

SUPPORTING INFORMATION

Probing the Solvent Shell with ^{195}Pt Chemical Shifts: Density Functional Molecular Dynamic Study of Pt^{II} and Pt^{IV} Anionic Complexes in Aqueous Solution

Lionel A. Truflandier and Jochen Autschbach
Department of Chemistry
312 Natural Sciences Complex
State University of New York at Buffalo
Buffalo, NY 14260-3000, USA
e-mail: jochena@buffalo.edu

1 Calculation of structural and dynamical properties

1.1 Radial distribution functions

The radial distribution function (RDF) $g_{ij}(r)$ for a pair of atoms ij is related to the probability of finding the atom pair a distance r apart, relative to the probability expected for a completely random distribution at the same density.¹ This definition can be expressed as an average over pairs, using the formal equation,

$$g_{ij}(r) = \frac{V}{N_{ij}} \left\langle \sum_i \sum_{j \neq i} \delta(\mathbf{r} - \mathbf{r}_{ij}) \right\rangle_{\text{configurations}} \quad (1)$$

where V is the volume of the cell and N_{ij} the number of atom pairs.¹ An efficient calculation of the RDF is based on the evaluation of atom pair probability $\delta\rho_{ij}(r)$, i.e. the number of ij pairs in the range $[r, r + \delta r]$. The calculation of $\delta\rho_{ij}$ is repeated for each configuration involved in the statistics, where the radius r is incremented by δr until the radial cutoff value r_c is reached. The latter is generally defined as the length of the box divided by two in order to respect the periodic image constraint.¹ As a result, $g_{ij}(r)$ is expressed as

$$g_{ij}(r) = \frac{V}{N_{ij}} \left\langle \sum_i \sum_{j \neq i} \frac{1}{4\pi r^2 \delta r} \delta\rho_{ij} \right\rangle_{\text{configurations}} \quad (2)$$

¹ $N_{ij} = N_i \times N_j$ when $i \neq j$ and $N_{ii} = N_i \times (N_i - 1)$ when $i = j$.

A number of 2048 configurations along with a radial step of 0.10 Å were used to generate the RDFs in this work. The RDFs expressed in eq. 2 are normalized such that g_{ij} approaches unity for large r .

1.2 Velocity auto-correlation functions and power spectra

The dynamical properties of a liquid such as the time integrals which are related to macroscopic transport coefficients can be evaluated from the velocity auto-correlation functions (VACFs). Their Fourier transformed amplitudes – often referred to as the “power density spectra” (PSD) or the “vibrational density of states” (VDOS) – yield the intensity of ro-vibrational excitation frequencies of the system at a given temperature.^{1,2} The normalized VACF, $C(t)$, is defined by

$$C(t) = \mathcal{N} \frac{\langle \sum_i \sum_{\alpha} v_{i\alpha}(t_i + t) v_{i\alpha}(t_i) \rangle_N}{\langle \sum_i \sum_{\alpha} v_{i\alpha}^2(t_i) \rangle_N} \quad (3)$$

where $v_{i\alpha}$ denotes the velocity component α of the atom i , i runs over the number N_t of time intervals t_i , and \mathcal{N} is a normalization factor given as $\mathcal{N} = 1/N_t N$, with N being the number of atoms. Considering that $C(t)$ is averaged over N , it is straightforward to decompose the velocity the VACFs into separate contributions; in our work, for instance, from the inorganic complex (Pt and ligand atoms) and from the solvent molecules (H and O atoms).

$$C(t) = C_{\text{complex}}(t) + C_{\text{H}_2\text{O}}(t) \quad (4)$$

Then the vibrational frequency spectrum $I(\omega)$ can be obtained by computing the following Fourier transform,³

$$I(\omega) = \frac{1}{2\pi} \int_0^{\infty} dt C(t) e^{i\omega t} \quad (5)$$

Power spectra presented in the paper were obtained using the maximum entropy method.⁴ Results were checked using more conventional Fourier transform methods involving data windowing functions such as the Bartlett window.⁵

2 Structural properties of bulk water

The bulk water structure related to the solvated $[\text{PtCl}_4]^{2-}$ system (noted $[\text{PtCl}_4]_{\text{sol}}^{2-}$) is compared to pure water simulations in Figure S1a-c. For example, considering the RDF of oxygen in water ($g_{\text{OO}}(r)$), the first peak position is at 2.70 Å with a height of 3.17 (Figure S1a), compared to the experimental values of 2.73 Å and 2.75 (vs. 2.71Å/3.30 from previous CP-aiMD). Likewise, the first minimum is at $g_{\text{OO}}^{\text{min}}(3.30) = 0.42$ in this study, which is also in good agreement with $g_{\text{OO}}^{\text{min}}(3.30) = 0.41$ from the CP-aiMD simulations of Grossman et al.^{6,7} Compared to the results obtained for $[\text{PtCl}_4]_{\text{sol}}^{2-}$, the overall liquid structure of water remains relatively unchanged despite the presence of the Pt complex. As observed for $[\text{PtCl}_4]_{\text{sol}}^{2-}$, peak positions and linewidths are globally conserved for the three RDFs. Nevertheless, the presence of the Pt-complex influences the behavior of the water shells as shown by the overstructured RDFs of S1a-c. The fact that these modifications seems be stronger at long range (around $r = 4$ Å) indicates that the difference observed between $[\text{PtCl}_4]_{\text{sol}}^{2-}$ and pure water are related to the densities of the liquid systems. From the comparison of the $g_{\text{HO}}(r)$ RDFs within the range of 1.0-1.5 Å (Figure S1a) we point out that, whereas for pure water a clear separation ($g_{\text{HO}}(1.2 \leq r \leq 1.3) = 0.0$) is observed between the O–H (≈ 1.5 Å) and O···H (≈ 1.7 Å) bond distance distributions, this property is not observed for $[\text{PtCl}_4]_{\text{sol}}^{2-}$ ($g_{\text{HO}}(1.2 \leq r \leq 1.3) = 0.1$). This result indicates the presence of intermediate O–H distances which might be related to H_2O molecules bonded to the $[\text{PtCl}_4]^{2-}$ anion and the existence of solvated H_3O^+ entities. We emphasize that these conclusions are transferable to the water liquid structure of the other solvated Pt-halides complexes.

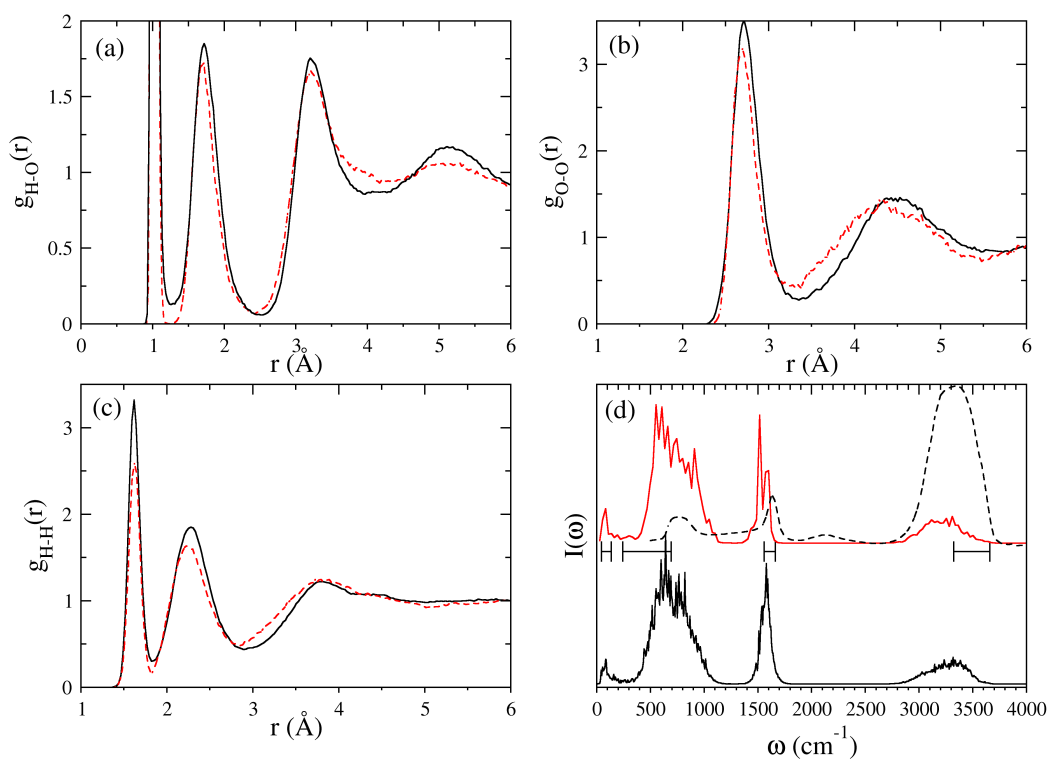


Figure S1: (a,b,c) Partial radial distribution functions of H_2O for the solvated $PtCl_4^{2-}$ complex (black solid line) and pure water (red dashed line). (d) Spectral density of the velocity auto-correlation functions of the solvated $[PtCl_4]^{2-}$ complex (black solid line) and pure water (red dashed line), along with the infra-red experimental spectrum (dashed line) from Ref. 8 and the peak widths of the experimental Raman spectrum (bars) from Ref. 9.

3 Additional data

3.1 H–X and and Pt–H Radial distribution functions

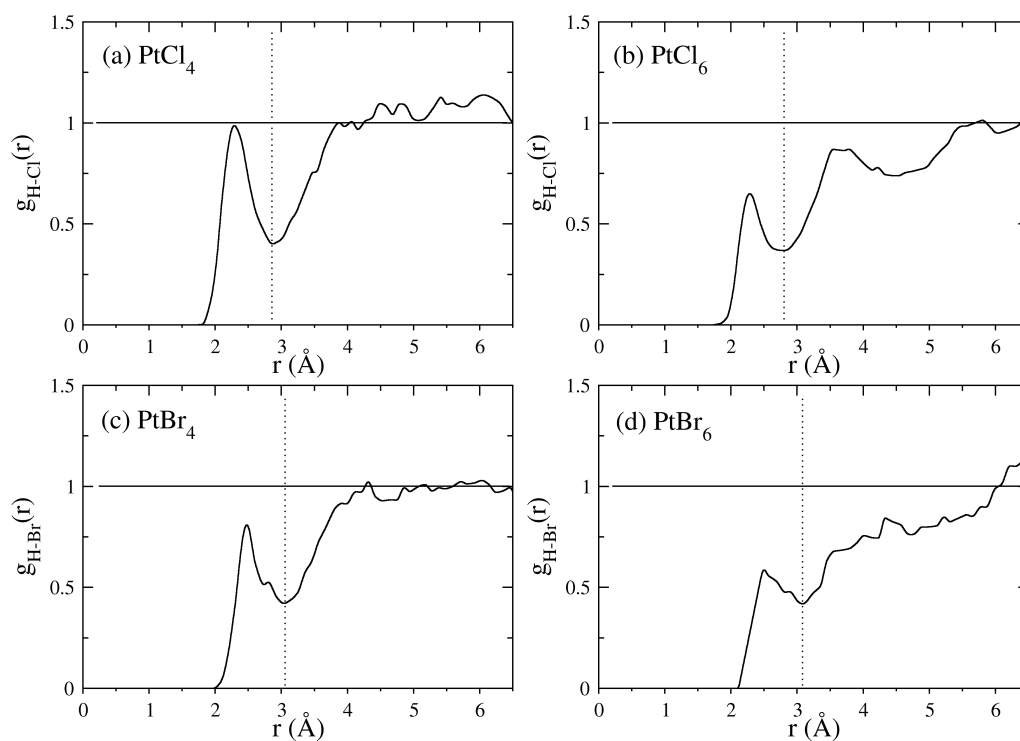


Figure S2: Partial radial distribution functions for H–X atom pairs with $X = \{\text{Cl}, \text{Br}\}$ for the various solvated $[\text{PtX}_n]^{2-}$ complexes. The vertical dotted lines indicate the integration radius used for the calculation of the H coordination number.

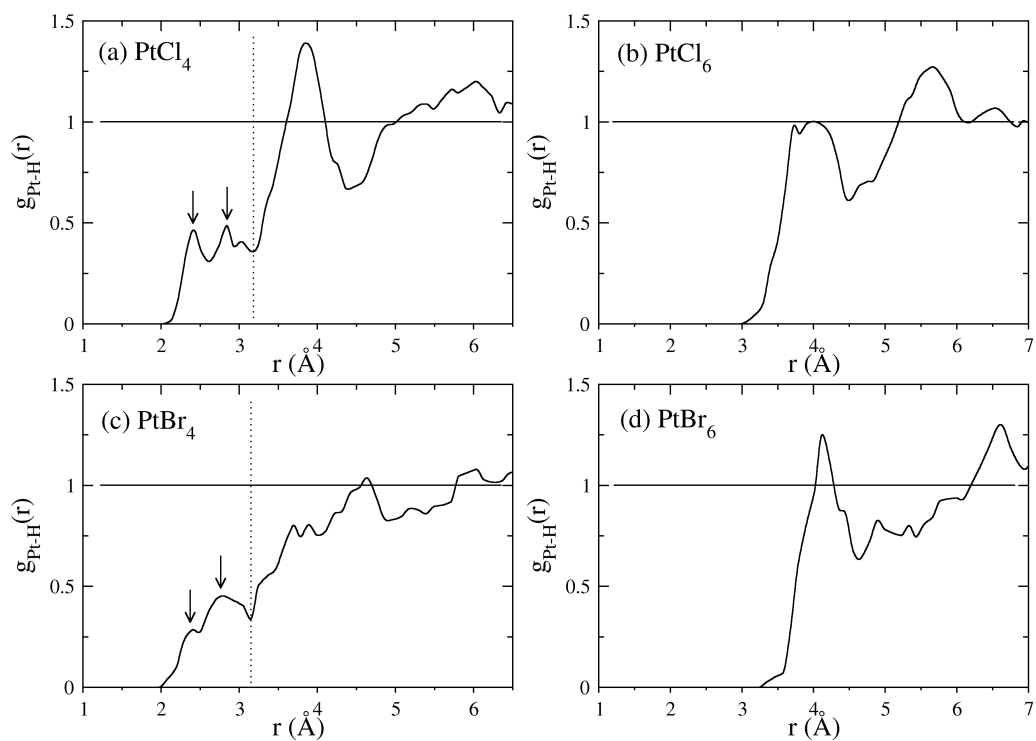


Figure S3: Partial radial distribution functions for Pt–H atom pairs for the various solvated $[\text{PtX}_n]^{2-}$ complexes. Arrows point out the presence of direct Pt←H₂O and/or Pt←OH₂ interactions along the axis perpendicular to the square-planar Pt complexes. The vertical dotted lines indicate the integration radius used for the calculation of the H coordination number.

3.2 Vibrational properties of $[\text{PtCl}_4]^{2-}$ and $[\text{Pt}(\text{CN})_4]^{2-}$ in water

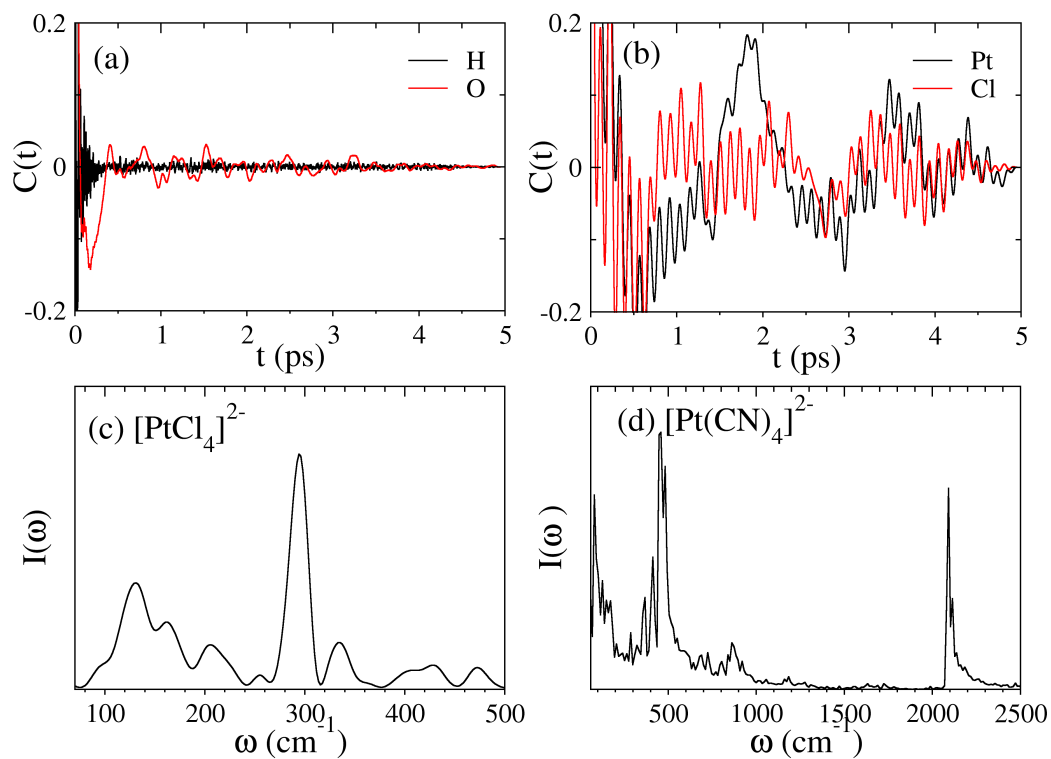


Figure S4: (a,b) Partial velocity auto-correlation functions $C(t)$ calculated for the four atomic species in $[\text{PtCl}_4]_{\text{sol}}^{2-}$. (c,d) Partial vibrational density of states $I(\omega)$ calculated for the isolated $[\text{PtCl}_4]^{2-}$ and $[\text{Pt}(\text{CN})_4]^{2-}$ complexes.

3.3 Theoretical ^{195}Pt isotropic shieldings and chemical shifts

Table S1: Theoretical ^{195}Pt isotropic shielding and chemical shift contributions calculated for the set of PtX_n^{2-} complexes, along with their statistical errors (in ppm).

Hamiltonian ^a	$[\text{PtCl}_6]^{2- b}$	$[\text{PtCl}_4]^{2-}$		$[\text{PtBr}_4]^{2-}$		$[\text{PtBr}_6]^{2-}$		$[\text{Pt}(\text{CN})_4]^{2-}$	
	σ_{av}^T ^c	σ_{av}^T	δ_{av}^T	σ_{av}^T	δ_{av}^T	σ_{av}^T	δ_{av}^T	σ_{av}^T	δ_{av}^T
SC	-2307	-913	-1391	-191	-2111	-1038	-1267	3038	-5346
SO	1340	2702	-1364	3665	-2329	3299	-1962	6068	-4728
	$\langle \sigma_{\text{bare}} \rangle$	$\langle \sigma_{\text{bare}} \rangle$	$\langle \delta_{\text{bare}} \rangle$	$\langle \sigma_{\text{bare}} \rangle$	$\langle \delta_{\text{bare}} \rangle$	$\langle \sigma_{\text{bare}} \rangle$	$\langle \delta_{\text{bare}} \rangle$	$\langle \sigma_{\text{bare}} \rangle$	$\langle \delta_{\text{bare}} \rangle$
SC	-2381 ± 46	-959 ± 47	-1419 ± 93	-323 ± 43	-2053 ± 89	-1139 ± 33	-1239 ± 79	2945 ± 7	-5314 ± 53
SO	1274 ± 40	2663 ± 37	-1391 ± 77	3554 ± 37	-2283 ± 77	3214 ± 27	-1943 ± 67	5978 ± 5	-4710 ± 45
	$\langle \sigma^T \rangle$	$\langle \sigma^T \rangle$	$\langle \delta^T \rangle$	$\langle \sigma^T \rangle$	$\langle \delta^T \rangle$	$\langle \sigma^T \rangle$	$\langle \delta^T \rangle$	$\langle \sigma^T \rangle$	$\langle \delta^T \rangle$
NR	426 ± 28	1536 ± 28	-1110 ± 56	2316 ± 24	-1890 ± 52	1714 ± 19	-1288 ± 47	3536 ± 7	-3111 ± 35
SC	-2063 ± 44	-278 ± 43	-1781 ± 87	209 ± 39	-2268 ± 83	-933 ± 30	-1128 ± 74	2932 ± 8	-4985 ± 52
SO	1576 ± 38	3235 ± 35	-1661 ± 73	4105 ± 33	-2533 ± 71	3405 ± 25	-1832 ± 63	5996 ± 6	-4426 ± 44
Expt.			-1623^{10}		-2672^{10}		-1882^{11}		-4746^{12}

^a The abbreviations SC and SO denote the scalar and spin-orbit ZORA Hamiltonian.

^b Reference system used for the calculation of the ^{195}Pt chemical shifts (see eq. (4) of the main paper).

^c See eq. (5) and (6) and text of the main paper for the definitions of σ_{av}^T , δ_{av}^T , $\langle \sigma_{\text{bare}} \rangle$ and $\langle \delta_{\text{bare}} \rangle$.

4 Complete references

4.1 Complete reference 27

Gaussian 03, Revision C.02, M. J. Frisch, G. W. Trucks, H. B. Schlegel, G. E. Scuseria, M. A. Robb, J. R. Cheeseman, J. A. Montgomery, Jr., T. Vreven, K. N. Kudin, J. C. Burant, J. M. Millam, S. S. Iyengar, J. Tomasi, V. Barone, B. Mennucci, M. Cossi, G. Scalmani, N. Rega, G.A. Petersson, H. Nakatsuji, M. Hada, M. Ehara, K. Toyota, R. Fukuda, J. Hasegawa, M. Ishida, T. Nakajima, Y. Honda, O. Kitao, H. Nakai, M. Klene, X. Li, J. E. Knox, H. P. Hratchian, J. B. Cross, C. Adamo, J. Jaramillo, R. Gomperts, R. E. Stratmann, O. Yazyev, A. J. Austin, R. Cammi, C. Pomelli, J. W. Ochterski, P. Y. Ayala, K. Morokuma, G. A. Voth, P. Salvador, J. J. Dannenberg, V. G. Zakrzewski, S. Dapprich, A. D. Daniels, M. C. Strain, O. Farkas, D. K. Malick, A. D. Rabuck, K. Raghavachari, J. B. Foresman, J. V. Ortiz, Q. Cui, A. G. Baboul, S. Clifford, J. Cioslowski, B. B. Stefanov, G. Liu, A. Liashenko, P. Piskorz, I. Komaromi, R. L. Martin, D. J. Fox, T. Keith, M. A. Al-Laham, C.Y. Peng, A. Nanayakkara, M. Challacombe, P. M. W. Gill, B. Johnson, W. Chen, M. W. Wong, C. Gonzalez, and J. A. Pople, Gaussian, Inc., Wallingford CT, 2004.

4.2 Complete reference 35

Amsterdam Density Functional, SCM, Theoretical Chemistry, Vrije Universiteit, Amsterdam, The Netherlands, <http://www.scm.com>, E. J. Baerends and J. Autschbach and A. Bérces and F. M. Bickelhaupt and C. Bo and P. M. Boerrigter and L. Cavallo and D. P. Chong and L. Deng and R. M. Dickson and D. E. Ellis and van Faassen, M. and L. Fan and T. H. Fischer and Fonseca Guerra, C. and van Gisbergen, S. J. A. and J. A. Groeneveld and O. V. Gritsenko and M. Grüning and F. E. Harris and van den Hoek, P. and C. R. Jacob and H. Jacobsen and L. Jensen and van Kessel, G. and F. Kootstra and van Lenthe, E. and D. A. McCormack and A. Michalak and J. Neugebauer and V. P. Osinga and S. Patchkovskii and P. H. T. Philipsen and D. Post and C. C. Pye and W. Ravenek and P. Ros and P. R. T. Schipper and G. Schreckenbach and J. G. Snijders and M. Solà and M. Swart and D. Swerhone and te Velde, G. and P. Vernooijs and L. Versluis and L. Visscher and O. Visser and F. Wang and T. A. Wesolowski and van Wezenbeek, E. and G. Wiesenekker and S.K. Wolff and T.K. Woo and A.L. Yakovlev and T. Ziegler.

References

- [1] Allen, M. P.; Tildesley, D. J. *Computer Simulation of Liquids*; Oxford University Press, USA: 1989.
- [2] P., P. K.; Marx, D. *Phys. Chem. Chem. Phys.* **2006**, 8, 573–586.
- [3] Noid, D. W.; Koszykowski, M. L.; Marcus, R. A. *J. Chem. Phys.* **1977**, 67, 404–408.
- [4] Childers, D. G. *Modern Spectrum Analysis*; John Wiley & Sons Inc: 1978.
- [5] Press, W. H.; Teukolsky, S. A.; Vetterling, W. T.; Flannery, B. P. *Numerical Recipes in Fortran 90, Vol. 2*; Cambridge University Press: 2 ed.; 1996.
- [6] Grossman, J. C.; Schwegler, E.; Draeger, E. W.; Gygi, F.; Galli, G. *J. Chem. Phys.* **2004**, 120, 300–311.
- [7] Schwegler, E.; Grossman, J. C.; Gygi, F.; Galli, G. *J. Chem. Phys.* **2004**, 121, 5400–5409.
- [8] Kim, J.; Schmitt, U. W.; Gruetzmacher, J. A.; Voth, G. A.; Scherer, N. E. *J. Chem. Phys.* **2002**, 116, 737–746.
- [9] Carey, D. M.; Korenowski, G. M. *J. Chem. Phys.* **1998**, 108, 2669–2675.
- [10] Matsumoto, K.; Arai, S.; Ochiai, M.; Chen, W.; Nakata, A.; Nakai, H.; Kinoshita, S. *Inorg. Chem.* **2005**, 44, 8552–8560.
- [11] Kramer, J.; Koch, K. R. *Inorg. Chem.* **2007**, 46, 7466–7476.
- [12] Maliarik, M.; Berg, K.; Glaser, J.; Sandstrom, M.; Toth, I. *Inorg. Chem.* **1998**, 37, 2910–2919.