

ELECTRONIC SUPPORTING INFORMATION

Thermogravimetric Analysis

Temp. Range (° C)	% wt. loss expt	% wt. loss calc	Assignment
0 – 250	6.92	6.78	Loss of 5 eq. H ₂ O
400 – 600	72.72	72.89	Loss of 2 eq. Re ₂ O ₇ UO ₂ remaining

TGA analysis for [U(ReO₄)₄].5H₂O (1)

Temp. Range (° C)	% wt. loss expt	% wt. loss calc	Assignment
0 – 250	5.79	5.82	Loss of 3 eq. CH ₃ CN
250 – 420	38.67	39.47	Loss of 3 eq. TPPO Mixed U & Re oxides remain

TGA analysis for [U(ReO₄)₄(TPPO)₃(CH₃CN)].2CH₃CN (5)

Temp. Range (° C)	% wt. loss expt	% wt. loss calc	Assignment
200 - 600	39.18	41.33	Loss of 4 eq. TBPO Mixed U & Re oxides remain

TGA analysis for [U(ReO₄)₄(TBPO)₄] (2)

Temp. Range (° C)	% wt. loss expt	% wt. Loss calc	Assignment
0 – 250	4.43	4.22	Loss of 2 eq. CH ₃ CN
300 - 700	46.29	39.47	Loss of DPPMO ₂ + Re ₂ O ₇ Mixed U & Re oxides remain

TGA analysis for [U(ReO₄)(DPPMO₂)₃(OH)][ReO₄]₂.2CH₃CN (6)

Temp. Range (° C)	% wt. Loss expt	% wt. Loss calc	Assignment
0 - 900	40.74	46.22	Loss of 4 eq. T ⁱ BP Mixed U & Re oxides remain

TGA analysis for [U(ReO₄)₄(TⁱBP)₄] (4)

Temp. Range (° C)	% wt. loss expt	% wt. loss calc	Assignment
150 - 900	35.72	37.0	Loss of 4 eq. TEP Mixed U & Re oxides remain

TGA analysis for [U(ReO₄)₄(TEP)₄] (3)

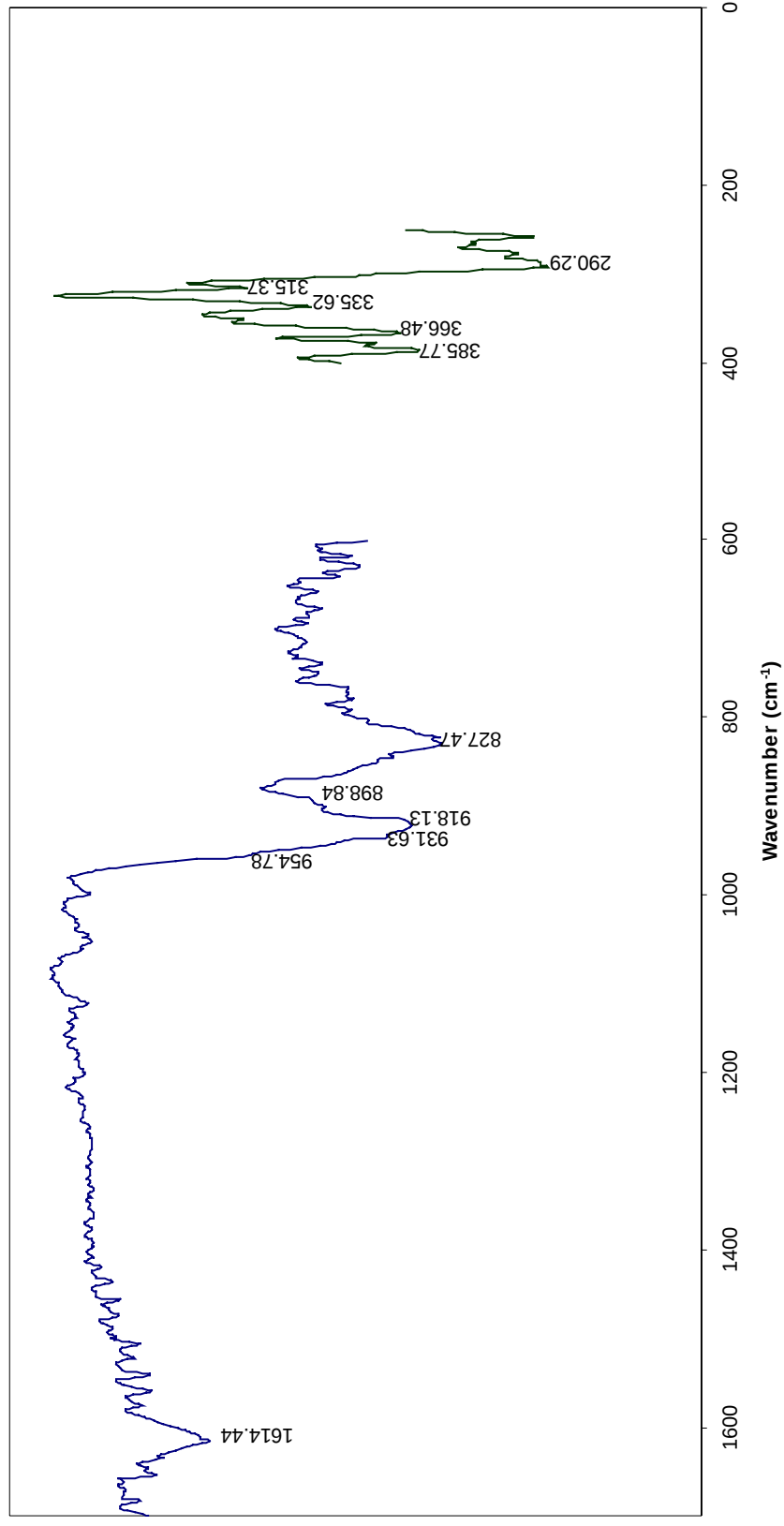
Space filling diagram of a portion of the lattice of $[\text{U}(\text{ReO}_4)_4(\text{TPPO})_3(\text{CH}_3\text{CN})]$ (5).

Packing diagram showing two molecules of **6** (left). Phenyl rings of DPPMO₂ ligands have been omitted for clarity. Space filling diagram of two molecules of **6** in the same orientation (right).

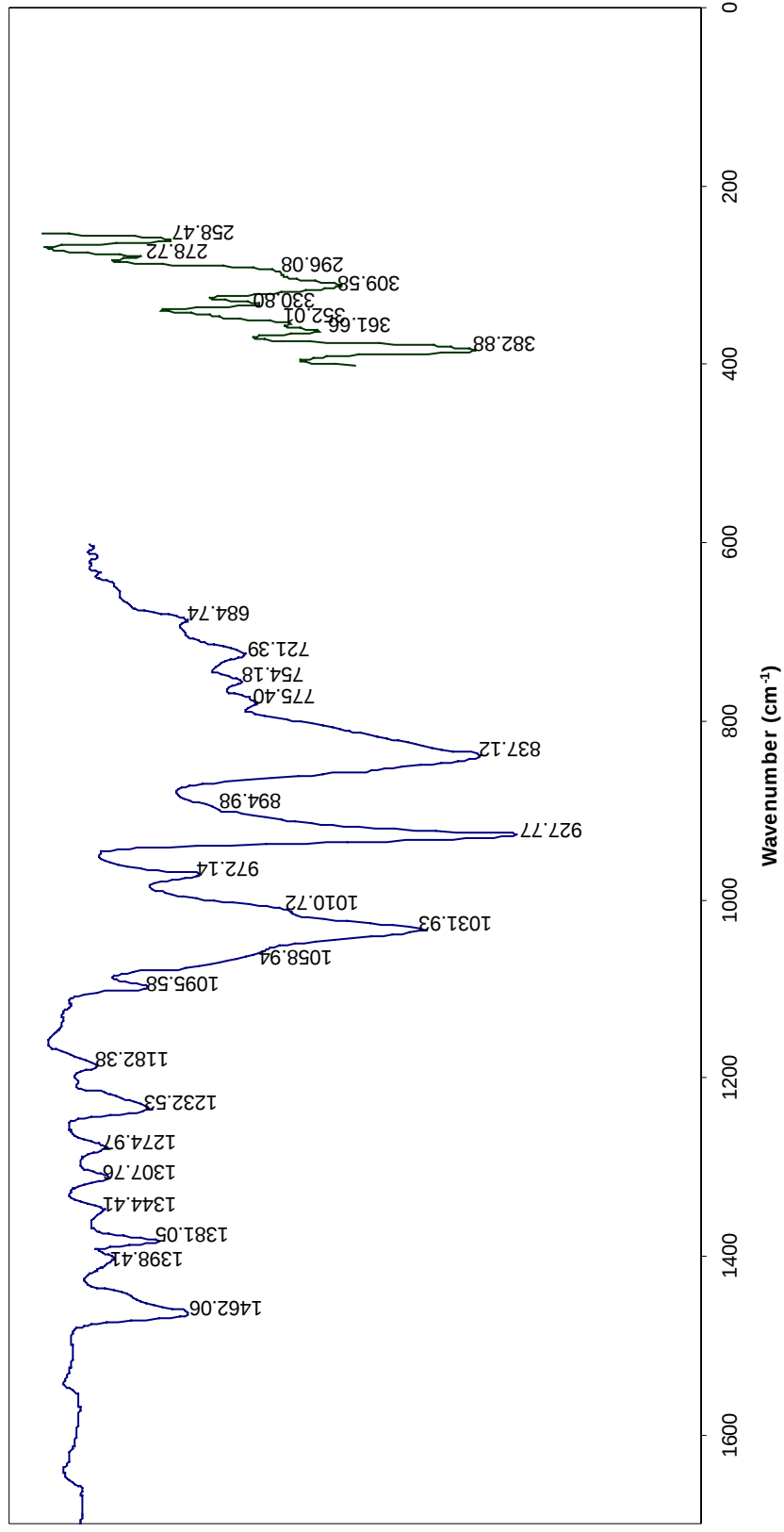
(a)

(b)

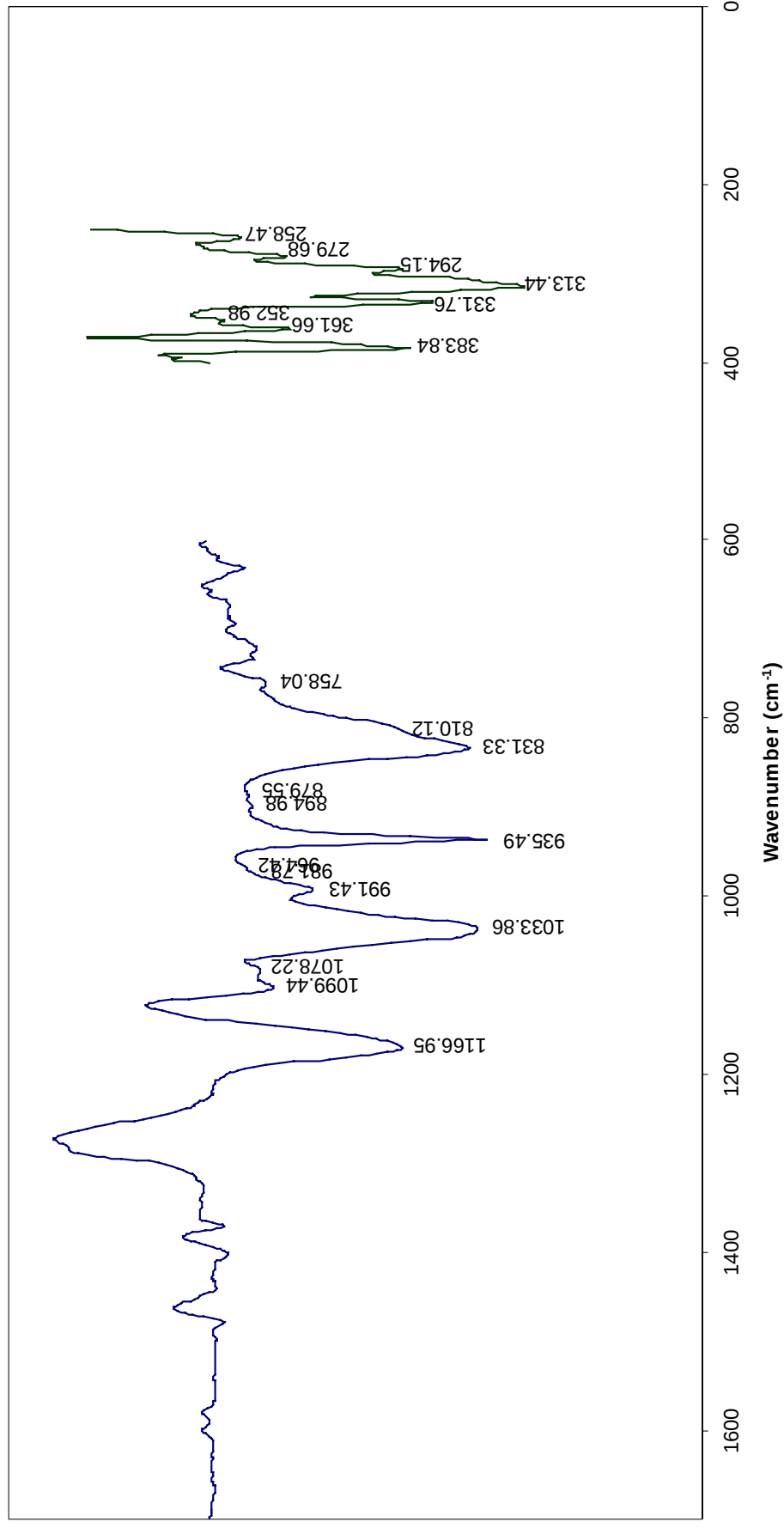
Mid- and far-infrared ATR (in transmission) spectra of solid $[\text{U}(\text{ReO}_4)_4] \cdot 6\text{H}_2\text{O}$ (**1**)



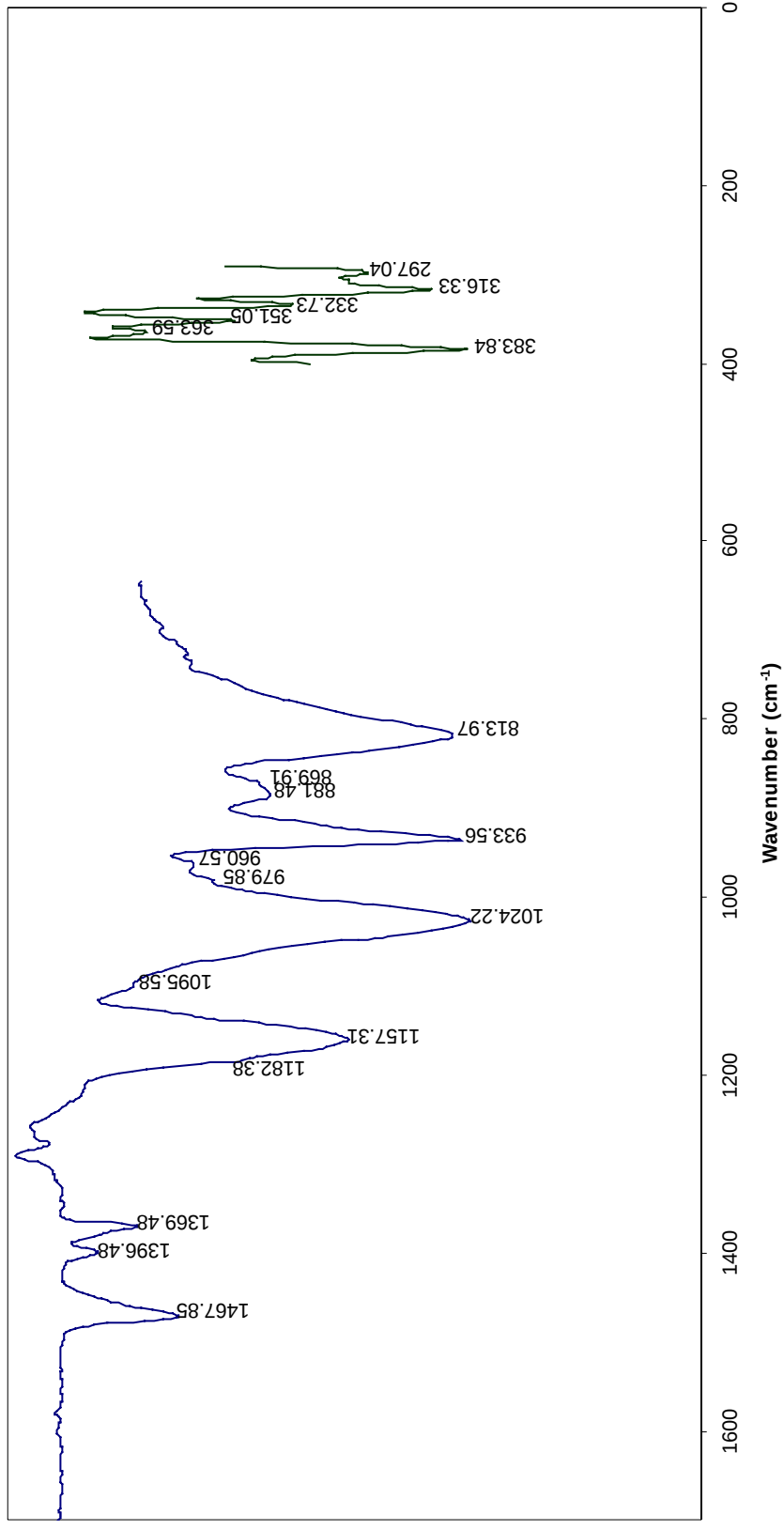
Mid- and far-infrared ATR (in transmission) spectra of solid $[\text{U}(\text{ReO}_4)_4(\text{TBPO})_4] \cdot (2)$



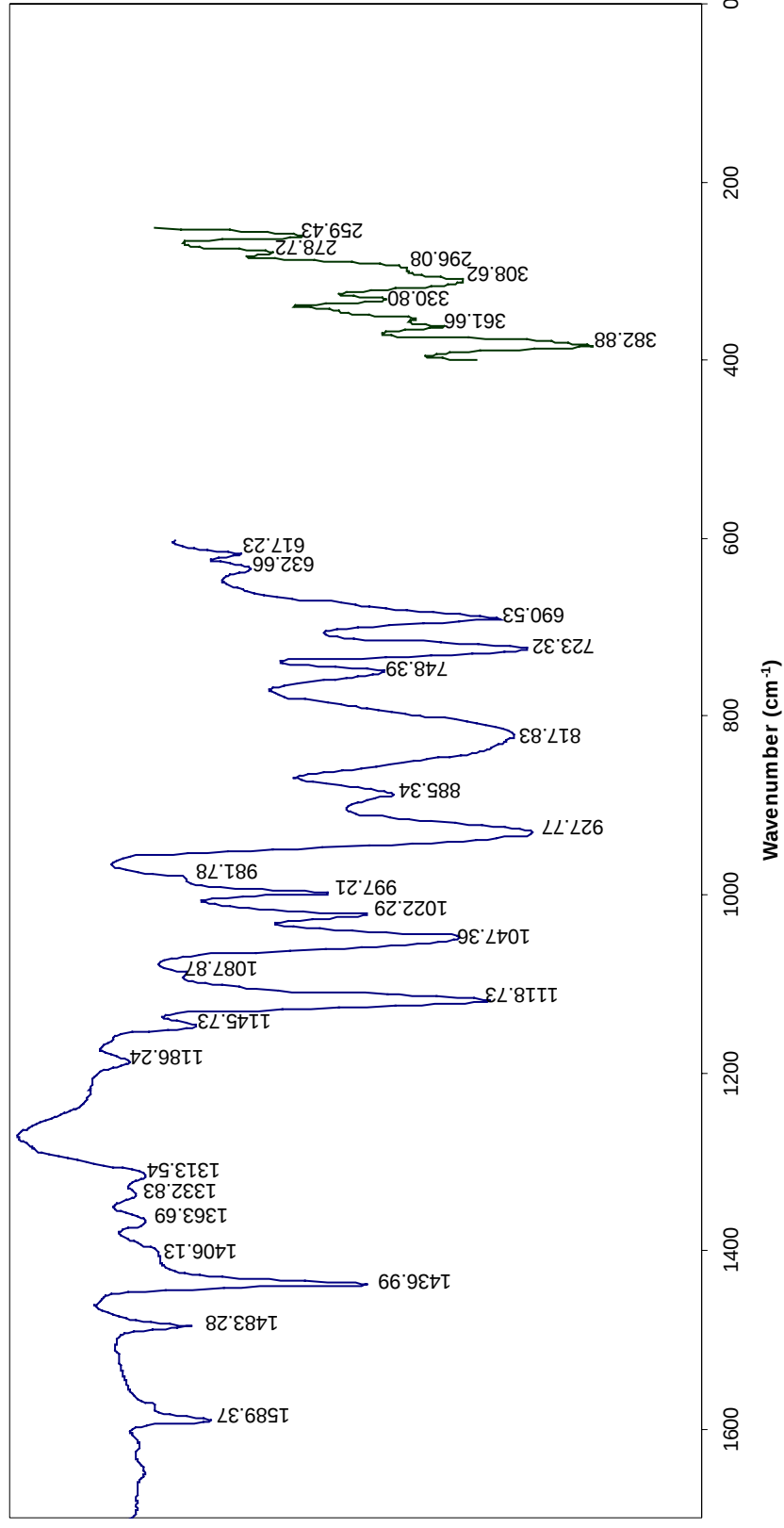
Mid- and far-infrared ATR (in transmission) spectra of solid $[\text{U}(\text{ReO}_4)_4(\text{TEP})_4]$ (3)



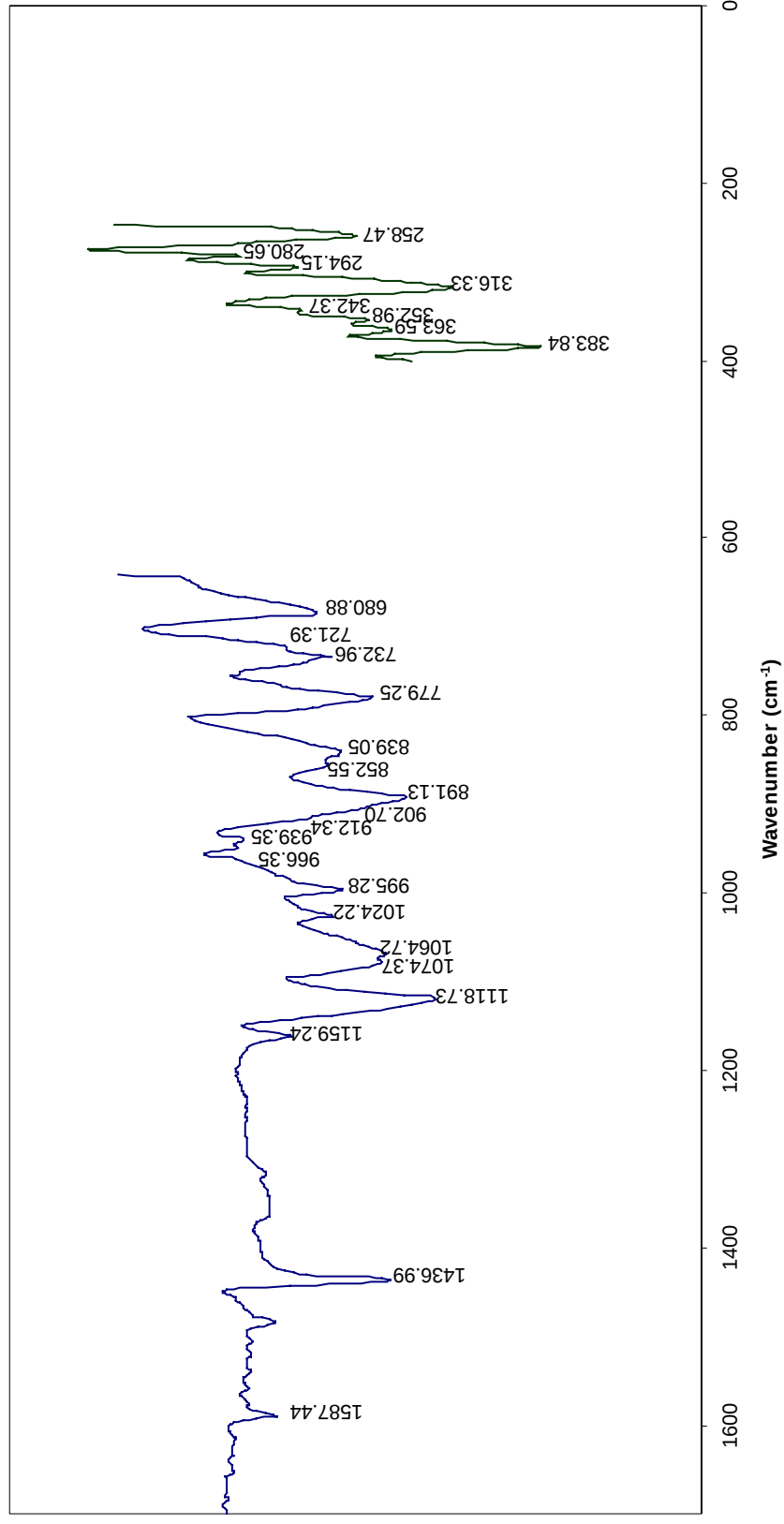
Mid- and far-infrared ATR (in transmission) spectra of solid $[\text{U}(\text{ReO}_4)_4(\text{TBP})_4]$ (**4**)



Mid- and far-infrared ATR (in transmission) spectra of solid $[\text{U}(\text{ReO}_4)_4(\text{TPPO})_3(\text{CH}_3\text{CN})]\cdot 2\text{CH}_3\text{CN}$ (**5**)



Mid- and far-infrared ATR (in transmission) spectra of solid $[\text{U}(\text{ReO}_4)(\text{DPPMO}_2)_3(\text{OH})](\text{ReO}_4)_2(\text{MeCN})_2$ (**6**)



P=O vibrations (cm^{-1}) in complexes **2–6** in comparison to the unbound ligand (solid state).

Compound	P=O Donor Ligand	Free Ligand	Coordinated Ligand
5	TPPO	1186	1047
2	TBPO	1155	1059
6	DPPMO ₂	1186	1064, 1074
4	T ⁱ BP	1280	1157
3	TEP	1260	1167

P=O donor ligand infrared vibrations for U^{IV} - perrhenato compounds (solid state).

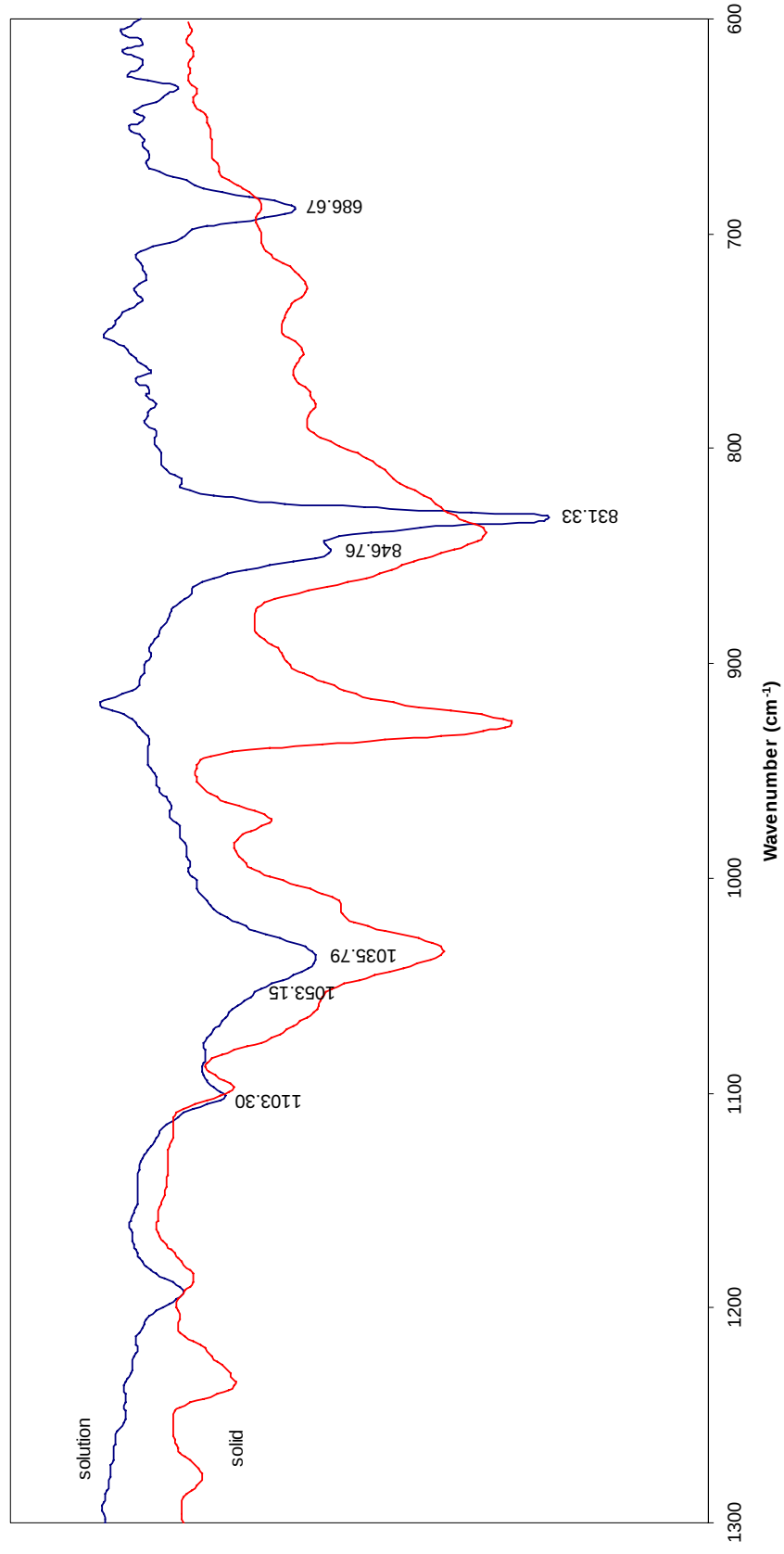
Compound	Vibrations (cm ⁻¹)
[U(ReO ₄) ₄ (TPPO) ₃ (CH ₃ CN)] (5)	1437, 1146, 1120, <u>1047</u> , 1022, 997, 818, 748, 732, 691
[U(ReO ₄) ₄ (TBPO) ₄] (2)	1462, 1233, 1096, <u>1059</u> , 1032, 1011, 837, 775
[U(ReO ₄)(DPPMO ₂) ₃ (OH)][ReO ₄] ₂ (6)	1437, 1159, 1119, <u>1074</u> , <u>1065</u> , 1024, 995, 853, 839, 779, 733, 721, 681
[U(ReO ₄) ₄ (T ⁱ BP) ₄] (4)	1468, 1369, 1182, <u>1157</u> , 1096, 1024, 814
[U(ReO ₄) ₄ (TEP) ₄] (3)	<u>1167</u> , 1099, 1078, 1034, 991, 831, 810, 758

NOTE: P=O stretch vibrations are underlined.

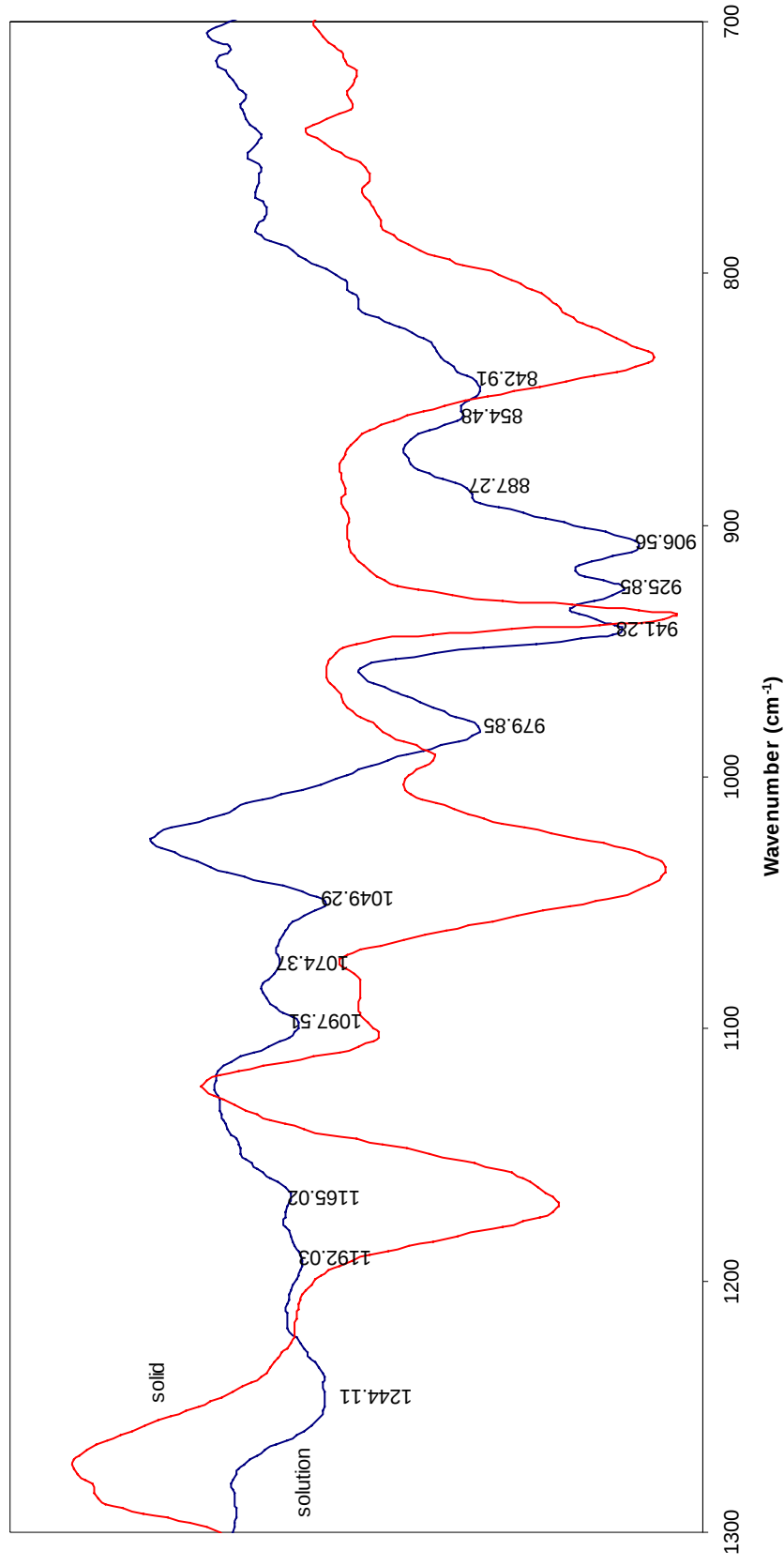
Re=O infrared vibrations (cm^{-1}) for U^{IV} perrhenate compounds **1** to **6** (solid state).

	$[\text{U}(\text{ReO}_4)_4 \cdot \text{H}_2\text{O}]$ (1)	$[\text{U}(\text{ReO}_4)_4(\text{TPPO})_3(\text{CH}_3\text{CN})]$ (5)	$[\text{U}(\text{ReO}_4)_4(\text{TBPO})_4]$ (2)	$[\text{U}(\text{ReO}_4)(\text{DPPMO}_2)_3(\text{OH})][\text{ReO}_4]_2$ (6)	$[\text{U}(\text{ReO}_4)_4(\text{TiBP})_4]$ (4)	$[\text{U}(\text{ReO}_4)_4(\text{TEP})_4]$ (3)
ν_1	955 (sh)	982 (sh)	972 (w)	966 (sh)	980 (vw)	982 (w)
ν_2	335(w)	331 (w)	331 (w)	342 (w)	333 (w)	332 (m)
ν_3	945 (sh) 932 (sh) 918 (s) 898 (sh)	928 (s) 885 (m)	928 (s) 895 (sh)	912 (sh) 903 (sh) 891 (s)	934 (s) 881 (w) 871 (w)	935 (s) 895 (vw) 881 (vw)
ν_4	315 (w) 290 (m)	309 (s) 296 (sh)	310 (w) 296 (sh)	316 (s) 294(w)	316 (s) 297 (w)	313 (m) 294 (w)
NOTE: (s) sharp; (m) medium; (w) weak; (vw) very weak; (sh) shoulder						

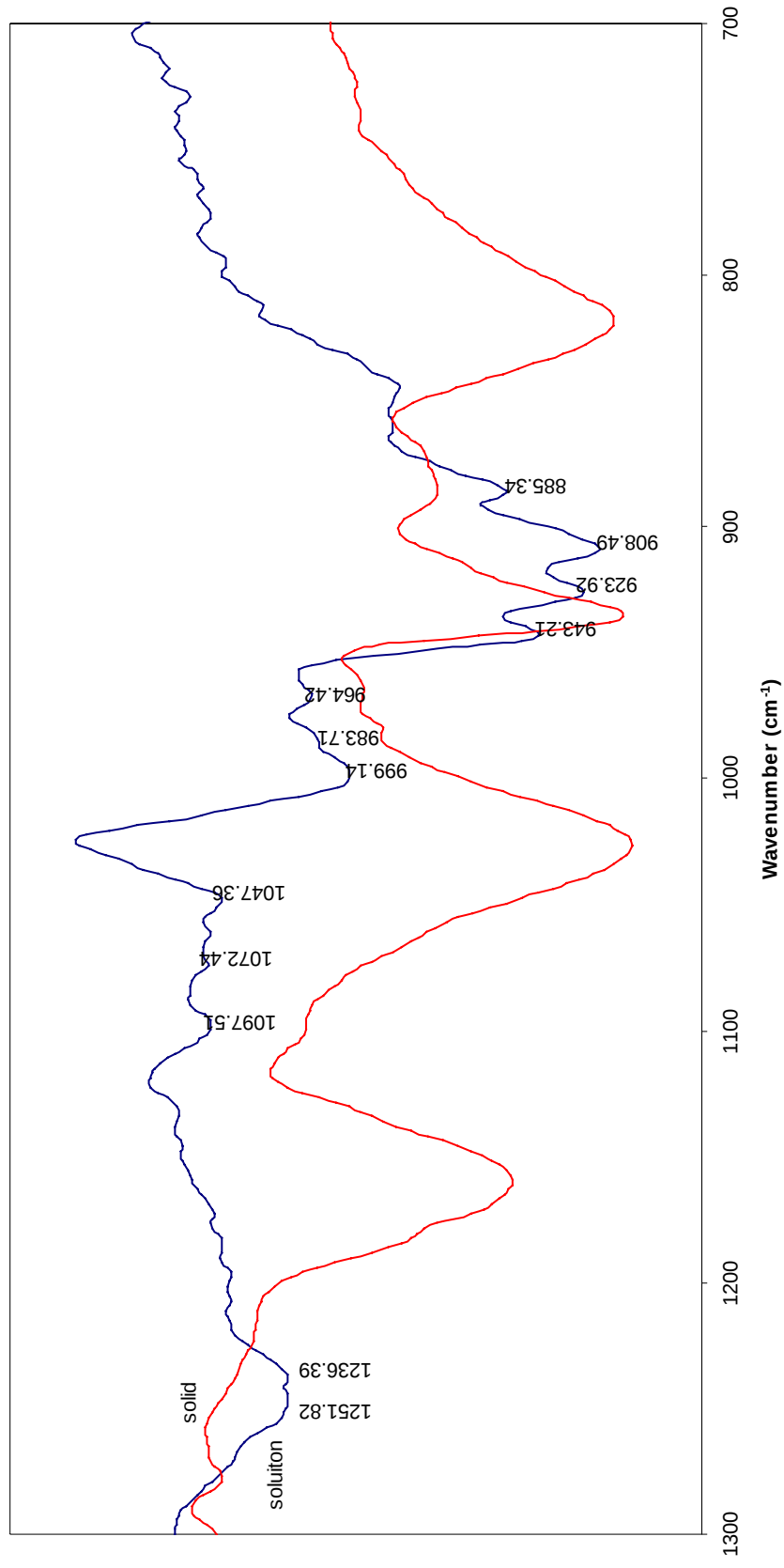
Mid-infrared ATR (in transmission) of $[\text{U}(\text{ReO}_4)_4(\text{TBPO})_4] \cdot (2)$ dissolved in MeCN (blue) and in solid state (red).



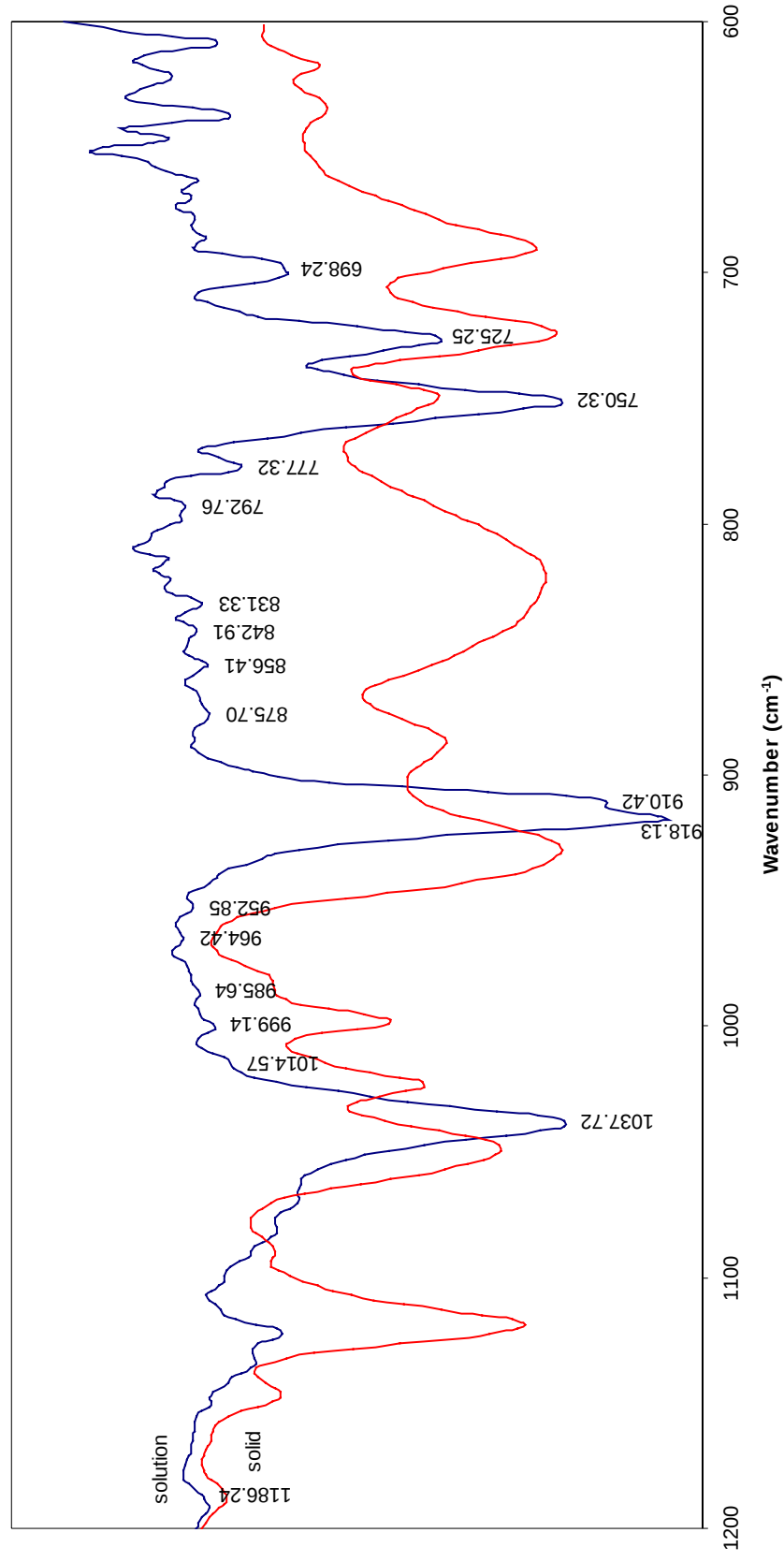
Mid-infrared ATR (in transmission) of $[\text{U}(\text{ReO}_4)_4(\text{TEP})_4]$ (**3**) dissolved in MeOH (blue) and in solid state (red).



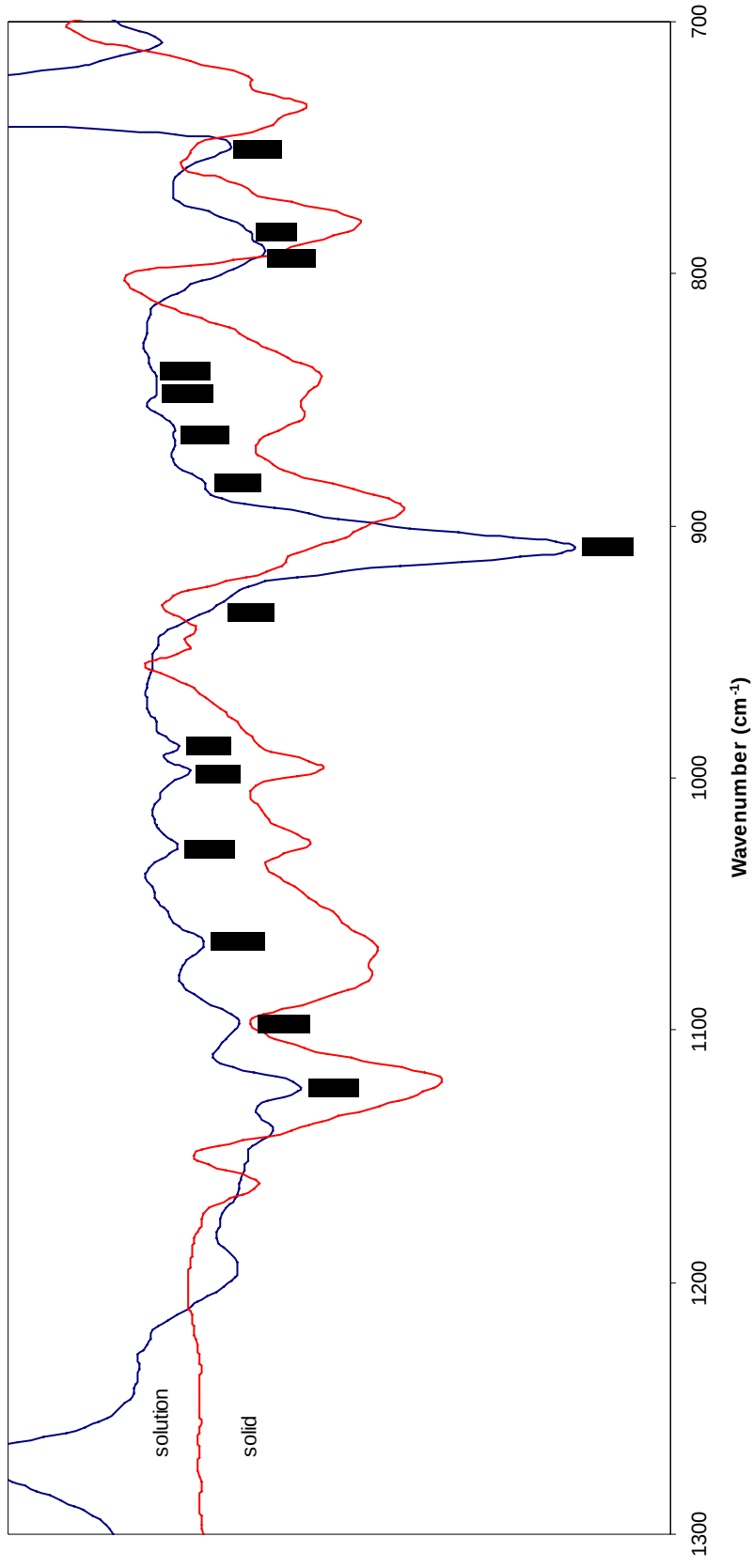
Mid-infrared ATR (in transmission) of $[\text{U}(\text{ReO}_4)_4(\text{TiBP})_4]$ (**4**) dissolved in MeOH (blue) and in solid state (red).



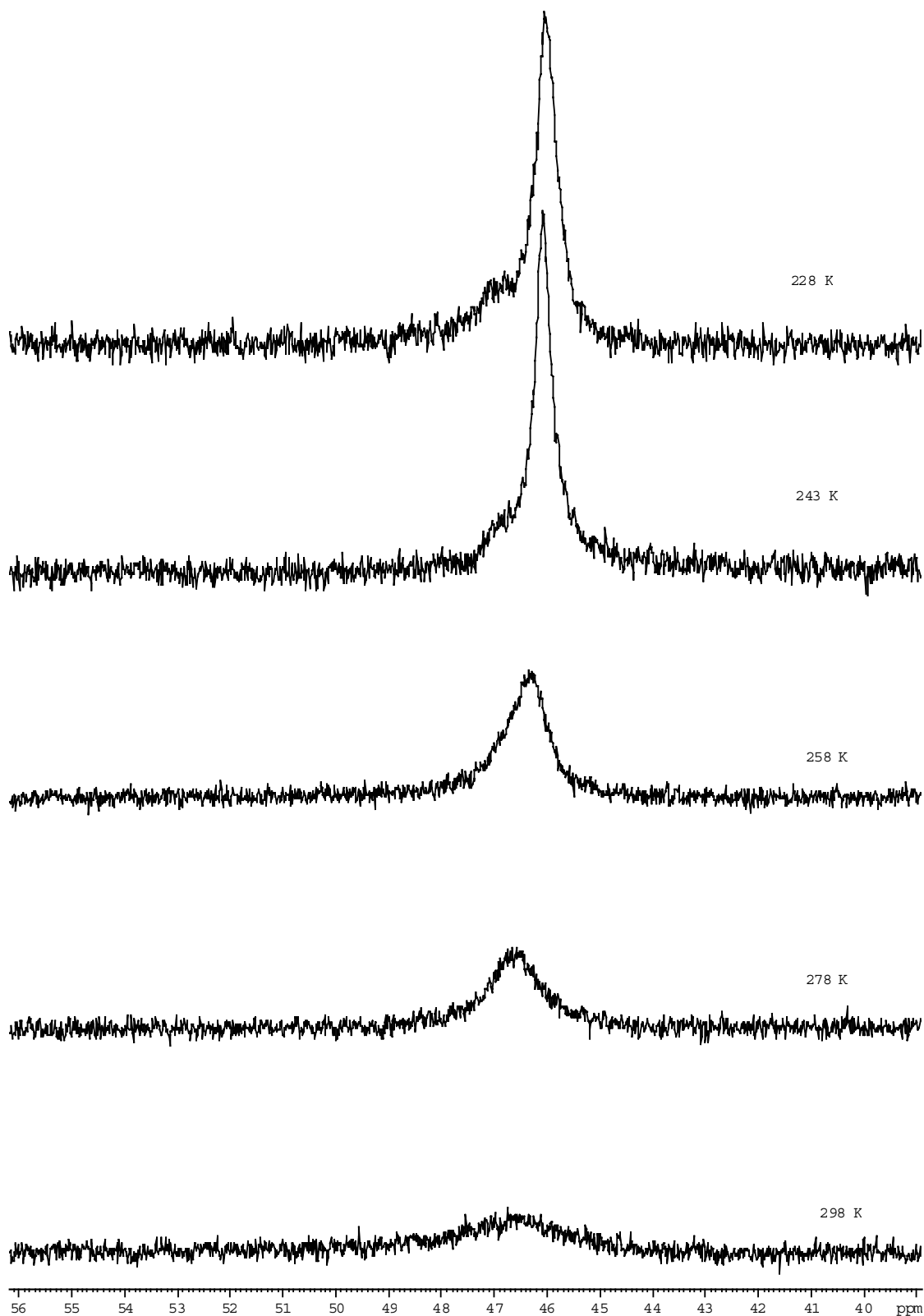
Mid-infrared ATR (in transmission) of $[\text{U}(\text{ReO}_4)_4(\text{TPPO})_3(\text{CH}_3\text{CN})] \cdot 2\text{CH}_3\text{CN}$ (5) dissolved in MeCN (blue) and in solid state (red).



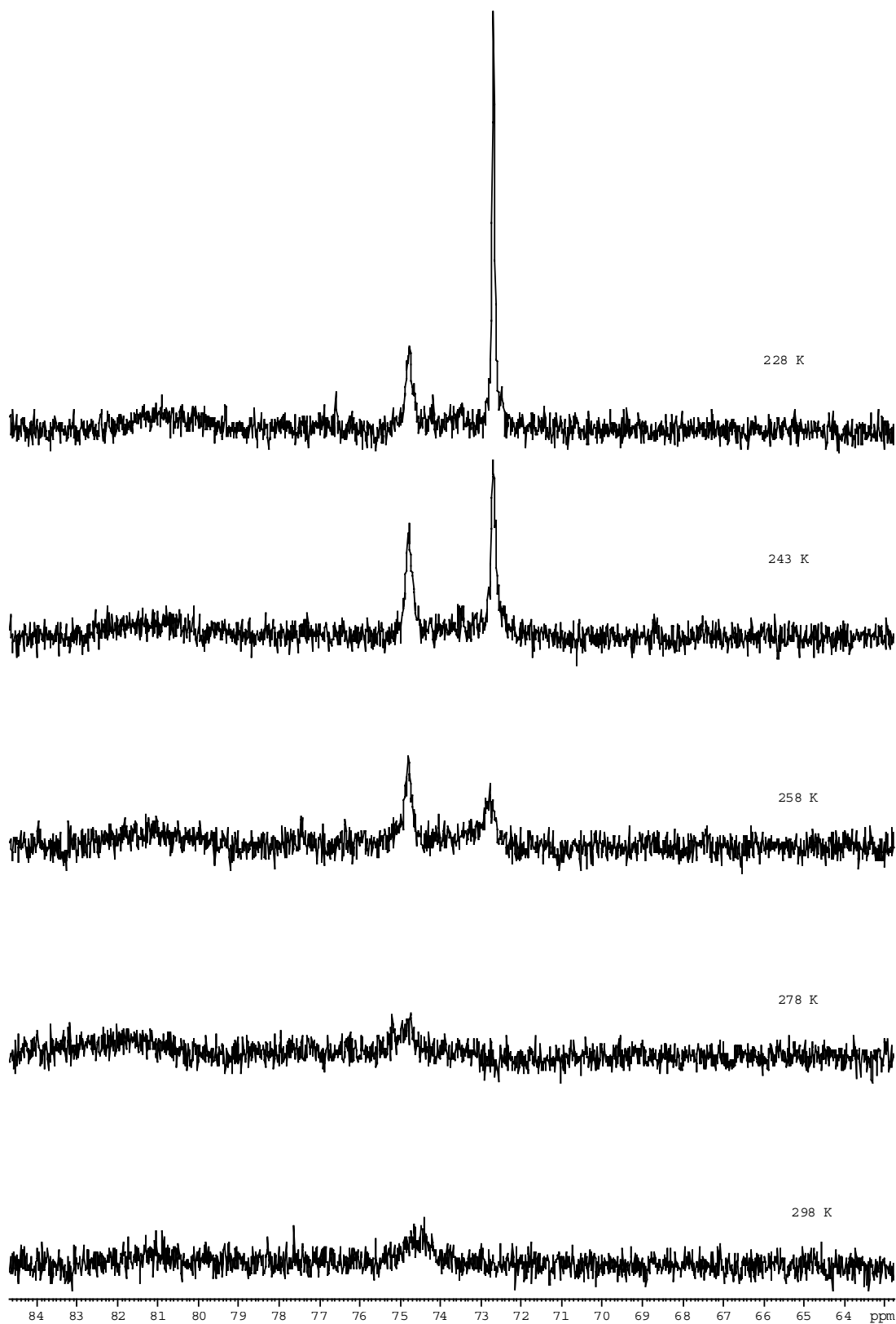
Mid-infrared ATR (in transmission) of $[\text{U}(\text{ReO}_4)(\text{DPPMO}_2)_3(\text{OH})](\text{ReO}_4)_2(\text{MeCN})_2$ (**6**) dissolved in pyridine (blue) and in solid state (red).



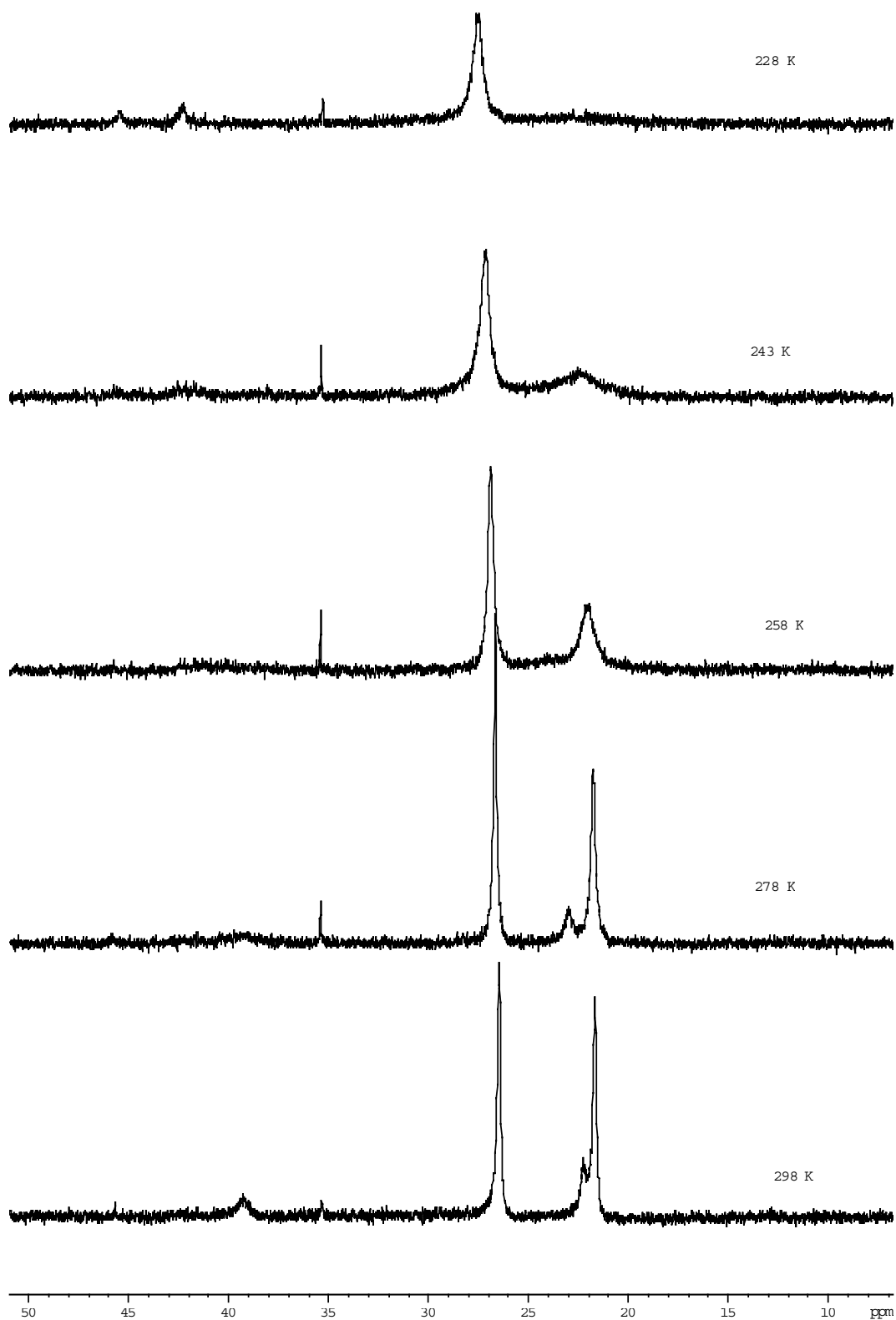
Solution state variable temperature (228-298 K) ^{31}P NMR spectra (162 MHz, 256 scans) for $[\text{U}(\text{ReO}_4)_4(\text{TPPO})_3(\text{CH}_3\text{CN})].2\text{CH}_3\text{CN}$ (5) in MeOD.



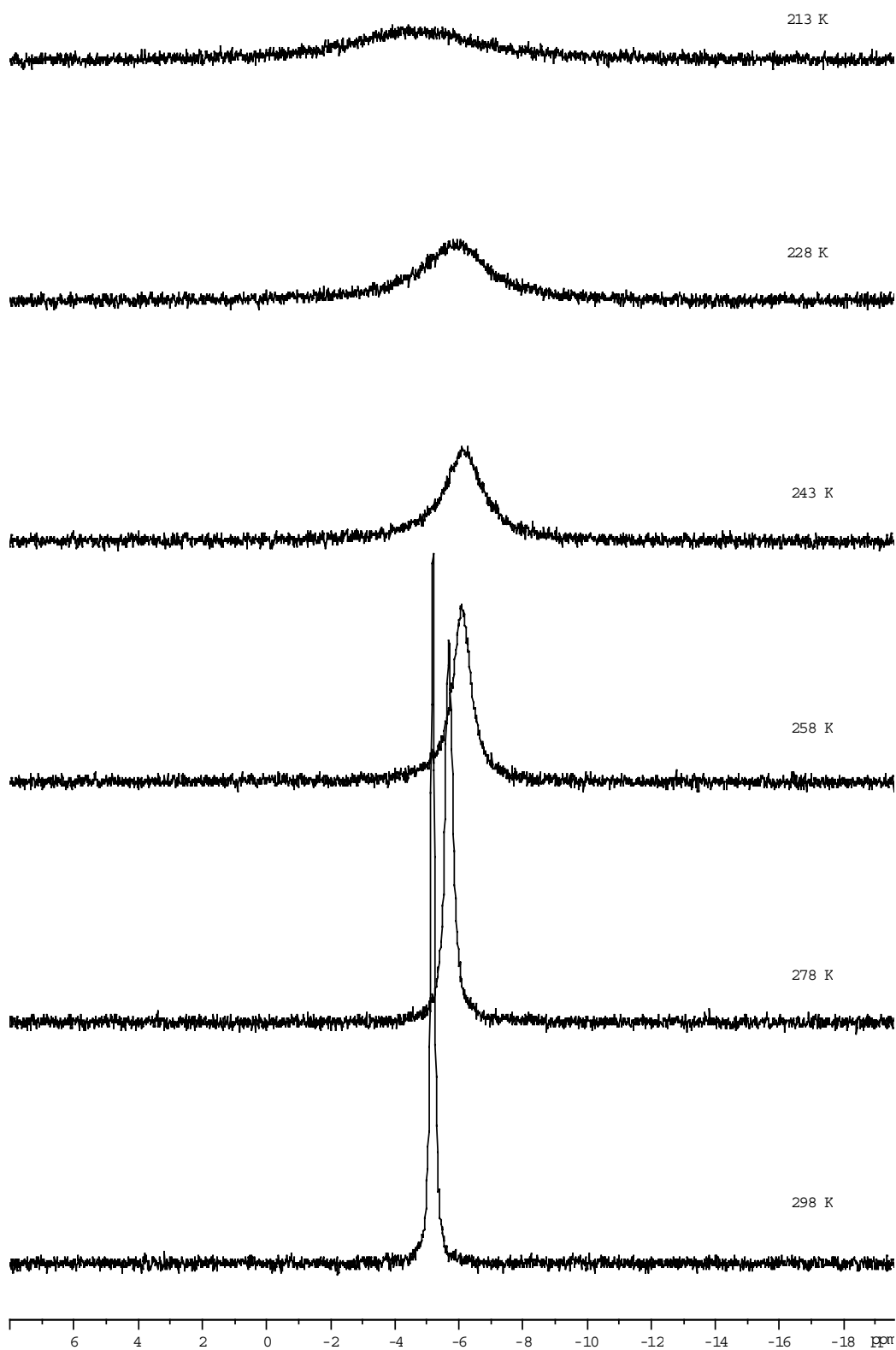
Solution state variable temperature (228-298 K) ^{31}P NMR spectra (162 MHz, 256 scans)
for $[\text{U}(\text{ReO}_4)_4(\text{TBPO})_4]$ (**2**) in CD_3CN .



Solution state variable temperature (228-298 K) ^{31}P NMR spectra (162 MHz, 16 scans) for $[\text{U}(\text{ReO}_4)(\text{DPPMO}_2)_3(\text{OH})][\text{ReO}_4]_2(\text{MeCN})_2$ (**6**) in pyridine.



Solution state variable temperature (213 -298 K) ^{31}P NMR spectra (162 MHz, 16 scans) for $[\text{U}(\text{ReO}_4)_4(\text{T}^i\text{BP})_4]$ (**4**) in MeOD.



Solution state variable temperature (213-298 K) ^{31}P NMR spectra (162 MHz, 16 scans) for $[\text{U}(\text{ReO}_4)_4(\text{TEP})_4]$ (**3**) in MeOD.

