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Dynamical Properties of CuBr$_2$ Aqueous Solutions by Inelastic Light Scattering†

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Vibrational dynamics for copper bromide aqueous solutions is studied as a function of concentration. Measurements were performed by the Jet Flow Raman Spectroscopy (JFRS) technique, that allows quantitative results for this highly absorbing electrolyte. Our analysis provides an interpretation for the low-frequency region in terms of a solid-like approach. Furthermore, the intramolecular O—H stretching region is analyzed on the basis of a solute imposed structure and the strong polarization of the water in the first hydration shell is shown.

I INTRODUCTION

The study of aqueous solutions of strong electrolytes forms a well-established chapter of the physical-chemistry of solution.[1] On the basis of a lot of works performed by Enderby and co-workers,[2] an intensive study has been performed by our group about the structural properties of II-I salts of transition metal (NiCl$_2$, CuCl$_2$, CuBr$_2$, ZnBr$_2$, ZnCl$_2$) aqueous solutions.

Under the working hypothesis that in this type of electrolyte, at very high concentrations, a structural super-arrangement exists, in which the structure of the hydrated crystals is reproduced, a large variety of experimental results based on thermodynamics,[3] transport[4] and ultrasonic[5] measurements, light[6] and neutron scattering,[7,8] and EXAFS[9,10] seems to indicate the possibility of a new point of view in describing the physical properties of these systems. Accordingly, the collective properties take an important role,

and the disordered liquid phase is considered more similar to the corresponding ordered phase, by which these ionic systems are well described as an ensemble of elementary excitations, rather than an ensemble of particles.[11]

On these basis and in contrast with the behaviour of alkaline-hearth metals halogenures, one has a picture for such a system as follows: ion-water complexes $(Me^{2+}(H_2O)p)$ and MeX_n^{2-n} formation (at low concentrations), interaction between the two different species and finally correlated "patches" of finite size creation with middle range order.

As far as the copper–bromide aqueous solutions are concerned, the structural properties have been recently investigated by EXAFS[9,10,12] spectroscopy that showed a four-fold planar coordination for the Cu^{2+} ions with an average Cu-Br distance of 2.39 Å (2.40 Å in the crystal). Furthermore a correlation up to two rectangular units exists in concentrated solutions, with a 50% of copper ions involved in this structure (at saturation). The remaining Cu^{2+} ions are hydrated with a mean coordination number of $3.5 \pm 0, 5 H_2O$ molecules (at saturation) or with $7 \pm 1 H_2O$ molecules (for $C < 0.5$ molar). For C=2 molar, only the 27% of copper ions are linked in the complexes under the hypothesis that the four-fold coordination do not change as a function of concentration. Small angle neutron scattering measurements[7] on the same system also indicate the existence of dynamically correlated regions of finite size.

The aim of the present work is to investigate in detail both the low frequency region and the O—H stretching band of Raman spectra, as a function of copper bromide concentration.

It will be shown that the VV component of the spectra gives evidence of characteristic frequencies of the $CuBr_4^{2-}$ complex together with those of the Cu-water bond.

The anisotropic Raman spectra is described in terms of a projected density of states,[13,14] that is the convolution of the true density of states $g(\omega)$ with the mode dependent matrix elements. Furthermore a quasi-elastic component is present, that can be interpreted in terms of structural relaxation for the system. Finally, from the H—O spectra evolution as a function of the concentration, the bonded water (i.e. the water attached to the cations in the nearby hydration) is found.

II EXPERIMENTAL PROCEDURE AND RESULTS

The solutions of $CuBr_2$ in H_2O are prepared by successive dilution starting from high purity materials, following the procedure elsewhere described.[6] The concentration of the saturated solutions turns out to be 4.56 molar analogous to literature[15] value. We have studied the 0.2, 0.8, 1.3, 2.0, 2.15,

2.3, 2.6, 3.0 and 3.9 molar concentration. In order to convert to molar fractions the concentrations expressed in molarity, the density of the various solutions has been experimentally measured for $T = 20°C$. The Raman spectra are detected by a double monocromator Spex Ramalog 5, together with an Ar^+ ion laser working at 5,145 Å; 4,880 Å, 4,765 Å and 4,579 Å of wavelength to detect some resonance effect. The mean power of the beam (about 400 mW) was continuously monitored.

The detecting system consist of a cooled photomultiplier RCA C31034 with flat response between 2,000 and 9,000 Å, and the output is analyzed by a single photon counting system and a Digital MINC 11 minicomputer. Due to the strong optical absorbtion of the $CuBr_2$ in water, we have used the jet flow technique (JFRS) elsewhere described.[16] We have shown that, by taking the scattering by a liquid layer of some tens of microns of thickness produced by a nozzle, simultaneous heating effect and focalization problem are avoided. In this manner for the first time, it has been possible to analyze the Raman scattering data for Copper Bromide solutions at high concentrations. The temperature is held constant at 20°C with an accuracy better than 0.1°C. The Raman spectra of $CuBr_2$ aqueous solutions have been taken for both VV and VH scattering geometries.

A peculiarity of this ionic system is the strong colour dependence on concentration. Without going into details on the complex nature of the optical absorbtion in these materials, we can say that the cation Cu^{2+}, in presence of different kinds of complexations alters and overlaps its electronic states giving rise to changes of the absorbance.[15]

Furthermore, through the strong absorbance of the samples, we had to make measurements of the absolute optical absorbance μ (cm^{-1}), results of which are shown in Figure 1 for three values of the concentration. For the absorbance spectra, in the region $4,000 \div 9,000$ Å, we have used a Perkin-Elmer 576 spectrometer with a liquid cell with a very small optical path.

The absorbance spectra, shown in Figure 1 are very structured showing edges at about 5,200 Å and 6,000 Å, and a marked maximum at 8,500 Å. The red centered band is due to the presence of quasi-covalent bonds between copper and oxygen of the first hydration shell, while the $4,000 \div 6,000$ Å band is imputable to the presence of ionic pairs.[15]

The detected Raman spectra are then corrected for the absorption, the entire spectral range investigated, and for every concentration, both the low frequency region ($15 \div 450$ cm^{-1} of Stokes shift) and the O—H stretching region ($2,800 \div 3,800$ cm^{-1}) are studied.

I_{VV} and I_{VH} Raman spectra for the 2.6 molar solutions are shown as an example, in Figure 2 for the low frequency contribution.

It is to be noted that the intramolecular and the intermolecular modes, connected to the Cu—Br and Cu—O bonds, are clearly visible in the VV
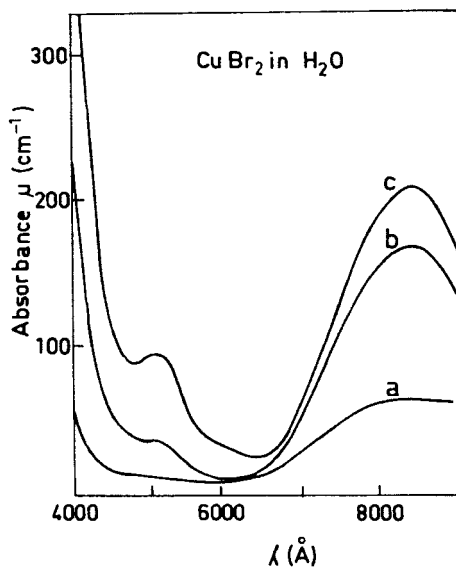
FIGURE 1   Optical absorbance μ (cm^{-1}) VS wavelength (Å) for copper bromide aqueous solutions. Curve a, b, c refers to 1.3, 2.0 and 2.3 molar, respectively.
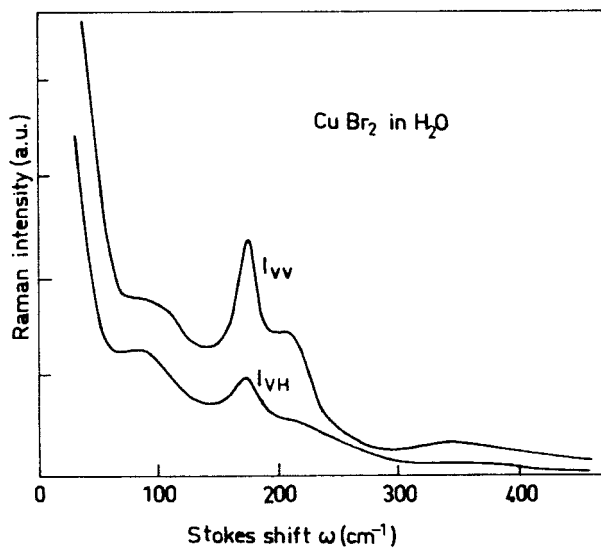

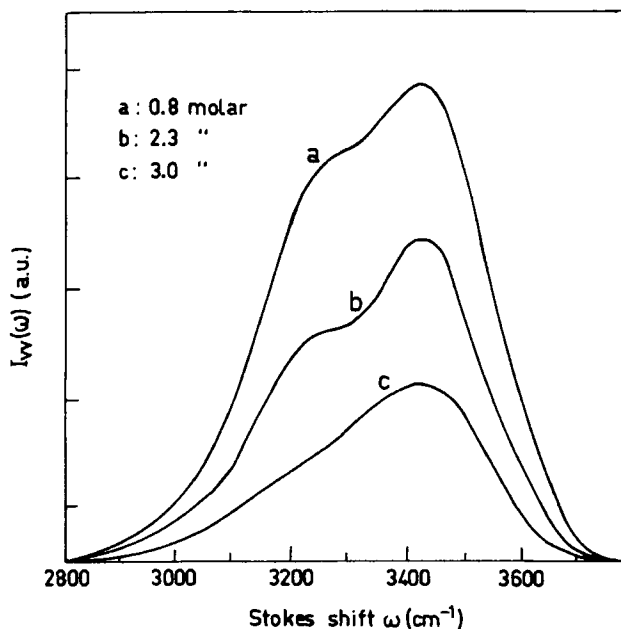FIGURE 2 I_{VV} and I_{VH} Raman spectra for CuBr$_2$ 2.6 molar (λ inc = 5145 Å).

FIGURE 3 Intramolecular O—H stretching band $[I_{VV}(\omega)]$ for copper bromide aqueous solutions at various concentrations. (λ inc = 4,888 Å).

configuration. In fact, for this scattering geometrie, the vibrational contributions are related to the isotropic part of the Raman scattering, and hence to all the collective excitations whose wave vector is in the optical range allowed ($Q \simeq 10^{-4}$ Å^{-1}).

In addition a not-shifted quasi-elastic contribution (Rayleigh wing) is also present, that is convoluted with the above mentioned spectral components. Furthermore, Figure 3 shows the evolution for different solute concentrations of the polarized O—H stretching band. We will discuss this spectral features in the next section.

III DISCUSSION

A Low frequency spectral region

With respect to the local arrangement of copper bromide aqueous solutions, the four-fold planar coordination in the structure gives rise to clearly visible bands in the VV spectrum.

In our system, only an intensity variation of the vibrational modes as concentration increases (shown in Figure 2 for the 2.6 M concentration) is observed.

The center frequency modes are: 172 cm^{-1}, 203 cm^{-1} and 82 cm^{-1}, moreover a large contribution is present in the range 300–400 cm^{-1} of Stokes shift. The above mentioned frequency are very close to those found for $(Et_4N)_2$ $(CuBr_4)$ salts[14] (85 cm^{-1}, 174 cm^{-1}, 216 cm^{-1}) and assigned to the $CuBr_4^{2-}$ complex. This fact strongly supports that the $CuBr_4^{2-}$ is the dominant species present in the solution. The large band centered at about 380 cm^{-1} is due to the Cu(II)—O[18] vibration indicating the presence of a cation-water coordination.

In order to understand how the structural properties of copper bromide aqueous solutions are connected to the dynamics of the vibrational modes, we have performed a detailed study on the polarized Raman contribution. In the context of the recent models for the analysis of Raman scattering in disordered systems[13,14,19] due to the breakdown of the crystalline momentum conservation selection rules, the anisotropic contribution to the spectra represents a smoothed out version of the one-phonon density of states of the corresponding crystals. The above concepts, although first developed for amorphous materials and glasses can be applied to the case of some liquid systems. In particular, for liquids like B_2O_3[13] and $ZnCl_2$[20] in which only a small number of bonds are broken upon the melting temperature, or for liquids like $SbCl_3$,[21] in which a chain of connected molecules creates a bond connectivity, or for liquids like concentrate electrolytic solutions[6,22] in which the structural arrangements are similar to that of the corresponding hydrated crystals. The vibrational modes are identified as "quasi-phononic" excitations in the instantaneous local structure for times that are of a lower magnitude than relaxational and diffusional times.

Furthermore a quasi-elastic component (Rayleigh wing) exists, that is characteristic of the liquid state. This latter contribution is connected to the Fourier transformate of the temporal correlation function of the polarizability tensor. Various microscopic mechanisms of scattering as jump diffusion, extended diffusion, structural relaxation, reorientational motions and so on, give rise to a not shifted contribution.[24]

Taking into account all the above-mentioned contributions, the $I_{VH}(\omega)$ can be written as follows:[20,21]

$$I_{VH}(\omega) \equiv I_{anis}^{Total}(\omega) = \mathscr{L}_R + \mathscr{L}_S + I_{anis}^{VIBR}(\omega) \qquad (1)$$

where:

$$\mathscr{L}_R = \frac{A_R \cdot \Gamma_R^2}{\Gamma_R^2 + \omega^2}, \quad \mathscr{L}_S = \frac{A_S \cdot \Gamma_S^2}{\Gamma_S^2 + \omega^2}$$

are lorentzian components by reorientational and structural relaxational processes and: $I_{anis}^{VIBR}(\omega) \propto P(\omega) \cdot n(\omega, T) \cdot 1/\omega \cdot g(\omega)$ is the solid-like contribution. (For the meaning of the symbols see e.g. Ref. (20).)

Generally, for "structure limited"[23] liquids, as our sample is, the structural relaxation time τ_S is lower than the reorientational relaxation time τ_R, giving a HWHM Γ_S of the lorentzian components, that is the only component detectable by Raman spectrometers. Then, following an already applied procedure,[20,21] it could be shown that, at very low Stokes shifts, the (1) becomes:

$$I_{\text{anis}}^{\text{Total}}(\omega) = \frac{A_S\Gamma_S^2}{\Gamma_S^2 + \omega^2} + C \tag{2}$$

If the (2) holds, fitting of the experimental data by the equations:

$$[I_{\text{anis}}^{\text{Total}}(\omega) - C]^{-1} = \frac{1}{A_S} + \frac{\omega^2}{A_S\Gamma_S^2} \tag{3}$$

we can find, for the obtained value of C, the lorentzian parameters A_s and Γ_s.

The fitting results showed in Figure 4 for a concentration of 2.6 molar, allow to obtain the values:

$$A_s = 265, \qquad \Gamma_s = 10.98 \text{ cm}^{-1}$$

Γ_s value gives a structural relaxation time $\tau_s = 0.48$ psec that is very close to the value founded by Litovitz et al., and may be analogously connected to the life time of the H-bond in the solution. This is a reasonable value, because at this concentration value the ratio salt molecules/water molecules is ~ 0.05, and the free water contribution is dominant on this aspect of the system dynamics.

We haven't performed a similar fitting for higher values of concentration, because the optical absorption increases more and more and does not allow
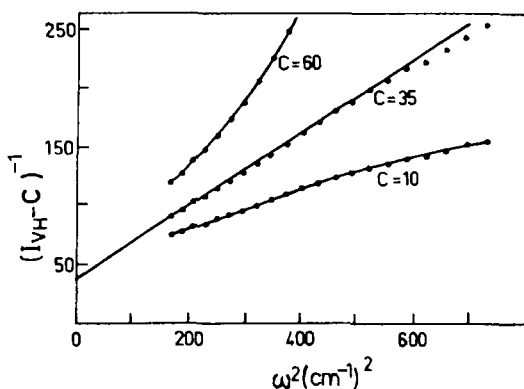

FIGURE 4 Fitting results with the Eq. (3) (see text), for the quasi-elastic lorentzian contribution to the anisotropic Raman scattering.
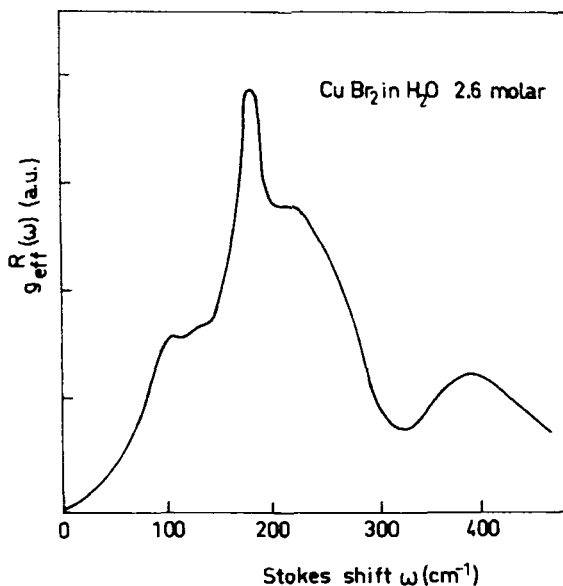
FIGURE 5 Raman effective density of states for the 2.6 molar copper bromide solution.

a quantitative fitting in the very low frequencies region. When the central lorentzian line is subtracted, the Raman effective density of states

$$g_{\text{eff}}^R(\omega) \propto I_{\text{anis}}^{\text{VIBR}}(\omega) \cdot \omega \cdot [n(\omega, T) + 1]^{-1}$$

is found, and the result for 2.6 molar copper bromide solutions is shown in Figure 5. It can be seen that the "optical" modes are clearly visible, other an ω^2 "acoustical" contribution that lies in the lower frequency spectrum. Finally, no effect was found in the resonance effects on this strongly absorbing copper bromide solutions, by changing the incident wavelength near the optical absorption edges.

This result is different from that found, on similar coloured electrolyte ($CuCl_2$), where a pre-resonance effect has been already detected[16] with a resulting enhancement of the total symmetric vibration $CuCl_4^{2-}$. This difference can be tentatively explained by a lower symmetry of the total symmetric vibration at 173 cm^{-1} connected with the complex $CuBr_4^{2-}$ (the depolarization ratio ρ is ~ 0.35) than the analogous highly symmetric ($\rho < 0.1$) vibrational band of $CuCl_2$ aqueous solutions.

The low symmetry observed for Cu–Br stretching band may be connected with the distortion of the rectangular complexes (EXAFS results) on the short contiguous sides due to their interaction.

B High frequency region analysis

The analysis of the intramolecular O—H stretching band for the copper bromide aqueous solutions is performed on the basis of the above-mentioned structural models for this kind of electrolyte. It is well known that the O—H vibrational band is quite sensitive to the structural modifications induced by the solute on the structure of the solvent. Figure 3 allows us to see, in fact, that the shape of the O—H stretching band changes continuously as the concentration increases.

Obviously, each curve of Figure 3 could be deconvoluted in the usual gaussian bands, each giving a different degree of polarization of the bond. In this case the correspective center frequency polarization, width and areas could be analyzed as a function of the solute concentration. Alternatively, if a structural point of view is assumed to explain the dynamical properties of our system, the modifications of the VV O—H stretching band may be induced by a suitable superposition of the pure water spectrum with the spectrum of the water strongly interacting with the ions (first hydration shell of water).

This latter contribution is due to bonded water, and it is connected with the middle range order structure locally similar to that of the crystalline status. To explain the O—H vibrational band for ZnBr$_2$ aqueous solutions, it is to be noted that a similar model has been successfully used already.[22]

It is easy to show that the percentage of free water (i.e. the water that is not implied in the imposed structure), may be expressed by:

$$\alpha = 1 - 10^{-3} \cdot n_H \cdot m \cdot M_0 \qquad (4)$$

where: M_0 is the water molecular weight, m is the molar concentration and n_H is the mean hydration number found by EXAFS measurements.[9,10,12] The α-weighed free water spectrum is then subtracted from the spectra for all the concentrations studied. In this manner the O—H stretching of the bonded water is obtained. It is to be noted that the bonded O—H spectra as a function of the concentration are surprisingly coincident. Figure 6 shows the obtained spectral form of this contribution. An inspection of Figure 6 allows us to draw the following results:

— The O—H water bonded spectrum is very similar to that of the O—H stretching band in the ZnBr$_2 \cdot \frac{1}{2}$H$_2$O melted crystal.[22] This fact confirms the working hypothesis that electrolytes of this kind have a very similar structural arrangement.

— The first moment of the distribution lies in the same spectral region of the O—H stretching of closed water (not tetrahedrically coordinated).

— The fact that the bonded O—H spectrum is coinciding at the various concentrations when the EXAFS n_H values are put into the Eq. (4), confirms
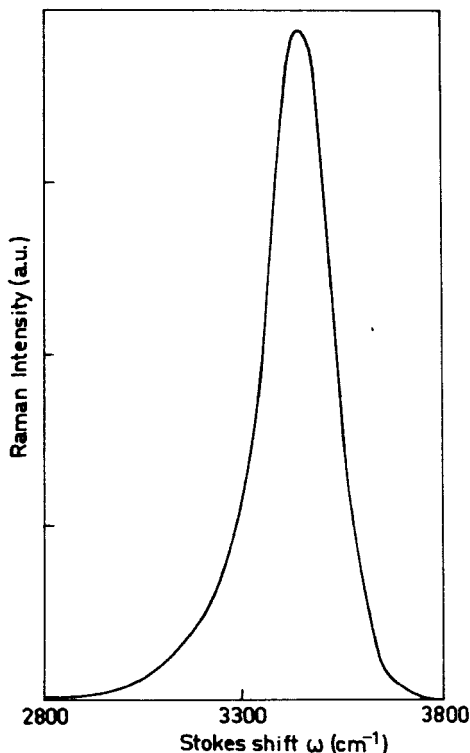
P. MIGLIARDO *et al.*

FIGURE 6   O—H bonded spectrum in the first hydration shell around the copper.

that local probes as scattering Raman, as far as intramolecular vibrations are concerned, and EXAFS are sensitive only to the first hydration shell around the ions.

IV   CONCLUDING REMARKS

The experimental measurements performed by means of the JFRS technique on aqueous solutions of $CuBr_2$ provides evidence of the presence of vibrational "optical" modes connected to the symmetry of the rectangular planar complexes $CuBr_4^{2-}$. Furthermore the presence of a vibrational structure due to copper-oxygen bond of the nearby hydration shell around the cation is shown. The anisotropic low frequency contribution is interpreted in terms of a collective point of view: a projected vibrational density of states is constructed for the system and both the "acoustical" and "optical" modes are found.

As far as the very low optical range is concerned, a central component in the $I_{VH}(\omega)$ is shown that is fitted by a lorentzian curve, which FWHM furnishes with a relaxational time $\tau = 0.48$ psec. This value is similar to that obtained by Montrose et al.[25] for hydrogenoid systems.

The high frequency region is interpreted in terms of two coexisting structural arrangements for the system: the first is a solute imposed one, similar to that of the crystalline state and the second one is the usual water structure. In connection with EXAFS measurements, the first contribution (bonded water) is derived and stochiometrically weighted as a function of the concentration.

Acknowledgments

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