

On the Microscopic Mechanism of Compton Scattering of BaCl₂ Solutions

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Abstract. Compton scattering of BaCl₂ solutions is studied in this article. And the electronic structure of some aqueous BaCl₂ solutions is analyzed profoundly according to the density functional theory. The microscopic mechanism of Compton Scattering of such solutions is discussed. And it is concluded that the microscopic mechanism of Compton scattering mainly includes these aspects: (i) Attenuation coefficient: the impact of attenuation coefficient on Compton scattered photon counts is: with concentrations the increasing of the solutions, the attenuation coefficient is increasing too. (ii) Electronic number density: with the decreasing of hydrated number of ions, the electronic density is approximately linear increasing. (iii) Mulliken atomic charge: it can be obtained that the bounded strength for the hydrated ion systems become increasing with the concentration increasing of solutions.

Introduction

Recent years have witnessed a great development in theory and applications of Compton scattering theories since their advancement.^[1] Our group's studies have shown that the relative number of photons Compton scattering is proportional to the electron density number of solutions, which can be written as^[2]

$$\Delta N = \phi_0 f_C f_{1x} f_{2x} \rho_x N_0 \left\{ x \left[\sum_i w_i \frac{Z_i}{A_i} \right] + (1-x) \left[\sum_{i'} w_{i'} \frac{Z_{i'}}{A_{i'}} \right] \right\} \frac{d\sigma_{KN}(\theta)}{d\Omega} S(q, Z) \Delta V \quad (1)$$

where ϕ_0 is the incident photon flux, x is the solution concentration, f_c is the compensation factor of container for photon scattering and absorption, and f_{1x} is the incoherent attenuation factor in incident direction of scatterer, and f_{2x} is the incoherent attenuation factor in exit direction of scatterers(affected by the solution concentration), ρ_x is the physical density, the parameter N_0 stands for Avogadro constant, and $\frac{d\sigma_{KN}(\theta)}{d\Omega}$ is the Klein-Nishina differential cross section, the function $S(q, Z)$ is the incoherent atomic scatter function. ΔV is the volume of electrolyte solution, Where ρ_x is the mass density of solution (affected by the solution concentration), and the $\left\{ x \left[\sum_i w_i \frac{Z_i}{A_i} \right] + (1-x) \left[\sum_{i'} w_{i'} \frac{Z_{i'}}{A_{i'}} \right] \right\}$ is the average ratio of scattering atomic number and atomic weight.

For BaCl₂ solutions, equation (1) is also suitable. In the article, Compton scattering of some aqueous BaCl₂ have been studied extensively. Firstly, the relationship between Compton scattering photon counts and concentration of the solutions were analyzed in theory in briefly. Secondly, the relationships were verified by the Compton scattering experiments of BaCl₂. And then the factors that impact Compton scattering photon counts have been explored from the microscopic

mechanism based on the density functional theory.

Some Approximations

The container of some aqueous BaCl₂ solutions is set to be cylindrical for convenient research. With the symmetry, both of f_{1x} and f_{2x} can be replaced by f_x . And the relationship between incoherent attenuation factor f_x and concentration is shown in Table 1,^[3] which based on that the distances d of incident and exit ray could be assumed to be a unit with symmetry of scattering, when the energy of the gamma ray is 661.5keV.

Table 1 The relationship between attenuation factor and concentration of aqueous BaCl₂ solutions

Concentration	0%	4.26%	8.52%	17.05%	18.94%	25.60%
x						
μ	8.939×10^{-2}	8.853×10^{-2}	8.767×10^{-2}	8.594×10^{-2}	8.555×10^{-2}	8.420×10^{-2}
$f_x = \exp(-\mu d)$	0.9145	0.9153	0.9161	0.9176	0.9180	0.9192

Note: the distance d was replaced by a unit distance

In consideration of some approximations, such as the relationship between mass density and concentrations is regarded as linear, and the concentration ranges from 0 to 0.25, the impact of concentration change on the mass density and the incoherent scatter factor can be approximated as linear. Therefore, the relationship between Compton scattering photon number and solution concentration under certain volume can be treated as linear relation by:

$$\Delta N = (Ax + B)\Delta V \quad (2)$$

where

$$A = f_c \phi_o N_0 2a \left(\sum_i w_i \frac{Z_i}{A_i} - \sum_{i'} w_{i'} \frac{Z_{i'}}{A_{i'}} \right) \frac{d\sigma_{KN}(\theta)}{d\Omega} \quad (3)$$

$$B = f_c \phi_o N_0 \left[b \left(\sum_i w_i \frac{Z_i}{A_i} - \sum_{i'} w_{i'} \frac{Z_{i'}}{A_{i'}} \right) + a \left(\sum_{i'} w_{i'} \frac{Z_{i'}}{A_{i'}} \right) \right] \frac{d\sigma_{KN}(\theta)}{d\Omega} \quad (4)$$

a and b in equation(4), (5) are two constants for a certain solution.

Experiments and Results

In these experiments the Compton scattering devices are employed, whose radiation source is a 137Cs with the energy 662 keV. The photons are collimated before they reach the scattered sample. Measurements of the scattered photons are carried out by using a high-resolution (less than 9 per cent in the studied energy range) NaI crystal detector, whose voltage is settled at a high value of 600 V. The collected photon events were recorded by a computer. The scatter angle θ is settled at 40° and 80°. At first, the background Compton scattering photon counts of empty container is collected, and then solutions' Compton scattering data are collected. For each test, the time to collect the scattered photons is 600 s. The test is repeated twice for each sample. The measurement results are fitted into linear with the least squares method after the background is cut off. And when the scatter angle θ is settled at 40°, the relationship between the scattered photon counts ΔN and the concentration x is

$$\Delta N = 14620.36 x + 35986.82 \quad (5)$$

when the scatter angle θ is settled at 80°, the linear expression is

$$\Delta N = 7903.22 x + 19548.38 \quad (6)$$

Our group considered that there were some factors which impacting the Compton scattering photon counts from a more microscopic point of view in order to truly reveal the nature of the Compton scattering mechanism.

Analysis of the Electronic Structure

Attenuation Coefficient: According to Eq.(1), Compton scattering photon number is proportional to f_{1x} , f_{2x} (f_{1x} is the attenuation factor of the incident beam, f_{2x} is the attenuation factor of the scattered beam). And attenuation coefficient of the scatterers is related to the energy of the incident light. When the energy of incident photon is 661.5 keV, the attenuation coefficient is shown in Table 1.

Hydration Number of Hydrated Ions: The literatures[4] show that the hydration numbers of Ba^{2+} and Cl^- in very dilute solutions are 8 and 6 which measured with X-ray diffraction method in experiments, respectively. Further, the ratio of free ions, hydrated ions (include low hydration number of hydrated ions and high hydration number of hydrated ions), free water molecules and molecular hydration will be changed with the change of solution concentration. That is to say, with the increasing of solution concentration, hydrated ions with low hydration number and free ions will be increasing, and hydrated ions with high hydration number and free water molecules will be decreasing. Therefore, it is reasonable to supposed that hydrated ions with low hydration number is relative with high concentration solutions and hydrated ions with high hydration number is relative with low concentration solutions.

Optimized Structure: The electronic structure of hydrated ions has been obtained by using the quantum chemistry program based the density functional theory (DFT)^[5-7]. During the calculations, it is necessary to considering the effect of the electronic structure of COSMO on solvent. It is a necessary step to optimize the hydrated ions geometry structure. After optimized the hydrated ions geometry structure, the relative parameters of electronic structure for hydrated ions can be calculated easily. And the optimized hydrated ions are shown from Fig. 1 (Note: the structure of hydrated chloride ion was shown in the reference[8]

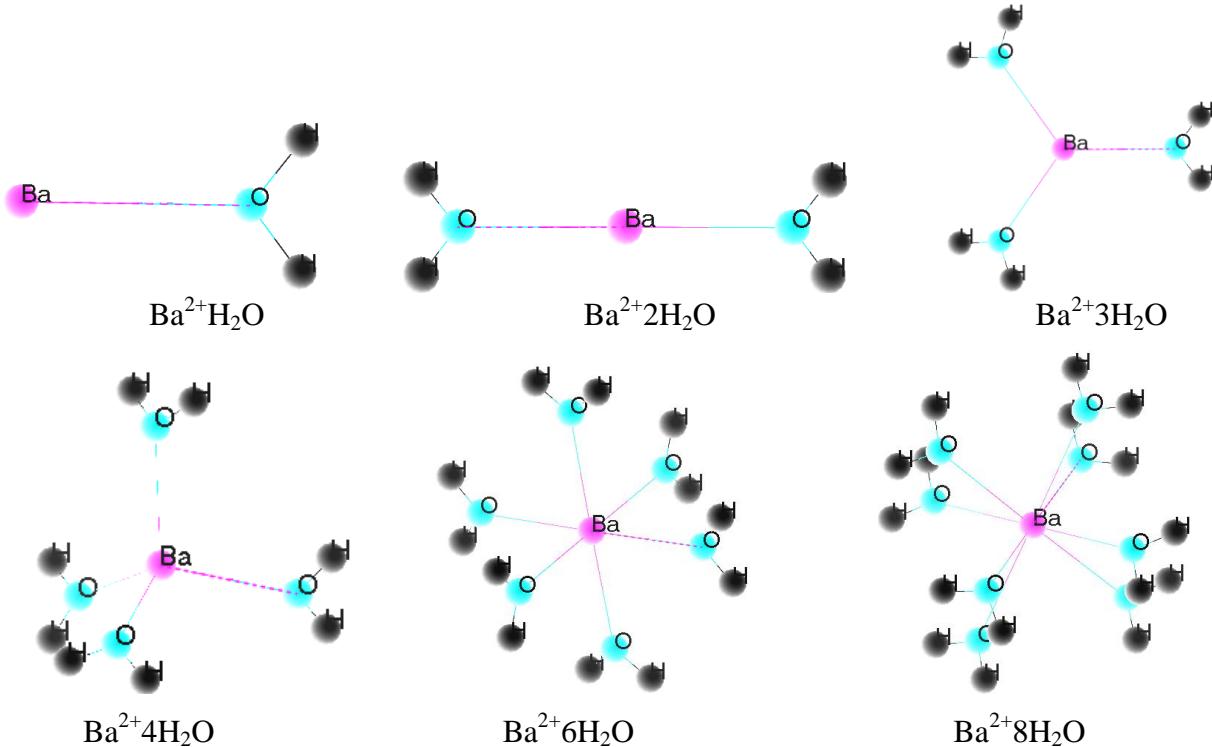


Figure 1. the optimized hydrated barium ion

The Distance between Hydration Ion and O atom: The following Table 2 shows the average distance between the central ion and the oxygen atoms in hydration water molecules of hydrated ions after optimized. From Table2, through compared the distance measured by experiment method with that computed by computation, these data are consistent each other. But with the decreasing of solution concentration, the average distances between hydration ion and O have a tendency to

increase.

Table 2 The average distance between hydration ion and O (Å)

coordination numbers	1	2	3	4	6	8	
	computational value						experimental value
Ba-O	2.712	2.726	2.744	2.740	2.775	2.886	2.80-2.90 ^[9]
Cl-O	3.078	3.162	3.187	3.192	3.267	3.292	3.14-3.29 ^[10]

Electronic Density: According to Equation(1), there was such a product part,

$$\rho_x N_0 \left\{ x \left[\sum_i w_i \frac{Z_i}{A_i} \right] + (1-x) \left[\sum_{i'} w_{i'} \frac{Z_{i'}}{A_{i'}} \right] \right\}$$

its actual physical meaning is electronic density. And based on the optimized hydrated ions, the electronic density can be calculated easily. The data of those ions are shown in Table 3.

Table 3 electronic density of hydrated barium ion and hydrated chloride ion ($\times 10^{29} \text{ m}^{-3}$)

	Ba ²⁺ H ₂ O	Ba ²⁺ 2H ₂ O	Ba ²⁺ 3H ₂ O	Ba ²⁺ 4H ₂ O	Ba ²⁺ 6H ₂ O	Ba ²⁺ 8H ₂ O
electronic density	11.012	9.390	8.960	7.967	7.172	6.328
	Cl ⁻ H ₂ O	Cl ⁻ 2H ₂ O	Cl ⁻ 3H ₂ O	Cl ⁻ 4H ₂ O	Cl ⁻ 6H ₂ O	Cl ⁻ 8H ₂ O
electronic density	6.476	6.197	5.802	5.768	5.352	5.083

With the decreasing of hydrated number, the electronic density is approximately linear increasing. Those are consistent with the experiments data on Fig. 1.

Mulliken Atomic Charges: Mulliken charge analysis is one of the most common charge analyses. The density matrix and atomic overlap matrix are used to partition charges among the atoms. This method is, however, very sensitive to the choice of basis set. In calculation, we select the DNP. The data is shown in Table 4.

Table 4 Mulliken atomic charges of hydrated barium ion and hydrated chloride ion (e)

Elem	Ba ⁺ H ₂ O	Ba ⁺ 2H ₂ O	Ba ⁺ 3H ₂ O	Ba ⁺ 4H ₂ O	Ba ⁺ 6H ₂ O	Ba ⁺ 8H ₂ O
Ba	1.914	1.852	1.768	1.702	1.643	1.577
O	-0.585	-0.591	-0.555	-0.586	-0.594	-0.582
H	0.335	0.332	0.316	0.330	0.327	0.318
Elem	Cl ⁻ H ₂ O	Cl ⁻ 2H ₂ O	Cl ⁻ 3H ₂ O	Cl ⁻ 4H ₂ O	Cl ⁻ 6H ₂ O	Cl ⁻ 8H ₂ O
Cl	-0.906	-0.837	-0.777	-0.738	-0.700	-0.692
O	-0.616	-0.607	-0.606	-0.603	-0.594	-0.591
H	0.261	0.263	0.266	0.268	0.272	0.276

According to Table 4, some rules can be seen as follows: (1)For the hydrated barium ion, the less the water molecule numbers of Ba²⁺ hydrate (higher concentration), the smaller the Ba²⁺ Mulliken atomic charge. It means that the electron will deviate from Ba²⁺, and the electrons bound from Ba²⁺ is weaker. But for O, the less the hydration numbers of Ba²⁺ hydrate, the stronger the O Mulliken atomic charge, and the electrons bound from O is stronger, i.e. the lower hydration numbers of Ba²⁺ is, the weaker electrons are bound. (2) According to the analyzing on the electronic structure of the hydrated ions above, it can be obtained that the bounded strength for the hydrated ion system becomes increasing with the concentration increasing of solutions.

Conclusions

And from equation (1), the Compton scattering occurred number is getting increasing with the concentrations increasing of the solutions. On the basis of the discussions above, it is concluded that the microscopic mechanism of Compton scattering mainly includes these aspects:

(i) Attenuation coefficient: the impact of attenuation coefficient on Compton scattered photon counts is: with concentrations the increasing of the solutions, the attenuation coefficient is increasing too. Further, the Compton scattered photon counts is in direct proportion to the attenuation coefficient from equation (1).

(ii) Electronic number density: with the decreasing of hydrated number of ions, the electronic density is approximately linear increasing. Those are consistent with the experiments data.

(iii) Mulliken atomic charge: according to the analyzing on the Mulliken atomic charge of the hydrated ions above, it can be obtained that the bounded strength for the hydrated ion systems become increasing with the concentration increasing of solutions.

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