Angewandte
Communications

Water Structuring Hot Paper

DOI: 10.1002/anie.201310266

Charge Asymmetry at Aqueous Hydrophobic Interfaces and Hydration Shells**

*Rüdiger Scheu, Blake M. Rankin, Yixing Chen, Kailash C. Jena, Dor Ben-Amotz, and Sylvie Roke**

The solvation of ions in a dielectric continuum is symmetric with respect to the sign of the ionic charge. Yet, many phenomena show indirect evidence that water may have a preference for negative charge: the vast majority of biological membrane interfaces are neutral or negatively charged,[1] water reorientation dynamics around anions and cations is different,[2] and the zero charge point of water is usually well below pH 7 at hydrophobic/water interfaces.[3] There is undoubtedly a link to the asymmetry of the water molecule. Here, we spectroscopically quantify differences between the structures of hydration shells and hydrophobic/water interfaces induced by ions of opposite charge but essentially identical molecular structure. We show that these two ions, tetraphenylborate (TPB^-) and tetraphenylarsonium (TPA^+), interact dramatically differently with water and its interface: The anion is preferentially hydrated and induces greater orientational order to water near hydrophobic interfaces. In contrast, the cation forms far fewer and weaker π–H bonds than the anion and strongly reduces the orientational order of water near a hydrophobic interface.

The vast majority of lipid (cell) membranes, macromolecules, and their interfaces are either neutral or negatively charged.[1] The hydrophobic–water surface carries a negative charge, and the point of zero charge of most interfaces occurs at very low pH values.[4–6] The hydration free energies[7–9] and entropies[8,10] of anions are calculated to be significantly more negative than those of cations of similar size. Moreover, the dynamics of water reorientation and hydrogen-bond exchange is quite different around positive and negative ions.[2,11] Both experiments and simulations indicate that ions of different size, structure, and charge partition differently at aqueous interfaces.[12,13] In addition to ion polarization, the surface potential at an air–water interface has been proposed to be one of the driving forces that favors anion adsorption.[9,14,15] Although specific ion (i.e. Hofmeister) effects exist for both negative and positive ions, and although they typically correlate with differences in size, polarizability, and/or charge density,[16] specific ion effects are generally smaller for positive ions than for negative ions,[17] thus suggesting an inherent asymmetry in the interaction of water with positive and negative ions. Yet, water is often treated as a dielectric continuum.[18]

The implied charge asymmetry is undoubtedly related to water's dipolar character and highly directional hydrogen-bonding proclivity. Although electrostatic interactions are symmetric with respect to charge exchange, hydrogen-bonding interactions are not symmetric with respect to solute charge, as water preferentially donates hydrogen bonds to anions ($O{-}H\cdots X^-$). Moreover, hydrogen bonding is highly cooperative (non-additive) in the sense that the average energy per hydrogen bond in water clusters increases non-linearly with the total number of hydrogen bonds.[19,20] Although the asymmetry between the interaction of water with positive and negative ions could play an important role in many biochemical and other aqueous chemical processes, such asymmetries are difficult to measure and to model theoretically on a molecular level. Here, we describe experiments that quantify charge asymmetry by measuring the difference between the structure of the hydrophobic/water interface and structure of the hydration shell induced by ions of very similar size, shape, and chemical structure, but opposite charge.

We seek to probe the existence and molecular foundation of the difference between the interactions of positive and negative ions with water and hydrophobic/water interfaces. To do so, we chose two ions, tetraphenylarsonium (TPA^+) and tetraphenylborate (TPB^-; Figure 1), which have opposite charges but otherwise very similar molecular structures. Numerous previous studies on these ions have assumed that they have essentially identical free energies of transfer across an interface between any arbitrary pair of solvents,[21–24] and the dielectric properties of solutions containing these ions are inferred to be very similar.[25] On the other hand, some theoretical calculations have concluded that TPB^- ions have a more favorable hydration energy than TPA^+ ions.[26] Here, we characterize experimentally the different influence of these two ions on water structure, as well as the corresponding difference in the strength and number of hydrogen bonds between water and the delocalized π orbitals of the phenyl rings (π-H bonding) by using Raman spectroscopy of the hydration shell. The effects of the ions on the interfacial

---

[*] Dr. R. Scheu, Y. Chen, Dr. K. C. Jena, Prof. Dr. S. Roke
Laboratory for fundamental BioPhotonics (LBP)
Institute of Bioengineering (IBI), School of Engineering (STI)
École Polytechnique Féderale de Lausanne (EPFL)
1015 Lausanne (Switzerland)
E-mail: sylvie.roke@epfl.ch

B. M. Rankin, Prof. Dr. D. Ben-Amotz
Purdue University, Department of Chemistry
West Lafayette, IN 47907 (USA)

[**] This work is supported by the Julia Jacobi Foundation, the Swiss National Science Foundation (grant number 200021_140472), the European Research Council (grant number 240556), the US National Science Foundation (CHE-1213338), and a PRF Research Grant from Purdue University. We thank John C. Conboy and Thomas L. Beck for useful discussions.

Supporting information for this article is available on the WWW under http://dx.doi.org/10.1002/anie.201310266.

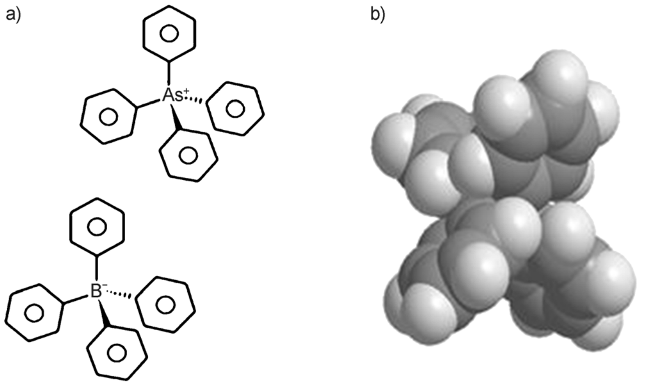

Figure 1. a) The chemical structure and b) a space-filling model of tetraphenylarsonium (TPA$^+$) and tetraphenylborate (TPB$^-$).

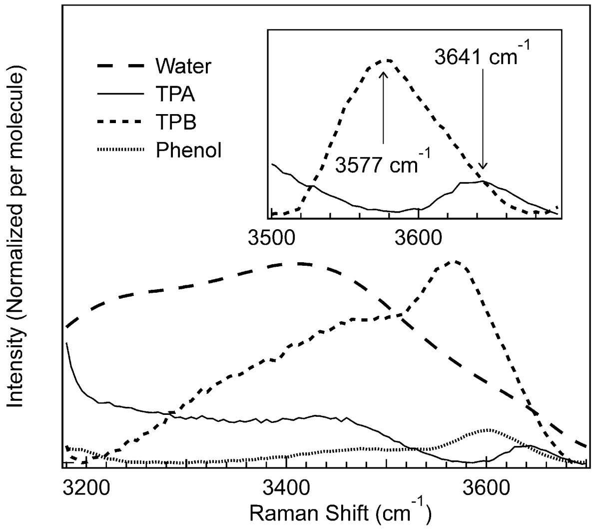

Figure 2. Hydration-shell spectra of oppositely charged ions of essentially identical structure. The O-H stretch Raman intensity (normalized per molecule) arising from the hydration shell of the negatively charged TPB$^-$ ions (-----) and positively charged TPA$^+$ ions (——) are compared with that of the neutral aromatic phenol dissolved in water (•••••). The Raman spectrum of bulk water (– – –) is shown for reference (arbitrarily scaled to approximately the same height as the TPB$^-$ spectrum). The inset shows the π-H bond bands of TPB$^-$ (-----) and TPA$^+$ (——), after subtraction of the hydrogen-bonded O-H background. The experimental concentrations of TPB$^-$ and TPA$^+$ are 0.1 M, while that of phenol is 0.5 M, but the hydration-shell spectra have been scaled to correspond to the same concentration.

properties of the charged hydrophobic/water interface is measured by probing the charge, water structure, and ionic surface structure of an aqueous ionic solution containing liquid (hexadecane) oil droplets (of ca. 100 nm radius) in water by electrokinetic mobility measurements, second harmonic scattering, and vibrational sum frequency scattering. Our results suggest that the interactions between water and negative ions cooperate, while for positive ions they counteract each other, thus rendering the negative interfaces more stable than the positive ones (as discussed below).

Interactions between water and solute molecules can be probed with Raman multivariate curve resolution (Raman-MCR)[27] to detect solute-correlated spectral changes in the O-H stretch band of water. For example, Raman-MCR has previously been used to detect changes in water structure around benzene and other hydrophobic[28] and ionic[29] solutes. Here, we report results obtained by using Raman-MCR to reveal differences between the hydration-shell structures of TPB$^-$ and TPA$^+$ and compare them to the hydration shell of phenol, which has a single uncharged phenyl ring. Note that previous studies have shown that the spectra of the hydration shells of phenol and benzene are essentially identical, and thus the OH head group of phenol has little influence on the following results.[30]

Figure 2 shows the hydration-shell spectra of the O-H stretch region of dilute solutions of TPB$^-$ ions, TPA$^+$ ions, and phenol, all normalized to the same solute concentration, and compared with the O-H stretch band of bulk water (see Figure 2 for further details). The Na$^+$ counterions have no observable effect on the water O-H band,[29] and the contribution of Cl$^-$ ions to the spectrum of the hydration shell of TPA$^+$ was removed by including NaCl in the water reference solution, at the same concentration as TPA$^+$, as previously described.[31] The phenol spectrum[30] displays a π-H bond band at about 3600 cm^{-1} (plus a weak red-shifted hydrogen-bonded O-H band). The number of π–H bonds per molecule can be estimated from the ratio of the area of the π-H-bonded O-H band to that of the aromatic C-H stretch mode, combined with the previously reported theoretical estimate that a π-H-bonded O-H mode has a Raman cross-section that is about 21 % larger than that of an aromatic C-H mode.[30] Thus, the fact that the π-H-bonded O-H band of TPB$^-$ has a 7 ± 1 times larger area than that of TPA$^+$ (as shown in the inset of Figure 2) implies that the π-H bond between water and TPB$^-$ is significantly stronger and more abundant than the π–H bond to TPA$^+$. The corresponding free energy difference is approximately $-kT\ln(7)\approx-2kT$ (-5 kJ mol^{-1} at room temperature), consistent with our observation that the π-H-bonded O-H band of TPB$^-$ is significantly red-shifted (by ca. 64 cm^{-1}) relative to that of TPA$^+$. It is further noteworthy that the probability of forming a π-H bond to each one of the phenyl rings of the TPA$^+$ ion is about five times lower than that to the neutral phenol molecule. Previous studies have demonstrated that π–H bonds between water and benzene are entropically stabilized, as they have a slightly less negative enthalpy than water–water hydrogen bonds, but a slightly more positive entropy.[30] Since the entropic contribution presumably varies little between the π–H bonds of phenol, TPA$^+$, and TPB$^-$, the probability difference is likely due to the corresponding π–H bond enthalpy difference, which makes sense, as the main difference between TPA$^+$ and TPB$^-$ is the sign of the total charge. Thus, the solvation shells of TPB$^-$ and TPA$^+$ are clearly quite different, with the TPA$^+$ ion having far fewer and weaker π-H bonds to water than does the TPB$^-$ ion.

To study the molecular structure of the ions and water at a hydrophobic/water interface, we used a solution containing nanoscopic liquid hexadecane droplets in an aqueous solution that contains either TPB$^-$ or TPA$^+$ ions. Such a system has an oil–water surface area of approximately 3000 cm^2 per mL. The surface charge was monitored by performing electrokinetic zeta potential measurements. The surface structure of the TPB$^-$ and TPA$^+$ ions at the oil–water interface was measured with vibrational sum frequency scattering (SFS), a vibrational coherent surface spectroscopy technique that measures the combined IR and Raman spectrum of molecules, which can only give rise to a signal in non-centrosymmetric environments such as interfaces.[32–34] The SF intensity for each vibrational mode scales quadratically with its surface density, multiplied by the square of the cosine of the tilt angle between the symmetry axis of the chemical group and the interface normal.[35,36] Vibrational modes associated with groups that lie in the surface plane are therefore not observed. We further probed the surface structure of water using second harmonic scattering (SHS), which probes the net orientational correlations of water dipoles along the surface normal, and is thus sensitive to the orientational directionality of water molecules in the interfacial region, induced, for example, by an electric field and/or hydrogen bonding.[37–39]

Figure 3 A shows SFS spectra of hexadecane nanodroplets in solutions of 10 mM TPB^- and TPA^+ in D_2O. The corresponding zeta potentials of the two solutions are −100 mV and +115 mV, respectively, which means the droplets have a comparable interfacial charge density. The counterions, Na^+ and Cl^-, are not interfacially active at a hydrophobic/water interface,[40] and since we use very low concentrations (1 ion per 5500 water molecules for the SFS experiments), we assume that they do not have any influence on the presented results. The SFS spectra display the C-H stretch modes of the phenyl rings of the tetraphenyl ions (2990–3100 cm^{-1}), as well as the high-frequency side of the interfacial hexadecane molecules (ca. 2850–2990 cm^{-1}). The SFS spectra for TPB^- and TPA^+ are similar below 2950 cm^{-1}, but are very different above 2950 cm^{-1}. The SFS intensity of TPB^- is more than ten times larger than that of TPA^+. The vibrational features of these ions can be assigned to combined C-H stretch modes originating from the individual phenyl rings (for more details see Refs. [41,42]).

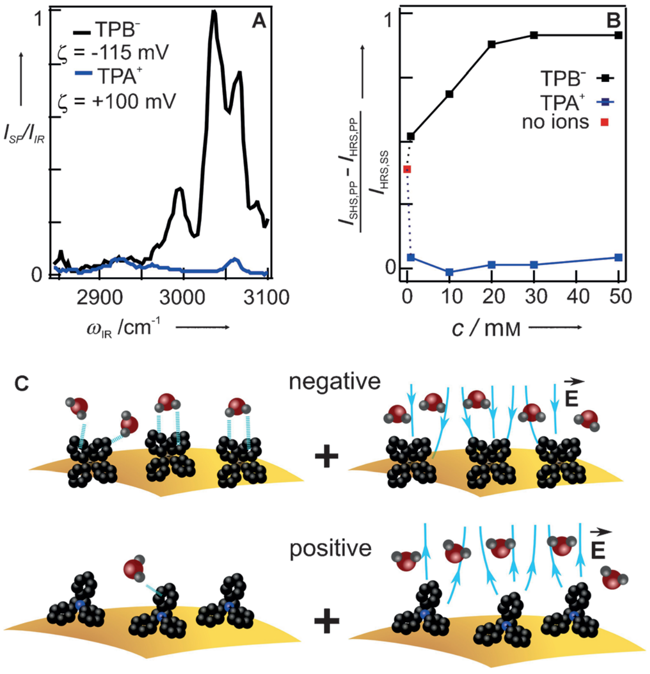

Figure 3. The interfacial structure of positively and negatively charged interfaces. A) SFS spectra (normalized intensity versus IR wavenumber, in ppp, with all beams polarized in the plane of incidence) of the oil droplet/solution interface. The D_2O solutions contain 10 mM of TPB^- (black) and TPA^+ ions (blue). The spectra are normalized to the C-H stretch modes of the oil. B) SHS intensities of droplet interfaces (pp polarization) with different concentrations of ions. The SH (hyper-Rayleigh) scattering signal from the oil-droplet-free salt solution has been subtracted from the data. The scattering angle was 35° with respect to the fundamental beam. The zeta potential of the pure oil droplets in water is about −50 mV. C) Illustration of the difference in surface hydration: for negative ions, the hydrogen bonding and electrostatic interactions cooperate (top), while for positive ions they do not (bottom). Note that the fourth phenyl ring of TPA^+ is pointing into the paper.

TPA^+ ions clearly produce a much weaker SFS signal, as well as a different surface vibrational signature, than the TPB^- ions, even though the interfacial number density of both ions is comparable. The difference in the spectral shape and intensity must therefore imply that the two ions adopt a very different surface structure. This is consistent with our hydration-shell spectra, which indicate that the TPB^- ions are better hydrated (more strongly π-H bonded) than TPA^+ ions in bulk solution, and so one might expect TPB^- to also be better hydrated than TPA^+ at the oil–water interface. Thus, one might expect the TPB^- ions to penetrate further into water than do the TPA^+ ions. It may also be significant that TPA^+ has slightly more flexible central As−C bonds,[43] relative to the B−C bonds of TPB^-. Some of the phenyl rings of TPA^+ may therefore be capable of adopting an approximately planar structure parallel to the interface (which would produce no SFS signal) which could explain the very weak SFS intensity of TPA^+.

The SHS results shown in Figure 3 B indicate that adsorption of TPB^- at the oil/water interface produces a much greater SHS signal than adsorption of an equal amount of TPA^+. Note that in each case the SHS signal of the corresponding solution (without oil droplets) has been subtracted. The very small SHS signal produced upon adsorption of TPA^+ indicates that this positively charged ion significantly decreases the interfacial ordering of water relative to that at the pure oil/water interface (as indicated by the red data point in Figure 3 B). In contrast, TPB^- increases the interfacial orientational ordering of water molecules (relative to that at the pure oil/water interface). Beyond a TPB^- concentration of 20 mM, the SHS intensity levels off, as the increased ionic strength of the solution results in a more effective screening of the surface electric field, and thus evidently limits the net interfacial orienational ordering of water.

The above observations may be explained by considering the combined influence of ion adsorption on both hydrogen bonding and electric field induced ordering (Figure 3 C). The negative TPB^- ions form strong π-H bonds to water (as shown in Figure 2) and thus are expected to preferentially orient water hydrogen atoms towards the oil/water interface (Figure 3 C, top left). Moreover, the DC electric field produced by adsorption of negative TPB^- ions will favor a similar dipolar orientation of water, as expected[38,44–46] (Figure 3 C, top right). In contrast, the weak π-H bonds between water and TPA^+ will tend to slightly favor orienting water hydrogen atoms towards the interface, while the DC electric field induced by TPA^+ adsorption will favor the opposite water orientation (Figure 3C, bottom). Thus, one expects both hydrogen bonding and electric field interactions to cooperatively order water when negative TPB^- ions are adsorbed, but to anti-cooperatively reduce water orientational order when positive TPA^+ ions are adsorbed.

In summary, we have quantified the charge asymmetry associated with the hydration of two oppositely charged ions of very similar molecular structure in water and on a hydrophobic/water interface. Our hydration-shell spectra reveal that water forms far fewer and weaker π-H bonds to the positively charged tetraphenylarsonium ion than to the negatively charged tetraphenylborate ion. Our vibrational sum frequency and second harmonic scattering results further reveal that the two ions adopt quite different structures and induce dramatically different interfacial water structures at an oil–water interface. Our observations are consistent with the cooperative (for negative ions) or anti-cooperative (for positive ions) interactions of electrostatic forces and hydrogen bonding. Our findings further imply that both molecular hydration shells and macroscopic oil–water interfaces are more strongly stabilized when they have a negative rather than a positive surface charge, in keeping with the predominance of negative charges at biological interfaces,[1] as well as the fact that electrokinetic mobility measurements imply that hydrophobic and air/water interfaces have a negative surface charge.[4–6]

Received: November 26, 2013
Revised: January 0, 2014

Keywords: emulsions · interfaces · ions · laser spectroscopy · water chemistry

---

[1] J. M. Berg, J. L. Tymoczko, L. Stryer, *Biochemistry*, New York, W. H. Freeman, **2002**.
[2] K. J. Tielrooij, N. Garcia-Araez, M. Bonn, H. J. Bakker, *Science* **2010**, *328*, 1006 – 1009.
[3] J. K. Beattie, A. M. Djerdjev, *Angew. Chem.* **2004**, *116*, 3652 – 3655; *Angew. Chem. Int. Ed.* **2004**, *43*, 3568 – 3571.
[4] R. J. Hunter, *Foundations of Colloid Science*, Oxford University Press, USA, **2001**.
[5] J. K. Beattie, A. M. Djerdjev, G. G. Warr, *Faraday Discuss.* **2009**, *141*, 31.
[6] R. Vácha, S. W. Rick, P. Jungwirth, A. G. F. de Beer, H. B. de Aguiar, J.-S. Samson, S. Roke, *J. Am. Chem. Soc.* **2011**, *133*, 10204 – 10210.
[7] G. Hummer, L. R. Pratt, A. E. Garcia, *J. Phys. Chem.* **1996**, *100*, 1206 – 1215.
[8] R. Lynden-Bell, J. Rasaiah, *J. Chem. Phys.* **1997**, *107*, 1981 – 1991.
[9] T. L. Beck, *Chem. Phys. Lett.* **2013**, *561 – 562*, 1 – 13.
[10] K. D. Collins, G. W. Neilson, J. E. Enderby, *Biophys. Chem.* **2007**, *128*, 95 – 104.
[11] D. Laage, G. Stirnemann, F. Sterpone, R. Rey, J. T. Hynes, *Annu. Rev. Phys. Chem.* **2011**, *62*, 395 – 416.
[12] W. Kunz, *Specific Ion Effects*, World Scientific Publishing Company, **2009**.
[13] D. J. Tobias, J. C. Hemminger, *Science* **2008**, *319*, 1197 – 1198.
[14] L. Horváth, T. Beu, M. Manghi, J. Palmeri, *J. Chem. Phys.* **2013**, *138*, 154702.
[15] M. D. Baer, A. C. Stern, Y. Levin, D. J. Tobias, C. J. Mundy, *J. Phys. Chem. Lett.* **2012**, *3*, 1565 – 1570.
[16] L. Vrbka, M. Mucha, B. Minofar, P. Jungwirth, E. C. Brown, D. J. Tobias, *Curr. Opin. Colloid Interface Sci.* **2004**, *9*, 67 – 73.
[17] S. C. Flores, J. Kherb, N. Konelick, X. Chen, P. S. Cremer, *J. Phys. Chem. C* **2012**, *116*, 5730 – 5734.
[18] J. N. Israelachvili, *Intermolecular and Surface Forces*, Academic Press, New York, **2011**.
[19] F. N. Keutsch, R. J. Saykally, *Proc. Natl. Acad. Sci. USA* **2001**, *98*, 10533 – 10540.
[20] L. V. Slipchenko†, M. S. Gordon, *Mol. Phys.* **2009**, *107*, 999 – 1016.
[21] E. Grunwald, G. Baughman, G. Kohnstam, *J. Am. Chem. Soc.* **1960**, *82*, 5801 – 5811.
[22] B. G. Cox, A. J. Parker, *J. Am. Chem. Soc.* **1973**, *95*, 402 – 407.
[23] A. Grossfield, P. Ren, J. W. Ponder, *J. Am. Chem. Soc.* **2003**, *125*, 15671 – 15682.
[24] J. C. Conboy, G. L. Richmond, *J. Phys. Chem. B* **1997**, *101*, 983 – 990.
[25] W. Wachter, R. Buchner, G. Hefter, *J. Phys. Chem. B* **2006**, *110*, 5147 – 5154.
[26] J. Schamberger, R. J. Clarke, *Biophys. J.* **2002**, *82*, 3081 – 3088.
[27] K. R. Fega, D. S. Wilcox, D. Ben-Amotz, *Appl. Spectrosc.* **2012**, *66*, 282 – 288.
[28] J. G. Davis, K. P. Gierszal, P. Wang, D. Ben-Amotz, *Nature* **2012**, *491*, 582 – 585.
[29] P. N. Perera, B. Browder, D. Ben-Amotz, *J. Phys. Chem. B* **2009**, *113*, 1805 – 1809.
[30] K. P. Gierszal, J. G. Davis, M. D. Hands, D. S. Wilcox, L. V. Slipchenko, D. Ben-Amotz, *J. Phys. Chem. Lett.* **2011**, *2*, 2930 – 2933.
[31] J. G. Davis, B. M. Rankin, K. P. Gierszal, D. Ben-Amotz, *Nat. Chem.* **2013**, *5*, 796 – 802.
[32] A. G. Lambert, P. B. Davies, D. J. Neivandt, *Appl. Spectr. Rev.* **2005**, *40*, 103 – 145.
[33] S. Roke, *ChemPhysChem* **2009**, *10*, 1380 – 1388.
[34] H. B. de Aguiar, A. G. F. de Beer, M. L. Strader, S. Roke, *J. Am. Chem. Soc.* **2010**, *132*, 2122 – 2123.
[35] X. Zhuang, P. B. Miranda, D. Kim, Y. R. Shen, *Phys. Rev. B* **1999**, *59*, 12632.
[36] A. G. F. de Beer, S. Roke, *J. Chem. Phys.* **2010**, *132*, 234702.
[37] R. K. Campen, A. K. Pymer, S. Nihonyanagi, E. Borguet, *J. Phys. Chem. C* **2010**, *114*, 18465 – 18473.
[38] K. C. Jena, P. A. Covert, D. K. Hore, *J. Phys. Chem. Lett.* **2011**, *2*, 1056 – 1061.
[39] E. C. Y. Yan, Y. Liu, K. B. Eisenthal, *J. Phys. Chem. B* **1998**, *102*, 6331 – 6336.
[40] M. Vazdar, E. Pluharová, P. E. Mason, R. Vácha, P. Jungwirth, *J. Phys. Chem. Lett.* **2012**, *3*, 2087 – 2091.
[41] G. Varsanyi, *Assignments for Vibrational Spectra of Benzene Derivatives*, Adam Hilger, London, **1974**.
[42] E. L. Hommel, H. C. Allen, *Analyst* **2003**, *128*, 750 – 755.
[43] R. Schurhammer, G. Wipff, *J. Phys. Chem. A* **2000**, *104*, 11159 – 11168.
[44] S. Ong, X. Zhao, K. B. Eisenthal, *Chem. Phys. Lett.* **1992**, *191*, 327 – 335.
[45] P. L. Hayes, J. N. Malin, C. T. Konek, F. M. Geiger, *J. Phys. Chem. A* **2008**, *112*, 660 – 668.
[46] A. G. F. de Beer, R. K. Campen, S. Roke, *Phys. Rev. B* **2010**, *82*, 235431.
[47] H. B. de Aguiar, J.-S. Samson, S. Roke, *Chem. Phys. Lett.* **2011**, *512*, 76 – 80.
[48] H. B. De Aguiar, R. Scheu, K. C. Jena, A. G. F. De Beer, S. Roke, *Phys. Chem. Chem. Phys.* **2012**, *14*, 6826 – 6832.
[49] N. Gomopoulos, C. Lütgebaucks, Q. Sun, C. Macias-Romero, S. Roke, *Opt. Express* **2013**, *21*, 815 – 821.