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Calculation of ^{17}O NMR shieldings in molecular models for crystalline MO , $\text{M} = \text{Mg, Ca, Sr}$, and in models for alkaline earth silicates

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Abstract ^{17}O NMR shieldings are calculated for the central O in the molecular model $\text{OM}_6(\text{OH})_{12}^{-2}$, for crystalline alkaline earth oxides, MO , where $\text{M} = \text{Mg, Ca, and Sr}$, using both Hartree–Fock and hybrid Hartree–Fock density-functional theory. Agreement of calculated and experimental NMR shifts of CaO and SrO compared to MgO is good, but only if the basis set on the M atoms has sufficient tight d polarization functions. Preliminary results are also presented for nonbridging O in the silicate $\text{Si}(\text{OH})_3\text{O}^-$ anion, perturbed by alkaline earth cations, giving trends which agree qualitatively with experiment.

Keywords $\text{MgO} \cdot \text{CaO} \cdot \text{SrO} \cdot \text{NMR} \cdot \text{Alkaline earth silicates} \cdot \text{Quantum calculation}$

Introduction

The ^{17}O NMR shielding of the central O in a molecular model, $\text{OMg}_6(\text{OH})_{12}^{-2}$, for crystalline MgO , periclase, was previously calculated (Tossell 1998) using Hartree–Fock and density functional methods (Jensen 1999). Agreement of calculated and experimental absolute shieldings was only fair, although an explanation was advanced for the deshielding of the O observed at elevated temperature (Fiske et al. 1994). Both HF and DFT approaches gave ^{17}O NMR shieldings which were too shielded compared to experiment by around 40–50 ppm.

In addition, unpublished studies by the author on the ^{17}O NMR shielding of the analogue CaO model yielded only a small difference between the O shieldings in the MgO and CaO models, inconsistent with the deshielding of about 247 ppm observed experimentally for CaO

compared to MgO (Turner et al. 1985). At the time it was not clear whether the reason for this discrepancy was the cluster model used, the quantum-mechanical method used to calculate the shielding, or the poor quality of the basis sets then available for Ca.

Although the difference in O NMR shift between MgO and CaO is itself interesting, perhaps a more significant difference is that between the O NMR shieldings of nonbridging Os (NBO) coordinated to either Mg or Ca in silicates (Timken et al. 1987). This difference is around 25 ppm, so that the NMR signature of the O can give information on which divalent cations are coordinated to the NBO and thus on the nature of cation ordering in silicate glasses and melts (Lee and Stebbins 2003).

In the past few years there have been some advances in our understanding of quantum-mechanical methods which can be used to calculate accurate NMR shifts, particularly for electronegative atoms like O and F (Cheeseman et al. 1996; Wilson et al. 1999; Liu and Nekvasil 2002). Cluster models even smaller than those used in Tossell (1998) have also yielded accurate relative shieldings for F in the alkali fluorides (Cai et al. 2002). There have also been improvements in the quality and availability of basis sets for heavier elements like Ca. It therefore seemed to be a good time to return to the problem of calculating the ^{17}O NMR shift of CaO . Since O in SrO was even more deshielded than in CaO (by roughly 100 ppm) and since several different basis sets are now available for Sr, it seemed useful to also consider SrO .

Computational methods

The cluster model chosen in $\text{OM}_6(\text{OH})_{12}^{-2}$, with a single central O, six nearest-neighbor M cations, 12 next-nearest-neighbor O anions, and 12 protons to give charge compensation, producing an overall charge of -2 . For consistency with previous results, the geometries were optimized for these clusters with a 3–21G basis (Hehre et al. 1986). For the MgO model cluster the optimization produced an Mg–O distance that was somewhat short (1.99 vs. 2.12 Å from the

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Table 1 Calculated and experimental ^{17}O NMR shieldings and shifts (in ppm) in $\text{OM}_6(\text{OH})_{12}^{-2}$ models for MO

Method/ MO	MgO			CaO			SrO		
	σ	$\Delta\sigma$	exp. rel. δ	σ	$\Delta\sigma$	exp. rel. δ	σ	$\Delta\sigma$	exp. rel. δ
pVDZ HF	316.0	0		107.1	208.9		11.4	304.6	
pVDZ B3LYP	290.9	0		-10.4	301.3		-75.2	366.1	
pVDZ average	303.4	0	0	48.4	255.1	247	-31.9	335.3	343

sum of ionic radii), while for the Ca and Sr clusters the optimized distances were 2.36 and 2.54 Å, respectively, compared to radii sums of 2.40 and 2.56 Å. Our previous studies of the MgO model (Tossell 1998) established that the calculated shielding changed rather slowly with Mg–O distance, so such a discrepancy should not be of great concern.

An alternative method for calculating NMR shieldings of crystalline solids employs a periodic approach (Mauri et al. 1996; Gregor et al. 1999) and would seem to be a natural choice for such a problem. However, this method has not yet been applied to ionic solids such as MgO. In addition, a cluster model provides more flexibility in applications to disordered environments in glasses, if appropriate clusters of manageable size can be defined.

In this work the NMR shieldings were calculated using two different coupled perturbation theory methods, based on HF theory or the B3LYP version of hybrid HF-DFT theory. In each case the GIAO method (Hinton et al. 1993) was used. All calculations were done with the software packages GAUSSIAN94 and GAUSSIAN98 (Frisch et al. 1994, 1998). Results were obtained with a number of different basis sets. There is considerable evidence that using valence electron only basis sets for atoms other than the central atom of interest can give acceptable results for F NMR shieldings (Cai et al. 2002), but in this work all-electron basis sets have been used for all atoms, to remove any concern about neglect of the core electron contributions. However, several conventional all-electron basis sets of the 6-31G (Hehre et al. 1986) type gave a badly underestimated value for the MgO – CaO shielding difference and adding conventional d polarization functions to those 6-31G bases improved this difference only slightly. Only when better basis sets are used, like those of Dolg et al. (1986) and Godbout et al. (1992), with better representations of the d orbitals, are results obtained in good agreement with experiment.

Results

Calculated and experimental ^{17}O NMR shieldings are given for the molecular cluster models of MgO, CaO, and SrO in Table 1, showing both HF and hybrid HF-DFT (B3LYP) results and their average for the best basis sets employed. These are basis sets of a structure similar to those of Dolg et al. (1986) and Godbout et al. (1992), which are designated pVDZ (DFT orbital) in the Extensible Computational Chemistry Environment Basis Set Database of the Environmental and Molecular Sciences Laboratory at the Pacific Northwest Laboratory. Note that the changes in shielding, σ , with respect to MgO are now in approximate agreement with experiment for both CaO and SrO. There is clearly a tendency for the HF results to give too small a shift and the B3LYP results too large a shift. Taking their average yields a result in better agreement with experiment.

Although this may initially seem an arbitrary procedure, it has been shown by Liu and Nekvasil (2002) to work very well empirically for F NMR shifts. Wilson

et al. (1999) and Wilson and Tozer (2002) have developed somewhat similar approaches, using exchange-correlation functionals intermediate between HF and DFT, within an uncoupled DFT formalism for the shielding. Their approach has a somewhat better theoretical foundation than our simple approach of averaging HF and B3LYP values, and has been found to work well for some small main-group molecules. It is possible to obtain essentially the same result as our HF, B3LYP average in a single calculation by simply constructing the appropriate hybrid functional within GAUSSIAN, but in this work we have performed separate HF and B3LYP calculations for all cases and then averaged the results.

The importance of basis set is illustrated in Table 2, where calculated shieldings are shown for the MgO and CaO cluster models using the HF method and several different basis sets. Basis set effects for the B3LYP calculations (not shown) are in the same direction and of very similar magnitude. For MgO the basis set dependence of the results is rather small, while it is quite large (amounting to more than 100 ppm) for CaO (and for SrO, not shown). In particular, to obtain a shielding in agreement with experiment for the CaO model it is necessary to employ a rather large set of d functions on the Ca, with several large exponent functions. For example, in the Dolg et al. (1986)-type basis sets there are five primitive d Gaussian functions on the Ca, with exponents of approximately 7.2, 1.9, 0.6, 0.2, and 0.05, contracted to two, i.e., a $(5d) \rightarrow [2d]$ d basis in standard notation. The Godbout et al. (1992) bases are of similar structure. By contrast, the 6-31G($2d$) basis has only two primitive d functions with exponents of 0.2 and 0.05. The reason for this difference in basis is straightforward – in 6-31G($2d$) the d functions are used as polarization functions, meant to better describe the bonding electron density. In the basis sets of Dolg et al. (1986) the d functions are required to correctly describe the energies

Table 2 Variation in calculated ^{17}O NMR shieldings (in ppm) with basis set, using 3-21G optimized geometries and HF method for $\text{OM}_6(\text{OH})_{12}^{-2}$ clusters

M	Mg	Ca
6-31G	333.3	328.4
6-31G(d)	317.8	205.8
6-31G($2d$)	314.3	179.1
pVDZ	($1d$) \rightarrow [$1d$] 316.0 ($2d$) \rightarrow [$2d$] 312.3	($5d$) \rightarrow [$2d$] 107.1 ($5d$) \rightarrow [$3d$] 100.0 ($3d$) \rightarrow [$2d$] 164.7

of excited states of ions of third-row elements (K–Br) in some of which d atomic orbitals are occupied. Thus, a much more flexible description of the d orbitals is needed. The importance of the two higher exponent d functions has been tested by removing them, producing the result labeled $(3d) \rightarrow [2d]$ in Table 2, which shows a shielding increase of about 57 ppm compared to the original Dolg et al. (1986) basis. By contrast, slightly uncontracting this d basis, by splitting the single tight Gaussian, i.e., producing a $(5d) \rightarrow [3d]$ set, gives only a 7-ppm change in shielding. For the MgO model, changing from one d function on both Mg and O to two functions, with an exponent ratio of 4:1, gives only a 3-ppm change in the O shielding, a much smaller effect than seen for the CaO model.

Many researchers have noted that results obtained using the GIAO method converge more rapidly with respect to basis set size than with other distributed origins methods. This is because the GIAO approach generates field-dependent functions which essentially provide additional functions of higher azimuthal quantum number than the original basis (Wolinski et al. 1990; Cheeseman et al. 1996). However, the compactness of the generated functions resembles that of the original, so tight functions are not produced from valence functions. Therefore, it may be necessary to explicitly include such tight functions in the basis.

It is also well known that the electronic structure of the conduction band is different in MgO and CaO. The low-energy part of the conduction band in MgO is essentially Mg s,p in character while there is considerable d contribution to the conduction band in CaO, as expected because of the low energy of the $3d$ atomic orbitals in Ca. This difference is seen in both early band theoretical studies (e.g., Bukowski 1982) and in the most recent studies (Yamasaki and Fujiwara 2002). It appears that an accurate representation of the virtual orbitals of the cluster model (the equivalent of the conduction band of the solid) is needed to correctly reproduce the ^{17}O NMR shielding.

It should be noted that this same cluster model with the pVDZ basis and the configuration interaction singles method (CIS: Foresman et al. 1992) gives lowest-energy optical excitation energies of 6.9 and 6.0 eV for the MgO and CaO cluster models, respectively, while the experimental band gaps are 7.8 and 7.1 eV in MgO and CaO and the band gaps obtained from sophisticated band calculations are 8.2 and 6.6 eV (Yamasaki and Fujiwara 2002). Thus, the energies and compositions of the virtual orbitals strongly influence the O NMR shielding. Previous experimental studies (Turner et al. 1985) identified crystallographic quantities, such as ionic radii, which could be correlated with the O NMR shifts, but such a correlation could not establish the electronic origin of these effects.

Finally, equilibrium geometries have been calculated using the HF method and SBK bases (Stevens et al. 1992) for clusters of the type $\text{Si}(\text{OH})_3\text{OM}(\text{OH}_2)_5$, in which a proton is removed from a silicic acid molecule,

$\text{Si}(\text{OH})_4$, and an almost fully hydrated M cation is bonded to it. NMR shieldings were then calculated using the pVDZ basis set, yielding shieldings at the O connecting Si and M of 291.2, 213.8, and 208.2 ppm, respectively, for $\text{M} = \text{Mg}, \text{Ca}$ and Sr . The calculated deshielding of this O (designated a nonbridging O, NBO, since it does not bridge between Si's) when Mg is replaced by Ca or Sr is in the direction seen experimentally, but is considerably larger than the experimental change, since the calculated change is around 70 and the experimental value only about 25 ppm. The effect of replacing Mg by Ca or Sr in this cluster may be exaggerated since the cluster allows closer approach of the O and the M atom than would be seen in the actual solids. For example, the calculated distances from M to O in these clusters are 1.84 and 2.00 Å, for the Mg and Ca cases, respectively, which are about 0.2 to 0.3 Å shorter than expected for such M–O distances in solids. To more accurately define this effect on NBO shieldings in silicates it will be necessary to consider clusters more representative of actual crystal structures. However, the basis sets and quantum-mechanical methods needed for accurate results are now determined, based on the present study of the MgO, CaO, SrO series.

Conclusions

The relative shieldings of O in MgO, CaO, and SrO can be semiquantitatively reproduced using a cluster approach and HF and hybrid HF-DFT methods. However, it is critically important to use a d orbital basis set on Ca or Sr which has a sufficient set of “tight” d functions. These functions are needed to properly represent the virtual orbitals of d type seen in the electronic structure of CaO and SrO solids.

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