Towards Systematically Improvable Models for Heavy Elements in Condensed Phase with Frozen Density Embedding

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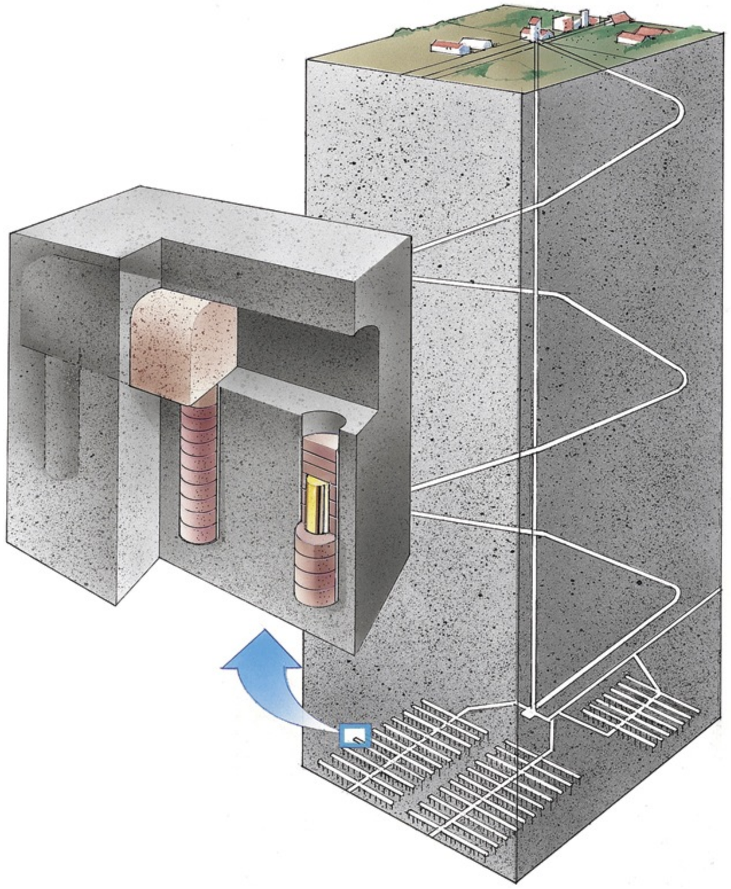
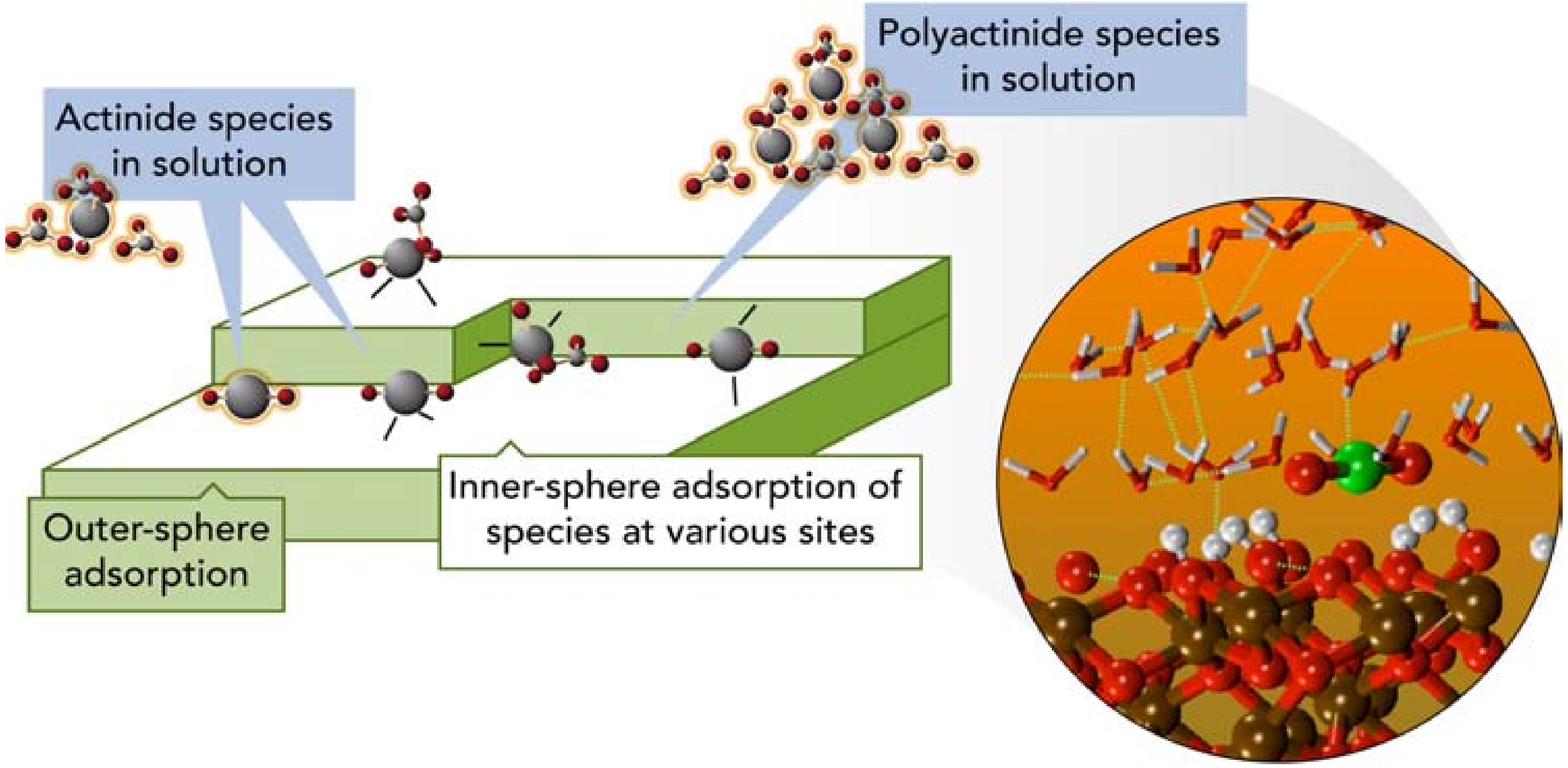
Actinides in Condensed Phase

- Understanding the behavoir of actinides (Ac) in condensed phase a key technological issue
  - Nuclear fuel cycle: optimization of separation processes
  - Waste disposal: interaction with clays in geological repositories, environment





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Actinides in Condensed Phase

- Experiments are difficult due to radioactivity

- Theoretical modeling: important but challenging
    - Correlation (close-lying f/d/p virtuals from Ac), relativistic (e.g. strong spin-orbit coupling) and environment effects (e.g. second solvation shell)
    - Interest in local properties (e.g. spectra): embedding methods (Gomes and Jacob, Annu. Rep. Prog. Chem., Sect. C: Phys. Chem. 2012, 108, 222 for an overview of different approaches)

Frozen Density Embedding

- Wesolowski and Warshel (J Phys Chem 1993, 97, 8050), reformulation of DFT (e.g. P. Cortona PRB 1992, 46, 2008)

- Total system (and total density) partitioned into subsystems

$$\rho_{\text{tot}} = \rho_{\text{I}} + \rho_{\text{II}} = \rho_{\text{I}} + \sum_{n} \rho_{\text{II;n}}$$

- Energy of total system rewritten as isolated subsystems energies plus interaction term

$$E[\rho_{\text{tot}}] = J[\rho_{\text{tot}}] + V_{\text{ne}}[\rho_{\text{tot}}] + T_s[\rho_{\text{tot}}] + E_{\text{xc}}[\rho_{\text{tot}}] \; = \; E[\rho_{\text{I}}] + E[\rho_{\text{II}}] + E_{\text{int}}[\rho_{\text{I}}, \rho_{\text{II}}]$$

- Subsystem energies

$$E_i[\rho_i] \; = \; \int \rho_i(\mathbf{r}) v^{i}_{\text{nuc}}(\mathbf{r}) d\mathbf{r} + \frac{1}{2} \iint \frac{\rho_i(\mathbf{r})\rho_i(\mathbf{r}')}{|\mathbf{r}-\mathbf{r}'|} d\mathbf{r}\, d\mathbf{r}' + \; E^{i}_{\text{nuc}} \; + \; E_{\text{xc}}[\rho_i] + T_s[\rho_i]$$

- Interaction energy

$$E_{\text{int}}[\rho_{\text{I}}, \rho_{\text{II}}] \; = \; \int \rho_{\text{I}}(\mathbf{r}) v^{\text{II}}_{\text{nuc}}(\mathbf{r}) d\mathbf{r} + \int \rho_{\text{II}}(\mathbf{r}) v^{\text{I}}_{\text{nuc}}(\mathbf{r}) d\mathbf{r} + E^{\text{I,II}}_{\text{nuc}} \; + \; \iint \frac{\rho_{\text{I}}(\mathbf{r})\rho_{\text{II}}(\mathbf{r}')}{|\mathbf{r}-\mathbf{r}'|} d\mathbf{r} d\mathbf{r}' + E^{\text{nadd}}_{\text{xck}}[\rho_{\text{I}}, \rho_{\text{II}}]$$

- Non-additive terms

$$E^{\text{nadd}}_{\text{xck}}[\rho_{\text{I}}, \rho_{\text{II}}] \; = \; E_{\text{xck}}[\rho_{\text{I}} + \rho_{\text{II}}] - E_{\text{xck}}[\rho_{\text{II}}] - E_{\text{xck}}[\rho_{\text{II}}]$$

Frozen Density Embedding

- Making the total energy stationary (wrt. I) yields KS-like equations

$$F^{\mathrm{KS;I}}\phi_p^I(\mathbf{r}) \;=\; \left[-\frac{1}{2}\Delta + v_{\mathrm{nuc}}^I(\mathbf{r}) + v_{\mathrm{H}} + v_{\mathrm{xc}}[\rho_I](\mathbf{r}) + v_{\mathrm{int}}^I(\mathbf{r})\right]\phi_p^I(\mathbf{r}) \;=\; \varepsilon_p^{\mathrm{KS;I}}\phi_p^I(\mathbf{r})$$

- Subsystems interact with each other via an effective embedding potential

$$v_{\mathrm{int}}^{\mathrm{I}}(\mathbf{r}) \;=\; \frac{\delta E_{\mathrm{int}}[\rho_{\mathrm{I}},\rho_{\mathrm{II}}]}{\delta\rho_{\mathrm{I}}} \;=\; v_{\mathrm{nuc}}^{\mathrm{II}}(\mathbf{r}) + \int\frac{\rho_{\mathrm{II}}(\mathbf{r}')}{|\mathbf{r}-\mathbf{r}'|}d\mathbf{r}' + \left[\left.\frac{\delta E_{\mathrm{xck}}^{\mathrm{nadd}}}{\delta\rho}\right|_{\rho_{\mathrm{tot}}} - \left.\frac{\delta E_{\mathrm{xck}}^{\mathrm{nadd}}}{\delta\rho}\right|_{\rho_{\mathrm{I}}}\right]$$

- Polarization of the environment: exchange I and II

- Generalization to WFT-in-DFT (e.g. Huang and Carter, JCP 2006, 125, 084102)

$$E_i[\rho_i] = E_{NN} + \langle\Psi_i|\hat{T} + \hat{V}_{\mathrm{nuc}} + \hat{V}_{\mathrm{ee}}|\Psi_i\rangle \qquad\qquad \rho_i \leftarrow \Psi_i^*\Psi_i$$

- Non-variational WF (Höfener, Gomes and Visscher, JCP 2012, 136, 044104; JCP 2013, 139, 104106)

$$L \;=\; \mathcal{L}_{\mathrm{I}} + E_{\mathrm{int}} + E_{\mathrm{II}}$$

$$\downarrow$$

$$\rho(\mathbf{t},\bar{\mathbf{t}}) = \langle\Lambda|\hat{\rho}|\mathrm{CC}\rangle = \left[\langle\mathrm{HF}| + \sum_{\mu_i}\bar{t}_{\mu_i}\langle\mu_i|e^{-T}\right]\hat{\rho}|\mathrm{CC}\rangle \quad\longrightarrow$$

$$0 \;=\; \frac{\partial L}{\partial\bar{t}_{\mu_i}} = \Omega_{\mu_i} + \sum_{pq}\langle p|v_{\mathrm{int}}^{\mathrm{I}}|q\rangle\langle\mu_i|\exp(-T)E_{pq}|\mathrm{CC}\rangle$$

$$0 \;=\; \frac{\partial L}{\partial t_{\mu_i}} = \langle\Lambda|[H,\tau_{\mu_i}]|\mathrm{CC}\rangle + \sum_{pq}\langle p|v_{\mathrm{int}}^{\mathrm{I}}|q\rangle\langle\Lambda|[E_{pq},\tau_{\mu_i}]|\mathrm{CC}\rangle$$

  - CC-in-CC straightforward (Höfener and Visscher, JCP 2012, 137, 204120)
  - Use only DFT densities: $F_{ab} \leftarrow \langle\phi_a|v_{\mathrm{int}}^{\mathrm{I}}(\mathbf{r})|\phi_b\rangle$ (Gomes, Jacob and Visscher, PCCP 2008, 10, 5353)

Excited states in Frozen Density Embedding

- ☐ Response theory (Casida and Wesolowski IJQC 2004, 96, 577; Neugebauer JCP 2007, 126, 134126)
  - ☐ Derivatives of the time-averaged quasienergy (Lagrangian): (JCP 2012, 136, 044104)

$$\{Q(t)\}_T = \{Q[\rho_{\mathrm{I}}](t)\}_T + \{Q[\rho_{\mathrm{II}}](t)\}_T + \{E_{\mathrm{int}}[\rho_{\mathrm{I}}, \rho_{\mathrm{II}}](t)\}_T$$

  - ☐ For DFT-in-DFT: $\rho(\boldsymbol{r},t) = \rho_{\mathrm{I}}(\boldsymbol{r},\boldsymbol{\kappa}_{\mathrm{I}}) + \rho_{\mathrm{II}}(\boldsymbol{r},\boldsymbol{\kappa}_{\mathrm{II}})$

$$\boldsymbol{F} = \frac{\partial^2\{Q^{(2)}\}_T}{\partial\boldsymbol{\kappa}^{(1)}\partial\boldsymbol{\kappa}^{(1)}} = \begin{pmatrix} \boldsymbol{F}_{\mathrm{I,I}} & \boldsymbol{F}_{\mathrm{II,I}} \\ \boldsymbol{F}_{\mathrm{I,II}} & \boldsymbol{F}_{\mathrm{II,II}} \end{pmatrix} = \begin{pmatrix} \boldsymbol{F}_{\mathrm{I}} & 0 \\ 0 & \boldsymbol{F}_{\mathrm{II}} \end{pmatrix} + \begin{pmatrix} \boldsymbol{F}^{\mathrm{I}}_{\mathrm{int}} & \boldsymbol{F}^{\mathrm{II,I}}_{\mathrm{int}} \\ \boldsymbol{F}^{\mathrm{I,II}}_{\mathrm{int}} & \boldsymbol{F}^{\mathrm{II}}_{\mathrm{int}} \end{pmatrix}$$

    - ☐ Approximation: only response of I (no subsystem coupling)

$$\boldsymbol{F} = \boldsymbol{F}_{\mathrm{I}} + \boldsymbol{F}^{\mathrm{I}}_{\mathrm{int}} = \frac{\partial^2\{Q^{(2)}\}_T}{\partial\boldsymbol{\kappa}^{(1)}_{\mathrm{I}}\partial\boldsymbol{\kappa}^{(1)}_{\mathrm{I}}} = \begin{pmatrix} \mathbf{A} & \mathbf{B} \\ \mathbf{B}^* & \mathbf{A}^* \end{pmatrix} - \omega \begin{pmatrix} \mathbf{1} & \mathbf{0} \\ \mathbf{0} & \mathbf{-1} \end{pmatrix}$$

$$A^{I,I}_{ia,jb} = \delta_{ij}\delta_{ab}(\varepsilon^I_a - \varepsilon^I_i) + 2(ia|bj) + (ia|f_{\mathrm{xc}}|bj) + (ia|\, w^{I,I}_{\mathrm{int}}\,|bj)$$

$$B^{I,I}_{ia,jb} = 2(ia|jb) + (ia|f_{\mathrm{xc}}|jb) + (ia|w^{I,I}_{\mathrm{int}}|jb)$$

$$(pq|w^{I,I}_{\mathrm{int}}|rs) = \iint \left[\left.\frac{\delta^2 E_{\mathrm{xck}}}{\delta\rho(\mathbf{r}')\delta\rho(\mathbf{r})}\right|_{\rho_{\mathrm{tot}}} - \left.\frac{\delta^2 E_{\mathrm{xck}}}{\delta\rho(\mathbf{r}')\delta\rho(\mathbf{r})}\right|_{\rho_{\mathrm{I}}} \right] \Omega_{pq}(\mathbf{r}')\Omega_{rs}(\mathbf{r})\, d\mathbf{r}d\mathbf{r}'$$

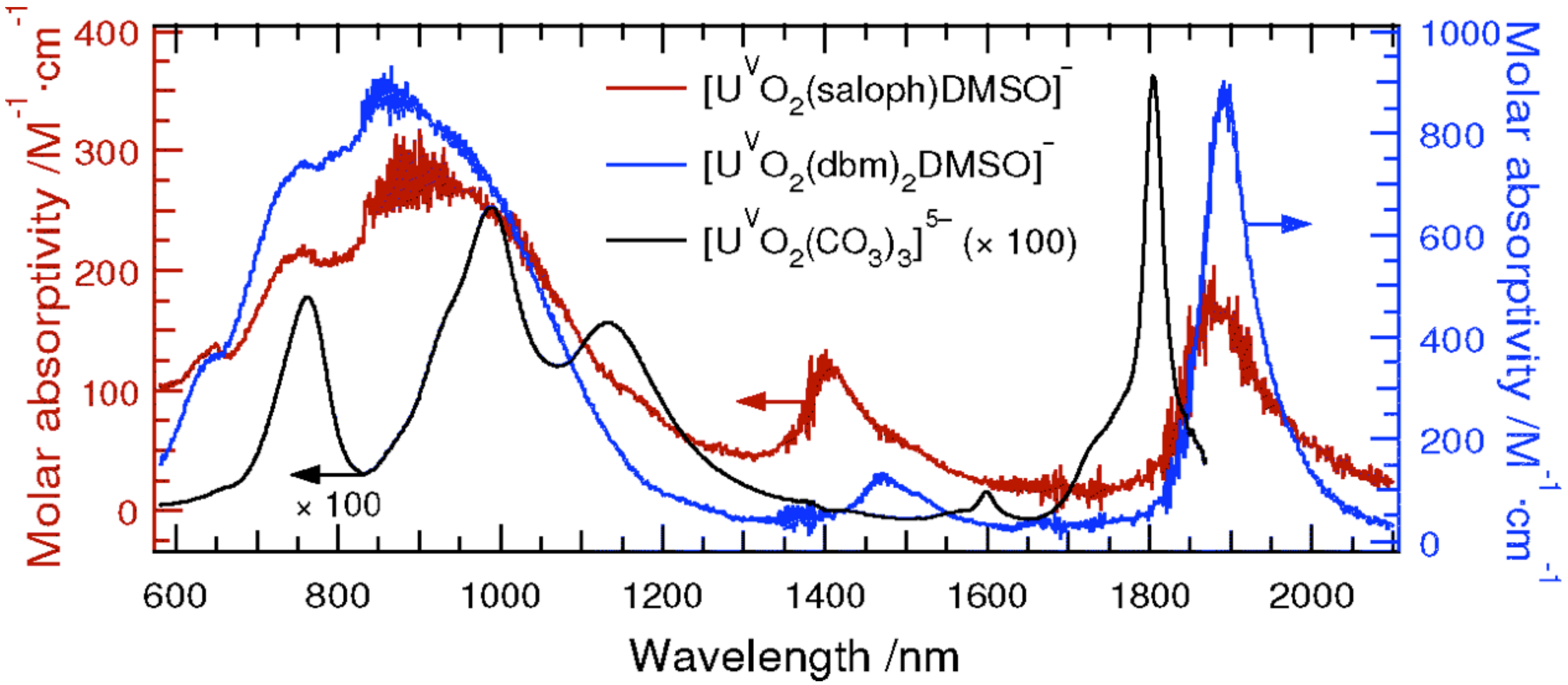
  - ☐ For CC-in-DFT, response of I: good approximation is eigenvalues of CC Jacobian with embedding contributions (JCP 2013, 139, 104106)

$${}^{\bar{t}t}A_{\mu_i,\nu_j} \leftarrow \sum_{pq} \langle p|v^{\mathrm{I}}_{\mathrm{int}}|q\rangle \langle\mu_i|\exp(-T)[E_{pq},\tau_{\nu_j}]|\mathrm{CC}\rangle + \frac{1}{2}\sum_{pq,rs}(pq|w^{I,I}_{\mathrm{int}}|rs)\langle\mu_i|\exp(-T)E_{pq}|\mathrm{CC}\rangle\langle\Lambda|[E_{rs},\tau_{\nu_j}]|\mathrm{CC}\rangle$$

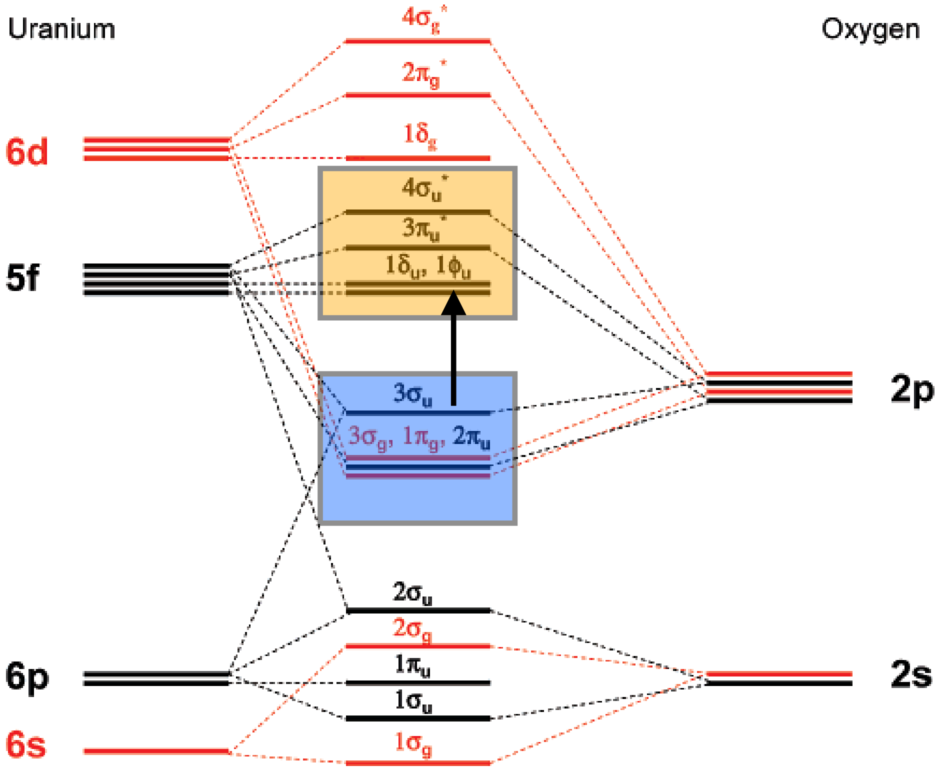
- ☐ Explicit calculation of excited states
  - ☐ used here, along with the fixed potential approximation $F_{ab} \leftarrow \langle\phi_a|v^{\mathrm{I}}_{\mathrm{int}}(\mathbf{r})|\phi_b\rangle$

A Focal Point: Uranyl Compounds

- The uranyl cation (UO_2^{n+}): the most important species in solution
  - Linear (very strong U-O bonds)
  - equatorial plane available for complexation
  - electronic spectra quite sensitive to ligands



Mizuoka K, Grenthe I and Ikeda Y Inorg. Chem. 2005, 44, 4472



Denning, JPCA 2007, 111, 4125

A test system for FDE: uranyl tetrachloride

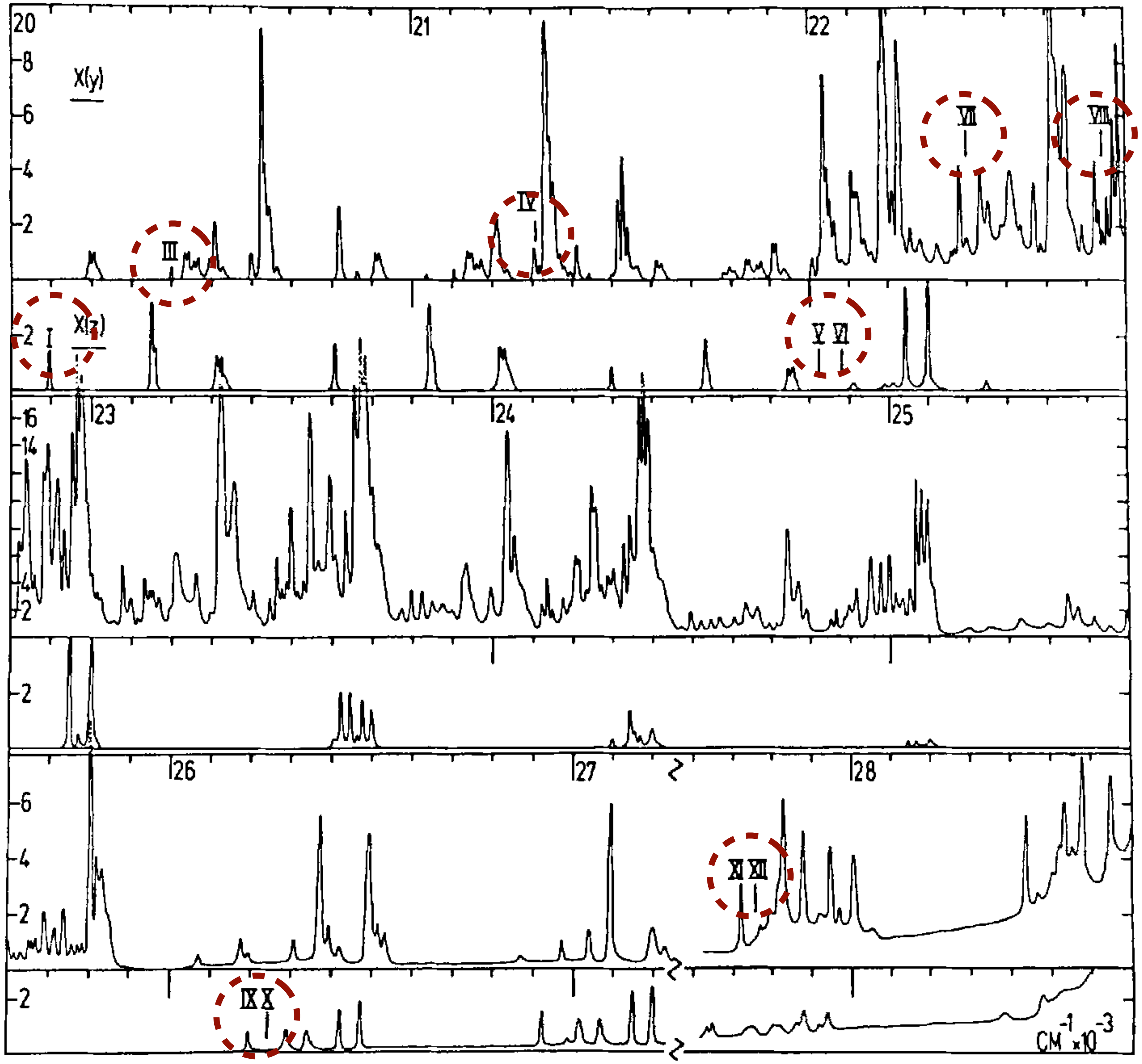


Fig. 4. Single crystal polarised absorption spectrum of $Cs_2UO_2Cl_4$ at 4.2 K; from Ref. [29]

R. G. Denning Structure and Bonding 79 : 1992

- Uranyl tetrachloride ($UO_2Cl_4^{2-}$)
  - High-quality measurements in the solid state ($Cs_2UO_2Cl_4$ crystal)
  - Photoelectron spectra for $UO_2Cl_4^{2-}$ in the gas phase now available
- Can a minimal(ist) approach (actinyl embedded in ligands) work?
  - Yes for f-f spectra of $NpO_2Cl_4^{2-}$ (Gomes, Jacob and Visscher, PCCP 2008, 10, 5353): very local
  - on uranyl chloride, low-lying excitations from bonding orbitals to U f orbitals: local enough?

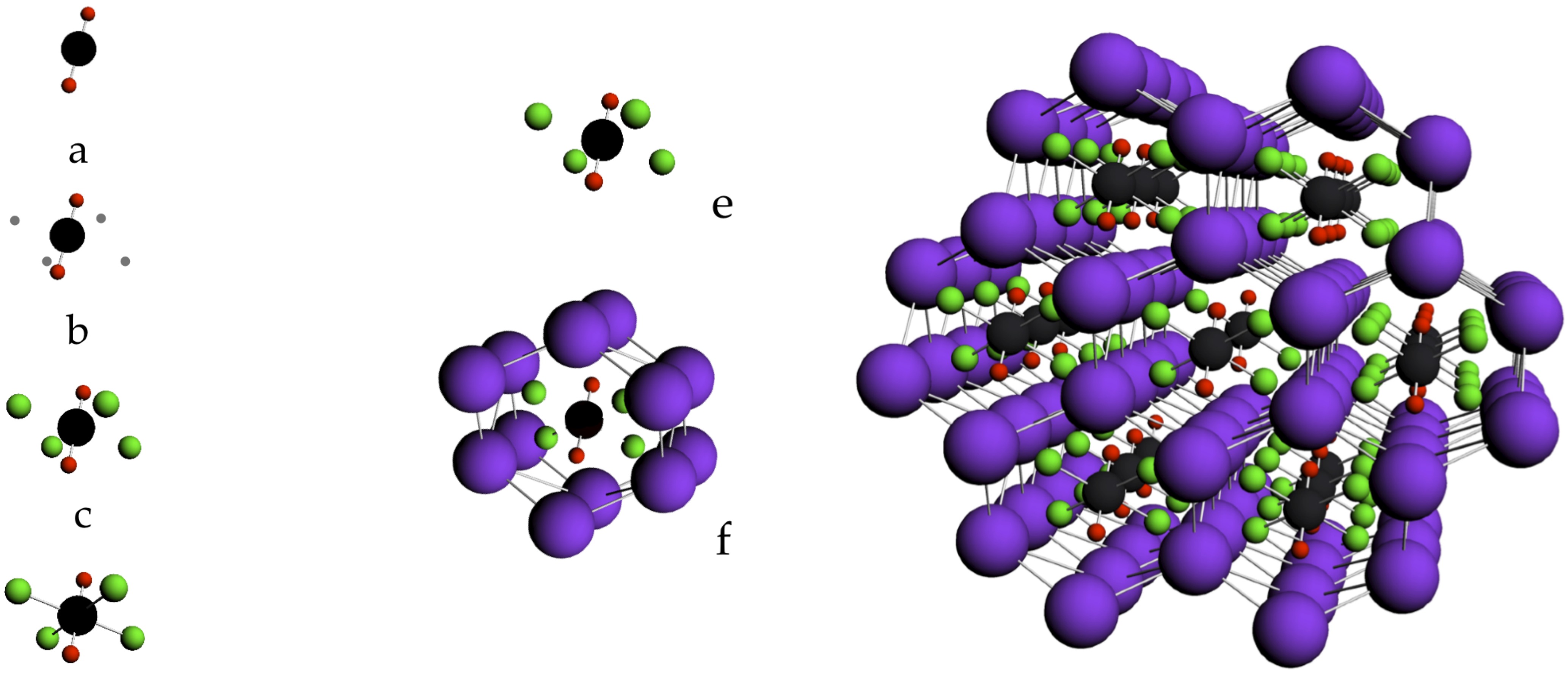
Computational Details

- Ground-state FDE calculations: ADF (www.scm.com), driven by PyADF (www.pyadf.org)
  - Spin-free ZORA Hamiltonian, TZ2P basis, SAOP model potential for subsystems
  - Freeze-thaw (20 iterations)
  - Non-additive terms calculated with PW91 XC / PW91k KEF ($E^{\mathrm{nadd}}_{\mathrm{xck}}[\rho_{\mathrm{I}}, \rho_{\mathrm{II}}] = E_{\mathrm{xck}}[\rho_{\mathrm{I}} + \rho_{\mathrm{II}}] - E_{\mathrm{xck}}[\rho_{\mathrm{II}}] - E_{\mathrm{xck}}[\rho_{\mathrm{II}}]$)

- Excitation energies: DIRAC (http://diracprogram.org)
  - Dirac-Coulomb Hamiltonian, triple-zeta basis (U: Dyall; O, Cl: Dunning)
  - Time-dependent CAM-B3LYP
  - Fock-space coupled cluster (IHFSCCSD) via sector (1h1p) (also sector (1h0p) for IPs)
    - 34 electrons correlated
    - model space with at least 5f, 6d (virtuals)
    - 2 virtual space truncations (Q_1: 5 a.u.=~120 virt., Q_2: 12 a.u.=~200 virt.)

Computational Details

- Two sets of structural models: $UO_2Cl_4^{2-}$ with (C_{2h}) and without the crystal environment (D_{4h})
  - Coordinates from X-ray structures (U-O: 1.774 A, U-Cl: 2.671 A)



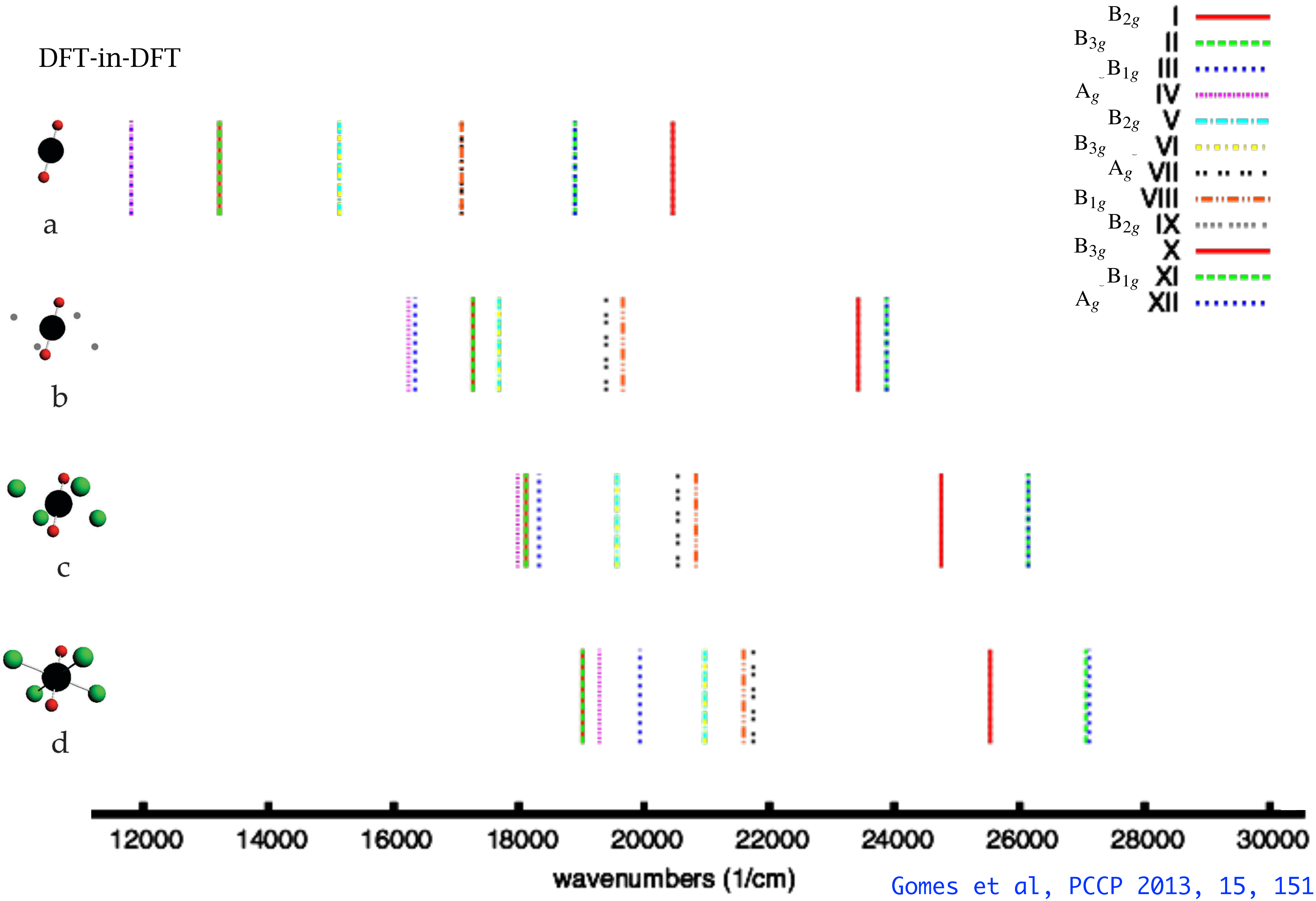
relaxed subsystems

frozen environment

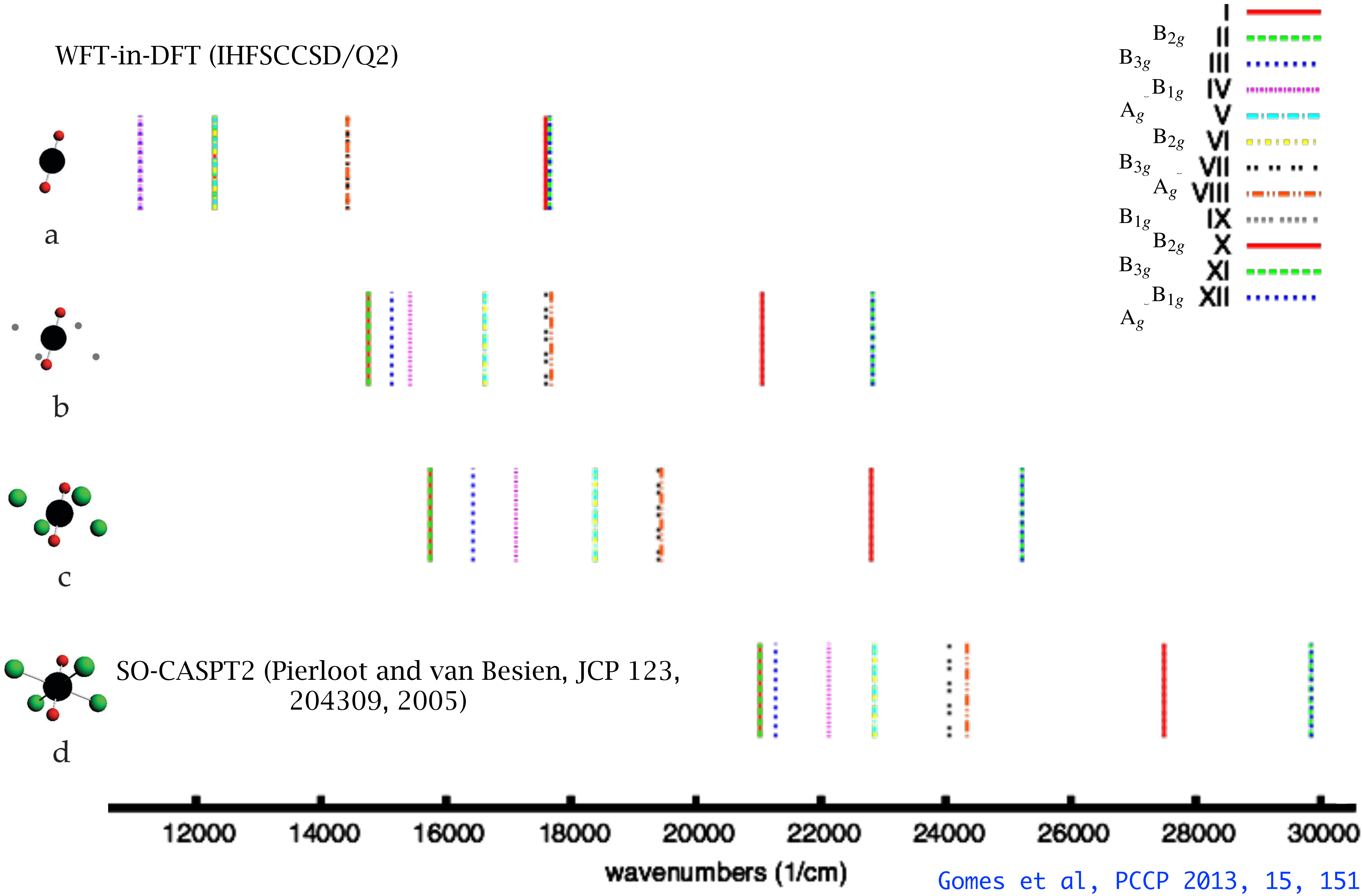
no environment

crystal environment

DFT-in-DFT

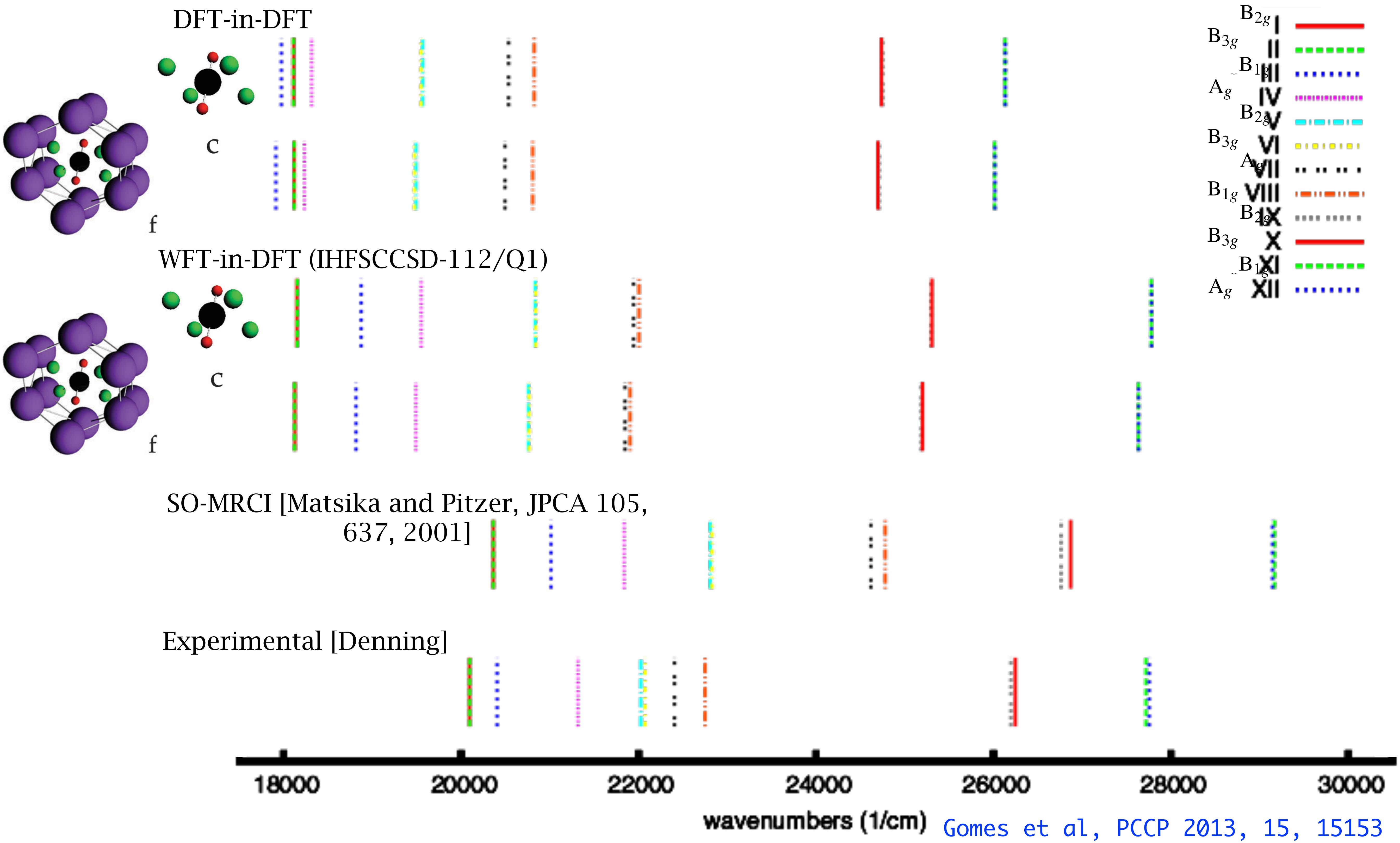


Gomes et al, PCCP 2013, 15, 15153


WFT-in-DFT (IHFSCCSD/Q2)

SO-CASPT2 (Pierloot and van Besien, JCP 123, 204309, 2005)

Gomes et al, PCCP 2013, 15, 15153



DFT-in-DFT

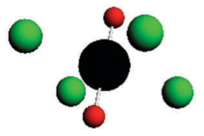
WFT-in-DFT (IHFSCCSD-112/Q1)

SO-MRCI [Matsika and Pitzer, JPCA 105, 637, 2001]

Experimental [Denning]

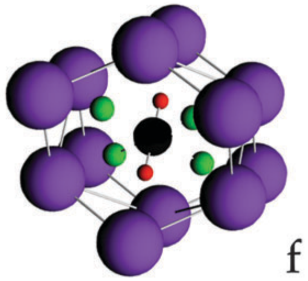
Gomes et al, PCCP 2013, 15, 15153

Ionization energies of Uranyl (Gas-phase and Crystal)



c

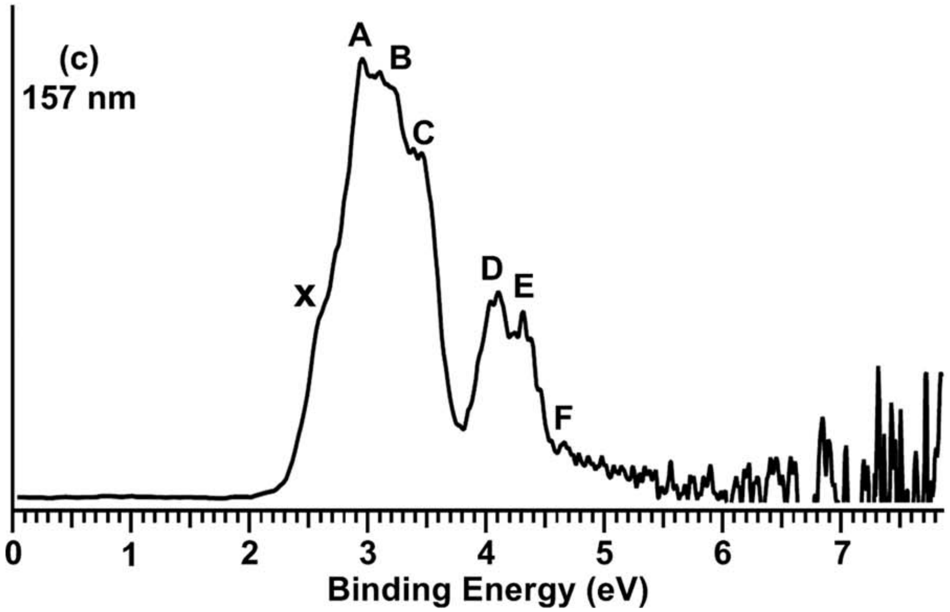
5.81 eV (IHFSCC/Q_1)
5.51 eV (IHFSCC/Q_2)
4.24 eV (CAM-B3LYP)
~5 eV (Exp.)



f

10.61 eV (IHFSCC/Q_1)

9.32 eV (CAM-B3LYP)
~9.4 eV (Exp.)



Dau et al, JCP 2012, 137, 064315

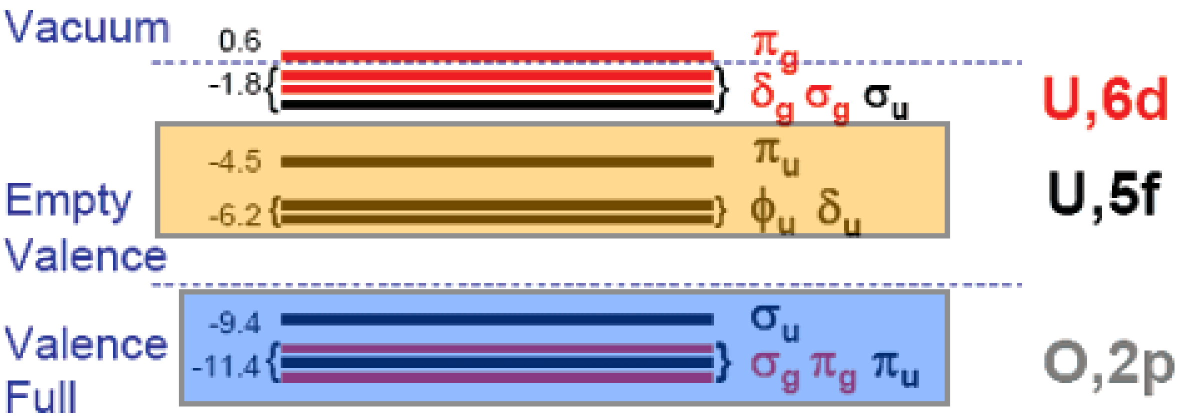
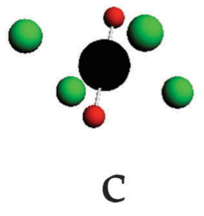


Figure 3. Experimental orbital energies in $Cs_2UO_2Cl_4$: *gerade* states, red; *ungerade* states, black.

Denning, JPC A 2007, 111, 4125

Ionization energies of Uranyl (Gas-phase and Crystal)



5.81 eV (IHFSCC/Q_1)
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4.24 eV (CAM-B3LYP)
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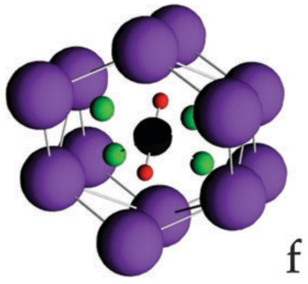
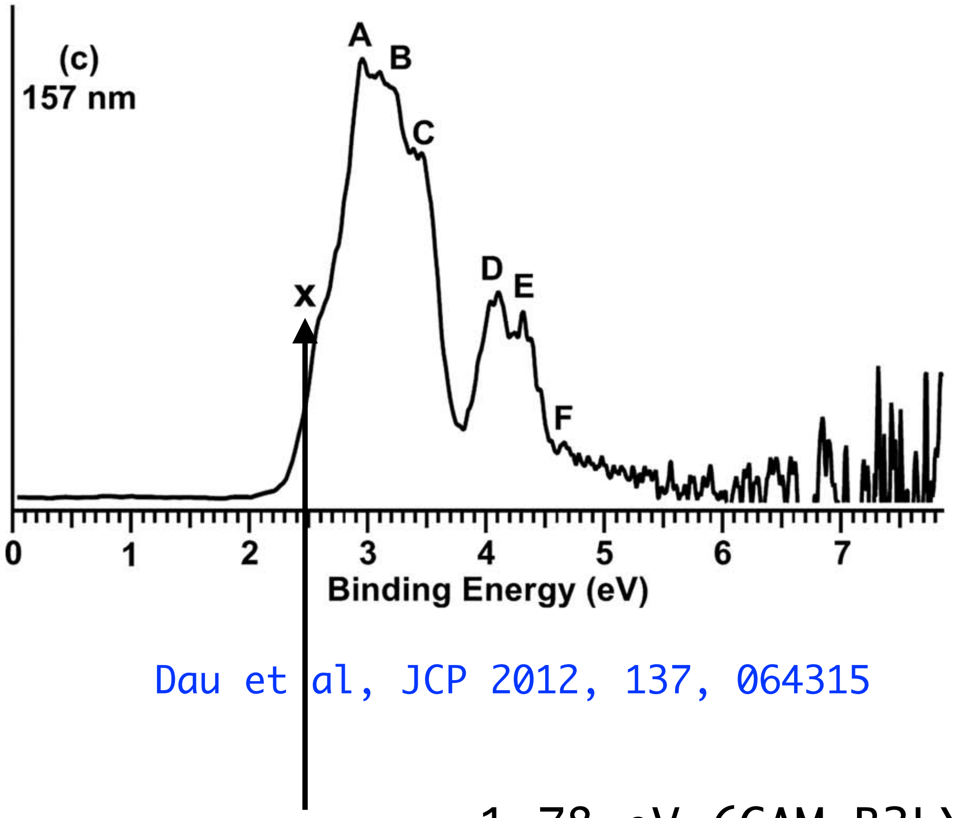


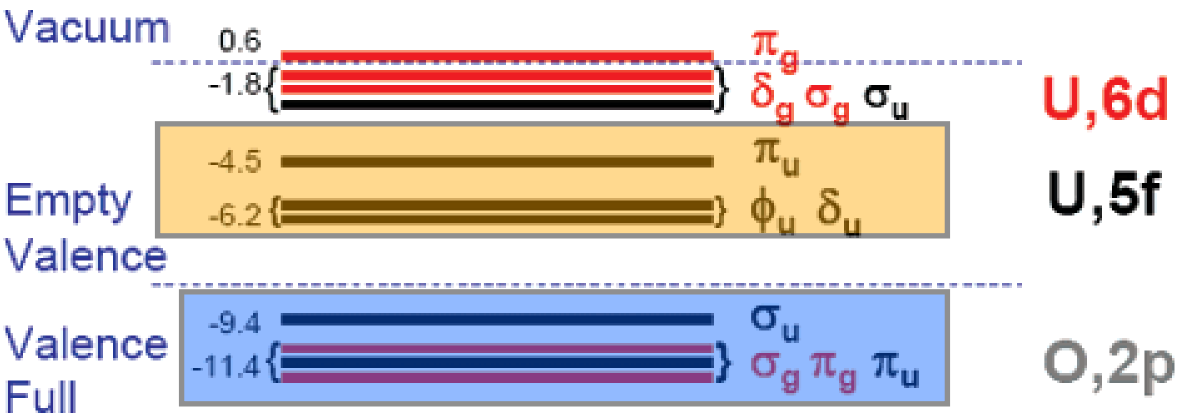
10.61 eV (IHFSCC/Q_1)

9.32 eV (CAM-B3LYP)
~9.4 eV (Exp.)



Dau et al, JCP 2012, 137, 064315

1.78 eV (CAM-B3LYP)
~2.4-2.5 eV (Exp.)



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Conclusions, Perspectives

- Subsystem methods (WFT/DFT-in-DFT) are quite useful to study AcO_2^{n+} systems in condensed phase
  - systematically modify the description of the surroundings
  - retain the quantum-mechanical character of “frozen” subsystems

- Fixed potential FDE and a minimal active region are a cost-effective approach

- Electronic structure approaches have a hard time describing the effects of electron correlation on the electronic spectra of $UO_2Cl_4^{2-}$

- In progress
  - a closer look at the at the origins of the red shift in FDE spectra for $UO_2Cl_4^{2-}$
  - exploring spectra of uranyl and other species with different ligands

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