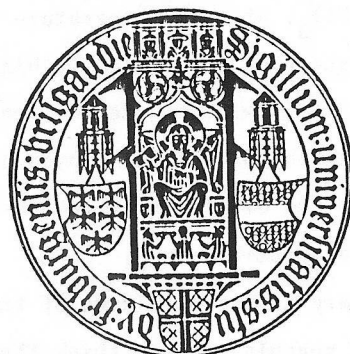


**PROCEEDINGS  
OF THE  
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ON  
RAMAN SPECTROSCOPY**

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**\*INTERFERENCE EFFECTS IN THE NH  
STRETCHING REGION OF AMINE HYDRO-  
HALIDES**

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The amine hydrohalides which contain strong hydrogen bonds of the  $N^+H \cdots X^-$  ( $X=Cl, Br, I$ ) type show rather different IR and Raman spectra in the  $NH_3$  stretching region around  $3000\text{ cm}^{-1}$ .

In fact the infrared spectra show a broad band (width  $\sim 800\text{ cm}^{-1}$ ) with superimposed a series of sharp peaks. On the contrary the Raman spectra, which have been studied in much less detail (1) are reported to consist of a series of strong and relatively sharp lines and a number of additional weak lines in the  $3000 - 2000\text{ cm}^{-1}$  spectral range.

We have measured single crystal IR and Raman spectra of ethylenediammonium chloride,  $(CH_2NH_3Cl)_2$ , at room temperature and the unpolarized Raman spectrum at  $10^\circ K$ . The spectral shapes in the higher frequency region are those above described. It is widely accepted that the rather complex spectral profiles originate from strong anharmonic interactions between fundamental stretching modes and overtones or combinations of lower lying modes which occur in the same spectral range.

The origin of the very different widths of the IR and Raman bands is however still a matter of speculation. We think that the broad band occurring in the IR spectra is mainly due to superimposed  $NH_3$  stretching modes (three  $NH_3$  stretching modes are expected around  $3000\text{ cm}^{-1}$ ), which are broadened through interaction with a multiphonon continuum encompassing a wide spectral range. The resulting broad features interact with sharp overtone and combination levels giving rise to the interference effects usually observed in these spectra. The interaction between the  $NH_3$  modes and the assumed multiphonon continuum should be weaker in the Raman effect with the result that the spectrum shows relatively sharp lines. The interaction between fundamentals and overtones and combinations should be here mainly of Fermi resonance type.

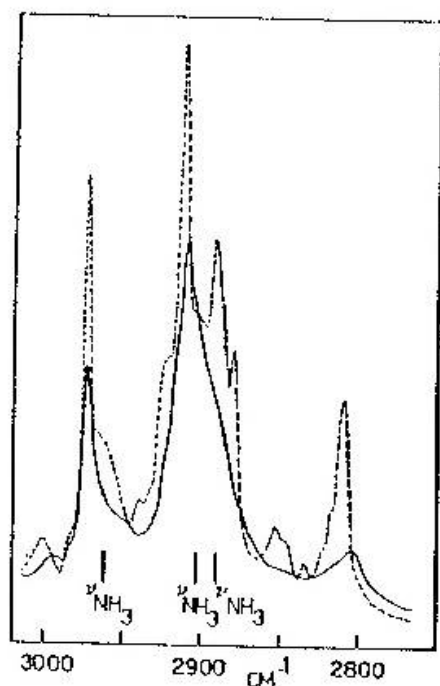


FIG. 1: Low (---) and room (—) temperature Raman spectra of  $(\text{CH}_2\text{NHCl})_2$  in the  $\nu_{\text{NH}_3}$  region.

Hence the Raman spectra are very important in order to localize the  $\text{NH}_3$  stretching mode frequencies.

From the comparison of the room and low temperature unpolarized Raman spectra ( see Fig. 1) we observed that the two Raman active  $\text{CH}_2$  stretching modes are sharper than the  $\text{NH}_3$  stretching modes and stronger, and do not change noticeably in frequency and width from 300 to 10°K.

The  $\text{NH}_3$  stretching modes depend more on temperature than the  $\text{CH}_2$  modes. The low temperature spectrum show a doublet below 2900  $\text{cm}^{-1}$  which can be assigned to one of the  $\text{NH}_3$  stretching modes. In fact a splitting into two components is expected on the basis of the  $\text{C}_i$  site and  $\text{C}_{2h}^5$  space group symmetry (2).

The other two  $\text{NH}_3$  stretching modes appear as relatively broad bands even at low temperature and superimposed on them there are the sharp lines due to the two  $\text{CH}_2$  modes and the other  $\text{NH}_3$  mode. The three  $\text{NH}_3$  stretching mode frequencies are indicated in the Figure with vertical bars.

Our assignment differs from a previous one (3) as far as  $\text{NH}_3$  stretching modes are concerned.

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