Supporting information for

Symmetry and dynamics of FHF^- anion in vacuum, in CD_2Cl_2 and in CCl_4. *Ab initio* MD study of fluctuating solvent-solute hydrogen and halogen bonds

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Figure S1. The distributions of $q_2 = r_{FH} + r_{FH}$, F…F and F…H distances for FHF^- in vacuum (top), in CH_2Cl_2 (middle) and in CCl_4 (bottom).

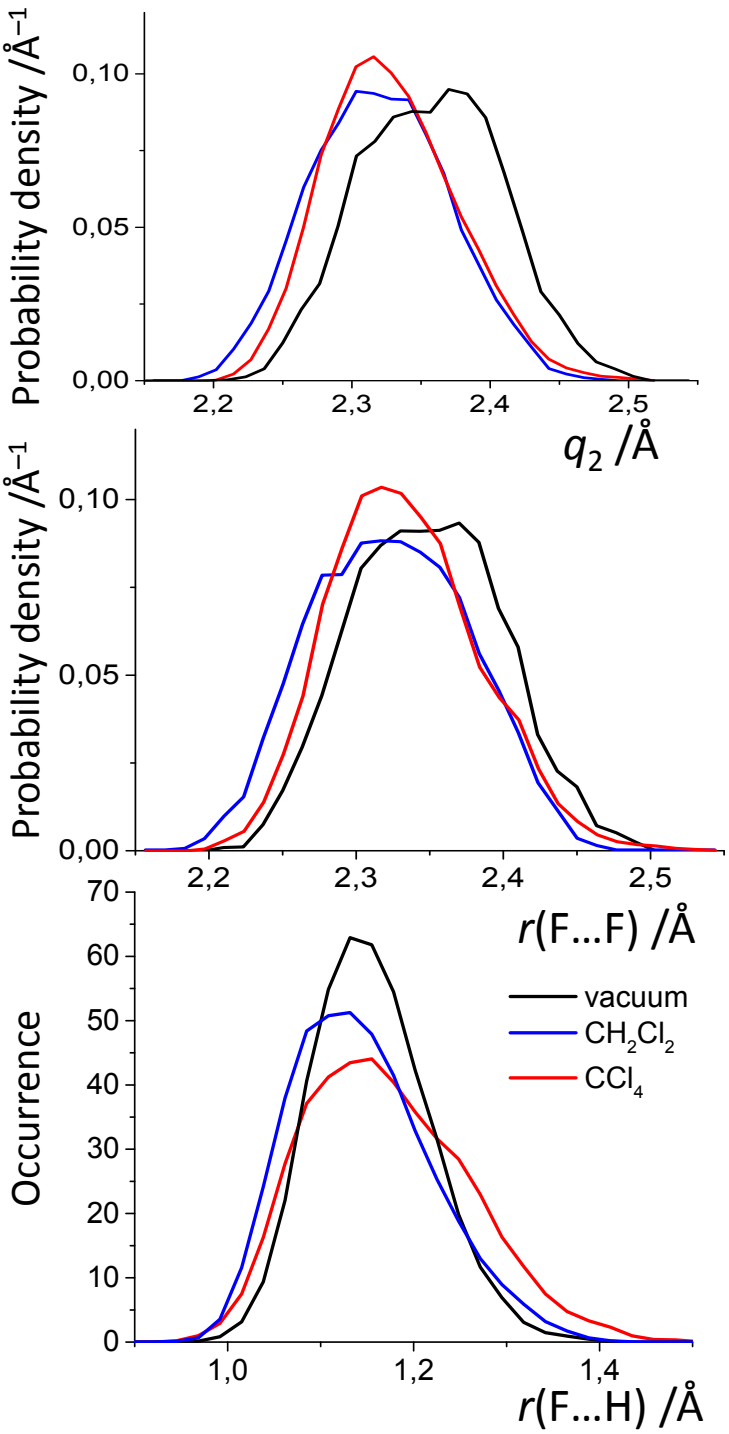

Table S1. The literature data on ^{1}H (relative to TMS) and ^{19}F (see the reference standard in the Table) NMR shieldings and chemical shifts of FHF^-anions in various environments.

System	δ^1H, ppm	^{19}F, ppm	Spectral ref.	Rescale to $CFCl_3$*	Ref.
FHF^- in $(CD_3)_2SO$ (296 K)	15.4	−145.3	Scale $(NaF)_{aq}$ = −122.4 ppm	−145.3	[a]
FHF^- bound in tricyclic encapsulating ligand (also $(CD_3)_2SO$) (296 K)	17.5	−152.1	Scale $(NaF)_{aq}$ = −122.4 ppm	−152.1	[a]
FHF^- Bu_4N^+ in CDF_3/CDF_2Cl (130 K)	16.60	−155.0	$CFCl_3$ scale	−155.0	[b]
FHF^- Bu_4N^+ in CD_3CN (253−343 K)	16.3	67÷71	Shielding vs. CF_3COOH	−143.5÷−147.5	[c]
FHF^- in KHF_2 crystal	16.6	+23.5 ± 9	C_6F_6 scale	−141.4 ± 9	[d]

* in some cases there is not enough data to be sure that the conversion is precise, so that the converted values should be taken with caution (ca. extra ±2 ppm).

[a] S.O. Kang, D. Powell, V.W. Day and K. Bowman-James, Trapped Bifluoride, *Angew. Chem. Int. Ed.*, 2006, **45**, 1921–1925.

[b] I.G. Shenderovich, H.-H. Limbach, S.N. Smirnov, P.M. Tolstoy, G.S. Denisov and N.S. Golubev, H/D isotope effects on the low-temperature NMR parameters and hydrogen bond geometries of $(FH)_2F^-$ and $(FH)_3F^-$ dissolved in CDF_3/CDF_2Cl, *Phys. Chem. Chem. Phys.*, 2002, **4**, 5488-5497.

[c] J.S. Martin and F.Y. Fujiwara, High Resolution Nuclear Magnetic Resonance Spectra of Bifluoride Ion and its Homologues, *Can. J. Chem.* 1971, **49**, 3071−3073.

[d] P. Van Hecke, H.W. Spiess, U. Haeberlen and S. Haussuehl, NMR Study of a Single Crystal of KHF_2. I. ^{1}H and ^{19}F Dipolar Spectra, J. Magn. Reson., 1976, 22, 93−102.

Table S2. Band positions in the power spectrum of FHF^- (FDF^-, as protons were simulated as deutrons) according to the normal mode analysis of the calculated trajectory performed in TRAVIS software. The power spectra are shown in Figure 7 in the main text.

System	Symmetric stretch ν_1, cm^{-1}	Bending ν_2, cm^{-1}	Asymmetric stretch ν_3, cm^{-1}
FDF^- in vacuum	572	911	1118
FDF^- in CH_2Cl_2	579	871	1159
FDF^- in CCl_4	559	860	1135