Supplementary Information

Review of Experimental GAPT and Infrared Atomic Charges in Molecules

Wagner E. Richter, Leonardo J. Duarte, Arnaldo F. Silva and Roy E. Bruns*

Instituto de Química, Universidade Estadual de Campinas (Unicamp),
CP 6154, 13083-970 Campinas-SP, Brazil

Table S1. Atomic polar tensor values determined from experimental infrared spectroscopic data (e). References reporting the original values in superscripts, original atom identification number for nonequivalent atoms in superscripts

X_2CY molecules

Molecule	C			Y			X_1				
	xx	yy	zz	xx	yy	zz	xx	yy	zz	xz	zx
F_2CO[1]	1.90 ± 0.04	0.53 ± 0.01	2.10 ± 0.05	–0.49 ± 0.01	–0.31 ± 0.00	–0.87 ± 0.03	–0.71 ± 0.01	–0.11 ± 0.00	–0.62 ± 0.01	–0.33 ± 0.01	–0.30 ± 0.01
Cl_2CO[1]	1.99 ± 0.04	0.20 ± 0.05	1.54 ± 0.08	–0.59 ± 0.01	–0.20 ± 0.02	–0.98 ± 0.03	–0.70 ± 0.02	0.00 ± 0.01	–0.28 ± 0.02	–0.33 ± 0.01	–0.23 ± 0.03
F_2CS[1]	1.36 ± 0.04	0.12 ± 0.01	2.01 ± 0.05	–0.11 ± 0.02	–0.04 ± 0.02	–0.64 ± 0.01	–0.62 ± 0.02	–0.04 ± 0.01	–0.68 ± 0.01	–0.34 ± 0.02	–0.40 ± 0.01
Cl_2CS[1]	1.28 ± 0.07	–0.15 ± 0.03	1.55 ± 0.05	–0.12 ± 0.02	0.04 ± 0.01	–0.77 ± 0.03	–0.58 ± 0.03	0.06 ± 0.01	–0.39 ± 0.01	–0.35 ± 0.02	–0.39 ± 0.02
Br_2CO[2]	1.58 ± 0.04	0.10 ± 0.01	1.40 ± 0.10	–0.83 ± 0.02	–0.17 ± 0.02	–1.10 ± 0.03	–0.37 ± 0.01	0.04 ± 0.02	–0.15 ± 0.03	–0.06 ± 0.02	–0.19 ± 004
H_2CO[3]	0.66	0.16	0.90	–0.41	–0.33	–0.74	–0.13	0.08	–0.08	0.06	0.10
H_2CO[3]	0.44	0.39	0.90	–0.24	–0.40	–0.74	–0.10	0.00	–0.08	0.16	0.10

*e-mail: bruns@iqm.unicamp.br

Dihaloethylenes

Molecule	Tensor				
	p_{xx}	p_{xz}	p_{yy}	p_{zx}	p_{zz}
cis-$C_2H_2F_2$[4,5]					
C_1	0.492 ± 0.048	0.404 ± 0.069	–0.063 ± 0.004	0.493 ± 0.038	0.511 ± 0.046
H_3	0.012 ± 0.037	–0.083 ± 0.037	0.159 ± 0.002	–0.012 ± 0.042	0.005 ± 0.041
F_4	–0.504 ± 0.042	0.512 ± 0.027	–0.096 ± 0.003	0.329 ± 0.0129	–0.516 ± 0.040
cis-$C_2H_2Cl_2$[6,7]					
C_1	0.299 ± 0.009	0.595 ± 0.028	–0.106 ± 0.003	0.379 ± 0.018	0.287 ± 0.004
H_3	0.010 ± 0.010	0.058 ± 0.008	0.147 ± 0.001	0.026 ± 0.010	–0.017 ± 0.002
Cl_4	–0.308 ± 0.011	0.379 ± 0.012	–0.041 ± 0.002	0.196 ± 0.003	–0.269 ± 0.006
1,1-$C_2H_2F_2$[8]					
C_1	–0.094 ± 0.153	0.0	–0.329 ± 0.006	0.0	–0.398 ± 0.074
C_2	1.383 ± 0.124	0.0	0.161 ± 0.014	0.0	1.386 ± 0.036
H_3[a]	0.147 ± 0.028	–0.151 ± 0.024	0.162 ± 0.001	0.039 ± 0.039	–0.094 ± 0.031
F_4[a]	–0.179 ± 0.017	0.171 ± 0.143	–0.078 ± 0.005	–0.010 ± 0.018	–1.013 ± 0.149

[a]Local coordinate system of reference 9.

Hydrocarbons

Molecule	Tensor				
	p_{xx}	p_{yy}	p_{zz}	p_{xy}	p_{yx}
CH_4[9]					
C	0.014 ± 0.014	0.014 ± 0.014	0.014 ± 0.014	0	0
H_2	–0.139 ± 0.008	0.064 ± 0.004	0.064 ± 0.004	0	0
H_3	0.041 ± 0.004	–0.115 ± 0.008	0.064 ± 0.004	0.063 ± 0.002	0.063 ± 0.002
CH_4[10]					
C	0.014	0.014	0.014	–	–
H_3	0.062	–0.113	0.040	0.062	0.100
C_2H_4[11]					
C	0.142	0.136	–0.246	0	0
H_1	–0.072	–0.068	0.122	–0.012	–0.032
C_2H_6[10]				p_{xz}	p_{zx}
C_4	0.121	0.121	–0.050	0	0
H_1	–0.123	0.039	0.021	–0.103	–0.082
C_3H_4 (propyne)[10]					
H_7	0.207	0.207	0.181	0	0
C_6	–0.251	–0.251	–0.437	0	0
H_1	0.059	0.097	–0.013	–0.027	–0.075
C_4	0.121	0.121	0.050	0	0
C_3H_4 (allene)[12,13]				p_{yz}	p_{zy}
C_1	–0.242 ± 0.037	–0.242 ± 0.037	0.580 ± 0.009	0	0
C_3	–0.252 ± 0.016	0.165 ± 0.057	–0.310 ± 0.014	0	0
H_7	0.154 ± 0.003	0.011 ± 0.029	0.010 ± 0.005	0.007 ± 0.021	–0.059 ± 0.011
C_3H_6[14]					
C_1	0.087	–0.161	0.125	0	0
H_1	0.082	–0.045	–0.063	0.078	0.028
C_6H_6 (benzene)[15,16]					
C_1	–0.063	0.102	–0.119	0	0
H_7	0.063	–0.102	0.119	0	0
C_4H_6 (2-butyne)[17]					
C_4	0.147	0.147	0.057	0	0
H_1	–0.070	0.088	–0.011	–0.034	–0.096
C_9	–0.174	–0.174	–0.025	0	0
C_3H_6 (cyclopropane)[14]					
C_1	0.087	–0.161	0.125	0	0
H_1	0.082	–0.045	–0.063	0.078	0.028

Linear molecules

Molecule	Tensor	
	p_{xx}	$p_{yy} = p_{zz}$
H–C≡C–H[18] → z		
H	0.183 ± 0.006	0.205 ± 0.003
C	–0.183 ± 0.006	–0.205 ± 0.003
H–C≡C–H[19] → z		
H	0.195	0.207
C	–0.195	–0.207
H–C≡C–H[17] → z		
H	0.187	0.208
C	–0.187	–0.208
H–C≡N[20] → z		
H	0.218 ± 0.004	0.237 ± 0.006
C	–0.292 ± 0.015	0.084 ± 0.008
N	0.074 ± 0.014	–0.321 ± 0.006
O=C=O[21] → z		
O	–0.236	–1.137
C	0.472	2.274
S=C=S[21] → z		
S	0.084	–1.200
C	–0.168	2.400
O=C=S[21] → z		
O	–0.103	–1.536
S	0.002	–0.809
C	0.101	2.345
N_1NO[21] → z		
N_1	–0.108	–0.626
O	–0.139	–1.237
N	0.247	1.863
ClCN[21] → z		
Cl	0.154	–0.420
N	–0.254	–0.097
C	0.093	0.517
BrCN[21] → z		
Br	0.193	–0.176
N	–0.226	–0.124
C	0.033	0.300

Other molecules

Molecule	Tensor				
	p_{xx}	p_{yy}	p_{zz}	p_{xy}	p_{yx}
SiH_4[22]					
Si	0.918	0.918	0.918	0	0
H_1	–0.189	–0.189	–0.308	0	0
SiH_4[23]				p_{yz}	p_{zy}
Si	0.904 ± 0.013	0.904 ± 0.013	0.904 ± 0.013	0	0
H_2	–0.226 ± 0.006	–0.226 ± 0.006	–0.226 ± 0.006	–0.015 ± 0.004	–0.015 ± 0.004
GeH_4[23]					
Ge	0.862 ± 0.009	0.862 ± 0.009	0.862 ± 0.009	0	0
H_2	–0.216 ± 0.003	–0.216 ± 0.003	–0.216 ± 0.003	–0.039 ± 0.002	–0.039 ± 0.002
SnH_4[23]					
Sn	1.016 ± 0.032	1.016 ± 0.032	1.016 ± 0.032	0	0
H_2	–0.254 ± 0.008	–0.254 ± 0.008	–0.254 ± 0.008	–0.047 ± 0.006	–0.047 ± 0.006
SiF_4[23]					
Si	2.215 ± 0.111	2.215 ± 0.111	2.215 ± 0.111	0	0
F_2	–0.554 ± 0.028	–0.554 ± 0.028	–0.554 ± 0.028	–0.070 ± 0.030	–0.070 ± 0.030
C_2H_3N (acetonitrile)[24]				p_{xz}	p_{zx}
C_1	0.144	0.144	0.042	0	0
H_1	–0.024	0.108	0.017	0.005	–0.040
C_2	0.061	0061	0.078	0	0
N	–0.331	–0.331	–0.171	0	0
H_2O[25]				p_{yz}	p_{zy}
O_3	–0.658	–0.460	–0.298	0	0
H_1	0.329	0.230	0.149	–0.077	–0.062
C_6F_6[15]				p_{xy}	p_{yx}
C_1	0.164	1.063	0.057	0	0
F_7	–0.104	–1.124	–0.057	0	0
NH_3[26]				p_{xz}	p_{zx}
N	0.110	0.110	–0.524	0	0
H_1	–0.101	0.027	0.175	–0.187	0.106
PH_3[26]					
P	0.318	0.318	0.434	0	0
H_1	–0.115	–0.097	–0.145	0.072	0.057
NF_3[27]					
N	1.433	1.433	0.595	0	0
F_1	–0.669	–0.287	–0.198	0.44	0.06

Other molecules (cont.)

Molecule	Tensor				
	p_{xx}	p_{yy}	p_{zz}	p_{xy}	p_{yx}
PF_3[27]					
P	1.824	1.824	1.573	0	0
F_1	–0.995	–0.221	–0.524	0.602	0.268
BF_3[28]					
B	1.86	1.86	0.83	–	–
F_1	–0.82	–0.42	–0.28	–	–
BCl_3[28]					
B	1.06	1.06	0.12	–	–
Cl_1	–0.55	–0.15	–0.04	–	–
C_2N_2[29]					
N_2	0.123	–0.245	–0.245	–	–
C_2	–0.123	0.245	0.245	–	–
SO_2[30]				p_{xz}	p_{zx}
O_1	–0.85	–0.235	–0.433	0.362	0.041
S	1.710	0.471	0.866	–	–
C_2H_4O (ethylene)oxide)[31]				p_{xy}	p_{yx}
O	–0.325	–0.868	–0.255	0	0
C_1	0.245	0.322	0.263	0.109	0.037
H_3	$p_{xx} = –0.042$ $p_{yy} = 0.056$ $p_{zz} = –0.068$ $p_{xy} = 0.037$ $p_{xz} = –0.085$ $p_{yx} = 0.040$ $p_{yz} = 0.031$ $p_{zx} = –0.039$ $p_{zy} = 0.037$				

Diatomic molecules[32,33]

Molecule	Atom	Tensor	
		p_{xx}	$p_{yy} = p_{zz}$
F–H → x	H	0.317	0.415
Cl–H → x	H	0.193	0.179
Br–H → x	H	0.100	0.121
I–H → x		0.011	0.055
Li–H → x	H	–0.473	–0.744
C≡O → x	O	–0.729	0.022
Li–F → x	F	–0.908	–0.837
Li–Cl → x	Cl	–0.820	–0.730
Na–F → x	F	–0.910	–0.878
Na–Cl → x	Cl	–0.844	–0.791
K–Cl → x	Cl	–0.891	–0.799
N≡O → x	O	–0.512	0.029

Halomethanes

Molecule	Tensor				
	p_{xx}	p_{yy}	p_{zz}	p_{xz}	p_{zx}
CH_3F[34]					
C	0.366	0.366	0.918	0	0
F	–0.277	–0.277	–0.882	0	0
H_1	–0.124	0.064	–0.002	–0.018	–0.076
CH_2F_2[35]				p_{yz}	p_{zy}
C	0.700	1.425	0.921	0	0
F_1	–0.272	–0.727	–0.465	0.348	0.218
H_1	–0.076	0.016	0.005	p_{xz} = –0.036	p_{zx} = –0.106
CHF_3[36]				p_{xz}	p_{zx}
C	1.730 ± 0.035	1.730 ± 0.035	1.095 ± 0.021	0	0
H_1	0.032 ± 0.006	0.032 ± 0.006	–0.072 ± 0.003	0	0
F_1	–0.885 ± 0.024	–0.290 ± 0.004	–0.341 ± 0.007	0.266 ± 0.012	0.106 ± 0.010
CF_4[37]				p_{yz}	p_{zy}
C	2.051	2.051	2.051	0	0
F_2	–0.512	–0.512	–0.512	–0.237	–0.237
CH_3Cl[38]				p_{xz}	p_{zx}
C	0.108	0.108	0.599	0	0
Cl	–0.176	–0.176	–0.451	0	0
H_1	–0.040	0.085	–0.049	–0.034	–0.058
CH_2Cl_2[39]				p_{yz}	p_{zy}
C	0.145	1.100	0.336	0	0
Cl_4	–0.114	–0.474	–0.157	–0.177	–0.066
H_2	0.041	–0.076	–0.011	p_{xz} = –0.033	p_{zx} = –0.047
$CHCl_3$[40,41]				p_{xz}	p_{zx}
C	1.128 ± 0.004	1.128 ± 0.004	0.213 ± 0.019	0	0
H	–0.055 ± 0.000	–0.055 ± 0.000	0.031 ± 0.020	0	0
Cl_1	–0.590 ± 0.018	–0.125 ± 0.021	–0.081 ± 0.002	0.285 ± 0.001	0.047 ± 0.016
CCl_4[42]				p_{yz}	p_{zy}
C	1.043	1.043	1.043	0	0
Cl_2	–0.261	–0.261	–0.261	–0.230	–0.230
CH_3Br[38]				p_{xz}	p_{zx}
C	0.056	0.056	0.519	0	0
Br	–0.145	–0.145	–0.322	0	0
H_1	–0.026	0.085	–0.066	–0.040	–0.050

Halomethanes (cont.)

Molecule	Tensor				
	p_{xx}	p_{yy}	p_{zz}	p_{xz}	p_{zx}
CH_3I[38]					
C	0.020	0.020	0.361	0	0
I	–0.115	–0.115	–0.112	0	0
H_1	0.018	0.044	–0.084	0.080	–0.037
$CFCl_3$[43]					
C	1.407	1.407	1.287	0	0
F	–0.285	–0.285	–0.887	0	0
Cl_1	–0.715	–0.033	–0.133	0.142	–0.024
CF_2Cl_2[43]					
C	1.356	1.837	1.716	0	0
F_1	–0.616	–0.373	–0.766	–0.327	–0.314
Cl_4	–0.062	–0.546	–0.092	0.222	0.120
CF_3Cl[43]					
C	1.806	1.806	2.486	0	0
Cl	–0.875	–0.048	–0.347	0	0
F_1	–0.875	–0.298	–0.713	0.318	0.297

Table S2. Charge and distance values used to calculate electrostatic potentials owing to neighboring atoms, V of Table 3

Molecule	Charge model			Bond distance / Å
	CHELPG	Mulliken	Zero flux	R(C–atom)
CH_4				
C	–0.328	–0.367	0.013	
H	0.082	0.092	–0.003	2.056
CH_3F				
C	0.191	0.115	0.650	
F	–0.282	–0.305	–0.699	2.605
H	0.031	0.063	0.016	2.058
CH_2F_2				
C	0.471	0.432	1.314	
F	–0.265	–0.262	–0.703	2.554
H	0.030	0.046	0.046	2.056
CHF_3				
C	0.665	0.611	2.021	
F	–0.238	–0.219	–0.704	2.514
H	0.049	0.047	0.091	2.052
CF_4				
C	0.861	0.730	2.786	
F	–0.215	–0.183	–0.696	2.486
CH_3Cl				
C	–0.126	–0.145	0.140	
Cl	–0.195	–0.206	–0.271	3.376
H	0.107	0.117	0.044	2.049
CH_2Cl_2				
C	–0.088	0.016	0.255	
Cl	–0.117	–0.149	–0.214	3.351
H	0.161	0.141	0.087	2.044
$CHCl_3$				
C	–0.118	0.122	0.363	
Cl	–0.036	–0.097	–0.163	3.286
H	0.225	0.168	0.124	2.246
CCl_4				
C	–0.295	0.199	0.466	
Cl	0.074	–0.050	–0.117	3.351

Table S2. Charge and distance values used to calculate electrostatic potentials owing to neighboring atoms, V of Table 3 (cont.)

Molecule	Charge model			Bond distance / Å
	CHELPG	Mulliken	Zero flux	R(C–atom)
CCl_3F				
C	–0.041	0.412	1.051	
F	–0.035	–0.188	–0.680	3.341
Cl	0.025	–0.075	–0.124	2.522
CCl_2F_2				
C	0.142	0.565	1.636	
F	–0.068	–0.185	–0.687	2.507
Cl	–0.003	–0.098	–0.131	3.333
$CClF_3$				
C	0.437	0.667	2.211	
F	–0.129	–0.184	–0.692	2.496
Cl	–0.050	–0.115	–0.135	3.323

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