A Family of Ionic Clusters in Zeolite Na-X

Paul A. Anderson and Peter P. Edwards

University Chemical Laboratory, Lensfield Road, Cambridge CB2 1EW, UK

Zeolite Na-X plays host to Na_5^{4+} and Na_6^{5+} clusters, each consisting of a single valence electron interacting with a number of ions.

The ESR spectrum of the compound resulting from the interaction of sodium vapour with zeolite Na-X was first reported in 1966 by Rabo *et al.*,[1] who found it to consist of a hyperfine pattern of nineteen lines, which they attributed to an Na_6^{5+} paramagnetic centre, analogous to the Na_4^{3+} previously observed in Na-Y by Kasai.[2] With Kasai[3] himself later reporting that different samples of Na/Na-X yielded an ESR spectrum containing between sixteen and nineteen lines, its original diagnosis as Na_6^{5+}, though widely accepted, was never entirely satisfactory.

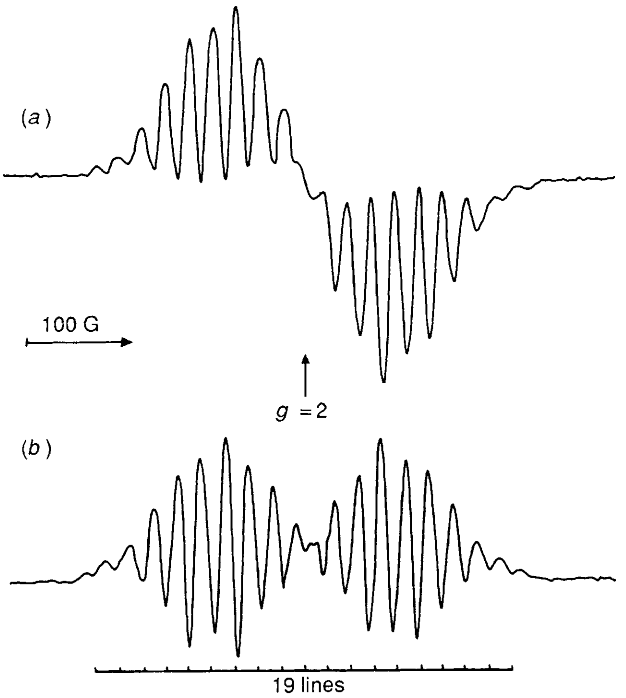

Fig. 1 The ESR spectrum at 298 K of Na/Na-X: (*a*) first derivative, and (*b*) second derivative

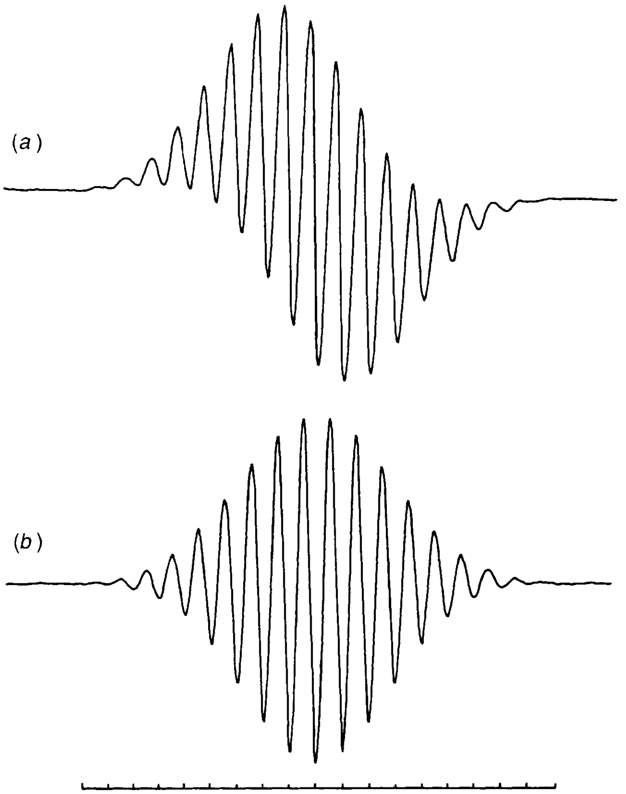

Fig. 2 The simulated ESR spectrum for an electron interacting with six equivalent sodium nuclei ($Na_6{}^{5+}$ centre): (*a*) first derivative, and (*b*) second derivative

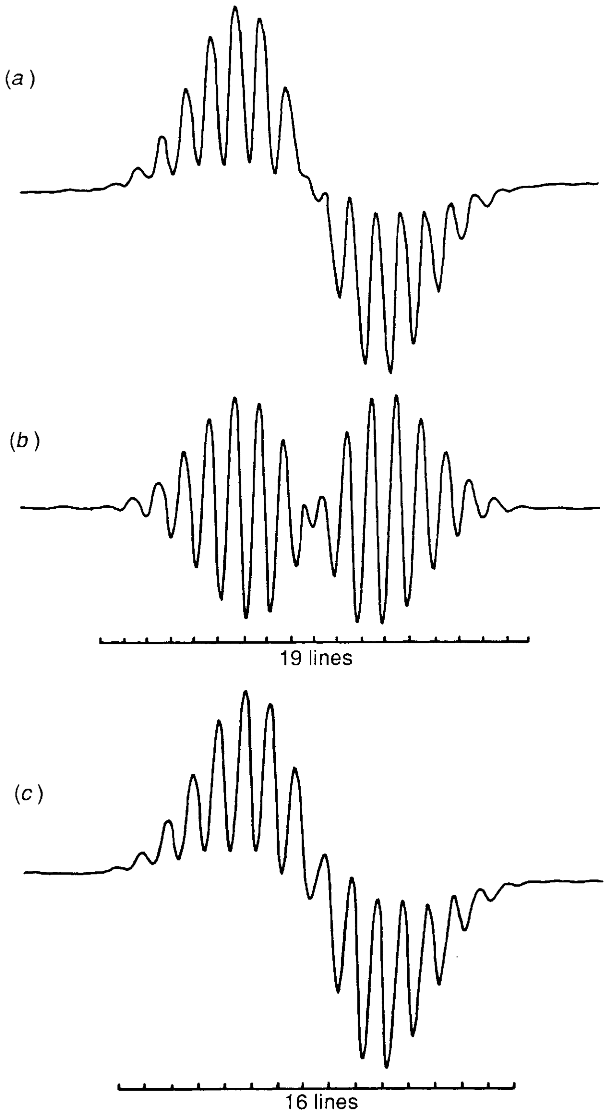

Fig. 3 The simulated ESR spectrum for an equal mixture of $Na_5{}^{4+}$ and $Na_6{}^{5+}$ centres: (*a*) first, and (*b*) second derivative. Also shown (*c*) is the simulated first derivative spectrum with a ratio of $Na_5{}^{4+}$ to $Na_6{}^{5+}$ of 1.25.

We have recorded the ESR spectra of a large number of M/Na-X compounds, where M = Na, K or Rb. The reactions were carried out in sealed, evacuated quartz reaction tubes, as described earlier by Harrison *et al.*,[4] and first and second derivative ESR spectra were recorded on a Varian E-109 spectrometer operating at X-band frequencies with 100 kHz field modulation; a typical example is shown in Fig. 1. The spectrum consisted of nineteen lines centred at $g = 2.0022 \pm 0.0003$ with a hyperfine splitting $a = 25.0 \pm 0.5$ G, which was slightly reduced at low temperature. For a single electron interacting with n equivalent nuclei of spin I, a hyperfine pattern consisting of $(2nI + 1)$ lines is expected. The first and second derivative spectrum simulated for an electron interacting with six sodium nuclei, using the linewidth and hyperfine parameter of the observed spectrum, is shown in Fig. 2. Although consisting of nineteen lines, it bears little resemblance to observed spectra such as those in Fig. 1; for, whereas the lines of the simulated spectrum grow in intensity towards the middle of the spectrum, those of the experimental spectrum increase at first and then decrease to near zero at the centre. In addition, like Kasai we have found that the number of hyperfine lines in the splitting pattern is often unclear. In one respect this is not uncommon, since the outer lines of a multiplet are the weakest and often indistinct, but the striking feature in this instance is that in some cases the spectrum appears to have a line at its centre of symmetry, while in others the lines straddle the free spin position. The most important pointer to the origin of these effects, however, is the comparative constancy of the overall profile regardless of how many lines the spectrum appears to contain. For example,

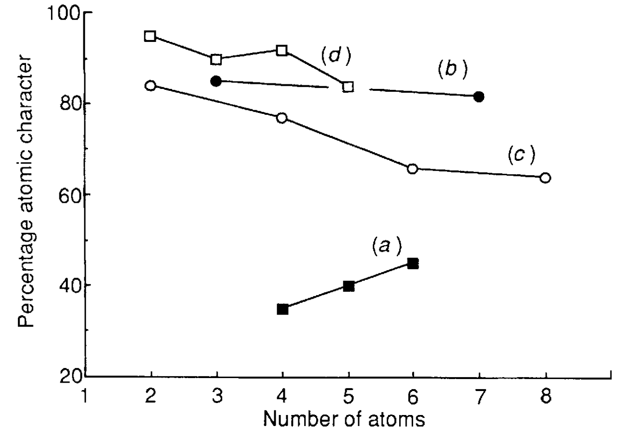

Fig. 4 The percentage atomic character as a function of the number of atoms for various types of cluster: (*a*) $Na_n^{(n-1)+}$ in Na-X, (*b*) Na_n in solid argon, (*c*) Ag_n^+ in zeolite A, and (*d*) $Ag_n^{(n-1)+}$ in frozen alcohols. (For references, see text.)

Fig. 3 shows simulations of the first and second derivative spectrum expected from a sample containing some electrons interacting with five sodium nuclei ($2nI + 1 = 16$ lines) and an equal number of others interacting with six ($2nI + 1 = 19$ lines). Not only is the simulated spectrum very similar to that shown in Fig. 1, but a slight adjustment in the relative proportion of the two centres enables a spectrum apparently consisting of sixteen lines to be obtained [Fig. 3(*c*)]. With the occasional addition of an underlying singlet, similar to those reported in other sodium zeolites,[4] virtually all the spectra we have observed from M/Na-X could be simulated.

The observation of such spectra even in samples exposed to extremely low concentrations of metal vapour strongly suggests that the centres responsible are, like Na_4^{3+}, single electron traps, and from the simulation studies the obvious conclusion is that these compounds contain both Na_5^{4+} and Na_6^{5+} clusters. From comparisons of real and simulated spectra it is clear that the ratio of Na_5^{4+} to Na_6^{5+} did not vary much, ranging approximately between 1.0 and 1.25. Better simulations were obtained if Gaussian rather than Lorentzian lines were used, suggesting that the lines may, like those of Na_4^{3+},[5] be inhomogeneously broadened. Although the reduction of Na-X by organolithium reagents is known to produce the Na_4^{3+} cluster,[6] attempts to simulate the spectrum of Na/Na-X including a contribution from Na_4^{3+} as well as the two higher centres only produced adequate results if the proportion of Na_4^{3+} included was small. This lack of firm evidence for the more usual Na_4^{3+} suggests that the new clusters may well also be located in the sodalite cage.

The quantity known as the 'percentage atomic character' of the clusters can be deduced from the comparison of their hyperfine splittings with that of a free atom.[7] The hyperfine splitting of Na_6^{5+} is 7.5% of that of the sodium atom, but the unpaired electron interacts with six sodium ions so the total value for Na_6^{5+} is 45%. Values for all three centres in Na-X are plotted as a function of the number of participating sodium atoms in Fig. 4. Also shown are data for neutral sodium clusters in solid argon,[8] and ionic silver clusters, in zeolite A[9] and in frozen alcohols.[10] For the neutral sodium clusters the values are high, but slightly lower than 100% owing to hybridization. Similar values obtain for a range of singly charged silver clusters in zeolite A, and even for several ionic silver clusters in frozen alcohol solutions, which like the centres in sodium zeolites have only one valence electron. In the case of silver the relatively large hyperfine splittings are an indication that the valence electrons remain closely associated with the cations and emphasize the molecular nature of the clusters. In contrast, the much lower values for the ionic clusters in Na-X indicate a much looser association between the ions and the valence electron, and are in fact typical of those measured for sodium F-centres.[11]

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