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Atomic Mean Dipole Moment Derivatives and GAPT Charges

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Mean dipole moment derivatives determined from gas-phase infrared fundamental intensity data for 30 molecules are compared with Generalized Atomic Polar Tensor (GAPT) charges calculated from wave functions obtained with 6-31G(d,p) and 6-311++G(3d,3p) basis sets at the Hartree−Fock, B3LYP density functional, and MP2 electron correlation levels. With very few exceptions, the MP2 results are in better agreement with the experimental values than are the B3LYP results calculated with the same basis set, although the differences between these calculated results are often small. The Hartree−Fock results deviate most from the experimental values. For all atoms studied here, C, H, F, Cl, N, O, and S, the MP2/6-311++G(3d,3p) results agree most closely with the experimental values with rms errors of 0.059, 0.013, 0.044, 0.045, 0.030, 0.041, and 0.014e respectively. Although the calculated results for charges between −0.5 and +0.5e seem to deviate randomly from the experimental results, calculated charges ranging from +0.5 to +2.0e tend to be slightly larger than the experimental values. This is a consequence of the fact that the MP2/6-311++G(3d,3p) calculations tend to overestimate infrared intensity sums for molecules with more polar bonds and intensity sums above 500 km mol^{-1}. The results reported here show that the calculated charge values seem to be converging to the experimental values as the basis set becomes more extensive, 6-31G(d,p) to 6-311++G(3d,3p), and as the electron correlation level becomes more complex, Hartree−Fock to B3LYP density functional to MP2. Experimental mean dipole moment derivative values are shown to be consistent with trends in atomic charge values expected from chemical arguments for the halomethanes, hydrocarbons and Group IV hydrides.

1. Introduction

It has long been a goal among chemists to reduce the information in the electronic densities of molecules to conceptually simple parameters allowing modeling applications to predict chemical reactivities. As a result, a large number of methods[1−35] have been proposed for calculating atomic charges from molecular wave functions. Many of these methods have been tested using a variety of basis sets at different levels of electron correlation treatment, and recently, density functional approaches have also been emphasized. However, conclusions about the reliability of specific calculational levels in assigning adequate charge values for atoms is difficult since no direct comparison between theoretically calculated and experimentally measured quantities has been made.

Recent theoretical investigations[36−42] have focused on obtaining atomic charges, called Generalized Atomic Polar Tensor (GAPT) charges, from mean dipole moment derivatives calculated from molecular wave functions. These quantities have been shown to satisfy the necessary fundamental conditions required of atomic charges, invariance with respect to molecular translations and rotations and summation to provide the net total charge of the molecule. Contrary to Mulliken-type charges, the GAPT charges are not directly related to the basis set chosen for the wave function calculation involved in their determinations. As a result, calculated GAPT charges are much less sensitive to basis set variations than are Mulliken charges.[36−42] Another advantage of this charge relative to others proposed until now is that it can be determined experimentally by measuring infrared fundamental intensities. In fact, infrared spectroscopists, in their attempts at describing molecular electronic density distributions, have been evaluating atomic polar tensors for some time,[43] providing a database that can be used for comparison with results obtained from quantum chemical calculations.

On the other hand, GAPT charges have been reported to be sensitive to the level of electron correlation treatment[41] especially for molecules with multiple bonds.[36] Density functional theory methods employing hybrid functionals, such as B3LYP, as well as Möller−Plesset 2 perturbation methods have been shown to reproduce electron correlation effects on atomic charges.[41] Furthermore, B3LYP/6-311++G(3df,3pd) and MP2/6-311++G(3df,3pd) intensity results have been shown to be in excellent agreement with those calculated using QCISD/6-311+G(3df,3pd).[44] These QCISD/6-311+G(3df,3pd) results are also in excellent agreement with CCSD(T)/TZ(2df,2pd) calculated intensities,[45] although both sets of results show large discrepancies upon comparison with experimental intensities. This is a cause of concern for several reasons. Intensity measurement errors can be large and thus prejudice comparison with theoretical values. Furthermore, accurate separation of the component intensities of overlapped bands is difficult and usually involves assumptions about band symmetry. Finally, quantum chemical intensities are calculated assuming harmonic vibrations and linear changes in dipole moments during vibrations, whereas the experimental intensities can be affected by dramatic anharmonic effects such as Fermi resonance.

The principal objective of this work is to compare results from experimental measurements, normally designated as mean dipole moment derivatives in the literature, with their corresponding quantities obtained from quantum chemical calculations, the GAPT charges. Convergence properties of the calculated charges, q_α^{GAPT}, to experimentally determined val-

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ues, $\bar{p}_\alpha$, will be investigated not only with respect to basis set changes but also to the electron correlation treatment level used in their determinations.

This study involves 30 molecules for which complete infrared fundamental intensity data are available in the gas phase. The atomic polar tensors (APT) of these molecules result in 34 carbon, 19 hydrogen, 9 fluorine, 9 chlorine, 3 nitrogen, 7 oxygen and 2 sulfur charges. The data set is more extensive than those of refs 41, 44, and 45. Some of the molecules, such as the hydrocarbons, have slightly polar bonds, whereas others, as in the fluorochloromethanes, have very polar bonds. Molecules having single, double, and triple bonds are included. This molecular variety is expected to result in very different mean dipole moment derivative values. As such, the variance in the derivative values is expected to be much larger than the one due to experimental errors in the intensities, hopefully permitting an examination of their values for their consistency with established concepts usually correlated with atomic charges, such as electronegativity, hybridization, and polarization effects. It should be remembered that a majority of the mean dipole moment derivatives studied here are averages of derivatives calculated from intensity values of isotopomers and are expected to be more precise than values obtained from the intensities of a single molecule. For this reason, comparison of experimental and theoretical mean derivatives can be more informative than comparison of individual infrared intensities.

2. 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:

$$A_i = \frac{N_A \pi}{3c^2}\left(\frac{\partial \vec{\mathrm{p}}}{\partial \mathrm{Q}_\mathrm{i}}\right)^2 \qquad (1)$$

N_A and c being Avogadro's number and the velocity of light, respectively.[46] The dipole moment derivatives can be transformed to atomic Cartesian coordinates using the expression[47,48]

$$\mathbf{P}_x = \mathbf{P}_Q \mathbf{L}^{-1}\mathbf{U}\mathbf{B} + \mathbf{P}_\rho \beta \qquad (2)$$

where $\mathbf{P}_Q$ is a $3 \times (3N - 6)$ matrix of the dipole moment derivatives obtained from the measured infrared intensities and $\mathbf{L}^{-1}$, $\mathbf{U}$, and $\mathbf{B}$ are well-known transformation matrixes commonly used in normal cooordinate analysis.[49] The $\mathbf{P}_\rho\beta$ product provides the rotational contributions to the polar tensor elements. As such, the polar tensor elements contained in $\mathbf{P}_x$ are obtained using the molecular geometry (the $\mathbf{B}$ and β matrixes), symmetry (the $\mathbf{U}$ matrix), vibrational frequencies and atomic masses (the normal coordinate $\mathbf{L}^{-1}$matrix), and permanent dipole moment values, as well as the experimentally measured infrared intensities.

The molecular polar tensor, $\mathbf{P}_x$, is a juxtaposition of APTs:

$$\mathbf{P}_x = \{\mathbf{P}_x^{(1)}\mathbf{P}_x^{(2)} \ldots \mathbf{P}_x^{(N)}\} \qquad (3)$$

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

$$\mathbf{P}^{(\alpha)}{}_X = \begin{pmatrix} \partial p_x/\partial x_\alpha & \partial p_x/\partial y_\alpha & \partial p_x/\partial z_\alpha \\ \partial p_y/\partial x_\alpha & \partial p_y/\partial y_\alpha & \partial p_y/\partial z_\alpha \\ \partial p_z/\partial x_\alpha & \partial p_z/\partial y_\alpha & \partial p_z/\partial z_\alpha \end{pmatrix} = \begin{pmatrix} p_{xx} & p_{xy} & p_{xz} \\ p_{yx} & p_{yy} & p_{yz} \\ p_{zx} & p_{zy} & p_{zz} \end{pmatrix} \qquad (4)$$

The mean dipole moment derivative of atom α, $\bar{p}_\alpha$, is simply one-third the trace of this matrix:[50]

$$\bar{p}_\alpha = 1/3(\partial p_x/\partial x_\alpha + \partial p_y/\partial y_\alpha + \partial p_z/\partial z_\alpha) \qquad (5)$$

The mean dipole moment derivatives studied in this work have been reported previously in the literature[50−65] and were calculated using the above equations. The GAPT charges[36] are also calculated using eq 5, where diagonal polar tensor elements from quantum chemical calculations are used instead of those derived from experimental intensities.

Two other APT invariants are frequently investigated in infrared intensity studies. The square of the atomic effective charge, $\chi_\alpha{}^2$, is 1/3 the trace of the matrix product of the APT by its transpose

$$\chi_\alpha^2 = 1/3\mathrm{Tr}(\mathrm{P}_x^{(\alpha)}\mathrm{P}_x^{(\alpha)\prime}) \qquad (6)$$

This is simply equal to 1/3 the sum of squares of the APT elements. This invariant can be directly related to the fundamental intensity sum of a molecule. The atomic anisotropy

$$\beta_\alpha^2 = 1/2[(p_{xx} - p_{yy})^2 + (p_{yy} - p_{zz})^2 + (p_{zz} - p_{xx})^2 + 3(p_{xy}^2 + p_{yz}^2 + p_{xz}^2 + p_{zx}^2 + p_{yx}^2 + p_{zy}^2)] \qquad (7)$$

has values that reflect molecular symmetry and can be related to $\bar{p}_\alpha$ and χ_α.

Theoretical calculations for the GAPT charges were performed using the Gaussian 94[66] and GAMESS−US[67] programs on IBM RISC 6000 and DEC ALPHA workstations. Theoretical equilibrium geometries were used to calculate all GAPT charges. Calculations were carried out at the HF/6-31+G(d,p), B3LYP/6-31+G(d,p), MP2/6-31+G(d,p), HF/6-311++G(3d,3p), B3LYP/6-311++G(3d,3p), and MP2/6-311++G(3d,3p) levels.

3. Results

Table 1 contains the results of GAPT charge calculations, q_α^{GAPT}, using 6-31+G(d,p) and 6-311++G(3d,3p) basis sets at the Hartree−Fock and Möller−Plesset 2 and B3LYP density functional levels for molecules containing carbon, hydrogen, fluorine, chlorine, nitrogen, oxygen, and sulfur atoms. Included in this table are values of mean dipole moment derivatives determined from infrared fundamental intensity measurements, root-mean-square (rms) errors for each combination of electron correlation treatment, and basis set levels for each of the atoms investigated.

Independent of the level used to treat electron correlation, the 6-311++G(3d,3p) results have smaller rms errors than those for the corresponding 6-31+G(d,p) calculations for all atoms except nitrogen, for which the B3LYP results are closer to the experimental values for the calculations with the smaller basis set. It should be noted, however, that only three nitrogen atoms have been included in our study. As expected for either basis set, the B3LYP and MP2 level calculations result in much more accurate estimates of the mean dipole moment derivatives than do those at the Hartree−Fock level for all the atoms tested. The MP2 results are found to be more accurate than those of the B3LYP calculations for all atoms when the 6-311++G(3d,3p) basis is used, although for some atoms the difference is not large. For example, the rms error for the B3LYP results of the fluorine atoms, 0.045e, is just slightly larger than the one for the MP2 results with a 0.044e error. This ordering does

TABLE 1: Comparation of Calculated and Experimental Mean Dipole Moment Derivatives (*e*)[a]

	6-31+G(d,p)			6-311++G(3d,3p)				
carbon	HF	B3LYP	MP2	HF	B3LYP	MP2	exp	refs
CH_4	0.061	−0.024	−0.010	0.073	0.007	0.002	0.016	51
CH_3F	0.709	0.592	0.598	0.554	0.554	0.550	0.541	50,52,53
CH_2F_2	1.301	1.167	1.172	1.219	1.090	1.089	1.014	54,55
CHF_3	1.807	1.666	1.675	1.719	1.580	1.584	1.523	54,56
CF_4	2.247	2.120	2.122	2.170	2.039	2.040	2.049	57
CH_3Cl	0.421	0.317	0.315	0.381	0.285	0.278	0.277	54,58
CH_2Cl_2	0.757	0.695	0.652	0.685	0.618	0.585	0.527	54
$CHCl_3$	1.051	1.074	0.980	0.964	0.966	0.898	0.827	54,59
CCl_4	1.301	1.435	1.294	1.206	1.301	1.194	1.043	60
CF_3Cl	2.098	1.993	1.970	1.989	1.878	1.863	1.907	54,61
CF_2Cl_2	1.893	1.837	1.781	1.771	1.705	1.668	1.636	54
$CFCl_3$	1.623	1.648	1.552	1.507	1.511	1.445	1.367	54
CH_3CH_3	0.141	0.095	0.087	0.136	0.092	0.079	0.063	54
C_2H_4O	0.373	0.311	0.286	0.354	0.293	0.265	0.277	54
C_3H_6	0.040	0.014	0.005	0.040	0.017	0.003	0.017	54
$C{*}H_3CN$	0.190	0.094	0.126	0.178	0.093	0.108	0.110	62
$C{*}H_3CCH$	0.215	0.125	0.146	0.201	0.120	0.125	0.104	54,63
CH_2CH_2	−0.074	−0.070	−0.074	−0.070	−0.066	−0.069	−0.055	54
$C{*}H_2CF_2$	−0.394	−0.356	−0.340	−0.362	−0.335	−0.323	−0.274	54
$CH_2C{*}F_2$	1.358	1.214	1.181	1.295	1.167	1.143	0.977	54
COH_2	0.796	0.689	0.606	0.768	0.675	0.596	0.593	54
COF_2	1.917	1.683	1.656	1.846	1.632	1.606	1.514	64
$COCl_2$	1.615	1.486	1.426	1.532	1.404	1.363	1.243	64
cis-$C_2H_2Cl_2$	0.219	0.194	0.176	0.210	0.181	0.169	0.182	54
CO	0.384	0.257	0.144	0.355	0.238	0.136	0.228	54
CO_2	1.572	1.168	1.069	1.538	1.175	1.075	1.073	54
CS_2	1.289	0.769	0.647	1.260	0.763	0.668	0.688	54
OCS	1.396	0.985	0.882	1.338	0.964	0.873	0.849	54
HCN	−0.022	−0.084	−0.130	0.014	−0.053	−0.097	−0.041	54
HCCH	−0.242	−0.226	−0.223	−0.226	−0.214	−0.209	−0.201	54,63,65
NCCN	0.225	0.175	0.095	0.182	0.182	0.109	0.122	54
$CH_3C{*}N$	0.117	0.101	−0.010	0.155	0.122	0.025	0.066	62
$CH_3C{*}CH$	−0.045	0.010	−0.050	−0.038	0.005	−0.043	−0.074	54,63
$CH_3CC{*}H$	−0.402	−0.390	−0.339	−0.373	−0.358	−0.313	−0.317	54,63
rms error[b]	0.2477	0.1373	0.1013	0.2031	0.0878	0.0593		
hydrogen	HF	B3LYP	MP2	HF	B3LYP	MP2	exp	refs
CH_4	−0.015	0.006	0.002	−0.018	−0.002	0.000	−0.004	51
CH_3F	−0.053	−0.023	−0.024	−0.017	−0.017	−0.016	−0.017	50,52,53
CH_2F_2	−0.046	−0.036	−0.038	−0.033	−0.023	−0.023	−0.018	54,55
CHF_3	−0.032	−0.025	−0.028	−0.020	−0.012	−0.013	0.004	54,56
CH_3Cl	−0.017	−0.006	−0.012	−0.010	0.000	−0.001	−0.002	54,58
CH_2Cl_2	−0.028	−0.019	−0.027	−0.014	−0.006	−0.008	−0.015	54
$CHCl_3$	−0.045	−0.038	−0.046	−0.033	−0.026	−0.029	−0.022	54,59
CH_3CH_3	−0.047	−0.032	−0.029	−0.045	−0.031	−0.026	−0.021	54
C_2H_4O	−0.022	−0.016	−0.010	−0.018	−0.012	−0.005	−0.018	54
C_3H_6	−0.020	−0.007	−0.002	−0.02	−0.008	−0.001	−0.008	54
CH_3CN	0.030	0.041	0.036	0.026	0.038	0.035	0.034	62
$CH{*}_3CCH$	−0.005	0.006	0.004	−0.005	0.006	0.007	0.029	54,63
$CH_3CCH{*}$	0.249	0.237	0.230	0.226	0.214	0.208	0.200	54
CH_2CH_2	0.037	0.035	0.037	0.035	0.033	0.034	0.027	54
CH_2CF_2	0.100	0.099	0.102	0.091	0.093	0.093	0.072	54
COH_2	−0.044	−0.054	−0.053	−0.034	−0.048	−0.044	−0.040	54
cis-$C_2H_2Cl_2$	0.050	0.052	0.051	0.046	0.048	0.048	0.021	54
HCN	0.293	0.277	0.275	0.270	0.256	0.255	0.231	54
HCCH	0.242	0.226	0.223	0.226	0.214	0.209	0.201	54,63,65
rms error[b]	0.0291	0.0210	0.0212	0.0192	0.0132	0.0128		
fluorine	HF	B3LYP	MP2	HF	B3LYP	MP2	exp	refs
CH_3F	−0.548	−0.524	−0.527	−0.503	−0.503	−0.501	−0.490	50,52,53
CH_2F_2	−0.605	−0.547	−0.548	−0.577	−0.522	−0.522	−0.488	54,55
CHF_3	−0.592	−0.547	−0.549	−0.566	−0.523	−0.524	−0.506	54,56
CF_4	−0.562	−0.530	−0.531	−0.542	−0.510	−0.510	−0.512	57
CF_3Cl	−0.609	−0.572	−0.572	−0.577	−0.540	−0.539	−0.590	54,61
CF_2Cl_2	−0.638	−0.599	−0.597	−0.594	−0.557	−0.553	−0.585	54
$CFCl_3$	−0.649	−0.612	−0.609	−0.596	−0.563	−0.556	−0.486	54
CH_2CF_2	−0.581	−0.528	−0.522	−0.558	−0.509	−0.503	−0.423	54
COF_2	−0.562	−0.521	−0.540	−0.537	−0.501	−0.516	−0.483	64
rms error[b]	0.0988	0.0628	0.0631	0.0716	0.0454	0.0442		

TABLE 1 (Continued)

chlorine	HF	B3LYP	MP2	HF	B3LYP	MP2	exp	refs
CH_3Cl	−0.369	−0.299	−0.280	−0.350	−0.284	−0.275	−0.271	54,58
CH_2Cl_2	−0.351	−0.328	−0.299	−0.328	−0.303	−0.284	−0.248	54
$CHCl_3$	−0.335	−0.346	−0.311	−0.310	−0.313	−0.289	−0.267	54,59
CCl_4	−0.325	−0.359	−0.323	−0.301	−0.325	−0.298	−0.261	60
CF_3Cl	−0.270	−0.278	−0.254	−0.258	−0.257	−0.246	−0.139	54,61
CF_2Cl_2	−0.308	−0.320	−0.293	−0.292	−0.296	−0.281	−0.233	54
$CFCl_3$	−0.325	−0.345	−0.314	−0.304	−0.316	−0.296	−0.294	54
$COCl_2$	−0.370	−0.379	−0.389	−0.345	−0.351	−0.368	−0.331	64
cis-$C_2H_2Cl_2$	−0.269	−0.246	−0.226	−0.255	−0.229	−0.218	−0.203	54
rms error[b]	0.0807	0.0794	0.0573	0.0639	0.0566	0.0454		

nitrogen	HF	B3LYP	MP2	HF	B3LYP	MP2	exp	refs
CH_3CN	−0.395	−0.319	−0.224	−0.410	−0.327	−0.239	−0.278	62
HCN	−0.272	−0.192	−0.145	−0.284	−0.203	−0.157	−0.189	54
NCCN	−0.225	−0.175	−0.095	−0.182	−0.182	−0.109	−0.122	54
rms error[b]	0.1020	0.0387	0.0431	0.1001	0.0454	0.0301		

oxygen	HF	B3LYP	MP2	HF	B3LYP	MP2	exp	refs
C_2H_4O	−0.656	−0.556	−0.531	−0.635	−0.535	−0.510	−0.483	54
COH_2	−0.708	−0.580	−0.499	−0.701	−0.579	−0.507	−0.513	54
COF_2	−0.793	−0.641	−0.576	−0.772	−0.631	−0.574	−0.549	64
$COCl_2$	−0.876	−0.729	−0.649	−0.841	−0.702	−0.627	−0.581	64
CO	−0.384	−0.257	−0.144	−0.355	−0.238	−0.136	−0.228	54
CO_2	−0.786	−0.584	−0.535	−0.769	−0.588	−0.537	−0.536	54
OCS	−0.891	−0.682	−0.595	−0.868	−0.675	−0.588	−0.581	54
rms error[b]	0.2383	0.0874	0.0464	0.2167	0.0756	0.0414		

sulfur	HF	B3LYP	MP2	HF	B3LYP	MP2	exp	refs
CS_2	−0.645	−0.385	−0.323	−0.630	−0.382	−0.334	−0.344	54
OCS	−0.505	−0.302	−0.287	−0.470	−0.289	−0.285	−0.268	54
rms error[b]	0.2709	0.0377	0.0200	0.2476	0.0307	0.0140		

[a] Unit of electrons, *e*. [b] Root-mean-square error, $\sqrt{\sum_{i=1}^{N}(q_i^{\mathrm{GAPT}}-\bar{p}_i)^2/N}$

not always occur for the smaller basis, for which the errors for the B3LYP level calculations are slightly smaller than the MP2 ones for the hydrogen, fluorine, and nitrogen atoms.

For the most accurate calculations, MP2/6-311++G(3d,3p) and B3LYP/6-311++G(3d,3p), it is of interest to compare error values for the different atoms. The rms errors for the carbon atoms, 0.059 and 0.088*e*, respectively, are much larger than the ones for the hydrogen atoms, 0.013*e* for both kinds of calculations. Probably, this owes to the fact that the carbon atomic charge values vary over a much larger range, −0.317 to +2.049*e*, than do the hydrogen ones, −0.040 to +0.231*e*. For carbon atoms in the hydrocarbon molecules, CH_4, C_2H_6, C_3H_6, and the methyl groups in CH_3CN and CH_3CCH,whose charges vary from +0.016 to 0.110*e*, the rms errors are 0.017 and 0.014*e*, respectively, for the B3LYP and MP2 level calculations. These errors have magnitudes very close to the errors for the hydrogen charges.

Recently, De Proft et al.[41] have reported results of GAPT charge calculations for a group of fifteen molecules. Common to their group of selected molecules and ours are C_2H_2, CH_4, CO, CO_2, H_2CO, and HCN. Their MP2/cc-pVDZ results have a 0.062*e* rms error compared with a 0.039*e* error for the MP2/6-311++G(3d,3p) results. The latter is close to the 0.034*e* error obtained for their QCISD GAPT charges. It is interesting that the B3LYP density functional results are quite accurate for these molecules. The B3LYP/cc-pVDZ and B3LYP /6-311++G(3d,3p) GAPT charges have 0.034*e* and 0.033*e* errors relative to the experimental values.

In Figure 1, the GAPT charges calculated using the MP2/6-311++G(3d,3p) wave functions are plotted against their experimental values. Although the differences between the calculated and experimental values are randomly distributed for the results with charge values between −0.5 and +0.5*e*, there exists a tendency for the calculated values to be larger than the experimental ones for some molecules having GAPT charges in the +0.5 to +2.0*e* range. This is even more clearly appreciated in the graph of the residual values, $q_\alpha^{\mathrm{GAPT}} - \bar{p}_\alpha$, in Figure 2. Although the residuals are randomly distributed for the derivatives with the smaller values, the larger ones show systematic positive deviations from the zero result. Of these, carbon GAPT charges for OCS, COF_2, $CFCl_3$, $COCl_2$, CCl_4, $CH_2C^*F_2$, and $CHCl_3$ exhibit the largest deviations from the lines representing exact agreement.

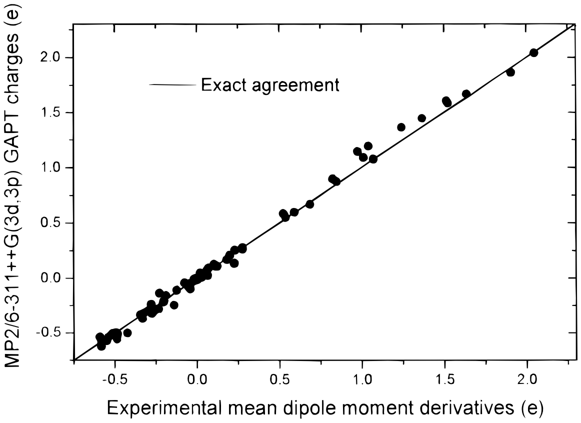

Figure 1. MP2/6-311++G(3d,3p) GAPT charges plotted against experimental mean dipole moment derivatives. Units of electrons, *e*.

The reason for this behavior can be more fully understood by comparing values calculated for the fundamental intensity

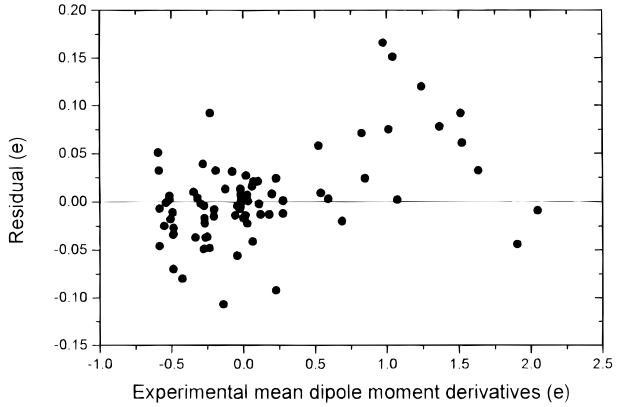

Figure 2. Residuals of calculated and experimental mean dipole moment derivatives plotted against the experimental derivative values. Units of electrons, *e*.

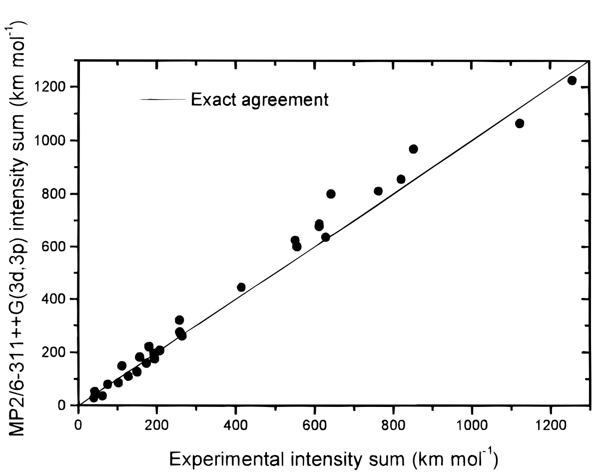

Figure 3. MP2/6-311++G(3d,3p) calculated intensity sums graphed against the experimental sums.

sums of these molecules with those determined experimentally. Crawford's G intensity sum rule[68]

$$\sum A_i - \Omega = \mathrm{K}\sum \chi_\alpha^2/m_\alpha \qquad (8)$$

relates the molecular intensity sum, $\sum A_i$, to a mass-weighted sum of the squared atomic effective charges, χ_α, where Ω is a rotational contribution and m_α represents the atomic masses. The effective charge is given by

$$\chi_\alpha^2 = \bar{p}_\alpha^2 + (2/9)\beta_\alpha^2 \qquad (9)$$

and is predominantly determined by the mean dipole moment derivative. Hence, high mean dipole moment derivative values are expected to be accompanied by high fundamental intensity sums.

Calculated and experimental intensity sum results[55,56,58,59,69−95] are given in Table 2 for the molecules of this study, and a graph of the MP2/6-311++G(3d,3p) sum values against the experimental ones is presented in Figure 3. Molecules with low infrared intensity sums show random displacements from the line representing exact agreement between calculated and experimental values whereas the calculated results for molecules with intensity sums larger than 500 km mol^{-1} tend to lie above this line, the calculated results being systematically larger than the experimental ones. The molecules for which the carbon

TABLE 2: Comparation of Calculated and Experimental Vibrational Intensity Sums (km mol^{-1})

	6-31G(d,p)			6-311++G(3d,3p)				
molecules	HF	B3LYP	MP2	HF	B3LYP	MP2	exp	refs
CH_4	158.0	134.6	109.6	142.2	102.3	85.2	102.2	69−72
CH_3F	297.0	229.5	210.9	210.0	210.0	195.2	193.6	73,74
CH_2F_2	609.6	507.2	498.5	551.4	454.9	444.8	415.0	55,75,76
CHF_3	1028.2	896.2	899.7	936.8	811.3	811.4	761.6	56,77,78
CF_4	1472.0	1322.7	1323.1	1375.6	1226.4	1225.8	1256.6	72,79,80
CH_3Cl	144.8	106.3	98.4	123.7	84.1	78.8	74.9	58,73,81,82
CH_2Cl_2	270.6	250.6	213.6	232.8	207.7	182.2	156.3	76,83
$CHCl_3$	405.1	440.5	362.3	356.3	373.0	320.7	258.0	59,84
CCl_4	469.5	578.2	467.9	408.9	481.8	*a*	322.2	84
CF_3Cl	1328.6	1203.6	1174.6	1207.6	1082.4	1064.2	1122.2	85,86
CF_2Cl_2	1081.4	1022.1	963.0	957.2	892.4	854.5	819.8	76
$CFCl_3$	774.7	802.2	713.6	675.3	682.9	626.0	550.0	87
CH_3CH_3	307.0	247.5	203.7	287.6	214.2	176.0	194.5	88
C_2H_4O	259.1	212.4	171.4	253.8	197.8	158.9	173.8	88
C_3H_6	193.7	466.0	134.6	179.4	140.3	109.8	127.1	88
CH_3CN	61.7	50.4	32.0	61.4	44.4	28.8	39.4	62
CH_3CCH	306.1	280.8	244.4	265.8	238.2	206.6	207.8	88
CH_2CH_2	203.5	173.5	161.2	175.7	145.0	127.2	149.7	88
CH_2CF_2	938.8	774.4	728.7	870.2	721.3	687.4	611.5	89
COH_2	358.2	328.0	252.4	365.9	331.9	261.3	264.7	91
COF_2	1324.0	1060.2	1020.2	1240.7	1002.3	968.2	851.8	88
$COCl_2$	1069.4	938.9	853.9	990.4	856.5	800.8	641.3	88
cis-$C_2H_2Cl_2$	299.4	284.0	248.8	267.9	243.3	221.4	180.3	90
CO	159.6	86.4	35.6	145.0	79.8	35.9	61.2	88
CO_2	1241.2	724.6	617.1	1211.4	739.6	636.4	628.0	92
CS_2	1537.8	669.5	563.6	1574.8	699.8	600.5	555.0	88
OCS	1366.5	769.1	656.8	1349.6	786.0	677.3	611.1	88
HCN	184.8	170.2	177.5	150.8	141.4	149.0	111.0	93
HCCH	369.8	321.3	314.5	321.8	287.4	275.1	259.0	94,95
NCCN	50.4	38.1	45.4	44.2	44.2	52.3	41.4	88
error	311.21	128.28	85.83	285.84	87.34	51.35		

[a] Calculation could not be executed on our workstation.

GAPT charges show the largest deviations from the experimental mean dipole moment derivatives in Figure 1, OCS, COF_2, $CFCl_3$, $COCl_2$, CH_2CF_2, and $CHCl_3$, also have the largest deviations of the calculated MP2/6-311++G(3d,3p) intensity sums from the experimental ones. The root-mean-square error for the intensity sums for these molecules, 99.0 km mol^{-1}, is about twice the error observed for all molecules studied, 51.4 km mol^{-1}.

Two interpretations are possible. The theoretical estimates are consistently too large, or the measured intensities are systematically too low. Incomplete pressure broadening was a major preoccupation in experimental works, especially for molecules with strong bands,[80] and could provoke intensity sum values lower than the correct ones. On the other hand, most of the intensity sum values in Table 1 are seen to decrease as the basis set is increased from 6-31+G(d,p) to 6-311++G(3d,3p) and as the electron correlation treatment level becomes more sophisticated. One could conclude that the calculated values are higher than the correct ones and tend to decrease as a more accurate description of the electronic densities in these molecules is attained, converging to the experimental values. The trend for IR intensities to decrease with improved treatment of electron correlation effects has been reported previously.[41,44,45] This trend has been explained by correlating decreasing intensity values with increasing equilibrium bond length predictions as electron correlation treatments become more complete.[45] However, these effects are only observable if sufficient balance between basis set size and electron correlation treatments exists.

It should also be remembered that the Gaussian and GAMESS computer programs provide results calculated within the limitations of the harmonic oscillator−linear dipole moment function approximations.[96] This could explain part of the discrepancies seen in Figures 1−3 and lower the errors reported in Tables 1 and 2. Furthermore, rotational corrections should be made in comparing theoretical and experimental mean dipole moment derivative results.[97] The application of these corrections could improve the correlation in Figure 1 but not the one in Figure 3.

A new feature introduced here is the comparison between experimental and theoretical intensity sums rather than comparisons between individual intensity values. Sum comparisons can be more informative. First, a major source of error in individual intensity determinations comes from separating overlapped bands into their component contributions.[73] The methyl halide molecules provide good examples for which a majority of fundamental bands are overlapped. Of the six fundamental bands in CH_3F, all are overlapped, ν_1 with ν_4, ν_2 with ν_5, and ν_3 with ν_6. Furthermore, the band separation error is 2/3 of the Beer's law plot error. A similar situation prevails for its isotopomer, CD_3F. More than two fundamentals can be overlapped as in CH_2F_2, where ν_3, ν_7 and ν_9 are all overlapped.[55] The use of molecular intensity sums for these molecules seems more appropriate for comparison with theoretical results than do individual intensity values.

It should be remembered that the experimental values have not been corrected for anharmonic effects, so that a completely rigorous comparison between experimental and calculated values cannot be made. Anharmonic corrections for intensities are more complicated than the corresponding ones for frequencies. Not only must anharmonic effects of the vibrations be taken into account but the intensity calculation should contemplate nonlinearity in the dipole moment functions.[46] Corrections of these effects for individual bands can be either positive or negative, and some cancellation might occur for fundamental intensity sums.

4. Discussion

Very recent studies[51,54] have shown that mean dipole moment derivatives obtained from experimental intensity measurements can be related to core electron binding energies of 1s carbon and *n*p ($n = 2,3,4$) heavier Group IV atoms by the simple potential model proposed by Siegbahn and co-workers[98]

$$E = k\bar{p}_C + \sum_{A \neq C} \bar{p}_A / R_{AC} \tag{10}$$

where E represents the binding energy, $\bar{p}_C$ and $\bar{p}_A$ mean moment derivatives of the atom being ionized and its neighboring atoms, respectively, and R_{AC}, the internuclear distance between atoms A and C. This relationship suggests that the mean dipole moment derivatives can be interpreted as atomic charges, at least for accurate estimations of electrostatic potentials close to nuclei, and hence as ionization energies of core electrons. In this discussion, focus is centered on how these derivatives vary with changes in traditional chemical valency parameters, such as electronegativity and degree of hybridization, in order to judge whether their behavior reflects the one expected for atomic charges.

The carbon atom mean dipole moment derivatives of the halomethanes vary from 0.016 to 2.051*e* and have been shown to be linearly related to the average electronegativity of their substituent atoms.[99] The terminal atom derivatives have relatively constant values for these molecules with $\bar{p}_H$ varying from 0.003 to −0.021*e*, $\bar{p}_F$ from −0.485 to −0.629*e*, and $\bar{p}_{Cl}$ from −0.148 to −0.294*e*. The mean dipole moment derivatives of CF_4, +2.051 and −0.512*e* for carbon and fluorine, respectively, are almost identical to Mulliken charges, +2.091 and −0.523.[99] The Mulliken charge procedure might be expected to be accurate for the CF_4 charges, since it is a very polar molecule with clear divisions between electronic densities around the C and F atoms. For this reason, large uncertainties in the calculated Mulliken charge values owing to the discrimination of overlap charge distributions are not expected.

The terminal atoms of the halomethanes also have mean derivatives showing a simple relationship with electronegativity. The $\bar{p}_X$ values of the X atoms in the CH_3X (X = F, Cl, Br, I, and H) molecules,[100] −0.502, −0.267,−0.137, −0.114, and −0.004*e*, are linearly related to their own electronegativities, 12.18, 9.38, 8.40, 8.10, and 7.17 on the Mulliken−Jaffe scale.[101] This behavior is expected for atomic charge values. Similar behavior is also observed for the X_2CO molecules (X = F, Cl, Br, H) with $\bar{p}_X$ values of −0.483, −0.331, −0.16, and −0.040*e*, respectively.[64,102] It is interesting that $\bar{p}_O = -0.554e$ is more negative than $\bar{p}_F = -0.482e$ in the F_2CO molecule. This is consistent with the fact that the oxygen atom appears to lie in the same direction as the negative pole of the F_2CO permanent dipole moment.[103]

Hydrocarbon molecules are the most appropriate to use for determining how mean dipole moment derivatives vary with changes in hybridization. The $\bar{p}_H$ values in ethane, ethylene, and acetylene are 0.021, 0.027, and 0.201*e*, respectively.[54] This trend correlates with the one for the acidities of these molecules. As the s character of the hybrid increases, the hydrogen atom becomes more positively charged. This is consistent with the facts that the CH bond lengths[104] decrease with increasing s character, with r_{CH} = 1.094, 1.087, and 1.060 Å in C_2H_6, C_2H_4, and C_2H_2, respectively, and that the hydrogen atom appears to become more negatively charged as the CH bond distance increases during molecular vibrations.[105] The same trend with hybridization is found for the $\bar{p}_H$ of CH_3CCH. The sp-bonded hydrogen has a mean derivative value of 0.200*e*, whereas the methyl group hydrogen has a 0.029*e* value. The hydrogen atom in HCN also has a very positive $\bar{p}_H$ value, $+0.231e$, that is even higher than the values found for HCCH and CH_3CCH. This is consistent with the fact that the CN group is expected to be more electronegative than the CH_3CC and HCC groups.

Electronegativity arguments are also consistent with the oxygen and sulfur mean dipole moment derivative values. Consider the CO_2 , OCS, and CS_2 molecules. The $\bar{p}_O$ values are -0.536 and $-0.581e$ for CO_2 and OCS, respectively, and the $\bar{p}_S$ values are -0.268 and $-0.344e$ for OCS and CS_2, respectively.[54]

Finally, these kinds of arguments have also been shown to be valid for the MH_4 (M = C, Si, Ge, and Sn) molecules.[51] Descending the periodic table for the Group IV elements corresponds to $\bar{p}_M$ values of 0.016, 0.904, 0.862, and 1.016*e*. In contrast to the monotonic decrease observed in the electronegativity values of the halogens as one goes down the table, the electronegativity values of Si and Ge are determined to be almost equal, with most tables reporting a germanium electronegativity value slightly higher than the one for silicon, in agreement with atomic charge interpretation of the observed mean dipole moment derivative values.[106]

5. Conclusions

Theoretical mean dipole moment derivative and intensity sum results tend to converge to their experimental values as basis set and electron correlation treatment levels improve. This is consistent with results that have been reported previously emphasizing individual intensity values. With the 6-311++G-(3d,3p) basis set, MP2 calculations deviate from experimental intensity sums by 51 km mol^{-1} or almost 15% of the average experimental intensity sum value. Most of the calculated values are larger than the experimental ones. The B3LYP density functional level results in almost twice this error, 87 km mol^{-1}. Depending on the application, this loss of accuracy might be compensated by shorter computational times. Comparison of theoretical and experimental intensity sums rather than individual intensity values eliminates uncertainties that can arise from overlapped fundamental band separations. Comparison of theoretically calculated GAPT charges with experimental mean dipole moment derivatives is also recommended, since the latter are averages of independent intensity measurements on isotopomers. Furthermore, the experimental mean dipole moment derivatives have values that exhibit behaviors upon changes in electronegativity and hybridization that are expected of atomic charges.

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