

A Comparison of the Experimental and *ab Initio* Values of the ^{17}O NMR Chemical Shifts in the Carbonyl Group

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New experimental and theoretical results are presented for the NMR shielding of oxygen in the carbonyl group. The experimental values clearly demonstrate that the solvent effects are very significant. The new results for the chemical shifts are in better agreement than the previous literature data with the corresponding *ab initio* values calculated for isolated molecules. © 1997 Academic Press

I. INTRODUCTION

The comparison of calculated and experimental results for NMR shielding constants is a complicated procedure. As discussed in detail by Jameson (1), it involves an analysis of rovibrational and temperature dependence of the shielding constant in the isolated molecule and, what makes it most difficult, an analysis of the effects of the environment. Most of the NMR experiments are done in the liquid phase and one must consider the solvent effect. Moreover, very often for small molecules one can obtain from the theory an accurate result but it is impossible to convert it to the chemical shift measured with respect to a (large) reference molecule.

So long as the *ab initio* calculations were not very accurate, the approximations within the theory determined the outcome of the comparison with experiment. In the past few years significant progress has been made in *ab initio* studies of NMR shielding constants; in particular various methods including correlation effects have been developed. Within the approximations using perturbation theory to describe electron correlation, a series of methods suitable for shielding calculations has been derived by Gauss and Stanton. It includes second (2, 3) and higher order (4) many-body perturbation (MBPT) schemes, a coupled cluster method including single and double excitations (CCSD) (5, 6) and the CCSD(T) approach—CCSD with a perturbative correction for triple excitations (7). Simultaneously, a formalism which enables the use of linear response methods for multiconfiguration SCF (MCSCF) wavefunctions (8) to study a variety of magnetic properties (see (9) and references therein), including NMR shielding constants (10), has been developed.

Whenever approximations are made, for example, a finite basis set is used, magnetic properties may depend on the arbitrary gauge origin of the magnetic field. In all the approaches discussed above, the computed shielding constants are gauge invariant since GIAOs (gauge invariant atomic orbitals) are used within the linear response formalism. Another advantage of the GIAOs is that, as shown by many numerical results (see, e.g., (10–12)), the convergence to the basis set limit is improved with respect to standard basis set expansions.

Ab initio calculations including electron correlation are significantly more difficult and expensive than the corresponding SCF studies. Unfortunately, for the shielding of atoms with lone pairs like nitrogen or oxygen in double bonds or aromatic systems the SCF results are often unreliable because the correlation effects can be on the order of 50–100 ppm (see, e.g., (6, 10, 13)). Thus, until now reliable calculations of ^{17}O shielding in the carbonyl group using large basis sets and correlated wavefunctions have been performed for very few molecules.

The experimental values of the oxygen chemical shifts are also scarce and often unverified. The natural ^{17}O abundance signal is extremely weak (1.08×10^{-5} as compared to ^1H) and relatively broad due to the quadrupole moment of ^{17}O nucleus. Therefore the ^{17}O measurements for samples of low concentration, like gases and solutions, require long accumulation times even now, when modern high field spectrometers are used.

As mentioned above, additional problems arise when the experimental and calculated shielding constants are compared. With some significant exceptions (CO, CO₂ and COS) (14) the ^{17}O NMR chemical shifts of carbonyl compounds were available only from pure liquids which are strongly self-associated (15). In the latter case intermolecular interactions change significantly the experimental results, so it is difficult to compare them with theoretical shielding calculations. We have tried to overcome this problem preparing our own set of ^{17}O chemical shift values for the studied molecules, based on measurements in cyclohexane (c-C₆H₁₂) solution. We presume that these measurements can be more

reliable as all of them were carried out under the same experimental conditions. Moreover, we believe that the use of cyclohexane as a solvent gives ^{17}O NMR shifts which are less modified by intermolecular forces and therefore better for the comparison with the calculated chemical shifts of carbonyl oxygens.

II. COMPUTATIONAL ASPECTS

All our ab initio calculations were done using the ACES II (16) program system. The theory underlying the calculation of shielding constants within the ACES II system and its implementation have been discussed in the works of Gauss and Stanton (2–7), and we refer to these works for their description.

We have used, similarly to our previous work (17), experimental geometries whenever available (there is one exception, see below). It is not simple to obtain accurate ab initio geometries for polyatomic molecules including the carbonyl group using perturbation theory methods. Another, more important advantage of using experimental geometries is that it is a systematic way to obtain shielding constants suitable for comparison with experimental data bypassing the problems of their dependence on rovibrational averaging and temperature.

The TZ2P (triple zeta + 2 polarization functions) basis set (18) was used, and GIAOs are always applied. We have also calculated the shielding constants using the smaller DZP (double zeta + polarization) basis. However, we find that the DZP results may be unreliable, sometimes they differ significantly even at the SCF level from the larger basis set values. Therefore, we report systematically only the TZ2P results. The calculations have been performed using the coupled cluster (CC) method, within the CCSD (CC singles and doubles) approximation. We have not applied the more accurate CCSD(T) approach and we have not used larger basis sets because that would make the calculations for the smaller molecules studied very time consuming and for the larger molecules practically impossible. A comparison with other results (see, e.g., Ref. (3)) indicates that the potential increase in the accuracy due to further extension of the basis set is rather small when chemical shifts are considered.

We use systematically the CO result of Ref. (19), $\sigma(\text{O}) = -59.3$ ppm, to establish the scale for the experimental values. To convert the absolute shielding to the chemical shift given with respect to liquid H_2O we have $\delta(\text{O in CO}) - \delta(\text{O in liquid H}_2\text{O}) = 350.1$ ppm (our result) or 350.2 ppm (14). We shall discuss the chemical shifts relative to CO, so these values are given only for comparison with other works.

We have recently analyzed the SCF results for the oxygen shielding constants in the carbonyl group (17). Reasonable agreement with experimental data has been obtained by scaling the SCF results, with three experimental gas phase values

used to determine the scaling coefficients. To analyze how good this estimate of correlation corrections was we apply the same procedure in this work and compare the results with the CCSD values. However, we use now our own experimental data for the reference molecules: $\sigma(\text{O}) = -59.3$ ppm in CO (applied to fix the scale, see above), $\sigma(\text{O}) = 225.6$ ppm in CO_2 , and $\sigma(\text{O}) = 90.9$ ppm in COS. The main difference between these and previous results is in the redefinition of ^{17}O scale.

III. EXPERIMENTAL

The natural abundance ^{17}O NMR spectra were recorded on a Varian UNITY plus-500 spectrometer operating at 67.889 MHz with $\pi/2$ pulse of approximately 11 μs , 37000 Hz (650 ppm) spectral width, and 20 ms acquisition time. Typically 1000 transients were collected for neat liquids and up to 500,000 for diluted or gaseous compounds. The temperature was stabilized at 298 K.

All chemical compounds were commercial products of the highest grade. Aldrich gases were used directly from lecture bottles. The liquid compounds were carefully dried and distilled just before the experiments. The molar ratio of solutes in cyclohexane was always lower than 0.03. The samples were placed in 4-mm o.d. glass tubes which were fixed in 5-mm o.d. NMR tubes (Wilmad 528PP). All gas samples (pure gases and their solutions in cyclohexane) were prepared by the condensation of gases from the calibrated part of a vacuum line and by sealing them in the 4-mm o.d. tubes. Nitromethane- d_3 was placed between the walls of the 4- and 5-mm o.d. tubes and served as the external references standard for all our ^{17}O NMR chemical shift measurements ($\delta = 606.56$ ppm relative to liquid water) and for the deuterium lock system.

IV. RESULTS AND DISCUSSION

A summary of the ab initio results is given in Table 1. The values of oxygen shielding are given first for all the compounds for which we present new experimental data and next for a few more molecules, included to enable a comparison with our previous work (17). We have also shown some of the recent theoretical values which have been obtained including correlation effects.

Our SCF results differ by less than 10 ppm from the previously reported values (17). Scaling to fit the CO, CO_2 , and COS data, we obtain for the TZ2P basis set the equation

$$\sigma(\text{O})^{\text{est}} = 0.928\sigma(\text{O})^{\text{SCF}} + 18.6 \text{ ppm}$$

in which both coefficients are similar to those in our previous work (see also (20, 21)). As shown by the CCSD results in Table 1, this estimate of the correlation corrections to $\sigma(\text{O})$ is very reasonable. Such estimates are particularly use-

TABLE 1
Calculated Values of the Oxygen Shielding Constants^a

Molecule	SCF	Estimate ^b	CCSD	Other works
CO	-84.80	-60.1	-45.41	-52.9, ^c -43.8 ^d
CO ₂	221.97	224.6	237.06	241.0, ^e 234.64 ^f
COS	79.83	92.7	103.42	105.91 ^f
CH ₃ CHO	-399.72	-352.5	-350.89	-291.7 ^e
(CH ₃) ₂ CO	-345.33	-302.0	-308.10	-279.8 ^e
H ₂ CCHCHO	-343.42	-300.2	-309.52	
HCONH ₂	-75.41	-51.4	-54.76	
HCHO	-448.64	-397.9	-378.30	-383.1 ^c
H ₂ CCO	-26.23	-5.8	-5.08	
HCOO ⁻	10.25	28.1	23.27	
HCOOH				
CO	-102.51	-76.6	-74.64	
OH	148.92		154.37	
HCOOCH ₃				
CO	-97.32	-71.8	-68.33	
OCH ₃	177.04		178.31	

^a Absolute shielding in ppm, TZ2P basis set results (this work).

^b SCF results scaled to reproduce the CO, CO₂, and COS experimental data, see text.

^c CCSD(T), Ref. (7).

^d MCSCF, Ref. (30).

^e MBPT(2), Ref. (3).

^f MC IGLO, Ref. (31).

ful when these effects are large, and $\sigma(\text{O})^{\text{SCF}}$ is a very poor approximation to the accurate result.

A comparison of various correlated results is complicated by strong basis set and geometry dependence of oxygen shielding. For CO and H₂CO, the CCSD values of (7) and the corresponding CCSD(T) results quoted in Table 1 are similar and this suggests that for small molecules the role of triple excitations is not very large. On the other hand, it has been suggested that the MBPT(2) approximation overestimates significantly the correlation corrections to the shielding (3, 22) and for CO₂, formaldehyde, and acetone our results are apparently more reliable than the quoted values.

To analyze the role of dimerization in HCONH₂ we have performed calculations for a centrosymmetric dimer structure with two hydrogen bonds. The geometry was taken from the calculations in Ref. (23), where it was optimized in the MP2 approximation with a DZ + 2P basis set. Recent calculations using a more advanced CCSD(T) approach (24) indicate that the MP2 method yields accurate dimerization energies for the considered geometrical structures of the dimer. Our CCSD calculation (with the DZP basis, the monomer results do not in this case differ significantly) shows a change of the oxygen shielding of 43.040 ppm with respect to the formamide monomer. We use this as a correction to estimate the TZ2P value of the shielding in the dimer.

V. ANALYSIS OF THE RESULTS

Table 2 presents our theoretical and experimental ^{17}O NMR chemical shifts in the carbonyl group expressed rela-

tive to carbon monoxide. The measurements were carried out for pure gaseous compounds (CO, CO₂, and COS) at low pressure and for neat liquids (HCONH₂, (CH₃)₂CO, H₂CCHCHO, and CH₃CHO). These results can be directly compared with some earlier data shown in the last column. Our measurements for the pure gases and liquid water are almost identical with the results given by Wasylshen *et al.* (14), the only difference of 0.8 ppm is seen for carbon dioxide. Let us note that the pressure of gases was not exactly the same; the results indicate that the density dependence of oxygen shifts is fairly modest. Thus the ^{17}O NMR experiments at low pressure give values that are very close to those of isolated molecules and can be safely used to compare with the results of ab initio calculations.

Table 2 presents also the ^{17}O NMR chemical shifts for all the investigated molecules in cyclohexane solutions. In contrast to CO, CO₂, and COS, for pure formamide, acetone, acrolein, and acetaldehyde the previous results are of lower accuracy and in a comparison with ab initio calculations should be replaced by these new values. As first shown by Tiffon *et al.* (25) the ^{17}O NMR chemical shift of acetone can be significantly changed by its self-association. It is certainly due to strong dipole-dipole interactions that an increase of oxygen shielding (approx. 16 ppm) is observed upon the dimerization of acetone molecules. We can undoubtedly assume that similar effects exist in the other pure liquids with carbonyl groups. It appears that the use of a nonpolar solvent like cyclohexane may help to solve the problem. At low concentration the solute molecules are mostly in the monomeric form and experience only dispersive forces. Then the expected solvent effect on oxygen shielding is smaller and dependent primarily on cyclohexane molecular properties (26). The values of the oxygen shifts may still not be perfect for direct comparison with the calculated shifts, but presumably are more appropriate than those for pure liquids.

For CO₂ and COS the calculated shifts relative to CO are in between those measured in the gas phase and those in solution. The correlation corrections are very different for these molecules, and they brought the ab initio results into agreement with experiment. Since the remaining differences are of the same size as the rovibrational corrections (see Ref. (19)) we cannot expect higher accuracy.

In the case of formamide the dilution effect was small and probably it means that the dimerization of HCONH₂ is extremely strong and takes place even in the solution of low concentration. Our theoretical value for the oxygen shift in the (HCONH₂)₂ dimer is much closer to the experimental result than the corresponding value for the monomer, in agreement with this hypothesis. Another confirmation comes from a recent ab initio and experimental study, which gives the results for a monomer and a trimer (27). Although a completely different ab initio approach (MCSCF wavefunction) and a different basis set have been used, the ^{17}O

TABLE 2
Theoretical and Experimental ^{17}O NMR Chemical Shifts Relative to Carbon Monoxide^a

	Theory CCSD TZ2P	Experiment		
		in $c\text{-C}_6\text{H}_{12}$ ^b	Neat substance ^c	Other works
CO_2	-282.47	-280.3	-284.9(g)	-285.7(g) ^d
COS	-148.82	-147.4	-150.2(g)	-150.2(g) ^d
CO	0.00	0.00 ^e	0.00(g)	0.00(g) ^d
HCONH ₂	9.35			
(HCONH ₂) ₂	-33.69 ^f	-49.9	-46.2(l)	-40 ^g
(CH ₃) ₂ CO	262.69	237.3	222.5(l)	219(l) ^g
H ₂ CCHCHO	264.11	243.7	234.6(l)	229 ^g
CH ₃ CHO	305.48	265.0	248.3(l)	242(l) ^g

^a In ppm, $\delta_i = \sigma(\text{CO}) - \sigma_i$.

^b The molar ratio of solutes was approximately 0.03.

^c (g), gaseous at 3 atm; (l), pure liquid.

^d Reference (14).

^e Deshielded (2.70 ppm) from gaseous CO.

^f Estimated from TZ2P and DZP calculations, see text.

^g Reference (15).

shielding in the monomer, -54.8 ppm, agrees very well with our CCSD result. The change observed for the central molecule in a linear trimer, calculated at the Hartree-Fock level, was $+46.2$ ppm. We find for the dimer in the SCF approximation $+54.8$ ppm and at the CCSD level $+43.0$ ppm. This change in ^{17}O shielding is very significant, it is primarily due to the formation of a hydrogen bond. Ab initio results indicate that the effect should be similar for different single $-\text{O} \cdots \text{H}-\text{N}$ hydrogen bonds, and we expect that the change of the ^{17}O shielding should be even larger when the oxygen atom enters two hydrogen bonds.

It is worth noticing that, as expected, the new oxygen shifts of acetone, acrolein, and acetaldehyde are much closer to the theoretical results than the measurements for pure liquids. Assuming that the result for an isolated molecule may be obtained by further extrapolation in the same direction, for these three compounds the final values would be in between the tabulated CCSD and cyclohexane solution results. We have previously estimated from the SCF calculations (17) the dimer to monomer change for acetone to be approximately 30 ppm (and we obtain a similar estimate now). The neat substance-cyclohexane solution shift observed here is 15 ppm. It is difficult to say whether the residual differences between the theoretical values and ^{17}O shifts of acetone, acrolein, and acetaldehyde in cyclohexane solution are due to approximations in the theory or to remaining intermolecular interactions in the solution; probably both effects should be considered. A potential source of discrepancy is that the geometry, in particular the CO double bond distance, may change in different solutions, and not necessarily in the same way for various molecules (the oxygen shielding derivative in CO is very large, approximately -900 ppm/Å (19)).

VI. CONCLUSIONS

There are recently various means to calculate ab initio shielding constants which should be directly comparable with experimental data. Successful attempts include for example calculations for dimers and other structures, rather than for an isolated molecule, as well as calculations for a solvated molecule and a combination of these approximations (see, for example (28, 29) and references therein).

In this work, we have taken a different approach to this problem. Our theoretical data used for comparison with experiment have been obtained systematically at the same level of approximation (basis set and wavefunction type) for all the molecules. In addition, we have used experimental molecular geometries and we compare finally the chemical shifts rather than analyze the shielding constants. Hopefully, this leads to a significant cancellation of any errors remaining in the ab initio calculation. Although for the smaller molecules one can undoubtedly perform nowadays more accurate calculations, we believe that it was more appropriate to use the same approximations for all the compounds studied.

At the same time, we have tried to obtain a set of experimental data which is best suited to compare with isolated molecule results of the calculation. We have shown that these new results are indeed approaching the corresponding ab initio values. The precision of our experimental data obtained from cyclohexane solutions is limited by the magnitude of solute-solvent interactions. Assuming that in this case only weak intermolecular forces affect the measured ^{17}O shielding, its uncertainty should be within a few parts per million. In addition, the present approach can be easily extended for other molecules. Measurement of the chemical shift for any compound in the cyclohexane solution, for

example, relative to liquid water, yields a reasonable approximation for the value in an isolated molecule.

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