

The High-frequency Hydroxy Region in H-Y Zeolites; A Comment on a Previous Communication and Corrigendum

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Deconvolution of the high-frequency (h.f.) i.r. hydroxy and deuterioxy stretching bands of H-Y and Na/H-X zeolites, using enhanced resolution Fourier Transform (F.T.) i.r. spectroscopy shows that more than one band may be recognised in some compositions, including the parent Y zeolite, in a previous communication up to five components having been reported; the previous results, for the hydroxy region, were influenced by incomplete compensation for water bands, and clear evidence is presented for the existence of two types of silanol in Y zeolites dealuminated with SiF_6^{2-} .

It has been suggested, on the basis of both theoretical¹ and numerical deconvolution of experimental results,² that the high-frequency (h.f.) i.r. band associated with $\bar{\nu}_{\text{OH}}$ for the bridged hydroxy groups in the large cages of zeolite Y is composed of several bands. In a recent paper³ we used enhanced resolution Fourier Transform (F.T.) i.r. spectroscopy to identify five major components, in the h.f. band, at 3660, 3650, 3642, 3636, and 3622 cm^{-1} . The relative intensities of the lower frequency bands were observed to increase with decreasing framework aluminium in accordance with the well known shift of the centre of the h.f. band to lower wavenumbers on dealumination of Y zeolite.⁴

If the above assignments are correct we should find a corresponding pattern in the i.r. spectra of the deuteriated materials. We have now extended our study to include a series of faujasite zeolites with Si/Al ratios varying from 1.2 to 8.3 which have been treated with D_2O vapour (17.8 mmHg). Self supporting discs of the $\text{NH}_4\text{-Y}$ (or $\text{Na/NH}_4\text{-X}$) zeolites were pretreated at 375 °C at 10^{-5} mbar (1 bar = 10^5 Pa) for four hours (Y-type) or at 275 °C and 10^{-5} mbar for three hours (X-type). Partial deuteration was achieved by exposing the discs to D_2O vapour (17.8 mmHg) at 100 °C for two minutes. The deuteration procedure was repeated after evacuation. Spectra were recorded after 500 scans, with 2 cm^{-1} resolution, using a Mattson Cygnus 100 FTIR spectrometer with a mercury cadmium telluride (MCT) detector.

Deconvoluted spectra are shown in Figure 1 and frequencies are given in Table 1. Spectra for the deuteriated zeolites appear as a single band for materials with a Si/Al ratio of 1.2 (Na/H-X), 1.75, and 4.5, and the centre of the single band moves to lower frequencies as Si/Al increases in agreement with many previous reports.⁴ In contrast, the spectra for deuteriated zeolites with framework Si/Al of 2.5 and 8.3 show clear evidence for two components in the h.f. band, in support of a localised as opposed to a co-operative model for bridged hydroxy groups. However, the present results for deuteriated materials (Figure 1b) do not show anything like the detail evident in our previous communication³ for the hydroxy spectra. It is now clear that the previous spectra are influenced by incomplete compensation for water vapour, since this

Table 1. Deconvoluted h.f. i.r. hydroxy and deuterioxy stretching bands of H-Y and Na/H-X zeolites (cm^{-1}).

	OH	OD
1.2	3658	2698
1.75	—	2694
2.5	3648 and 3639	2687 and 2682
4.5	3634	2681
8.3	3639 and 3631	2682 and 2677

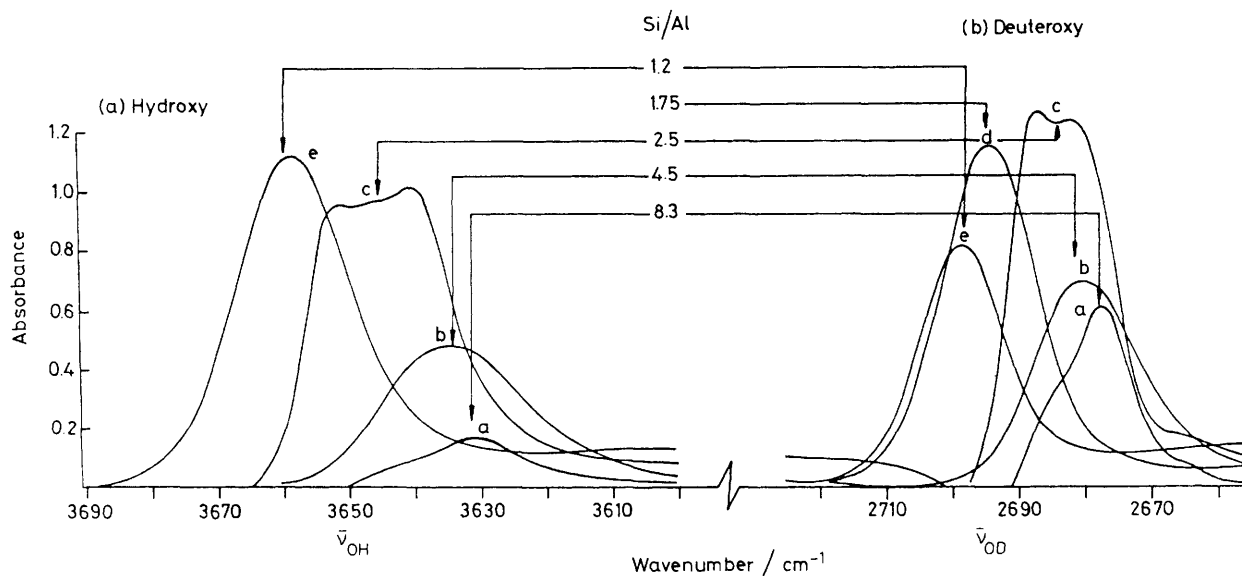


Figure 1. Deconvoluted h.f. i.r. hydroxy (a) and deuterioxy (b) stretching bands of H-Y and NaH-X zeolites; Si/Al ratios from 1.2 to 8.3.

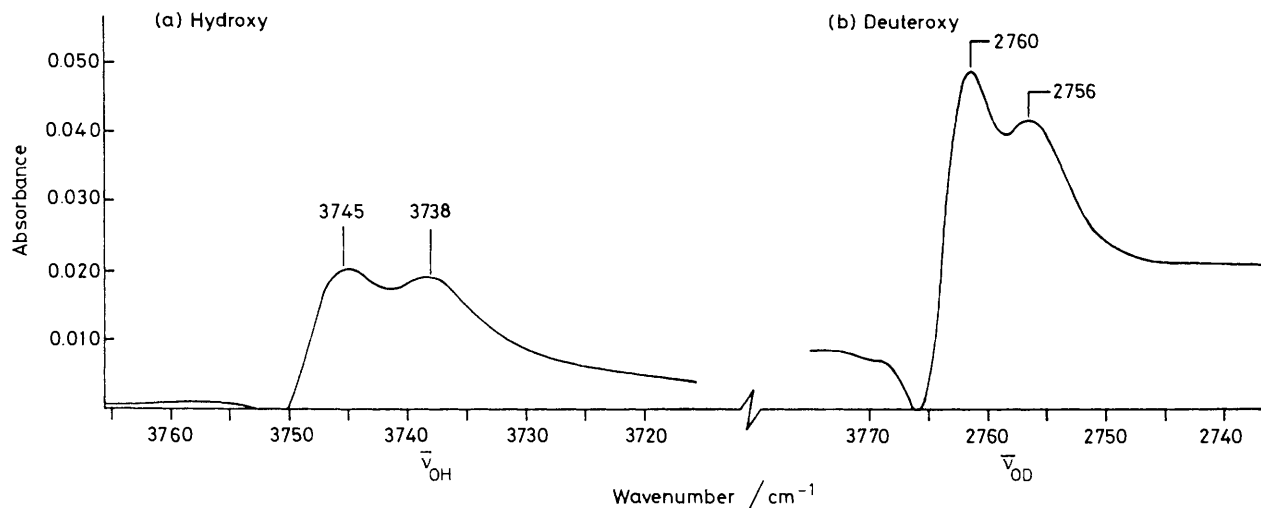


Figure 2. Deconvoluted i.r. hydroxy (a) and deuterioxy (b) stretching bands for chain terminating (HO/DO)-Si \equiv groups in H-Y zeolite (Si/Al = 4.5) dealuminated using (NH₄)₂SiF₆.

cannot influence the deuteriated spectra and since results using a very careful and complete purging of the system with dry air give deconvoluted spectra for the hydroxy region (Figure 1a) which are closely analogous to the corresponding OD spectra (Figure 1b). When considering the properties of zeolites dealuminated with SiF₆²⁻ it is possible that inhomogeneity in composition may affect the results, but this is most unlikely for the parent NH₄-Y (Si/Al = 2.5). At this point, therefore, it is clear that results in our first communication³ are complicated by incomplete compensation of water vapour bands and they appear to emphasise strongly the non-cooperative nature of zeolite hydroxy groups by identifying several components in the h.f. band. Moreover, the role of water vapour has been confirmed by admitting it to a completely dry spectrometer.⁵ The present results, however, do provide evidence for separate components contributing to the overall hydroxy band, as required by a localized model for Brønsted sites, but a quantitative evaluation requires further work.

In the case of silanols (HO-Si \equiv) deconvolution (Figure 2) clearly reveals two separate bands with $\bar{\nu}_{OH} = 3745$ and 3738 cm⁻¹, and corresponding bands $\bar{\nu}_{OD} = 2760$ and 2756 cm⁻¹, for zeolite Y dealuminated with SiF₆²⁻. The band at 3745 cm⁻¹ is assigned to terminal (HO-Si \equiv) in zeolites or in hydrated silica⁴ so that the band at 3738 cm⁻¹ may be assigned to internal silanols arising from incomplete substitution of silicon during treatment with SiF₆²⁻. This assignment coincides

with that by Dakta⁶ for the internal silanols in H-ZSM-5. Internal silanols in H-ZSM-5 have been identified, using ¹H and ²⁹Si cross-polarisation m.a.s.-n.m.r.,⁷ as HOSi(OSi \equiv)₃ and to a lesser extent (HO)₂Si(OSi \equiv)₂ units.

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References

- 1 V. B. Kazansky, in 'Structure and Reactivity of Modified Zeolites,' eds. P. A. Jacobs, N. I. Jaeger, P. Jiru, V. B. Kazansky, and G. Schulz-Ekloff, Elsevier, 1981, p. 61.
- 2 D. Dombrowski, J. Hoffman, J. Fruwert, and T. Stock, *J. Chem. Soc., Faraday Trans. 1*, 1985, **81**, 2257.
- 3 J. Dwyer, K. Karim, W. Kayali, D. Milward, and P. J. O'Malley, *J. Chem. Soc., Chem. Commun.*, 1988, 594.
- 4 J. W. Ward, in 'Zeolite Chemistry and Catalysis,' ed. J. A. Rabo, ACS Monograph 171, 1976, p. 118.
- 5 N. E. Thompson, unpublished work.
- 6 J. Dakta and E. Tuznik, *Zeolites*, 1985, **5**, 230.
- 7 G. L. Woolery, L. B. Alemany, R. M. Dessau, and A. W. Chester, *Zeolites*, 1986, **6**, 14.