

## NOTE

## The Interpretation of the Multiplet Band Structure of the $\nu(\text{OH})$ Stretching Frequencies of Silica and Alumina Surfaces

The application of infrared spectroscopy to the study of adsorption processes has provided a detailed understanding of the nature of the active sites on adsorbent surfaces and of the species which occur during the adsorption of a variety of materials upon them. The surfaces which have been studied most are those of high area silicas and aluminas (see, for example, review monographs by Little (1) and Hair (2)). In all cases the  $3\ \mu$  spectral region is characterized by multiplet frequencies which are usually attributed to surface hydroxyl groups of several kinds.

For example, absorption bands at 3800, 3744, and 3700  $\text{cm}^{-1}$  found (3) on alumina aerogel are considered to arise from hydroxyl groups in different environments. The highest frequency is assigned to a hydroxyl group with four oxide ions as nearest neighbors, the middle frequency to one with two nearest neighbor oxide ions, and the lowest frequency to a hydroxyl group with no adjacent oxide ions. With another sample of alumina additional surface hydroxyl groups were identified (4) at 3780 and 3733  $\text{cm}^{-1}$  and assigned to the presence of three and one nearest neighbor oxide ions respectively. Zeolites (5) have also been found to have three or more bands which are interpreted as arising from three types of surface hydroxyl groups; there is however, no complete agreement for their assignments. The central band, about 3690  $\text{cm}^{-1}$ , is close to the 3710  $\text{cm}^{-1}$  feature observed on alumina and is therefore attributed to an aluminol grouping. The band at 3740  $\text{cm}^{-1}$  correlates with the free silanol vibration found on silica gel but is not perturbed by physically

adsorbed substances; its exact origin is thus uncertain. Many other examples exist (1, 2) of multiplet  $\nu(\text{OH})$  frequencies all of which utilize an interpretation based on each band arising from (a) differently bound hydroxyl groups, or (b) hydroxyl groups in different environments.

The purpose of this note is to point out an alternative interpretation which is equally valid in most cases and which does not appear to have been considered by adsorption workers utilizing the infrared technique. This is that multiplet frequencies in the  $\nu(\text{OH})$  stretching region can arise from combination sum-and-difference modes of low frequency vibrations.

Such an interpretation has been used by Hexter (6, 7) to explain the structure in the hydroxyl band of brucite observed by Mara and Sutherland (8). The spectrum of crystalline brucite  $[\text{Mg}(\text{OH})_2]$  shows the amazing feature of no less than 16 absorption lines in the region 2-5  $\mu$ , whereas the theory of infrared spectra of crystals would predict only one in this region. This pattern of frequencies has been interpreted (6, 7) in terms of "heads" at frequency separations from the center of the spectrum of simple multiples of a derived low-frequency librational mode. An analysis of the similar spectrum of portlandite  $[\text{Ca}(\text{OH})_2]$  produced perfectly compatible results. A similar interpretation has also been invoked by Hallam and Jones (9) to explain satellite bands observed in the  $\nu(\text{OH})$  region for the vapour spectra of some fluoroalkanols. In this case sum-and-difference modes ( $\nu_{(\text{OH})} \pm \nu_{\text{low}}$ ) are observed, flanking the main  $\nu(\text{O}-\text{H})$  peak at 3660  $\text{cm}^{-1}$  (for trifluoro-

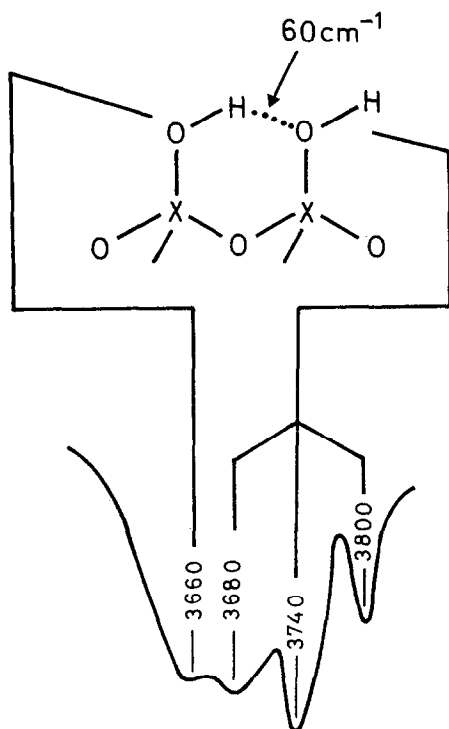


Fig. 1. Typical pattern of  $\nu(\text{OH})$  frequencies, interpreted in terms of two types of surface OH groups. ethanol vapour); the low frequency mode  $\nu_{\text{low}}$  at  $\sim 120 \text{ cm}^{-1}$  is the H-bond frequency or a torsional mode.

If then we consider a hypothetical spectral pattern of a surface, as depicted in Fig.

1, it could be interpreted in terms of only two types of surface OH groups, two of the four features being attributed to sum-and-difference modes of a hydrogen bond frequency at  $60 \text{ cm}^{-1}$ .

#### REFERENCES

1. LITTLE, L. H., "Infrared Spectra of Adsorbed Species," Academic Press, New York (1966).
2. HAIR, M. L., "Infrared Spectroscopy in Surface Chemistry," Dekker, New York (1967).
3. PERI, J. B., AND HANNAN, R. B., *J. Phys. Chem.* **64**, 1526 (1960).
4. PERI, J. B., *J. Phys. Chem.* **69**, 211 (1965).
5. CARTER, J. L., LUCCHESI, P. J., AND YATES, D. J. C., *J. Phys. Chem.* **68**, 1385 (1964).
6. HEXTER, R. M., AND DOWS, D. A., *J. Chem. Phys.* **25**, 504 (1956).
7. HEXTER, R. M., *J. Opt. Soc. Am.* **48**, 770 (1958).
8. MARA, R. T., AND SUTHERLAND, G. B. B. M., *J. Opt. Soc. Am.* **43**, 1100 (1953); **46**, 465 (1956).
9. HALLAM, H. E., AND JONES, D., paper presented at Sixth European Congress of Molecular Spectroscopy, Copenhagen (1964) *Conference Abstracts*, p. 86; JONES, D., Ph.D. thesis, University of Wales (1965).

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