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Influence of Intermolecular Interactions on Nuclear Magnetic Shielding Constants of OCS

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The gauge-included atomic orbital (GIAO) method has been applied within the coupled Hartree-Fock (CHF) approximation to compute ^{13}C, ^{17}O and ^{33}S NMR chemical shifts for solid OCS. Increasing clusters of OCS molecules taken out of crystal lattice have been used in an additive approximation to estimate the effect of intermolecular interactions on shielding of the carbon, oxygen and sulphur nuclei. There is a very good agreement achieved for NMR chemical shifts between the results of calculations and experimental measurements obtained for ^{13}C and also some discrepancies for ^{17}O and ^{33}S nuclei, probably due to deficiency of *ab-initio* calculations (lack of electron correlation). The results reveal that the ^{33}S NMR signal of OCS is strongly dependent on intermolecular interactions.

Key words: ^{13}C, ^{17}O and ^{33}S NMR spectroscopy, nuclear magnetic shielding, GIAO-CHF calculations, intermolecular interactions, solid OCS structure

Intermolecular interactions have significant effects on measured NMR shielding constants. The nuclear shielding constants are determined by electronic distribution around the nuclei of interest. The scale of these effects depends mainly on the quality of observed nucleus and also on the character of intermolecular interactions [1]. Incredible progress of modern computing methods of quantum chemistry within last years supplies effective methods of computing shielding tensors of nuclei. They allow obtaining precise and accurate values on shielding surfaces of small singular molecules [2,3] and to model changes of shielding constant values, due to intermolecular interactions in the condensed phase. Our previous papers [4–6] have proved that joint application of the GIAO-CHF [7] method in Wolinski's *et al.* [8] version and the supermolecular approximation gives fairly good results. Such an approach allows *ab-initio* calculations for quite large fragments of crystal lattices as it was shown for water [9], solid ammonia [10,11], methylamine [12], ammonium nitrate [13] and acetylene [14]. Certain problems appear in molecular systems, where the total shielding effects can be computed in a correct manner only when an electron correlation is taken into account, for example in the case of the O atom in carbonyl group [15,16]. Molecule of the carbonyl sulfide (OCS) belongs to such systems, but it

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is the unique chemical compound which can be currently used as a reference standard for the experimental scale of absolute shielding in ^{33}S NMR spectroscopy [17]. Such application of OCS requires careful studies on intermolecular contributions to nuclear magnetic shielding of sulphur.

Carbonyl sulfide crystallizes in a special position in the trigonal R 3m(R) space group with three molecules in the unit cell [18]. The unit cell parameters of OCS are the following: $a = b = c = 4.063$ Å and $\alpha = \beta = \gamma = 90°$. Structural details of this structure have been established on the basis of neutron powder diffraction data collected at 90 K. There is only one independent OCS molecule in the crystal lattice and we will analyse increasing clusters of OCS molecules, what constitute close environment of the central OCS molecule. It appears that there are 6 symmetry related OCS molecules in the first environment shell 4.063 Å far from the first central molecule. 6 other molecules of OCS form the second shell that is 5.288 Å distant from the central molecule. The third molecular shell is formed by 2 molecules located on a straight line 5.861 Å far from the central molecule on both its sites. The intermolecular distance is measured as an S…S internuclear distance with the S atoms coming from two different molecules. The arrangement of molecules in the OCS lattice is shown in Fig. 1.

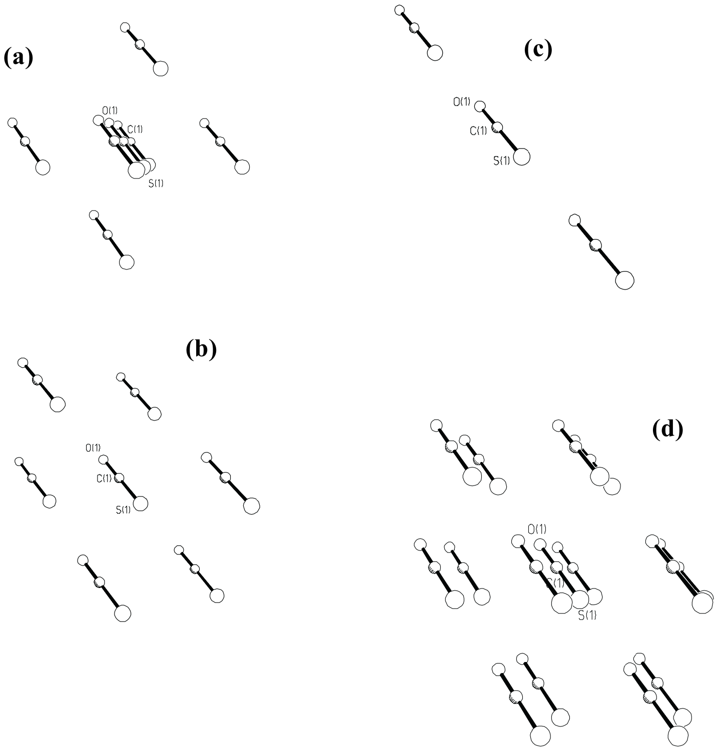

Figure 1. Packing of OCS molecules in crystal lattice at 90 K [18]: (a) 1st environment of central (labeled) OCS molecule 4.063 Å far from the central OCS molecule, (b) 2nd shell of OCS molecules 5.288 Å far from the central one, (c) 3rd shell of OCS molecules 5.861 Å from the central OCS molecule, (d) all three environments of the central OCS molecule together.

Here, OCS is formed of linear molecules with the CO and CS bond lengths equal to 1.161 Å and 1.559 Å, respectively. Such clusters, as those described above, can serve as good model systems to study the influence of intermolecular interactions on shielding of ^{13}C, ^{17}O and ^{33}S nuclei. All the chemical shifts of OCS can also be measured in the gas phase and the liquid state. This allows comparing the calculated theoretical shielding changes on condensation with experimental results of these effects for different nuclei in the same molecule and this is the aim of our work.

EXPERIMENTAL AND CALCULATION DETAILS

Experimental. Measurements of ^{13}C and ^{17}O NMR chemical shifts were accomplished using VARIAN UNITYplus-500 spectrometer and default set of parameters. ^{33}S NMR chemical shifts were also measured in the similar way in order to verify earlier data [19] and to obtain all the gas-to-liquid shifts in the same experimental conditions. NMR samples were prepared by condensation of OCS gas (Aldrich) from the calibrated part of a vacuum line and they were sealed in 8 mm o.d. glass tubes about 5 cm long containing separately gaseous (at ~8 atm) and liquid OCS. The volumes of sample tubes and the vacuum line were measured using mercury. The sealed samples were fitted into standard 10 mm o.d. thin-walled NMR tubes (Wilmad 513-5PP) with liquid DMSO-d_6 in the annular space for the reference standard and deuterium lock system. All the measurements of NMR chemical shifts were carried out at temperature of 298 K.

Calculations. The GIAO-CHF approach [7] with the improvement of Woliński *et al.* [8] was applied for calculations of NMR shielding tensors using the GAUSSIAN 94 [20]. The basis set applied for this study was of double dzeta quality as proposed by Hansen and Bouman [21]: (721/221/1) = [3s, 3p, 1d] for atoms C, O and (531111/22211/1) = [6s, 5p, 1d] for S. It should be noticed that the present results may contain superposition errors due to incompleteness of the basis set, but our previous studies [10–15] have shown that the magnitude of superposition errors was negligible for similar calculations of ^{1}H, ^{13}C and ^{15}N shielding in other solid systems. It can be presumed that the supermolecular approximation may still give reasonable results also for the magnetic shielding of oxygen and sulphur nuclei. The calculations were performed on the IBM RISK System/6000 work station.

RESULTS AND DISCUSSION

Calculated shielding constants [$\sigma = (\sigma_{11} + \sigma_{22} + \sigma_{33})/3$] for the central molecule OCS in different environments are shown in Table 1. The first two lines contain data for isolated molecules: (1) in the gas phase and (2) taken from a crystal. It is obvious that our present study based on the CHF approximation cannot deliver accurate results for the absolute shielding constants in the OCS molecule. However, our values of $\sigma_C = 17.7$ ppm, $\sigma_O = 86.3$ ppm and $\sigma_S = 809.6$ ppm correspond with the best quality calculations of *ab initio* calculations for OCS (33.3, 98.8 and 809.0 ppm, respectively) and with the experimental data (30.0, 88.1 and 817 ppm, respectively) [22]. On the basis of present results in Table 1 one can also say that the shielding of carbon, oxygen and sulphur slightly decreases firstly because of changes in the geometry of the OCS molecule on lowering temperature down to 90 K [22]. Then profound decrease of shielding of all three nuclei takes place when the molecules of OCS of the first shell are taken into account, *cf.* Table 1 and Fig. 2. As expected the deshielding effect is the largest for a sulphur nucleus and the smallest for a carbon nucleus.

Table 1. GIAO-CHF shielding constants [ppm] of ^{13}C, ^{17}O and ^{33}S nuclei in an OCS molecule as a function of different molecular environment.

OCS shielding constant	σ_C	σ_O	σ_S
Gas phase[(a)]	17.7	86.3	809.6
Molecule isolated from crystal	17.0	85.1	807.8
1st environment of central (labeled) OCS molecule	13.6	72.4	779.5
2st environment of central (labeled) OCS molecule	17.1	79.9	808.2
3st environment of central (labeled) OCS molecule	16.6	90.1	803.9

[(a)] For the experimental geometry of the OCS molecule [27] with chemical bonds O–C: 1.1572 Å and C–S: 1.5606 Å.

The next neighbourhood of molecules (6 molecules of shell two and 2 molecules of shell three) has a far less influence, although alignment of three OCS molecules in one line significantly increases the shielding of the oxygen atom and improves also the two other results. This is why an almost complete model of the OCS crystal lattice should contain at least three molecular shells. The total effect of OCS condensation has been estimated assuming full additivity of contributions coming from three above structures. Our latest results for ammonia [11] prove that such an assumption rather overestimates the amount of real effect. This is what one can observe when theoretical results are compared with the experimental ones (see Table 2).

Table 2. Comparison of calculated intermolecular effects in ^{13}C, ^{17}O and ^{33}S shielding constants [ppm] with experimental values measured for condensed OCS.

Δ of shielding constant	$\Delta\sigma_C$	$\Delta\sigma_O$	$\Delta\sigma_S$
Calculated[(a)]	–5.1	–15.1	–35.4
Experimental[(b)]	–4.0	–7.3	–19.5[(c)]

[(a)] Estimated assuming additivity of interactions within first three shells of molecular environment of an OCS molecule in crystal.

[(b)] Measured as a difference of chemical shifts in the liquid and gas phases assuming correction on differences in volume magnetic susceptibility [28].

[(c)] ± 8.0 ppm.

In conclusion, we want to point out that both the model of crystal and the approximations applied lead to a good agreement achieved for NMR chemical shifts between the results of calculations and experimental measurements obtained for ^{13}C. The discrepancies for ^{17}O and ^{33}S nuclei are larger and well seen in Fig. 2. One of the main reasons of these discrepancies is the CHF approximation, which does not include to present calculations of the electron correlation, which is so important for the carbonyl oxygen [16] and sulphur atoms. However, our approximate results describe fairly well the influence of intermolecular interactions on the shielding of oxygen and sulphur nuclei in OCS crystal lattice. They point out the correct direction of shielding changes due to the environment. We can presume that the same range of magnitude of

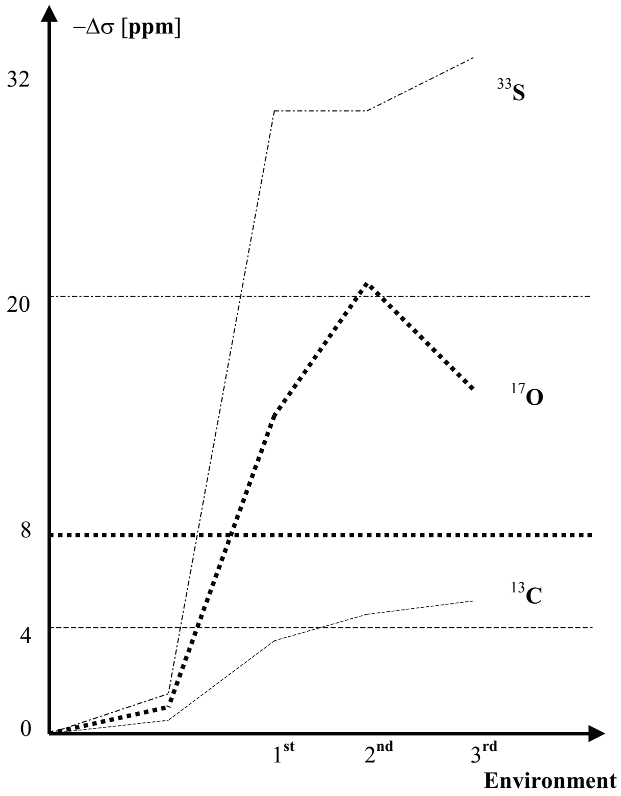

Figure 2. Changes of shielding constants as a function of increasing number of molecules in the environment of the central OCS molecule. The horizontal lines describe the experimental gas-to-liquid shifts for C, O and S nuclei, *cf.* Table 2. It is important to admit that the ^{33}S gas-to-liquid shift is known with relatively low accuracy, $\Delta\sigma = -19.5 \pm 8.0$ ppm.

shielding will be observed whenever OCS molecules are condensed. Then it is a very important information for ^{33}S NMR spectroscopy. The absolute magnetic shielding of a sulphur nucleus has experimentally been determined only for an OCS molecule and it is based on the spin-rotation constant measured by molecular-beam experiment and Flygare's procedure [17,23–25]. This gives the absolute ^{33}S shielding in OCS equal to 843 ± 12 ppm in Wasylishen's original scale [17] or to more reliable value of 817 ± 12 ppm, if the diamagnetic contribution of the shielding is better estimated [22]. Application of the present ^{33}S shielding scale remains limited, because the appropriate $\sigma_0(T)$ parameter for an isolated OCS molecule has never been measured. A linear OCS molecule gives poor ^{33}S measurements in the gas phase, its NMR signal is very broad due to a large quadrupole coupling constant, $eq_oQ = -29.91$ MHz [26]. It is really difficult to perform precise NMR measurements for such a signal. Now, our theoretical and experimental results jointly confirm that the ^{33}S NMR signal of OCS is strongly dependent on intermolecular interactions.

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