

LETTER TO THE EDITOR

Optical and Raman investigation of $\text{NH}_4\text{Cl}:\text{Cu}^{2+}$

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Abstract. We have explored the centre II formed in $\text{NH}_4\text{Cl}:\text{Cu}^{2+}$ crystals by means of optical absorption and Raman spectroscopy. The crystal-field spectrum of centre II is shown to be composed of three bands, consistent with its D_{4h} symmetry. An analysis of peak positions suggests $\text{NH}_3\text{--Cu}^{2+}$ and $\text{Cl}^-\text{--Cu}^{2+}$ distances close to 1.9 and 2.4 Å respectively. At 14 K the crystal-field bands assigned as $b_{2g}(xy) \rightarrow a_{1g}$ and $e_g(xz; yz) \rightarrow a_{1g}$ show nice vibronic progressions corresponding to $\Omega = 400 \pm 15 \text{ cm}^{-1}$. Raman spectroscopy reveals the presence of a sharp peak corresponding to $\Omega_0 = 445 \text{ cm}^{-1}$. Both Ω and Ω_0 frequencies are associated with the $\text{NH}_3\text{--Cu}^{2+}$ symmetric stretching of the $[\text{CuCl}_4(\text{NH}_3)_2]^{2-}$ unit. This difference reflects higher $\text{NH}_3\text{--Cu}^{2+}$ distances for the excited states due to the promotion of an additional electron to the strongly anti-bonding a_{1g} level.

In the realm of transition-metal impurities in insulator materials the vibrational modes associated with the impurity are usually less known than the corresponding localised electronic levels. To obtain experimental information on localised vibrational modes is, however, desirable for gaining a better insight into the nature and geometry of the centre associated with the impurity. This information concerns not only the electronic ground state, explored through infrared and Raman spectroscopy, but also the excited states whose vibrational frequencies can be measured in the optical spectra provided vibronic progressions are observed in it when the temperature is lowered.

Here we report information on the $\text{NH}_3\text{--Cu}^{2+}$ stretching frequency of centre II in $\text{NH}_4\text{Cl}:\text{Cu}^{2+}$ derived from Raman and optical absorption measurements. These data support the model of centre II depicted in figure 1, which was previously established through EPR [1] and ENDOR [2] spectroscopy.

Besides this previous characterisation of centre II and its simplicity, we are interested in this centre because it has a *peculiar* electronic situation [1–3]: the unpaired electron in this tetragonal Cu^{2+} centre is not placed in the anti-bonding b_{1g} level ($\sim x^2 - y^2$) but in the a_{1g} level ($\sim 3z^2 - r^2$) as a consequence of the stronger crystal field due to the axial NH_3 molecules. On the other hand, centre II has proved to be a sensitive probe for detecting the phase transition at 242.3 K undergone by the NH_4Cl lattice [4–7].

Although centre II has been well explored through EPR and ENDOR techniques, less attention has been paid to its optical and vibrational properties. As regards the former, only two of the three crystal-field bands of the tetragonal centre II have been reported

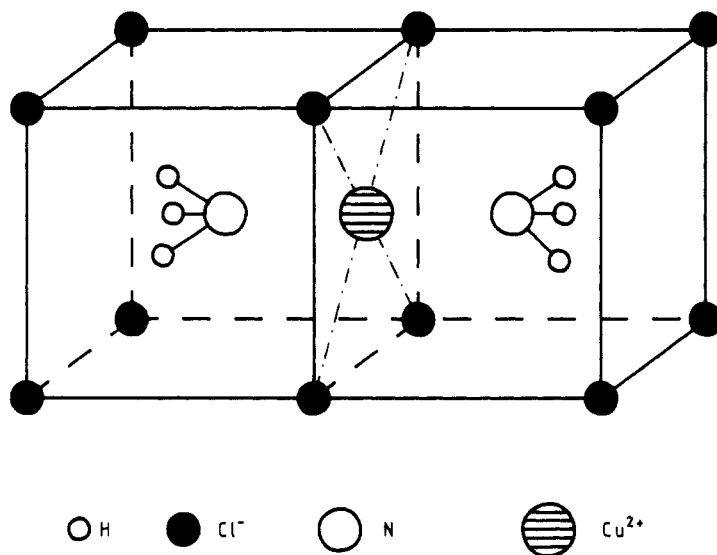


Figure 1. Model of centre II. Cu²⁺ is placed interstitially at the centre of a (100) face. The nearest neighbours are two 'axial' NH₃ molecules and four 'equatorial' Cl⁻ anions.

[6] while up to now no data on its charge-transfer bands have been available [7]. As far as the vibrational properties of centre II are concerned, no data have been reported to our knowledge.

Aside from the evidence of three crystal-field bands in the optical absorption (OA) spectrum of centre II we report here the finding of nice vibronic progressions in the low-temperature OA spectrum and of a Raman peak clearly associated with the centre. The comparison between the two sets of data give us useful information on the change of the NH₃-Cu²⁺ stretching frequency on passing from the electronic ground states ²A_{1g} to the excited states ²B_{1g} and ²E_g.

NH₄Cl crystals of good optical quality have been grown by slow evaporation of saturated solutions at room temperature. Urea was added to avoid dendritic growth.

Centre II was formed by adding to the solution CuCl₂·2H₂O and concentrated ammonia (pH ≈ 8). It can also be formed by adding CuCl to the solution due to the dismutation of Cu⁺ in water solutions. The presence of centre II as the main species in our samples was ascertained by EPR measurements.

Optical data were recorded using a Perkin-Elmer Lambda 9 spectrophotometer. The Raman spectra were taken with the 4762 Å line of a Kr⁺ laser where the sample absorption is a minimum. A double monochromator and photon-counting electronics were used.

Temperatures down to 14 K were achieved by means of an Air Products CSA-202 E closed-circuit cryostat.

Several samples have been explored, the most heavily doped of them having about 10000 ppm of Cu²⁺.

In figure 2 the crystal-field spectrum of centre II measured at room temperature is depicted. That spectrum, which is coincident with the one reported in [6], exhibits one maximum at 13700 cm⁻¹ and a shoulder at about 9500 cm⁻¹. Nevertheless around the maxima placed at 13700 cm⁻¹ the experimental spectrum is not symmetric, suggesting that a third gaussian band may be masked in it.

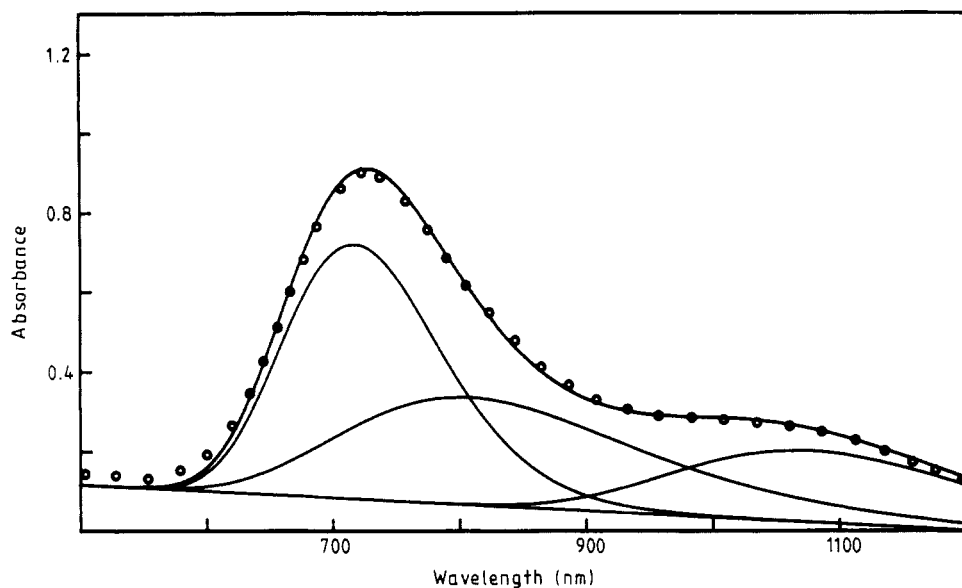


Figure 2. Simulation of the optical absorption spectrum of $\text{NH}_4\text{Cl}:\text{Cu}^{2+}$ (centre II) at room temperature by three gaussian bands whose maxima lie at $\lambda_1 = 717$ nm, $\lambda_2 = 806$ nm and $\lambda_3 = 1075$ nm. The corresponding half-widths (γ) are the following: $\gamma_1 = 2800$ cm^{-1} , $\gamma_2 = 4100$ cm^{-1} and $\gamma_3 = 2400$ cm^{-1} . Circles: experimental points; curves: simulated spectrum.

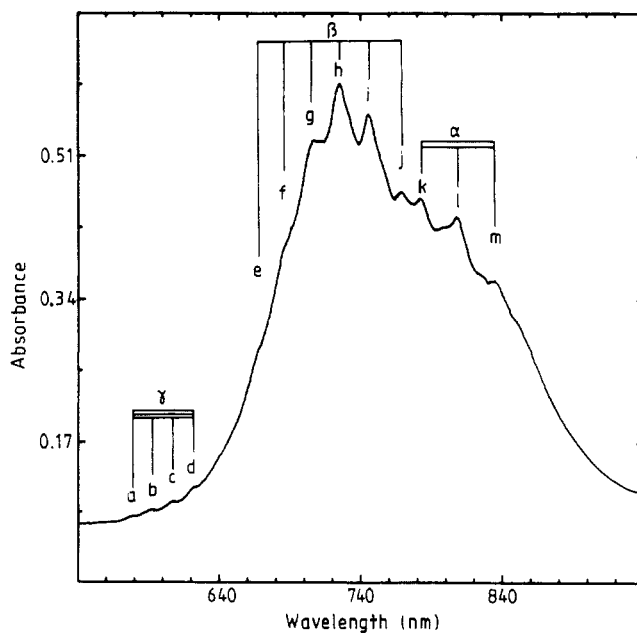


Figure 3. The crystal-field spectrum of centre II in the 540–940 nm region at 14 K. Vibronic progressions can be observed.

This situation can be greatly clarified by looking at the spectrum measured at 14 K. In the 540–940 nm spectral region (figure 3) several vibronic progressions involving the same phonon frequency $\Omega = 400 \pm 15 \text{ cm}^{-1}$ are detected. These progressions are still better seen by looking at the second-derivative spectrum (figure 4). No progressions are detected in the 950–1200 nm spectral region. The shape of the experimental spectrum shown in figure 2 as well as the fact that progressions α and β do not have the same origin support the proposal of the existence of *two* bands overlapping in the 540–940 nm region.

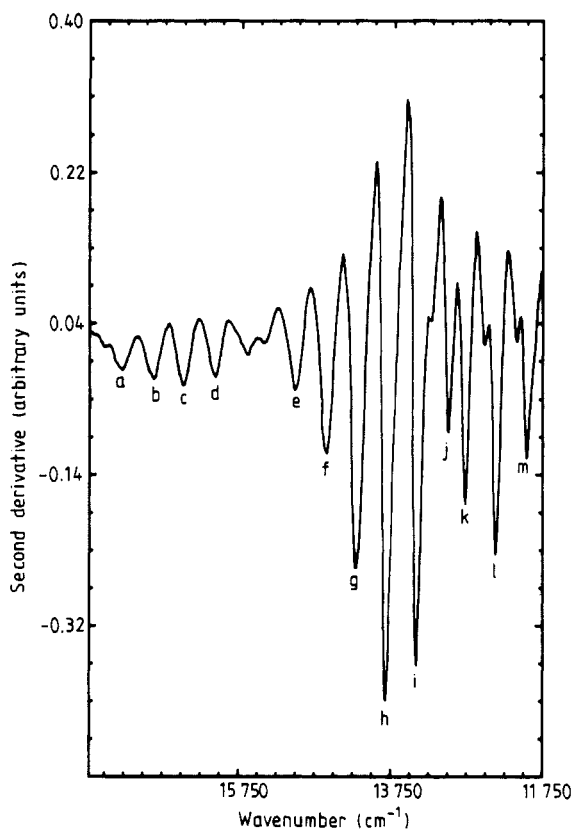


Figure 4. The second derivative of the spectrum depicted in figure 3 corresponding to the region where vibronic progressions appear.

Bearing these facts in mind, the room-temperature experimental spectrum can be simulated as the sum of three gaussian bands (figure 2) peaking at $E_1 = 13950$, $E_2 = 12400$ and $E_3 = 9300 \text{ cm}^{-1}$. These peaks are assigned as corresponding, respectively, to the three $e_g(xz; yz) \rightarrow a_{1g}$, $b_{2g}(xy) \rightarrow a_{1g}$ and $b_{1g} \rightarrow a_{1g}$ transitions expected for the present Cu^{2+} system involving D_{4h} symmetry. This assignment is supported by a simple crystal-field-like calculation which uses parameters derived from systems containing $[\text{CuCl}_4]^{2-}$ [8] and $[\text{Cu}(\text{NH}_3)_4]^{2+}$ units [9].

In this way the experimental values [8] of the three crystal-field parameters Dq , Ds and Dt for the square planar $[\text{CuCl}_4]^{2-}$ having a $\text{Cu}^{2+}-\text{Cl}^-$ distance $R_{\text{eq}} = 2.265 \text{ \AA}$, are equal to $Dq = 1250 \text{ cm}^{-1}$, $Ds = 2671 \text{ cm}^{-1}$ and $Dt = 1242 \text{ cm}^{-1}$. The parameters Dq , Ds and Dt for the $[\text{CuCl}_4(\text{NH}_3)_2]^{2-}$ unit can be obtained via the addition of those arising

from the four equatorial Cl^- anions and those from the two axial NH_3 molecules. The former are derived from the correspondence with a $[\text{CuCl}_4]^{2-}$ unit with $R_{\text{eq}} = 2.265 \text{ \AA}$ and assuming that Dq and Dt scale as R_{eq}^{-5} while Ds scales as R_{eq}^{-3} , following crystal-field theory [10].

Now it is necessary to stress that although crystal-field theory predicts values of $10Dq$ that are clearly smaller than the experimental ones, it has been demonstrated experimentally [11, 12] as well as by SCF calculations on octahedral systems [13, 14] that $10Dq$ depends in fact upon R^{-n} where n is not far from five. As an example, recent experimental studies of the optical spectrum of Mn^{2+} in several fluoroperovskites have led to the conclusion that $n = 4.7$ for the $[\text{MnF}_6]^{4-}$ unit [12, 13]. These arguments then give some support to our assumption of the dependence of the Ds , Dt and Dq parameters on R_{eq} for the four Cl^- anions.

The parameters Ds and Dt corresponding to the two axial ligands can be easily derived from those for a square planar situation. In fact both Ds and Dt for the axial ligands have the opposite values to those obtained in a square planar geometry with the same metal–ligand distance.

The values $Ds = 2243 \text{ cm}^{-1}$ and $Dt = 946 \text{ cm}^{-1}$ corresponding to $[\text{Cu}(\text{NH}_3)_4]^{2+}$ and $R_{\text{eq}} = 2.0 \text{ \AA}$ have been derived from experimental results for salts involving $[\text{Cu}(\text{NH}_3)_4]^{2+}$ units [9]. As the axial NH_3 are neutral molecules we have assumed that Ds and Dt depend in this case on R_{ax}^{-4} and R_{ax}^{-6} respectively.

With this model we have estimated the peak positions of the three crystal-field bands corresponding to centre II as a function of R_{eq} and R_{ax} . These parameters have been varied in the range $2.30\text{--}2.50 \text{ \AA}$ for R_{eq} and $1.80\text{--}2.05 \text{ \AA}$ for R_{ax} . If $R_{\text{eq}} = 2.30 \text{ \AA}$, a_{1g} lies above b_{1g} only for $R_{\text{ax}} < 1.95 \text{ \AA}$. This situation is favoured when R_{eq} increases. In these cases it has been found that the ordering of crystal-field transitions estimated via the present model is *always* that proposed in our previous assignment. Moreover this model predicts that the $b_{2g} \rightarrow a_{1g}$ and $e_g \rightarrow a_{1g}$ transitions are close, the separation between them being always less than 2000 cm^{-1} .

Taking $R_{\text{eq}} = 2.45 \text{ \AA}$ and $R_{\text{ax}} = 1.90 \text{ \AA}$ we find $E_1 = 13600 \text{ cm}^{-1}$, $E_2 = 13300 \text{ cm}^{-1}$ and $E_3 = 5000 \text{ cm}^{-1}$. The first two transitions are actually closer to the experimental ones than the $b_{1g} \rightarrow a_{1g}$ transition. This kind of discrepancy due to the simplicity of the model has been noticed in other Cu^{2+} systems [15].

The figures for R_{eq} and R_{ax} obtained through this analysis are reasonable. In this sense one would expect a $\text{Cu}^{2+}\text{--Cl}^-$ distance higher than that found in CuCl_4^{2-} due to the additional presence of the two axial NH_3 molecules. This kind of phenomenon has been noticed [15] on passing from CuCl_4^{2-} to $\text{CdCl}_2\cdot\text{Cu}^{2+}$ where Cu^{2+} is surrounded by an elongated octahedron of Cl^- rather than only by four equatorial Cl^- ions. On the other hand, two axial NH_3 molecules can be at a smaller distance from Cu^{2+} than in the case of $\text{Cu}(\text{NH}_3)_4^{2+}$. In this sense it is worth noting here that if the nitrogen atoms of centre II depicted in figure 1 were just at the centre of the cube then R_{ax} would be equal to 1.94 \AA .

The experimental arguments reported here as well as the indications given by the theoretical model both support the assertion that the $b_{2g} \rightarrow a_{1g}$ and $e_g \rightarrow a_{1g}$ transitions of centre II in fact lie very close. This conclusion is at variance with the suggestion made in [6] assuming that the $b_{2g} \rightarrow a_{1g}$ transition lies at much higher energy than the other crystal-field transitions.

As already remarked, the crystal-field spectrum of centre II at 14 K shows nice vibronic progressions corresponding to a phonon frequency $\Omega = 400 \pm 15 \text{ cm}^{-1}$ characteristic of electronic excited states. The frequency is much higher than that corresponding

to the symmetric stretching of the CuCl_4^{2-} unit ($\Omega = 280 \text{ cm}^{-1}$) [8] while it can reasonably be associated [16] with the $\text{NH}_3\text{--Cu}^{2+}$ symmetric stretching of centre II. This view is supported by the selection rules followed by vibronic progressions, which appear due to the coupling of an electronic excited state with one vibrational mode. An orbital singlet state, such as ${}^2\text{B}_{2g}$, can only be coupled to A_{1g} vibrational local modes while an electronic state ${}^2\text{E}_g$ can be coupled to modes belonging to A_{1g} , A_{2g} , B_{1g} or B_{2g} . Then the only common local mode for both ${}^2\text{B}_{2g}$ and ${}^2\text{E}_g$ electronic excited states is A_{1g} . Moreover *no* A_{2g} , B_{1g} or B_{2g} modes can be built from the axial NH_3 molecules.

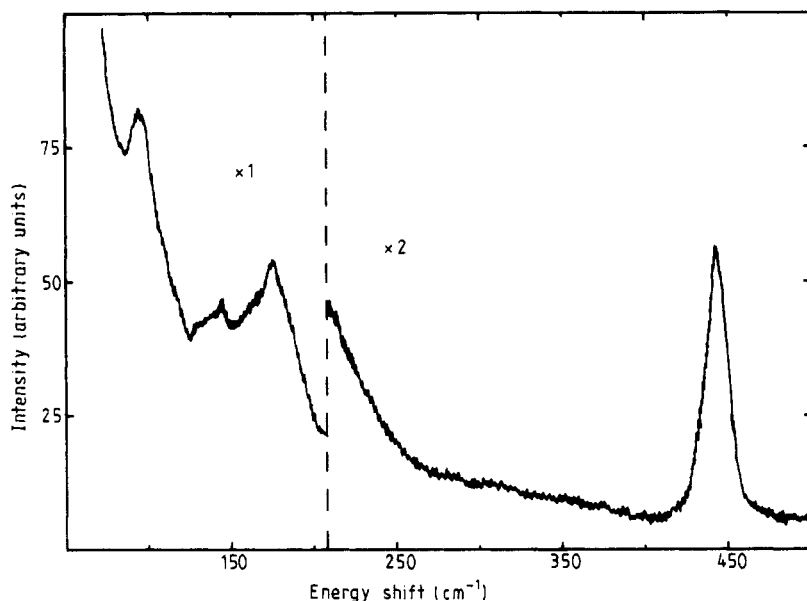


Figure 5. The Raman spectrum ($X(\text{YY})\bar{X}$) of $\text{NH}_4\text{Cl}:\text{Cu}^{2+}$ (centre II). For an explanation see the text. $T = 300 \text{ K}$.

To obtain complementary information on vibrational local modes of centre II corresponding to the ground state ${}^2\text{A}_{1g}$ we have also performed Raman measurements on several samples. Figure 5 shows the room-temperature Raman spectrum for the sample with the highest Cu^{2+} concentration. It corresponds to a parallel configuration $X(\text{YY})\bar{X}$ where only the A_{1g} and B_{1g} modes of centre II are allowed. Besides the second-order Raman spectrum (below 250 cm^{-1}) due to the NH_4Cl host crystal, a sharp peak at 445 cm^{-1} appears whose intensity decreases with decreasing Cu^{2+} concentration. This peak almost disappears in a perpendicular configuration $X(\text{YZ})\bar{X}$ which only allows E_g and B_{2g} vibrational modes for the three different orientations of centre II in NH_4Cl .

These arguments, the value of the frequency $\Omega_0 = 445 \text{ cm}^{-1}$ and the impossibility of building a B_{1g} vibrational local mode from the axial NH_3 molecules lead us to the conclusion that it corresponds in fact to the $\text{NH}_3\text{--Cu}^{2+}$ symmetric stretching frequency for the ground electronic state. This means that this frequency experiences a decrease of about 10% on passing from the ground state ${}^2\text{A}_{1g}$ to the excited states ${}^2\text{B}_{2g}$ or ${}^2\text{E}_g$. This discrepancy cannot be attributed to the different temperatures at which Raman and OA measurements have been carried out. In fact, at 80 K the Raman spectrum leads to a value $\Omega_0 = 457 \text{ cm}^{-1}$ implying a still greater difference from Ω .

The softening of the $\text{NH}_3\text{-Cu}^{2+}$ A_{1g} frequency on passing from the ground state ${}^2A_{1g}$ to the excited states ${}^2B_{2g}$ and 2E_g can be understood qualitatively by inspecting the changes of electronic structure involved. In both cases there is a promotion of a π -electron to a a_{1g} level with a stronger anti-bonding character. The appearance of one additional electron in this a_{1g} level leads to an increase of the $\text{NH}_3\text{-Cu}^{2+}$ distance tending to decrease the energy of that level. The higher value of the $\text{NH}_3\text{-Cu}^{2+}$ distance for the relaxed 2E_g and ${}^2B_{2g}$ states will probably induce a softening on the above-mentioned A_{1g} mode.

In the case of $(\text{N-mpH})_2\text{CuCl}_4$ [8], NiCl_2 [17] and K_2PtCl_4 [18] systems relative softenings equal to 4%, 3% and 13% respectively have been observed.

As a final point we would like to comment on the possible nature of the progressions called γ in figure 3, which are different from the progression β because they cannot be associated with the same origin. The existence of different electronic origins in such a spectral region can arise from (i) the influence of spin-orbit coupling upon the 2E_g state [19] and (ii) the presence of different odd vibration modes activating the parity-forbidden ${}^2A_{1g} \rightarrow {}^2E_g$ transition. Further work is necessary to clarify this point.

In conclusion we can say that the analysis of crystal-field and Raman spectra of centre II is consistent with the structural model proposed for it. In particular the vibrational progressions detected in the low-temperature crystal-field spectrum and the Raman spectrum give *direct* support to the proposal that NH_3 is present in the centre.

Studies of $\text{NH}_4\text{Br}:\text{Cu}^{2+}$ crystals grown in a similar way have been started. A detailed account of the vibrational progressions observed in the first experiments will be reported in the near future.

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