Supplementary material: An atom in molecules study of infrared intensity enhancements in fundamental donor stretching bands on hydrogen bond formation.

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Table S1: Bond lengths (Å) and angles (°).

System	distance/angle	CCSD/aug-cc-pVTZ	CCSD/cc-pVQZ-mod	Exp.
HF	r(HF)	0.918	0.914	0.917[a]
HCl	r(HCl)	1.276	1.273	1.275[a]
HCN	r(HC)	1.065	1.064	1.066[a]
	r(CN)	1.153	1.149	1.153[a]
HNC	r(HN)	0.995	0.993	0.996[b]
	r(NC)	1.168	1.165	1.168[b]
H_2O	r(HO)	0.959	0.955	0.958[a]
	Θ(HOH)	104.4	104.4	104.5[a]
HF…HF	$r(HF)_{donor}$	0.923	0.918	
	$r(HF)_{acceptor}$	0.920	0.916	
	r(F…H)	1.842	1.841	
	r(F…F)	2.75	2.75	2.72 ± 0.03[c]
	$\Theta(H\text{-}F_{donor}\ldots F)$	7	7	10 ± 6[c]
	$\Theta(H\text{-}F_{acceptor}\ldots F)$	111	111	117 ± 6[c]
HCl…HCl	$r(HCl)_{donor}$	1.279	1.276	
	$r(HCl)_{acceptor}$	1.278	1.275	
	r(Cl…H)	2.588	2.636	
	r(Cl…Cl)	3.848	3.892	3.746[d]
	$\Theta(H\text{-}Cl_{donor}\ldots Cl)$	8	8	9[d]
	$\Theta(H\text{-}Cl_{acceptor}\ldots Cl)$	88.2	88.4	90.2[d]
HCN…HCN	$r(HC)_{donor}$	1.070	1.070	1.246[e]
	$r(CN)_{donor}$	1.153	1.150	1.140[e]
	$r(HC)_{acceptor}$	1.066	1.065	1.063[e]
	$r(CN)_{acceptor}$	1.151	1.148	1.123[e]
	r(N…H)	2.255	2.240	2.075[e]
	r(N…N)	4.488	4.460	4.461[e]
HNC…HNC	$r(HN)_{donor}$	1.008	1.006	
	$r(NC)_{donor}$	1.167	1.164	
	$r(HN)_{acceptor}$	0.996	0.995	
	$r(NC)_{acceptor}$	1.163	1.160	
	r(C…H)	2.111	2.120	
HCN…HF	$r(HF)_{donor}$	0.929	0.923	
	$r(HC)_{acceptor}$	1.066	1.065	
	$r(CN)_{acceptor}$	1.149	1.146	
	r(N…H)	1.868	1.883	
	r(N…F)	2.796	2.806	2.796[f]
HF…HCl	$r(HCl)_{donor}$	1.280	1.277	
	$r(HF)_{acceptor}$	0.920	0.915	
	r(F…H)	2.096	2.097	2.12[g]
	r(Cl…F)	3.37	3.36	3.37[g]
	$\Theta(H\text{-}Cl_{donor}\ldots F)$	6	7	
	$\Theta(H\text{-}F_{acceptor}\ldots Cl)$	117	115	130[g]
H_2O…HF	$r(HF)_{donor}$	0.930	0.926	
	$r(OH)_{acceptor}$	0.958	0.954	
	r(O…H)	1.741	1.741	
	r(O…F)	2.67	2.65	2.662[h]
	$\Theta(H\text{-}F_{donor}\ldots O)$	0.4	0.5	

[a] Haynes, W.M., Ed., CRC Handbook of Chemistry and Physics; 93st Ed. (Internet Version 2013); CRC Press/Taylor and Francis, Boca Raton, FL.

[b] Okabayashi, T.; Tanimoto, M. Millimeter and Submilliter-Wave Spectroscopy of HNC and DNC in the Vibrationally Excided-States. *J. Chem. Phys.* **1993**, *99*, 3268-3271.

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[d] Semiempirical values from Elrod, M.J.; Saykally, R.J. Determination of the Intermolecular Potential-Energy Surface for $(HCl)_2$ from Vibration-Rotation-Tunneling Spectra. *J. Chem. Phys.* **1995**, *103*, 933-949.
[e] Ruoff, R.S.; Emilsson, T.; Chuang, C.; Klots, T.D.; Gutowsky, H.S. Experimental Separation of Torsional and Charge Redistribution Effects in Rotational Spectra of HCN Dimers. *Chem. Phys. Letters* **1987**, *138*, 553-558.
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The largest deviations in bond lengths (roughly 0.2 Å) are observed for two values of the HCN**…**HCN dimer but, as discussed in the experimental data source,[e] they can be explained by inaccuracies in microwave derived distances since the hydrogen from the donor molecule is very close to the center of mass.

Table S2: QTAIM charges obtained from CCSD/cc-pVQZ-mod calculations at equilibrium geometries.

System	Atom[a]	q_i (*e*)	System	Atom[a]	q_i (*e*)
HF	H	0.753	HNC…HNC	H_d	0.585
HCl	H	0.256		N_d	-1.615
HCN	H	0.191		C_d	1.000
	C	1.015		H_a	0.566
	N	-1.207		N_a	-1.556
HNC	H	0.551		C_a	1.020
	N	-1.581	HCN…HF	H_d	0.774
	C	1.030		F_d	-0.801
H_2O	H	0.588		H_a	0.214
	O	-1.176		C_a	1.059
HF…HF	H_d	0.774		N_a	-1.247
	F_d	-0.785	HF…HCl	H_d	0.299
	H_a	0.770		Cl_d	-0.303
	F_a	-0.759		H_a	0.764
HCl…HCl	H_d	0.274		F_a	-0.761
	Cl_d	-0.285	H_2O…HF	H_d	0.782
	H_a	0.267		F_d	-0.806
	Cl_a	-0.256		H_a	0.616
HCN…HCN	H_d	0.247		O_a	-1.207
	C_d	0.984			
	N_d	-1.242			
	H_a	0.208			
	C_a	1.043			
	N_a	-1.240			

[a] The letters “a” and “d” refer to acceptor and donor monomers, respectively.

Table S3: Ratio between square roots of fundamental infrared intensities of HX_{donor} stretching modes in dimers (D) and monomers (M) along with the equivalent ratio from p_{zz}^{H} elements of donor monomers as obtained from CCSD/cc-pVQZ-mod calculations.

Dimers	$\sqrt{A^D/A^M}$	p_{zz}^D/p_{zz}^M
HF…HF	1.97	1.90
HCl…HCl	2.14	2.14
HCN…HCN	2.17	2.28
HNC…HNC	2.12	2.31
HCN…HF	2.66	2.69
HF…HCl	2.21	2.20
H_2O…HF	2.55	2.63

Table S4: Variations in QTAIM/CCFDF contributions to the infrared intensities of X-H stretching modes (km mol^{-1}) due to dimerization according only to p_{zz}^{H} elements of donor monomers as obtained from CCSD/cc-pVQZ-mod calculations.

Dimers		QTAIM/CCFDF[a]							
Y…HX	Attrib.	$\Delta(A^C)$	$\Delta(A^{CF})$	$\Delta(A^{DF})$	$\Delta(A^{C\times CF})$	$\Delta(A^{C\times DF})$	$\Delta(A^{CF\times DF})$	$\Delta(A^{CFterms})$	Tot
HF…HF	HF_{donor}	31.2	-248.0	30.7	301.3	92.4	62.7	116.1	270.4
HCl…HCl	HCl_{donor}	9.3	127.9	-59.8	86.3	19.4	-52.9	161.4	130.2
HCN…HCN	HC_{donor}	24.0	450.9	31.0	210.9	-79.2	-387.5	274.3	250.2
HNC…HNC	HN_{donor}	37.8	353.5	-2.0	603.7	-8.2	-206.4	750.9	778.6
HCN…HF	HF_{donor}	31.9	-446.3	-10.2	800.2	-20.0	288.9	642.8	644.5
HF…HCl	HCl_{donor}	23.2	114.0	-57.8	105.9	-2.4	-45.0	174.9	137.9
H_2O…HF	HF_{donor}	44.0	-401.9	39.6	623.5	118.8	190.2	411.8	614.2

[a] $\Delta(A^i) = A^i(dimer) - A^i(monomer)$.

Table S5: Atomic terms of the QTAIM/CCFDF analysis of the polar tensor elements (*e*) associated with parallel dipole moment derivatives for displacements of the bridge hydrogen along the X-H axis from CCSD/cc-pVQZ-mod calculations.[a]

Monomer	q_{Hd}	$-R_{XHd}\frac{\partial q_X}{\partial z_{Hd}}$	$R_{YHd}\frac{\partial q_Y}{\partial z_{Hd}}$	$\frac{\partial m_{Hd,z}}{\partial z_{Hd}}$	$\frac{\partial m_{X,z}}{\partial z_{Hd}}$	$\frac{\partial m_{Y,z}}{\partial z_{Hd}}$	Other atoms		Tot
							CF	DF	
HF	0.753	-0.691	-	-0.074	0.338	-	-	-	0.326
HCl	0.256	0.423	-	0.077	-0.562	-	-	-	0.194
HCN	0.191	0.536	-	0.075	-0.656	-	0.130	-0.029	0.247
HNC	0.551	-0.127	-	0.066	-0.258	-	0.211	-0.015	0.427
Dimer	q_{Hd}	$-R_{XHd}\frac{\partial q_X}{\partial z_{Hd}}$	$R_{YHd}\frac{\partial q_Y}{\partial z_{Hd}}$	$\frac{\partial m_{Hd,z}}{\partial z_{Hd}}$	$\frac{\partial m_{X,z}}{\partial z_{Hd}}$	$\frac{\partial m_{Y,z}}{\partial z_{Hd}}$	CF	DF	Tot
HF…HF	0.774	-0.534	-0.018	-0.015	0.283	0.049	0.079	0.002	0.619
HCl…HCl	0.274	0.486	0.023	0.102	-0.556	0.037	0.048	-0.001	0.414
HCN…HCN	0.247	0.559	-0.066	0.110	-0.696	-0.008	0.459	-0.042	0.564
HNC…HNC	0.585	-0.020	0.007	0.092	-0.292	-0.015	0.621	0.013	0.991
HCN…HF	0.774	-0.473	-0.072	-0.012	0.282	-0.009	0.403	-0.017	0.876
HF…HCl	0.299	0.517	-0.027	0.119	-0.566	0.025	0.054	0.002	0.423
H_2O…HF	0.782	-0.444	-0.059	0.005	0.275	0.035	0.247	0.018	0.858

[a] The letter "d" labelling some of the terms refers to donor monomers.

Table S6: Contributions from charge, charge flux (donor, charge transfer and acceptor) and polarization changes (donor and acceptor) as given by the QTAIM/CCFDF analysis of the polar tensor elements (*e*) associated with parallel dipole moment derivatives for displacements of the bridge hydrogen along the X-H axis from CCSD/cc-pVQZ-mod calculations.[a]

Monomer	q_{Hd}	$\sum_{i\in d} z_{iHd}\frac{\partial q_i}{\partial z_{Hd}}$	$\sum_{i\in a} z_{YHd}\frac{\partial q_i}{\partial z_{Hd}}$	$\sum_{i\in a} z_{iY}\frac{\partial q_i}{\partial z_{Hd}}$	$\sum_{i\in d}\frac{\partial m_{i,z}}{\partial z_{Hd}}$	$\sum_{i\in a}\frac{\partial m_{i,z}}{\partial z_{Hd}}$	Tot
HF	0.753	-0.691	-	-	0.264	-	0.326
HCl	0.256	0.423	-	-	-0.485	-	0.194
HCN	0.191	0.666	-	-	-0.610	-	0.247
HNC	0.551	0.084	-	-	-0.208	-	0.427
Dimer	q_{Hd}	$\sum_{i\in d} z_{iHd}\frac{\partial q_i}{\partial z_{Hd}}$	$\sum_{i\in a} z_{YHd}\frac{\partial q_i}{\partial z_{Hd}}$	$\sum_{i\in a} z_{iY}\frac{\partial q_i}{\partial z_{Hd}}$	$\sum_{i\in d}\frac{\partial m_{i,z}}{\partial z_{Hd}}$	$\sum_{i\in a}\frac{\partial m_{i,z}}{\partial z_{Hd}}$	Tot
HF…HF	0.774	-0.534	0.053	0.008	0.268	0.051	0.619
HCl…HCl	0.274	0.486	0.076	-0.005	-0.454	0.036	0.414
HCN…HCN	0.247	0.794	0.066	0.092	-0.620	-0.015	0.564
HNC…HNC	0.585	0.289	0.191	0.128	-0.185	-0.017	0.991
HCN…HF	0.774	-0.473	0.148	0.183	0.270	-0.026	0.876
HF…HCl	0.299	0.517	0.020	0.007	-0.447	0.027	0.423
H_2O…HF	0.782	-0.444	0.127	0.061	0.280	0.053	0.858

[a] The letters “a” and “d” labelling some of the terms refer to acceptor and donor monomers, respectively.