

An ab initio calculation of O-17, H-1 and H-2 NMR parameters for various types of OH groups in hydrous silicates

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Ab initio molecular orbital calculations have been performed on clusters to investigate the NMR characteristics of hydroxyls (OH) that are possibly present in hydrous silicates. The calculated ^{17}O and ^2H quadrupolar coupling constants (QCC) and ^1H chemical shift for SiOH, AlOH and bridging OH's (Si(OH)Al, Al(OH)Al) all show good (and the same) correlation with the O-H and H-bonding (O-H...O) distances, and are also in good agreement with experimental data for OH groups with similar O-H...O distances in crystalline phases. SiOH and Si(OH)Al can form H-bonding of a range of O-H...O distances (down to 2.45Å); Their ^{17}O and ^1H (^2H) NMR parameter values are similar and vary widely. AlOH tends not to behave as a H-donor, and thus gives large ^{17}O and ^2H QCC, and small ^1H chemical shift.

The ^{17}O and ^1H (^2H) NMR are potentially useful techniques that might shed light on the water dissolution mechanisms in hydrous silicate melts. In order to understand the NMR characteristics of various types of hydroxyls (OH) that are possibly present in hydrous silicates, we have performed ab initio molecular orbital calculations on clusters of various sizes. The clusters have been optimized with the density functional theory (B3LYP/6-311+G(2df,p)), which yields satisfactory geometries, in particular, O-H and H-bonding (O-H...O) distances. The NMR parameters have been calculated at HF/6-311+G(2df,p). The calculated ^{17}O and ^2H quadrupolar coupling constants (QCC), and ^1H chemical shift for SiOH, AlOH and bridging OH's (SiOHAl, AlOHAl) all show good (and the same) correlation with the O-H and H-bonding (O-H...O) distances: Hydroxyls with stronger H-bonding tend to yield smaller ^{17}O and ^2H QCC's and larger ^1H chemical shift. The calculated values for all three parameters are in good agreement with available experimental NMR data for OH groups with similar O-H...O distances in crystalline phases. SiOH and Si(OH)Al could form H-bonding of a range of strengths from weak to very strong (O-H...O distance down to 2.45 Å); Their ^{17}O and ^1H (^2H) NMR parameter values thus vary widely. For example, the ^{17}O QCC, ^2H QCC and ^1H chemical shift for SiOH without H-bonding are around 8 MHz, 310 kHz and 2 ppm respectively; those for SiOH with a O-H...O distance of 2.45 Å are 4 MHz, 65 kHz and 17 ppm respectively. This large dependence of ^{17}O and ^1H (^2H) NMR parameters on H-bonding strengths suggests that the latter must be kept in mind for NMR spectral interpretation. AlOH have a tendency not to form strong Al-O-H...O type H-bonding, and thus give relatively large ^{17}O QCC (7-9 MHz), large ^2H QCC (276-330 kHz) and small ^1H chemical shift (-1.8 - 2.5 ppm).

It is known that the O-H stretching frequency values for hydroxyls show similar dependence on H-bonding strengths. Thus, ^{17}O , ^1H and ^2H NMR, as well as vibrational spectroscopy are complementary to one other and all yield information about the strength of H-bonding. Because these different techniques are sensitive to motions with different frequencies, a comprehensive study using all these techniques may yield information about both the H-bonding strength and the dynamics of the dissolved water species.

On the basis of our calculation results, together with information for H-bonding strengths estimated from experimental vibrational spectra and ^1H NMR data, we were able to predict ^{17}O NMR parameters for hydroxyls in hydrous silicate glasses and gels. The observed ^{17}O NMR peaks for silica gel and hydrous albite glass, that have been attributed to SiOH, are significantly narrower than expected from ^{17}O QCC, suggesting that at least some of the SiOH, if present, must be non-rigid. The observed broad ^{17}O NMR peaks for hydrous albite and alkali silicate glasses, originally attributed to molecular H_2O , could equally well be ascribed to rigid hydroxyls with weak H-bonding.