Hyperconjugation

International Edition: DOI: 10.1002/anie.201609437
German Edition: DOI: 10.1002/ange.201609437

Low-Frequency CH Stretch Vibrations of Free Alkoxide Ions

*Jos Oomens, Giel Berden, and Thomas Hellman Morton**

Abstract: *CH stretches in hydrocarbon cations often shift to lower frequencies relative to neutral molecules, because they do not have sufficient electrons to give every bond an electron pair. A parallel effect in negatively charged species has not been previously observed. Here we show that CH bond weakening occurs in alkoxide anions as a consequence of hyperconjugation. The reasoning differs somewhat from the case of positively charged ions, but the net effect is the same: to lower CH stretching frequencies by hundreds of wavenumbers.*

Many introductory texts begin the discussion of molecular vibrations by treating the elongation and contraction of CH bonds. CH stretches tend to couple to only a slight extent with motions of other atoms besides carbon and hydrogen, and few other vibrations overlap the CH stretch region. Because nitrogen and oxygen bind more strongly to hydrogen than does carbon (and other elements bind more loosely), the low mass of hydrogen causes excitation of CH stretches to occupy a distinctive domain of the electromagnetic spectrum, $3040\,\mathrm{cm}^{-1} \pm 11\,\%$ for an uncharged molecule. Here we describe experiments, which demonstrate that adding electric charge (in anions) has the same effect as removing electron density (in cations): to lower CH stretching frequencies by hundreds of wavenumbers.

Removing electron density diminishes bond strengths. CH stretches occur at lower frequencies in positively charged ions such as protonated methane,[1] protonated ethylene,[2] protonated acetylene,[3] or the radical cations of hydrocarbons, alcohols, and ethers.[4] For instance, in gaseous CH_5^+, whose lowest CH stretch occurs near $2500\,\mathrm{cm}^{-1}$, 8 valence electrons have to form 5 bonds, if all bonds become equivalent. In these cations fewer than 2 electrons are available for each bond, rendering CH bonds weaker than in neutrals. We present data to reveal that in isolated, *negatively* charged alkoxide ions the charged oxygen tends to *donate* electron density to the adjacent carbon to form a partial C=O linkage, causing that carbon atom's bond to hydrogen to weaken. The net result of *increased* electron density in anions lowers the α-CH stretch fundamentals in these cases, to an extent comparable to the consequence of removing electrons in the cationic examples. The result is an almost unprecedented red-shift for the CH stretch vibration, which we here verify experimentally.

A number of textbooks point out that the CH stretching vibrations of aldehydes have the lowest frequency among CH stretches of neutral molecules ($\nu_{\mathrm{OC-H}} = 2700\text{–}2750\,\mathrm{cm}^{-1}$).[5] As described below (and displayed in Figure 1), pure CH stretches in gaseous alkoxides occur at much lower frequencies, being observed in a series of free alkoxide ions. This shift to the red illustrates the profound effect that covalent

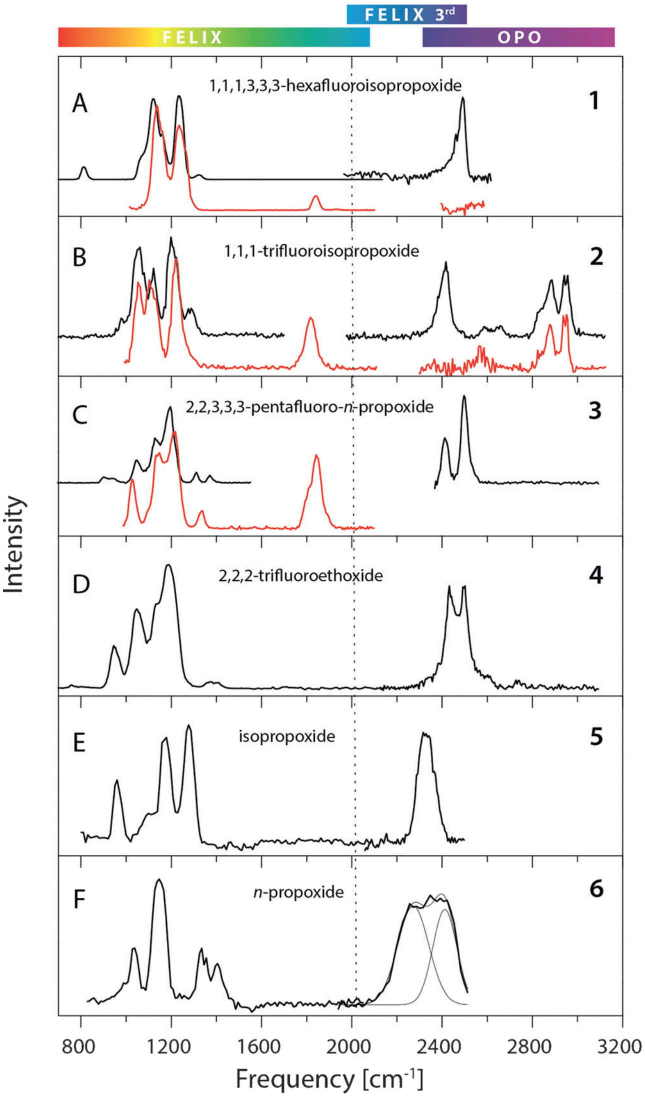


Figure 1. IR multiple photon dissociation (IRMPD) spectra of six alkoxide anions. Traces in red correspond to deuterated analogues, $(CF_3)_2CDO$ (**1**-*d*), $CF_3(CH_3)CDO$ (**2**-*d*), and $CF_3CF_2CD_2O$ (**3**-d_2) anions, respectively.

---

[*] Prof. T. H. Morton
Department of Chemistry, University of California, Riverside
Riverside, CA 92521-0403 (USA)
E-mail: morton@citrus.ucr.edu

Prof. Dr. J. Oomens, Dr. G. Berden
Radboud University, Institute for Molecules and Materials, FELIX
Laboratory, Toernooiveld 7c, 6525ED Nijmegen (The Netherlands)

Prof. Dr. J. Oomens
van't Hoff Institute for Molecular Sciences, University of Amsterdam
Science Park 904, 1098XH Amsterdam (The Netherlands)

Supporting information and the ORCID identification number(s) for the author(s) of this article can be found under http://dx.doi.org/10.1002/anie.201609437.

attachment to a negatively charged oxygen atom has on nearby single bonds, when the charge is not partially compensated by a counterion.

Recently these laboratories reported density functional (DFT) calculations that predict a red shift of hundreds of wavenumbers for the α-CH stretching frequencies of free alkoxide ions relative to their alkali metal salts.[6] Here we present experimental confirmation of those predictions using inter alia the free electron laser for infrared experiments (FELIX). Some of these CH stretches occur even lower than the lowest CH stretch of protonated methane (CH_5^+).[1] Figure 1 and Table 1 summarize the experimental results and Figure 2 compares a pair of results with theory. Because the spectra were recorded at room temperature, hot bands (excitations arising from states above the lowest level) are sometimes seen as shoulders to the red of the principal peak, but are not tabulated below. Combination bands and overtones are also not tabulated.

Table 1: Observed CH stretch frequencies compared with density functional theory (DFT).

	Exptl[a]	Scaled Harmonic[b]	Anharmonic[b]
$(CF_3)_2CHO^-$ (**1**)	2490[c]	2491	2403
$CF_3CH(CH_3)O^-$ (**2**)	2415[d,e,f]	2448	2268
$CF_3CF_2CH_2O^-$ (**3**)	2413, 2498[e]	2443, 2506	2327, 2436
$CF_3CH_2O^-$ (**4**)	2436, 2498[c,d,g]	2425, 2489	2264, 2394
$(CH_3)_2CHO^-$ (**5**)	2328[d]	2377	2256
$CH_3CH_2CH_2O^-$ (**6**)	2272, 2412[d]	2337, 2428	2204,2323

[a] Experimental uncertainty of ±5 cm^{-1}. Where more than one experimental technique has been used, the observed absorptions coincide. [b] DFT calculations performed at B3LYP/aug-cc-PVTZ. Anharmonic frequencies are unscaled.[9] Harmonic frequencies scaled by 0.95.[11] [c] IRMPD spectroscopy using a commercial benchtop optical parametric oscillator with additional activation by a cw CO_2 laser. [d] IRMPD spectroscopy using the 3rd harmonic of a free-electron laser without additional activation. [e] IRMPD spectroscopy using a commercial benchtop optical parametric oscillator without additional activation. [f] Principally parent anion depletion via IR-induced electron detachment. [g] IRMPD spectroscopy using the 3rd harmonic of a free-electron laser with additional activation by a cw CO_2 laser.

Alkoxide ions of interest were mass isolated in the ICR cell of a FTMS, followed by irradiation with tunable IR lasers that scanned over the frequency domains of interest. Figure 1 displays the spectra. Alcohols containing trifluoromethyl groups have sufficient acidity for electrospray (ESI) mass spectrometry of methanol or methanol:water solutions (containing triethylamine) to produce their gaseous conjugate base anions.[7] The unfluorinated alkanols, though, are not acidic enough for this to work, and their conjugate bases were produced by gas phase deprotonation in the ICR cell with CF_3^-, produced, in turn, by irradiation of ESI-generated $CF_3CH_2O^-$ with the output of a cw CO_2 laser. While ethanol does not react via this ion–molecule reaction, the two isomers of propanol (C_3H_8O) go to completion to form their respective alkoxide anions. IR multiple photon dissociation (IRMPD) spectra were obtained either using a commercial benchtop optical parametric oscillator/amplifier (OPO/OPA) laser (scanned over the domain 2300–3100 cm^{-1}) or with the output of the free-electron laser FELIX[8] operating in fundamental (700–2100 cm^{-1}) or 3rd harmonic mode (2000–2500 cm^{-1}).

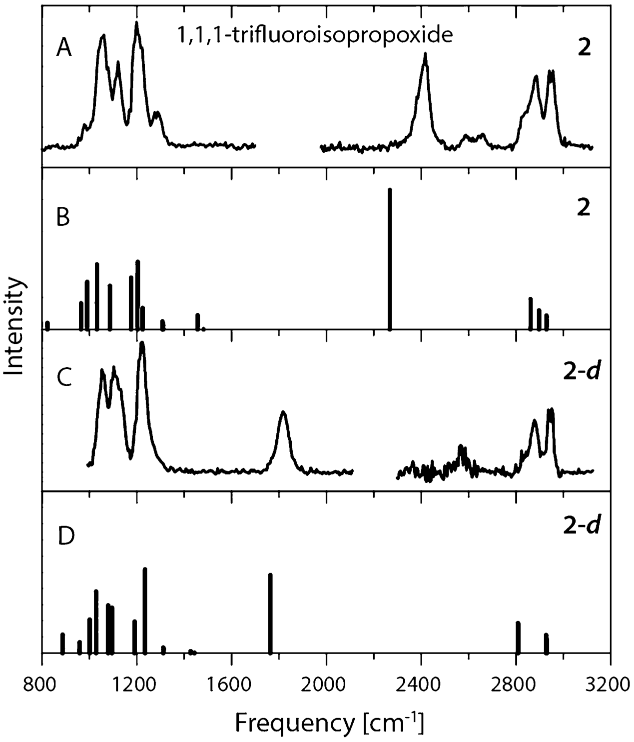


Figure 2. A,C) Experimental IRMPD spectra of 1,1,1-trifluoroisopropoxide ion (**2**) in the gas phase (A), along with its respective d_1 analogue, **2**-*d* (C) based on depletion of the parent ions via electron detachment. B,D) Unscaled anharmonic vibrations of **2** and **2**-*d* (stick spectra with harmonic intensities) predicted at B3LYP/AUG-cc-pVTZ.

The IRMPD spectra of fluorinated isopropoxides provide a good starting point. The IRMPD spectra of 1,1,1,3,3,3-hexafluoroisopropoxide (**1**, *m*/*z* 167) and its deuterated analogue (**1**-*d*, *m*/*z* 168) show a CH stretch for **1** at 2490 cm^{-1} (which is closely reproduced by both scaled harmonic and unscaled anharmonic calculations, see Table 1) and a CD stretch for **1**-*d* at 1820 cm^{-1}. Because this ion has no hydrogens apart from the α-position, the scan stops at 2500 cm^{-1}. The experimental spectra of 1,1,1-trifluoroisopropoxide (**2**, *m*/*z* 113) and its α-d_1 analogue, 1,1,1-trifluoro-2-propoxide-2-*d* (**2**-*d*, *m*/*z* 114) are reproduced both in Figures 1 and 2 (panels A and C) for comparison with plots of the calculated, unscaled anharmonic frequencies of **2** and **2**-*d* (Figure 2, panels B and D). The calculations give much poorer agreement with experiment in this case. There are three methyl vibrations in these ions (which can be seen in both Figures 1 and 2) at 2885, 2940, and 2955 cm^{-1}(±5 cm^{-1}), as well as weak combination bands between 2650 and 2750 cm^{-1}. These bands occur at nearly the same positions in **2**-*d*. It is clear from Figures 1 and 2 that the 2415 cm^{-1} absorption of **2** disappears in the spectrum of **2**-*d*. While the methyl CH stretches in the 2800–3000 cm^{-1} range are reliably reproduced by calculation, the calculated anharmonic α-CH absorption of **2** is nearly 150 cm^{-1} *lower* than observed.[9] The scaled harmonic value is approximately 35 cm^{-1} *higher* than observed. In any event, the experimental αCH stretch of the alkoxide occurs at a frequency more than 500 cm^{-1} lower than the α-CH stretch of the neutral alcohol.[10]

While IR excitation of unfluorinated alkoxides leads to expulsion of H_2 to produce the corresponding enolate anion, fluorinated alkoxides, by contrast, dissociate to give CF_3^-, except for **3** and **3**-d_2 which give $CF_3CF_2^-$ and HF (or DF) loss. For primary alkoxides the presence of two α-hydrogens implies a pair of low-frequency CH stretches. In the case of 2,2,3,3,3-pentafluoro-*n*-propoxide (**3**, illustrated in panel C of Figure 1) and 2,2,2-trifluoroethoxide (**4**, illustrated in panel D of Figure 1) the two bands are resolved and have widths comparable to the absorption profiles of the secondary alkoxides (for each of which a single band appears in this domain). Isopropoxide (**5**, illustrated in panel E of Figure 1) has only one hydrogen α to the oxygen, so a single band is observed in the domain 1900–2300 cm^{-1}, but *n*-propoxide (**6**, illustrated in panel F of Figure 1) displays two barely resolved bands. The broader profile for this species is possibly due to a combination of effects including a) a wider rotational envelope due to the larger rotational constants for the unfluorinated species; b) enhanced multiple-photon excitation due to closely spaced absorptions; and c) rapid interconversion of the two mirror-image *gauche* conformations (which transposes the two α-hydrogens) on a timescale comparable to the separation between the two bands. Panel F of Figure 1 shows their deconvolution, while Table 1 lists the frequencies of the two bands for *n*-propoxide that result. *n*-Propoxide and 2,2,3,3,3-pentafluoro-*n*-propoxide possess more than one conformation, but DFT calculations[9] suggest that in both cases the *gauche* geometry (chiral) predominates over the antiperiplanar geometry (achiral) by at least a factor of 10 at room temperature.

As tabulated, the α-hydrogens of free alkoxide anions absorb at frequencies at least 200 cm^{-1} below aldehyde CH stretches. Animation of calculated normal modes indicates that these lower CH stretch fundamentals still remain uncoupled from other molecular motions. Typically, IR bands measured by IRMPD spectroscopy exhibit a small red shift as compared to bands recorded using linear absorption methods because of the effects of anharmonicity. Although some previous IRMPD studies have reported shifts up to 35 cm^{-1}, for weakly bound systems this shift is often very small.[12] From the accurate experiment/theory correspondence of the bands other than the α-CH stretches (see Figure 2) we estimate this shift to be virtually negligible here.

Comparison of experimental with predicted theoretical band positions in Table 1 reveals that conventionally scaled DFT harmonic frequencies[11] tend to give a closer fit to CH stretches than do unscaled DFT anharmonic calculations using the same basis set. It had previously been proposed that unscaled anharmonic predictions might offer the closest match to experiment,[13] but the present case provides a counterexample.

By contrast, the most intense absorptions in the fingerprint region, the CO stretches, are not badly fitted by the unscaled anharmonic calculations, predicted at 1204 cm^{-1} for **2** and 1235 cm^{-1} for **2**-*d*. Note that the shift to the blue with deuteration conforms to experiment. CO stretches are also not badly predicted by calculation for the other anions in Table 1, as our prior paper[6] reports for ions **1** and **4** and also found here for ions **3**, **5**, and **6** (predicted at 1199, 1181, and 1161 cm^{-1}, respectively).

Although α-CH stretches in alkoxide ions shift dramatically, α-methylene HCH scissors and wagging motions do not appear to do so. As Figure 1 shows, for example, in ion **3** they occur quite close to the predicted anharmonic values of 1461 cm^{-1} (HCH bend) and 1398 cm^{-1} (HCH wag), not far from where they are observed in the corresponding neutral alcohol.[14] In other words, the weakening of CH bonds seems to manifest itself only in stretching motions.

Table 2 summarizes calculated CH and CO bond lengths for the minimum energy geometries of the alkanols and their corresponding alkoxides. The CH bond lengths are in the order of 0.04 Å longer in the alkoxide anions, while the CO bond lengths are in the order of 0.09 Å shorter. The distances do not change very much among the various conformations of the alkanols.

As previously reported, the C−O bond orders calculated by the atoms in molecules (AIM) method for anions **1** and **4** have values of $n = 1.4$–1.5.[6] This increase, compared to bond orders close to $n = 1$ in the parent alcohols, necessitates a compensatory weakening of the α-CH bonds. Such a phenomenon has been recognized for neutrals (both in ground and electronically excited states) and positively charged ions long ago[15,16] but has remained controversial for negatively charged ions, despite many attempts to put it on the same footing as for cations.[17] Many chemists accept the idea that hydrogen can act as an electron source in hyperconjugation. Here we have shown cases where hydrogen acts as an electron sink.

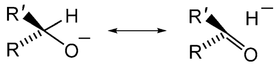
In terms of Lewis structures, negative ion hyperconjugation has been described in terms of a single-bond/no-bond formalism (the same as for cations), where a substituent bears a negative instead of a positive charge. One problem with this picture is that pentadecafluoroadamantane has greater gas phase acidity (both experimentally and theoretically)[18] than anticipated, despite the fact that there are no fluorine atoms *anti*-periplanar to the one C−H bond.[16] That is to say, electron-withdrawing substituents lead to mixing of the effects of hyperconjugation and those of electronegativity.

Table 2: Calculated α-CH and CO bond lengths (B3LYP/AUG-cc-pVTZ) for minimum energy geometries of alkanols (ROH) and their corresponding alkoxide ions (RO^-) in the gas phase.

R	CH (alkanol)	CO (alkanol)	CO (alkoxide)	CH (alkoxide)
$(CF_3)_2CH$ (C_s symm)	1.09455	1.39935	1.30716	1.12950
$CF_3CH(CH_3)$	1.09575[a]	1.41475[a]	1.32228	1.13199
$CF_3CF_2CH_2$ (*gauche*)	1.08799, 1.09470[b]	1.40579[b]	1.32127	1.12815, 1.13089
CF_3CH_2	1.08337, 1.09374[a]	1.40627[a]	1.32110 (C_s symm)	1.13096
$(CH_3)_2CH$	1.09748[c]	1.43519[c]	1.33454	1.13686
$CH_3CH_2CH_2$	1.09656 (*anti*, C_s symm)	1.42917	1.33320 (*gauche*)	1.13360, 1.13884

[a] OH synclinal between the CF_3 and the α-CH. [b] OH synclinal between the CF_2 and the α-CH, nearly parallel to one of the CF bonds of the CF_2. [c] OH synclinal between the CH_3 and the α-CH.

In general, many previous examples that invoke negative ion hyperconjugation involve strongly electronegative substituents such as halogens[19] (which also undergo E1cb elimination in competition with producing stable anions). The data presented here demonstrate negative hyperconjugation in stable alkoxides, which involves hydrogen instead of halogens. "No-bond" Lewis structures, as drawn to the right in Equation (1), reinforce the parallels between positive and negative ions.



(1)

Acknowledgements

The authors are grateful to the FELIX staff for their skill in helping perform the IRMPD experiments, particularly Dr. A.F.G. van der Meer and Dr. B. Redlich. J.O. acknowledges the Nederlandse Organisatie voor Wetenschappelijk Onderzoek (NWO) for VICI grant no. 724.011.002 and thanks the Stichting Physica for support.

Keywords: anions · hyperconjugation · IRMPD action spectroscopy · IR spectroscopy · mass spectrometry

How to cite: *Angew. Chem. Int. Ed.* **2017**, *56*, 217–220
Angew. Chem. **2017**, *129*, 223–226

---

[1] S. Ivanov, O. Asvany, A. Witt, E. Hugo, G. Mathias, B. Redlich, D. Marx, S. Schlemmer, *Nat. Chem.* **2010**, *2*, 298.

[2] A. M. Ricks, G. E. Douberly, P. v. R. Schleyer, M. A. Duncan, *Chem. Phys. Lett.* **2009**, *480*, 17.

[3] G. E. Douberly, A. M. Ricks, B. W. Ticknor, W. C. McKee, P. v. R. Schleyer, M. A. Duncan, *J. Phys. Chem. A* **2008**, *112*, 1897.

[4] a) J. D. Mosley, J. W. Young, M. Huang, A. B. McCoy, M. A. Duncan, *J. Chem. Phys.* **2015**, *142*, 114301; b) Y. Matsuda, H. Hariaya, M. Xie, K. Takahashi, A. Fujii, *Chem. Phys. Lett.* **2015**, *640*, 215; c) M. Xie, Y. Matsuda, A. Fujii, *J. Phys. Chem. A* **2015**, *119*, 5668; d) Y. Matsuda, T. Endo, N. Mikami, A. Fujii, A. Morita, K. Takahashi, *J. Phys. Chem. A* **2015**, *119*, 4885; e) M. Xie, Y. Matsuda, A. Fujii, *J. Phys. Chem. A* **2016**, *120*, 6351.

[5] See, for example, K. Nakanishi, P. H. Solomon, *Infrared Absorption Spectroscopy*, Holden-Day, San Francisco, **1977**; D. Lin-Vien, N. B. Colthup, W. G. Fately, J. C. Grasselli, *The Handbook of Infrared and Raman Characteristic Frequencies of Organic Molecules*, Academic Press, San Diego, **1991**.

[6] J. Oomens, G. Berden, T. H. Morton, *ChemPhysChem* **2015**, *16*, 1992.

[7] See, for example, A. Shokri, X. B. Wang, S. R. Kass, *J. Am. Chem. Soc.* **2013**, *135*, 9525.

[8] D. Oepts, A. F. G. van der Meer, P. W. van Amersfoort, *Infrared Phys. Technol.* **1995**, *36*, 297.

[9] T. Fornaro, M. Biczysko, S. Monti, V. Barone, *Phys. Chem. Chem. Phys.* **2014**, *16*, 10112 and references therein.

[10] J. Murto, A. Kivinen, K. Edelmann, E. Hassinen, *Spectrochim. Acta Part A* **1975**, *31*, 479.

[11] J. P. Merrick, D. Moran, L. Radom, *J. Phys. Chem. A* **2007**, *111*, 11683.

[12] a) J. Oomens, A. G. G. M. Tielens, B. G. Sartakov, G. von Helden, G. Meijer, *Astrophys. J.* **2003**, *591*, 968; b) M. Z. Kamrath, E. Garand, P. A. Jordan, C. M. Leavitt, A. B. Wolk, M. J. van Stipdonk, S. J. Miller, M. A. Johnson, *J. Am. Chem. Soc.* **2011**, *133*, 6440.

[13] T. H. Morton, *Inorg. Chim. Acta* **2011**, *369*, 140.

[14] P. J. Godin, A. Cabaj, L. H. Xu, K. LeBris, K. Strong, *J. Quant. Spectrosc. Radiative* **2017**, *186*, 150.

[15] a) R. S. Mulliken, *J. Chem. Phys.* **1939**, *7*, 359; b) R. S. Mulliken, C. A. Rieke, W. G. Brown, *J. Am. Chem. Soc.* **1941**, *63*, 41.

[16] a) R. Hoffmann, L. Radom, J. A. Pople, P. v. R. Schleyer, W. J. Hehre, L. Salem, *J. Am. Chem. Soc.* **1972**, *94*, 6221; b) T. Chiba, K. Okuyama, A. Fujii, *J. Phys. Chem. A* **2016**, *120*, 5573.

[17] See, for example, P. v. R. Schleyer, A. J. Kos, *Tetrahedron* **1983**, *39*, 1141.

[18] M. Zhang, M. M. Rahman Badal, M. Pasikowska, T. Sonoda, M. Mishima, H. Fukaya, T. Ono, H.-U. Siehl, J.-L. Abboud, I. A. Koppel, *Bull. Chem. Soc. Jpn.* **2014**, *87*, 825.

[19] See, for example, M. E. Crestoni, B. Chiavarino, J. Lemaire, P. Maitre, S. Fornarini, *Chem. Phys.* **2012**, *398*, 118.

Manuscript received: September 27, 2016
Final Article published: November 30, 2016