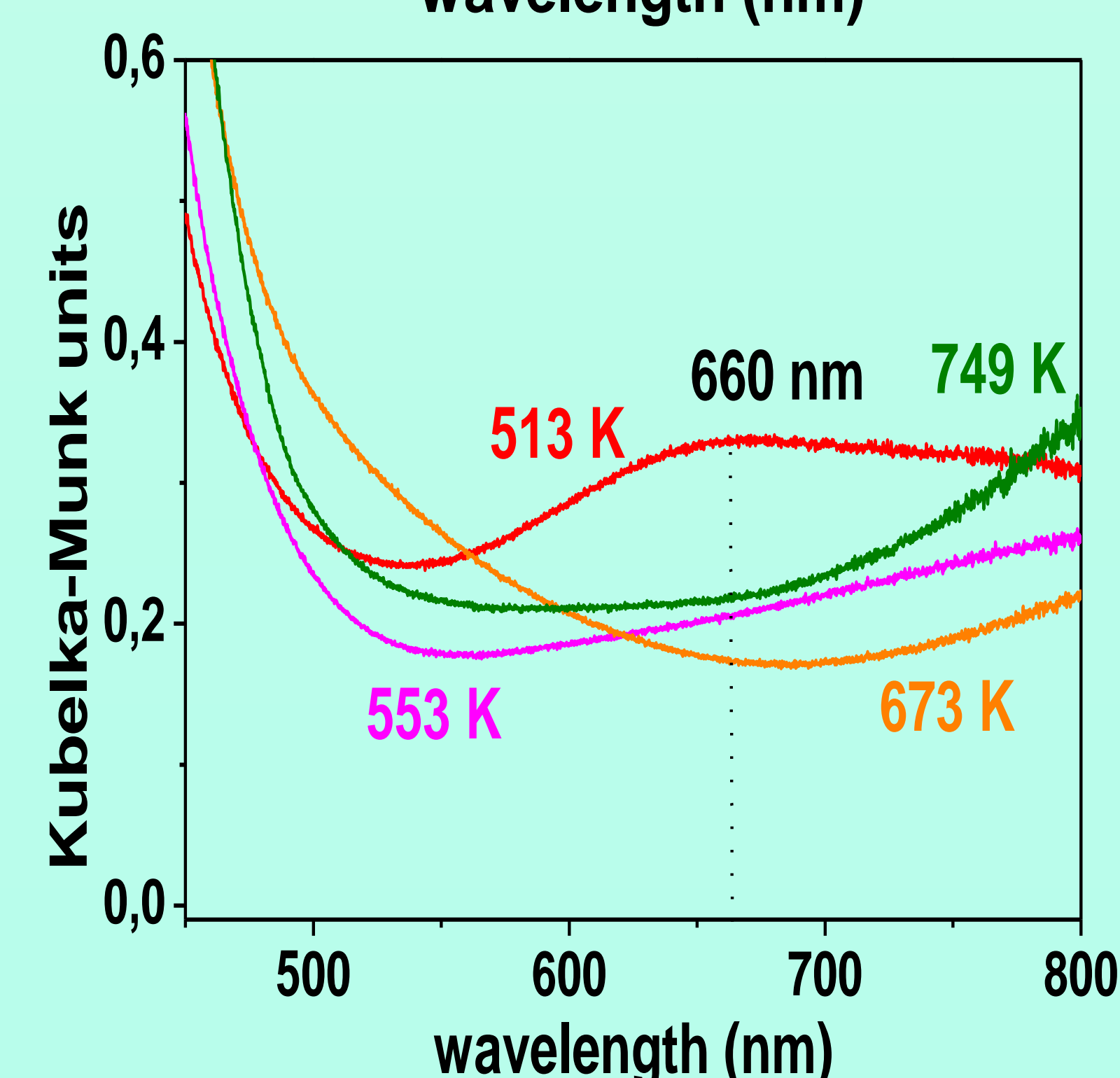


Supramolecular Mo<sub>36</sub> prepared from 0.7 mol/L AHM with 1 mol/L HNO<sub>3</sub> at 30°C



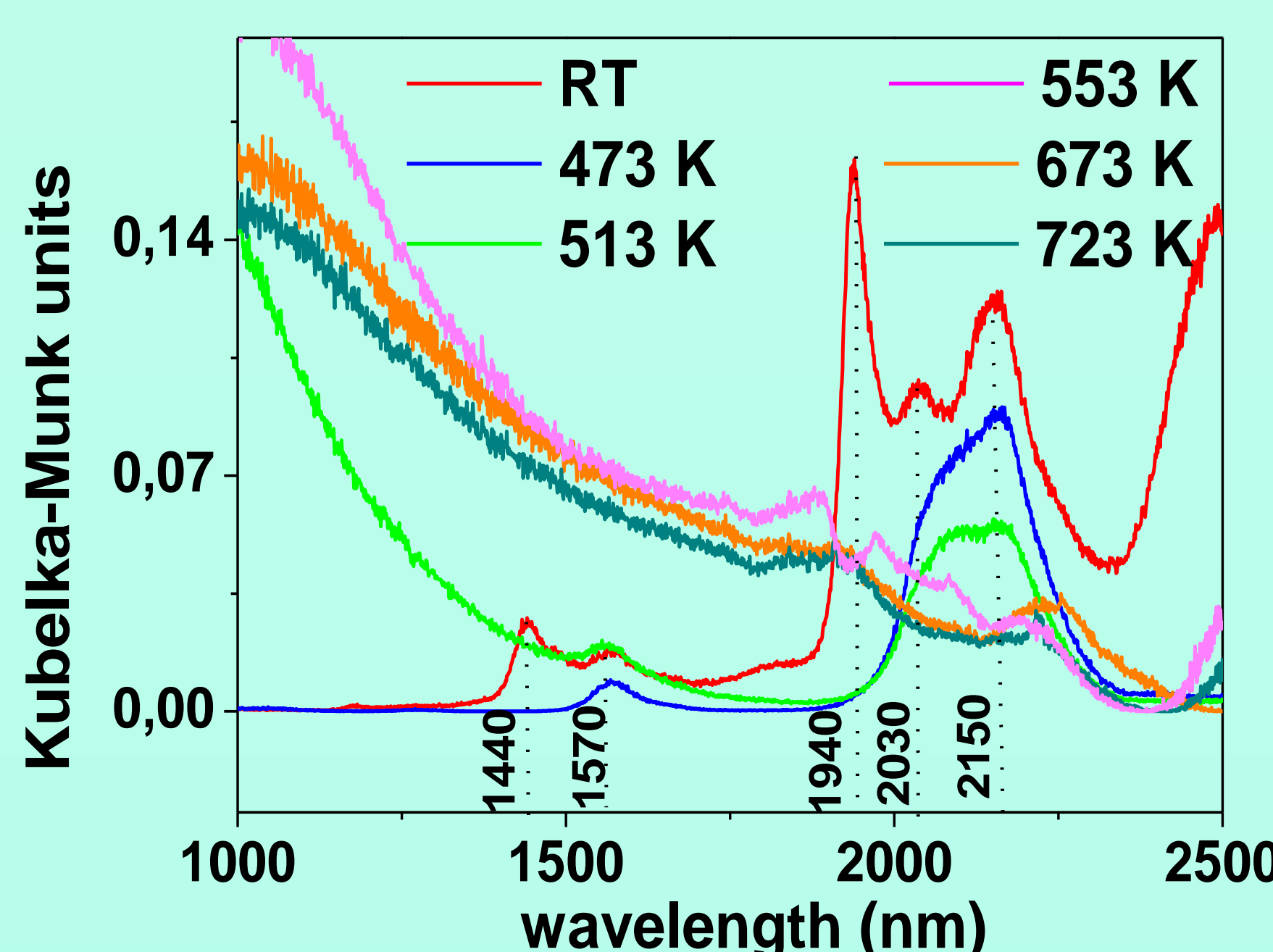
Spectra recorded from room temperature up to 673 K under flow of Helium

Spectra recorded from room temperature up to 749 K under flow of 21 % oxygen in Helium



High temperature spectroscopy

Supramolecular Mo<sub>36</sub> prepared from 0.7 mol/L AHM with 1 mol/L HNO<sub>3</sub> at 50°C



Spectra recorded from room temperature up to 723 K under flow of 21 % oxygen in Helium