Hydrogen Bonds

DOI: 10.1002/anie.201200508

Low-Frequency Vibrational Modes of Protic Molten Salts and Ionic Liquids: Detecting and Quantifying Hydrogen Bonds**

*Koichi Fumino, Elena Reichert, Kai Wittler, Rolf Hempelmann, and Ralf Ludwig**

Over the past decade ionic liquids (ILs) have attracted much attention in science and technology. Potential areas of application include novel syntheses, electrolyte devices, photochemical cells, separation, and catalysis.[1–3] Protic ionic liquids (PILs) are an important subgroup of ionic liquids formed by a combination of equimolar amounts of a Brønsted acid and a Brønsted base.[4–10] The key property that distinguishes PILs from other ILs is the proton transfer from the acid to the base, leading to the presence of proton-donor and proton-acceptor sites, which can be used to build a hydrogen-bond network. PILs have a number of unique properties in contrast to other ILs, just as water is different from "normal" molecular liquids. Thus, PILs are a perfect system to study the presence and strength of hydrogen bonding. The number of H-bond donors, the interaction strength, and the network formation can be varied as desired.

Intermolecular interactions between molecules and ions can be studied by experimental methods covering the suitable frequency range between 1 and 300 cm^{-1} (0.03 to 9 THz). The variety of methods includes optical heterodyne-detected Raman-induced Kerr-effect spectroscopy, terahertz (THz) spectroscopy, dielectric relaxation spectroscopy, low-energy neutron scattering, and far-infrared (FIR) spectroscopy as well as Raman spectroscopy.[11–17] Recently, we could show for aprotic ionic liquids that terahertz (THz) and far-infrared (FIR) spectroscopy cover best the frequency range which includes vibrational bands describing the strength of anion–cation interactions.[18] Moreover, a frequency shift due to hydrogen- bond-enhanced anion–cation interaction could be observed.[19] However, because of high molecular weights and large numbers of molecular units the density of overlapping states can be very high in this frequency range. The interpretation of the resultant low-frequency spectra absolutely requires theoretical modeling to deduce the origins of spectral absorptions and to assign intra- and intermolecular vibrational modes. For that purpose ab initio quantum chemistry or density functional theory (DFT) calculations on ion-pair clusters of ionic liquids as well as classical or quantum chemical molecular dynamics simulations have been reported.[20–27] However, there are still substantial problems with evaluating the low-frequency spectra. Small frequency shifts of these broad bands can stem from either the cation or the anion of the ionic liquid. In addition, contributions from different kinds of intermolecular interactions cannot be distinguished properly. This is why some researchers suggest that these bands arise from long-range electrostatic interaction rather than hydrogen bonding.[28,29]

For that reason we investigated a selected set of protic ionic liquids. If the PILs were liquid at room temperature, we measured them in the liquid state, otherwise in the solid state as pellets. Some of the systems may be termed protic molten salts because they exhibit melting points above 100 °C. They all include trialkylammonium cations as the Brønsted base which exhibits only a single N–H group as a possible H-bond donor (see SI1 in the Supporting Information). Because protic ionic liquids are expected to form stronger H-bonds than aprotic ionic liquids, we hoped to observe a well separated vibrational band that can be clearly assigned to N–H···anion hydrogen bonds. For some of the methyl ammonium nitrates Raman and infrared spectra in the low-frequency range were measured previously.[30,31] Owing to the lack of systematic variation of the number of possible H-bonds as well as supporting DFT calculated frequencies, the vibrational modes could be only crudely assigned to "translational and librational motions of cations and anions".

First we measured the FIR spectra of tetramethylammonium nitrate $[(CH_3)_4N][NO_3]$ and trimethylammonium nitrate $[(CH_3)_3NH][NO_3]$ (see Figure 1a and also SI2). For $[(CH_3)_4N][NO_3]$ a broad vibrational band is observed which is generally attributed to librational contributions of interacting ions. Intramolecular vibrational motions of the ammonium cation and the nitrate anion are not anticipated in this frequency range. The spectrum of $[(CH_3)_3NH][NO_3]$ shows a similar band at around 100 cm^{-1}, but additionally a distinct vibrational mode at 171 cm^{-1}. Because no vibrations can be associated with the ions, this band represents a vibration associated with an anion–cation interaction and can be clearly assigned to the $^{+}N{-}H\cdots NO_3^{-}$ hydrogen bond.

This finding is supported by DFT-calculated frequencies of aggregates $[(CH_3)_3NH][NO_3]_n$ with $n = 2, 4, 6, 8, 10$. For comparison with the measured spectrum, the calculated FIR spectra were also simulated by applying a width at half maximum of 10 cm^{-1} for the Lorentzian functions for each

---

[*] Dr. K. Fumino, Dipl.-Chem. K. Wittler, Prof. Dr. R. Ludwig
Universität Rostock, Institut für Chemie
Abteilung für Physikalische Chemie
Dr.-Lorenz-Weg 1, 18059, Rostock (Germany)
E-mail: ralf.ludwig@uni-rostock.de

Prof. Dr. R. Ludwig
Leibniz-Institut für Katalyse an der Universität Rostock e.V.
Albert-Einstein-Strasse 29a, 18059 Rostock (Germany)

Dr. E. Reichert,[+] Prof. Dr. R. Hempelmann
Universität des Saarlandes, Physikalische Chemie
D-66123 Saarbrücken (Germany)

[+] Current address:
Polystone Chemical GmbH, 66440 Blieskastel (Germany)

[**] This work was supported by the DFG priority programme 1191 "Ionic Liquids" and by the DFG Sonderforschungsbereich SFB 652.

Supporting information for this article is available on the WWW under http://dx.doi.org/10.1002/anie.201200508.

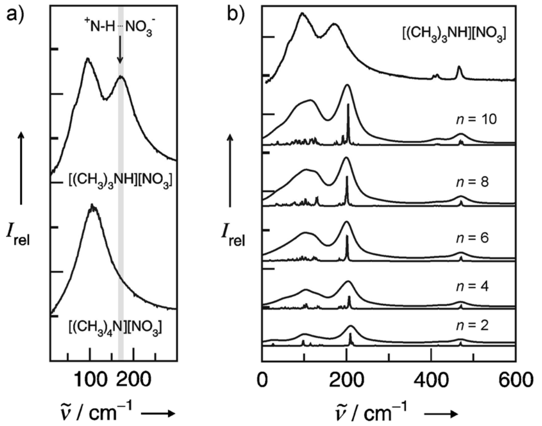

Figure 1. a) FIR spectra of the protic ionic liquids $[(CH_3)_3NH][NO_3]$ (top) and $[(CH_3)_4N][NO_3]$ (bottom) measured with pellets. The additional vibrational band at 171 cm^{-1} in the spectrum can be assigned to the $^+N{-}H\cdots NO_3^-$ intermolecular interaction (indicated by the arrow) and is consequently missing in the spectrum for $[(CH_3)_3N][NO_3]$. b) Calculated FIR spectra of clusters of ion pairs of $[(CH_3)_3NH][NO_3]_n$ with $n = 2, 4, 6, 8, 10$. The calculated spectra were also simulated by using a width at half maximum of 10 cm^{-1} for each vibrational mode. No cluster size dependence beyond the ion-pair tetramer is observed. The simulated spectra perfectly reproduce the measured spectrum (top).

vibrational mode (Figure 1b). Although the frequencies are calculated in the harmonic approximation and no correction is applied, the calculated IR spectra perfectly resemble the measured spectra. Contributions above 400 cm^{-1} are intramolecular in nature and can be certainly assigned to bending vibrational modes of the trimethylammonium cation. Contributions at about 100 cm^{-1} describe unspecific librational motions indicated by low intensities in the calculated spectra. The most important result is that the additional vibrational band measured at 171 cm^{-1} is also observed in the calculated spectra for each cluster. There is no further shift in the frequency of this band with increasing cluster size beyond the tetramer. The major vibrational bands are better separated in the calculated than in the measured spectra; this is likely a result of the matrix effect in the pellets. At this point we can conclude that the distinct vibrational band at 171 cm^{-1} is well isolated and that it can be certainly assigned to the $^+N{-}H\cdots NO_3^-$ hydrogen bond.

After detection of the H-bond by FIR we can now try to quantify the strength of this interaction. Steiner pointed out that hydrogen bonds with mainly ionic and little covalent nature are not classified as "strong" despite high dissociation energies.[32] Instead, they might be termed ionic with a moderate hydrogen bond formed on top. We now show that this "on top" H-bond energy can be calculated. For clusters of tetramethylammonium nitrate $([(CH_3)_4][NO_3])_n$ and trimethylammonium nitrate $([(CH_3)_3NH][NO_3])_n$ up to $n = 6$ the binding energies per ion pair were calculated und corrected for the basis set superposition error (see SI3). As already noticed in the calculated IR spectra, also the binding energies do not further change for clusters larger than tetramers (Figure 1b).

There are mainly three contributions to this interaction: Coulomb forces, hydrogen bonding, and dispersion forces. The Coulomb and dispersion forces should be similar for the two PILs. It may be argued that the additional methyl group in $[(CH_3)_4N][NO_3]$ leads to larger dispersion forces than in $[(CH_3)_3NH][NO_3]$. To check this argument we applied Grimme's new DFT-D3 method for calculating noncovalent interactions.[33] The intermolecular dispersion forces per ion-pair for both PILs only differ by 2 $kJ\,mol^{-1}$ (see SI4). Thus the main difference in energy is due to the presence of hydrogen bonding in $[(CH_3)_3NH][NO_3]$. From the energy difference of the two PIL clusters we now obtain a reliable measure of the H-bond strength. As shown in the inlay of Figure 2, it is estimated to be 49.4 $kJ\,mol^{-1}$. If the dispersion correction is taken into account, the H-bond energy decreases to 47.3 $kJ\,mol^{-1}$. Such an H-bond strength is usually classified to lie between moderate and strong H-bonds.[32]

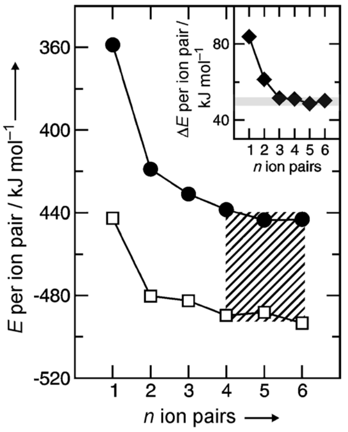

Figure 2. DFT-calculated cluster energies per ion pair for $[(CH_3)_4N][NO_3]_n$ (●) and $[(CH_3)_3NH][NO_3]_n$ (□) with $n = 1$–6. The energy difference between clusters of similar size of the two PILs (see inset) represent the H-bond strength of the $^+N{-}H\cdots NO_3^-$ interaction in $[(CH_3)_3NH][NO_3]$. The H-bond energy is quantified to be 49.4 $kJ\,mol^{-1}$. The slightly higher dispersion energies in clusters $[(CH_3)_4N][NO_3]_n$ due to the additional methyl group of the cation reduces the H-bond energy by only about 2 $kJ\,mol^{-1}$.

After detecting and quantifying the H-bond strength in PILs, we now discuss the origin of frequency shifts in the FIR spectra. Of course, following the equation of the simple harmonic oscillator $\nu = 1/2\pi\,(k/\mu)^{1/2}$, frequency shifts can stem from both different reduced masses as well as changing force constants which indicates the interaction strength. To sort out this problem we measured the FIR spectra of trialkylammonium methylsulfonate $[R_3NH][CH_3SO_3]$ with the alkyl groups R = methyl, ethyl, propyl, and butyl. We synthesized these PILs in order to study the systematic replacement of alkyl groups at the ammonium cations (see SI5). Moreover, the methyl sulfonate anion $CH_3SO_3^-$ forms a weaker interaction with the cation and also increases the degree of motional freedom resulting in lower melting points and "ionic liquids" per definition. Thus, we hold the anion constant and vary the cation. This way the mass increases with the mass of the ammonium cation and its alkyl chains.

If it is assumed that the force constant for stretching of the hydrogen bond does not vary much along the series of trialkylammonium cations, and that the whole mass of each partner should be used in calculating the frequencies, than these frequencies should decrease significantly with increasing molecular weight (Figure 3a). For the set of chosen ammonium cations, a significant frequency shift from 160.3 cm^{-1} down to 122 cm^{-1} for tributylammonium methylsulfonate is expected because of increasing reduced masses. It has been reported for alcohols that the frequencies do not decrease in this way and that the vibration is to a large extent localized.[34,35] This seems to be also true for PILs, where only a moderate shift down to 142.3 cm^{-1} is observed. Instead, the measured frequency shifts reflect the decreasing calculated binding energies of the tetrameric clusters due to the positive "inductive effect" (Figure 3b). In chemistry, the inductive effect is an observable effect of the transmission of charge through a chain of atoms in a molecule by electrostatic induction. The effect can be either positive or negative. The increasing length of the alkyl chain from the methyl to the butyl group in the ammonium cation increases the electron-releasing character and results in weaker hydrogen bonds. The higher the electron density at the ammonium nitrogen, the less charge can be transferred into the N−H antibonding orbital. Weinhold's natural bond orbital (NBO) analysis shows that the $n_O \rightarrow \sigma^*_{NH}$ "donor–acceptor" interaction energies can be related to the calculated overall interaction energies.[36,37] This indicates that the decreasing H-bond strength and not the increasing reduced masses causes the red shift of the intermolecular frequencies (see SI6).

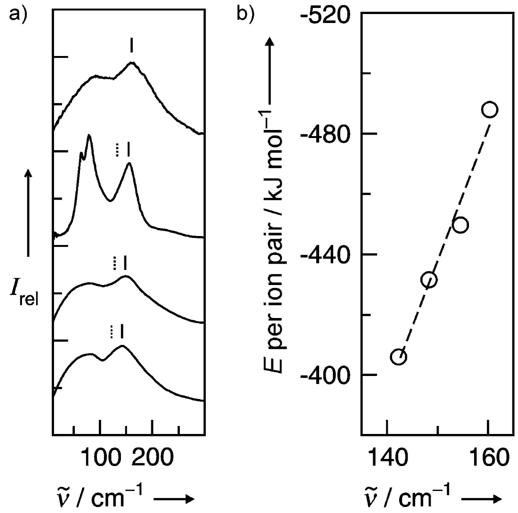

Figure 3. a) FIR spectra of the PILs trialkylammonium methylsulfonate [R_3NH][CH_3SO_3] with R=Me, Et, Pr, Bu in pellets or in the liquid (Et) state. In all cases, the additional vibrational bands between 140 and 160 cm^{-1} can be assigned to the $^{+}$N−H···$CH_3SO_3^{-}$ intermolecular interaction. Starting from the maximum frequency at 160 cm^{-1} for [$(CH_3)_3NH$][CH_3SO_3], the predicted frequency shifts due to the increased reduced masses (•••••) are significantly stronger than the measured ones. b) The DFT-calculated cluster energies per ion pair for the PIL tetramers are plotted versus the frequency of the H-bond vibrational mode. The nearly linear behavior indicates that the frequency shift is related to the interaction strength rather than to the reduced masses of the different cations.

Another set of experiments also indicates that the vibration is to a large extent localized. In [$(CH_3)_3NH$][NO_3] the methyl groups can be successively replaced by ethyl groups increasing the reduced mass as well as increasing the electron-pushing effect. Instead of a predicted frequency shift of $\Delta\nu = 27$ cm^{-1} due to the increasing reduced mass, only a slight shifts of $\Delta\nu = 6$ cm^{-1} is observed for this series. Again, the measured frequency shift can be explained by weaker hydrogen bonds as a result of the inductive effect (+I; Figure 4a).

However, a significant shift towards higher wavenumbers indicating increasing H-bond strength is expected with increasing interaction potential of the anion. Starting with [$(CH_3)_3NH$][CH_3SO_3], we replaced the anion methylsulfonate ($CH_3SO_3^-$) by nitrate (NO_3^-) and chloride (Cl^-) in these PILs. As shown in Figure 4b the observed shift to higher wavenumbers with decreasing reduced mass is significantly lower that predicted ($\Delta\nu = 23.8$ cm^{-1} versus $\Delta\nu = 55.8$ cm^{-1}). Instead, the blue shift in the intermolecular frequencies can

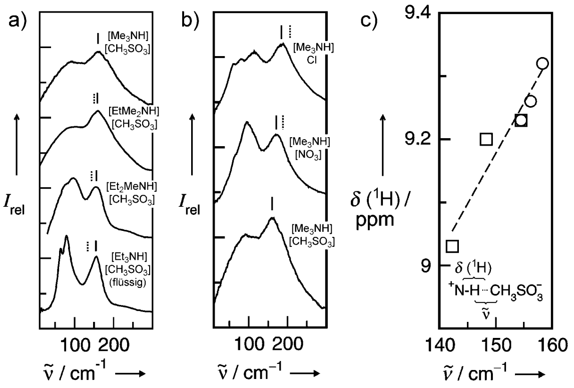

Figure 4. a) FIR spectra of the protic ionic liquids trimethyl-, methyldiethyl-, dimethylethyl-, and triethylammonium methylsulfonate in pellets or in the liquid state. In all cases, the additional vibrational bands in the range between 154 and 160 cm^{-1} can be assigned to the $^{+}$N−H···$CH_3SO_3^{-}$ intermolecular interaction. Starting from the maximum frequency at 160 cm^{-1} for [$(CH_3)_3NH$][CH_3SO_3], the predicted frequency shifts due to reduced masses (•••••) are significantly stronger than measured ones. b) FIR spectra of trimethylammonium salts of $CH_3SO_3^-$, NO_3^-, and Cl^- in the pellet state. In all cases, the additional vibrational bands in the range between 160 and 184 cm^{-1} can be assigned to the $^{+}$N−H ··anion intermolecular interaction. Starting from the maximum frequency at 160 cm^{-1} for [$(CH_3)_3NH$][CH_3SO_3], the predicted frequency shifts due to decreasing reduced masses (•••••) are significantly stronger than the measured shifts. c) Chemical shifts δ(^{1}H) for the N−H proton plotted versus the FIR frequencies of trialkylammonium methylsulfonates [R_3NH][CH_3SO_3]. The fact that the two properties show nearly linear behavior strongly suggests that the FIR vibrational modes are independent of the varied reduced mass of the cation. The $^{+}$N−H···anion intermolecular interaction is local in nature and the frequency shifts can be related to the inductive effect due to the different electron-pushing substituents. Stronger interaction results in NMR downfield proton chemical shifts and higher FIR frequencies. It should be noted that the accuracy of the proton chemical shifts and the intermolecular frequencies is in the order of ±0.01 ppm and ±1 cm^{-1}, respectively and thus within the size of the symbols.

be explained by stronger anion–cation interaction in the anion order $CH_3SO_3^- < NO_3^- < Cl^-$.

The ultimate proof for the locality and the directionality of the hydrogen bonds in PILs is given by relating the FIR vibrational frequencies to spectroscopic properties that do not depend on the reduced mass of the ions. Such a sensitive probe of hydrogen bonding is the ^{1}H NMR chemical shift $\delta(^1H)$ of the trialkylammonium cations. As shown in Figure 4c a nearly linear relation is found for the two properties. Decreasing interaction strength leads to upfield proton chemical shifts and red-shifted FIR frequencies. If the expected FIR frequencies due to different reduced masses are plotted versus $\delta(^1H)$, deviation from linearity is found (SI7).

The interaction is local and directional in nature and frequency shifts can be related to different interaction strengths as a result of varying anions or inductive effects by variation of the alkyl groups at the cation. For all PILs the H-bond vibrational modes can be located in the 140–180 cm^{-1} range of the far-infrared spectra. This is about the frequency range observed for the O–H···O intermolecular vibrations of water.[38–41] How can that be, although the H-bonds in PILs (47 $kJ\,mol^{-1}$) are about two times stronger than those in water (22 $kJ\,mol^{-1}$)? In contrast to PILs, the intermolecular interaction in water depends on the reduced mass because of its low molecular weight. The calculated force constants and the corresponding reduced masses of the low vibrational frequencies of a water dimer are compared with those of the simple PIL ion pair $[(CH_3)_3NH][NO_3]$. The ratios $[(CH_3)_3NH][NO_3]/H_2O$ for the force constants (2.16) and the reduced masses (2.12) are similar (see SI8). The significantly lower reduced mass of water compensates for its small force constants, resulting in intermolecular vibrational modes for water and PILs in the same frequency range.

Experimental Section

The FTIR measurements were performed with a Bruker Vertex 70 FTIR spectrometer equipped with an extension for measurements in the FIR region that consists a multilayer Mylar beam splitter, a room-temperature DLATGS detector with preamplifier, and polyethylene (PE) windows for the internal optical path. The accessible spectral region for this configuration lies between 30 and 680 cm^{-1} (0.3 and 20.3 THz). Further improvement could be achieved by using a high-pressure mercury lamp and a silica beam splitter. This configuration allowed measurements down to 10 cm^{-1} and significantly better signal-to-noise ratios. The solid PILs were mixed with polyethylene powder and measured as pellets in the FIR region.

The frequencies of the configurations were calculated at the DFT level B3LYP, using the internal stored 6-31+G* basis set of the Gaussian09 program.[42] The binding energies were corrected for the basis set superposition error (BSSE).[43] Grimme's DFT-D3 method was applied for calculating dispersion forces.[33]

The synthesis of six alkylammonium methylsulfonate protic ion liquids is described in the Supporting information. All the other compounds were purchased from Sigma–Aldrich, Steinheim.

Received: January 18, 2012
Revised: March 9, 2012
Published online: May 4, 2012

Keywords: DFT calculations · FTIR spectroscopy · hydrogen bonds · ionic liquids · water

---

[1] F. Endres, S. Z. El Abedin, *Phys. Chem. Chem. Phys.* **2006**, *8*, 2101.
[2] R. D. Rogers, K. R. Seddon, *Science* **2003**, *302*, 792–793.
[3] P. Wasserscheid, T. Welton, *Ionic Liquids in Synthesis*, 2nd ed., Wiley-VCH, Weinheim, **2008**.
[4] T. L. Greaves, C. J. Drummond, *Chem. Rev.* **2008**, *108*, 206–237.
[5] E. Bodo, P. Postorino, S. Mangialardo, G. Piacente, F. Ramondo, F. Bosi, P. Ballirano, R. Caminiti, *J. Phys. Chem. B* **2011**, *115*, 13149–13161.
[6] C. A. Angell, N. Byrne, J.-P. Belieres, *Acc. Chem. Res.* **2007**, *40*, 1228–1236.
[7] W. Xu, C. A. Angell, *Science* **2003**, *302*, 422–425.
[8] M. Yoshizawa, W. Xu, C. A. Angell, *J. Am. Chem. Soc.* **2003**, *125*, 15411–15419.
[9] J. Stoimenovski, E. I. Izgorodina, D. R. MacFarlane, *Phys. Chem. Chem. Phys.* **2010**, *12*, 10341–10347.
[10] A. Wulf, K. Fumino, R. Ludwig, *Angew. Chem.* **2009**, *121*, 3230–3233; *Angew. Chem. Int. Ed.* **2009**, *48*, 3184–3186.
[11] H. Shirota, E. W. Castner, Jr., *J. Phys. Chem. A* **2005**, *109*, 9388–9392.
[12] H. Shirota, H. Fukuzawa, T. Fujisawa, J. F. Wishart, *J. Phys. Chem. B* **2010**, *114*, 9400–9412.
[13] D. A. Turton, J. Hunger, A. Stoppy, G. Hefter, A. Thoman, M. Walther, R. Buchner, K. Wynne, *J. Am. Chem. Soc.* **2009**, *131*, 11140–11146.
[14] C. Daguenet, P. J. Dyson, I. Krossing, A. Oleinikowa, J. Slattery, C. Wakai, H. Weingärtner, *J. Phys. Chem. B* **2006**, *110*, 12682–12688.
[15] B. S. Hudson, *J. Phys. Chem. A* **2011**, *115*, 3949–3960.
[16] C. Roth, T. Peppel, K. Fumino, M. Köckerling, R. Ludwig, *Angew. Chem.* **2010**, *122*, 10419–10423; *Angew. Chem. Int. Ed.* **2010**, *49*, 10221–10224.
[17] K. Iwata, H. Okajima, S. Saha, H. Hamaguchi, *Acc. Chem. Res.* **2007**, *40*, 1174–1181.
[18] R. Ludwig, A. Wulf, K. Fumino, P. F. Taday, *ChemPhysChem* **2010**, *11*, 349–353.
[19] A. Wulf, K. Fumino, R. Ludwig, *Angew. Chem.* **2010**, *122*, 459–463; *Angew. Chem. Int. Ed.* **2010**, *49*, 449–453.
[20] P. A. Hunt, B. Kirchner, T. Welton, *Chem. Eur. J.* **2006**, *12*, 6762–6775.
[21] F. Dommert, J. Schmidt, B. Qiao, Y. Zhao, C. Krekeler, L. Delle Site, R. Berger, C. Holm, *J. Chem. Phys.* **2008**, *129*, 224501.
[22] P. A. Hunt, I. R. Gould, B. Kirchner, *Aust. J. Chem.* **2007**, *60*, 9–14.
[23] S. Zahn, J. Thar, B. Kirchner, *J. Chem. Phys.* **2010**, *132*, 124506.
[24] E. I. Izgorodina, *Phys. Chem. Chem. Phys.* **2010**, *13*, 4189–41207.
[25] H. V. Spohr, G. N. Patey, *J. Chem. Phys.* **2010**, *132*, 154504.
[26] T. Köddermann, K. Fumino, R. Ludwig, J. N. C. Lopes, A. A. H. Pádua, *ChemPhysChem* **2009**, *10*, 1181–1186.
[27] S. S. Sarangi, S. K. Reddy, S. Balasubramanian, *J. Phys. Chem. B* **2011**, *115*, 1874–1880.
[28] T. Buffeteau, J. Grondin, Y. Danten, J.-C. Lassègue, *J. Phys. Chem. B* **2010**, *114*, 7587–7592.
[29] J. Grondin, J.-C. Lassègue, D. Cavagnat, T. Buffeteau, P. Johansson, R. Holomb, *J. Raman Spectrosc.* **2011**, *42*, 733–743.
[30] M. Mylrajan, T. K. K. Srinivasan, *J. Chem. Phys.* **1988**, *89*, 1634–1641.
[31] M. Mylrajan, T. K. K. Srinivasan, *J. Phys. C* **1988**, *21*, 1673–1690.
[32] T. Steiner, *Angew. Chem.* **2002**, *114*, 50–80; *Angew. Chem. Int. Ed.* **2002**, *41*, 48–76.
[33] S. Grimme, J. Antony, S. Ehrlich, H. Krieg, *J. Chem. Phys.* **2010**, *132*, 154104.

[34] W. J. Hurley, I. D. Kuntz, Jr., G. E. Leroi, *J. Am. Chem. Soc.* **1966**, *88*, 3199–3202.

[35] R. F. Lake, H. W. Thompson, *Proc. R. Soc. London Ser. A* **1966**, *291*, 469–477.

[36] E. Reed, L. A. Curtiss, F. Weinhold, *Chem. Rev.* **1988**, *88*, 899–926.

[37] F. Weinhold, C. R. Landis, *Valency and Bonding: A Natural Bond Orbital Donor–Acceptor Perspective*, Cambridge, University Press, Cambridge, **2005**.

[38] V. I. Gaiduk, J. K. Vij, *Phys. Chem. Chem. Phys.* **2001**, *3*, 5173–5181.

[39] N. Miura, T. Kitagawa, K. I. Nishikawa, A. Moon, *Joint 30th International Conference in Infrared and Millimeter Waves and 13th International Conference on Terahertz Electronics*, **2005**.

[40] V. I. Gaiduk, D. S. F. Crothers, *J. Mol. Liq.* **2006**, *128*, 145–160.

[41] J.-B. Brubach, A. Mermet, A. Filabozzi, A. Gerschel, P. Roy, *J. Chem. Phys.* **2005**, *122*, 184509.

[42] Gaussian 09 (Revision B.01), M. J. Frisch, et al., see the Supporting Information.

[43] S. Boys, F. Bernardi, *Mol. Phys.* **1970**, *19*, 553–566.