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Alkyl Radicals as Hydrogen Bond Acceptors: Computational Evidence

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Abstract: Spectroscopic, energetic and structural information obtained by DFT and G3-type computational studies demonstrates that charged proton donors can form moderately strong hydrogen bonds to simple alkyl radicals. The presence of these bonds stabilizes the adducts and modifies their structure, and gives rise to pronounced shifts of IR stretching frequencies and to increased absorption intensities. The hydrogen bond acceptor properties of alkyl radicals equal those of many conventional acceptors, e.g., the bond length changes and IR red-shifts suggest that *tert*-butyl radicals are slightly better acceptors than formaldehyde molecules, while propyl radicals are as good as H_2O. The hydrogen bond strength appears to depend on the proton affinity of the proton donor and on the ionization energy of the acceptor alkyl radical, not on the donor−acceptor proton affinity difference, reflecting that the charge-transfer aspects of hydrogen bonding are particularly conspicuous when the acceptor polarity and basicity is low.

Introduction

Hydrogen bonding is an important hydrogen atom mediated stabilizing interaction that influences the structure, function and dynamics of many chemical and biological systems in the gaseous, liquid and solid state.[1−3] The physical properties of hydrogen bonds can vary considerably, and so can the criteria by which hydrogen bonding in a specific system may be recognized. The formation of typical moderate or strong conventional hydrogen bonds is relatively easily verified, because the presence of these bonds substantially modifies the structural, energetic and spectroscopic properties of the system in question, giving rise to lengthened donor H bonds, to red-shifts of the IR stretching vibrational frequencies of these bonds with attendant increase in intensity, and to significant stabilization.[1−3]

The acceptor atom in moderate and strong hydrogen bonds is commonly expected to be an electronegative atom with an accessible lone pair,[1,4,5] but it has been demonstrated that hydrogen bonding can also involve a variety of unconventional closed-shell acceptor molecules[6] as well as alkyl radicals.[7] In this respect, spectroscopic studies have indicated that weak hydrogen bonds form between HF and methyl radicals when CH_4 reacts with F_2 in low-temperature noble gases,[7] and computational studies of these and related systems have confirmed that alkyl radicals can participate in hydrogen bonding but that the bonds will be relatively weak.[8−10] However, hydrogen bonds are often stronger in ionic systems,[11,12] and it was recently suggested that protonated aminoalkyl radicals exhibit intramolecular hydrogen bonds of moderate strength between the NH^+ and the radical carbon atom.[13] A few earlier results point in the same direction; Holmes,[14] Gil,[15] and Audier[16] and their co-workers found that $CH_3\bullet$ radicals can be bonded to H_3O^+ and $CH_3OH_2^+$ in the gas phase, and Bouchoux and Choret[17] and Semialjac et al.[18] presented computational evidence to suggest intramolecular hydrogen bonding to radical carbon

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(1) Jeffrey, G. A. *An Introduction to Hydrogen Bonding*; Oxford University Press: New York, 1997.
(2) Steiner, T. *Angew. Chem., Int. Ed.* **2002**, *41*, 48.
(3) Scheiner, S. *Hydrogen Bonding, a Theoretical Perspective*; Oxford University Press: New York, 1997.
(4) Pauling, L. *The Nature of the Chemical Bond*; Cornell University Press: Ithaca, NY, 1939.
(5) Gordon, M. S.; Jensen, J. H. *Acc. Chem. Res.* **1996**, *29*, 536.
(6) (a) Alkorta, I.; Rozas, I.; Elguero, J. *Chem. Soc. Rev.* **1998**, *27*, 163. (b) Rozas, I.; Alkorta, I.; Elguero, J. *J. Am. Chem. Soc.* **2000**, *122*, 11154.
(7) (a) Jacox, M. E. *Chem. Phys.* **1979**, *42*, 133. (b) Misochko, E. Y.; Benderskii, V. A.; Goldschleger, A. U.; Akimov, A. V.; Shestakov, A. F. *J. Am. Chem. Soc.* **1995**, *117*, 11997. (c) Merritt, J. M.; Rudić, S.; Miller, R. E. *J. Chem. Phys.* **2006**, *124*, 084301.
(8) Chen, Y.; Tschuikow-Roux, E.; Rauk, A. *J. Phys. Chem.* **1991**, *95*, 9832.
(9) Alkorta, I.; Rozas, I.; Elguero, J. *Ber. Bunsen-Ges.* **1998**, *102*, 429.
(10) (a) Tachikawa, H. *J. Phys. Chem. A* **1998**, *102*, 7065. (b) Igarashi, M.; Ishibashi, T.; Tachikawa, H. *J. Mol. Struct.* **2002**, *594*, 61. (c) Wang, B.-Q.; Li, Z.-R.; Wu, D.; Hao, X.-Y.; Li, R.-J.; Sun, C.-C. *Chem. Phys. Lett.* **2003**, *375*, 91. (d) Tang, K.; Shi, F. Q. *Int. J. Quantum Chem.* **2007**, *107*, 665. (e) Raghavendra, B.; Arunan, E. *J. Phys. Chem. A* **2007**, *111*, 9699. (f) Li, Q.; An, X.; Luan, F.; Li, W.; Gong, B.; Cheng, J.; Sun, J. *J. Chem. Phys.* **2008**, *128*, 154102. (g) An, X.; Liu, H.; Li, Q.; Gong, B.; Cheng, J. *J. Phys. Chem. A* **2008**, *112*, 5258. (h) Crespo-Otero, R.; Sanchez-Garzia, E.; Suardiaz, R.; Montero, L. A.; Sander, W. *Chem. Phys.* **2008**, *353*, 193. (i) Li, Q.; An, X.; Gong, B.; Cheng, J. *J. Mol. Struct.* **2008**, *866*, 11.
(11) Meot-Ner (Mautner), M. *Chem. Rev.* **2005**, *105*, 213.
(12) (a) Gilli, G.; Gilli, P. *J. Mol. Struct.* **2000**, *552*, 1. (b) Gilli, P.; Pretto, L.; Gilli, G. *J. Mol. Struct.* **2007**, *844*, 328. (c) Gilli, P.; Pretto, L.; Bertolasi, V.; Gilli, G. *Acc. Chem. Res.* **2009**, *42*, 33.
(13) Hammerum, S.; Nielsen, C. B. *J. Phys. Chem. A* **2005**, *109*, 12046.
(14) (a) Cao, J.; Sun, W.; Holmes, J. L. *Int. J. Mass Spectrom.* **2002**, *217*, 179. (b) Wang, X.; Sun, W.; Holmes, J. L. *J. Phys. Chem. A* **2006**, *110*, 8409.
(15) Gil, A.; Sodupe, M.; Bertran, J. *Chem. Phys. Lett.* **2004**, *395*, 27.
(16) (a) Nedev, H.; van der Rest, G.; Mourgues, P.; Audier, H. E. *Eur. J. Mass Spectrom.* **2003**, *9*, 319. (b) Nedev, H.; van der Rest, G.; Mourgues, P.; Audier, H. E. *Int. J. Mass Spectrom.* **2004**, *231*, 197.
(17) Bouchoux, G.; Choret, N. *Int. J. Mass Spectrom.* **2000**, *201*, 161.
(18) Semialjac, M.; Loos, J.; Schröder, D.; Schwarz, H. *Int. J. Mass Spectrom.* **2002**, *214*, 129.

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in distonic isomers of alcohol and amide radical cations; Mayer and co-workers[19] suggested that ionization of the van der Waals dimer of dimethylamine can give rise to adduct ions bonded by NH•••C hydrogen bonds.

Hydrogen bonding is not a simple phenomenon but the collective expression of several intermolecular interactions; the relative importance of each of these varies from system to system. Using Morokuma's classification,[20] the important stabilizing contributions to hydrogen bonding are electrostatic interactions and charge transfer. The electrostatic interactions are particularly prominent when the acceptor molecule is basic or highly polar, whereas the contributions to hydrogen bonding that arise from covalent interactions (charge transfer) stand out more clearly when the acceptor molecule is neither. It is, hence, to be expected that the covalent interactions will be particularly conspicuous when ionic proton donors form hydrogen bonds to nonpolar acceptor molecules such as alkyl radicals.

The changes brought about by hydrogen bonding with regard to structure, energy and IR spectroscopic properties are conveniently examined computationally, and the present study uses composite high-level ab initio methods to examine these properties, in order to demonstrate that alkyl radicals can be good hydrogen bond acceptors. These methods also allow the details of the bonding in adducts of ionic proton donors and alkyl radicals to be studied. In particular, the atoms-in-molecules (AIM[21,22]) and natural bond orbital (NBO[23,24]) methods make it possible to substantiate the presence of hydrogen bonds and to examine their origin. Hydrogen bonding to heteroatom-centered radicals[25,26] has not been included in the present studies.

The present paper is organized in two main parts: in the first, the formation of moderate or strong hydrogen bonds from charged proton donors to simple alkyl radicals is examined, with particular emphasis on the stabilization and structural changes that hydrogen bonding brings about. In the second, the various contributions to the hydrogen bonding interactions in ionic alkyl radical adducts are discussed, especially the relationship between the adduct stabilization and the ionic interactions, the fragment deformation, and the proton affinity and ionization energy of the components.

Computational Methods

Standard ab initio molecular orbital calculations were carried out with the Gaussian 03 suite of programs.[27] Structures and vibrational frequencies of the hydrogen-bonded adducts were determined with the B3LYP and MP2 methods, employing the 6-31+G(d,p) basis set.[28] The electronic energies determined with the G3 and G3//B3LYP composite methods[29] were used to derive 298 K heats of formation within the ideal gas, rigid rotor and harmonic oscillator models as described by Nicolaides et al.,[30] and to determine proton affinities and vertical ionization energies. The properties of hydrogen-bonded systems are not all well reproduced by calculations at the Hartree−Fock level,[31] and the structures and vibrational frequencies used in the G3 calculations were therefore determined at the MP2(full)/6-31+G(d,p) level (frequencies scaled[32] by 0.937). The auxiliary thermochemical data were taken from Chase's compilation.[33] Unless otherwise indicated, all discussion in this paper of molecular structure and vibrational frequencies is based on the results of B3LYP/6-31+G(d,p) calculations (not scaled), while the thermochemistry is based on the G3//B3LYP results. Spin contamination was not an issue for the systems considered here.

The stabilization of the hydrogen-bonded adducts (E_{stab}) was calculated as $\Sigma\Delta H_f$(components) − ΔH_f(adduct), employing for consistency the G3//B3LYP heats of formation of the components as well as the adducts. It is possible to define the adduct bond strength so as to include the deformation energy (or fragment relaxation),[34−36] that is, to explicitly account for the fact that the structure of the components in the adduct is different from the structure of the free components. However, by choosing to express the adduct stabilization as the negative of the enthalpy of association we retain the relationship to conventional definitions of bond strength, even though a comprehensive description of the adduct interactions requires that the deformation is properly accounted for.

Proton affinities were determined as the difference between the G3//B3LYP energies of the base and the protonated base, adding 5/2 RT (6.2 kJ mol^{-1}). Vertical ionization energies were determined as the difference between the electronic G3 energies of the radical and the corresponding cation with the frozen structure of the radical, ignoring vibrational energy contributions.

The calculated harmonic vibrational frequencies provide an estimate[37] of the red-shift of the O−H or N−H stretching vibrations that accompanies hydrogen bonding. The red-shift was determined relative to not-hydrogen-bonded OH (or NH) in the same adduct, if possible, otherwise relative to the OH (NH) vibrations of the isolated proton donor in question, using the unscaled frequencies. The harmonic stretching frequencies can exhibit coupling to other modes when the IR stretch of the hydrogen bonding O−H (or N−H) is around 3000 cm^{-1}, which occasionally interferes with determination of the red-shift. However, it is often possible to assess the 'true' harmonic red-shift by 'virtual isotope labeling', that is, by

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(19) (a) Mayer, P. M.; Keister, J. W.; Baer, T.; Evans, M.; Ng, C. Y.; Hsu, C.-W. *J. Phys. Chem. A* **1997**, *101*, 1270. (b) Mayer, P. M. *Int. J. Mass Spectrom.* **2002**, *218*, 1.

(20) (a) Kitaura, K.; Morokuma, K. *Int. J. Quantum Chem.* **1976**, *10*, 305. (b) Umeyama, H.; Morokuma, K. *J. Am. Chem. Soc.* **1977**, *99*, 1316. (c) Morokuma, K. *Acc. Chem. Res.* **1977**, *10*, 294.

(21) Bader, R. A. W. *Atoms in Molecules*; Clarendon Press: Oxford, UK, 1990.

(22) Koch, U.; Popelier, P. L. A. *J. Phys. Chem.* **1995**, *99*, 9747.

(23) Reed, A. E.; Curtiss, L. A.; Weinhold, F. *Chem. Rev.* **1988**, *88*, 899.

(24) Weinhold, F.; Landis, C. R. *Valency and Bonding*; Cambridge University Press: Cambridge, UK, 2005.

(25) (a) Aloisio, S.; Francisco, J. S. *Acc. Chem. Res.* **2000**, *33*, 825. (b) Hansen, J. C.; Francisco, J. S. *ChemPhysChem* **2002**, *3*, 833.

(26) Qi, X.-J.; Lin, L.; Fu, Y.; Guo, Q.-X. *Struct. Chem.* **2005**, *16*, 347.

(27) Frisch, M. J.; et al., *Gaussian 03*, rev. C2; Gaussian Inc: Wallingford, CT, 2004.

(28) (a) Del Bene, J. E.; Person, W. B.; Szczepaniak, K. *J. Phys. Chem.* **1995**, *99*, 10705. (b) Pan, Y. P.; McAllister, M. A. *J. Mol. Struct.* **1998**, *427*, 221. (c) Koné, M.; Illien, B.; Graton, J.; Laurence, C. *J. Phys. Chem. A* **2005**, *109*, 11907.

(29) (a) Curtiss, L. A.; Raghavachari, K.; Redfern, P. C.; Rassolov, V.; Pople, J. A. *J. Chem. Phys.* **1998**, *109*, 7764. (b) Baboul, A. G.; Curtiss, L. A.; Redfern, P. C.; Raghavachari, K. *J. Chem. Phys.* **1999**, *110*, 7650. (c) Curtiss, L. A.; Redfern, P. C.; Rassolov, V.; Kedziora, G.; Pople, J. A. *J. Chem. Phys.* **2001**, *114*, 9287.

(30) Nicolaides, A.; Rauk, A.; Glukhovtsev, M. N.; Radom, L. *J. Phys. Chem.* **1996**, *100*, 17460.

(31) Del Bene, J. E.; Shavitt, I. In *Molecular Interactions* Scheiner, S., Ed.; Wiley: New York, 1997; pp 157−179.

(32) Scott, A. P.; Radom, L. *J. Phys. Chem.* **1996**, *100*, 16502.

(33) Chase, M. W., Jr. *NIST-JANAF Thermochemical Tables*, 4th ed.; Journal of Physical Chemical Reference Data; National Institute of Standards and Technology and the American Institute of Physics: Melville, NY, 1998; Monograph No. 9.

(34) (a) Guerra, C. F.; Bickelhaupt, F. M. *Angew. Chem., Int. Ed.* **1999**, *38*, 2942. (b) Guerra, C. F.; Bickelhaupt, F. M.; Snijders, J. G.; Baerends, E. J. *Chem.−Eur. J.* **1999**, *5*, 3581. (c) Guerra, C. F.; Bickelhaupt, F. M. *Angew. Chem., Int. Ed.* **2002**, *41*, 2092.

(35) Grabowski, S. J. *Ann. Rep. Prog. Chem., Sect. C* **2006**, *102*, 131.

(36) (a) Xantheas, S. S. *J. Chem. Phys.* **1996**, *104*, 8821. (b) Bowen, J. P.; Sorensen, J. B.; Kirschner, K. N. *J. Chem. Educ.* **2007**, *84*, 1225.

(37) (a) Adesokan, A. A.; Gerber, R. B. *J. Phys. Chem. A* **2009**, *113*, 1905. (b) Oh, H.-B.; Lin, C.; Hwang, H. Y.; Zhai, H.; Breuker, K.; Zabroushov, V.; Carpenter, B. K.; McLafferty, F. W. *J. Am. Chem. Soc.* **2005**, *127*, 4076. (c) Buckingham, A. D.; Del Bene, J. E.; McDowell, S. A. C. *Chem. Phys. Lett.* **2008**, *463*, 1.

Table 1. Calculated Stabilization[a] of Hydrogen-Bonded Alkyl Radical Adducts, D−H$^+$···A•

donor (PA)	CH_3• (522)	C_2H_5• (611)	C_3H_7• (686)	*iso*-C_3H_7• (675)	*sec*-C_4H_9• (725)	*tert*-C_4H_9• (708)
H_2O (689)	58 (4)	85 (5)	87 (6)	104 (8)	105 (8)	120 (10)
$CH_2{=}O$ (712)	50 (4)	75 (5)	79 (6)	95 (7)	100 [7]	111 [10]
HCN (713)	43 (3)	67 (5)	70 (5)	85 (7)	89 [7]	102 [8]
HCOOH (743)	43 (4)	66 (5)	69 (6)	82 (8)	87 [8]	97 (10)
CH_3OH (755)	45 (4)	68 (5)	71 (6)	84 (7)	90 [8]	100 (9)
CH_3CHO (772)	43 (3)	65 (5)	68 (6)	81 (7)	86 [8]	95 [9]
C_2H_5OH (777)	43 (3)	64 (5)	66 (6)	78 (7)		
$HCOOCH_3$ (783)	38 (3)	58 (5)				
CH_3CN (784)	34 (3)	53 (4)	55 [5]	68 [6]		
CH_3COOH (788)	36 (4)	56 (5)	59 [6]	70 [7]	83 [9]	
$(CH_3)_2O$ (793)	41 (4)	61 (5)	64 [6]	76 [7]	81 [7]	91 [9]
C_2H_5CN (796)	33 (3)	52 (4)				
$C_2H_5OCH_3$ (810)	36 (4)	56 [5]	68 [7]			
$(CH_3)_2CO$ (815)	33 (3)	53 (5)	55 [5]	66 [7]		
$HCONH_2$ (833)	33 (3)	52 (5)	53 [5]	64 [6]		
NH_3 (856)	28 (2)	44 (3)	46 (3)	55 (4)	59 [5]	66 (6)
CH_3CONH_2 (869)	29 (3)	45 [5]	56 [4]			
$CH_2{=}NH$ (870)	26 (2)	41 (3)	43 (4)	52 (4)	56 [5]	63 [6]
CH_3NH_2 (902)	24 (3)	38 (3)	40 (4)	49 (4)	53 [5]	59 [6]
$CH_3\mathit{N}{=}CH_2$ (903)	24 (2)	38 (3)	39 [4]	48 [4]		
$CH_3CH{=}NH$ (909)	21 (2)	35 (3)	36 [3]	45 [4]		
$(CH_3)_2NH$ (932)	23 (3)	37 (4)	38 [4]	47 [5]	56 [5]	

[a] Stabilization determined as $\Sigma\Delta H_f$(components) − ΔH_f(adduct), G3//B3LYP, kJ mol^{-1} (298 K); G3 counterpoise corrections in parentheses, G3(MP2) corrections in square brackets. The carboxylic acid adducts are bonded via the *E* OH group.

calculation of the vibrational properties of suitably deuterium substituted analogs, a technique also used by others.[38] One example is the red-shift upon formation of the NH_4^+···CH_3• adduct, which was determined as the difference between the calculated N−H stretching wavenumbers of D_3NH^+···CH_3• and HD_2ND^+···CH_3•. The harmonic approximation may cause the red-shift to be underestimated, considering that anharmonicity particularly affects stretching of the donor-hydrogen bond.[37]

The magnitude of the bond length changes and the red-shift determined for the OH (NH) groups depends to some extent on the method of calculation; in nearly all cases, the changes relative to that of the not-hydrogen-bonded O−H are smaller when the MP2 method is used than with B3LYP. This often reflects small differences between the calculated positions of the bonding hydrogen atoms; the distances between the heavy atoms involved are less sensitive to the method of calculation.

Estimates of possible basis set superposition errors (BSSE) were obtained by the counterpoise (cp) method[39] as implemented in Gaussian 03. The cp corrections to the G3 results were obtained for each of the component calculations and summed in the same manner as the electronic energies in a G3-type calculation.[29] The cp corrections are not included in the tabulated stabilization energies but are given separately, because it is open to question whether they should be applied in unmodified form to results obtained for reasonably strongly bonded ionic systems.[40] It is interesting to observe that for each of the 138 ionic adducts included in the present study the cp correction appears to amount to slightly less than 10% of the calculated stabilization energy, with surprising consistency; very nearly the same corrections apply to the G3 and the G3(MP2) energies.

Analysis of the properties of hydrogen-bonded adducts with the AIM approach[21,22] and with the NBO method[23,24] were performed with the facilities available in Gaussian 03. As an aid to the interpretation, extensive use has been made of the Molden and Xaim programs.[41,42]

The Formation of Hydrogen Bonds to Alkyl Radicals

The presence of hydrogen bonds in adducts of ionic proton donors and alkyl radicals is demonstrated by the stabilization of the adducts and by their structural and IR spectroscopic properties; additional evidence is provided by results obtained with the AIM and NBO methods.

The Enthalpy of Adduct Formation. The results in Table 1 show that the formation of adducts of charged proton donors and alkyl radicals is accompanied by significant stabilization, up to more than 100 kJ mol^{-1}. The stabilization is strong evidence to support that hydrogen bonds are formed, but it is not in itself a direct measure of the strength of these bonds; other elements contribute, in particular the ionic interactions that necessarily accompany the formation of adducts of charged species (discussed below).

The results presented in Table 1 agree well with those obtained with more demanding methods, e.g., the stabilization of H_3O^+···CH_3• and NH_4•···CH_3• determined with CCSD(T)/aug-cc-pVTZ//MP2/aug-cc-pVTZ calculations is within 3 kJ mol^{-1} of that obtained with G3//B3LYP.

The stabilization of simple ionic adducts of alkanes and alkyl radicals depends directly on whether hydrogen bonds can be formed (Table 2): adducts of the hydrogen bond donors H_3O^+ and NH_4^+ are better stabilized than the adducts of Na^+ and K^+, respectively, and adducts of the hydrogen bond acceptors CH_3• and *tert*-C_4H_9• are better stabilized than the adducts of CH_4 and C_4H_{10}. One example is that the stabilization of [H_3O^+ *tert*-C_4H_9•] is some 70 kJ mol^{-1} higher than that of [H_3O^+ C_4H_{10}]; the

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(38) Kryachko, E. S.; Zeegers-Huyskens, T. *J. Phys. Chem. A* **2003**, *107*, 7546.

(39) (a) Boys, S. F.; Bernardi, F. *Mol. Phys.* **1970**, *19*, 553. (b) Jensen, F. *Introduction to Computational Chemistry*, 2nd. ed.; Wiley: Chichester, UK, 2007.

(40) (a) Masamura, M. *Theor. Chem. Acc.* **2001**, *106*, 301. (b) Cramer, C. J. *Essentials of Computational Chemistry*; Wiley: Chicester, UK, 2002.

(41) Schaftenaar, G.; Noordik, J. H. *J. Comput.-Aided Mol. Design* **2000**, *14*, 123.

(42) Ortiz Alba, J. C.; Jané, C. B. *Xaim*; Universitat Rovira i Virgili, Tarragona, Spain; http://www.quimica.urv.es/XAIM.

Table 2. Bond Lengths and Stabilization of Simple Adducts of Cations and Hydrocarbons[a]

	CH_3•		CH_4		*tert*-C_4H_9•		*iso*-C_4H_{10}	
	E_{stab}	r_{C-X}	E_{stab}	r_{C-X}	E_{stab}	r_{C-X}	E_{stab}	r_{C-X}
H_3O^+	58	2.79	36[b]	2.94	120	2.67	51	3.16
Na^+	40	2.67	31[c]	2.59	76	2.56	52	2.71
K^+	22	3.13	15	3.14	50	3.09	29	3.31
NH_4^+	28	3.07	16	3.27	66	2.93	25	3.48

[a] Adduct stabilization, $E_{stab} = \Sigma\Delta H_f(\text{components}) - \Delta H_f(\text{adduct})$, determined with G3//B3LYP (kJ mol^{-1}, 298 K); heavy atom separation in Å determined with B3LYP/6-31+G(d,p) calculations. [b] Experimental value 33 kJ mol^{-1} (ref 43). [c] Experimental value 30 kJ mol^{-1} (ref 44).

difference for the corresponding Na^+ adducts in which hydrogen bonding is not possible is only 24 kJ mol^{-1}.

Bond Length Change; IR Red-Shift. Additional illustration that alkyl radicals can be good hydrogen bond acceptors is provided by the properties of the ternary adduct of H_3O^+ with H_2O and *tert*-C_4H_9• (Figure 1). The changes of bond lengths and IR absorption indicate that the interaction between H_3O^+ and *tert*-C_4H_9• is at least as strong as the interaction between H_3O^+ and H_2O.

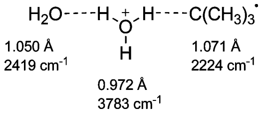

Figure 1. Ternary adduct of H_3O^+ with H_2O and *tert*-C_4H_9•; bond lengths in Å, IR absorption in cm^{-1} (B3LYP/6-31+G(d,p)).

The modification of the IR properties that accompanies hydrogen bonding was recognized early,[45] and the red-shift is seen as the signature of conventional hydrogen bonding.[2,31,46,47] The strength of the hydrogen bond is often taken to be related to the bond length changes that cause the IR frequency shifts and to the absorption intensity increase.[1,2,46−51]

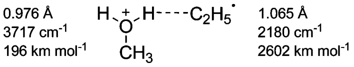

Figure 2. Adduct of protonated methanol and an ethyl radical; bond lengths and IR properties from B3LYP/6-31+G(d,p) calculations.

Table 3. Calculated Harmonic IR Wavenumbers (cm^{-1}), Absorption Intensities (km mol^{-1}) and Bond Length Differences (Å) of Hydrogen-Bonded and Free H in the $-OH_2^+$ and $-NH_2^+$ Groups of Simple Adducts

	ν_{hb}	int$_{hb}$	ν_{free}	int$_{free}$	Δr
$HC(OH)_2^+\cdots CH_3$•	2608	2322	3642	241	0.053
$HC(OH)_2^+\cdots C_2H_5$•	2078	2816	3653	227	0.091
$CH_3OH_2^+\cdots CH_3$•	2649	1927	3711	230	0.057
$CH_3OH_2^+\cdots$*i*-C_3H_7•	1830	2701	3725	176	0.120
$(CH_3)_2NH_2^+\cdots CH_3$•	3070	662	3462	68	0.021
$(CH_3)_2NH_2^+\cdots$*t*-C_4H_9•	2755	1434	3467	56	0.040

B3LYP/6-31+G(d,p) results; the adducts of protonated formic acid are bonded via the *E* OH group. Additional examples are found in Tables S10−S12 of the Supporting Information.

Table 4. AIM Electron Density (ρ) and Laplacian (∇^2) at the Bond Critical Point of Hydrogen Bonds in Representative Alkyl Radical Adducts[a]

H_3O^+	ρ	∇^2	$CH_3OH_2^+$	ρ	∇^2
CH_3•	0.052	0.0188	CH_3•	0.043	0.0335
C_2H_5•	0.075	−0.0255	C_2H_5•	0.058	0.0148
iso-C_3H_7•	0.097	−0.0905	*iso*-C_3H_7•	0.070	−0.0103
tert-C_4H_9•	0.111	−0.1394	*tert*-C_4H_9•	0.081	−0.0361

$(CH_3)_2OH^+$	ρ	∇^2	NH_4^+	ρ	∇^2
CH_3•	0.038	0.0384	CH_3•	0.027	0.0397
C_2H_5•	0.050	0.0289	C_2H_5•	0.035	0.0396
iso-C_3H_7•	0.058	0.0167	*iso*-C_3H_7•	0.041	0.0370
tert-C_4H_9•	0.064	0.0046	*tert*-C_4H_9•	0.046	0.0335

[a] Atomic units; based on B3LYP/6-31+G(d,p) wave functions.

The formation of alkyl radical adducts is uniformly accompanied by an increase in the donor O−H or N−H bond lengths; the magnitude of the change roughly follows the adduct stabilization. Correspondingly, the calculated harmonic O−H or N−H stretching vibrations of the adducts exhibit large red-shifts relative to those of the individual donor molecules, in some cases more than 2000 cm^{-1}, and the IR intensities show a remarkable increase (often by more than a factor of 10), exemplified in Table 3. As emphasized by Iogansen,[49] the intensity change is an independent measure of hydrogen bond strength, and the red-shift obeys Badger's rule.[52] It is in a way paradoxical that the property that reliably signals conventional hydrogen bonding is in fact a measure of the weakening of the bond that the hydrogen bond partially replaces. However, the elongation and attendant weakening of the donor-hydrogen bond is accompanied by strengthened bonding to the acceptor atom; larger O−H bond length change and red-shift, smaller H···C distance.

AIM and NBO. The presence of hydrogen bonds in adducts of alkyl radicals is also supported by the results of AIM calculations that describe the topology of the electron density.[21] The criteria outlined by Koch and Popelier[22] provide empirical guidelines to decide whether to consider a particular interaction to be a 'hydrogen bond'. The most widely used of these criteria stipulates that the value of the Laplacian of the electron density at the bond critical point should be between 0.024 and 0.139 au. The results in Table 4 illustrate that the bonding in the less well stabilized adducts (primary alkyl radical acceptors, high proton affinity donors) belongs in this category. Bonding in the better stabilized adducts is apparently stronger than normally encountered in the hydrogen-bonded systems considered by Koch and Popelier,[22] considering that application of their criteria would suggest almost covalent bonding in a number of adducts,

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(43) Bennett, S. L.; Field, F. H. *J. Am. Chem. Soc.* **1972**, *94*, 5188. (a) Holmes, J. L. (ref 14) refers to an unpublished value, 42 kJ mol^{-1} (attributed to McMahon, T. B.).

(44) Castleman, A. W.; Peterson, K. I.; Upschulte, B. L.; Schilling, F. J. *Int. J. Mass Spectrom. Ion Phys.* **1983**, *47*, 203.

(45) (a) Hilbert, G. E.; Wulf, O. R.; Hendricks, S. B.; Liddel, U. *J. Am. Chem. Soc.* **1936**, *58*, 548. (b) Hendricks, S. B.; Wulf, O. R.; Hilbert, G. E.; Liddel, U. *J. Am. Chem. Soc.* **1936**, *58*, 1991. (c) Badger, R. M.; Bauer, S. H. *J. Chem. Phys.* **1937**, *5*, 839.

(46) (a) Allerhand, A.; Schleyer, P. v. R. *J. Am. Chem. Soc.* **1963**, *85*, 1715. (b) Pimentel, C. G.; McClellan, A. L. *The Hydrogen Bond*; Freeman: San Francisco, 1960; (c) Fuster, F.; Silvi, B. *Theor. Chem. Acc.* **2000**, *104*, 13.

(47) Thompson, W. H.; Hynes, J. T. *J. Am. Chem. Soc.* **2000**, *122*, 6278.

(48) (a) Ratajczak, H.; Orville-Thomas, W. J.; Rao, C. N. R. *Chem. Phys.* **1976**, *17*, 197. (b) Rao, C. N. R.; Dwivedi, P. C.; Ratajczak, H.; Orville-Thomas, W. J. *J. Chem. Soc., Faraday Trans. 2* **1974**, 955.

(49) Iogansen, A. V. *Spectrochim. Acta* **1999**, *55*, 1585.

(50) Swanton, D. J.; Bacskay, G. B.; Hush, N. S. *Chem. Phys.* **1983**, *82*, 303.

(51) Joseph, J.; Jemmis, E. D. *J. Am. Chem. Soc.* **2007**, *129*, 4620.

(52) (a) Badger, R. M. *J. Chem. Phys.* **1934**, *2*, 128. (b) Badger, R. M. *J. Chem. Phys.* **1935**, *3*, 710. (c) Lippincott, E. R.; Schroeder, R. *J. Chem. Phys.* **1955**, *23*, 1099. (d) Schroeder, R.; Lippincott, E. R. *J. Phys. Chem.* **1957**, *51*, 921.

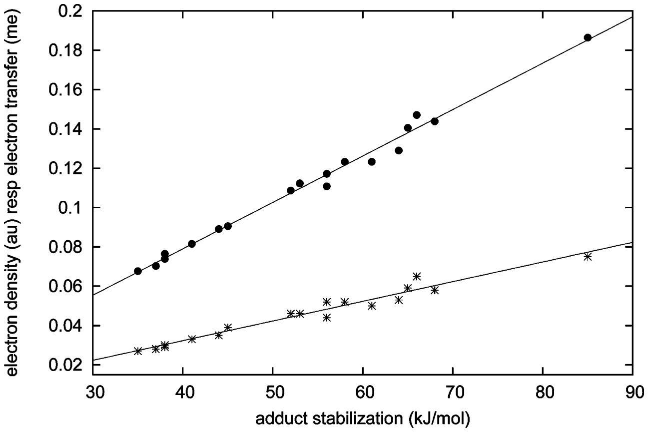

Figure 3. Relationship between stabilization (kJ mol^{-1}) and AIM electron density at the bond critical point (atomic units) for adducts of ethyl radicals and the protonated donors of Table 1 (stars), and between stabilization and NBO electron transfer (%) to the donor OH (NH) σ^* orbital for the same adducts (circles). Results for adducts of protonated nitriles and protonated formaldehyde omitted.

as the Laplacians of the electron density at the bond critical point of the hydrogen bonds have negative values (Table 4). Figure 3 illustrates that the electron density appears to be correlated to the adduct stabilization, as also observed for other hydrogen-bonded adducts.[22,53,54]

The covalent contribution to conventional hydrogen bonding arises from charge-transfer interactions between the acceptor and the σ^* orbital of the D−H bond.[23] The NBO method[24] makes it possible to examine these so-called non-Lewis interactions in the alkyl radical adducts. We find that charge-transfer from the singly occupied carbon orbital to the OH (NH) σ^* orbital contributes significantly to the bonding, as originally suggested by Chen et al.[8] The results shown in Figure 3 indicate that the magnitude of the non-Lewis interaction is correlated to the adduct stabilization.

Carpenter and Weinhold[55] emphasized that the NBO description of open-shell species gives rise to different Lewis-structures for different spin. With regard to hydrogen-bonded alkyl radical adducts, this can manifest itself in exaggerated form, as different connectivity with different spin. The bonding between the components in some adducts is in fact so strong that the open-shell NBO results for the α-spin cases imply two-electron covalent bonding between the donor hydrogen and the alkyl radical, in contrast to the β-spin results. An intermediate situation is encountered in a few instances, in that the α-spin NBO results suggest that the bonding resembles the transition state for hydrogen atom transfer. Related problems were noticed by Karpichev et al.;[56] these aspects merit further study.

Structure of Hydrogen-Bonded Alkyl Radical Adducts. The hydrogen bonds in the alkyl radical adducts are almost linear; the D−H−A angles are typically 170−175°. The heavy-atom distances range from ~2.7 Å in the more strongly bonded adducts such as $H_3O^+\cdots$*tert*-C_4H_9• to ~3.2 Å in adducts such as $(CH_3)_2NH_2^+\cdots CH_3$•. The distance is in most cases slightly less when determined by B3LYP calculations than by MP2 calculations (typically ~2% difference). The position of the bonding hydrogen atom also varies with the method of calculation; the donor-hydrogen bond length determined with the B3LYP method can be up to 5% longer than that obtained by MP2 calculations; correspondingly, the calculated red-shifts are smaller in the latter case. The stabilization energies are, however, not particularly sensitive to these structural differences, except when the bond length changes are particularly pronounced, such as when proton transfer would be thermoneutral or even exothermic.

		B3LYP	MP2
$H_2O\cdots H^+\cdots C_4H_9^\bullet$	r_{OH}	1.233 Å	1.113 Å
	r_{CH}	1.420 Å	1.547 Å

Figure 4. [H_3O^+ *sec*-butyl•] adduct; the calculated position of the bonding hydrogen does not reflect the proton affinities; PA(H_2O) 689 kJ mol^{-1}, PA(*sec*-C_4H_9) 725 kJ mol^{-1}.

The more strongly bonded adducts appear to be single-minimum species, that is, we have not been able to obtain evidence for the existence of $D\cdots H{-}A^{+\bullet}$ adducts alongside $D{-}H^+\cdots A$•, except in a few instances where the alkyl radical proton affinity is higher than that of the donor, and even in these instances, the existence of both forms of the adduct could not be confirmed with all computational models employed. Perhaps surprisingly, the hydrogen is often closer to the less basic component (Figure 4), which affords an additional indication that the proton affinities of the components provide a key to the structure of the hydrogen-bonded adducts only when the proton affinity difference is considerable.[54,57−60]

Stabilization of Hydrogen-Bonded Alkyl Radical Adducts

The enthalpy change that accompanies the formation of hydrogen-bonded adducts depends on the interactions between the components of the adduct and on the structural changes that each of the components undergo as a result of adduct formation.

Ionic Interactions. The stabilization that results from the interaction of a polarizable molecule or radical with a nearby charged species can be quite substantial, regardless of any hydrogen bonding. The dipole moment of most alkyl radicals is sufficiently small that ion−dipole interactions will not be important, but interactions with higher-order multipoles and with induced multipoles must be taken into account, particularly when the alkyl radical and the ion are in close proximity.[61] It is possible to estimate the magnitude of the ionic interactions in these systems by considering the adducts of alkyl radicals with sodium and potassium ions, in which hydrogen bonding cannot occur.

The size of K^+ and NH_4^+ ions is about the same, and they would be expected to exhibit similar ionic interactions with neutral molecules. Experimental studies have provided confirmation that the stabilization of gas-phase adducts of NH_4^+ with polar and nonpolar molecules is almost the same as the stabilization of the corresponding K^+-adducts.[62] It follows that

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(53) (a) Mó, Y.; Yáñez, M.; Elguero, J. *J. Chem. Phys.* **1992**, *97*, 6628. (b) Espinosa, E.; Souhassou, M.; Lachekar, H.; Lecomte, C. *Acta Crystallogr.* **1999**, *B55*, 563. (c) Grabowski, S. J. *Monatsh. Chem.* **2002**, *133*, 1373.

(54) Olesen, S. G.; Hammerum, S. *Europ. J. Mass Spectrom.* **2009**, *15*, 239.

(55) Carpenter, J. E.; Weinhold, F. *J. Mol. Struct.* **1988**, *169*, 41.

(56) Karpichev, B.; Reisler, H.; Krylov, A. I.; Diri, K. *J. Phys. Chem. A* **2008**, *112*, 9965.

(57) Fridgen, T. D. *J. Phys. Chem. A* **2006**, *110*, 6122. (b) Burt, M. B.; Fridgen, T. D. *J. Phys. Chem. A* **2007**, *111*, 10738.

(58) Scheiner, S. *Acc. Chem. Res.* **1994**, *27*, 402.

(59) (a) Bouma, W. J.; Radom, L. *Chem* **1979**, *64*, 216. (b) Pross, A.; Radom, L. *J. Am. Chem. Soc.* **1981**, *103*, 6049.

(60) Gardenier, G. H.; Roscioli, J. R.; Johnson, M. A. *J. Phys. Chem. A* **2008**, *112*, 12022.

hydrogen bonding in the NH_4^+-adducts can only account for a minor part of the stabilizing interactions. The results in Table 2 demonstrate that this is also the case for alkyl radical adducts; subtraction of the stabilization of the K^+-adducts from the stabilization of the NH_4^+-adducts provides an indication that the strength of the hydrogen bonds between NH_4^+ and CH_3• or *tert*-C_4H_9• is about 5 and 15 kJ mol^{-1}, respectively, i.e., somewhat less[63] than that between two H_2O molecules, ~20 kJ mol^{-1}. However, even though only limited stabilization accompanies the formation of hydrogen-bonded adducts of ammonium ions, the interactions in these and related systems may nonetheless turn out to be important, not least because enzyme-catalyzed reactions involving carbon radicals often take place at physiological pH, in the presence of $-NH_3^+$ and related groups.

Na^+ and H_3O^+ ions are not as similar as K^+ and NH_4^+, but the difference between the stabilization of their alkyl radical adducts does afford some measure of the hydrogen bond strength in the H_3O^+ adducts. The [CH_3• H_3O^+] adduct is stabilized by 18 kJ mol^{-1} relative to [CH_3• Na^+], and the [*tert*-C_4H_9• H_3O^+] adduct by 44 kJ mol^{-1} relative to [*tert*-C_4H_9• Na^+] (Table 2), in very good agreement with the bonding of Na^+ and H_3O^+ to even-electron hydrogen bond acceptors.[62b]

Taking these results to be indicative, the contributions from hydrogen bonding and from ionic interactions to the binding of the better stabilized alkyl radical adducts (Table 1) appear to be of the same order of magnitude. However, the ionic interactions could well account for the major part of the stabilization of relatively weakly bonded adducts, just as the ionic interactions may dominate when the acceptor component of a hydrogen-bonded adduct possesses an appreciable dipole moment; Steiner's characterization[2] may be appropriate in these instances, "ionic interactions with a hydrogen bond on top". However, the presence of even substantial ionic contributions will not obscure systematic variations of the hydrogen bond contribution to the stabilization of alkyl radical adducts.

Deformation. The structure of the components of the adduct is modified as the result of the hydrogen bonding, and the overall stabilization reflects the attractive interactions between the deformed components as well as the energy of deformation:[54]

$$E_{\text{stab}} = E_{\text{ion}} + E_{\text{HB}} - E_{\text{def}} \tag{1}$$

The change of the energy of the adduct that is brought about by deformation can be assessed by considering adducts of 'frozen' donors. Taking [*tert*-C_4H_9• H_3O^+] as an example, the adduct is 16 kJ mol^{-1} less stable when the H_3O^+ component is not allowed to relax and adopt the preferred adduct structure. However, the energy of the H_3O^+ itself is some 42 kJ mol^{-1} higher when it possesses the adduct structure than when a free species. A simplistic interpretation of these results suggests that some 58 kJ mol^{-1} of the strength of the hydrogen bond is required to compensate for the deformation of the H_3O^+ component.

The deformation is primarily by elongation of the O−H bond. The attendant lowering of the energy of the O−H σ^* orbital makes charge transfer interactions with the alkyl radical more favorable,[47] strengthening the hydrogen bond. This is corroborated by the results of NBO calculations on the free and constrained adducts; relaxation appears to bring about a quadrupled charge transfer contribution. Increasing deformation is hence accompanied by increased hydrogen bonding, and these changes influence the adduct stabilization in opposite directions. Their contribution is therefore easily underestimated, but they should be evaluated separately, as deformation applies to the individual components, whereas hydrogen bonding is part of the interaction between the components.

The magnitude of the ionic interactions depends *inter alia* on the separation of the adduct components and hence implicitly on the strength of the hydrogen bond, which draws the components closer together. The deformation, elongation of the D−H bond, is also related to the strength of the hydrogen bond. In other words, the factors that determine the strength of the hydrogen bond will also influence the other two right-hand terms of eq 1, and hence be directly reflected in the magnitude of the stabilization energy, though in all likelihood not in a simple (linear) fashion.

Basing a crude estimate of the strength of the ionic interactions in [*tert*-C_4H_9• H_3O^+] on the stabilization of the [*tert*-C_4H_9• Na^+] adduct, 76 kJ mol^{-1} (Table 2), and taking the energy of deformation to be 42 kJ mol^{-1} (above), eq 1 yields an estimated hydrogen bond strength of 86 kJ mol^{-1}. However, these values should not be taken any further than to substantiate that the hydrogen bonding and the ionic interactions in the [*tert*-C_4H_9• H_3O^+] adduct are about equally strong, and that a considerable part of the contribution of the hydrogen bond to the adduct stabilization is offset by the deformation. A better estimate would require use of one of the energy decomposition schemes that explicitly account for deformation.[64,65]

D···H···A: The Donor Proton Affinity. The stabilization of hydrogen-bonded alkyl radical adducts is correlated to the acidity of the proton donor (the columns of Table 1 are arranged according to ascending donor proton affinity); the stronger acids form the better stabilized adducts. In even-electron systems, the strength of the hydrogen bond is often taken to be correlated to the difference between the proton affinities of donor and acceptor.[11,66−71] There is, however, some disagreement with regard to whether the correlation is linear and whether the donor and acceptor proton affinities should be weighted differently.[72−] For ionic systems, the different interpretations could well reflect

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(61) (a) Cybulski, S. M.; Scheiner, S. *J. Phys. Chem.* **1989**, *93*, 6565. (b) Solcà, N.; Dopfer, O. *J. Phys. Chem. A* **2005**, *109*, 6174. (c) Qian, W.; Krimm, S. *J. Phys. Chem. A* **2005**, *109*, 5608. (d) Stone, A. J. *The Theory of Intramolecular Forces*; Oxford University Press: Oxford, UK, 1996.

(62) (a) Liebman, J. F.; Romm, M. J.; Meot-Ner (Mautner), M.; Cybulski, S. M.; Scheiner, S. *J. Phys. Chem.* **1991**, *95*, 1112. (b) Meot-Ner (Mautner), M.; Sieck, L. W.; Liebman, J. F.; Scheiner, S. *J. Phys. Chem.* **1996**, *100*, 6445.

(63) Goebbert, D. J.; Wenthold, P. G. *Europ. J. Mass Spectrom.* **2004**, *10*, 837.

(64) Pendás, A. M.; Blanco, M. A.; Francisco, E. *J. Chem. Phys.* **2006**, *125*, 184112.

(65) (a) Glendening, E. D.; Streitwieser, A. *J. Chem. Phys.* **1994**, *100*, 2900. (b) Glendening, E. D. *J. Phys. Chem. A* **2005**, *109*, 11936.

(66) Larson, J. W.; McMahon, T. B. *J. Am. Chem. Soc.* **1982**, *104*, 6255.

(67) (a) Davidson, W. R.; Sunner, J.; Kebarle, P. *J. Am. Chem. Soc.* **1979**, *101*, 1675. (b) Desmeules, P. J.; Allen, L. C. *J. Chem. Phys.* **1980**, *72*, 4731.

(68) (a) Chen, J.; McAllister, M. A.; Lee, J. K.; Houk, K. N. *J. Org. Chem.* **1998**, *63*, 4611. (b) Shan, S.; Loh, S.; Herschlag, D. *Science* **1996**, *272*, 97.

(69) (a) Meot-Ner (Mautner), M. *J. Am. Chem. Soc.* **1984**, *106*, 1257. (b) Speller, C. V.; Meot-Ner (Mautner), M. *J. Phys. Chem.* **1985**, *89*, 5217. (c) Meot-Ner (Mautner), M.; Sieck, L. W. *J. Phys. Chem.* **1985**, *89*, 5222.

(70) Mayer, P. M. *J. Phys. Chem. A* **1999**, *103*, 5905.

(71) Lankau, T.; Yu, C.-H. *Phys. Chem. Chem. Phys.* **2007**, *9*, 299.

(72) Remer, L. C.; Jensen, J. H. *J. Phys. Chem. A* **2000**, *104*, 9266.

(73) Özen, A. S.; De Proft, F.; Aviyente, V.; Geerlings, P. *J. Phys. Chem. A* **2006**, *110*, 5860.

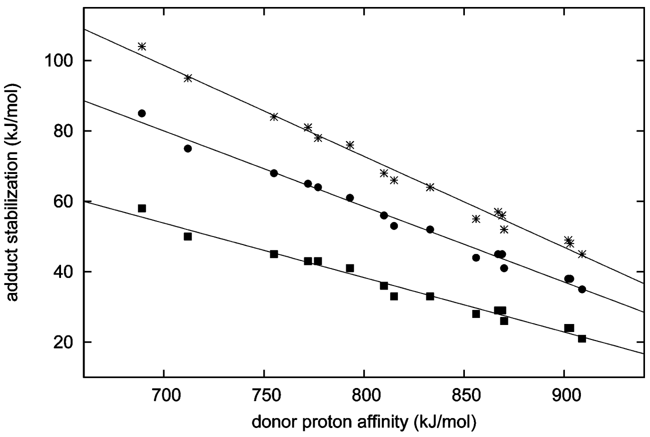

Figure 5. Relationship between adduct stabilization (kJ mol^{-1}) and donor proton affinity (kJ mol^{-1}) of methyl (boxes), ethyl (circles) and isopropyl (stars) radical adducts; data for adducts of protonated nitriles and carboxylic acids omitted.

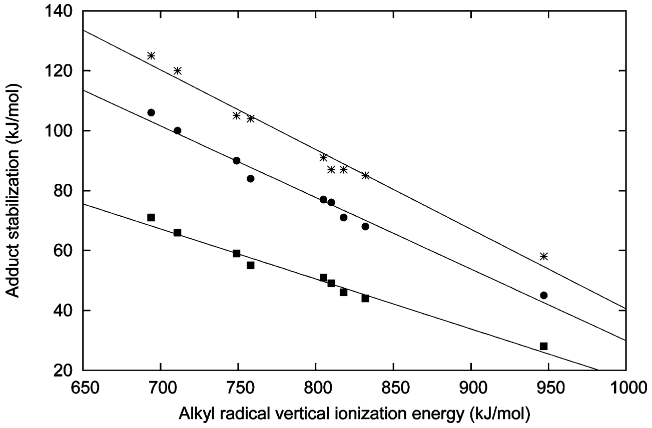

Figure 6. Relationship between adduct stabilization (kJ mol^{-1}) and the alkyl radical vertical ionization energy (kJ mol^{-1}); the alkyl radicals of Table 3 with H_3O^+ (stars), $CH_3OH_2^+$ (circles) and NH_4^+ (boxes).

that the observed correlations are with adduct stabilization, not directly with the strength of the hydrogen bond.[54] The relationship between adduct stabilization and the proton affinity of the donor also manifests itself as a relationship between IR red-shift and proton affinity.[7978]

For each alkyl radical the relationship between adduct stabilization and donor proton affinity appears to be approximately linear (see Figure 5). Intuitively, it appears reasonable that the strength of the hydrogen bond would be related to the acidity of the donor, or in other words, that the incipient bond to the acceptor can be stronger when the donor-hydrogen bond is less strong. It is less obvious that the strength of the incipient bonding to the H^+ acceptor site would be directly related to the thermochemical consequences of completed H^+ transfer, which is what the proton affinity difference measures. The assumption that such a relationship would exist is not necessarily productive;[80] proton affinity describes the (enthalpy) relation between reactants and products of a proton transfer reaction, whereas hydrogen bonding is determined by the interactions between the reactants prior to a possible proton transfer.

D···H···A: The Acceptor Ionization Energy. Many of the observations that are taken to indicate that the proton affinity difference determines the strength of hydrogen bonds concern interactions between similar molecules. In such systems it is reasonable to expect that the same properties determine the donor and acceptor contributions to the stabilization; e.g., the proton affinity of both components of an $ROH\cdots H^+\cdots HOR'$ adduct. However, in contrast to the situation for many hydrogen-bonded even-electron systems, the stabilization of alkyl radical adducts appears not to depend on the proton affinity of the acceptor. This is illustrated by the properties of the adducts of the ethyl, propyl and isopropyl radicals (Table 1). There is only little difference between the stabilization of the C_2H_5• and C_3H_7• adducts, in spite of a 75 kJ mol^{-1} proton affinity difference. At the same time, the proton affinity difference between the C_3H_7• and *iso*-C_3H_7• radicals is only 11 kJ mol^{-1}, but their adducts are significantly differently stabilized.

Instead, the adduct stabilization varies with the degree of branching at the radical carbon, tertiary radicals forming the more stable adducts and methyl radicals the least stable (cf. Table 1). The stabilization appears to be almost linearly related to the alkyl radical vertical ionization energy (Figure 6), in apparent agreement with a number of early suggestions that the strength of hydrogen bonds can depend on the ionization energy of the H-acceptor molecule.[48,81−86] This view, that hydrogen bonding can be regarded as a donor−acceptor interaction closely related to charge-transfer has been all but ignored for a number of years. However, it draws attention to (possibly in exaggerated form) one aspect of the currently accepted description of the hydrogen bond, that there is a significant covalent contribution arising from partial electron transfer from the hydrogen bond acceptor to the donor O−H or N−H σ^* orbital.[23,24,34,65,87]

Considering that adduct stabilization appears not to depend on the acceptor proton affinity, a relationship with the

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(74) (a) Caldwell, G.; Rozeboom, M. D.; Kiplinger, J. P.; Bartmess, J. E. *J. Am. Chem. Soc.* **1984**, *106*, 4660. (b) Zeegers-Huyskens, T. *J. Mol. Struct.* **1986**, *135*, 93. (c) Nguyen, M. T.; Leroux, N.; Zeegers-Huyskens, T. *J. Mol. Struct.* **1997**, *404*, 75. (d) Zeegers-Huyskens, T. *J. Org. Chem.* **1999**, *64*, 4946. (e) Chandra, A. K.; Zeegers-Huyskens, T. *J. Org. Chem.* **2003**, *68*, 3618. (f) Chandra, A. K.; Nguyen, M. T.; Zeegers-Huyskens, T. *J. Phys. Chem. A* **1998**, *102*, 6010.

(75) Bian, L. *J. Phys. Chem. A* **2003**, *107*, 11517.

(76) Chan, B.; Del Bene, J. E.; Radom, L. *J. Am. Chem. Soc.* **2007**, *129*, 12197.

(77) (a) Zeegers-Huyskens, T. *Chem. Phys. Lett.* **1986**, *129*, 172. (b) Zeegers-Huyskens, T. *J. Mol. Struct.* **1988**, *177*, 125.

(78) (a) Humbel, S. *J. Phys. Chem. A* **2002**, *106*, 5517. (b) Humbel, S.; Hoffmann, N.; Côte, I.; Bouquart, J. *Chem.—Eur. J.* **2000**, *6*, 1592.

(79) (a) Gordy, W.; Stanford, S. C. *J. Chem. Phys.* **1940**, *8*, 170. (b) Hammett, L. P. *J. Chem. Phys.* **1940**, *8*, 644. (c) Ault, B. S.; Steinback, E.; Pimentel, G. C. *J. Phys. Chem.* **1975**, *79*, 615. (d) Barnes, A. J. *J. Mol. Struct.* **1983**, *100*, 259. (e) Zeegers-Huyskens, T. *J. Mol. Liq.* **1995**, *67*, 33. (f) Fridgen, T. D.; MacAleese, L.; Maitre, P.; McMahon, T. B.; Boissel, P.; Lemaire, J. *Phys. Chem. Chem. Phys.* **2005**, *7*, 2747. (g) Roscioli, J. R.; McCunn, L. R.; Johnson, M. A. *Science* **2007**, *316*, 249.

(80) Chan, B.; Del Bene, J. E.; Elguero, J.; Radom, L. *J. Phys. Chem. A* **2005**, *109*, 5509.

(81) Tsubomura, H. *Bull. Chem. Soc. Jpn.* **1954**, *27*, 445.

(82) (a) Coulson, C. A.; Danielsson, U. *Ark. Fys.* **1954**, *8*, 239. (b) Coulson, C. A.; Danielsson, U. *Ark. Fys.* **1954**, *8*, 245. (c) Coulson, C. A. *Research, Sci. Appl. Ind.* **1957**, *10*, 149. (d) Coulson, C. A.; In *Hydrogen Bonding*; Hadzi, D., Ed.; Pergamon Press: London, 1959; pp 339−355.

(83) Puranik, P. G.; Kumar, V. *Proc. Ind. Acad. Sci.* **1963**, *58*, 29.

(84) Szczepaniak, K.; Tramer, A. *J. Phys. Chem.* **1967**, *71*, 3035.

(85) (a) Ratajczak, H. *J. Phys. Chem.* **1972**, *76*, 3000. (b) Ratajczak, H.; Orville-Thomas, W. J. *J. Chem. Phys.* **1973**, *58*, 911. (c) Ratajczak, H.; Orville-Thomas, W. J. *J. Mol. Struct.* **1975**, *26*, 387.

(86) Allen, L. C. *J. Am. Chem. Soc.* **1975**, *97*, 6921.

(87) Alabugin, I. V.; Manoharan, M.; Peabody, S.; Weinhold, F. *J. Am. Chem. Soc.* **2003**, *125*, 5973.

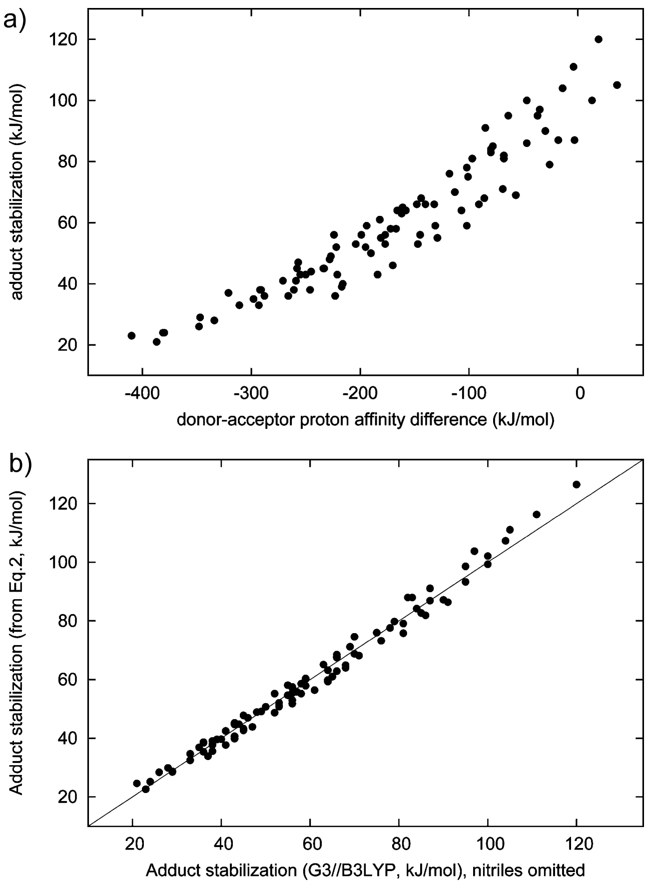

Figure 7. (a) Putative relationship between adduct stabilization and the donor−acceptor proton affinity difference; (b) relationship shown in eq 2. Based on data from Table 1 (nitriles omitted); the straight line in (b) illustrates a hypothetical perfect correspondence.

donor−acceptor proton affinity difference is not expected (Figure 7a). A simple linear correlation between adduct stabilization and PA(donor) and IE(acceptor) with an accuracy of a few kJ mol^{-1} was also not found. However, a reasonable correspondence (Figure 7b) is obtained if a logarithmic relationship is assumed, eq 2; a similar approach was suggested by Zeegers-Huyskens.[77]

$$\ln E_{\text{stab}} = 9.876 - 0.0037\ \text{PA(donor)} - 0.0035\ \text{IE(alkyl radical)} \quad (2)$$

Equation 2 may not account comprehensively for all interactions involved in the stabilization of hydrogen-bonded adducts of alkyl radicals, but the conspicuous correspondence shown in Figure 7b strongly suggests that PA(donor) and IE(acceptor) are major elements of the adduct stabilization, and that any additional important factors will yield (almost) constant contributions or vary monotonically with PA or IE. In particular, no significant improvement is obtained by including a contribution from PA(acceptor) in eq 2, that is, by considering a possibly weighted ΔPA.[74,75]

To find that the adduct stabilization and in turn the hydrogen bond strength depends on the ionization energy of the acceptor rather than on the proton affinity does not constitute a radical departure from the conventional description of hydrogen bonding. In a manner of speaking, both IE and PA reflect the energetics of making electrons available; Maksić and Vianello[88] have discussed the relationship between the two, which is behind the trend visible in Figure 7a. The connection between stabilization and the alkyl radical ionization energy reflects that the charge transfer aspect of hydrogen bonding assumes particular importance in adducts of charged proton donors; the distance between the components is lowered by the attractive ionic interactions, and the energy of the O−H σ^* orbital will be lowered by protonation, both making the hydrogen bond charge transfer interactions more favorable. Furthermore, charge transfer could well be especially favorable in ionic systems, since it will entail dispersal of charge rather than charge separation.

Systematic Deviations. The ionic contribution to the stabilization of adducts of certain donors can give rise to anomalies, in particular when the charge can be delocalized. The adducts of alkyl radicals and protonated nitriles are less well stabilized than expected from simple proton affinity considerations (see Table 1), but the NH bond length changes suggest that the strength of the nitrile hydrogen bonds is consistent with the nitrile proton affinity; the reason for the diminished adduct stabilization could be that delocalization of the charge in the protonated nitrile attenuates the contributions arising from ionic interactions.

Related effects may cause adducts of protonated carboxylic acids to exhibit a small but consistent deviation from the expected correlation between stabilization and IR red-shift. The adducts that involve the *E* OH group are uniformly slightly more stable (by 2−4 kJ mol^{-1}) than those involving the *Z* OH group. However, the calculated O−H bond lengths, IR red-shifts, and IR intensities indicate that the latter adducts possess the stronger hydrogen bonds. Very similar differences are observed with a range of even-electron acceptor molecules;[54] it was suggested that the ionic interactions in the *E* and *Z* adducts particularly favored lengthening of the *Z* OH bond. Differences between the stabilization of neutral hydrogen-bonded water adducts of carboxylic acid conformers were reported earlier by Rablen et al.[89]

The adducts of protonated carboxylic acids also appear to be slightly less stable than the donor proton affinity would indicate, which suggests diminished ionic interactions in the carboxylic acid adducts, possibly because of delocalization of charge. A similar suggestion was made by Larson and McMahon[66] for protonated carboxylic acid dimers.

Alkyl Radicals vs Even-Electron Acceptors. Formaldehyde and the *tert*-butyl radical have about the same proton affinity (712 and 708 kJ mol^{-1}), and hydrogen bonding from methanol to these two acceptors result in similar O−H bond length changes and IR red-shifts (Table 5). That is also the case when protonated methanol is the donor, and when formic acid and protonated formic acid are the donors. Water and the propyl radical also have about the same proton affinity (689 and 686 kJ mol^{-1}), and the results in Table 5 show that their acceptor properties toward methanol and protonated methanol are quite similar.

These observations illustrate that charged proton donors form stronger hydrogen bonds and confirm that alkyl radicals as hydrogen bond acceptors compare well with common even-electron acceptors. The similarity with regard to acceptor properties is also illustrated by the properties of ternary hydrogen-bonded adducts (Table 6 and Figure 1). In these, the

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(88) (a) Maksić, Z. B.; Vianello, R. *J. Phys. Chem. A* **2002**, *106*, 419. (b) Deakyne, C. *Int. J. Mass Spectrom.* **2003**, *227*, 601.

(89) Rablen, P. R.; Lockman, J. W.; Jorgensen, W. L. *J. Phys. Chem. A* **1998**, *102*, 3782.

Table 5. Comparison of Bond Length Changes and IR Red-Shifts in Even- and Odd-Electron Hydrogen-Bonded Adducts[a]

	CH_3OH		$CH_3OH_2^+$	
	Δr_{OH}	$\Delta \nu_{OH}$	Δr_{OH}	$\Delta \nu_{OH}$
CH_2O	0.006	116	0.123	>1850
tert-C_4H_9•	0.008	183	0.238	>2200
H_2O	0.007	126	0.101	1627
n-C_3H_7•	0.007	149	0.102	1717

	HCOOH		$HC(OH)_2^+$	
	Δr_{OH}	$\Delta \nu_{OH}$	Δr_{OH}	$\Delta \nu_{OH}$
CH_2O	0.019	383	0.126	>2300
tert-C_4H_9•	0.018	389	0.161	>2400
H_2O	0.013	260	0.104	1706
iso-C_3H_7•	0.015	358	0.131	>2000

[a] Δr in Å, $\Delta \nu$ in cm^{-1}; B3LYP/6-31+G(d,p) calculations. H-bonding to protonated formic acid via the *E* OH group.

Table 6. Hydrogen Bond Lengths and IR Absorption Wavenumbers of Ternary Alkyl Radical Adducts[a]

	$\nu_{OH(C)}$	$\nu_{OH(O)}$	$r_{OH(C)}$	$r_{OH(O)}$	r_{CO} (r_{CN})
$H_2O\cdots H_3O^+\cdots$*tert*-C_4H_9•	2114	2419	1.071	1.050	2.74
$H_2O\cdots CH_3OH_2^+\cdots$*tert*-$C_4H_9$•	2375	2744	1.047	1.028	2.78
$H_2O\cdots NH_4^+\cdots$*tert*-C_4H_9•	2703	3012	1.068	1.051	3.00
$H_2O\cdots H_3O^+\cdots$*iso*-C_3H_7•	2324[b]	2317[b]	1.054	1.058	2.77
$H_2O\cdots CH_3OH_2^+\cdots$*iso*-$C_3H_7$•	2545[c]	2684[c]	1.037	1.031	2.81
$H_2O\cdots NH_4^+\cdots$*iso*-C_3H_7•	2805	2987	1.062	1.053	3.04

[a] ν in cm^{-1}, r in Å; B3LYP/6-31+G(d,p) calculations. [b] Derived from calculations describing the H_2DO^+ adducts. [c] Derived from calculations describing the CH_3OHD^+ adducts.

ionic core, H_3O^+, $CH_3OH_2^+$ and NH_4^+, forms hydrogen bonds to two neutral components, and the O−H (N−H) bond lengths and IR red-shifts indicate that the hydrogen bonds to the *tert*-butyl radicals are stronger than those to H_2O. The bond lengths and red-shifts of the isopropyl adducts show that this and H_2O form about equally strong hydrogen bonds to charged donors.

The hydrogen bonds in the ternary adducts are less strong than those in the corresponding binary adducts, giving rise to smaller bond length changes and red-shifts. The reason is that $H_5O_2^+$ is a less strong acid than H_3O^+ and therefore forms hydrogen bonds that are less strong.

Summary and Conclusions

Strong ionic proton donors form moderate to strong hydrogen bonds to alkyl radicals, which causes changes of structure and IR properties that are in line with the criteria outlined by Jeffrey[1] for hydrogen-bonded even-electron systems. The interactions that give rise to hydrogen bonding in alkyl radical adducts are the same as those that result in hydrogen bonds between closed-shell species; however, the charge transfer (or covalent) contributions stand out more clearly since the electrostatic contribution to the hydrogen bonding is diminished when the acceptor molecule is nonpolar and nonbasic. The importance of charge-transfer interactions is emphasized by the finding that adduct stabilization is correlated to the acceptor ionization energy rather than to the proton affinity.

The presence of the charge strongly influences the properties of the adducts, in part because the attraction between ions and neutral molecules reduces the distance between the adduct components, and thereby particularly facilitates covalent interactions, in part because charge transfer within ionic adducts causes charge dispersal, not charge separation. NBO analysis shows that charge-transfer between the singly occupied alkyl radical orbital and the donor-H σ^* orbital is the predominant non-Lewis interaction in the hydrogen-bonded adduct. However, modern energy decomposition methods would be required in order to obtain a reliable estimate of the magnitude of this interaction and a companion estimate of the magnitude of the electrostatic contribution and the ionic interactions.

The adduct stabilization is determined by the ionic interactions and the hydrogen bonding, less the deformation energy. It follows that the strength of the hydrogen bond is not given by the stabilization of the adduct. However, the factors that contribute to the strength of the hydrogen bond will also influence the ionic interactions and the deformation, and the hydrogen bond strength is therefore correlated to the stabilization, even though the functional form is unclear.

The deformation by elongation of the D−H bond destabilizes the donor component; at the same time, the charge-transfer interaction with the acceptor is strengthened as the energy of the D−H σ^* orbital falls. The two effects cancel each other to a considerable extent, which could be the reason why their contribution to hydrogen bonding interactions have been underestimated.

The strength of the interaction between proton donors and hydrogen bond acceptors depends on the properties of the acceptors as electron donors and as proton acceptors, that is, on their ability to serve as one- and two-electron donors. For alkyl radicals, the one-electron properties dominate, inasmuch as the stabilization of hydrogen-bonded alkyl radical adducts depends on the ionization energy of the radical, not on the proton affinity.

The acceptor properties of alkyl radicals equal those of common, conventional hydrogen bond acceptors. In isolated systems, H_2O and *iso*-C_3H_7• appear to form equally good hydrogen bonds, and those formed by *tert*-C_4H_9• will be even better. However, hydrogen bonding is one of several intermolecular interactions, and other factors may favor interaction with polar molecules over that with nonpolar alkyl radicals, particularly in condensed phase. Yet, recent studies[90] have uncovered evidence of hydrogen atom transfer from water and alcohols to alkyl radicals in the presence of Lewis acids, furnishing additional evidence that alkyl radicals experience bonding to acidic hydrogens.

Supporting Information Available: The complete citation for ref 27. Tables S1−S8: structural, vibrational and energetic data for hydrogen-bonded adducts of alkyl radicals and ionic hydrogen bond donors obtained with B3LYP/6-31+G(d,p) and MP2(full)/6-31+G(d,p) calculations and with the G3 and G3//B3LYP composite methods. Table S9: auxiliary thermochemistry employed to determine adduct stabilization (G3//B3LYP results). Tables S10−S13: representative IR red-shifts and bond length changes of OH and NH groups in adducts of protonated alcohols, amines and carbonyl compounds.This material is available free of charge via the Internet at http://pubs.acs.org.

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(90) (a) Spiegel, D. A.; Wiberg, K. B.; Schacherer, L. N.; Medeiros, M. R.; Wood, J. L. *J. Am. Chem. Soc.* **2005**, *127*, 12513. (b) Pozzi, D.; Scanlan, E. M.; Renaud, P. *J. Am. Chem. Soc.* **2005**, *127*, 14204. (c) Cuerva, J. M.; Campaña, A. G.; Justicia, J.; Rosales, A.; Oller-López, J. L.; Robles, R.; Cárdenas, D. J.; Buñuel, E.; Oltra, J. E. *Angew. Chem., Int. Ed.* **2006**, *45*, 5522. (d) Tantawy, W.; Zipse, H. *Eur. J. Org. Chem.* **2007**, 5817.