Effect of Electronic Structure on Compton Scattering of MgCl2 Solutions

Fan sisi[1], Luo Guang[1a*]

[1] College of Physics and Electronic Engineering of Chongqing Normal University, Chongqing 400047, P. R. China

[a*]corresponding author: photoncn@cqnu.edu.cn

Abstract-Based on the Compton scattering theoretical and experimental research, Compton scattering of MgCl2 solution is studied in this article. And the electronic structure of some aqueous MgCl2 solutions is analyzed profoundly according to the density functional theory. It is concluded that the factors affecting the counts of Compton scattering photon include the mass density, the scattering attenuation factor and the concentration of a solution, especially include the other two factors, (i) Electronic number density: with the decreasing of hydrated number of ions, the electronic density is approximately linear increasing; (ii) 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.

Keywords-Compton scattering; electron density; electronic structure; MgCl2 solution

I. INTRODUCTION

The study of Compton scattering[1] has always become the hot point research at home and abroad since the Compton scattering was proposed. Studies have shown that the relative number of photons Compton scattering photon counts ΔN is proportional to the solution concentration x，which can be written as[2]

$$\Delta N = \{ f_C \phi_o N_0 2a(\sum_i w_i Z_i / A_i - \sum_{i'} w_{i'} Z_{i'} / A_{i'}) d\sigma_{KN}(\theta) / d\Omega x + f_C \phi_o N_0 [b(\sum_i w_i Z_i / A_i - \sum_{i'} w_{i'} Z_{i'} / A_{i'}) + a(\sum_{i'} w_{i'} Z_{i'} / A_{i'})] d\sigma_{KN}(\theta) / d\Omega \} \Delta V \quad (1)$$

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, 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, $\sum_i w_i Z_i / A_i$ and $\sum_{i'} w_{i'} Z_{i'} / A_{i'}$ are the average ratio of scattering atomic number and atomic weight of solute molecules and soluble molecules, *a* and *b* are two constants for a certain solution.

For $MgCl_2$ solutions, equation(1) is also suitable. In the article, Compton scattering of some aqueous $MgCl_2$ solutions have been studied extensively. The relationships were verified by the Compton scattering experiments of $MgCl_2$ solutions, and then the factors that impact Compton scattering photon counts have been explored from the electronic structure based on the density functional theory.

II. EXPERIMENTS AND RESULTS

In these experiments the Compton scattering devices are employed, whose radiation source is a ^{137}Cs 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 those results can be shown in Fig.1.

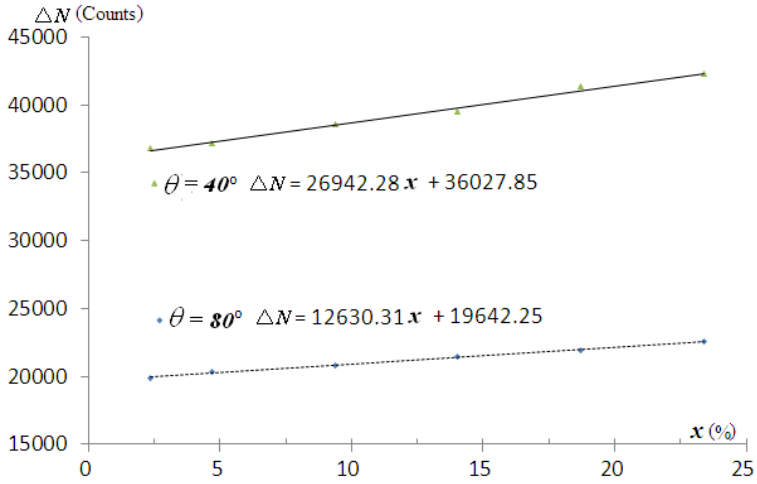

Figure 1. The relation between the scattered photon counts and the concentration of $MgCl_2$ solutions at the scattering angle 40° and 80°

As shown from Fig.1, the relationship between $MgCl_2$ solution concentrations and Compton scattering photon counts is linear. This is consistent with the equation (1).

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

III. ANALYSIS OF THE ELECTRONIC STRUCTURE

A. Hydration number of hydrated ions:

When the solute molecules are dissolved into the aqueous solution to form an ion, and the hydrated ion is formed. There are free ions, hydrated ions (include low hydration number of hydrated ions and high hydration number of hydrated ions), free water molecules and molecular hydration in a certain concentration solution. And those particles ratio keep in a dynamic balance. With the increase of solution concentration, the number of water molecules in $MgCl_2$ decreased, and the ratio of the number of water molecules and the number of ions decreased. It can be concluded that, with the increase of solution concentration, the hydration number of $Mg^{2+}$and Cl^- will reduce. The literatures[5-6] show that the hydration numbers of both of $Mg^{2+}$and Cl^- in very dilute solutions are 6 which measured with X-ray diffraction method in experiments. The hydration number should be smaller than the above experimental value for common solutions. 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 lower hydration number is relative with higher concentration solutions and hydrated ions with higher hydration number is relative with lower concentration solutions.

B. Optimized structure:

The electronic structure of hydrated ions has been obtained by using the quantum chemistry program based the density functional theory (DFT)[7-9]. 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.2 (Note: the structure of hydrated chloride ion was shown in the reference[8])

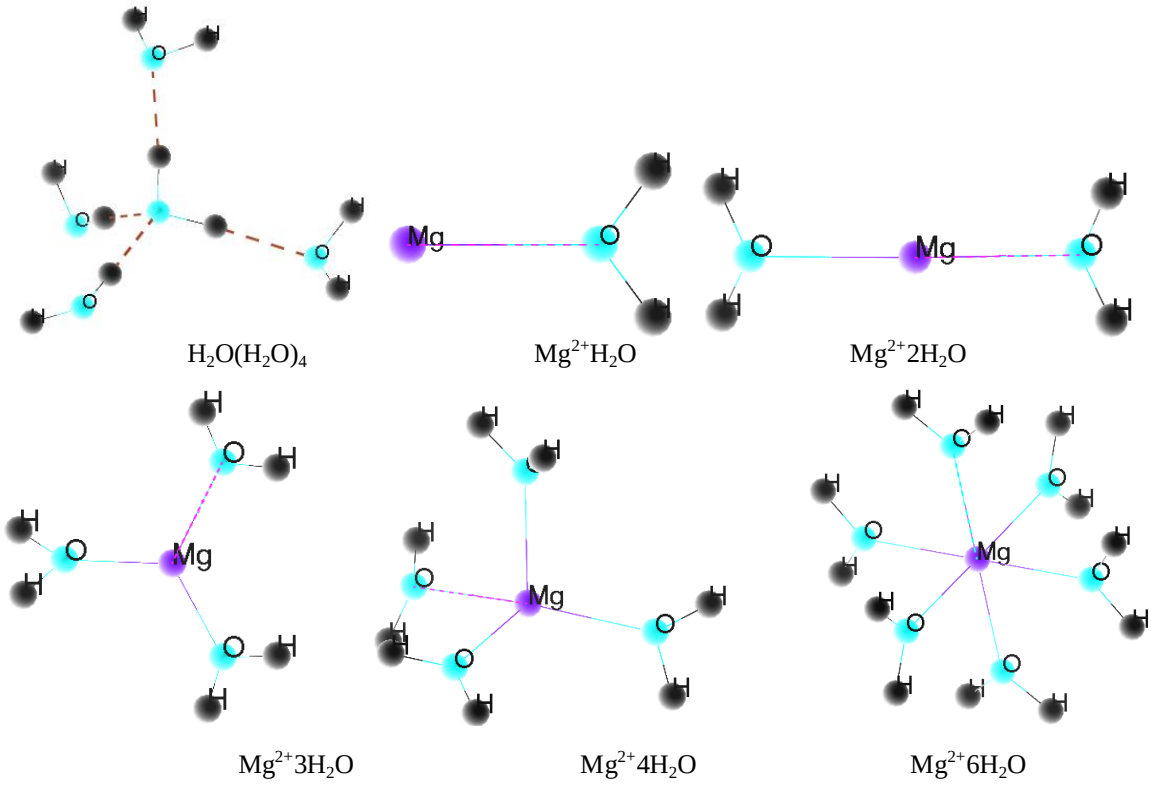

Figure 2. the optimized hydrated water molecule and hydrated magnesium ion

C. The Distance between hydration ion and O atom:

The following table 1 shows the average distance between the central ion and the oxygen atoms in hydration water molecules of hydrated ions after optimized. From table 1, 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 I THE AVERAGE DISTANCE BETWEEN HYDRATION ION AND O (Å)

coordination number	1	2	3	4	6	8	
			computational value				experimental value
Mg-O	2.067	2.081	2.046	2.058	2.111	—	2.09[11]
Cl-O	3.078	3.162	3.187	3.192	3.267	3.292	3.14-3.29[12]

D. Electronic density:

According to Equation (1), there was such terms, $\sum_i w_i Z_i / A_i$ and $\sum_{i'} w_{i'} Z_{i'} / A_{i'}$ which denoted 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 2.

TABLE II ELECTRONIC DENSITY OF HYDRATED MAGNESIUM ION AND HYDRATED CHLORIDE ION (X1029M-3)

	$Mg^{2+}H_2O$	$Mg^{2+}2H_2O$	$Mg^{2+}3H_2O$	$Mg^{2+}4H_2O$	$Mg^{2+}6H_2O$	
electronic density	5.522	5.490	5.448	5.405	5.313	
	Cl^-H_2O	Cl^-2H_2O	Cl^-3H_2O	Cl^-4H_2O	Cl^-6H_2O	Cl^-8H_2O
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.

E. 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 3.

TABLE III MULLIKEN ATOMIC CHARGES OF HYDRATED MAGNESIUM ION AND CHLORIDE ION (E)

Elem	$Mg^{+}H_2O$	$Mg^{+}2H_2O$	$Mg^{+}3H_2O$	$Mg^{+}4H_2O$	$Mg^{+}6H_2O$	$(H_2O)_5$
Mg	1.860	1.718	1.561	1.412	1.248	-
O	-0.547	-0.546	-0.508	-0.538	-0.537	-0.596
H	0.344	0.344	0.328	0.342	0.330	0.298
Elem	$Cl^{-}H_2O$	$Cl^{-}2H_2O$	$Cl^{-}3H_2O$	$Cl^{-}4H_2O$	$Cl^{-}6H_2O$	$Cl^{-}8H_2O$
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 3, some rules can be seen as follows: for the hydrated magnesium ion, the less the water molecule numbers of Mg^{2+} hydrate (higher concentration), the smaller the Mg^{2+} Mulliken atomic charge. It means that the electron will deviate from Mg^{2+}, and the electrons bound from Mg^{2+} is weaker. But for O, the less the hydration numbers of Mg^{2+} hydrate, the stronger the O Mulliken atomic charge, and the electrons bound from O is stronger, i.e. the lower hydration numbers of Mg^{2+} is, the weaker electrons are bound.

IV. CONCLUSIONS

And from Equation (1), the Compton scattering occurred number is getting increasing with the concentrations increasing of the solutions. Furthermore, on the basis of the discussions above, it is concluded that the electronic structure of Compton scattering mainly includes these aspects: (i) 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. (ii) 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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