

NOTES

Reevaluation of Proton Positions in Hydrogen Faujasite

Protons attached to oxygens of the aluminosilicate framework are believed to take part in catalytic reactions of molecules sorbed in zeolite molecular sieves. Numerous infrared studies utilized the T-OH stretching frequencies (T denotes tetrahedral Si and Al) to infer the positions of the framework hydroxyls, and data from other techniques provided supporting evidence. Olson and Dempsey (1) attempted to locate protons in dehydrated hydrogen faujasite prepared by thermal decomposition of the ammonium-exchanged form. From single-crystal X-ray diffraction data, they obtained the following T-O distances and standard deviations: T-O1, 1.653 ± 0.002 Å; T-O2, 1.634 ± 0.001 ; T-O3, 1.663 ± 0.002 ; T-O4, 1.623 ± 0.002 . By assuming that the T-OH bond is 0.08 Å longer than a T-O bond, they concluded that the 59 protons/unit cell were attached to O1 and O3. From an X-ray diffraction study of powders of $\text{Na}_2\text{H}_{54}\text{-Y}$ zeolite, Gallezot and Imelik (2) found long T-O distances for O(2) and O(3), but refinement of parameters from cubic powder patterns is so uncertain because of peak overlaps that the Olson-Dempsey data are preferred.

Many faujasite-type zeolites showed three infrared peaks ascribed to T-OH [e.g. (3)], namely, a minor one at 3750 cm^{-1} assigned to surface species, and two strong bands at 3650 [high frequency (HF) band] and 3550 cm^{-1} [low frequency (LF) band]. The HF band was assigned to a proton pointing into the supercage from O1 and the LF band to a proton pointing into the sodalite cage from O3 because (a) molecules too large to enter the sodalite unit per-

turbed only the HF band (4), and (b) the LF band developed preferentially at high exchange levels of H^+ (actually NH_4^+ originally) for Na^+ (5). However, a high-resolution infrared study by Jacobs and Uytterhoeven (6) of the hydroxyl bands of the dehydrated hydrogen zeolites X and Y showed that the LF band was much broader than the HF band and was asymmetric, implying that it was composed of more than one peak.

We now show how the Olson-Dempsey and Jacobs-Uytterhoeven data can be reconciled by adjusting the T-O distances for perturbations related to framework geometry thereby allowing protons to be attached to all four types of framework oxygens.

The correlations between T-O distances and both the T-O-T and O-T-O angles of framework silicates can be interpreted in terms of molecular orbital and ionic bonding. A comprehensive study of feldspars by Gibbs *et al.* (7) is instructive in showing the relative contributions of Si, Al ordering, cation bonding, and framework geometry to the T-O distances of aluminosilicate frameworks. Similar effects occur in the zeolite mordenite (8, 9, 10), especially for H-mordenite. For each T-O distance, the deviation $\Delta(\text{T-O})$ from the mean of the four distances for that tetrahedron was calculated and plotted against (a) the secant of the adjacent T-O-T angle, and (b) the mean of the three adjacent O-T-O angles (Fig. 1). A good linear correlation was found for both plots with the following equations and correlation coefficients:

TABLE 1
Observed and Adjusted T-O Distances in H-Faujasite^a

	Observed	T-O-T	$\langle\text{O-T-O}\rangle_3$	a	b	c
T-01	1.653(2)	138.6(3)	109.17	1.643	1.647	1.645
T-02	1.634(1)	147.4(3)	109.57	1.644	1.635	1.639
T-03	1.663(2)	139.7(3)	108.77	1.657	1.652	1.654
T-04	1.623(2)	145.3(3)	110.37	1.629	1.637	1.633

^a Columns a, b and c show values adjusted by Eqs. (4), (5), and (6). Error in parentheses to same significance level as last figure. Distances in Å, angles in degrees.

$$\Delta(\text{T-O}) = -0.13249 \sec(\text{T-O-T}) - 0.15238 \langle\text{O-T-O}\rangle_3 \quad (1)$$

$$\Delta(\text{T-O}) = -0.01513 \langle\text{O-T-O}\rangle_3 + 1.65564 \quad (2)$$

A double regression gave a slightly better correlation coefficient 0.967 and the equation,

$$\Delta(\text{T-O}) = -0.05885 \sec(\text{T-O-T}) - 0.00904 \langle\text{O-T-O}\rangle_3 + 0.92155 \quad (3)$$

The secant of T-O-T gives a better correlation than the angle itself, and its use can be justified in terms of molecular orbital theory (7, 10). Use of $\Delta(\text{T-O})$ eliminates the effect of Si, Al distribution among the various tetrahedra. There are no exchangeable cations to affect the T-O distances. Figure 1c shows good agreement between observed values for $\Delta(\text{T-O})$ in H-mordenite and those calculated from the double-regression equation, with the implication that the protons are randomly distributed among the framework oxygens within experimental error. Similar trends have been found in other framework silicates, and all have been semiquantitatively explained by semi-empirical extended Hückel molecular orbital calculations of T_5O_{16} clusters with T-O-T and O-T-O angles set at the observed values but with all T-O distances set equal (7, 10).

If the above correlations for H-mordenite also apply to H-faujasite, the T-O distances of the latter can be adjusted for the perturbation from its framework anisotropy before interpreting $\Delta(\text{T-O})$ in terms of

proton positions. Table 1 shows adjusted T-O distances for H-faujasite using the slopes of the regression equations to give the following adjustments

$$-0.13249[\sec(\text{T-O-T}) - \text{mean sec}(\text{T-O-T})] \quad (4)$$

$$+0.01513[\langle\text{O-T-O}\rangle_3 - \text{mean}\langle\text{O-T-O}\rangle_3] \quad (5)$$

$$-0.05885[\sec(\text{T-O-T}) - \text{mean sec}(\text{T-O-T})] + 0.00904[\langle\text{O-T-O}\rangle_3 - \text{mean}\langle\text{O-T-O}\rangle_3] \quad (6)$$

Note that only the slope, and not the intercept is used. No matter which equation is used, the range of adjusted T-O distances is less than that for the unadjusted T-O distances (0.028, 0.015, and 0.019 vs 0.040 Å). The T-O3 distance remains the longest, but the relative order of the other three distances varies with the type of adjustment. Because regression Eq. (3) gave the best fit for H-mordenite, we shall use adjusted values from it (Table 1, col. c) to estimate the proton distribution in H-faujasite assuming 59 protons/unit cell and that T-OH is longer than T-O by 0.08 Å. For a linear relation between bond length and proton population, the predicted proton populations are: O1, 17; O2, 10; O3, 28; O4, 3.

Jacobs (11) estimated the number of protons attached to the framework oxygens from the area of the infrared absorption peak while taking into account the differences in the integrated absorption coeffi-

cients (3). For a 90% exchanged sample the following distribution was obtained: O1, 15.6; O3, 18.0; and O2 + O4, 16.7. Taking into account that on further exchange the protons are preferentially attached to O3 (5, 6), extrapolation to full exchange gives O1, 15.6; O3, 23.6; and O2 + O4, 16.7. This agrees satisfactorily with the present estimates of 17, 28 and 13 when account is taken of the uncertainties of the relation between bond length and framework geometry, especially when protons are attached to framework oxygens.

We conclude by emphasizing the uncertainties in the present calculation, but suggest that it can reconcile the difference between the earlier interpretations of the infrared and X-ray data. Particularly desirable would be a single-crystal neutron diffraction study to locate the protons directly. Natural faujasite crystals over 1 mm long are available but whether they would survive ion-exchange with NH_4^+ and dehydration to H-faujasite is not known. In

the meantime, we suggest that there is some uncertainty in the detailed location of protons in H-faujasite and synthetic equivalents, though the basic concept of protons projecting into both the supercage and the sodalite cage still stands.

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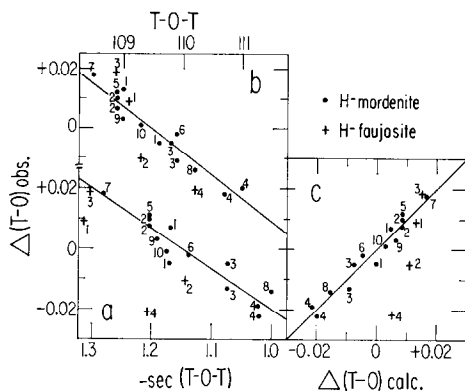


FIG. 1. Correlations between observed $\Delta(T-O)$ and (a) $-\text{secant}(T-O-T)$, (b) $(O-T-O)_a$, and (c) $\Delta(T-O)$ calculated from regression Eq. (3). Distances in Å. Small numbers are labels for oxygen atoms; note that some oxygens have two independent T-O distances, whereas others have only one. In (a) and (b), the lines are the regression Eqs. (1) and (2). In (c), the line represents equality of observed and calculated $\Delta(T-O)$. Data for H-faujasite are plotted to show that they do not obey the regressions for H-mordenite, and hence must require an additional contribution.