Angewandte
International Edition Chemie

DOI: 10.1002/anie.201003662

Water Clusters

Infrared Spectra and Hydrogen-Bonded Network Structures of Large Protonated Water Clusters $H^+(H_2O)_n$ ($n = 20$–200)[**]

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Because H-bonding causes unique properties of water, structures of H-bonded water networks are of fundamental interest. For molecular-level understanding of H-bonded network structures in water and aqueous solutions, water clusters $(H_2O)_n$ and hydrated clusters $M(H_2O)_n$ (M: solute) in the gas phase have been extensively studied.[1–22] These clusters are microscopic models for bulk water and aqueous solutions, respectively, and they provide detailed structural information on H-bonded networks. It is expected that investigation of cluster structures for each cluster size n would lead to insight into the bulk picture. Because H-bonding environments are sensitively reflected in OH stretching frequencies of water, IR spectroscopy of size-selected clusters is a powerful tool to elucidate size-dependent H-bonded water network structures.[1,5–12,14,15]

In the case of neutral clusters such as $(H_2O)_n$, rigorous size selection is difficult and has been practically limited to n values up to ten.[1,12] These sizes are too small to construct bulky water networks, which contain interior and four-coordinate (4-coord) water molecules. Because 4-coord water would be in the majority in bulk water, as in hexagonal ice,[23] spectral identification of 4-coord water is a key to studying large-scale H-bonded water networks. Studies of larger clusters are thus required.

For ionic clusters, on the other hand, application of mass spectrometric techniques removes the difficulty of size selection and opens the way to study larger clusters ($n > 10$), which were first studied in protonated water clusters $H^+(H_2O)_n$ ($n \lesssim 30$).[5–7,9] They are models for the hydrated proton and provide structural information about water networks around an excess proton. Studies on $H^+(H_2O)_n$ ($n \lesssim 30$) have shown that clusters larger than $n \approx 10$ form closed net (multiple ring) structures, and they develop into closed cage structures with a dramatic decrease in 2-coord water molecules at $n = 21$.[5–7,9] This network development of $H^+(H_2O)_n$ has been discussed by analyzing free (non-H-bonded) OH stretching bands corresponding to the 1–3-coord water molecules. In larger clusters, 4-coord water is expected to be dominant; however, no direct observations have been reported. Because 4-coord water molecules do not have a free OH group, analyses of the H-bonded OH stretching region are required to reveal their contribution for more bulky networks. Previously, we succeeded in extending the application of size-selected IR spectroscopy to $n = 100$, but only free OH bands were covered.[10] For $H^+(H_2O)_n$, IR spectra in the H-bonded OH region have been reported only for clusters with $n \leq 27$ so far.[5,6]

In the case of other hydrated clusters, Williams et al. have reported IR spectra of $Ca^{2+}(H_2O)_{n\leq 69}$ and $SO_4^{2-}(H_2O)_{n\leq 80}$.[14,19] These are the largest cationic and anionic clusters investigated by size-selected IR spectroscopy in the whole OH stretching region. In these studies, the center of the H-bonded OH stretching band was found to approach that of bulk water with increasing cluster size; however, the band width of the H-bonded OH stretching band accounts only for part of the bulk spectrum, possibly because the doubly positively charged Ca^{2+} and/or negatively charged SO_4^{2-} ions strongly affect water networks. It is expected that, in much larger clusters with a singly charged ion, the ion effect would be further diluted and the cluster structure would be much closer to those of neat water networks.

To identify the 4-coord water, and to discuss less perturbed H-bonded network structures of hundreds of water molecules, we report here IR spectra of precisely size selected, large $H^+(H_2O)_n$ in the OH stretching region (2200–4000 cm^{-1}) up to a size of $n = 200$, which is expected to be large enough to form a bulklike H-bonded network in which 4-coord water is dominant. For example, the lowest-energy structures of $(H_2O)_n$ ($n \lesssim 1000$) on the empirical potential-energy surface have been reported, and these studies suggested that crystal cores are formed in the size region of a few hundred water molecules or more.[2–4,22] We show clear spectroscopic signatures for the abundance of the interior (4-coord) water. Furthermore, the fact that IR spectral patterns approach those of supercooled water and ice with increasing cluster size suggests formation of more ordered H-bonded network structures.

Figure 1a shows IR photodissociation spectra of $H^+(H_2O)_n$ ($n = 20$–200). Depths of cluster-ion depletion, caused by the vibrational predissociation, are plotted as a function of the IR wavenumber. The spectra of $H^+(H_2O)_{20,21}$ are similar to those reported previously.[10] Bands around 3700 and

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[**] We are grateful to Dr. M. Hayashi in CCMS, National Taiwan University, Taiwan for his help to the data analyses. We also thank Dr. J.-L. Kuo in IAMS, Academia Sinica, Taiwan for stimulating discussion. This study was supported by the Grant-in-Aid for Scientific Research (Project No. 19056001 from MEXT Japan, and Nos. 205015, 20550005, and 2235001 from JSPS), and the Mitsubishi Foundation. K.M. is supported by JSPS Research Fellowships for Young Scientists. Most of the calculations were performed by using supercomputing resources at Cyberscience Center, Tohoku University.

Supporting information for this article is available on the WWW under http://dx.doi.org/10.1002/anie.201003662.

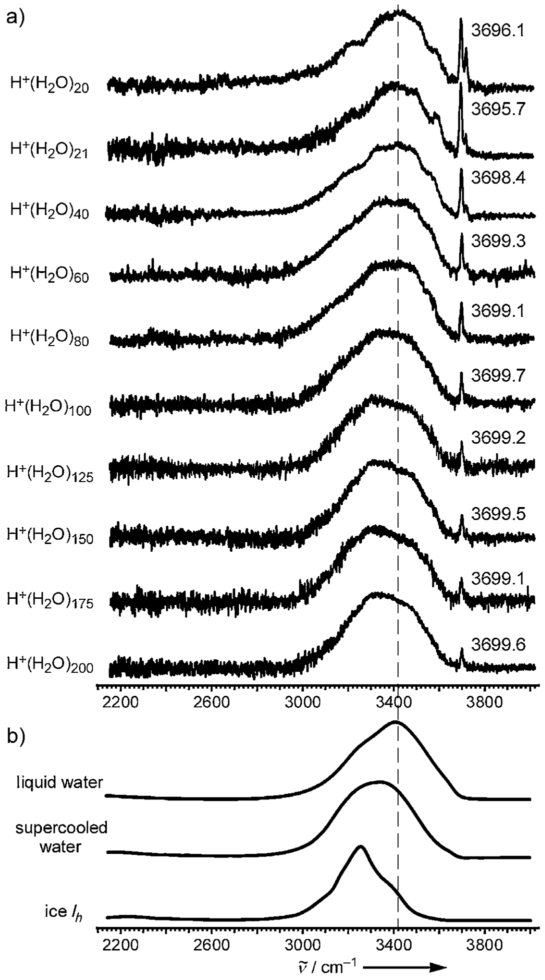

Figure 1. a) IR photodissociation spectra of $H^+(H_2O)_n$ ($n = 20$–200) in the OH stretching region. These spectra were measured by monitoring the depletion of the size-selected cluster ions of interest due to vibrational predissociation. Depletion depths are plotted. Peak positions of free OH bands are indicated in cm^{-1}. b) IR spectra of liquid water (298 K), supercooled water (240 K), and hexagonal ice (235 K). These spectra are reproduced by reported numerical data.[26,27] The dashed line is a guide to the eye.

3720 cm^{-1} are assigned to the free OH stretchin vibrations of 3-coord and 2-coord water molecules, respectively. Broad bands below 3600 cm^{-1} are H-bonded OH stretching vibrations. As in previous studies, the 2-coord water band is much weaker than the 3-coord band in $n \geq 21$ clusters.[5–7,9–11] By comparison with the previous IR study on $H^+(H_2O)_{21}$ formed under various conditions and theoretical studies, we estimate that clusters observed here have finite temperatures of 150–200 K.[9,17,18] The behavior of the free OH band shows that closed cage (neither chain nor net) networks are maintained at least up to $n = 200$ and that clusters with $n \geq 21$ consist mainly of 3- or 4-coord water molecules. In large clusters, the free OH band is attributed only to 3-coord water molecules, while the H-bonded OH band is attributed to 3- and 4-coord water molecules. As is clearly seen in Figure 1 a, the relative intensity of the free OH band decreases with increasing cluster size. This means that 4-coord water becomes dominant in larger clusters.[2–4]

For a detailed investigation of the band position of 4-coord water molecules, we carried out density functional (DFT) calculations at the B3LYP/6-31+G(d) level.[24] We calculated structures and their IR spectra for $H^+(H_2O)_{60}$ as a typical example of a large cluster (Figure 2). First, we constructed a cluster consisting only of 3-coord water molecules. In this case, a buckyball-like hollow cage (Figure 2b) is a possible structure, as Ludwig and Appelhagen introduced for $(H_2O)_{60}$.[25] Its simulated spectrum shows almost flat intensity distribution in the 2950–3550 cm^{-1} region and it clearly disagrees with the experimental spectrum. Such disagreement implies that a contribution of 4-coord water molecules is necessary to reproduce the observed spectrum.

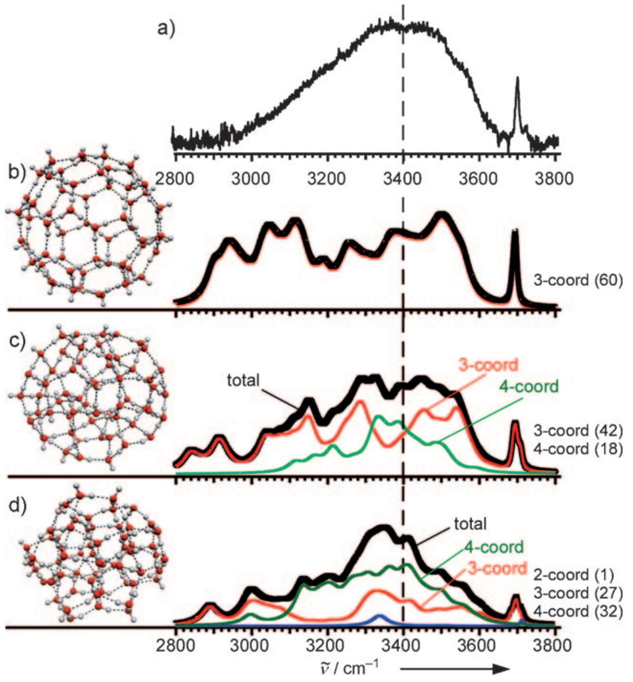

Figure 2. a) Experimental spectra of $H^+(H_2O)_{60}$. b–d) Calculated model cluster structures of $H^+(H_2O)_{60}$ and their IR spectra obtained at the B3LYP/6-31+G(d) level with a scale factor of 0.9736. Curves in blue, red, and green indicate decomposition of the spectra to 2-, 3-, and 4-coord water molecules, respectively. Curves in black indicate the simulated spectra due to the sum of the individual components. To simulate spectra, Lorentzian functions of 10 and 50 cm^{-1} full width at half-maximum were used for free and H-bonded OH stretching vibrations, respectively.

Then, we calculated two model structures having 18 and 32 water molecules in 4-coord sites (Figure 2 c,d). The corresponding spectra (black curves in Figure 2 c,d) are in better agreement with the experimental one. In these spectra, we decomposed bands into the contributions of the 3- and 4-coord water molecules. We analyzed each normal mode and identified the local OH oscillator having the largest amplitude. Then this normal mode was categorized into the class of coordination to which the water molecule of the largest contribution belongs. In Figure 2 c and d, the red and green curves indicate the spectral contributions of the 3- and 4-

coord water molecules, respectively. The 3-coord bands are similar to those in Figure 2 b, that is, the spectrum of "pure" 3-coord water. On the other hand, the 4-coord bands have a narrower intensity distribution, with a maximum in the 3300–3400 cm^{-1} region. These analyses agree with our expectation that 4-coord water contributes to experimental spectra, which also have a maximum in the 3300–3400 cm^{-1} region. Of course, the observed spectrum is attributed to an ensemble of many structural isomers. In addition, the calculated structures are not necessarily actual spectral carriers. As a qualitative trend, however, nice agreement between the observed and calculated spectra is seen, and it demonstrates that the contribution of 4-coord water is essential to reproduce the band shape of the observed spectrum.

Note that IR spectra of $H^+(H_2O)_{20,21}$, for which 4-coord bands have not been discussed, also show similar band shapes to that of $H^+(H_2O)_{60}$. This suggests even these smaller clusters, at least $H^+(H_2O)_{n\geq21}$, also contain 4-coord water molecules. (For $H^+(H_2O)_{n\leq20}$, the situation is complicated because quite a few 2-coord water molecules exist, and their contribution to the IR band is expected to overlap with that of the 4-coord water molecules.[21]) For $H^+(H_2O)_{21}$, the reported structure is a dodecahedral cage enclosing one water molecule (see Figure S1 in the Supporting Information). In such a structure, one interior and four surrounding water molecules are 4-coord. The band shape analysis for $H^+(H_2O)_{21}$ (Figure S1, Supporting Information) agrees with this structure.

In addition to the consideration of coordination numbers, H-bonded network structures should be discussed. In the experimental IR spectra (Figure 1), a low-frequency shift of the H-bonded band and a small high-frequency shift of the free OH band are observed with increasing cluster size. To interpret these results, we compare the spectra with those of bulk water and water surface.

Figure 1 compares experimental IR spectra of $H^+(H_2O)_n$ (Figure 1 a) and previously reported IR spectra of liquid water, supercooled water, and hexagonal ice (Figure 1 b).[26,27] Although free OH bands are absent in the bulk spectra, H-bonded bands of the $n \lesssim 60$ clusters are similar to that of liquid water in their absorption maxima and band centers. On the other hand, in larger clusters, the maximum and center of the band are shifted to about 3300 cm^{-1}, that is, closer to those of supercooled water and hexagonal ice. Hexagonal ice has a crystal structure consisting only of 4-coord water molecules, and it is assumed that supercooled water has partially ordered (crystalline) networks.[28] These results thus suggest that $H^+(H_2O)_n$ forms liquidlike, disordered structures at smaller sizes ($n \leq$ tens), but at least partially crystalline structures at larger sizes ($n \gtrsim 100$). Because the number of H-bonds is not maximized in hexagonal crystalline structures, clusters of tens of water molecules or smaller favor four- or five-membered ring motifs. Hexagonal networks (six-membered ring motifs) have the advantage of constructing larger, more ordered networks. Note that the development of four-membered ring motifs is inherently limited to one direction (fused-cubic structures only),[13] and it is difficult to avoid defects in constructing large-scale networks consisting only of five-membered rings. In accordance with these discussions, we suggest that formation of crystalline structures occurs in $H^+(H_2O)_n$ clusters with hundreds of water molecules. Such formation of a crystalline core in large clusters has been predicted by theoretical searches for low-energy structures and IR spectroscopy on average size-controlled clusters,[2–4,22] and the present results are consistent with these previous studies.

Figure 3 plots the free OH stretching frequencies as a function of the cluster size. In the region of $n \lesssim 60$, free OH frequencies show a clear high-frequency shift, while the frequency becomes constant in the larger-sized region. Because a lower free OH frequency is generally expected when surrounding H-bonds are stronger,[13,16] the high-frequency shift in Figure 3 shows weakening of H-bonds in the networks. The H-bond strength in $H^+(H_2O)_n$ clusters is enhanced by the charge of the excess proton. This shift is thus accounted for by dilution of the effect of the excess proton. The frequency seems to converge to 3699–3700 cm^{-1}. In the previous study on $H^+(H_2O)_n$ ($n \leq 100$), from the fact that the OH frequency of 3699–3700 cm^{-1} is much lower than the previously reported value of about 3718 cm^{-1} for $(H_2O)_{\langle n\rangle=40,111}$ ($\langle n\rangle$: average size, Figure 3),[4] we concluded that an excess proton affects the structures of H-bonded network even in large clusters ($n = 100$).[10] To obtain more accurate data on the free OH frequency of large neutral water clusters, we recently measured free OH frequencies of phenol–$(H_2O)_n$ clusters, in which the perturbation from phenol is negligible.[13] Figure 3 shows that the free OH frequency of phenol–$(H_2O)_{n-1}$ (and benzene–$(H_2O)_8$) approaches that of $H^+(H_2O)_n$ at least in the $n \lesssim 50$ region, that is, the structures of $H^+(H_2O)_n$ are more similar to those of $(H_2O)_n$ than previously expected.

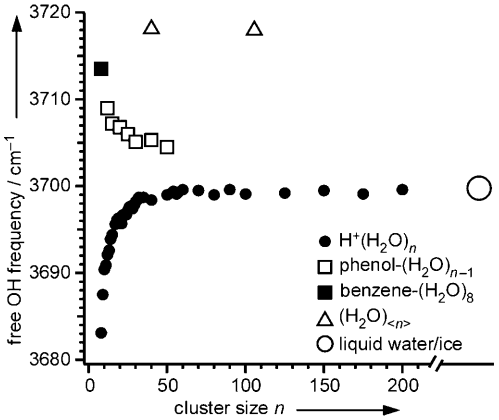

Figure 3. Size-dependent free OH frequencies of $H^+(H_2O)_n$ (●) compared with those of phenol–$(H_2O)_{n-1}$ (□),[13] benzene–$(H_2O)_8$ (■),[12] $(H_2O)_{\langle n\rangle}$ (△),[4] and condensed-phase liquid water and ice (○).[29–32]

The free OH band is also detectable in condensed-phase liquid water and ice surfaces by using sum-frequency generation (SFG) spectroscopy and IR reflection–absorption spectroscopy (IRRAS).[29–32] The reported value for liquid water and ice is about 3700 cm^{-1} (Figure 3). Since this value is essentially the same as that of large $H^+(H_2O)_n$, we suggest that the surface structure of the large clusters is comparable to those of condensed-phase water and ice. This is in contrast to the average-size-controlled study on large $(H_2O)_{\langle n\rangle}$ clusters ($\langle n\rangle < 10^6$), in which free OH frequencies converged to about 3692 cm^{-1}.[2] One possible cause of this difference is the lower temperature of neutral $(H_2O)_{\langle n\rangle}$, cooled in a cell at 4.2–140 K.[2] $H^+(H_2O)_n$ are estimated to have higher temperatures (ca. 150–200 K),[9,17,18] and this temperature range is much closer to those in condensed-phase experiments.

In summary, we have studied large-scale H-bonded water network structures by measuring the IR spectra of precisely size selected, protonated water clusters $H^+(H_2O)_n$ up to $n = 200$ at an estimated temperature of 150–200 K. To the best of our knowledge, $n = 200$ is the largest size investigated by size-selected IR spectroscopy. In IR spectra, we identified the 4-coord and 3-coord water bands. We also showed that the abundance of 4-coord water molecules gradually increases with increasing cluster size. In the interior of the clusters, as has been seen in size-averaged $(H_2O)_{\langle n\rangle}$ studies,[2] indications of crystal-core formation are observed. The free OH frequency suggests that the surface structures of the large clusters are similar to those of liquid water and ice. The observed spectra are expected to be a benchmark for studies concerning large-scale H-bonded networks involving tens to hundreds of water molecules.

Experimental Section

The experimental methods, except for the improved ion source, have been described elsewhere.[5,10] Briefly, $H^+(H_2O)_n$ were generated by supersonic jet expansion. The gaseous mixture of H_2O and He (total pressure 9.5 MPa) was expanded into a vacuum chamber through a pulsed valve (Even–Lavie valve[33]). The gas pulse was crossed by an electron beam of 200 eV generated by an electron gun (Omegatron Co.) in the collisional region of the jet. Cluster ions grew larger in the following collisions and were simultaneously cooled. Ions of interest were selected by a mass spectrometer and irradiated by coherent IR light (Laser Vision OPO/OPA). Vibrational predissociation causes depletion of the parent-ion intensity. IR spectra were measured by monitoring the parent-ion intensity as a function of the IR wavelength.

Received: June 16, 2010
Revised: October 7, 2010

Keywords: density functional calculations · hydrogen bonds · IR spectroscopy · mass spectrometry · water chemistry

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[1] U. Buck, F. Huisken, *Chem. Rev.* **2000**, *100*, 3863 – 3890.
[2] V. Buch, S. Bauerecker, J. P. Devlin, U. Buck, J. K. Kazimirski, *Int. Rev. Phys. Chem.* **2004**, *23*, 375 – 433.
[3] J. K. Kazimirski, V. Buch, *J. Phys. Chem. A* **2003**, *107*, 9762 – 9775.
[4] C. Steinbach, P. Andersson, J. K. Kazimirski, U. Buck, V. Buch, T. A. Beu, *J. Phys. Chem. A* **2004**, *108*, 6165 – 6174.
[5] M. Miyazaki, A. Fujii, T. Ebata, N. Mikami, *Science* **2004**, *304*, 1134 – 1137.
[6] J. W. Shin, N. I. Hammer, E. G. Diken, M. A. Johnson, R. S. Walters, T. D. Jaeger, M. A. Duncan, R. A. Christie, K. D. Jordan, *Science* **2004**, *304*, 1137 – 1140.
[7] H. C. Chang, C. C. Wu, J. L. Kuo, *Int. Rev. Phys. Chem.* **2005**, *24*, 553 – 578.
[8] J. M. Headrick, E. G. Diken, R. S. Walters, N. I. Hammer, R. A. Christie, J. Cui, E. M. Myshakin, M. A. Duncan, M. A. Johnson, K. D. Jordan, *Science* **2005**, *308*, 1765 – 1769.
[9] C.-C. Wu, C.-K. Lin, H.-C. Chang, J.-C. Jiang, J.-L. Kuo, M. L. Klein, *J. Chem. Phys.* **2005**, *122*, 074315.
[10] K. Mizuse, A. Fujii, N. Mikami, *J. Chem. Phys.* **2007**, *126*, 231101.
[11] G. E. Douberly, A. M. Ricks, M. A. Duncan, *J. Phys. Chem. A* **2009**, *113*, 8449 – 8453.
[12] C. J. Gruenloh, J. R. Carney, C. A. Arrington, T. S. Zwier, S. Y. Fredericks, K. D. Jordan, *Science* **1997**, *276*, 1678 – 1681.
[13] K. Mizuse, T. Hamashima, A. Fujii, *J. Phys. Chem. A* **2009**, *113*, 12134 – 12141.
[14] M. F. Bush, R. J. Saykally, E. R. Williams, *J. Am. Chem. Soc.* **2008**, *130*, 15482 – 15489.
[15] J. M. Lisy, *J. Chem. Phys.* **2006**, *125*, 132302.
[16] J. C. Jiang, J. C. Chang, B. C. Wang, S. H. Lin, Y. T. Lee, H. C. Chang, *Chem. Phys. Lett.* **1998**, *289*, 373 – 382.
[17] J.-L. Kuo, M. L. Klein, *J. Chem. Phys.* **2005**, *122*, 024516.
[18] N. J. Singh, M. Park, S. K. Min, S. B. Suh, K. S. Kim, *Angew. Chem.* **2006**, *118*, 3879 – 3884; *Angew. Chem. Int. Ed.* **2006**, *45*, 3795 – 3800.
[19] J. T. O'Brien, J. S. Prell, M. F. Bush, E. R. Williams, *J. Am. Chem. Soc.* **2010**, *132*, 8248 – 8249.
[20] J. C. Jiang, Y. S. Wang, H. C. Chang, S. H. Lin, Y. T. Lee, G. Niedner-Schatteburg, *J. Am. Chem. Soc.* **2000**, *122*, 1398 – 1410.
[21] A. Lenz, L. Ojamäe, *J. Phys. Chem. A* **2006**, *110*, 13388 – 13393.
[22] B. Bandow, B. Hartke, *J. Phys. Chem. A* **2006**, *110*, 5809 – 5822.
[23] Y. Maréchal, *The Hydrogen Bond and the Water Molecule*, Elsevier, Amsterdam, **2007**.
[24] Gaussian 03 (Revision E.01), M. J. Frisch et al., see the Supporting Information.
[25] R. Ludwig, A. Appelhagen, *Angew. Chem.* **2005**, *117*, 821 – 826; *Angew. Chem. Int. Ed.* **2005**, *44*, 811 – 815.
[26] A. Y. Zasetsky, A. F. Khalizov, M. E. Earle, J. J. Sloan, *J. Phys. Chem. A* **2005**, *109*, 2760 – 2764.
[27] J. E. Bertie, Z. Lan, *Appl. Spectrosc.* **1996**, *50*, 1047 – 1057.
[28] A. Y. Zasetsky, A. F. Khalizov, J. J. Sloan, *J. Chem. Phys.* **2004**, *121*, 6941 – 6947.
[29] Q. Du, R. Superfine, E. Freysz, Y. R. Shen, *Phys. Rev. Lett.* **1993**, *70*, 2313 – 2316.
[30] L. Schriver-Mazzuoli, A. Schriver, A. Hallou, *J. Mol. Struct.* **2000**, *554*, 289 – 300.
[31] X. Wei, P. B. Miranda, Y. R. Shen, *Phys. Rev. Lett.* **2001**, *86*, 1554 – 1557.
[32] T. L. Tarbuck, S. T. Ota, G. L. Richmond, *J. Am. Chem. Soc.* **2006**, *128*, 14519 – 14527.
[33] U. Even, J. Jortner, D. Noy, N. Lavie, C. Cossart-Magos, *J. Chem. Phys.* **2000**, *112*, 8068 – 8071.