Location of Cations in Zeolites by Infrared and Raman Spectroscopy

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Summary For various hydrated monovalent cation-exchanged forms of the synthetic zeolite Linde A a linear relationship has been found between the frequency of some of the framework vibrations and the reciprocal of the sum of the cation and framework oxygen ionic radii; this regularity implies that the Tl^+, Ag^+, and Li^+ ions probably occupy similar positions in the crystal structures to those determined for the Na^+ and K^+ ions by *X*-ray crystallography.

It is well known that the catalytic and molecular sieve properties of zeolites are markedly affected by the particular cation present, which is required to balance the negative framework charge. Hence, knowledge of the siting of the cations in zeolites is important in understanding zeolitic properties. We have attempted to gain information on cation positions indirectly by studying their effect on the modes of vibration of the alumino-silicate framework.

Raman and i.r. spectra of hydrated Li^+, Na^+, Ag^+, K^+, and Tl^+ exchanged forms of Linde A have been measured in the region 1500—200 cm^{-1}. The most pronounced effect of the exchangeable cation is its influence on frequency and intensity of the vibrational modes of the $Si(Al)O_4$ tetrahedral primary framework building units. Tentative vibrational assignments are based on i.r. studies by Flanigen *et al.*,[1] on a wide range of zeolites with different framework structures. According to these authors, the $Si(Al)O_4$ symmetric stretching modes, $\nu_1(A_1)$ should lie between *ca.* 650 and 720 cm^{-1}, and $Si(Al)O_4$ bending modes $\nu_4(T_2)$ between 420 and 500 cm^{-1}.[1] However, our Raman spectra show that the bands in the ν_1 symmetric region (670—736 cm^{-1}) are consistently lower in intensity than those in the ν_4 region (Figure 1), whereas one normally expects more relative intensity from symmetric modes in Raman spectra. At present, we shall use these tentative assignments for discussion purposes.

The frequencies of the $\nu_1(A_1)$ symmetric stretching vibration and the $\nu_4(T_2)$ bending vibration of the $Si(Al)O_4$ tetrahedra can be linearly correlated with the reciprocal of the sum of the cation and framework oxygen ionic radii, $1/[r(\text{cation}) + r(O^{2-})]$ (see Figure 2).

X-Ray diffraction studies on hydrated NaA[2,3] and KA[4] have shown that only eight of the twelve exchangeable cations appear to interact significantly with the framework. These eight cations are all sited on the three-fold axes of the cubic unit cell near the centres of the sodalite cage six-rings. Since these cations would be expected to have the greatest influence on the lattice vibrations, the observed frequency shifts are therefore an approximate measure of the distance between the cation and the sodalite cage six-ring oxygen atoms.

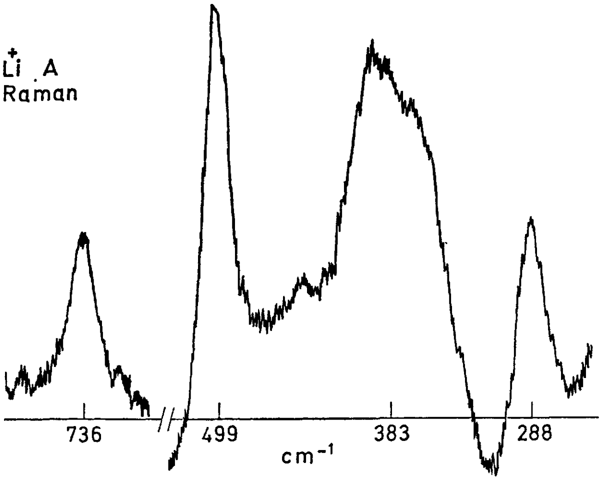

Figure 1. *Raman spectrum of* Li^+ *exchanged Linde A from* 250—785 cm^{-1}; *weaker bands are also observed at* 209, 940, 983, *and* 1074 cm^{-1}. *Spex Ramalog*, 5145 Å *laser excitation with* 100 *mW at the sample*, 10 cm^{-1} *resolution, scan speed* 100 cm^{-1} *min*.

Thus for the Li^+, Ag^+, and Tl^+ exchanged forms of Linde A the cations are probably also at these sites at a position on the three-fold axes such that the distance between the cation and the three closest six-ring oxygen atoms is approximately equal to the sum of their ionic radii (*i.e.* TlA, 2·80; AgA, 2·66; LiA, 2·00 Å).

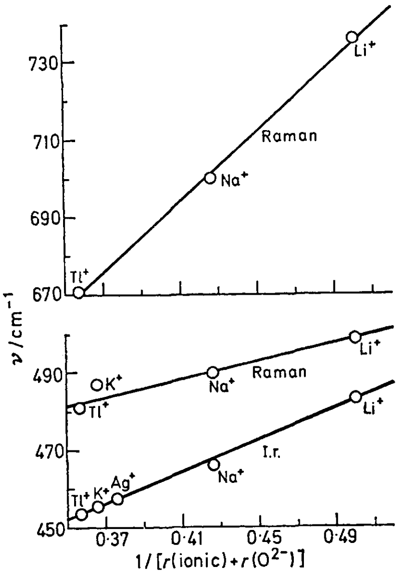

FIGURE 2. *Frequency shifts of lattice vibrations for monovalent exchanged Linde A as observed by Raman and i.r. spectroscopy. (The Raman spectra of* K^+ *and* Ag^+ *forms were so weak that only the absorption at* 487 *cm*$^{-1}$ *for the* K^+ *form was observable.)*

The linear relationship between the inverse of the cation–framework distance and the frequency shifts of the lattice vibrations indicates that the perturbation is due to the electrostatic potential of the cation at the framework. This is further supported by the fact that the frequencies are shifted to higher wavenumbers with decreasing ionic radius.

As shown in Figure 1, if the observed Raman bands in the region 480—500 cm^{-1} are due to the $\nu_4(T_2)$,Si(Al)O_4 bending vibration then they are all shifted to higher wavenumbers relative to the i.r. This shift might be understood on the basis that the observed absorption profiles in both i.r. and Raman are an envelope of these unresolved vibrations from SiO_4 and AlO_4^- tetrahedra. Due to the differences in polarisability and dipole moment of these groups their relative contributions to the observed composite Raman and i.r. bands would be expected to be different.

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