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Nuclear magnetic resonance chemical shifts using optimized geometries

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Isotropic chemical shifts and shift anisotropies for carbon, nitrogen, oxygen, and fluorine in first-row-atom molecules have been calculated in the perturbed Hartree–Fock gauge including atomic orbital scheme for both experimental and optimized molecular structures using a 6-311G* basis for heavy atoms and a scaled 4-31G basis for hydrogen. Structure optimization leads to the expected shortening of bond lengths, which is accompanied by an increase in the isotropic chemical shifts. The increased shifts show much improved agreement with gas phase experimental values for nitrogen and oxygen, while the results for carbon are only mildly affected and remain good; shift anisotropies for all species tend to decrease in magnitude and also generally improve. Fluorine is anomalous, its increasing shifts upon structure optimization moving further away from experiment at this level of basis set. The trend in the optimized isotropic shifts is explained in terms of the general tendency for atoms in the right-hand portion of the first row of the periodic table to have negative shift derivatives with bond extension.

I. INTRODUCTION

Coupled Hartree–Fock theory with moderately sized basis sets and local gauge origins is providing a better and better description of the nuclear magnetic resonance chemical shift for both first- and second-row atoms.^{1–15} Calculations involving ¹³C are beginning to approach experimental error,¹⁶ and will require better experimental values with which to compare. With these apparent successes, however, a number of systems which yield somewhat accurate results on a relative scale still disagree significantly with experimental values on an absolute scale. These are illustrated for first-row molecules by compounds containing nitrogen and oxygen situated in multiple bonds; carbon in CO usually departs significantly from experiment, and fluorine calculations in general are lacking in accuracy on an absolute scale. The calculated nitrogen and oxygen results are significantly lower (too paramagnetic) than observed values. Schindler,⁶ in an extensive set of calculations involving nitrogen, recently showed that even the use of very large basis sets in the Hartree–Fock approximation did not alleviate this problem, and concluded that electron correlation would be required in order to achieve better agreement with experiment.

In virtually all calculations reported to date experimental geometries have been employed for the molecules studied. A recent study¹⁷ of the first- and second-row hydrides did employ optimized structures, which, at the level of basis set employed {6-311G* = [4s,3p,d] for heavy atoms, 4-31G = [2s] for hydrogen} agreed well with those geometries which were known. Several years ago in a study⁸ involving chemical shifts and bond modification effects for some small first-row-atom molecules it was pointed out that, due to the size of the chemical shift derivative, significant changes would occur for the chemical shift depending on whether one used the experimental or an optimized geometry. Since that time our ability to handle larger systems has improved, and more and better gas phase data are available with which to compare calculated results. Accordingly, in

this paper we report the results of a series of calculations on molecules containing carbon, nitrogen, oxygen, and fluorine employing both experimental structures and those optimized at the same level of (moderately sized) basis at which the chemical shift is calculated. Our results show that the degree of goodness of reproducing carbon shifts is not affected, but that results for the previously pathological cases involving nitrogen and oxygen are very much improved. The results for fluorine still remain an enigma at the level of basis set employed here. Our results suggest that larger basis sets or inclusion of correlation may be important for the reproduction of the fluorine chemical shifts, but that the conventional coupled Hartree–Fock approach may be quite adequate for the other elements of the first long row of the periodic table, provided optimized geometries at a suitably high level of basis are employed.

II. DETAILS OF THE CALCULATIONS

The chemical shift calculations for a set of selected molecules containing only hydrogen and first-row atoms were carried out using Ditchfield's gauge including atomic orbital perturbed coupled Hartree–Fock approach¹⁸ using both experimental^{19,20} and optimized molecular structures. Parameters from the experimental structures were employed as input for the geometry optimizations. All bond lengths and internal angles were allowed to vary subject to constraints of molecular symmetry. The basis sets employed for this study are those which were previously^{8,17} found to be efficient for chemical shift calculations for first-row atoms, and are due to Hehre *et al.*²¹: 4-31G for hydrogen {(31) = [2s]}, and 6-311G*{(6311/311/1) = [4s,3p,d]} for first-row atoms. Six cartesian *d* functions were used; the recommended hydrogen scale factors were employed, but no scale factors were used for the heavy atoms.

Geometry optimizations were carried out using the GAUSSIAN-86 program²² which employs the Berny optimiz-

ation method.²³ The default convergence limits for forces [$3E-4$ Hartree/(bohr or rad)] and displacements ($1.2E-3$ bohr or rad) were used. The convergence limit for self-consistent-field energies was $1E-9$ hartrees. Final density matrices for experimental and optimized structures calculated by the GAUSSIAN-86 program were used as input for the chemical shift calculations. The chemical shift program is a modified version of Ditchfield's original program (based on an early member of the GAUSSIAN series) recoded to be more space efficient and to handle up to 120 atomic orbitals.²⁴

We have tried to be particularly careful in this study to compare our isotropic shift results calculated for a rigid molecule in its experimental or optimized equilibrium form only to measured *gas phase* results on an absolute scale. Although some experimental estimates of σ_e are available, most results are reported for σ_0 , the gas phase shift typically at 300 K. The absolute shielding scales and primary references are those of Jameson and Jameson¹⁶ for carbon [$\sigma_0(\text{CO}) = 1.0 \pm 1.2$ ppm], Jameson *et al.*²⁵ for nitrogen [$\sigma_0(\text{NH}_3) = 264.54 \pm 0.05$], Wasylishen *et al.*²⁶ for oxygen [$\sigma_0(\text{CO}) = -42.3 \pm 17.2$ ppm], and Jameson and co-workers^{27,28} for fluorine [$\sigma_0(\text{HF}) = 410 \pm 6$ ppm]. Gas phase data available from other sources have been converted to these absolute scales using data given in these primary references. Data for butane are reported since, along with liquid phase data,²⁹ corrections for liquid-to-gas changes in the chemical shift are available.³⁰ To the extent that future changes to these primary standards occur, so, too, all the reported data relative to these standards will be modified.

Some other experimental isotropic shift data (usually liquid phase data) are given for certain cases, but are not employed in the error analysis. In addition, in the tables containing the calculated and observed chemical shifts and shift anisotropies a variety of calculated shifts for which no experimental data are available are included for reference and later comparison to observed values when available.

III. RESULTS AND DISCUSSION

A. Structure, energy, and dipole moment changes

As is well known, carbon, nitrogen, oxygen, and fluorine bond lengths tend to be smaller than experimental values in the Hartree-Fock approximation. Bonds involving electronegative first-row atoms such as NO, OO, OF, and FF are known to shorten considerably upon optimization.²¹ For the 31 molecules optimized in the present study the average change in bonds involving hydrogen was -0.0101 Å (with a standard deviation of 0.0072 Å, 34 cases), while that for bonds between heavy (nonhydrogen) atoms changed by -0.0232 Å (with a standard deviation of 0.0196 Å, 33 cases) on the average. The distribution of heavy atom bond length changes is a reasonable one with the exception of the molecules OF_2 and F_2 where large changes of -0.0730 and -0.0892 Å, respectively, were found. If these outliers are removed from the analysis, an average heavy atom bond length change of -0.0200 Å is obtained with a standard deviation of 0.0133 Å. In addition to the OF_2 and F_2 molecules, NNO showed a NN bond length change of -0.0430 Å, and in NF_3 and NF bond length changed by -0.0463 Å.

The largest *positive* bond length changes observed were those for CH_3CN where the CC bond changed by $+0.0077$ Å, and in acetone, where the CC bond increased by $+0.0079$ Å. With few exceptions, changes in angles were small and less than 1° ; the largest change was in HCOOH where the COH angle increased by 3.2° .

The average energy lowering upon optimization was -1.56 kcal/mole with a standard deviation of 1.51 kcal/mole. Those molecules showing the greatest decrease in energy included NNO (-3.60), H_2CO (-3.74), NF_3 (-3.76), F_2 (-3.94), and OF_2 (-5.49).

Dipole moments were also calculated and compared to averaged gas phase data.³¹ For both experimental and optimized geometries the calculated moments were larger than those observed experimentally. Upon optimization, 17 moments decreased (moved toward experiment), while 4 increased (moved further away from experiment). The root mean square error (rmse) for the experimental structures was 0.34 D and was reduced to 0.28 D for the optimized structures.

Bonds involving fluorine are well known to cause many of the difficulties observed in comparing Hartree-Fock results with experiments.²¹ The F_2 molecule is cited as a "worst case" in the determination of theoretical vibrational frequencies, and is significantly improved by including correlation at the MP2/631G* level. The bond-breaking energy in the HF molecule seems to approach the Hartree-Fock limit slower than other AH systems, and HOF and F_2 are predicted to be thermodynamically unstable with respect to OF and FF bond cleavage. Because the structures of OF_2 and F_2 depart so much from experiment, they were excluded from the analyses which follow.

B. Chemical shifts

The key results of the present study are contained in this section. In discussing the degree of agreement between calculated and observed chemical shifts, one must keep in mind the fact that we are comparing calculations carried out on rigid molecules in their equilibrium nuclear configuration (either experimental or optimized) with experimental chemical shifts for molecules at finite temperatures (typically 300 K) that are rotating and vibrating in the gas phase. Rovibrational effects at room temperatures can be significant and are dominated generally by zero-point energy effects. For carbon, Jameson and Jameson¹⁶ report corrections to the isotropic shift for species such as CH_4 , CO, CO_2 , to be -3.3 , -2.0 , and -1.5 ppm, respectively. Laws *et al.*³² give a correction for the nitrogen molecule of -3.4 ppm. While these corrections are relatively small in terms of our current ability to calculate chemical shifts, they are noticeable and should be taken into account in a more rigorous analysis. Shifts for other species can be much larger. Jameson and Osten report corrections for fluorine at 300 K of -9.5 to -18.0 ppm in some haloethanes³³ and -6.8 to -15.4 in some halomethanes.³⁴ Ditchfield³⁵ calculates a -11.2 ppm correction for fluorine in HF at 300 K, while Fowler and Raynes³⁶ report a -13.1 ppm zero-point correction for oxygen in H_2O . These negative corrections are

consistent with the idea of bond stretching in the presence of rovibrational effects coupled with the negative shift derivatives with respect to bond length modification found for species on the right-hand side of the first row of the periodic table.^{8,17} Ideal calculations, then, involving molecules in their rigid equilibrium geometry would be expected to be perhaps 3–5 ppm more positive than experiment for species like carbon and nitrogen, and perhaps as much as 10–15 ppm more positive for nuclei such as oxygen and fluorine.

In our compilations of data, comparisons are given only for results obtained for gas phase studies. A few liquid phase data are presented for information, but are not used in the error analysis. Changes from liquid to gas phase are generally not known, and can be sizeable and varied.

Experimental chemical shifts and those calculated for both experimental and optimized geometries are contained in Table I. There is a great amount of experimental data for carbon that has in the past been reasonably well calculated; there are relatively fewer experimental data available for the remaining nuclei. In the table a rmse is cited, as well as the standard deviations (sd) and average error (\bar{x}). The rmse gives a measure of the absolute error between calculated and observed shifts, while the standard deviation is a measure of agreement between the two quantities on a *relative* basis.

The results for carbon in Table I show that, for the 22 experimentally known shifts, changes in the statistical quantities are relatively minor. The rmse is virtually unchanged, the standard deviation does improve somewhat, and the average error changes from being just slightly positive to that range where one would expect it to be on the basis of rovibrational effects. CO is calculated much better than in the past, although there are other cases which get significantly worse; CH₃F maintains a large error, the error increasing from 13.2 to 16.6 ppm going from experimental to the optimized geometry. Carbon, it would appear, is relatively insensitive to whether one uses experimental or optimized geometries, although the average error does move in that direction one would expect. Expressing the rmse as a percentage of the shift range for those species contained in Table I, one finds an error of 3.5% and 3.7% for experimental and optimized geometries, respectively.

The chemical shift data in Table I for nitrogen and oxygen show significant improvement when optimized geometries are used rather than experimental ones. The rmse for nitrogen decreases from 31.5 to 12.2 ppm, while the standard deviation is reduced from 17.8 to 8.7 ppm. The average error moves up, as expected, but is still negative. Multiply bonded nitrogen nuclei change more than those involved in single bonds, and the improved rmse represent now 3.7% of the total nitrogen shift range, a figure virtually identical to that for carbon.

Oxygen, although having only five experimental data with which to compare, also shows significant improvement. The rmse is reduced from 30.3 to 13.6 ppm; the standard deviation remains approximately constant, while the mean error moves up, however, like that for nitrogen, still remains negative. The single bond case (water) changes relatively little while those involving multiple bonds show the biggest change. As mentioned earlier, OF₂ is left out of the analysis

since it is considered to be an outlier due to its drastic reduction in OF bond length upon optimization; this severe decrease in bond length causes a much too large increase in the chemical shift. If one uses the shift range excluding the very negative value of OF₂, the rmse represents 3.5% of the modified chemical shift range, a figure in close agreement with the results for nitrogen and carbon.

The final set of data in Table I concerning fluorine shows that, even excluding the OF₂ and F₂ molecules, the rmse and the standard deviation increase upon structure optimization. Even excluding NF₃, which shows a very large shift error using the optimized geometry, does not help that much. All the shifts move up, as expected, but they are generally too high to begin with and, accordingly, get worse. Excluding the last three molecules in the table one finds the rmse to be 13.2% of the modified shift range, a figure much higher than those for the other three nuclei studied. This figure may actually be a bit pessimistic since the shift range for fluorine if one includes F₂ is the largest of all nuclei investigated. That is to say, it may be that much harder to calculate accurate fluorine shifts because the range is so much greater than that of other nuclei. Nevertheless, at our level of basis the inability of Hartree–Fock, either with experimental or optimized structures, to reproduce chemical shifts at a level of accuracy similar to that for carbon, nitrogen, and oxygen, suggests that inclusion of correlation may be required in this instance. On the other hand, Fleischer and Schindler,⁴⁰ using larger basis sets than we, find noticeably better agreement with experiment for a large series of fluorine compounds calculated at experimental geometries, and conclude that correlation effects may not be so important for fluorine as for other species. Generally speaking, the use of extended basis sets at experimental geometries has not shown significant improvement for other first-row nuclei.

An explanation of why the chemical shifts from optimized structures are improved over those from experimental geometries is to be found from the behavior of the shift upon bond stretching and shrinking. We have carried out a study of bond modification effects on some first-row-atom containing molecules⁸ (using experimental geometries), and first- and second-row hydrides¹⁷ (using optimized geometries) and find reasonably good agreement between theory and experiment for σ' , the derivative of the isotropic chemical shift with bond length change. The shift derivatives tend to always be negative for carbon, nitrogen, oxygen, and fluorine, apparently a property associated with these species residing in the right-hand portion of the periodic table, and are dominated by the paramagnetic portion of the shift. The absolute values of the shift derivatives tend to be larger for oxygen than for nitrogen, and larger for nitrogen than carbon. The shift derivatives ranges found are –6.3 to –537.9 ppm/Å for carbon, –625.4 to –1132.5 ppm/Å for nitrogen, and –1166.3 to –1726.5 (only two cases) for oxygen. Fluorine, also with only two cases, is somewhat anomalous, showing a shift derivative of –131.4 ppm/Å for HF and the very large value of –2782 ppm/Å for F₂. Aside from the two fluorine examples, the shift derivatives are correlated with the shifts themselves, the shift derivative becoming more negative as the isotropic shift algebraically

TABLE I. Experimental and theoretical isotropic chemical shifts (in ppm) for carbon, nitrogen, oxygen, and fluorine calculated for both experimental and optimized geometries. Unless specifically noted, the experimental data are taken from Ref. 16 for carbon, Ref. 25 for nitrogen, Ref. 26 for oxygen, and from Refs. 27 and 28 for fluorine.

	Calculated shifts		Observed shifts	
	Experimental structure	Optimized structure	Gas phase	Other
A. Carbon				
(CH ₂) ₃	197.6	199.1	...	189.7 ^a
CH ₄	194.7	196.4	195.1	
CH ₃ CN	191.4	194.5	187.7	
CH ₃ CH ₃	183.5	186.2	180.9	
CH ₃ CH ₂ CH ₂ CH ₃	173.7	179.7	173.1 ^b	
CH ₃ CH ₂ CH ₃	178.8	178.6	170.9	
CH ₃ CH ₂ CH ₃	176.5	177.5	169.2	
CH ₃ CH ₂ CH ₂ CH ₃	165.1	170.1	159.7 ^b	
CH ₃ NH ₂	164.3	166.8	158.3	
(CH ₃) ₂ CO	167.5	167.6	158.0	
CH ₃ CHO	167.7	166.9	157.2	
CH ₃ OH	147.1	149.3	136.6	
CHCH	117.8	119.9	117.2	
CH ₃ F	130.0	133.4	116.8	
CH ₂ CCH ₂	115.2	118.3	115.2	
CH ₂ F ₂	97.9	102.4	...	
CHF ₃	91.1	95.4	...	
HCN	75.2	81.6	82.1	
CH ₃ CN	67.9	75.1	73.8	
CH ₂ CH ₂	62.5	67.9	64.5	
F ₂ CO	56.4	61.9	...	
CO ₂	54.6	62.7	58.8	
H(CO)OH	28.5	38.0	...	17.7 ^c
H ₂ CO	4.4	14.2	...	- 9.3 ^d
CN ⁻	1.5	15.6	...	
CO	- 20.6	- 8.0	1.0	
CH ₃ CHO	- 7.2	6.3	- 6.7	
(CH ₃) ₂ CO	- 17.2	- 2.3	- 13.1	
CH ₂ CCH ₂	- 37.1	- 31.8	- 29.3	
rmse	7.8	8.2		
sd	7.7	5.7		
\bar{x}	1.1	5.9		
B. Nitrogen				
NH ₃	262.6	266.5	264.5	
CH ₃ NH ₂	252.4	257.2	250.0	
NNO	61.9	89.0	99.5	
NNO	- 27.8	- 2.0	11.3	
CH ₃ CN	- 41.5	- 24.8	- 9.1	
HCN	- 46.4	- 31.1	- 20.4	
CN ⁻	- 74.1	- 50.9	...	- 29.7 ^e
NF ₃	- 91.1	- 51.8	...	
N ₂	- 109.4	- 80.0	- 61.6	
rmse	31.5	12.2		
sd	17.8	8.7		
\bar{x}	- 26.1	- 8.5		
C. Oxygen				
CH ₃ OH	348.9	353.1	...	
H ₂ O	331.3	339.7	344.0	
CO ₂	220.0	240.8	243.4	
NNO	168.7	219.4	200.5	
H(CO)OH	153.7	172.5	...	
F ₂ CO	17.3	44.2	...	
CO	- 86.5	- 61.3	- 42.3	
H(CO)OH	- 105.5	- 74.0	...	
(CH ₃) ₂ CO	- 371.7	- 325.4	...	
CH ₃ CHO	- 401.3	- 345.5	...	
OF ₂	- 415.3	- 219.5	- 473.1	
H ₂ CO	- 422.7	- 406.2	...	- 312.1 ^f

TABLE I *continued*).

	Calculated shifts		Observed shifts	
	Experimental structure	Optimized structure	Gas phase	Other
rmse ^a	30.3	13.6		
sd	11.6	13.5		
\bar{x}	-28.0	-1.7		
D. Fluorine				
CH ₃ F	491.5	497.0	471.0	
HF	416.5	423.3	410.0	
CH ₂ F ₂	371.3	378.3	339.1	
CHF ₃	307.1	314.7	274.1	
F ₂ CO	239.5	258.0	221.6	
NF ₃	136.5	190.6	50.3	
OF ₂	31.0	148.4	-52.3	
F ₂	-181.4	33.9	-232.8	
rmse ^h	41.5	64.6 ⁱ		
sd	25.6	41.8		
\bar{x}	32.7	49.3		

^a Estimated from liquid phase data (Ref. 29) and the average liquid-to-gas correction for propane (Ref. 37).

^b Liquid phase data (Ref. 29) corrected to the gas phase (Ref. 30).

^c Liquid phase data (Ref. 29).

^d An "estimated" result mentioned in Ref. 38.

^e In 0.4 M KCN, Ref. 39.

^f Estimated in Ref. 26 from additivity arguments.

^g Analysis excludes OF₂.

^h Analysis excludes OF₂ and F₂.

ⁱ Exclusion of NF₃ as well as OF₂ and F₂ yields: rmse, 32.8; sd, 10.3; \bar{x} , 31.1.

decreases. In fact, from the available data, a single curve can be drawn through the data in a σ vs σ' plot for carbon, nitrogen, and oxygen nuclei treated together.

The implications for the present study are clear. Oxygen and nitrogen shifts tend to be too low; carbon is about right, using experimental geometries. Optimized geometries tend to shorten bonds, and angle changes are for the most part minimal (and apparently have a small effect on shifts for first-row atoms). Shortened bonds will raise (algebraically) nitrogen and oxygen shifts because their shift derivatives are large, and will only modestly affect carbon since its shift derivatives are smaller. Atoms associated with multiple bonds tend to have larger shift derivatives and, accordingly, will show a greater sensitivity to bond shortening.

Of equal if not greater importance to the isotropic shifts are the shift anisotropies. While the isotropic shift is an average of the three principle elements of the shift tensor, the shift anisotropy involves differences of the diagonal elements. While errors may be averaged out in the isotropic shift, this is less likely to happen for the anisotropy. Shift anisotropies, thus, are a more severe test of theory. Unfortunately, shift anisotropies are also harder to measure, and generally must be determined from studies on either solids or liquid crystals so that effects of the environment are not so clear as for gas phase species. Our calculated anisotropies for both experimental and optimized geometries are given in Table II along with the root mean square error, standard deviation, and mean error in the comparison of the relatively few experimental values known for the class of molecules

studied here. The experimental data have been taken in the main from the compilation of Jameson.⁴¹ Where more than one experimental value is quoted, comparisons are made to the average value.

The results for the anisotropies parallel those of the isotropic shifts. For the sixteen listed experimental anisotropies for carbon, nine remain about the same and seven improve in going from experimental to optimized geometries, the rmse changing from 18.3 to 12.4 ppm. For nitrogen and oxygen there are only a total of seven known anisotropies, but while the results for NH₃ are virtually unchanged, all the other error decrease significantly, and indeed, are in the same range of error as that for the optimized isotropic shift. Aside from F₂, the fluorine cases are not badly calculated, but F₂ is pathological due evidently to its overly large decrease in bond length upon optimization. We note that for all species the average change in anisotropy is negative upon structure optimization.

Although the experimental data are sparse, comparison with experiment for the anisotropies is consistent with that for the isotropic shifts, and suggests that, with the exception of fluorine, the various elements of the shift tensor are better calculated in the optimized structures.

C. Experimental versus optimized structures

When calculating a specific property for a molecule, should one use the experimental structure or the structure optimized within the theoretical model employed? There ap-

TABLE II. Chemical shift anisotropies (ppm) calculated for both experimental and optimized molecular geometries. The shift anisotropy $\Delta\sigma$ is defined as $\Delta\sigma = \sigma_{\parallel} - \sigma_{\perp}$ when axial symmetry is present, or as $\Delta\sigma = \sigma_{33} - \frac{1}{2}(\sigma_{22} + \sigma_{11})$, $\sigma_{33} > \sigma_{22} > \sigma_{11}$. Experimental data are denoted as solid phase (s), liquid crystal (lc), or a combination of spin-rotation data and theoretical diamagnetic shielding. Unless noted under the reference column, the experimental data are taken from the compilation of Jameson (Ref. 41) which contains the original references.

	Experimental structure	Calculated $\Delta\sigma$	Optimized structure	Observed $\Delta\sigma$	Ref.
A. Carbon					
(CH ₂) ₃	56.4	55.9	48 ± 3(s)	42	
CH ₃ CN	12.8	13.6	5 ± 10(1c)	43	
CH ₃ CH ₃	10.8	10.3	...		
CH ₃ CH ₂ CH ₂ CH ₃	22.1	22.2	...		
CH ₃ CH ₂ CH ₃	22.6	22.8	...		
CH ₃ CH ₂ CH ₃	6.4	6.6	...		
CH ₃ CH ₂ CH ₂ CH ₃	26.3	20.9	...		
CH ₃ NH ₂	38.9	38.6	...		
(CH ₃) ₂ CO	46.4	46.9	50 ± 10(s)	44	
CH ₃ CHO	44.0	45.8	47.5 ± 5(s)	45	
CH ₃ OH	64.0	62.6	63(s)		
CHCH	241.9	239.8	240 ± 5(s)	45	
CH ₃ F	86.3	85.4	90(s), 87.4 ± 3.5(1c)	45,46	
CH ₂ CCH ₂	100.4	99.3	94.5(s)	47	
CH ₂ F ₂	26.2	26.4	...		
CHF ₃	-11.1	-11.8	...		
HCN	304.2	296.2	284.6 ± 20(1c)		
CH ₃ CN	343.0	329.7	311 ± 30(1c)	43	
CH ₂ CH ₂	173.9	168.9	153(s)	47	
F ₂ CO	172.4	163.8	...		
OCO	342.9	333.5	335(s)	47	
H(CO)OH	108.0	98.8	...		
H ₂ CO	183.6	165.1	...		
CN ⁻	414.1	394.5	...		
CO	438.0	420.6	405.5 ± 1.4(sr), 406 ± 30(s), 353	47	
CH ₃ CHO	190.0	172.8	174 ± 5(s)	45	
(CH ₃) ₂ CO	209.3	185.9	193 ± 10(s)	44	
CH ₂ CCH ₂	74.0	78.9	58(s)	45	
rmse	18.3	12.4			
sd	13.7	10.6			
\bar{x}	12.1	6.4			
B. Nitrogen					
NH ₃	-38.7	-41.7	-40(sr)		
CH ₃ NH ₂	47.7	50.5	...		
NNO	420.7	382.4	368 ± 15(1c)	48	
NNO	566.4	530.6	508 ± 15(1c)	48	
CH ₃ CN	520.7	506.9	...		
HCN	579.1	557.2	563.8 ± 8(sr)		
CN ⁻	626.2	592.5	...		
NF ₃	124.9	107.4	...		
N ₂	672.3	629.8	676 ± 20(sr), 603 ± 28(s)		
rmse	38.7	13.1			
sd	21.7	12.5			
\bar{x}	32.1	3.8			
C. Oxygen					
H ₂ O	40.2	39.4	...		
CH ₃ OH	101.2	105.6	...		
OCO	292.3	262.1	...		
NNO	374.1	299.0	...		
H(CO)OH	199.6	187.3	...		
F ₂ CO	400.0	382.6	...		
CO	746.0	708.8	676.1(sr)		
H(CO)OH	612.7	585.0	...		
(CH ₃) ₂ CO	1073.9	1020.6	...		
CH ₃ CHO	1176.9	1104.0	...		
H ₂ CO	1298.5	1271.4	1252(sr)		
OF ₂	183.5	139.5	...		
rmse	59.3	26.9			
sd	11.7	6.6			
\bar{x}	58.2	26.1			

TABLE II. (continued.)

Experimental structure		Calculated $\Delta\sigma$	Optimized structure	Observed $\Delta\sigma$	Ref.
D. Fluorine					
CH ₃ F	- 75.6	- 85.1	- 60.8 ± 15(sr), - 90 ± 4(1c)	44	
HF	99.4	89.4	93.7 ± 0.5(sr), 108(sr)		
CH ₂ F ₂	159.5	161.7	...		
CHF ₃	113.5	100.4	...		
F ₂ CO	210.7	180.8	...		
NF ₃	355.2	273.2	...		
OF ₂	584.3	415.4	...		
F ₂	1005.2	684.5	1050 ± 50(s)		
rmse ^a	1.0	10.6			
sd	0.6	0.9			
\bar{x}	- 0.8	- 10.6			

^a F₂ excluded from analysis.

pears to be no clear cut answer to this question; particular answers depend on particular circumstances. One could well argue that for consistency's sake the theoretical model should be used in all regards, including that determining the equilibrium structure to be employed. On the other hand, by carrying out a property calculation using the known structure, it is argued that at least this aspect of the overall determination is correct, since optimized structures are not quite the same as the experimental ones. Of course, there are experimental errors associated with molecular structure determination, and it has been stated that looking for agreement much beyond 0.01 Å or 1° is, at this juncture, not worthwhile.²¹ For the present basis sets employed, errors ranging from 0.00 to 0.05 Å are observed in bond lengths, representing errors as large as 4%, excluding the outlying cases of OF₂ and F₂, where errors of 5 and 6% occur. Finally, as a predictive tool it could be argued that one should use those structures (experimental or optimized) that allow the best predictions.

Structural effects are often systematic and can be corrected for. The same is true for chemical shifts, often reported on a relative scale. However, ultimately one wants agreement with experiment on an *absolute* basis, so that a probe of the fundamental causes will have, in some sense, an absolute meaning. It is felt by some^{49,50} that to calculate vibrational frequencies that agree well with experiments, experimental or empirically adjusted reference structures should be employed due to difficulties inherent in the Hartree-Fock procedure. Contrary, to this view, others²¹ argue that since the calculation of harmonic frequencies assumes one is at a minimum on the potential energy surface, the theoretically determined structure (and minima) should be used. Structural features like rotational barriers require optimized structures. On the other hand, electric dipole moments which are sensitive to structure are also sensitive to the basis set involved, and it has been suggested that in cases like this it may be best to use experimental structures.²¹ We note that the 21 molecules with nonvanishing moments studied here showed improved values in going from experimental to optimized geometries, although the error is still large.

The goal of chemical shift calculations is not only to provide a useful predictive tool, but also to present a base for a better fundamental understanding of the phenomenon. A proper understanding will require accurate calculations carried out with suitable basis sets, a knowledge of the need to include correlation and the effects of rotation and vibration, and answers to questions such as the appropriate geometry to employ. In the present study, as far as the calculation of fluorine chemical shifts are involved, it seems to make relatively little difference whether one uses experimental or optimized structures; they are, for our basis, not calculated very well. Larger basis sets⁴⁰ and/or inclusion of correlation effects will be important for this nucleus. Fluorine, in the case of chemical shifts, continues to be a thorn in the side of the Hartree-Fock approach. For carbon, nitrogen, and oxygen, however, the use of optimized structures results in a general improvement of both isotropic shifts and shift anisotropies, and results exhibiting trends which are consistent among these three nuclei. For these species either by argument of consistency with the theoretical model or of practicality as a predictive tool, it would appear that the structure of choice is that optimized rather than that observed experimentally.

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