# Hydration Phenomena in a Concentrated Aqueous Solution of $Ce(NO_3)_3$. X-ray Diffraction and Raman Spectroscopy

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The scattering of X-rays from a concentrated $Ce(NO_3)_3$ aqueous solution has been measured and analyzed. The experimental correlation function appears to be mainly characterized by the hydration of the cation: peaks at about 2.55 and 4.65 Å. Good agreement with experimental data is achieved through a model in which the Ce(III) ions have a first and a second hydration shell and also the nitrate group is considered hydrated. Complex formation between cation and anion is confirmed by using Raman spectroscopy.

## 1. Introduction

Recent reviews [1–4] have shown that X-ray and neutron diffraction studies have provided useful information about the state of divalent and trivalent small cations in aqueous solution. Recently Habenschuss and Spedding [5–7] presented results of an extensive X-ray study for ten rare earth (except the $Ce^{+3}$ ion) chloride solutions, indicating that the inner sphere water coordination of the rare earth ions in aqueous solution decreases from nine to eight, due to the decreasing rare earth ionic radii. As the information about the structural behaviour of the Ce(III) ion in aqueous solution is very poor, a study on it seems interesting. For this purpose we decided to investigate a 2 Molar $Ce(NO_3)_3$ solution. In perchlorate solutions of Ce(III) Fratiello et al. [8] declare that "the spectral evidence for inner-shell complex formation leads to the possibility of a greater maximum hydration number than 6 for this species".

Another aim of our work was to determine the behaviour of the nitrate ion in conditions different from those studied earlier, and at the same time to check whether direct interactions between cation and anion exist. As far as this anion is concerned, the diffractometric studies generally lead to the conclusion that the $NO_3^-$–$H_2O$ interactions are weak. In presence of trivalent cations, as in solutions of $Cr(NO_3)_3$ [9] and $Fe(NO_3)_3$ [10], they can be totally masked by the strong cationic contributions, while in solutions of $Al(NO_3)_3$ [11], it was found necessary to introduce discrete interactions between $NO_3^-$ and the solvent. These interactions can be seen clearly in solutions of $NH_4NO_3$ [12]. Indeed, the nitrate ion can be very sensitive to the structure formed around the counterion because of its geometry, its tendency to create ion pairs, and its capability to form H-bonds even if they are weak; moreover, it can be very sensitive to variation in concentration. As regards complex-formation, a survey of the literature [13] on the behaviour of Ce(III) in nitrate solutions points to Ce–$ONO_2$ contacts. This phenomenon has been studied in sulphate solutions of divalent and trivalent cations [14–16]; in these the presence of a peak in the correlation function $G(r)$, attributable to the cation-S interaction (in the range 3.3–3.6 Å) has been crucial to show the inner-complex formation. The presence of a peak due to the Ce–N interaction should show the phenomenon.

Raman spectroscopic studies also can provide significant structural information an aqueous electrolyte solutions; in particular, spectroscopic criteria for distinguishing between the formation of direct, or contact, ion pairs and solvent-separated ion pairs have been established with metal nitrate solutions [17–18]. Raman measurements were also carried out on the same solution.

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## 2. Experimental Results

### 2.1. X-ray Scattering Measurements and Data Treatment

The solution studied was obtained by dissolving a weighted amount of $Ce(NO_3)_3 \cdot 6H_2O$ (Merck reagent grade) in distilled water. Cerium and $NO_3^-$ contents were determined by standard methods [19–20]. The composition of the solution investigated is given in Table 1. X-ray scattering data were obtained at 22 ± 1 °C on a $\vartheta-\vartheta$ diffractometer equipped with a Mo X-ray tube (wavelength = 0.7107 Å). The observed range of scattering angles ($2\vartheta$) was from 3° to 140°, corresponding to the range $0.5 \leqq s \leqq 16.58$ Å$^{-1}$, where $s = (4\pi/\lambda)\sin\vartheta$ is the scattering variable. The measured intensities were corrected for background, polarization and absorption [21], and smoothed by fourth differences [22]. The Compton contribution was evaluated by a semiempirical method [23] in order to account for the monochromator discrimination. The corrected intensities were scaled to the independent scattering factor for the solution, using both the analytical method [24] and visual comparison. The structure function was then constructed according to

$$i(s) = \left[I_{\text{e.u.}}(s) - \sum_{i=1}^{m} x_i f_i^2\right] \Big/ \left[\sum_{i=1}^{m} x_i f_i\right]^2, \quad (1)$$

where $f_i$ are the atomic scattering amplitudes corrected for anomalous dispersion, $x_i$ are the stoichiometric coefficients in a structural unit containing $m$ kinds of atoms, and $I_{\text{e.u.}}$ is the intensity in electron units. The scattering factors were computed according to an analytical formula using the coefficients proposed by Hajdu [25] for $H_2O$, by Cromer and Mann [26] for $N$, and Cromer and Waber [27] for O. For the Ce atom they were taken from International Tables [28]. The experimental correlation function $G(r)$ was obtained $i(s)$ by Fourier transformation according to

$$G(r) = 1 + (2\pi^2 \varrho_0 r)^{-1} \int_{s_{\max}}^{s_{\min}} s\,i(s)\sin(s\,r)\,\mathrm{d}s\,, \quad (2)$$

where $r$ is the interatomic distance, $s_{\min}$ and $s_{\max}$ are the lower and upper limits of the experimental data, and $\varrho_0$ is the bulk number density of the stoichiometric units.

Before calculating the final correlation function, the structure $s\,i(s)$ was corrected for residual systematic errors by means of a procedure described by Levy, Danford and Narten [23]. The method is based on the removal of the peaks present in $G(r)$ at small values of $r$, and is more effective if a sufficiently extended range of distances can be used to this end. Therefore, in addition to unphysical ripples, the peaks due to the N–O and O–O (from the $NO_3^-$ group) distances were also removed from $G(r)$, following a procedure used elsewhere [11, 12, 29], since these contributions are obvious and not very important for the interpretation of the results. No convergence factor was used in calculating the Fourier transformation.

Table 1. Composition of the solution in moles/l. $d$ is the density and $\mu$ the linear absorption coefficient calculated for MoK$\alpha$ radiation.

| $[Ce^{3+}]$ | $[NO_3^-]$ | $[H_2O]$ | $d$(g cm$^{-3}$) | $\mu$(cm$^{-1}$) |
|---|---|---|---|---|
| 2.0 | 6.0 | 50.723 | 1.566 | 15.063 |

### 2.2. Raman Spectroscopic Measurements

The Raman apparatus consisted of a CRL-CR2 argon laser, a 25–100 Dual Monochromator from Jarol-Ash, a cooled FW-130 photomultipliar from ITT and a home-made digital data acquisition system. The wavelength breadth of the apparatus did not change appreciably the Raman spectral shapes of our measurements. Spectral resolution was 3 cm$^{-1}$. The solution to be investigated was contained in a Beckman 5 cm$^3$ cylindrical cell and the beam was continuously monitored after a single passage through the cell. In order to avoid local heating causing density and concentration fluctuations, the laser light was defocussed to give a beam of about 5 mm radius. The spectra recorded in this way were reproducible in time. The Raman laser spectrometer has been described extensively elsewhere [30].

## 3. Analysis of the Results

### 3.1. Correlation Function

The experimental structure function $s\,i(s)$ and the resulting correlation function $G(r)$ are plotted in Figs. 1 and 2, respectively (points). An inspection of $G(r)$ allows the first qualitative information to be obtained. In it three well-resolved peaks can be distinguished with their maxima centered at about 2.55, 3.05 and 4.65 Å.

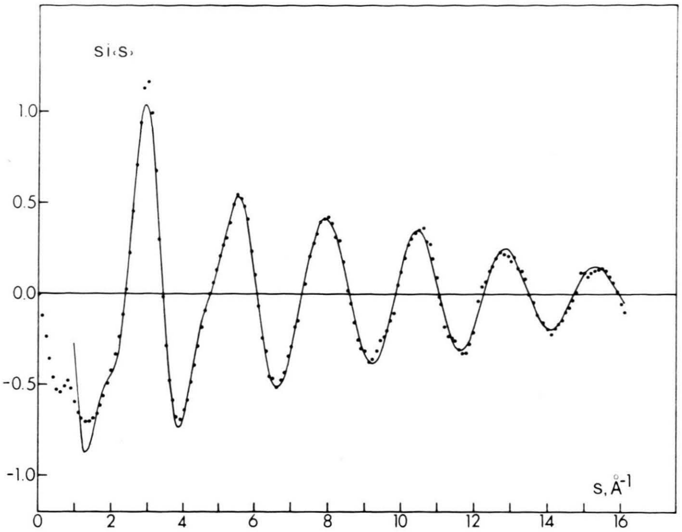

Fig. 1. Observed structure function (···) compared with that of the best fit from model 2 (——).

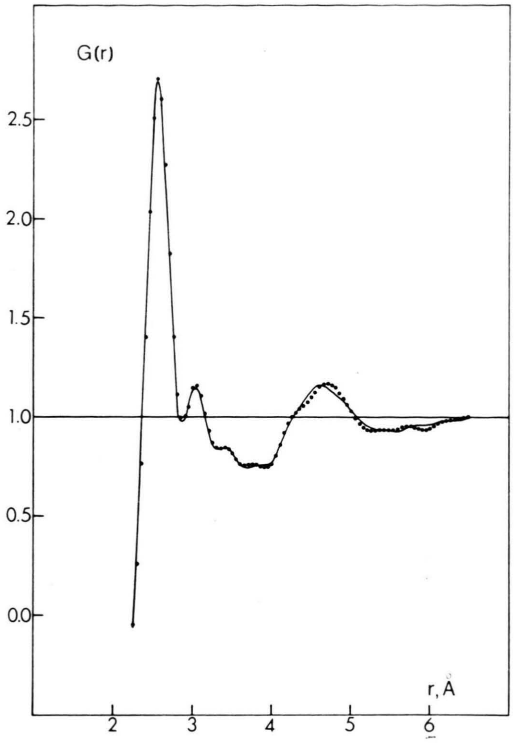

Fig. 2. Observed (···) and model (——) distance spectra obtained from Fourier transformation of the corresponing structure functions in Figure 1.

The peak at 2.55 Å is diagnostic of the $Ce^{3+}$–$H_2O$ distances, both on the basis of the ionic radii of the species and as found in the crystal structures of $Ce(H_2O)_5(NO_3)_3 \cdot H_2O$ [31] and $CeCl_3(H_2O)_7$ [32].

The peak centered at about 3.05 Å is certainly caused by nearest-neighbour interactions $H_2O$–$H_2O$. Contributions could also come from interactions between the oxygen atoms of the nitrate ion and anionic hydration water molecules. Concerning the attribution of the large peak at about 4.65 Å, it is less direct than that of the two preceding peaks. The presence of peaks around 4–5 Å is not enough to state that a second hydration shell is present around the cation, since various kinds of O–O distances fall in this range. The presence of the second hydration shell has been shown for many divalent [15, 33, 34] and trivalent [9–11, 16] ions with small ionic radii, and also for the $Sr^{2+}$ ion [35]. We think that also in this case, its position and especially its height suggest that $Ce^{3+}$ ions must be involved.

A small peak at about 3.4 Å is also present in the correlation function; it can be ascribed to the N–$H_2O$ interactions since its value is not too different from that expected for the N–$H_2O$ pair supposing that the water molecules around the anion occupy positions directed by tetrahedral angles. This distance has been found in aqueous solutions [11, 12]. Another possible origin of this peak are the Ce–N interactions, indicating the presence of cation-anion contact phenomena in our solution. The value of the Ce–N distance depends on the $NO_3^-$ orientation.

Peaks from larger intermolecular distances are absent. As in previous investigations on concentrated solutions, the order phenomena observable in the experimental correlation curves concern ionic hydration exclusively.

### 3.2. Raman Data

In Fig. 3 we report the spectrum obtained for the studied solution in the range 600–800 cm$^{-1}$. Two bands are present at about 720 and 740 cm$^{-1}$. The first one is assumed [17, 18] to derive essentially from unbound nitrate ($\nu_4$: doubly degenerate mode). The coordination of the nitrate group to a metal leads to a lowering of the symmetry of the nitrate ion which may result in the removal of the degener-

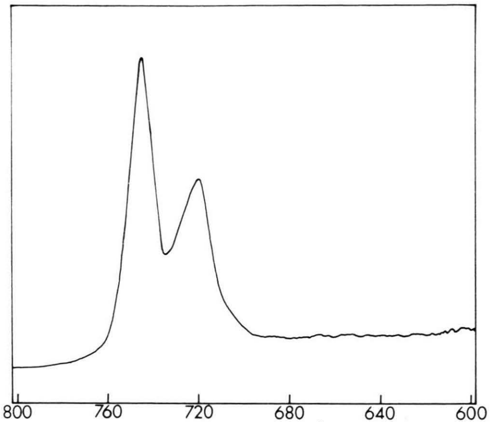

Fig. 3. Raman spectrum of the 2.0 M $Ce(NO_3)_3$ solution.

acy of certain vibrations and in the appearance of forbidden (on the basis of a $D_{3h}$ point group) Raman bands. The second band (740 cm$^{-1}$) in the region of the $\nu_4$ frequency is regarded as that arising from a new species of nitrate: a bound nitrate ion [17, 18]. The presence of the two bands confirms the attribution of the peak in the correlation function $G(r)$ at about 3.4 Å both to the $N-H_2O$ and $Ce-N$ interactions.

### *3.3. Models*

In order to get more detailed information than that directly deducible from the experimental $G(r)$, the usual analysis based on the calculation of a model structure function, which was systematically refined against experimental data, has been used. This synthetic structure function was constructed according to the formula used by Narten and Levy [36] and proposed by Debye a long time ago:

$$i(s) = \sum_{i=1}^{m} \sum_{j=1}^{n_i} x_i f_i f_j \left[ \sum_{i=1}^{m} x_i f_i \right]^{-2} \cdot \exp\left(-\tfrac{1}{2}\sigma_{ij}^2 s^2\right) \sin(s\, r_{ij})/s\, r_{ij}\,, \qquad (3)$$

where $m$ is the number of atoms in the stoichiometric unit, $n_i$ the number of atoms with discrete structure "seen" by an origin atom of $i$ type; $r_{ij}$ the mean radial distance of the $j$th atom from an origin atom of $i$ type and $\sigma_{ij}$ the mean-squares deviation for the distance $r_{ij}$. The least squares refinements were carried out using the $s$ intervall 1.5 – 16.2 Å$^{-1}$, the function

$$U = \sum_{s_{\min}}^{s_{\max}} \left(i(s)_{\text{obs}} - i(s)_{\text{calc}}\right)^2 \qquad (4)$$

being minimized by means of the LSHS program; this is based on the classical Gauss-Newton linearization method as modified by Marquardt [37]. This program is a personal version of one of the authors, in Fortran IV, that allows the simultaneous fitting of the parameters with a calculation time less then the least squares programs previously used.

The quantitative analysis has been made in different steps. Since the structural information about the first hydration of the cerium(III) ion in nitrate aqueous solutions is inexistent, a first preliminary calculations has been carried out. In it only three independent parameters have been introduced, i.e. the distance $Ce-H_2O$ ($r_{Ce-H_2O_I}$), the root-mean-squares deviation of the distance ($\sigma_{Ce-H_2O_I}$), and the coordination number ($n_{Ce-H_2O_I}$). Sixteen calculations have been carried out, with $s_{\max}$ fixed, but varying $s_{\min}$ from 1 to 8.5 Å$^{-1}$ with steps 0.5. The obtained values for the three parameters do not give univocal indications. Indeed the obtained values for the $Ce-H_2O$ distance are almost constant, on the contrary the pairs of the $n$ and $\sigma$ values obtained vary with the $s_{\min}$ value used. The values for the $Ce-H_2O$ distance are between 2.575 Å for $s_{\min} = 1$ and 2.547 for $s_{\min} = 8.5$ Å$^{-1}$. The pairs of $n$ and $\sigma$ vary from 7.4 and 0.126 for $s_{\min} = 1$ to 5.1 and 0.098 for $s_{\min} = 8.5$ Å$^{-1}$.

These variations are due to the presence in the structure function $i(s)$, at high $s$ values, of other contributions besides that considered. These contributions cannot be omitted in the calculations.

On the basis of the results of these preliminary calculations and of the qualitative analysis of $G(r)$ and of the Raman spectrum two complete calculations were then carried out. In both calculations we introduced the following contributions:

a) Interactions between Ce(III) and first-neighbour water molecules,
b) Interactions between Ce(III) and second-neighbour water molecules,
c) Interactions between $N$ atoms (from nitrate ions) and water molecules,
d) Interactions between Ce(III) and nitrate ions.

The two models differ in the description of the interactions $H_2O-H_2O$, $H_2O_I-H_2O_{II}$ and $O-H_2O$.

In the first model we assumed a single contribution $H_2O-H_2O$. In the second model these contributions are considered separately. For the description of cation and anion hydration no symmetry is assumed. The following parameters were therefore introduced in the models:

First shell around the cation:

The $Ce-H_2O_I$ distance ($r_{Ce-H_2O_I}$) and its root-mean-squares deviation $\sigma_{Ce-H_2O_I}$ and the coordination number $n_{Ce-H_2O_I}$ are independent parameters together with distance, root-mean-squares deviation and $n$ for $H_2O-H_2O$ pertaining to the cation hydration shell.

Second shell around the cation:

The $Ce-H_2O_{II}$ distance ($r_{Ce-H_2O_{II}}$) and its root-mean-squares deviation $\sigma_{Ce-H_2O_{II}}$ and the coordination number ($n_{Ce-H_2O_{II}}$) are parameters together with the distance ($r_{H_2O_I-H_2O_{II}}$) and the root-mean-squares deviation $\sigma_{H_2O_I-H_2O_{II}}$ for the $H_2O-H_2O$ molecules that pertain to the subsequent hydration shells and are directly H-bonded; while the coordination number $n_{H_2O_I-H_2O_{II}}$ is related to $N_{Ce-H_2O_{II}}$ by the relationship $n_{H_2O_I-H_2O_{II}} = n_{Ce-H_2O_{II}}/n_{Ce-H_2O_I}$.

## Anionic hydration

The $N-H_2O$ distance ($r_{N-H_2O}$), its root-mean-squares deviation $\sigma_{N-H_2O}$ and the coordination number $n_{N-H_2O}$ are independent parameters together with the distance ($r_{O-H_2O}$) and root-mean-squares deviation $\sigma_{O-H_2O}$ for $O-H_2O$ contacts; while the coordination number $n_{O-H_2O}$ is related to $n_{N-H_2O}$ by the relationship $n_{O-H_2O} = n_{N-H_2O}/3$.

## Cerium-nitrate contacts

The $Ce-O_2$, $Ce-N$ and $Ce-O_3$ distances $\left(\begin{array}{l} \quad O_2 \\ Ce{-}O_1 \end{array}\!\!>N{-}O_3\right)$ are parameters, while the root-mean-squares deviations of the distances $\sigma_{Ce-O_2}$ and $\sigma_{Ce-N}$ are fixed equal to $\sigma_{N-H_2O}$, and $\sigma_{Ce-O_3}$ equal to $\sigma_{Ce-H_2O_{II}}$. The $Ce-O_1$ distance was assimilated to $Ce-H_2O_I$. These approximations have been used for decreasing the number of parameters; for this reason also $\sigma_{H_2O_I-H_2O_{II}}$ is equal to $\sigma_{O-H_2O}$. The number of coordinated nitrate groups is 0.9; this value has been calculated by using the equilibrium constants [13].

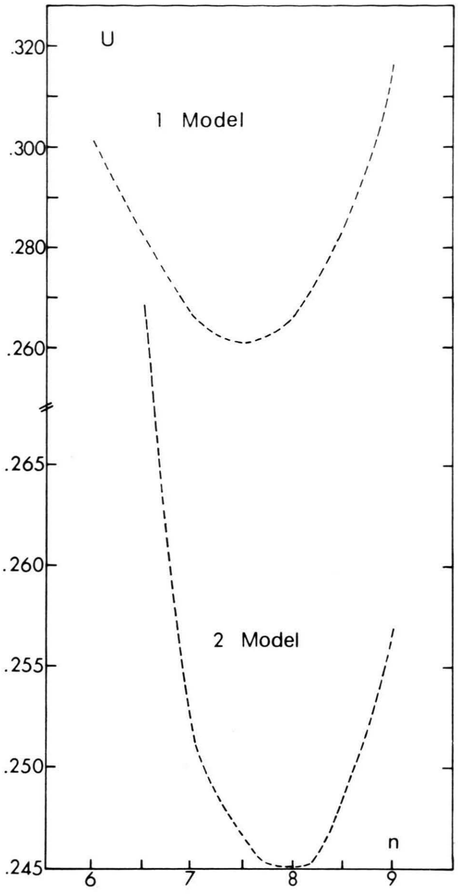

Fig. 4. The $U$ values, defined in (4), for the two models as a functions of $n_{Ce-H_2O_I}$.

A number of refinements were carried out using the $s$ intervall 1.5–16.2 $Å^{-1}$. $n_{Ce-H_2O_I}$ in each calculation was fixed while the whole parameter set was refined. The $n_{Ce-H_2O_I}$ values vary from 6 to 9 with steps 0.2. Figure 4 shows $U$ vs. $n$ for the two models. The function reaches its minimum at $n = 7.5$ in the first case and 8 in the second one. The $U$ function varies not much for $n_{Ce-H_2O_I}$ (between 7 and 8).

The best structure function from the second model is given in Fig. 1 (solid line). In order to have a comparison between the correlation functions, the theoretical $si(s)$ was connected to the experimental data at $s = 1.6$ $Å^{-1}$ and then Fourier transformed. In Fig. 2 the correlation function thus obtained (solid line) is plotted against the one from the experimental data (points). In Table 2 we report the values of the parameters obtained with the two models.

Table 2. Mean distances $r$(Å) and root-mean-squares deviation $\sigma$(Å) for the discrete interactions used in the final calculation of the synthetic functions from the two models are given. Standard errors for the refined parameters are given in parenthesis. $n$ is the coordination number.

| Parameters | Model 1 | Model 2 |
|---|---|---|
| $r_{\mathrm{Ce-H_2O_I}}$ | 2.552 (2) | 2.555 (2) |
| $\sigma_{\mathrm{Ce-H_2O_I}}$ | 0.120 (1) | 0.121 (1) |
| $n_{\mathrm{Ce-H_2O_I}}$ | 7.5 | 8.0 |
| $r_{\mathrm{Ce-H_2O_{II}}}$ | 4.56 (1) | 4.57 (2) |
| $\sigma_{\mathrm{Ce-H_2O_{II}}}$ | 0.41 (1) | 0.39 (2) |
| $n_{\mathrm{Ce-H_2O_{II}}}$ | 15.5 (7) | 15.1 (6) |
| $r_{\mathrm{Ce-O_2}}$ | 3.51 (2) | 3.51 (2) |
| $r_{\mathrm{Ce-N}}$ | 3.44 (2) | 3.44 (2) |
| $r_{\mathrm{Ce-O_3}}$ | 4.62 (2) | 4.61 (3) |
| $r_{\mathrm{N-H_2O}}$ | 3.40 (3) | 3.50 (5) |
| $\sigma_{\mathrm{N-H_2O}}$ | 0.28 (2) | 0.26 (2) |
| $n_{\mathrm{N-H_2O}}$ | 7.0 (4) | 7.7 (6) |
| $r_{\mathrm{H_2O-H_2O}}$ | 2.94 (1) | 3.13 (2) |
| $\sigma_{\mathrm{H_2O-H_2O}}$ | 0.197 (5) | 0.130 (5) |
| $r_{\mathrm{H_2O_I-H_2O_{II}}}$ | – | 2.90 (1) |
| $\sigma_{\mathrm{H_2O_I-H_2O_{II}}}$ | – | 0.136 (4) |
| $r_{\mathrm{O-H_2O}}$ | – | 2.89 (2) |

## 4. Remarks

The present study on a concentrated $Ce(NO_3)_3$ solution shows the presence of a first and a second shell of water molcules around cerium(III) together with the presence of cerium-nitrate contacts. It was also necessary to introduce some anion-solvent contacts as in the case of the solution of $Al(NO_3)_3$ [11]. The two alternative models show that the coordination numbers of Ce(III) vary with the used model and that it is very difficult to give unambiguously an answer with X-ray diffraction technique. In this connection it is very meaningful to compare the theoretical correlation functions (Fig. 5) obtained from the two models; they are substantially identical. The possible reason for this difficulty is that the contribution of the cation-$H_2O_I$ superimposes the $H_2O-H_2O$ and $O-H_2O$ contributions.

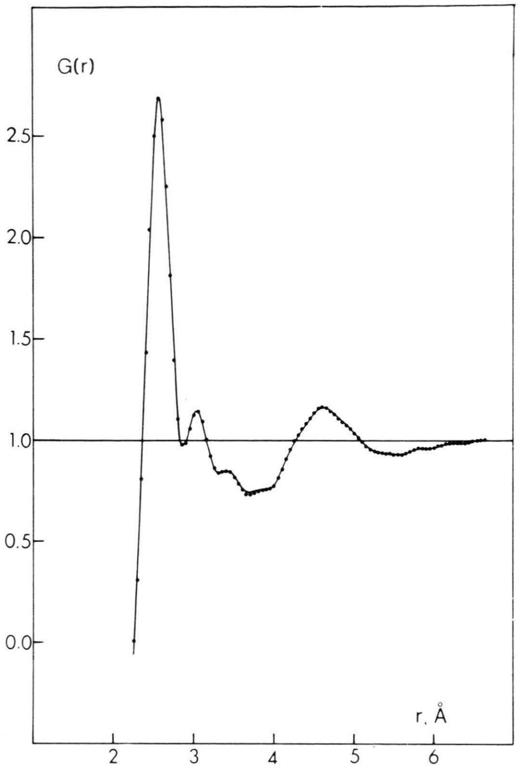

Fig. 5. Theoretical correlation functions obtained from model 1 (···) and model 2 (——).

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