J. Am. Chem. Soc. **2000,** *122,* 1231−1232

NMR Spin−Spin Coupling Constants for Hydrogen Bonds of $[F(HF)_n]^-$, $n = 1-4$, Clusters

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Received September 9, 1999
Revised Manuscript Received December 16, 1999

Introduction. A currently fascinating question pertains to the magnitude of coupling constants between two electronegative atoms through hydrogen bonds,[1] and what this might say about the covalent character of the hydrogen bond. In biological systems, hydrogen bonds between N and O atoms are of great interest,[1] but the first observed couplings of this type were reported by Limbach and co-workers for hydrogen-bonded anionic clusters of the type $[F(HF)_n]^-$, $n = 1-4$, in aprotic media.[2] They observed both one-bond couplings between the hydrogen-bonded proton and the two heavy atoms of a hydrogen bridge ($^{(1)}J$(HF)), as well as the two-bond couplings between heavy atoms ($^{(2)}J$(FF)). Prior NMR experiments were successful only in resolving the one-bond coupling of the type $^{(1)}J$(HF) for the most stable isomer $[FHF]^-$.[3,4] The $^{(2)}J$(FF) is experimentally inaccessible because of the magnetic equivalency of the coupled F nuclei, so only predictive theory can provide the value. However, attempts to calculate the coupling constants with the currently very popular density functional theory (SOS-DFT) methods, or even multi-configuration linear response (MCLR) (applicable only to the smallest biflouride system), were unsuccessful. Here, we report reliable equation-of-motion coupled-cluster (EOM-CC) results for this $^{(1)}J$ and $^{(2)}J$ coupling constant of $[FHF]^-$ and its higher homologues $[F(HF)_n]^-$, $n = 1-4$.

In previous work we have shown that EOM-CC[5] with good basis sets[6] typically provide NMR coupling constants for a wide range of different couplings to within about 10%.[7] We have used this fact to predict the $^{(1)}J$(CC) coupling for the previously unobserved coupling constants for the pentacoordinate C in the nonclassical 2-norbornyl carbocation.[8] We also predicted the coupling constants including that for the bridged H in the experimentally unknown (nonclassical) ethyl carbenium ion.[9] In the case of $[FHF]^-$, the $^{(2)}J$(FF) coupling constant is also inaccessible, but accurate EOM-CC provides its value. Furthermore, we address the higher homologues through $[F(HF)_4]^-$ to discuss the change of sign of the F−H coupling constant with increasing bond distance and size of the F−F couplings.

Results. The geometries of $[F(HF)_n]^-$, $n = 1-4$, are optimized at the CCSD(T)/aug-cc-pVDZ level ((5s,2p)/[3s,2p] for H and (10s,5p,2d)/[4s,3p,2d] for F).[10,11] The NMR spin−spin coupling constants are calculated at the EOM-CCSD level using Ahlrichs qz2p basis set sets[6] ((7s,2p)/[4s,2p] for H and (11s,7p,2d)/[6s,4p,2d] for F) which has been calibrated for this property. All calculations were performed using the ACES II program system.[12]

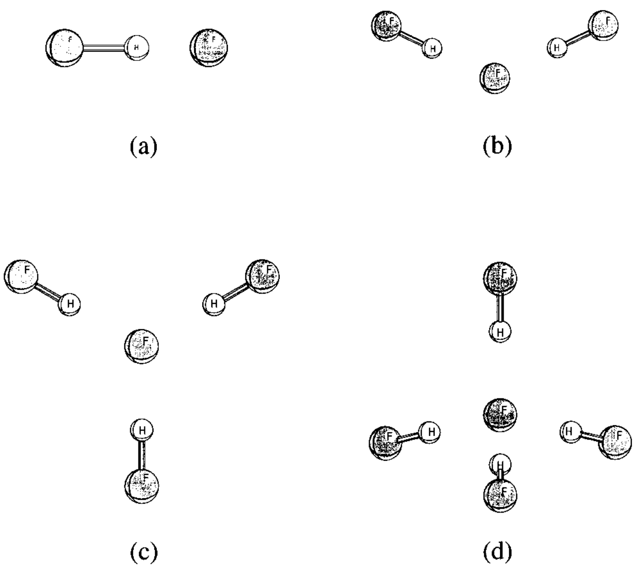

Figure 1. The structures of the hydrogen bonded $[F(HF)_n]^-$, $n = 1-4$, clusters. The FHF bond angles are 180° and the FF distance is the sum of the two HF distances given in Table 1.

The CCSD(T)/aug-cc-pVDZ geometries and EOM-CCSD/qz2p coupling constants are presented in Table 1, and the optimized structures are also presented in Figure 1. The MP(2)/6-31G+(p,d) geometries, DFT (MCLR for $[FHF]^-$), and experimentally measured NMR spin−spin coupling constants from Limbach et al.[2] are also reported in Table 1 for comparison. The geometries, to a large extent, are unaffected by the improved level of correlation and the basis sets, meaning they are essentially converged. The optimized gas-phase geometries and NMR results confirm that the equilibrium structures of $[F(HF)_n]^-$, $n = 1-4$, clusters in solution exhibit $D_{\infty h}$, C_{2v}, D_{3h}, and T_d symmetry (see Figure 1). As Limbach and co-workers indicated, the calculated gas-phase geometries compare well with the experimentally measured geometries of the crystalline salts of $[F(HF)_n]^-$, $n = 1-4$, clusters (see ref 1 in Limbach et al.[2]).

Unlike the SOS-DFT results which frequently have the wrong sign, the agreement of calculated EOM-CCSD spin−spin couplings with experiment is quite good. The EOM-CCSD results for $^{(1)}J$(HF′) (F′ indicates the central fluorine atom) of $[FHF]^-$ of 100 Hz compare well with the experimentally measured value of 124 ± 3 Hz (see below for a discussion about error bars). We predict the gas-phase result for the experimentally inaccessible $^{(2)}J$(FF) coupling constant of $[FHF]^-$ to be 225 Hz. Based on Figure 3 (solid line) in ref 2 a value slightly larger that 200 Hz can be extrapolated for $^{(2)}J$(FF) in $[FHF]^-$. This extrapolated value compares well with 225 Hz presented here. Unlike the SOS-DFT, the EOM-CCSD method accurately predicts the absolute sign of all the couplings reported. The SOS-DFT results do show the correct sign change of the $^{(1)}J$(HF) coupling. Flourine, of course, is more difficult for some DFT methods than other atoms.

Consistent with our previous observations,[7] though the Fermi-contact (FC) term is the largest contribution, the $^{(1)}J$(HF) and

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[12] ACES II program is a product of the Quantum Theory Project, University of Florida Authors: J. F. Stanton, J. Gauss, J. D. Watts, M. Nooijen, N. Oliphant, S. A. Perera, P. G. Szalay, W. J. Lauderdale, S. R. Gwaltney, S. Beck, A. Balková, D. E. Bernholdt, K.-K. Baeck, H. Sekino, P. Rozyczko, C. Huber, and R. J. Bartlett. Integral packages included are VMOL (J. Almlöf and P. Taylor); VPROPS (P. R. Taylor); and a modified version of the ABACUS integral derivative package (T. U. Helgaker, H. J. Aa. Jensen, J. Olsen, P. Jørgensen, and P. R. Taylor.).

10.1021/ja993275r CCC: $19.00

Table 1. Calculated Optimized Geometries at the CCSD(T)/aug-cc-pVDZ Level and Experimental and Calculated NMR Spin−Spin Coupling Constants of $[\mathrm{F(HF)}_n]^-$, $n = 1-4$, Clusters

	$[\mathrm{FHF}]^-$	$[\mathrm{F(FH)}_2]^-$	$[\mathrm{F(FH)}_3]^-$	$[\mathrm{F(FH)}_4]^-$
symmetry	$D_{\infty h}$	C_{2v}	D_{3h}	T_d
r(F−H), Å	1.1517 (1.1495^a)	1.3705 (1.349^a)	1.4604 (1.451^a)	1.5373 (1.540^a)
r(F···H), Å	1.1517 (1.1495^a)	1.0037 (1.012^a)	0.9704 (0.979^a)	0.9577 (0.961^a)
a(H−F−H)	linear	128.8 (130.2^a)	120.0	109.5

	MCLR^a	EOM-CCSD	exp^a	DFT^a	EOM-CCSD	exp^a	DFT^a	EOM-CCSD	exp^a	DFT^a	EOM-CCSD^b	exp^a
$^{(1)}J$(HF′), Hz	6,133	100	124 ± 3	−71	−45	−24 ± 3	−72	−57	−41 ± 4	−63.4	−57	<10
$^{(2)}J$(FF), Hz	−133,385	225		−73	179	146 ± 4	−100	101	92 ± 5	−144	11	<15
$^{(1)}J$(HF), Hz	6,133	100	124 ± 3	229	388	354 ± 3	300	426	430 ± 4	336	492	480 ± 5

[a] The values are taken from ref 2. [b] Small spin-dipole contribution is not included.

$^{(2)}J$(FF) coupling constants have large contributions from the paramagenatic spin−orbit (PSO) and spin−dipole (SD) terms. In particular, the absolute average PSO contributions can be as large as 23% of the total for the $^{(1)}J$(HF) and $^{(2)}J$(FF) coupling constants. Relative to FC, SD, and PSO contributions the diamagnetic spin−orbit (DSO) contribution is insignificant for the $^{(2)}J$(FF) couplings. However, the absolute average of the DSO contribution is about 4% of the total for the $^{(1)}J$(HF) coupling constants. The MCLR results reported for $[\mathrm{FHF}]^-$ by Limbach et al.[2] are unrealistic and are inconsistent with MCLR results for small molecules.[13]

The absolute mean deviation of EOM-CCSD results from experiment for the set of $[\mathrm{F(HF)}_n]^-$, $n = 1-4$, clusters is 25 Hz or 23%. This is somewhat larger than our previously established error bars for the EOM-CCSD method,[7] though that work did not address F−F coupling. However, some of the couplings considered here involve bonds that are weak and highly anharmonic, leading to large zero-point vibrational corrections. In our calculations the effects of the medium are also neglected, but we believe that more of the error is due to vibrational effects rather than to the medium effects. This assertion is supported by the observation that the calculated gas-phase geometries show very little deviation from the geometries established from measurements on crystalline salts.[2] Also, the deviations of calculated results from experiment decrease as the cluster size increases. Presumably, with the large clusters being more compact, the vibrational motions are more restricted. Of course, consideration of vibrational effects could be added in future work, as has been done to some extent for SOS-DFT.[14]

We demonstrate that EOM-CCSD confirms the experimental assignments of F−H−F couplings. Furthermore, we predict the experimentally unknown $^{(2)}J$(FF) for $[\mathrm{FHF}]^-$ to be 225 Hz. We also show that the MCLR results for the $[\mathrm{FHF}]^-$ ion are in error by 1−2 orders of magnitude!

Acknowledgment. This work was supported by the United States Air Force office of Scientific Research (Grant No. F49620-98-1-0116). Authors thank Dr. Hans-Heinrich Limbach for sending reprints of his papers, and Mr. Ken Wilson for generating the figure. We also thank the DoD HPC shared Resource Center (HPCMO) for providing computer facilities.

JA993275R

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