Ethylene Adsorbed by Silver Exchanged 13X Zeolite; an Inelastic Neutron Scattering Study

By JOSEPH HOWARD, THOMAS C. WADDINGTON,* and CHRISTOPHER J. WRIGHT†
(*Department of Chemistry, University of Durham, and †A.E.R.E., Harwell*)

Summary Vibrations of ethylene on a zeolite surface have been observed, at two different coverages, by incoherent inelastic neutron scattering.

USING the 6H spectrometer[1] at A.E.R.E., Harwell, incoherent inelastic neutron scattering spectra of ethylene adsorbed on silver-exchanged 13X zeolite have been measured. The zeolite is relatively transparent to neutrons but it will absorb ethylene so that the total sample cross section increases by up to twelve times. The ethylene exists as discrete molecules within the zeolite framework[2] and at 110 K the strong interaction between the silver ions and the ethylene leads to sharp vibrational transitions associated with the motion of the ethylene with respect to the surface. To our knowledge this is the first spectroscopic observation of such vibrations for a molecule other than water.[3] The zeolite was ion-exchanged repeatedly with $AgNO_3$ solution,[4] washed, and then degassed to a final pressure below 5×10^{-6} Torr at 450 °C. Spectra were measured, at a pressure of 500 Torr of ethylene and again after the same sample had been evacuated for 30 min. Isotherm data show that under these experimental conditions 8·0 and 4·4 ethylene molecules respectively are adsorbed per supercage.[5] These numbers correspond closely to the numbers of silver ions of types II plus III (8·75) and of type III (4·75), per supercage,[6,7] so it is deduced that at these pressures type II plus III sites and type III sites respectively are occupied by the ethylene. The heats of adsorption of ethylene on the type III and type II sites are 18·1 and *ca.* 12·5 kcal mol^{-1} respectively.[2]

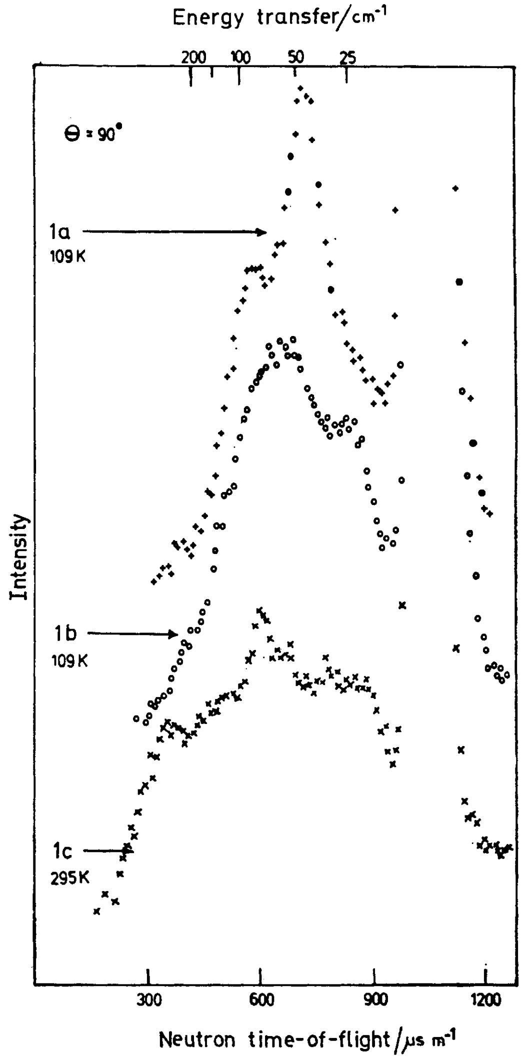

FIGURE 1. Neutron time-of-flight spectra of (a) ethylene adsorbed on Ag–13X zeolite at low pressure, (b) ethylene adsorbed on Ag–13X zeolite at a pressure of 500 Torr, and (c) Ag–13X zeolite.

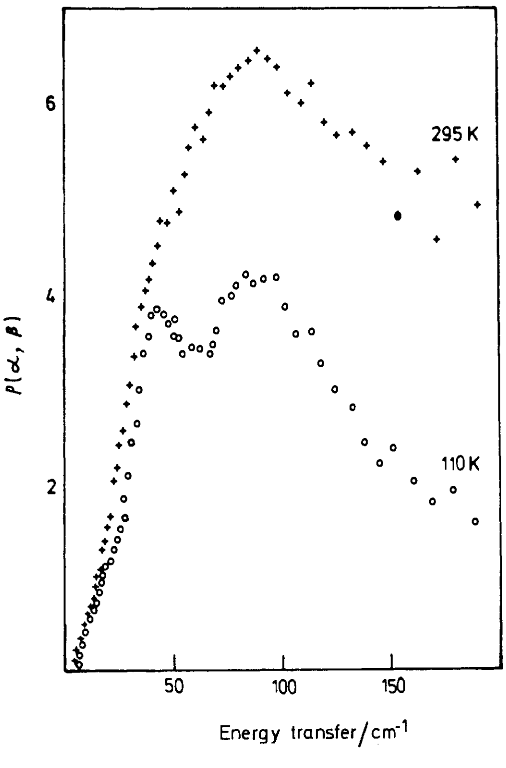

FIGURE 2. $P(\alpha,\beta)$ for ethylene adsorbed at low pressure, on Ag–13X zeolite at 295 K and 110 K.

The spectra in the Figure 1 show the corrected neutron counts, with sample container and degassed zeolite spectra subtracted in the cases of Figures 1a and 1b, and the sample container subtracted in the case of Figure 1c, plotted as a function of scattered neutron time-of-flight. For the ethylene adsorbed on type III sites a transition is found at 40 cm^{-1} (Figure 1a). At the higher pressure of ethylene, when type II sites are also occupied, transitions occur at 56 and 22 cm^{-1} (Figure 1b). Our interpretation of this spectrum is that a vibration of the more weakly bound species, on type II sites, occurs at 22 cm^{-1} and a vibration of the more strongly bound species, on the type III sites, occurs at 56 cm^{-1}. These vibrations may well be hindered rotations of the ethylene molecule as observed in the neutron spectra of model compounds;[8,9] however measurements using deuteriated samples of ethylene are in progress to check this hypothesis. The vibration of ethylene on the type III site has shifted from 40 to 56 cm^{-1} on increasing the coverage, perhaps owing to steric crowding in the supercage.

We have investigated the possibility that the peak at 80 cm^{-1} in Figure 1a is the first overtone of the vibration whose fundamental occurs at 40 cm^{-1}. The intensity of a fundamental and a first overtone, both of energy ω, are proportional to T and T^2 respectively. Figure 2 shows that with increase in temperature the Boltzmann factor-compensated scattering $P(\alpha,\beta)$‡ at 80 cm^{-1} increases considerably faster than that at 40 cm^{-1}. This is to be expected if a significant proportion of the intensity, at 80 cm^{-1}, is due to a first overtone. At constant temperature the intensities of a fundamental and first overtone, both of energy ω, are represented by $A\exp(-Q^2C)$ and $BQ^2\exp(-Q^2C)$ respectively. We have separated one and two quantum scattering by taking $P(\alpha,\beta)$ data obtained at constant energy transfer, ω, and different momentum transfers, Q, and fitting them to the expression $(A + BQ^2)\exp(-Q^2C)$.[10]

This separation confirms the presence, at 80 cm^{-1} of both a fundamental and first overtone with their contributions to the intensity being approximately equal at 110 K. However, because of the poor resolution exact quantitative comparisons cannot be made. The spectrum of the degassed zeolite (Figure 1c), which arises from coherent scattering, shows features at a range of energies down to 15 cm^{-1}, and because of this we have to allow the possibility that the measured vibrations at 80 and 20 cm^{-1} are due to zeolite vibrations which differ between the type II and III sites, and which are being amplified by interaction with the adsorbed gas.

However, this fails to explain the sharp peak at 40 cm^{-1} in the case of the strongly bound ethylene, since no corresponding sharp feature occurs in the zeolite spectrum.

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‡ $P(\alpha,\beta) = [2\beta\sinh(\beta/2)/\alpha] \times [(\delta^2\sigma/\delta\Omega\delta\omega)k_B\mathrm{T}] \times [(4\pi/\sigma)\exp(\beta/2)]$ where $\alpha = h^2Q^2/2Mk_BT$; $\beta = h\omega/k_BT$; k_B, the Boltzman constant; M, the mass of the scattering atom; T, the absolute temperature; σ, the cross-section; and Ω, the angle of scatter.

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