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Infrared spectra of HCl adsorbed on high-area alkali-metal halides: dependence of the effective surface ionicities on the ionic radius ratio

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The adsorption of HCl on the surfaces of a wide range of high-area alkali-metal halides gave broad HCl absorption bands caused by hydrogen bonding to the surface halide ions. The decrease in wavenumbers of the absorptions at near-monolayer coverage, $\Delta\nu$(HCl), relative to the value for gas-phase HCl, used as a measure of the strength of the hydrogen bonding, showed systematic variations as a function of anion for a given cation, or *vice versa*. The values of $\Delta\nu$(HCl) were shown to correlate with the radius ratio, $r^+ : r^-$, of the anions. A scale of the effective surface ionicities of the alkali-metal halides, relative to CsCl assumed to have unit ionicity, was derived from the relative $\Delta\nu$(HCl) values. The resulting scale gives a linear correlation with the charge separations in the gaseous diatomic alkali-metal halides as calculated earlier from the analysis of their dipole moments.

Introduction

In earlier publications from this laboratory[1,2] studies were made of the adsorption of hydrogen halides on alkali-metal surfaces using the technique of infrared spectroscopy. the principal bands obtained were identified as arising from the ν(HX) (X = Cl, Br or I) stretching modes of the hydrohalide molecules hydrogen bonded to halide ions of the surface. The strengths of the hydrogen-bonding interactions, as reflected in the changes in the ν(HX) wavenumbers of the adsorbed molecules relative to that of the hydrohalide in the gas phase, showed regular behaviour. For example, for a series of alkali-metal chlorides, M^+Cl^-, the strength of hydrogen bonding of HCl to Cl^- increased as M^+ followed the sequence Li^+, Na^+, K^+, Cs^+. This is what is to be expected if the increasing matching of the radii of the M^+ ions and Cl^- along the series leads to an increasing ionic character of the crystal structure.

In this paper we use HCl as a single probe in order to investigate more systematically the electron availabilities of the anion sites of a wide range of alkali-metal halide surfaces through the strengths of its hydrogen-bonding interactions. In the earlier work it was found that interactions of a hydrohalide with an ionic alkali-metal halide that was lower in the Periodic Table than that providing the anion, *e.g.* HCl on NaF or HBr on NaCl, led to halogen exchange between the gas phase and the surfaces.[1,2] By choosing HCl as our probe we were hence able to study its interactions with chloride, bromide and iodide, but not with fluoride ions.

Experimental

As in the earlier work,[1,2] high surface area deposits of the alkali-metal halides were prepared by high-temperature sublimation and condensation on a halide window cooled to 82 K. The films prepared in this manner were largely amorphous, but were transformed into quasi-crystalline deposits by annealing for up to 24 h at 193 K using solid CO_2–acetone as refrigerant. Depositions were made in a cylindrical copper chamber with infrared transparent windows. The windows were attached by Araldite epoxy resin to thin copper bellows soldered to the copper cylinder; the flexibility of the bellows avoided stress fracturing of the windows during thermal cycling between 77 K and ambient temperatures. The hermetic adsorption chamber was itself suspended in an external vacuum chamber with infrared windows which acted as a thermal shield during the low-temperature procedures. Both the inner adsorption chamber and the vacuum shield were demountable by ground-glass joints sealed with Apiezon vacuum grease.

Adsorbents were sublimed onto the inner surfaces of the adsorption chamber from a silica cup held within a tantalum wire-spiral furnace coil mounted to the side or below the optical path. Powdered adsorbents were pre-dried at 388 K for extended periods and then pressed into pellets at 15 000 psi for 20 s (1 psi = 6.8947×10^3 Pa) in a sample die held at the same temperature. Very hygroscopic materials were handled in dry nitrogen. Thermocouples of chromel–alumel and copper–constantin were used to measure the temperatures of the furnace cupola and of the window of the adsorption chamber respectively. After final assembly of the full cell, the adsorbent was held at *ca.* 373 K for an extended period during evacuation. The adsorption chamber was then cooled slowly to 82 K with liquid nitrogen. Sublimation was carried out in stages until about a 10% drop in transmission had occurred. Where necessary, the temporary adsorption of CO was used to estimate the area of adsorbent available. The earlier work[1,2] showed that, after annealing, surface areas of such deposits were in the range of 200–240 $m^2\ g^{-1}$. Electron microscopy showed quasi-crystalline deposits; these have been shown to have dominant (100) surface planes.[3]

Hydrogen chloride was adsorbed in controlled volumetric doses up to near saturation at equilibrium pressures of up to 10 Torr (1 Torr = 133.32 Pa); infrared spectra were recorded at each stage. Desorption, with the recording of spectra, was also carried out in stages down to evacuation of the gas phase and then during warming.

The HCl gas (97%) was obtained in a lecture bottle from Matheson. Adsorbents were purchased at the highest advertised purities as follows: BDH Chemicals, KX and NaCl (99.9%), CsBr (99.5%), CsI (99%); Hopkins Williams, CsCl (98%); Koch-Light, RbX series (99.8%). Infrared spectra were recorded between 4000 and 600 cm^{-1} using a Perkin-Elmer 621 spectrometer.

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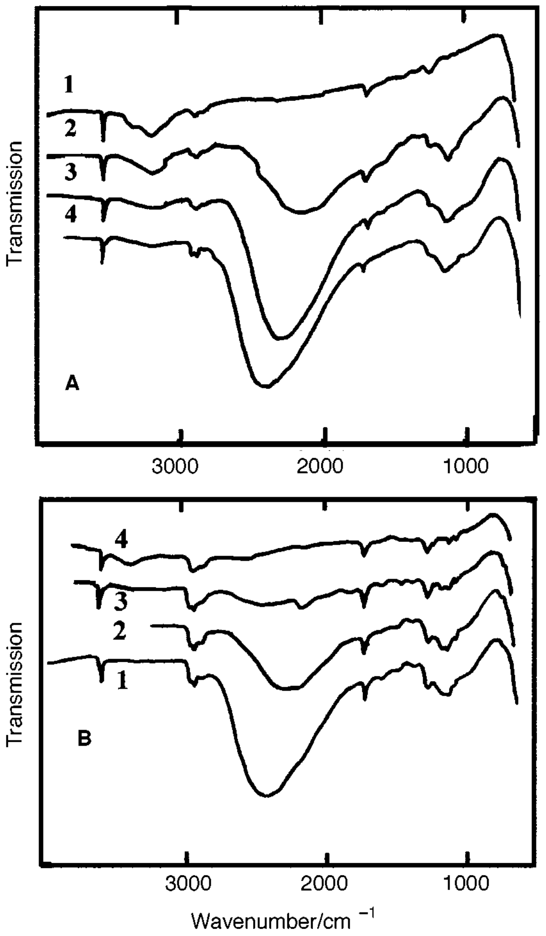

Fig. 1 Infrared spectra of HCl adsorbed on high-area KCl at 193 K. (1) Background spectrum; (2) 3rd dose, 0.0 Torr; (3) 6th dose, 1.3 Torr; (4) 8th dose, 6.5 Torr equilibrium pressure. B: Spectra of HCl on KCl obtained during evacuation. (1) 6.5 Torr; (2) evacuation at 193 K for 58 min; (3) warming during evacuation; (4) room temperature with evacuation. The spectra are displaced for clarity.

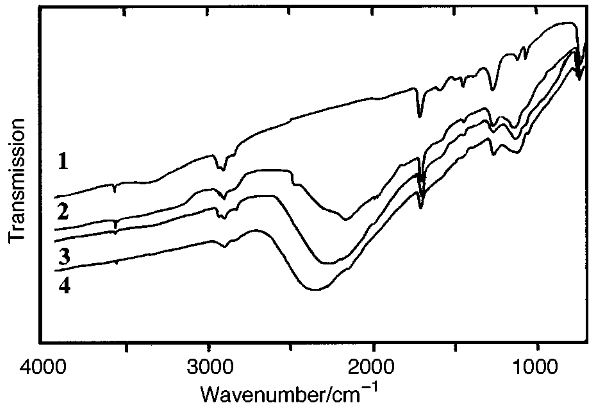

Fig. 2 Infrared spectra of HCl adsorbed on high-area RbCl at 193 K: (1) background spectrum; (2) 0.05 Torr; (3) 0.46 Torr; (4) 4.60 Torr equilibrium pressures. The background transmission level decreased with increased dosage.

Table 1 The Pauling electronegativity differences, $\Delta\chi_P$; the wavenumber lowerings, $\Delta\nu$(HCl), the radius ratios, $r^+:r^-$, and the derived effective surface ionicities for HCl adsorbed on the surfaces of a range of alkali-metal halides

Halide	$\Delta\chi_P$	$\Delta\nu$(HCl)/ cm^{-1}	$r^+:r^-$	Effective surface ionicity
LiCl	2.18	(285)	0.54	0.50
NaCl	2.23	385	0.70	0.67
KCl	2.34	465	0.91	0.81
RbCl	2.34	495	0.99	0.86
CsCl	2.37	575	1.13	[1.00]
NaBr	2.03	(355)	0.64	0.62
KBr	2.14	405	0.84	0.70
RbBr	2.14	455	0.91	0.79
CsBr	2.17	550	1.03	0.96
NaI	1.73	(295)	0.56	0.51
KI	1.84	375	0.74	0.65
RbI	1.84	405	0.81	0.70
CsI	1.87	515	0.91	0.90

The numbers shown in parentheses are $\Delta\nu$(HCl) values from ref. 2; the value in square brackets is the assumed unit ionicity of CsCl; all entries are rounded off to three significant figures.

Results

We add to the earlier work by Smart and Sheppard[1,2] a more comprehensive investigation of HCl adsorbed on a wide range of alkali-metal halides. Typical infrared spectra in the region 4000 to 600 cm^{-1} are shown in Fig. 1 for the HCl/KCl system as a function of increasing dosage at 193 K (Fig. 1A), with the equilibrium pressures listed in each case, and of decreasing coverage (Fig. 1B) brought about by progressive desorption through pressure reduction followed by pumping and warming to room temperature. The separate transmission spectra are displaced with respect to each other for clarity of presentation. Similar results for progressive adsorption of HCl on RbCl, also at 193 K, are shown in Fig. 2. In this case each dose of HCl led to a reduction of background transmission so there was no need for spectral displacements. The latter phenomenon also occurred with the HCl/CsBr system, but not with the others. It is probably attributable to further crystallization of the deposit caused by the heat of adsorption. In the HCl/RbCl series of spectra a sharp and weak band at 740 cm^{-1} was formed during the first few dosages of HCl. It was not removed by subsequent evacuation. Similar bands were not observed from the other halides.

It is seen that the wavenumbers of the broad absorption bands from the adsorbed HCl molecules that are hydrogen bonded to the surface anions vary with the degree of coverage. The observed absorption maxima move to higher wavenumbers with increasing coverage indicating that the first doses of HCl are more strongly held than the later ones. Electron microscopic studies of sintering of the original quasi-amorphous deposits revealed the partial development of recognizable crystal planes at the temperature, *ca.* 190 K, that preceded the infrared experiments. The first-covered and more active adsorption sites are expected to be the halide ions on the edges or corners of crystallites, or on defects on the crystal planes. Increasing coverage by HCl led to the superposition of the higher wavenumber absorptions on top of the lower wavenumber ones, generating bands that are asymmetric to lower wavenumbers. For the lowest coverages there can also be contributions from H_3O^+ species (see below). Therefore, for consistency, we list in Table 1 the peak positions in the form of the wavenumber differences, $\Delta\nu$(HCl), from the values for gaseous HCl (2885 cm^{-1}), *i.e.* $\Delta\nu(\text{HCl}) = \nu(\text{HCl gas}) - \nu(\text{HCl adsorbed})$, observed when the equilibrium pressures of gas-phase HCl were between 2 and 10 Torr, corresponding to near-monolayer coverage. The greater value for $\Delta\nu$(HCl) for HCl on NaCl, given in Table 1, relative to that reported by Smart and Sheppard,[2] relates to our more systematic choice of higher coverage data. Some additional data from the latter authors, for other members of the alkali-metal halide system, are incorporated in Table 1. These are given in parentheses because of uncertainties in the coverage used. For the alkali-metal halides studied, Table 1 lists additionally the Pauling electronegativity difference, $\Delta\chi_P$, between the alkali metal and the halide, the ionic radius ratio, $r^+:r^-$ and estimated surface ionicities derived from the $\Delta\nu$(HCl) values

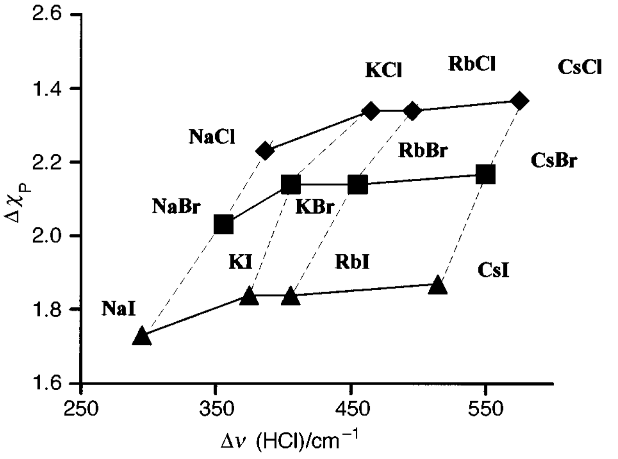

Fig. 3 The wavenumber lowering, Δν(HCl), of the absorption band of adsorbed hydrogen-bonded HCl relative to the gas-phase value of 2885 cm^{-1}, displayed as a function of the Pauling electronegativity difference, $\Delta\chi_p$ of the alkali-metal halide.

(see later discussion). The electronegativity scale used was that given by Pauling,[4] and the ionic radii, from which the ratios were calculated, were those tabulated by Shannon and Prewitt.[5,6] Other well known tabulations of electronegativities or ionic radii gave similar patterns or correlations with respect to the values of Δν(HCl).[7]

The spectra in Figs. 1 and 2 show a number of additional weak and sharp bands which remain unchanged during adsorption processes. Most of these are attributable to traces of Araldite resin used to seal the windows onto the inner copper adsorption chamber. An exception is a sharp absorption at 3580 cm^{-1} which arises from the bond-stretching mode of OH$^-$ groups within the cell windows. Additional broad and weak OH absorptions centred in the 3400–3250 cm^{-1} region, the precise position depending on the alkali-metal halide, denote the presence of traces of adsorbed water which are difficult entirely to exclude from the more hygroscopic materials. These bands weaken rapidly as the first few doses of HCl are adsorbed. At the same time, new broad absorptions centred between 1120 and 1150 cm^{-1}, with shoulders near *ca.* 950 cm^{-1}, grow in intensity. Following Smart and Sheppard,[2] who introduced HCl to water that had been deliberately adsorbed on NaCl, we assign the *ca.* 1135 cm^{-1} absorptions to the ν_2 symmetrical deformation mode of H_3O^+ from surface-generated H_3O^+ Cl^-. The very broad ν(OH) absorptions from H_3O^+ species[2] contribute to the low-wavenumber tail of the growing broad absorptions from the HCl molecules hydrogen bonded to the halide surface anions. Other weak absorptions near 1600 cm^{-1} probably correspond to ν_4 of the H_3O^+ species.[8]

Discussion

Factors expected to favour the ionic nature of the alkali-metal halides include the electronegativity difference between the metal and the halogen, and the relative sizes of the anion and the cation expressed in terms of the radius ratio $r^+:r^-$. Only Cs^+ and Rb^+ are comparable in size to Cl^-, the smallest anion studied. The smaller cations can be expected to reduce the effective ionicity by electrical polarization of the larger anions. The wavelength difference, Δν(HCl), for the adsorbed HCl is expected to increase with the increasing effective surface ionicity of a given halide ion.

Fig. 3 is a plot of Δν(HCl) *vs.* the Pauling electronegativity difference, $\Delta\chi_P$, for the set of alkali-metal halides. If the polarization of the cations were unimportant it would be expected that, for example, the value of Δν(HCl) would be similar for all the chlorides as related to the electron density of an undistorted chloride ion. In fact, the differences are seen to be very large even though for Cs^+, Rb^+ and K^+ the values of $\Delta\chi_P$ are closely similar. Clearly polarization effects are important. Similar variations apply to the data for the other anions.

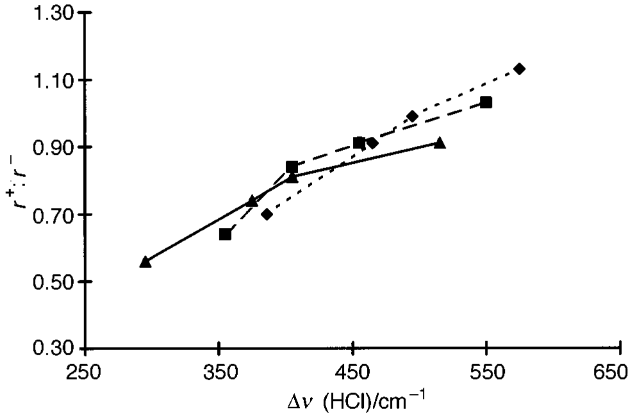

Fig. 4 The wavenumber lowering of adsorbed HCl, Δν(HCl), plotted as a function of the radius ratios, $r^+:r^-$, of the alkali-metal halide. ◆, Chlorides; ■, bromides; ▲, iodides.

The effect of the relative sizes of cations and anions in determining effective surface ionicities is explored in Fig. 4, where Δν(HCl) is plotted against the radius ratio $r^+:r^-$. There is seen to be a quasi-linear relationship between these two quantities, implying that the radius ratio is the factor of principal importance. The linear-type trend is also seen approximately to extrapolate back to zero values for the two variables which, for very small values of $r^+:r^-$, would correspond effectively to covalent bonding.

Overall, it would seem that the electronegativity differences are sufficiently great in all cases to give high charge transfer from alkali metal to halide in the absence of moderation by the polarization of the anions caused by the disparities in the ionic radii. It seems reasonable to use Δν(HCl) as a measure of the effective surface ionicities. Since CsCl involves the most electropositive and electronegative elements, and because its radius ratio is close to one (the ionic radii are average values and not precise), it seems reasonable to assume that its greatest value for Δν(HCl) approximates to full ionicity. With the value for CsCl taken as unity, the reduced values of the effective surface ionicities of the other alkali-metal halides, derived proportionately from the Δν(HCl) values, are listed in the last column of Table 1.

Matcha and King[9] earlier made a detailed analysis of the electrical dipole moments of the alkali-metal halides as diatomic molecules. From this they derived a quantity *f* where 2*f* represents the charge difference between the two atoms. This is clearly also a measure of ionicity in the diatomic forms of the alkali-metal halides and would be expected to be related to our estimated ionicities in the ionic solids. Fig. 5 shows that indeed there is a very satisfactory straight-line relationship between these two quantities, in the cases where data for both are available, and this adds weight to our analysis. The *f* values for the diatomic halides show that these are also highly ionic. Fig. 5 implies that the ionicities of the crystalline halides fall off much more rapidly with radius ratio than is the case for the diatomic species. It appears that the combined effect of the multiple cations surrounding an anion in the crystalline case more rapidly reduces the ionicity as reflected in the electron density of the anion that is available for hydrogen bonding.

A possible explanation for the additional absorption at 740 cm^{-1} observed with the RbCl system is that a small amount of symmetrical $ClHCl^-$ ions have formed on an atypical surface site. These are the Type II species observed by Evans and Lo[10] for a number of HX complexes with ionic halides. Ault[11] has observed a strong and sharp absorption at 723 cm^{-1} from such a species from matrix-isolated Cs^+ $ClHCl^-$. Spectra from the

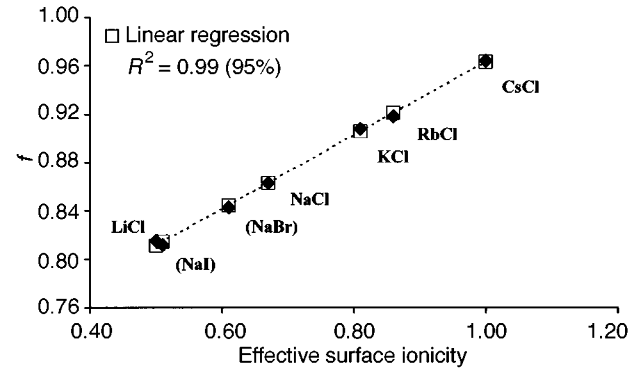

Fig. 5 A plot of the surface ionicities (see text) of the alkali-metal halides [estimated from the $\Delta\nu$(HCl) values relative to that for CsCl assumed to represent unit ionicity] relative to the f values ($2f$ = charge separation) derived by Matcha and King[9] from an analysis of the dipole moments of the gaseous diatomic alkali-metal halides. The dotted line and squares represent the linear regression data with an R^2 of 0.99 at 95% confidence level, $f = 0.6596 + 0.3035$ (ionicity).

particularly stable FHF^- species have been observed for the HCl adsorption on NaF.[2]

Conclusion

The adsorption of HCl on the surfaces of a wide range of high-area alkali-metal halides gives broad absorption bands from HCl hydrogen bonding to the surface halide ions. When obtained at near-monolayer coverage, the magnitudes of the decrease in wavenumbers of the absorption maxima, $\Delta\nu$(HCl) relative to the value for gas-phase HCl, provide a measure of the relative strengths of the hydrogen bonding. This quantity correlates poorly with the electronegativity differences between the metal and halogen elements, but well with the radius ratio, $r^+:r^-$, of cation to anion. This shows that effective surface ionicities of the alkali-metal halides are reduced by polarization of the larger anions by the smaller cations. Assuming that the case of CsCl approximates to unit ionicity, the $\Delta\nu$(HCl) values were used to derive values for the surface ionicities of the other alkali-metal halides. These quantities are shown to give a linear correlation with respect to the charge separations in the gaseous diatomic alkali-metal halides derived from the analysis of their measured dipole moments.

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