Rationalisation of the IR stretching frequencies of Brønsted acid centres in microporous solids

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The relative position of the O–H stretching frequency of Brønsted acid sites in microporous solids is found to be correlated with the gradient norm of the electrostatic potential and, unlike previous attempts to provide a unified picture of the vibrational properties in such solids, the correlation is found for all structural and compositional variants studied to date.

Both aluminosilicate and aluminophosphate-based crystalline microporous solids can be prepared so that they possess acidic properties, rendering them suitable as solid acid catalysts. The predominant acid function in such materials is a Brønsted acid centre characterised by a protonated oxygen bridging two tetrahedrally coordinated atoms, T–O(H)–T′, where T is typically Si, Al, P. The relative acidity of different centres is typically estimated from the IR vibrational frequency of the hydroxyl bond, ν(O–H) and, more realistically, through the shift in this frequency on the sorption of small probe molecules.[1] Over the years, a number of attempts have been made to provide a rationalisation of the relative position of the stretching frequency of the Brønsted hydroxyl, ν(O–H), with the use of Sanderson electronegativity[2] being the most successful. However, this approach is found only to be valid for low concentrations of acid sites when the acid centres can be considered homogeneous and cannot, therefore, be applicable in the case of either low Si/Al zeolites,[3] or for SAPO materials, where Si-islands can form. Furthermore, the electronegativity is dependant only on composition[2] and hence differences in acidity between different structures with the same composition cannot be accounted for. Deviations are also found once acid sites are considered to be 'perturbed' as a consequence of being present in small cavities. In such cases, a $1/r^2$ relationship between the bathochromic shift observed and near neighbour oxygen distances in the same ring as the acid site has been proposed.[2] The latter observation has been taken by many authors as suggesting that the shift is proportional to the size of the cavity in which the proton vibrates and have assigned IR bands based on this assumption alone, without any consideration of the local environment not part of the immediate cavity. However, no general descriptor or rationalisation has been suggested which is consistent regardless of material structure and composition. Furthermore, there exists little theoretical evaluation of the correlations described above.

We have applied standard lattice energy minimisation and Mott–Littleton methodologies[4] to determine the equilibrium geometries of acid sites in a variety of structures and compositions of both aluminosilicates and silicoaluminophosphates and subsequently used a lattice dynamics approach to calculate the vibrational properties; the GULP code[5] was used throughout. The model consists of formally charged ions which also interact through short-range interatomic potentials (two- and three-body terms) coupled with a shell model description of polarisation; the parameters used are those of Sanders *et al.*[6] and Gale and Henson,[7] with the hydroxyl model being a modification of that derived for NaOH.[8, 9] The model has been extensively demonstrated to reproduce experimental structures and also gives good agreement with experimental vibrational properties; although a -150 cm^{-1} correction for anharmonicity is required for O–H stretching frequencies.[9] The results presented here have been corrected thus unless otherwise stated.

The ability of the model to reproduce the experimentally observed vibrational properties is illustrated in Fig. 1. Not only are the relative shifts in ν(O–H) between the different structures reproduced but also the range of vibrations noted within a structure are in good agreement. Our calculations also reproduce the observed bands; for example, in SSZ-13 we calculate two bands at 3593 and 3575 cm^{-1} and in mordenite we observe two bands at 3600 and 3572 cm^{-1}, compared to 3603, 3579 and 3612, 3585 cm^{-1} respectively from experiment. Similarly, we calculate shifts to lower wavenumber with decreasing Si/Al in FAU.

Thus, together with previous studies, the data strongly suggests that this particular potential model is suitable for determining the relative positions of vibration frequencies across a broad range of microporous systems. But what properties of the structure correlate with the resulting vibrations? Do the calculated sites and geometries correlate with features such as cavity size discussed above?

We previously demonstrated that short-range interactions which manifest themselves as local geometry changes, particularly in the T–O–T′ bond angle are not adequate to identify variations in vibrational properties.[10] For example, identical T–O–T′ angles at different sites within the same structure can

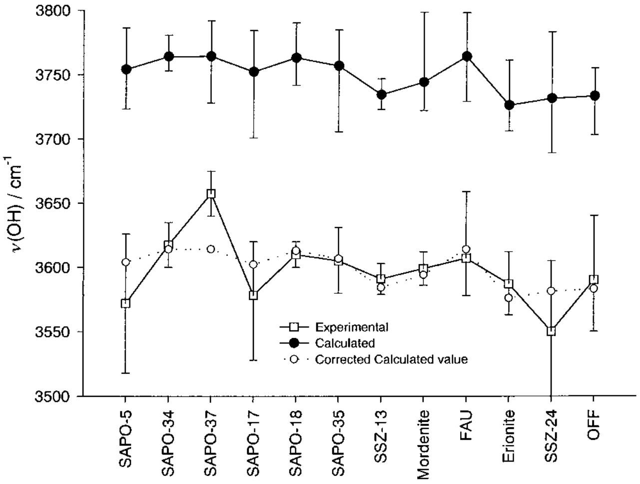

Fig. 1. Comparison of calculated (●) and experimental (□) ν(O–H) values. Shown as data points are the mean values of all noted signals; from experiment each peak position noted in published spectra has been included, whilst our calculations include all sites considered regardless of relative energy. The bars signify the minimum and maximum values found with no consideration of relative peak strength (in the case of experiment) or likely population (in the case of the calculated values). Once the anharmonicity correction term[9] of -150 cm^{-1} is applied to the calculated values (○), close agreement is found with the experimental value of ν(O–H).

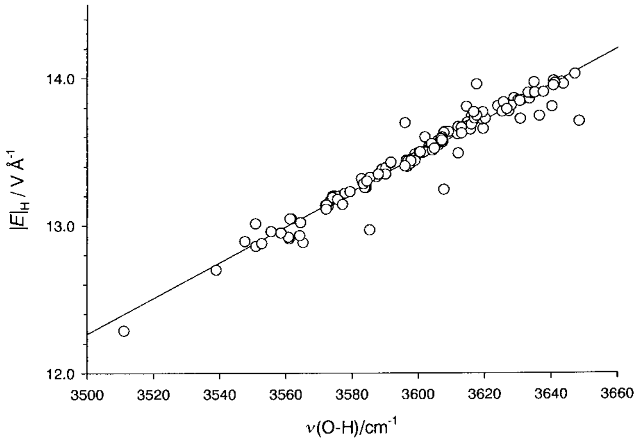

Fig. 2 Correlation of the gradient norm of the electrostatic potential at the proton ($|E|_H$) with the calculated stretching frequency (corrected for anharmonicity), ν(O–H). Acid centres considered include; isolated sites in high Si/Al aluminosilicates, sites in low Si/Al and in Si/Al = 1 aluminosilicates and isolated and island sites of SAPOs, in the structure types indicated in Fig. 1.

possess radically different values of ν(O–H). Instead, we consider (as have others) that the long-range Coulombic interactions are dominant and have previously observed a remarkable correlation between ν(O–H) and the gradient norm of the electrostatic potential at the proton, $|E|_H$, when considering the acidity of SAPOs.[10,11] Extending this idea to the range of structures now considered, it is clear from Fig. 2 that such a correlation appears quite general. We do not, however, observe a consistent correlation between ν(O–H) and the size of the cavity in which the proton is vibrating (Fig. 3) as is often claimed. Furthermore, we do not find that consideration of near neighbour O–H distances[2] can be used to identify likely shifts in ν(O–H). For example, we observe a number of cases where we obtain almost identical ν(O–H) for protons vibrating within different sized cavities of the same material; in SAPO-17 we calculate that protons in both 8MR and 6MR sites vibrate at 3613–3616 cm^{-1}, whilst we also determined other sites in 6MR vibrating at a lower value of 3592 cm^{-1}.[11] In SAPO-35 we determined that three of the lowest frequency vibrations, at 3607 cm^{-1}, are present in 8MR whilst a proton in a 6MR gave a signal at 3616 cm^{-1},[11] which may have been expected to shift to lower values if the cavity size and reduction in nearest oxygen distances arguments held.[2] This apparent lack of correlation can be readily rationalised; consideration of the cavity size does not take into account the interactions between the proton and oxygens which are 'behind' the proton; and near-neighbour oxygens not directly in the same ring may be closer, and thus more influential, than those in the ring, particularly for larger cavities.

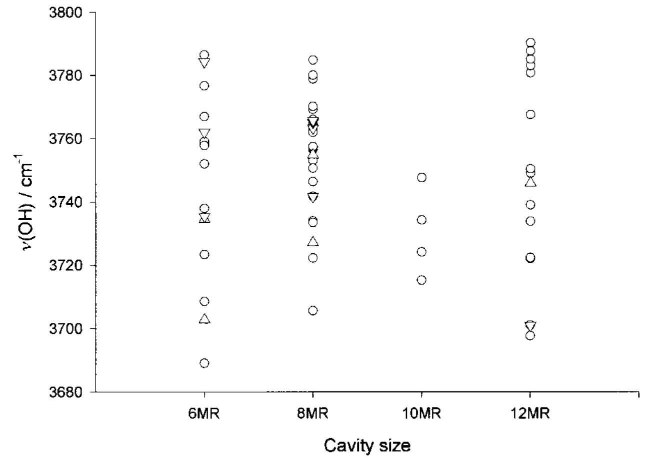

Fig. 3 Calculated vibrational frequencies and cavity size for isolated Brønsted acid sites. All data are presented as open circles whilst highlighted are the values for SAPO-17 (▽) and Offretite (△) which clearly show that cavity size alone cannot account for the relative position of ν(O–H); similar-sized cavities exhibit a wide range of values, whilst in some materials protons in large cavities have higher ν(O–H) than smaller cavities.

In summary therefore, we have identified that interatomic potential calculations are able to reproduce the vibrational properties of Brønsted acid sites in a wide structural and compositional range of microporous solids. We find that the relative position of ν(O–H) can be correlated with the gradient norm of the electrostatic potential at the proton, providing a direct correlation between the structure and the resulting vibration. Note, however, that simple consideration of the electrostatic potential of the framework 'hosting' the acid sites does not provide such insights; lattice relaxation is significant. Thus, we believe, these calculations can be used to verify and assign observed IR bands to specific acid sites in such structures. Furthermore, they may indeed provide a unifying rationalisation of stretching frequencies in such materials. Current work is focused on understanding further the correlation with electrostatic potential and the contribution of the electrostatic field to proton transfer.

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