Atomic Mean Dipole Moment Derivative and Anisotropic Contributions to Molecular Infrared Intensity Sums

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Atomic anisotropies determined from gas-phase infrared fundamental intensity data for 30 molecules are compared with anisotropies calculated from wave functions obtained with 6-31+G(d,p) and 6-311++G(3d,3p) basis sets at the Hartree−Fock, B3LYP density functional and MP2 electron correlation levels. The discrepancies between the experimental and theoretical anisotropy values are up to 30 times larger than those found for the mean dipole moment derivatives. Although a change in the basis set from 6-31+G(d,p) to 6-311++G(3d,3p) has small effects on the anisotropy values, they are quite sensitive to the inclusion of post-Hartree−Fock electron correlation treatment. Although the calculated results for anisotropies with values $<0.7e^2$ deviate randomly from the experimental results, calculated anisotropies with higher values tend to overestimate the experimental values. Molecules with double bonds (CH_2CF_2, COH_2, COF_2, $COCl_2$, *cis*-$C_2H_2Cl_2$, CO_2, CS_2, and OCS) are found to have high atomic anisotropies and large anisotropic contributions to the experimental intensity sums, whereas these contributions are much smaller for molecules containing triple bonds. Mean dipole moment derivative contributions are predominant over anisotropic ones for the fluorochloromethanes and fluorine-rich fluoromethanes. These results are interpreted using an atoms-in-molecules charge/charge flux/dipole flux decomposition of the dipole moment derivatives of CO, CO_2, CS_2, OCS, HCN, C_2H_2, and C_2N_2. Large positive weighted charge flux and dipole flux contributions are canceled to a large extent by large negative weighted charge flux−dipole flux interaction terms for all these molecules. Whereas this cancellation is only partial for the double-bonded molecules, it is almost perfect for the triple-bonded ones.

Introduction

Polar tensors[1,2] have been determined for almost all molecules for which complete experimental gas-phase fundamental intensity data are available. Not only have the polar tensors provided an unambiguous calculational scheme for obtaining dipole moment derivatives from intensities, but they have also provided parameters that are amenable to interpretation in terms of the electronic structures of molecules. Crawford's G sum rule relates the effective charges to the total fundamental infrared intensity sum[3]

$$\sum A_i = K\sum_{\alpha}\frac{\chi_\alpha^2}{m_\alpha} - \Omega \tag{1}$$

where m_α represents the αth atomic mass and the sum is taken over all the atoms in the molecule. Ω is a rotational correction to the sum, and K is a constant. Three rotationally invariant parameters[4] are commonly determined from each atomic polar tensor of the molecular tensor: $\bar{p}_\alpha$, the atomic mean dipole moment derivative, β_α^2, the atomic anisotropy, and χ_α, the atomic effective charge. The atomic effective charge is related to the atomic mean derivative and the atomic anisotropy by

$$\chi_\alpha^2 = \bar{p}_\alpha^2 + \frac{2}{9}\beta_\alpha^2 \tag{2}$$

Substitution of eq 2 into eq 1 results in an intensity sum partitioning into two contributions besides the rotational term: inverse mass weighted sums of squares of the atomic mean dipole moment derivatives and the atomic anisotropies.

$$\sum A_i = K\sum_{\alpha}\frac{\bar{p}_\alpha^2}{m_\alpha} + \frac{2K}{9}\sum_{\alpha}\frac{\beta_\alpha^2}{m_\alpha} - \Omega \tag{3}$$

The first term might be considered to be a contribution to the intensity sum from net atomic charges. The atomic mean dipole moment derivatives have been shown to have mathematical properties similar to those expected of atomic charges.[5] Furthermore, their successful use[6,7] in Siegbahn's simple potential model[8] for predicting ionization energies of core electrons shows they are closely related to atomic charges.

The charge/charge flux/overlap (CCFO) model interpretation of derivatives used during the last 30 years by spectroscopists to understand infrared fundamental intensities points to three contributions to the mean derivative: (1) displacements of equilibrium atomic charges, (2) intramolecular charge transfers,

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and (3) changes in the polarization of charges during the molecular vibration.[9] The second and third contributions are expected to be important in determining atomic anisotropies and their contributions to the intensity sum, whereas the equilibrium charge only affects the mean dipole moment derivative and its contribution to the intensity sum.

A few years ago,[10] our group reported atomic mean dipole moment derivatives calculated from the polar tensors of 30 molecules. All these molecules are polyatomic except CO, and in all, 34 carbon, 19 hydrogen, 9 fluorine, 9 chlorine, 3 nitrogen, 7 oxygen, and 2 sulfur mean dipole moment derivatives were reported. These mean derivatives, obtained from only experimental data, are in excellent agreement, within ~0.05*e*, with MP2/6-311++G(3d,3p) molecular orbital estimates. To complement this mean dipole moment derivative study, the corresponding atomic anisotropies obtained from experimental data are reported here. Atomic mean dipole moment derivative and anisotropic contributions to the infrared intensity sums of these molecules are evaluated, and their relative importance is assessed. One of our main objectives is to understand why some of these molecules have large atomic anisotropies whereas others have very small ones. Molecules with large anisotropic contributions are identified and their common electronic structural properties characterized. Molecules with dominating isotropic mean derivative contributions might be expected to have electronic structures accurately described by simple atomic charge models. On the other hand, large anisotropic contributions to the intensity sums suggest that the molecular electronic structure must be described by including parameters containing directional information, such as those contained in atomic electric moments. To do this, we have applied an atoms-in-molecules (AIM) charge/charge flux/dipole flux decomposition[11] to the infrared intensity parameters of some of the molecules investigated in this work. The dipole flux part of this model substitutes the overlap term of the CCFO model.

The accuracy of quantum chemical calculations of atomic anisotropies is also investigated. This study also complements our previous one on the sensitivities of the atomic mean dipole moment derivatives to basis set changes and different electron correlation treatment levels. Since absolute intensities are difficult to measure in the laboratory, accurate quantum chemical estimates of polar tensors and their invariant quantities are especially relevant to understanding molecular electronic structures.

Calculations

Within the harmonic oscillator−linear dipole moment approximations, the measured fundamental infrared intensity, A_i, is proportional to the square of the dipole moment derivative with respect to its associated normal coordinate, Q_i,

$$A_i = \frac{N_A \pi}{3c^2}\left(\frac{\partial \vec{p}}{\partial Q_i}\right)^2 \qquad i = 1, 2, \ldots, 3N - 6 \tag{4}$$

where N_A and c are Avogadro's number and the velocity of light, respectively.[12] The dipole moment derivatives can be transformed to atomic Cartesian coordinates using the expression[1]

$$\boldsymbol{P}_x = \boldsymbol{P}_Q \boldsymbol{L}^{-1} \boldsymbol{U} \boldsymbol{B} + \boldsymbol{P}_\rho \beta \tag{5}$$

where $\boldsymbol{P}_Q$ is a 3 × (3N − 6) matrix of dipole moment derivatives obtained from the measured infrared intensities and $\boldsymbol{L}^{-1}$, $\boldsymbol{U}$, and $\boldsymbol{B}$ are well-known transformation matrices commonly used in normal coordinate analysis.[13] The $\boldsymbol{P}_\rho\beta$ product provides the rotational contributions to the polar tensor elements. As such, the polar tensor elements contained in $\boldsymbol{P}_x$ are obtained using the molecular geometry (the $\boldsymbol{B}$ and β matrices), symmetry (the $\boldsymbol{U}$ matrix), vibrational frequencies and atomic masses (the normal coordinate $\boldsymbol{L}^{-1}$ matrix), and permanent dipole moment values (the $\boldsymbol{P}_\rho$ matrix), as well as the experimentally measured intensities.

The molecular polar tensor, $\boldsymbol{P}_x$, is a juxtaposition of the atomic polar tensors (APTs)

$$\boldsymbol{P}_x = \{\boldsymbol{P}_x^{(1)} \boldsymbol{P}_x^{(2)}, \ldots, \boldsymbol{P}_x^{(N)}\} \tag{6}$$

with N being the number of atoms in the molecule. Each APT contains the derivatives of the molecular dipole moment with respect to atomic Cartesian coordinates.

$$\boldsymbol{P}_x^{(\alpha)} = \begin{pmatrix} \frac{\partial p_x}{\partial x_\alpha} & \frac{\partial p_x}{\partial y_\alpha} & \frac{\partial p_x}{\partial z_\alpha} \\ \frac{\partial p_y}{\partial x_\alpha} & \frac{\partial p_y}{\partial y_\alpha} & \frac{\partial p_y}{\partial z_\alpha} \\ \frac{\partial p_z}{\partial x_\alpha} & \frac{\partial p_z}{\partial y_\alpha} & \frac{\partial p_z}{\partial z_\alpha} \end{pmatrix} = \begin{pmatrix} p_{xx}^{(\alpha)} & p_{xy}^{(\alpha)} & p_{xz}^{(\alpha)} \\ p_{yx}^{(\alpha)} & p_{yy}^{(\alpha)} & p_{yz}^{(\alpha)} \\ p_{zx}^{(\alpha)} & p_{zy}^{(\alpha)} & p_{zz}^{(\alpha)} \end{pmatrix} \tag{7}$$

The mean dipole moment derivative of atom α, $\bar{p}_\alpha$, is simply one-third the trace of the atomic polar tensor.[14]

$$\bar{p}_\alpha = {}^1/_3(p_{xx}^{(\alpha)} + p_{yy}^{(\alpha)} + p_{zz}^{(\alpha)}) \tag{8}$$

The atomic effective charge is one-third the trace of the product of the atomic polar tensor and its transpose, that is, the square root of one-third the sum of squares of all the polar tensor elements.

The polar tensors for all the atomic anisotropies reported here have been reported previously in the literature.[6,14−28] The atomic anisotropy can be calculated directly from the atomic polar tensor.[14]

$$\beta_\alpha^2 = {}^1/_2[(p_{xx}^{(\alpha)} - p_{yy}^{(\alpha)})^2 + (p_{yy}^{(\alpha)} - p_{zz}^{(\alpha)})^2 + (p_{zz}^{(\alpha)} - p_{xx}^{(\alpha)})^2] + {}^3/_2(p_{xy}^{(\alpha)2} + p_{yz}^{(\alpha)2} + p_{xz}^{(\alpha)2} + p_{zx}^{(\alpha)2} + p_{yx}^{(\alpha)2} + p_{zy}^{(\alpha)2}) \tag{9}$$

Theoretical calculations of the polar tensors were performed using the Gaussian 94[29] and GAMESS-US[30] programs on IBM RISC 6000 and DEC ALPHA workstations. The methods used in these calculations were Hartree−Fock, Möller−Plesset 2, and B3LYP density functionals using 6-31+G(d,p) and 6-311++G(3d,3p) basis sets. All calculations were carried out at the theoretical equilibrium geometries. Atomic charges and atomic dipoles were obtained directly from the Gaussian program. The fluxes were calculated numerically from 0.01 Å geometrical distortions. Individual contributions to the atomic anisotropies were calculated using the FORTRAN 77 program written in our laboratory.

Results

Tables 1−3 contain atomic anisotropy values of atomic polar tensors determined from experimental intensities as well as those calculated using 6-31+G(d,p) and 6-311++G(3d,3p) basis sets at the Hartree−Fock, Möller−Plesset 2, and B3LYP density functional levels for 30 molecules. Tables 1 and 2 contain values for the carbon and hydrogen atoms, respectively, and Table 3 holds values for the fluorine, chlorine, nitrogen, oxygen, and

TABLE 1: Comparison of the Calculated and Experimental Anisotropy Values (e^2 Values)[a] for Carbon Atoms

	6-31+G(d,p)			6-311++G(3d,3p)				
carbon	HF	B3LYP	MP2	HF	B3LYP	MP2	exptl	refs
CH_4	0.000	0.000	0.000	0.000	0.000	0.000	0.000[b]	15
CH_3F	0.342	0.408	0.379	0.432	0.362	0.352	0.336	14, 16, 17
CH_2F_2	0.557	0.621	0.612	0.489	0.534	0.531	0.415	6
CHF_3	0.398	0.530	0.542	0.343	0.460	0.471	0.327	6, 19
CF_4	0.000	0.000	0.000	0.000	0.000	0.000	0.000[b]	20
CH_3Cl	0.543	0.368	0.319	0.468	0.304	0.288	0.246	6, 21
CH_2Cl_2	1.390	1.510	1.173	1.323	1.355	1.138	0.764	6
$CHCl_3$	1.316	1.659	1.302	1.311	1.550	1.306	0.869	6, 22
CCl_4	0.000	0.000	0.000	0.000	0.000	0.000	0.000[b]	23
CF_3Cl	0.423	0.341	0.318	0.539	0.438	0.438	0.402	24
CF_2Cl_2	0.356	0.335	0.310	0.438	0.403	0.393	0.245	24
$CFCl_3$	0.125	0.152	0.137	0.172	0.197	0.180	0.035	24
CH_3CH_3	0.006	0.001	0.002	0.004	0.001	0.001	0.036	6
C_2H_4O	0.042	0.047	0.033	0.038	0.040	0.028	0.025	6
C_3H_6	0.148	0.084	0.096	0.121	0.074	0.085	0.072	6
$C*H_3CN$	0.000	0.013	0.005	0.000	0.012	0.004	0.010	25
$C*H_3CCH$	0.001	0.000	0.000	0.000	0.002	0.000	0.006	6
CH_2CH_2	0.191	0.159	0.153	0.161	0.130	0.118	0.119	6
$C*H_2CF_2$	0.197	0.133	0.085	0.229	0.158	0.119	0.076	6
CH_2C*F_2	2.772	2.418	2.173	2.802	2.359	2.217	1.498	6
COH_2	0.731	0.659	0.454	0.805	0.687	0.501	0.539	6
COF_2	2.673	2.595	2.468	2.642	2.484	2.415	2.132	27
$COCl_2$	3.595	3.764	3.576	3.561	3.561	3.516	2.599	27
cis-$C_2H_2Cl_2$	1.543	1.523	1.270	1.409	1.320	1.153	0.792	6
CO	1.026	0.616	0.286	0.966	0.588	0.303	0.564	6
CO_2	5.546	3.587	3.144	5.617	3.717	3.349	3.247	6
CS_2	16.427	7.745	6.880	17.339	8.260	7.328	6.595	6
OCS	9.891	5.968	5.476	10.317	6.381	5.813	5.036	6
HCN	0.033	0.066	0.139	0.062	0.108	0.195	0.141	6
HCCH	0.001	0.001	0.001	0.000	0.000	0.000	0.000	6, 26, 28
NCCN	0.022	0.052	0.185	0.071	0.071	0.206	0.135	6
CH_3C*N	0.040	0.047	0.003	0.030	0.036	0.003	0.000	25
CH_3C*CH	0.160	0.217	0.098	0.193	0.254	0.144	0.145	6
CH_3CC*H	0.067	0.061	0.022	0.090	0.085	0.045	0.047	6
rms error[c]	2.048	0.462	0.290	2.222	0.502	0.322		

[a] Units of squared electrons, e^2. [b] These values are zero by symmetry and were not included in the rms error calculation. [c] Root-mean-square error, $\sqrt{\sum_{i=1}^{N}(\beta_i^2(\text{calc})-\beta_i^2(\text{exp}))^2/N}$.

TABLE 2: Comparison of the Calculated and Experimental Anisotropy Values (e^2 Values)[a] for Hydrogen Atoms

	6-31+G(d,p)			6-311++G(3d,3p)				
hydrogen	HF	B3LYP	MP2	HF	B3LYP	MP2	exptl	refs
CH_4	0.060	0.052	0.042	0.053	0.040	0.033	0.039	15
CH_3F	0.044	0.041	0.032	0.047	0.038	0.033	0.040	14, 16, 17
CH_2F_2	0.023	0.022	0.016	0.030	0.026	0.022	0.026	6
CHF_3	0.005	0.005	0.003	0.008	0.007	0.005	0.008	6, 19
CH_3Cl	0.035	0.032	0.030	0.030	0.025	0.023	0.024	6, 21
CH_2Cl_2	0.024	0.022	0.021	0.020	0.016	0.016	0.007	6
$CHCl_3$	0.020	0.015	0.014	0.019	0.016	0.016	0.008	6, 22
CH_3CH_3	0.067	0.058	0.048	0.063	0.050	0.042	0.050	6
C_2H_4O	0.039	0.040	0.031	0.042	0.038	0.029	0.033	6
C_3H_6	0.042	0.039	0.031	0.039	0.033	0.025	0.029	6
CH_3CN	0.018	0.017	0.014	0.017	0.014	0.012	0.016	25
CH_3^*CCH	0.032	0.032	0.026	0.030	0.027	0.022	0.030	6
CH_3CCH*	0.004	0.002	0.003	0.001	0.000	0.000	0.001	6
CH_2CH_2	0.064	0.054	0.049	0.055	0.045	0.038	0.042	6
CH_2CF_2	0.033	0.024	0.022	0.028	0.020	0.017	0.099	6
COH_2	0.074	0.096	0.086	0.085	0.101	0.091	0.089	6
cis-$C_2H_2Cl_2$	0.055	0.048	0.048	0.046	0.039	0.040	0.047	6
HCN	0.000	0.001	0.001	0.001	0.000	0.000	0.000	6
HCCH	0.001	0.001	0.001	0.000	0.000	0.000	0.000	6, 26, 28
rms error[b]	0.019	0.019	0.018	0.018	0.019	0.019		

[a] Units of squared electrons, e^2. [b] Root-mean-square error, $\sqrt{\sum_{i=1}^{N}(\beta_i^2(\text{calc})-\beta_i^2(\text{exp}))^2/N}$.

TABLE 3: Comparison of the Calculated and Experimental Anisotropy Values (e^2 Values)[a] for Fluorine, Chlorine, Nitrogen, Oxygen, and Sulfur Atoms

	6-31+G(d,p)			6-311++G(3d,3p)				
fluorine	HF	B3LYP	MP2	HF	B3LYP	MP2	exptl	refs
CH_3F	0.486	0.441	0.387	0.575	0.430	0.392	0.442	14, 16, 17
CH_2F_2	0.557	0.524	0.476	0.554	0.513	0.480	0.410	6
CHF_3	0.483	0.516	0.480	0.477	0.501	0.479	0.428	6, 19
CF_4	0.348	0.399	0.379	0.341	0.389	0.377	0.506	20
CF_3Cl	0.493	0.526	0.487	0.483	0.508	0.484	0.462	24
CF_2Cl_2	0.501	0.548	0.493	0.475	0.508	0.473	0.392	24
$CFCl_3$	0.438	0.507	0.433	0.393	0.445	0.401	0.318	24
CH_2CF_2	1.306	1.105	1.002	1.284	1.067	1.010	0.834	6
COF_2	0.776	0.828	0.867	0.760	0.789	0.839	0.635	27
rms error[b]	0.189	0.152	0.121	0.182	0.124	0.112		

	6-31+G(d,p)			6-311++G(3d,3p)				
chlorine	HF	B3LYP	MP2	HF	B3LYP	MP2	exptl	refs
CH_3Cl	0.190	0.101	0.075	0.179	0.094	0.080	0.079	6, 21
CH_2Cl_2	0.320	0.360	0.257	0.327	0.345	0.275	0.170	6
$CHCl_3$	0.343	0.471	0.343	0.360	0.456	0.368	0.306	6, 22
CCl_4	0.293	0.452	0.334	0.325	0.456	0.377	0.476	23
CF_3Cl	0.262	0.333	0.315	0.283	0.341	0.336	0.080	24
CF_2Cl_2	0.365	0.460	0.410	0.386	0.458	0.432	0.347	24
$CFCl_3$	0.356	0.484	0.403	0.383	0.484	0.433	0.457	24
$COCl_2$	0.803	1.012	1.038	0.812	0.956	1.014	0.760	27
cis-$C_2H_2Cl_2$	0.475	0.483	0.394	0.442	0.421	0.364	0.338	6
rms error[b]	0.122	0.159	0.138	0.117	0.142	0.135		

	6-31+G(d,p)			6-311++G(3d,3p)				
nitrogen	HF	B3LYP	MP2	HF	B3LYP	MP2	exptl	refs
CH_3CN	0.018	0.000	0.046	0.009	0.000	0.054	0.026	25
HCN	0.033	0.082	0.164	0.051	0.110	0.198	0.156	6
NCCN	0.022	0.052	0.185	0.071	0.071	0.206	0.135	6
rms error[b]	0.097	0.066	0.031	0.072	0.048	0.050		

	6-31+G(d,p)			6-311++G(3d,3p)				
oxygen	HF	B3LYP	MP2	HF	B3LYP	MP2	exptl	refs
C_2H_4O	0.486	0.332	0.284	0.454	0.306	0.269	0.338	6
COH_2	0.440	0.301	0.107	0.513	0.338	0.156	0.198	6
COF_2	0.508	0.376	0.231	0.524	0.389	0.265	0.217	27
$COCl_2$	1.177	0.968	0.621	1.182	0.931	0.646	0.462	27
CO	1.026	0.616	0.286	0.966	0.588	0.303	0.564	6
CO_2	1.385	0.897	0.787	1.404	0.929	0.837	0.812	6
OCS	3.956	2.500	2.022	4.141	2.641	2.176	2.053	6
rms error[b]	0.831	0.267	0.128	0.894	0.0300	0.134		

	6-31+G(d,p)			6-311++G(3d,3p)				
sulfur	HF	B3LYP	MP2	HF	B3LYP	MP2	exptl	refs
CS_2	4.109	1.935	1.719	4.335	2.065	1.833	1.649	6
OCS	1.334	0.741	0.843	1.385	0.812	0.876	0.658	6
rms error[b]	1.804	0.211	0.140	1.968	0.314	0.202		

[a] Units of squared electrons, e^2. [b] Root-mean-square error, $\sqrt{\sum_{i=1}^{N}(\beta_i^2(\text{calc})-\beta_i^2(\text{exp}))^2/N}$.

sulfur atoms. Included in all these tables are the root-mean-square errors in β_α^2 for all levels of the theoretical calculations.

Several conclusions can be drawn from these tables and the corresponding ones in ref 10 for the atomic mean dipole moment derivatives. First, the root-mean-square errors in β_α^2 are much larger than those found for the atomic mean derivatives. This is also true for the square roots of these errors that have the same units as the $\bar{p}_\alpha$ errors and are up to 30 times larger. It must be remembered, however, that the atomic anisotropy values probably have larger propagated errors from experimental uncertainties than the mean derivative values. Second, the errors in β_α^2 are not very sensitive to the two basis sets used here. In fact, the errors are a bit larger for results obtained from calculations with the more extensive 6-311++G(3d,3p) basis set for the carbon, oxygen, and sulfur anisotropies. This contrasts with the errors found for the atomic mean dipole derivatives. For all the atoms studied, the errors in the mean derivatives

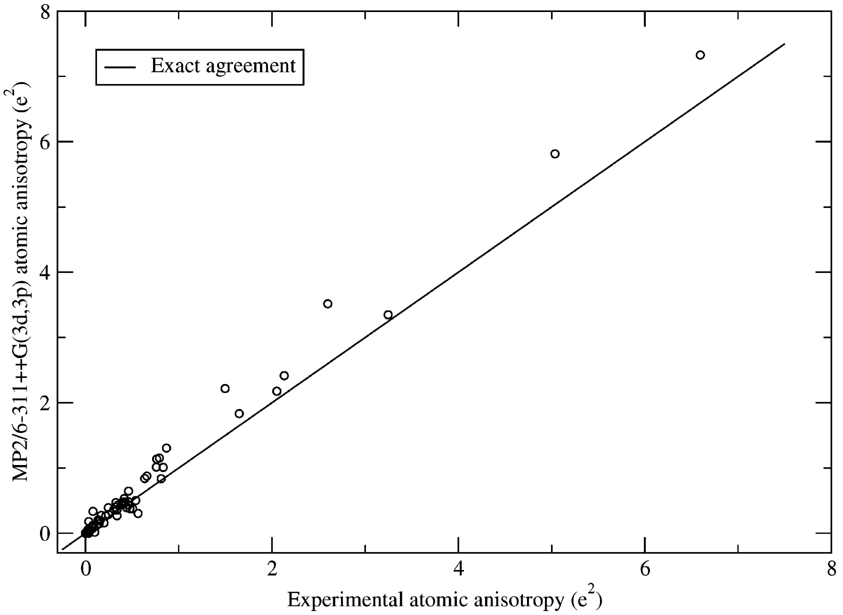

Figure 1. Graph of the experimental and MP2/6-311++G(3d,3p) anisotropies (e^2 values).

obtained with this more extensive basis set were smaller than those for the calculations with the 6-31+G(d,p) basis set. Third, the root-mean-square errors are very sensitive to the inclusion of post-Hartree−Fock electron correlation treatment for all atoms except hydrogen, for which the errors of the Hartree−Fock (HF) calculations are almost exactly the same as those for the B3LYP and MP2 calculations using both basis sets. For the carbon, fluorine, nitrogen, oxygen, and sulfur atoms, the B3LYP and MP2 results have errors that are significantly smaller than those of the HF results. On the other hand, the B3LYP and MP2 results for the chlorine anisotropies have slightly larger errors than those of the HF results for both basis sets.

In Figure 1, the anisotropy values calculated using the MP2/6-311++G(3d,3p) wave functions are plotted against the experimental values. Although the differences between the calculated and experimental values appear to be randomly distributed for anisotropy values below $0.7e^2$, the theoretical anisotropies with higher values tend to overestimate the experimental values. These residuals between theoretical and experimental anisotropy values are similar to those found for the mean dipole moment derivatives, random between −0.5 and 0.5*e* with a tendency for overestimation of the larger mean derivatives. Residuals show even more positive deviations for the results of the other wave functions, as can be verified in Tables 1−3. Recalling eqs 8 and 9, it seems clear that the wave functions used in this study overestimate individual dipole moment derivatives, especially those associated with the carbon atoms with high positive atomic charges such as those in the fluorochloromethanes, CO_2, CS_2, OCS, COF_2, and CH_2CF_2. These results also explain why intensity sums for these molecules tend to be overestimated, as has been reported in ref 10, where the same basis set and electron correlation treatment levels were used.

In Figure 2, the positive square roots of the experimental anisotropies are plotted against the experimental mean dipole moment derivatives. The most striking feature of the graph is the large variance in the carbon values compared with those for the other atoms. The carbon points have both the largest atomic mean dipole moment derivatives and anisotropies. The larger mean derivatives are found for the fluorochloromethanes, as reported recently.[10] However, the fluorochloromethane carbons have anisotropies <1 in spite of the high values of the individual polar tensor elements. Carbon atoms with experimental anisotropies >1 are found for the CO_2, CS_2, OCS, COF_2, and $COCl_2$ molecules and for the carbon atom bound to the fluorines of the 1,1-$C_2H_2F_2$ molecule. All these molecules contain double bonds and, with the exception of CS_2, contain a much more electronegative element than carbon. This is strikingly clear for the carbon anisotropies of 1,1-$C_2H_2F_2$. The anisotropy of the carbon atom bonded to the fluorines, $1.498e^2$, is much larger than the one for carbon bonded to the hydrogens, $0.076e^2$. The latter is similar to the carbon anisotropy in ethylene, $0.119e^2$. Moderate carbon anisotropy values are also found for the other double-bonded molecules where carbon is bonded to atoms other than hydrogen, 0.79 and $0.54e^2$, for *cis*-$C_2H_2Cl_2$ and H_2CO, respectively.

The three molecules with adjacent double bonds, CO_2, OCS, and CS_2 have high anisotropies for all their atoms. The CS_2 molecule has the highest anisotropies, 6.595 and $1.649e^2$, for carbon and sulfur, respectively. The carbon, sulfur, and oxygen atoms of OCS also have high anisotropy values, 5.036, 0.658, and $2.053e^2$, respectively. The 3.247 and $0.812e^2$ anisotropies for the carbon and oxygen atoms of CO_2 are lower than their corresponding values in OCS. For these three molecules, the anisotropy values increase as the electronegativity differences of the atoms decrease.

Anisotropy values in molecules with triple bonds are much lower than those found in molecules with double bonds. The carbon and oxygen anisotropies in CO are the same, $0.564e^2$, since the atomic polar tensors in a neutral molecule sum to give the null tensor. The carbon and nitrogen anisotropies for the triple bonds in HCN, C_2H_2, C_2N_2, and CH_3CN are all lower than $0.16e^2$.

Terminal atoms, except those for molecules containing double bonds, have moderate anisotropy values. The fluorine atoms have anisotropies ranging from 0.32 to $0.83e^2$ and appear on the left-hand side of Figure 2 with mean dipole moment values close to −0.5*e*. The anisotropies of the chlorine atoms have a somewhat larger range, $0.08{-}0.76e^2$, and have points in Figure 2 positioned close to the mean derivative value −0.25*e*. The

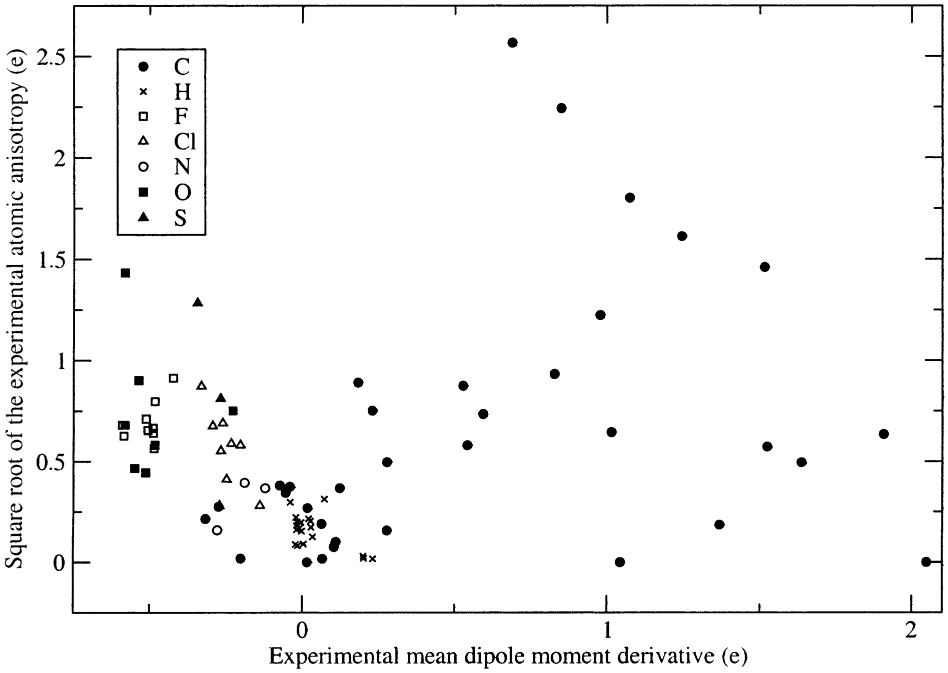

Figure 2. Graph of the positive square root of the experimental atomic anisotropies and their corresponding atomic mean dipole moment derivatives.

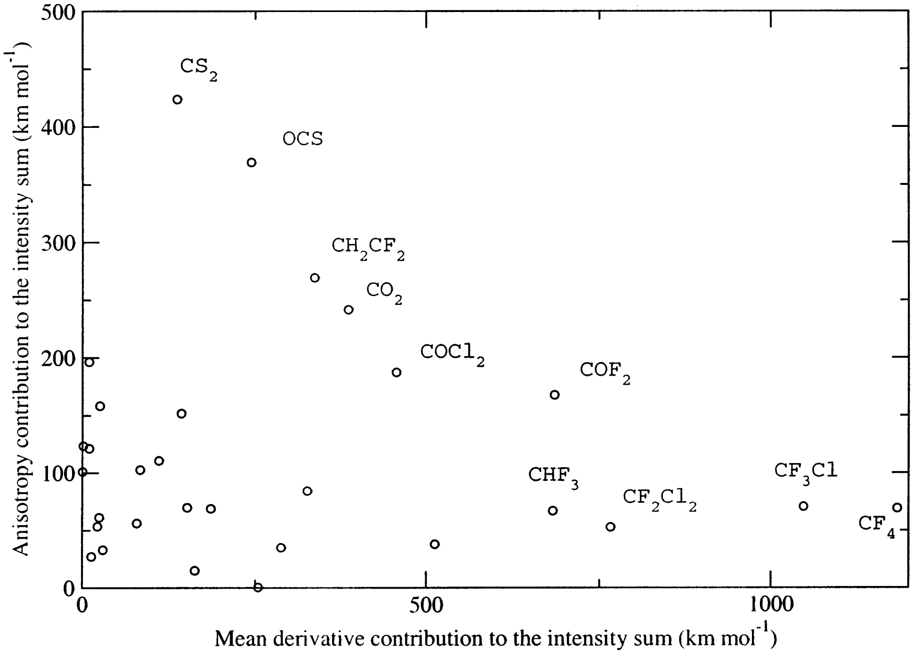

Figure 3. Graph of the atomic mean dipole moment derivative and anisotropy contributions to the experimental intensity sums (kilometers per mole).

hydrogen atoms have the smallest anisotropies, as one might expect. They range from 0.00 to 0.10e^2 and have mean derivatives around the zero value.

Symmetry, of course, plays an important role in determining anisotropies. For the T_d molecules, such as CH$_4$, CF$_4$, and CCl$_4$, included in our study, symmetry requires that the central atom anisotropy be zero. However, symmetry does not seem to be an important factor in determining anisotropies of linear molecules. Eq 9 reduces to a simple equation

$$\beta_\alpha^2 = (p_\parallel^{(\alpha)} - p_\perp^{(\alpha)})^2 \qquad (10)$$

for these molecules. For the triple bonds investigated here, the parallel and perpendicular derivatives are not much different. However, large differences are found for these values in the double-bond-containing molecules, as already demonstrated.

The importance of the anisotropy contributions to the molecular intensity sums can be studied using Table 4 and Figure 3. Table 4 contains atomic mean dipole moment derivative and anisotropy contributions to the intensity sums for carbon and terminal atoms calculated from the experimental data in Tables 1−3 and in Table 1 of our study of the corresponding mean dipole moment derivatives.[10] Figure 3 contains a graph of the total mean dipole moment derivative intensity sum contribution plotted against the anisotropic contribution. High anisotropic but relatively moderate-to-low mean derivative contributions are found for molecules with double bonds, CO$_2$, CS$_2$, OCS, 1,1-C$_2$H$_2$F$_2$, COF$_2$, and COCl$_2$.

TABLE 4: Mean Dipole Moment Derivative, Anisotropy, and Rotational Contributions to the Experimental Intensity Sums (km mol^{-1})

	carbon atoms		terminal atoms				
molecules	$K\Sigma\bar{p}_\alpha/m_\alpha$	$(^2/_9)K\Sigma\beta_\alpha^2/m_\alpha$	$K\Sigma\bar{p}_\alpha/m_\alpha$	$(^2/_9)K\Sigma\beta_\alpha^2/m_\alpha$	Ω	total[a]	ΣA_i exptl[a]
CH_4	0.06	0.00	0.19	101.11	0.00	101.36	100.98
CH_3F	71.27	18.20	39.48	92.50	14.88	206.57	192.70
CH_2F_2	250.37	22.44	75.20	61.87	19.17	390.71	413.60
CHF_3	564.81	17.70	118.29	49.24	4.72	745.32	766.64
CF_4	1022.32	0.00	161.43	69.18	0.00	1252.93	1256.62
CH_3Cl	18.68	13.31	6.09	47.92	7.93	78.07	78.31
CH_2Cl_2	67.63	41.33	11.45	14.89	7.50	127.80	138.90
$CHCl_3$	166.54	47.00	19.05	21.93	0.59	253.93	257.96
CCl_4	264.89	0.00	22.48	34.91	0.00	322.28	322.20
CF_3Cl	885.53	21.75	162.36	48.91	0.14	1118.41	1122.14
CF_2Cl_2	651.73	13.26	114.33	39.53	0.13	818.72	807.80
$CFCl_3$	455.03	1.87	57.75	36.01	0.09	550.57	554.11
CH_3CH_3	1.93	3.95	7.68	192.38	0.00	205.94	202.60
C_2H_4O	37.37	2.70	46.41	100.08	11.83	174.73	173.84
C_3H_6	0.21	11.75	1.11	111.80	0.00	124.87	122.50
CH_3CN	4.01	0.58	26.20	32.39	23.49	39.69	39.45
CH_3CCH	28.44	10.69	123.38	59.18	0.88	220.81	207.80
CH_2CH_2	1.47	12.88	8.46	108.39	0.00	131.20	129.43
CH_2CF_2	250.71	85.19	85.17	184.18	2.45	602.80	611.50
COH_2	85.63	29.15	57.39	122.56	33.00	261.73	264.17
COF_2	558.15	115.34	126.93	52.28	1.33	851.37	851.70
$COCl_2$	376.22	140.61	79.78	46.66	1.17	642.10	641.40
cis-$C_2H_2Cl_2$	16.13	85.72	9.36	72.54	3.91	179.84	180.30
CO	12.66	30.52	9.50	22.91	0.12	75.47	61.2
CO_2	280.35	175.71	105.04	65.96	0.00	627.06	628.00
CS_2	115.26	356.84	21.59	66.84	0.00	560.53	561.71
OCS	175.52	272.48	68.26	96.75	0.52	612.49	624.90
HCN	0.41	7.61	162.28	7.43	66.27	111.46	111.00
HCCH	19.68	0.04	234.45	0.47	0.00	254.64	255.64
NCCN	7.25	14.66	6.22	12.57	0.00	40.70	40.83

[a] Exact agreement does not occur between the entries in these columns, since the next-to-last column contains results obtained using $\bar{p}_\alpha$ and β_α^2 values obtained from isotopomers, whereas the intensity sum is a simple average of the isotopomer sums.

The fluorochloromethanes and fluorine-rich fluoromethanes have low anisotropic contributions but very high mean derivative ones. The largest mean derivative contribution (1183.8 km mol^{-1} for CF_4) is almost 3 times larger than the largest anisotropic contribution (423.6 km mol^{-1} for CS_2). Most of the molecules not mentioned above have relatively small contributions from both sources, <200 km mol^{-1}.

Discussion

Some years ago, Bader and collaborators[11] proposed that infrared gas-phase fundamental intensities can be quantitatively calculated using an atoms-in-molecules charge/charge flux/dipole flux decomposition. Here, this dipole derivative decomposition is applied to the polar tensor invariants, $\bar{p}_\alpha$ and β_α^2. Diagonal polar tensor elements can be partitioned into charge, weighted charge flux, and dipole flux terms

$$p_{xx}^{(\alpha)} = \frac{\partial p_x}{\partial x_\alpha} = q_\alpha + \sum_i x_i \frac{\partial q_i}{\partial x_\alpha} + \sum_i \frac{\partial m_{i,x}}{\partial x_\alpha} \qquad (11)$$

whereas off-diagonal ones have contributions from only the last two terms.

$$p_{yx}^{(\alpha)} = \frac{\partial p_y}{\partial x_\alpha} = \sum y_i \frac{\partial q_i}{\partial x_\alpha} + \sum_i \frac{\partial m_{i,y}}{\partial x_\alpha} \qquad (12)$$

These expressions can be substituted into eqs 8 and 9 to obtain charge/charge flux/dipole flux contributions to the atomic mean dipole moment derivatives and anisotropies. In this way, these invariant quantities and their contributions to the experimental intensity sums can be understood at a more fundamental level.

In this work, one of our objectives is to understand why some molecules have large anisotropic contributions to their intensity sums. For this reason, our study treats some of the simpler molecules contained in Table 4 and Figure 3. Linear molecules with both large and low anisotropic contributions were chosen, CS_2, OCS, CO_2, CO, HCN, C_2H_2, and C_2N_2. Furthermore, charge, charge flux, and dipole flux interpretations of atomic mean dipole moment derivatives were also made in order to understand why these derivatives seem to vary with the electronegativities of substituent atoms.[10]

The atomic mean dipole moment derivative has been demonstrated to have the mathematical properties expected of an atomic charge and sometimes is called the GAPT (generalized atomic polar tensor) charge.[5] The charge/charge flux/dipole flux model interpretation attributes three contributions

$$\bar{p}_\alpha = q_\alpha + \frac{1}{3}\sum_r\left(\sum_i r_i \frac{\partial q_i}{\partial r_\alpha}\right) + \frac{1}{3}\sum_r\left(\sum_i \frac{\partial m_{i,r}}{\partial r_\alpha}\right) \qquad (13)$$

to the mean derivative. The first term represents the contribution from the atomic charge of the displaced atom, q_α. The second one is a sum over all atoms in the molecule, i, and for all directions, $r = x$, y, and z, of weighted charge fluxes, $r_i(\partial q_i/\partial r_\alpha)$. The last term is a sum over all the atomic dipole fluxes in the molecule along x, y, and z, $\partial m_{i,r}/\partial r_\alpha$, where $m_{i,r}$ represents the dipole of the ith atom provoked along the rth Cartesian axis when the αth atom is displaced in that direction. For the atomic mean dipole derivative to be the same as the atomic charge, the weighted charge flux and dipole flux contributions must be negligible or cancel one another.

The charge/charge flux/dipole flux decomposition provides a more complex interpretation of the atomic anisotropy, partitioning it into weighted charge flux, dipole flux, and weighted charge flux−dipole flux interaction contributions

$$\begin{aligned}\beta_\alpha^2 = {} & \sum_r\left(\sum_i r_i \frac{\partial q_i}{\partial r_\alpha}\right)^2 - \frac{1}{2}\sum_r\sum_{r'}\left(\sum_i r_i \frac{\partial q_i}{\partial r_\alpha}\right)\left(\sum_i r_i' \frac{\partial q_i}{\partial r_\alpha'}\right) - \\ & \frac{3}{2}\sum_r\sum_{r'}\left(\sum_i r_i \frac{\partial q_i}{\partial r_\alpha'}\right)^2 + \sum_r\left(\sum_i \frac{\partial m_{i,r}}{\partial r_\alpha}\right)^2 - \\ & \frac{1}{2}\sum_r\sum_{r'}\left(\sum_i \frac{\partial m_{i,r}}{\partial r_\alpha}\right)\left(\sum_i \frac{\partial m_{i,r'}}{\partial r_\alpha'}\right) + \frac{3}{2}\sum_r\sum_{r'}\left(\sum_i \frac{\partial m_{i,r}}{\partial r_\alpha'}\right)^2 + \\ & 2\sum_r\left(\sum_i r_i \frac{\partial q_i}{\partial r_\alpha}\right)\left(\sum_i \frac{\partial m_{i,r}}{\partial r_\alpha}\right) - \frac{1}{2}\sum_r\sum_{r'}\left(\sum_i r_i \frac{\partial q_i}{\partial r_\alpha}\right)\left(\sum_i \frac{\partial m_{i,r'}}{\partial r_\alpha'}\right) + \\ & 3\sum_r\sum_{r'}\left(\sum_i r_i \frac{\partial q_i}{\partial r_\alpha'}\right)\left(\sum_i \frac{\partial m_{i,r}}{\partial r_\alpha'}\right)\end{aligned} \qquad (14)$$

where the indexes r and r', representing Cartesian coordinates, are always different. This equation shows that each of the above contributions can be further subdivided into three contributions depending on the directions of the fluxes involved and the geometrical weightings.

The first three terms represent weighted charge flux contributions involving: (1) the sum of squares of atomic charge fluxes weighted by their associated Cartesian atomic coordinates of the same direction as the flux, (2) the sum of products of charge fluxes in perpendicular directions each weighted by its associated Cartesian coordinate in the flux direction, and (3) the sum of squares of atomic charge fluxes weighted by atomic Cartesian coordinates of directions perpendicular to the charge flux. For

TABLE 5: Charge/Charge Flux/Dipole Flux Contributions to the Atomic Mean Dipole Moment Derivatives and Anisotropies

		mean dipole moment derivative (e)				anisotropy (e^2)			
		charge	weighted charge flux	dipole flux	total	weighted charge flux	dipole flux	flux interaction	total
CO	C	1.101	−0.519	−0.444	0.138	2.428	4.473	−6.591	0.310
	O	−1.101	0.519	0.444	−0.138	2.428	4.473	−6.591	0.310
CO_2	C	2.137	−0.935	−0.124	1.078	7.873	21.604	−26.084	3.393
	O	−1.068	0.466	0.061	−0.542	1.952	5.410	−6.499	0.863
CS_2	C	−1.096	2.840	−1.074	0.670	72.617	33.745	−99.004	7.358
	S	0.548	−1.423	0.536	−0.339	18.221	8.422	−24.775	1.868
OCS	C	0.524	0.930	−0.582	0.872	7.792	0.136	−2.060	5.868
	O	−1.018	0.239	0.188	−0.590	0.515	4.805	−3.148	2.172
	S	0.494	−1.162	0.388	−0.280	12.152	6.579	−17.883	0.848
HCN	H	0.169	0.311	−0.220	0.260	0.872	0.861	−1.733	0.000
	C	0.799	−1.446	0.543	−0.104	18.832	15.054	−33.675	0.211
	N	−0.968	1.135	−0.324	−0.157	11.599	8.756	−20.155	0.200
C_2H_2	C	−0.121	−0.310	0.214	−0.217	0.865	0.835	−1.700	0.000
	H	0.121	0.310	−0.214	0.217	0.865	0.835	−1.700	0.000
C_2N_2	C	0.836	−1.155	0.429	0.110	12.007	9.072	−20.874	0.205
	N	−0.836	1.155	−0.429	−0.110	12.007	9.072	−20.874	0.205

the linear molecules treated here, placed along a Cartesian axis, only the first has nonzero contributions to the atomic anisotropy. This occurs because linear molecules only exhibit charge fluxes along their molecular axes.

The contributions involving only atomic dipole fluxes are (1) a sum of squares of dipole fluxes in the same direction as the atomic displacement, (2) a sum of products of these dipole fluxes where the factors correspond to perpendicular atomic displacements, and (3) a sum of squares of dipole fluxes provoked in directions perpendicular to the atomic displacement. This last contribution is zero by symmetry arguments for linear molecules oriented along Cartesian axes.

The weighted charge flux−dipole flux interactions consist of three terms: (1) sums of products of parallel charge and dipole fluxes provoked by atomic displacements in the flux direction, (2) sums of products of perpendicular weighted charge and unweighted dipole fluxes each provoked by atomic displacements in their respective flux directions, and (3) sums of products of charge flux weighted by coordinates perpendicular to the direction of atomic displacement and atomic dipole fluxes provoked perpendicularly to the atomic displacement. This last term is zero for linear molecules oriented along a Cartesian axis, since they have zero $r_i(\partial q_i/\partial r'_\alpha)$ and $\partial m_{i,r}/\partial r'_\alpha$ fluxes.

Table 5 contains values of charge, weighted charge flux, and dipole flux contributions to the mean dipole moment derivative and weighted charge flux, dipole flux, and weighted charge flux−dipole flux interaction contributions to the atomic anisotropy. These contributions were calculated using atoms-in-molecules (AIM) atomic charges and dipoles obtained by applying the formalism proposed by Bader.[31,32]

A measure of the numerical accuracy of the charge/charge flux/dipole flux decomposition in determining the atomic anisotropies can be obtained upon comparing the values in the last column of Table 5 with the corresponding MP2/6-311++G(3d,3p) anisotropies calculated directly from the molecular wave function and given in the second-to-last columns of Tables 1−3. A root-mean-square (rms) error of 0.024e^2 is quite small, considering the anisotropy values vary from 0.000 to 7.358e^2. A similar error analysis for the mean dipole moment derivatives results in a 0.006e rms error upon comparing them to mean derivatives calculated from AIM parameters (fourth numerical column in Table 5) with values obtained directly from the molecular wave functions (second-to-last numerical column in Table 1 of ref 10). A larger rms error is found upon comparing the anisotropy values calculated using the AIM parameters with the experimental anisotropy values, 0.311e^2. This shows that the lack of agreement here is caused by limitations in the wave functions used in our calculations. Thus, the use of higher quality wave functions can be expected to improve the agreement between experimental and charge/charge flux/dipole flux results for both atomic mean dipole moment derivatives and anisotropies. However, considering that this rms error is only 4.2% of the calculated anisotropy range of values in Table 5, this agreement is satisfactory.

Inspection of the values in the first four numerical columns of this table leads to a charge/charge flux/dipole flux interpretation of the mean dipole moment derivative. Weighted charge flux and dipole flux contributions are large, and at least one of these is opposite in sign to the AIM atomic charge. As such, the magnitudes of the mean dipole moment derivatives are usually smaller than those of the atomic charge. The weighted charge flux is of opposite sign to the atomic charge in all cases but four in the table, the carbon atom of OCS, the hydrogen atom of HCN, and both the carbon and hydrogen atoms of C_2H_2. The magnitudes of the dipole fluxes are always smaller than those of their corresponding charge fluxes, although they are still appreciable.

Mean dipole moment contributions to the intensity sums seem to reflect electronegativity differences in the CO_2, OCS, and CS_2 molecules, as can be seen in Figure 3 and Table 4. The carbon mean dipole moment derivative contributions to the intensity sums, 280.35, 175.52, and 115.26 km mol^{-1}, are proportional to the squares of the $\bar{p}_C$ values in Table 5, 1.078, 0.872, and 0.670e, respectively. However, these are not proportional to the squares of the AIM carbon charges of 4.567e^2 for CO_2, 0.275e^2 for OCS, and 1.201e^2 for CS_2. Coincidently, these carbon intensity sum contributions have the same ordering as the AIM carbon charges, $q_C(CO_2) = 2.137e > q_C(OCS) = 0.524e > q_C(CS_2) = -1.096e$.

The order of the terminal atom mean dipole moment derivative contributions, 105.04 km mol^{-1} for CO_2, 68.26 km mol^{-1} for OCS, and 21.59 km mol^{-1} for CS_2, is the same as the sum of squares of either the terminal atom mean dipole moment derivatives or the AIM atomic charges. The oxygen and sulfur mean derivatives are about −0.55 and −0.30e, whereas the AIM atomic charges are around −1.05 and +0.52e. It is interesting that the carbon and sulfur mean derivatives and atomic charges in CS_2 have opposite signs, carbon having a negative AIM charge but a positive mean derivative and sulfur having a positive AIM charge but a negative mean derivative.

The C_2H_2 and C_2N_2 molecules also provide an interesting comparison. The electronegativity difference between carbon and nitrogen is larger than the one between carbon and hydrogen. However, the mean dipole moment derivative contribution from all atoms to the intensity sum is much larger for C_2H_2, 254.13 km mol^{-1}, compared with 13.47 km mol^{-1} for C_2N_2. The carbon mean dipole moment derivative intensity sum contribution is 19.68 km mol^{-1} for C_2H_2 and only 7.25 km mol^{-1} for C_2N_2, in agreement with their calculated carbon mean derivative values of -0.217 and $+0.110e$, respectively. However, the carbon AIM charge in C_2N_2 is much larger, $0.836e$, than it is in C_2H_2, $-0.121e$.

Figure 3 and the data in Table 4 clearly show mean derivative contributions decreasing as the sum of the electronegativities of the substituent atoms decreases in the fluorochloromethanes. Since these molecules have only single carbon−halogen bonds, they provide an interesting family of molecules for studying the importance of charge/charge flux/dipole flux contributions to the mean dipole moment derivatives.

As mentioned in the Results section, anisotropic contributions to the intensity sums of CO_2, OCS, and CS_2 are very large compared with those for HCN, C_2H_2, and C_2N_2. For CS_2, the total anisotropic contribution to the intensity sum is 423.68 km mol^{-1} compared with only 136.85 km mol^{-1} for the mean dipole moment derivative contribution. This contrasts with data for most of the substituted methanes for which the mean derivative contributions are far more important. Methane and methyl chloride are the notable exceptions, as might be expected. Therefore, it is worthwhile examining the data in Table 5 to understand why the CO_2, OCS, and CS_2 anisotropic contributions are so large and those for HCN, C_2H_2, and C_2N_2 are so small.

Large positive anisotropic contributions for all the atoms in these molecules can be observed for the weighted charge flux and dipole flux contributions in contrast to the large negative weighted charge flux−dipole flux cross-terms. Although these terms partially cancel each other out, relatively large atomic anisotropic values do result, especially for the carbon and sulfur atoms, as shown in Table 5.

Relatively small weighted charge flux, dipole flux, and weighted charge flux−dipole flux interaction contributions are found for the H atoms in HCN and C_2H_2. These contributions cancel each other out, resulting in null hydrogen atomic anisotropies for these molecules. The carbon and nitrogen atoms have large weighted charge flux, dipole flux, and weighted charge flux−dipole flux interaction contributions for the HCN and C_2N_2 molecules. Just as for the CO_2, OCS, and CS_2 molecules, all the weighted charge flux and dipole flux contributions are positive for HCN, C_2H_2, and C_2N_2, whereas the weighted charge flux−dipole flux interaction contributions are negative. These contributions almost exactly cancel each other out, resulting in very small anisotropic contributions to the intensity sums.

Further investigation of the various contributions to the mean dipole moment derivative and anisotropic intensity sums are being carried out in our laboratory using AIM atomic charges and dipoles and their fluxes for the rest of the molecules given in the tables and figures of this paper. This should provide further understanding of the electronic factors contributing to the infrared fundamental intensities of molecules in the gas phase.

Conclusion

The comparison between experimental anisotropy data, resulting from the fundamental infrared intensities, and their calculated estimates for carbon, hydrogen, fluorine, chlorine, nitrogen, oxygen, and sulfur atoms in 30 molecules shows that these quantities are, like the mean dipole moment derivatives, highly dependent on the electron correlation level employed in the calculations. MP2 and B3LYP results are almost always in better agreement with the experimental values than those of the Hartree−Fock method. On the other hand, the anisotropy results appear to be insensitive to the two basis sets employed in these calculations, 6-31+G(d,p) and 6-311++G(3d,3p).

Carbon atoms participating in double bonds with oxygen and sulfur, CO_2, CS_2, OCS, COF_2, and $COCl_2$, present the highest anisotropy values, indicating that the dipole moment derivatives for the stretching modes of these bonds are very different than the derivatives from the perpendicular modes. On the other hand, carbon atoms participating in single and triple bonds of the molecules studied here usually have lower anisotropic contributions. Hydrogen atoms always show the lowest anisotropies which might be due to their unit nuclear charge and, consequently, their low electronegativities.

Moreover, the electronic source of the highly anisotropic CO_2, CS_2, and OCS data, according to a charge/charge flux/dipole flux decomposition of the dipole moment derivatives using the AIM formalism, is a partial canceling of large positively weighted charge flux and dipole flux contributions with large negatively weighted charge flux−dipole flux cross-contributions. For the HCN, C_2H_2, and C_2N_2 molecules with low atomic anisotropic contributions to the infrared intensities, this cancellation is almost perfect.

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