

## Adsorption of Hydrogen Halides on Alkali Halide Surfaces as studied by Infrared Spectroscopy

By R. ST. C. SMART and N. SHEPPARD\*

(School of Chemical Sciences, University of East Anglia, Norwich, NOR 88C)

ALKALI HALIDES have well-defined crystal surfaces and are transparent over extended regions of the i.r. spectrum. Kosirovski and Folman<sup>1</sup> have pioneered the preparation of high-surface-area materials of this type in a form suitable for spectroscopic study. By using a cell of similar, but somewhat simplified, design we have studied the adsorption of hydrogen halides on to several alkali halide surfaces by i.r. spectroscopy. The films are deposited from the vapour at  $-196^\circ$  and sintered at  $-80^\circ$  to reduce surface heterogeneity; after this treatment the samples have specific areas *ca.* 200 m.<sup>2</sup>g.<sup>-1</sup>.

The principal mode of adsorption is typified by HCl on a

ionic character associated with Cl atoms in the surface layer.

Caesium chloride, with a low lattice frequency and strong hydrogen bonding to HCl, provides a particularly favourable opportunity for the direct observation of the Cl<sup>-</sup> . . . H-Cl hydrogen bond stretching frequency, which is directly related to the strength of bonding to the surface. Figure 1 shows a band at 218 cm.<sup>-1</sup> which can be assigned to this vibration. A band at the intermediate frequency of 1160 cm.<sup>-1</sup> (Figure 1) is probably to be assigned to the vibrational motion of the hydrogen atom perpendicular to the Cl . . . Cl line.

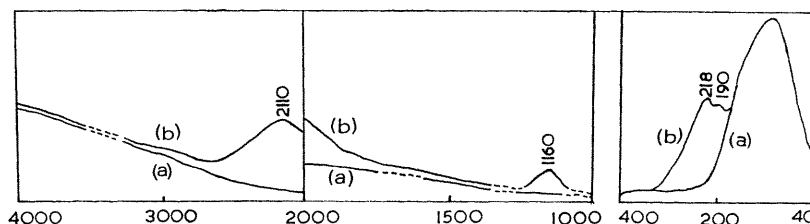


FIGURE 1. *I.r. spectra from (a) a CsCl film at  $-80^\circ$ ; (b) the same after admitting 10 torr HCl at  $-80^\circ$ .*

series of chlorides. Here a broad i.r. band, clearly arising from hydrogen-bonding of HCl to the surface (probably to Cl<sup>-</sup> ions), occurs at a much lower frequency than the gas-phase HCl bond-stretching fundamental at 2886 cm.<sup>-1</sup> (Figure 1). For surfaces of LiCl, NaCl, and CsCl the frequency-lowering caused by hydrogen bonding is 356, 435, and 776 cm.<sup>-1</sup> respectively. The considerable increase in strength of hydrogen bonding from LiCl to CsCl is attributed, at least partially, to the increasing degree of

The sequence NaCl, NaBr, and NaI give low-frequency shifts of the  $\nu_{\text{HCl}}$  vibration of 435, 355, and 295 cm.<sup>-1</sup> respectively. These results show that the effective proton accepting power of Cl<sup>-</sup>, Br<sup>-</sup>, and I<sup>-</sup> ions in these salts decreases in this order, as expected.

Although the principal adsorption through hydrogen bonding is of a physical nature (the adsorbed HCl can, for example, readily be removed from the chloride surfaces by pumping), the i.r. spectra also provide direct evidence that

proton mobility and transfer occurs readily from the hydrogen halides on these surfaces. Thus, when HBr is adsorbed on NaCl we have found that the i.r. spectrum is the same as that from HCl on NaBr. The proton transfer reaction has been verified by the detection of HCl alone in the gas phase by mass spectrometry. Such a reaction has previously been shown for HCl over NaCl<sup>2</sup> by the use of isotopic techniques.

Particularly clear-cut spectroscopic evidence for proton transfer is obtained when HCl (or DCl) is adsorbed on high surface-area NaF or KF. The spectrum observed (see Figure 2) is from FHF<sup>-</sup> (or FDF<sup>-</sup>) and not from hydrogen-bonded HCl. The frequencies of the main bands observed by absorption of HCl on NaF are given below in comparison with the analogous bands of crystalline NaHF<sub>2</sub> listed in brackets:<sup>3</sup>  $\nu_3$  1600 (1600);  $\nu_2$ ,  $\nu_2'$  1260, 1225 (1212);  $\nu_1$  530 cm.<sup>-1</sup> (600 cm.<sup>-1</sup>; KHF<sub>2</sub><sup>4</sup>). The breadth of the i.r. bands obtained, even at low surface coverage, suggest that isolated FHF<sup>-</sup> ions (as obtained by matrix isolation

techniques<sup>3-5</sup>) are not present. Alternatively there may be a range of sites with different FHF distances. It seems more probable that the surface reaction occurs in patches, possibly centred on initially active sites.

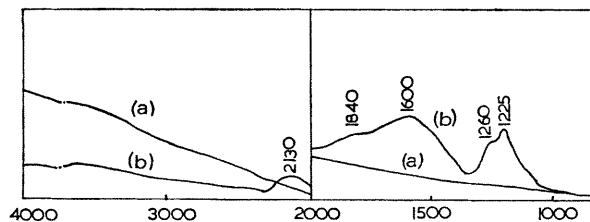


FIGURE 2. I.r. spectra from (a) an NaF film at  $-80^\circ$ ; (b) the same after admitting 10 torr HCl at  $-80^\circ$ .

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