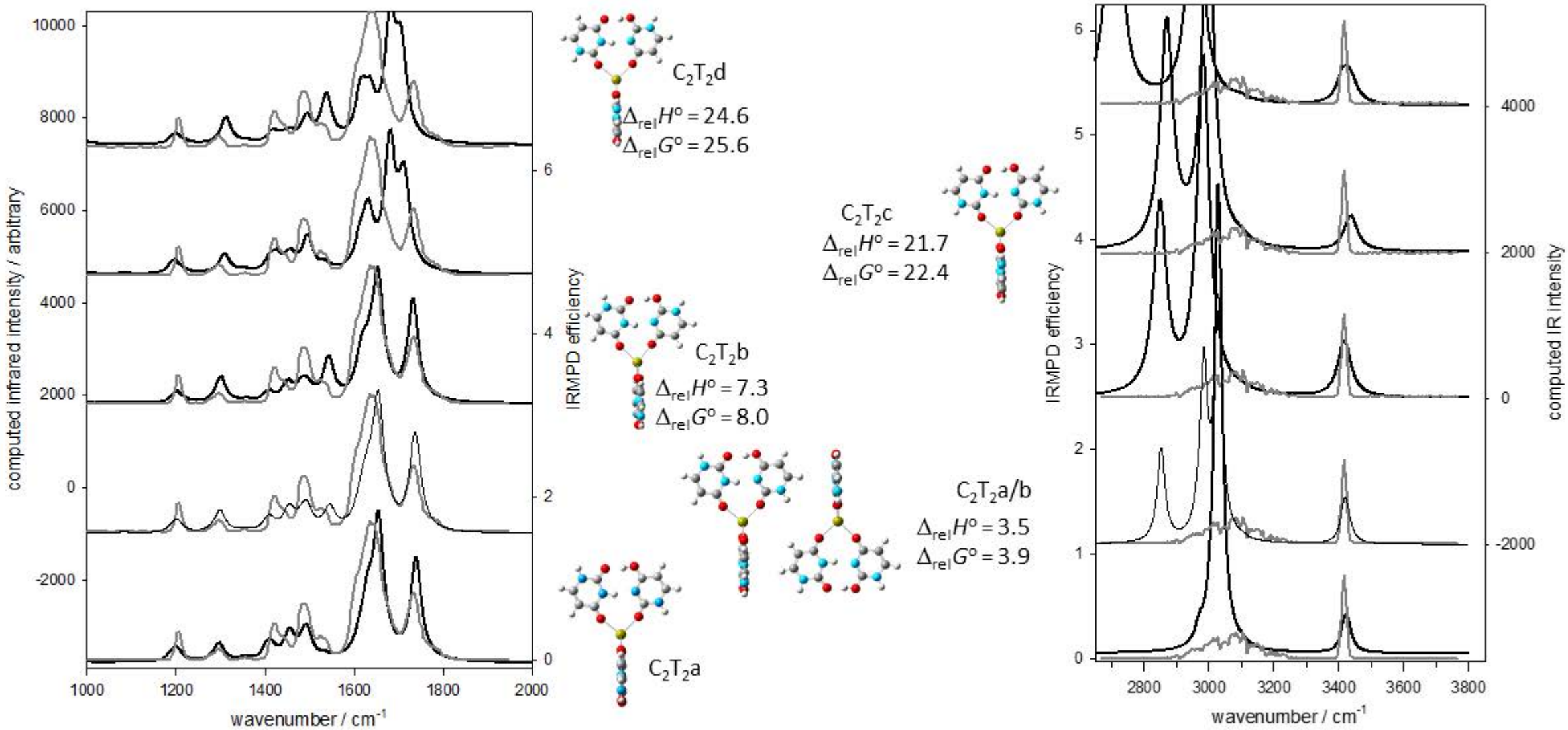
Electronic Supplementary Material (ESI) for Physical Chemistry Chemical Physics.

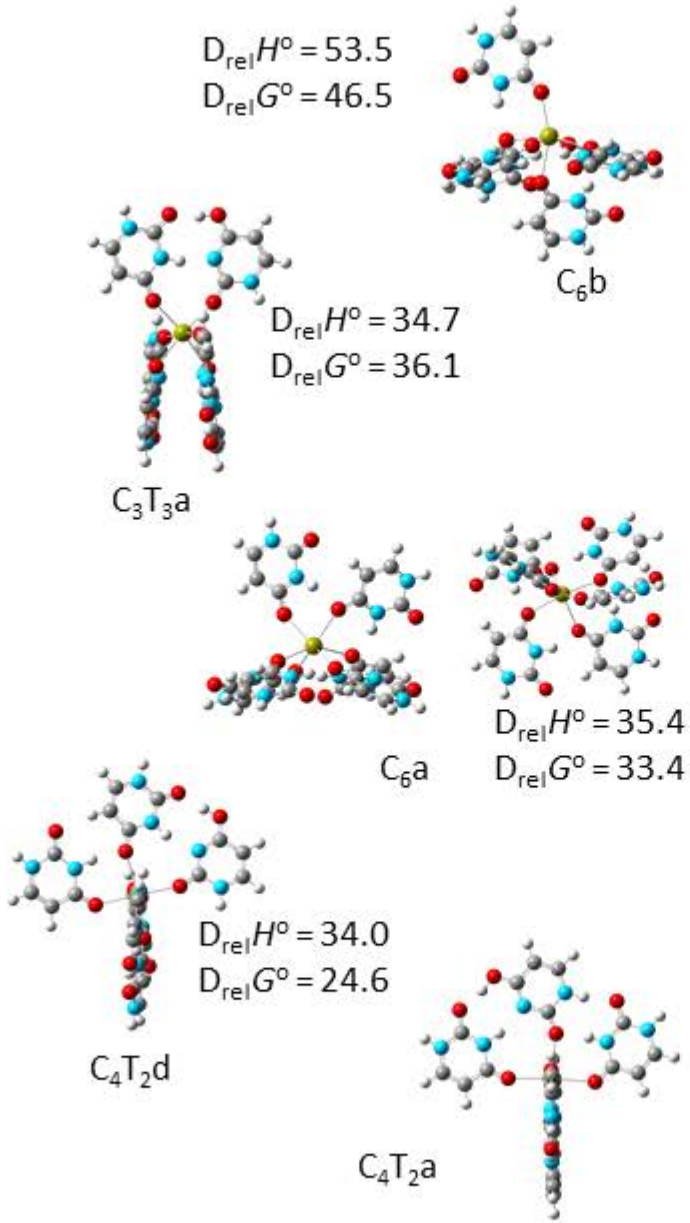
Figure S1



Comparison of the experimental IRMPD spectrum (grey trace) for U_4Ca^{2+} and the B3LYP/6-31+G(d,p) computed IR spectra (black traces) for five different isomers. The 298 K enthalpies and Gibbs energies relative to structure C_2T_2a are also shown (also computed using B3LYP/6-31+G(d,p)).

Figure S2

Comparison of the experimental IRMPD spectrum in the C-H/N-H/O-H stretch region (grey trace) for U_6Ca^{2+} and the B3LYP/6-31+G(d,p) computed IR spectra (black traces) for five different isomers. The 298 K enthalpies and Gibbs energies relative to structure C_4T_2a are also shown (also computed using B3LYP/6-31+G(d,p)). The experimental spectrum is complimentary to that in the fingerprint region seen in Figure 3.



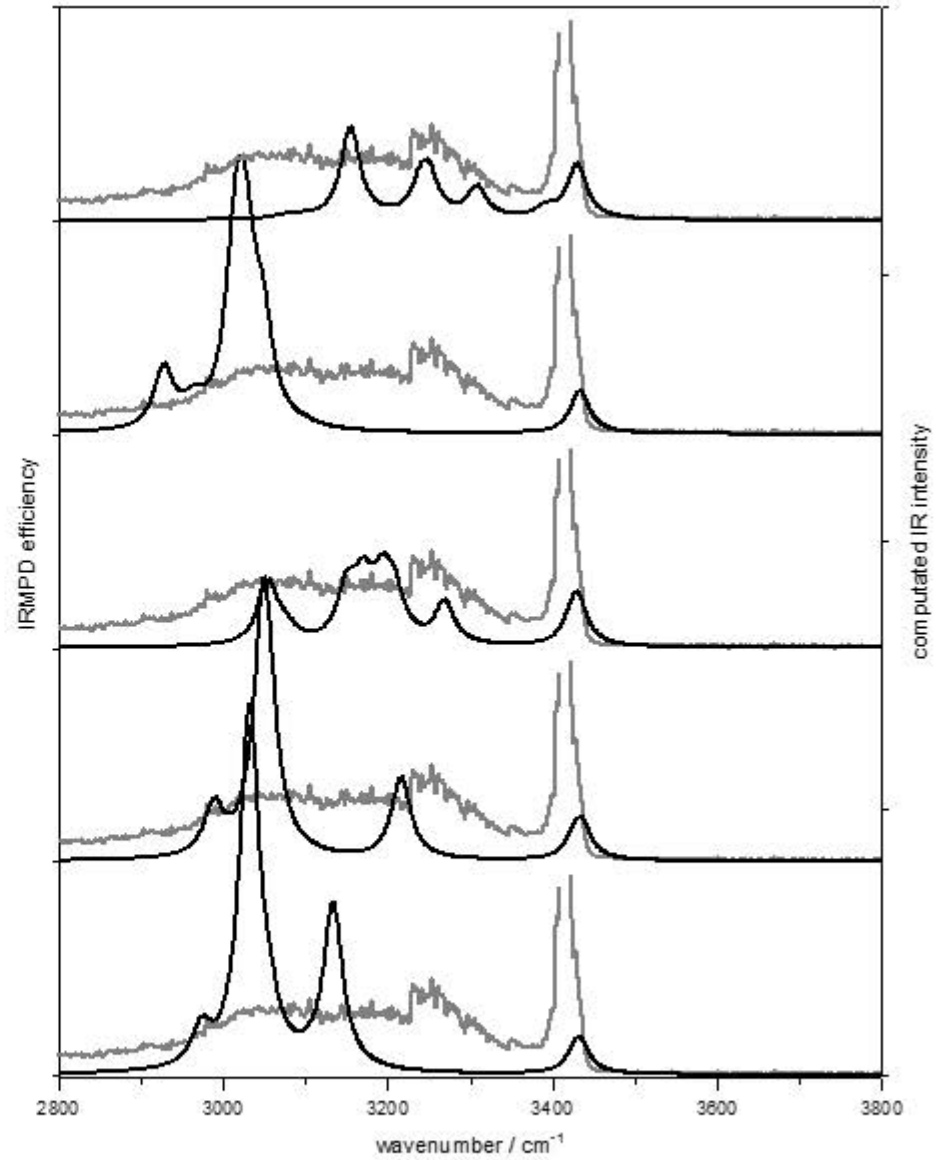
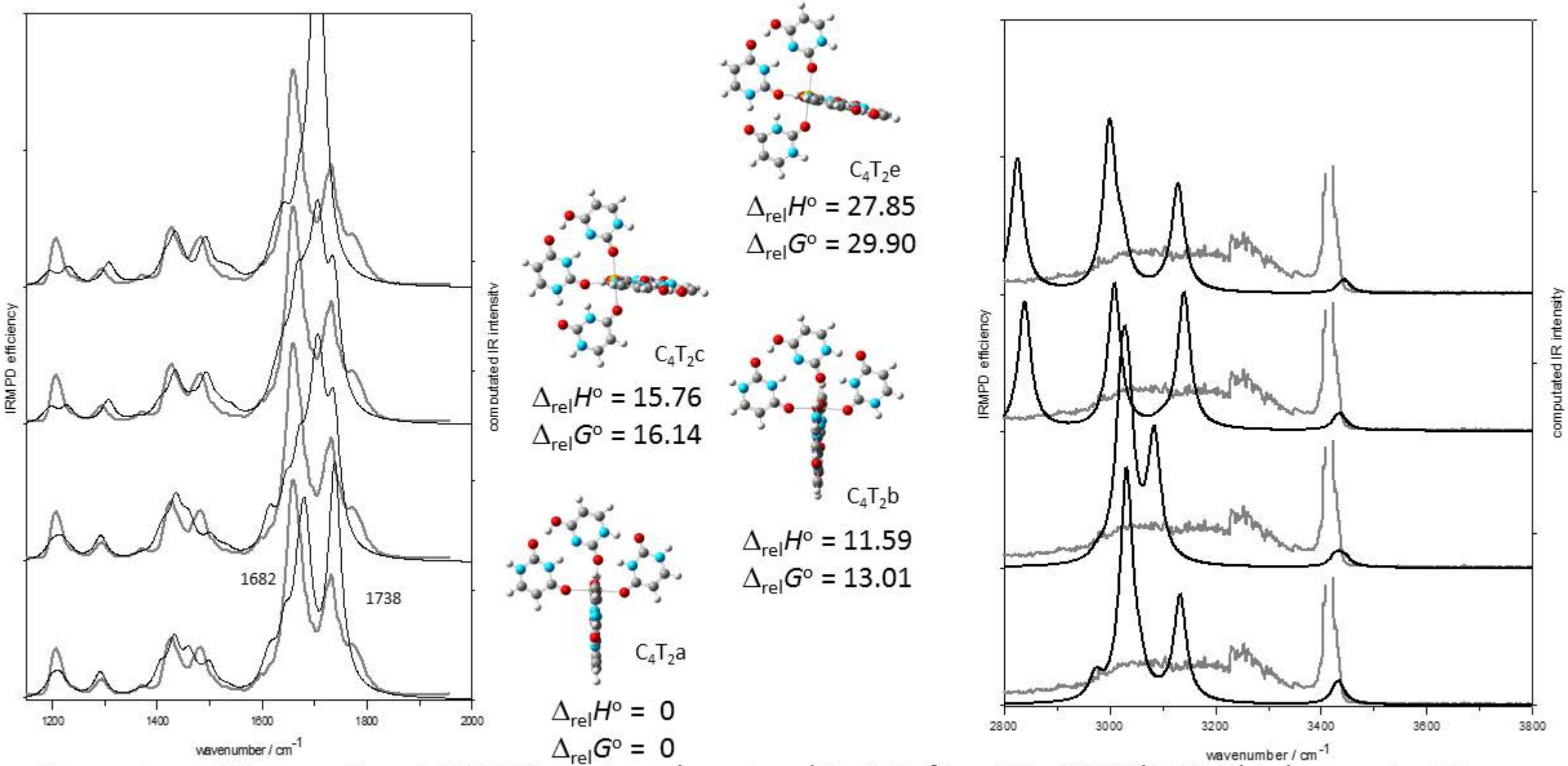
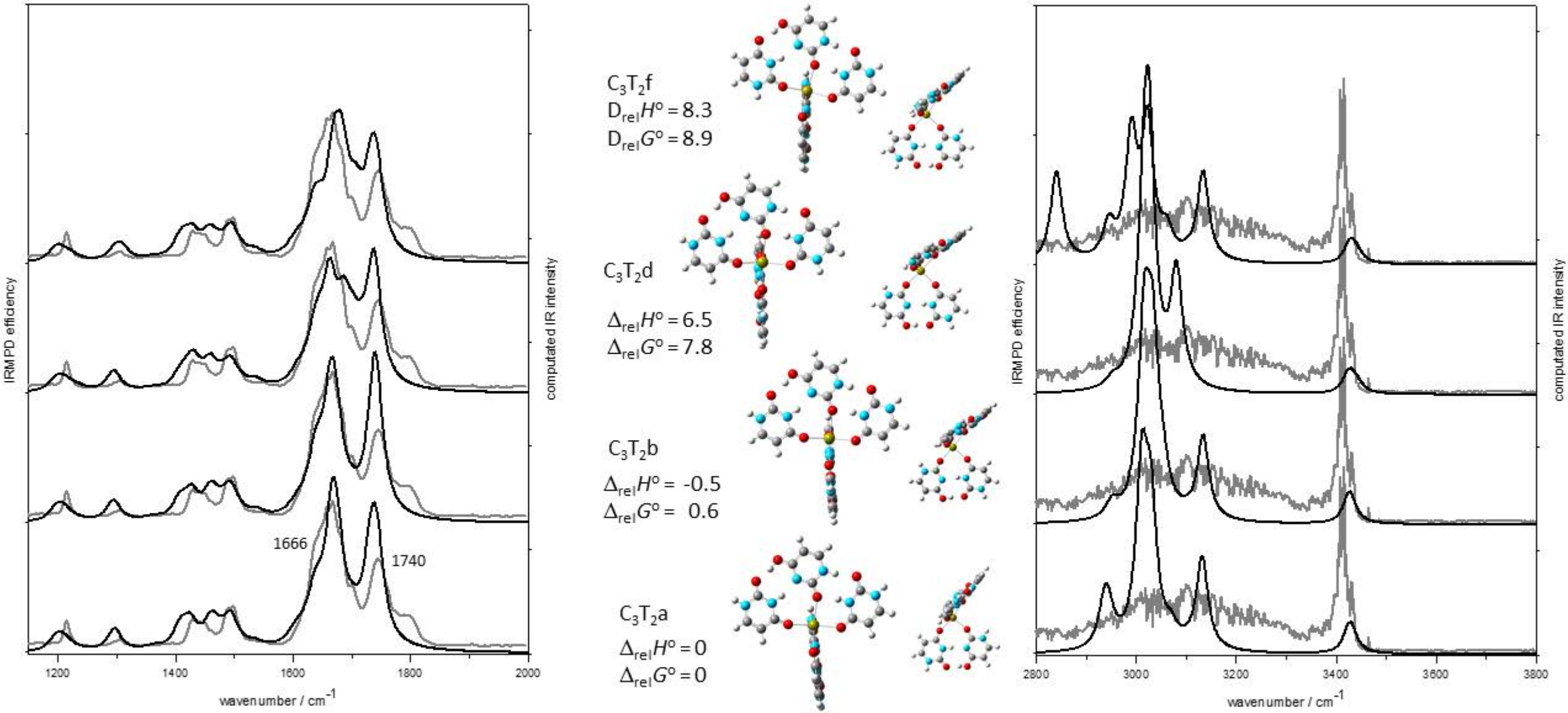


Figure S3



Comparison of the experimental IRMPD spectrum (grey trace) for U_6Ca^{2+} and the B3LYP/6-31+G(d,p) computed IR spectra (black traces) for four different isomers. The 298 K enthalpies and Gibbs energies relative to structure C_4T_2a are also shown (also computed using B3LYP/6-31+G(d,p)).

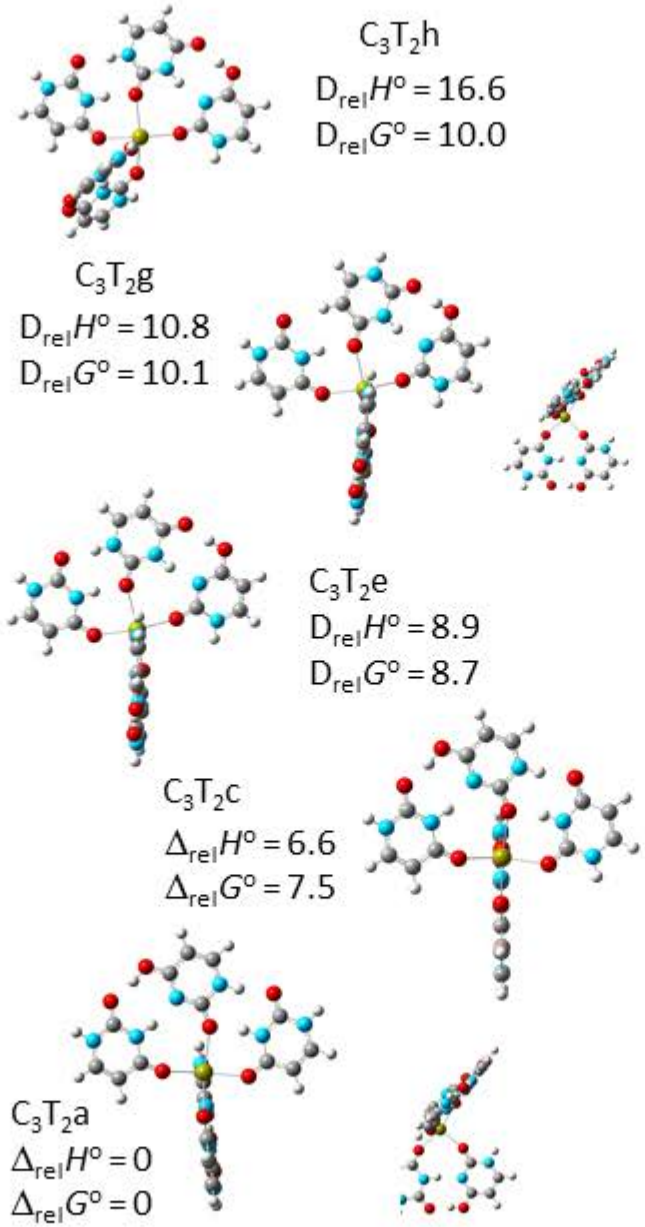
Figure S4



Comparison of the experimental IRMPD spectrum (grey trace) for U_5Ca^{2+} and the B3LYP/6-31+G(d,p) computed IR spectra (black traces) for four different isomers. The 298 K enthalpies and Gibbs energies relative to structure C_3T_2a are also shown (also computed using B3LYP/6-31+G(d,p)).

Figure S5

Comparison of the experimental IRMPD spectrum in the C-H/N-H/O-H stretch region (grey trace) for U_5Ca^{2+} and the B3LYP/6-31+G(d,p) computed IR spectra (black traces) for five different isomers. The 298 K enthalpies and Gibbs energies relative to structure C_3T_2a are also shown (also computed using B3LYP/6-31+G(d,p)). The experimental spectrum is complimentary to that in the fingerprint region seen in Figure 4.



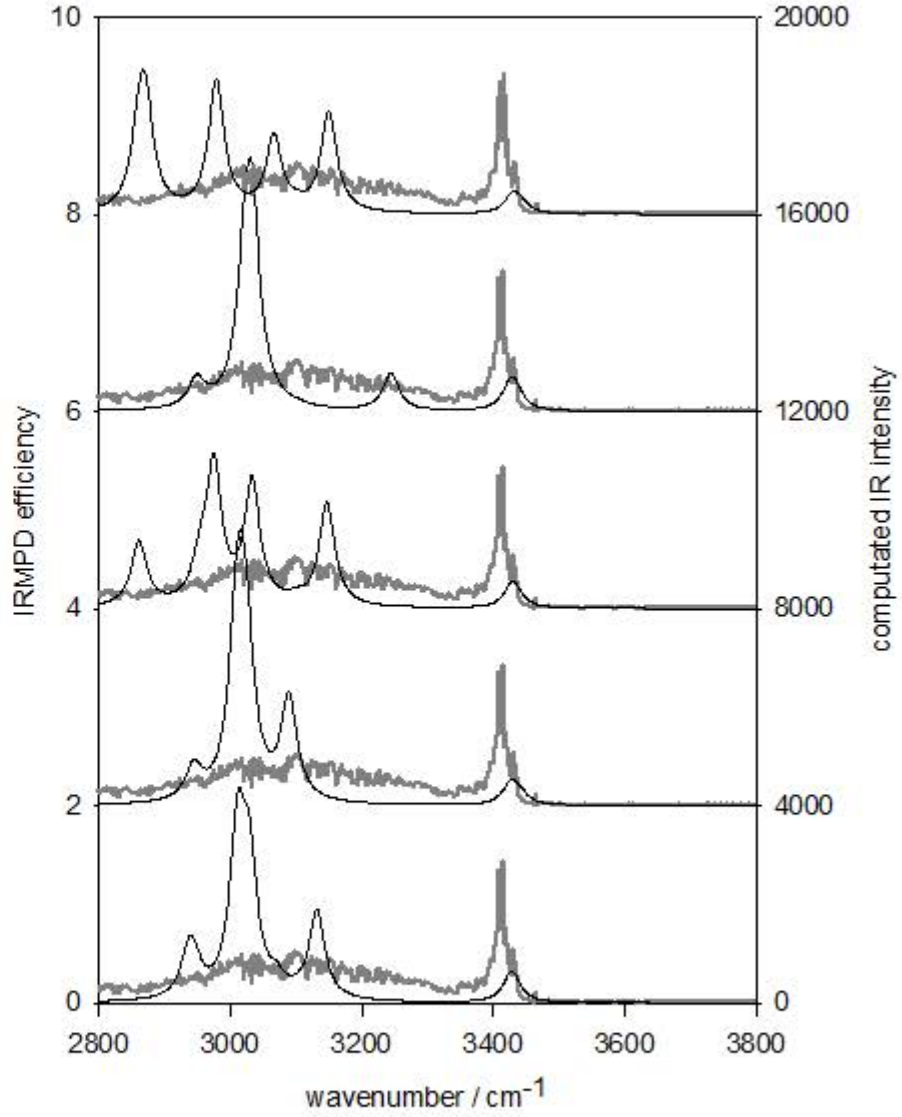
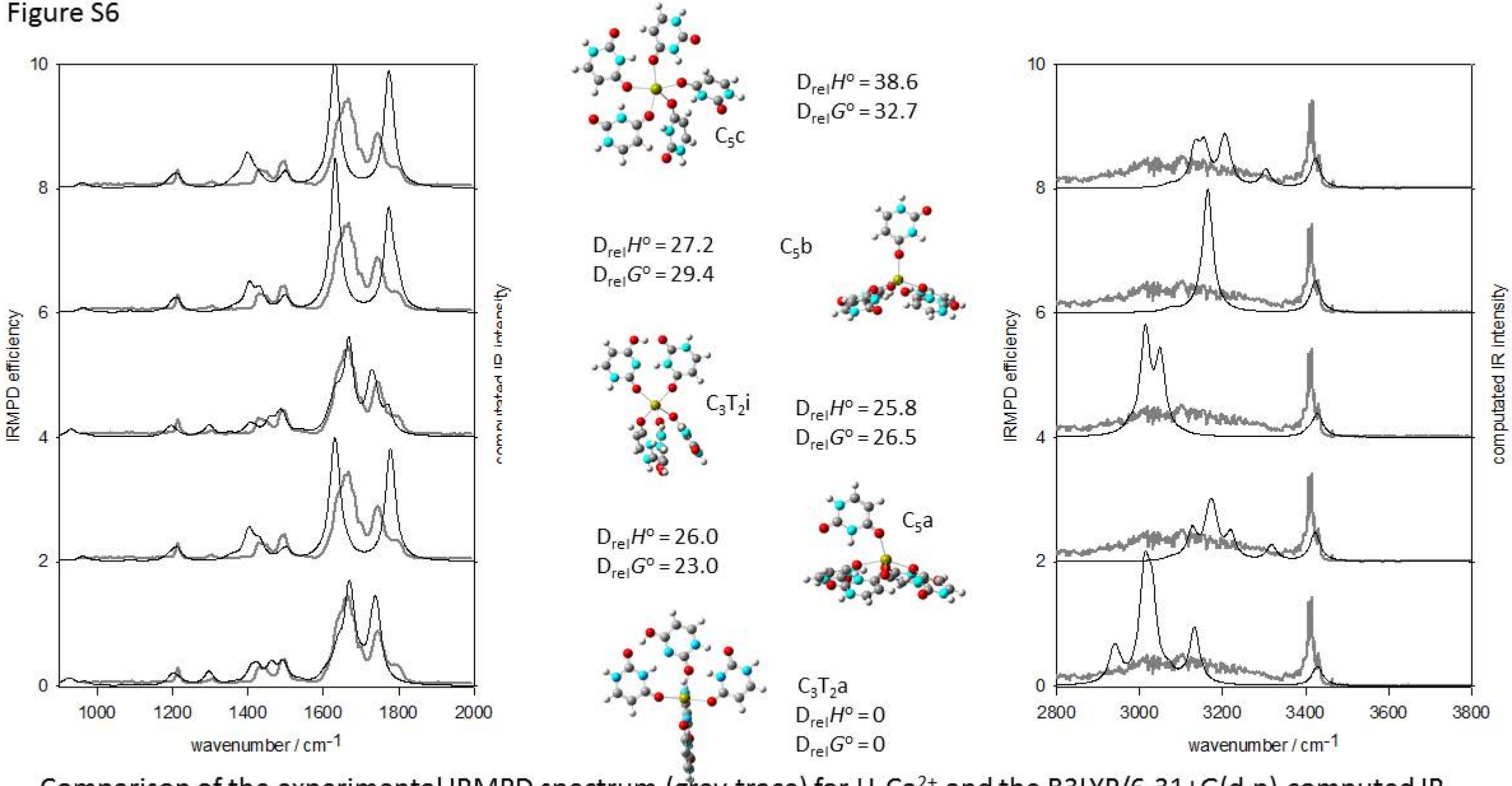
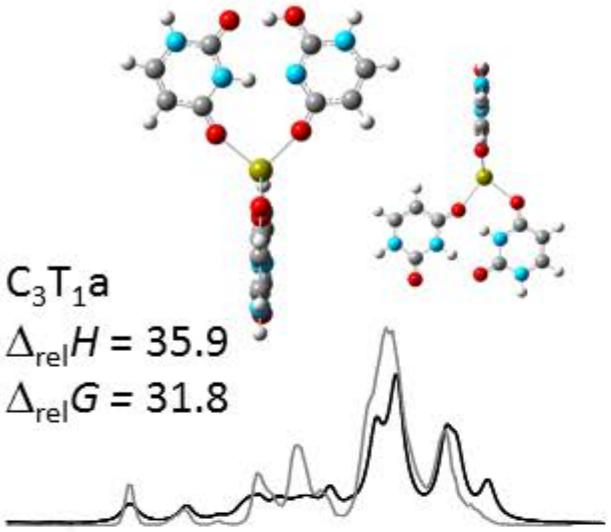


Figure S6

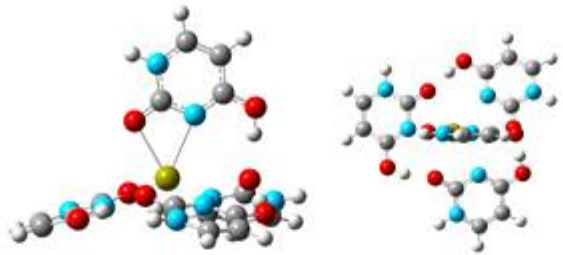


Comparison of the experimental IRMPD spectrum (grey trace) for U_5Ca^{2+} and the B3LYP/6-31+G(d,p) computed IR spectra (black traces) for five different isomers. The 298 K enthalpies and Gibbs energies relative to structure C_3T_2a are also shown (also computed using B3LYP/6-31+G(d,p)).

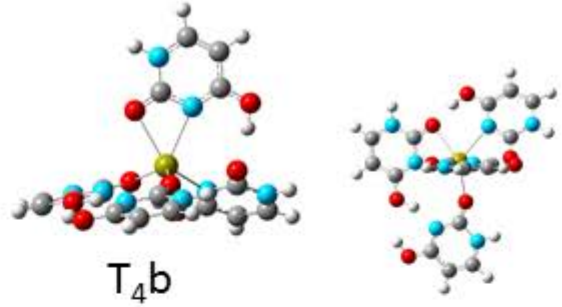
Figure S7



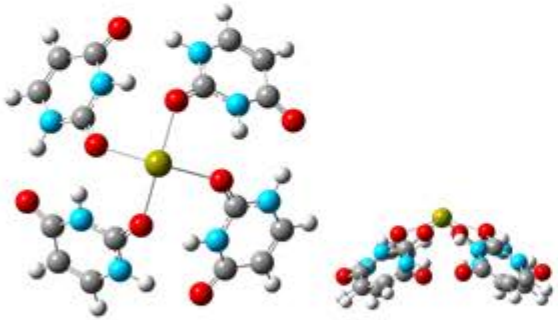
C_3T_1a
$\Delta_{rel}H = 35.9$
$\Delta_{rel}G = 31.8$



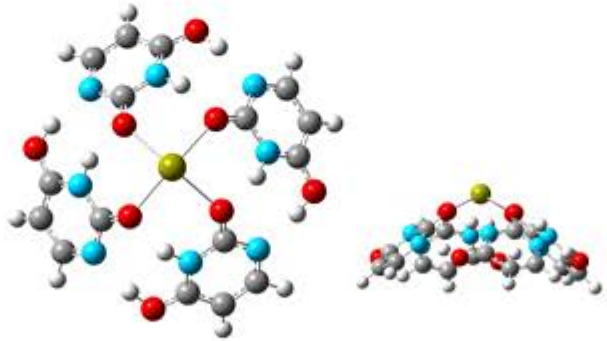
T_4a
$\Delta_{rel}H = 62.8$
$\Delta_{rel}G = 70.7$



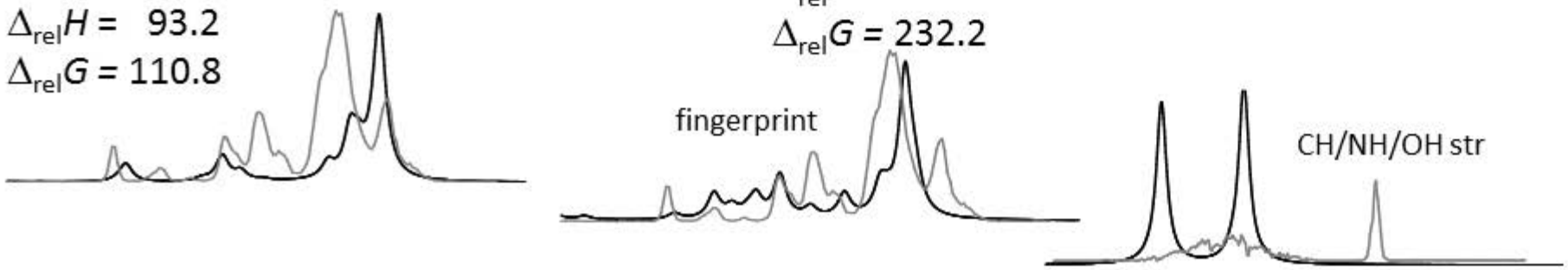
T_4b
$\Delta_{rel}H = 70.0$
$\Delta_{rel}G = 71.9$



C_4d
$\Delta_{rel}H = 93.2$
$\Delta_{rel}G = 110.8$

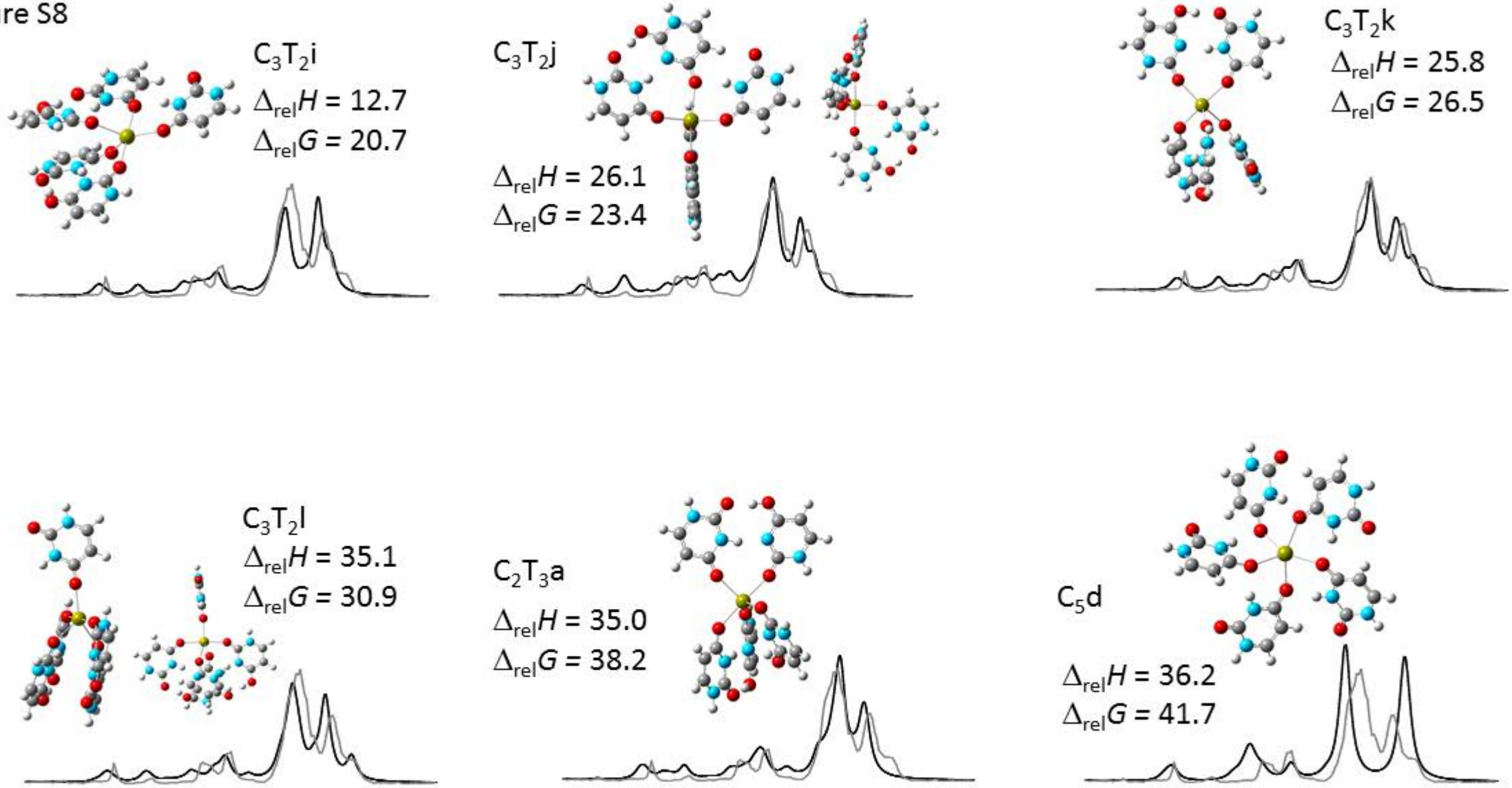


T_4c
$\Delta_{rel}H = 203.0$
$\Delta_{rel}G = 232.2$



Some other higher energy U_4Ca^{2+} structures along with their energies and 298 K Gibbs energies relative to C_2T_2a and computed IR spectra (black trace) compared to the experimental IRMPD spectrum (grey trace).

Figure S8



Some other higher energy U_5Ca^{2+} structures along with their energies and 298 K Gibbs energies relative to C_3T_2a and computed IR spectra (black trace) compared to the experimental IRMPD spectrum (grey trace).

Figure S8 continued

C_5e

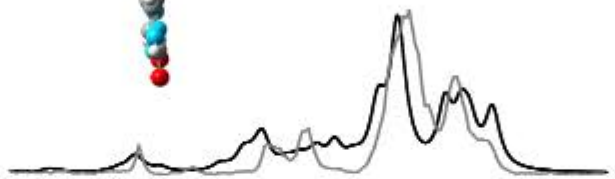
$\Delta_{rel}H$ = 64.0

$\Delta_{rel}G$ = 73.4

C_5f

$\Delta_{rel}H$ = 117.9

$\Delta_{rel}G$ = 104.7



T_5a

$\Delta_{rel}H$ = 276.4

$\Delta_{rel}G$ = 250.5

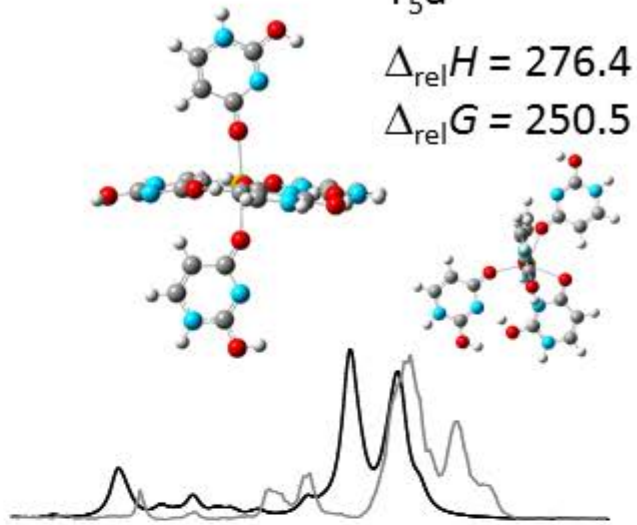
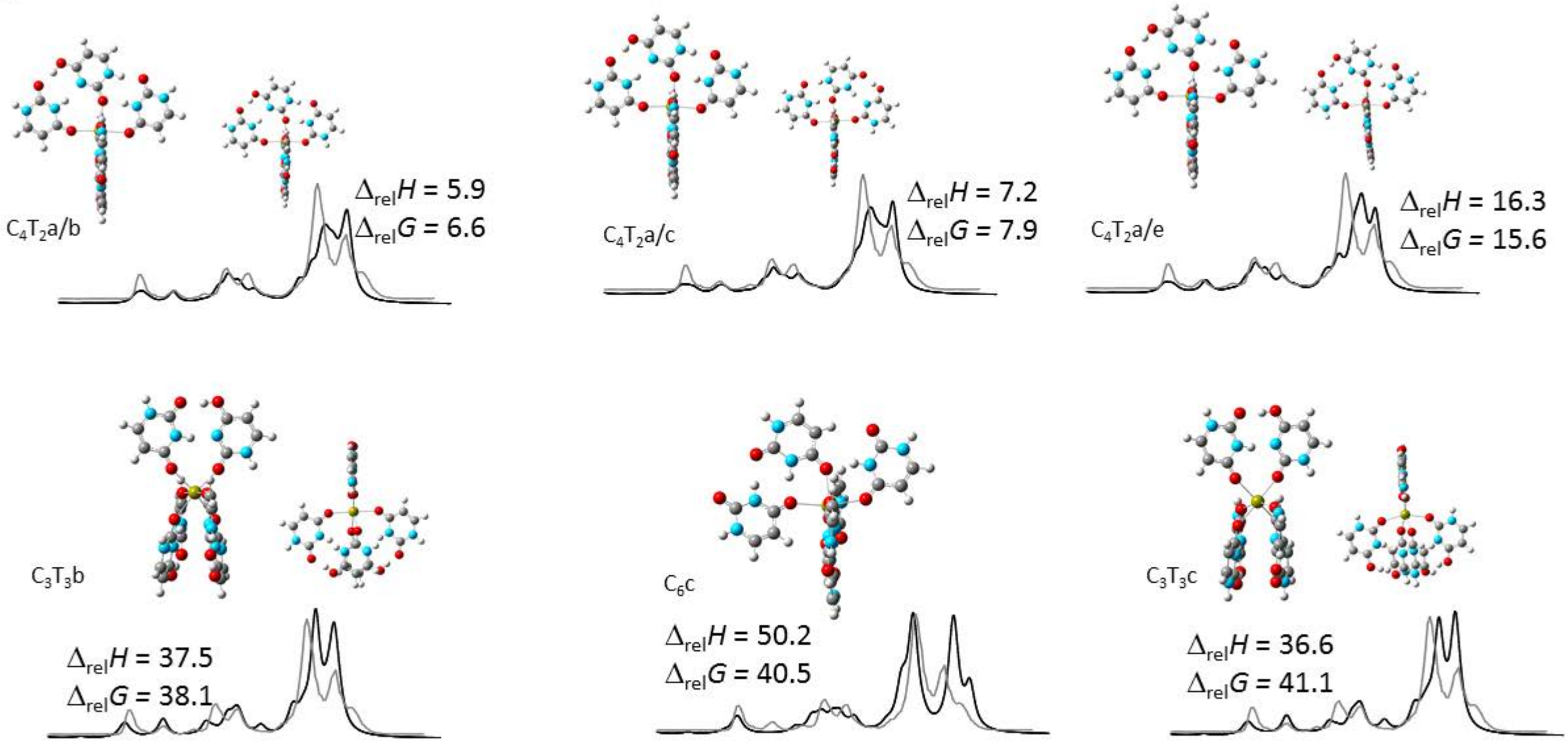
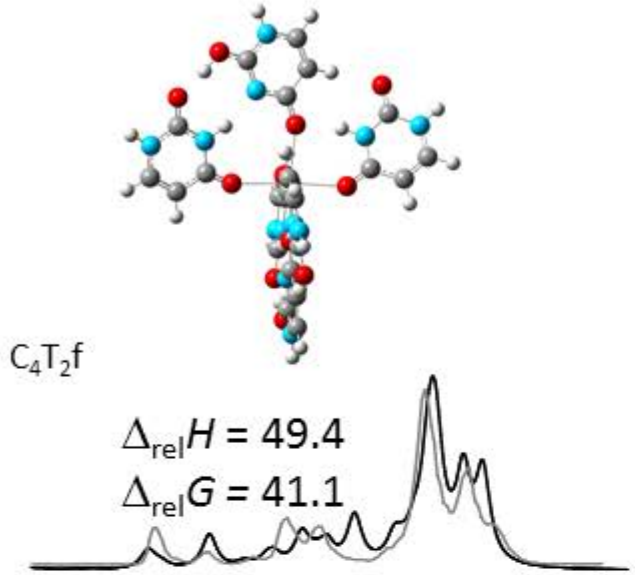


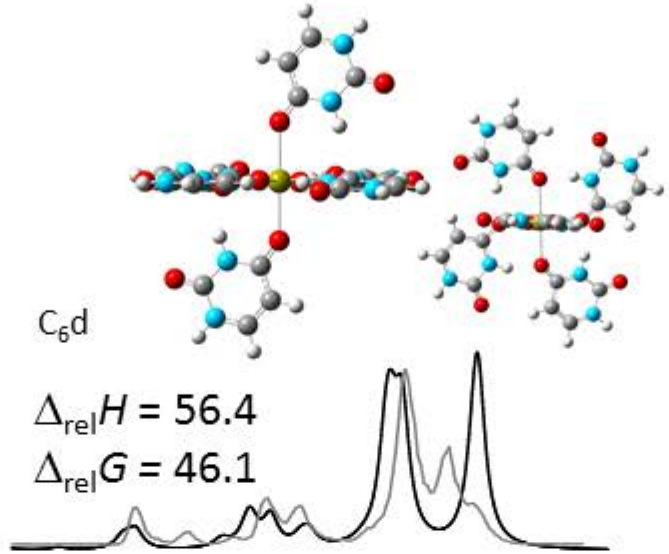
Figure S9

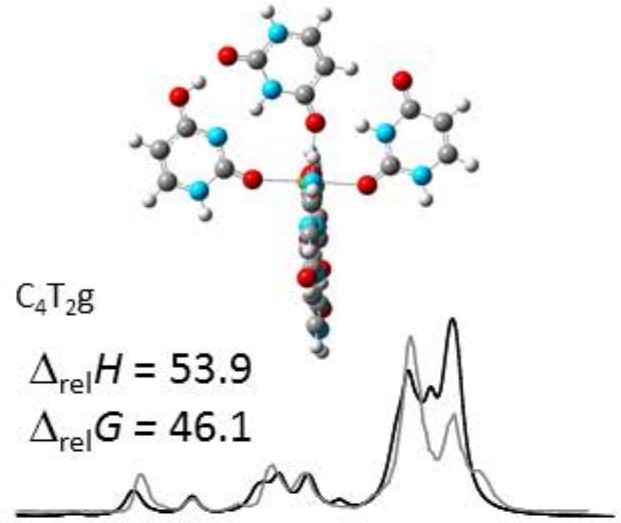


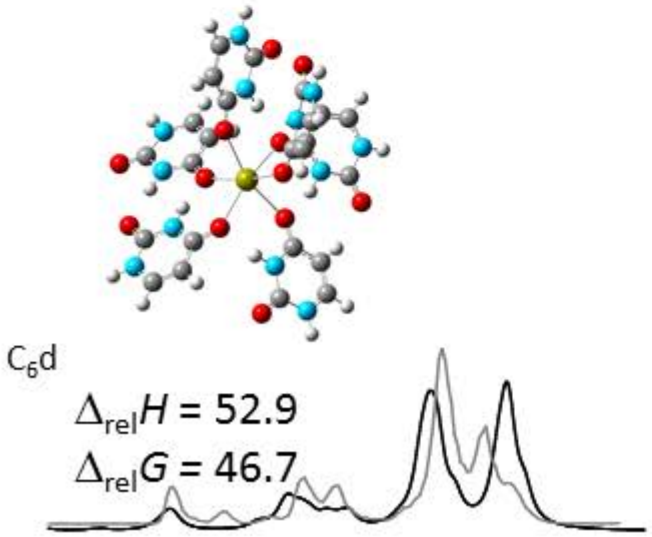
Some other higher energy U_6Ca^{2+} structures along with their energies and 298 K Gibbs energies relative to C_4T_2a and computed IR spectra (black trace) compared to the experimental IRMPD spectrum (grey trace).

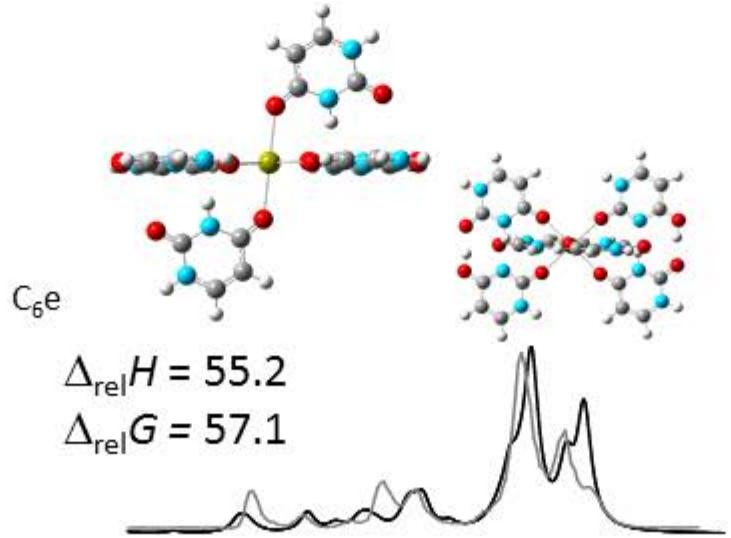
Figure S9 continued











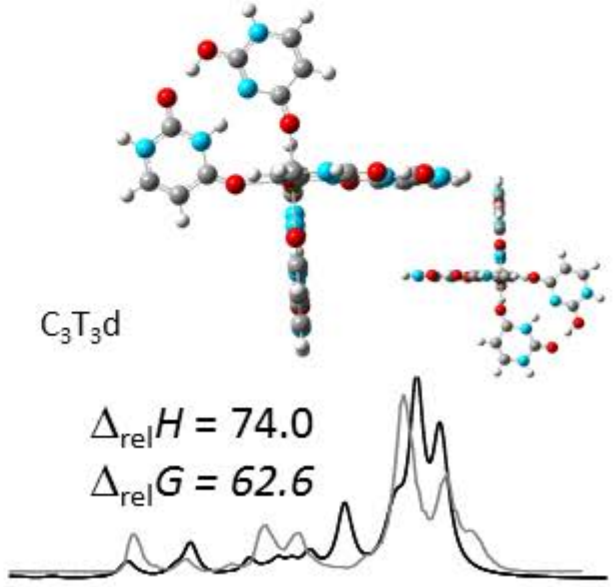


Figure S9 continued

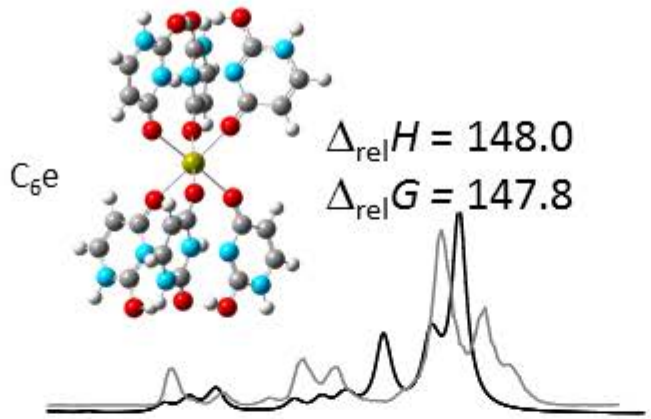


Figure S10. Mass spectra following 3420 cm^{-1} irradiation of isolated A) U_4Ca^{2+}, B) U_5Ca^{2+}, and C) U_6Ca^{2+}.

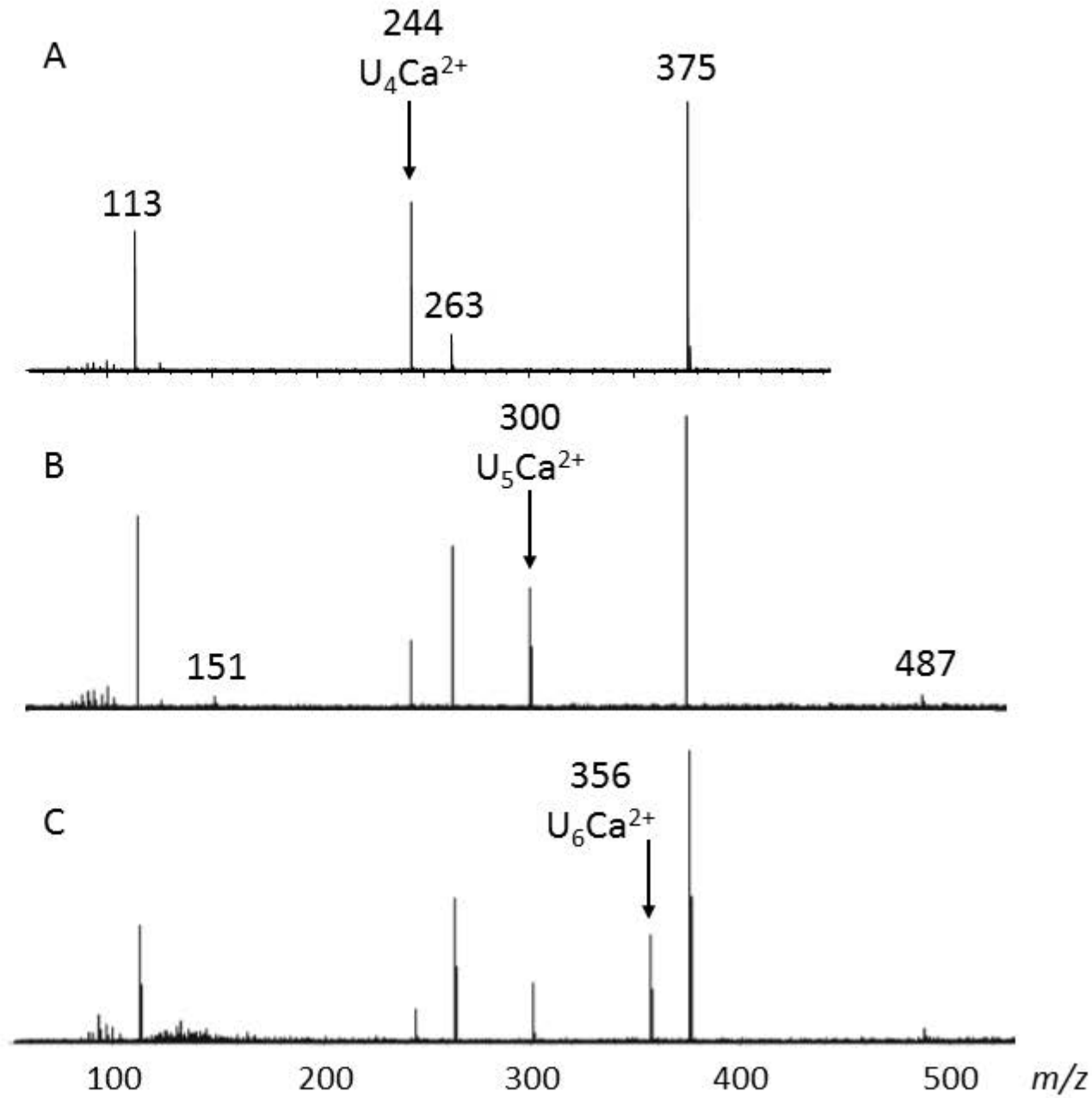


Table S1: Comparison of basis set on the 298 K energetics (top relative enthalpies, bottom relative Gibbs energies) in kJ mol^{-1} of some U_5Ca^{2+} structures.

Structure	B3LYPD3/6-31+G(d,p)	B3LYPD3/6-311+G(3df,3pd)
C_3T_2a	0.0 0.0	0.0 0.0
C_3T_2b	-0.5 +0.6	-0.4 +0.6
C_3T_2d	6.5 7.8	7.0 8.3
C_3T_2c	6.6 7.5	7.1 8.0
C_3T_2f	8.3 8.9	8.6 9.3
C_3T_2e	8.9 8.7	8.8 8.6

Table S2: Comparison of basis set on the 298 K energetics (top relative enthalpies, bottom relative Gibbs energies) in kJ mol^{-1} of some U_6Ca^{2+} structures.

Structure	B3LYPD3/6-31+G(d,p)	B3LYPD3/6-311+G(3df,3pd)
T_4C_2a	0.0 0.0	0.0 0.0
T_4C_2b	11.6 13.1	12.2 13.7
T_4C_2c	15.8 16.1	15.7 16.1
T_4C_2d	34.0 24.6	32.7 23.3
T_4C_2e	27.9 29.9	28.7 30.8
T_4C_2f	34.7 36.1	31.9 33.2