



## XRD-DFA Analysis of data on discrete units of micro-molecules: Applied on $C_{52}H_{60}N_4S_8Zn_2$

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### ABSTRACT

X-ray diffraction (XRD) technique due to its strength for providing visualized atomic model of molecules stands as first in the field of characterization of new synthesized molecules. Here, the analysis of diffraction data on discrete units of new, not yet fairly known structure of molecule  $C_{52}H_{60}N_4S_8Zn_2$  is performed to obtain a quantitative view of the structure of the system. Notes regarding the layer shape of the molecule are mentioned. First, a qualitative discussion of the type of intra-molecular order is given. Then, the nano-particle's size definitions, via different approaches of coherence, correlation, etc. are addressed. Each of the different defined values is obtained and difference between them and their interpretation will be discussed. Debye function analysis (DFA) is employed to approximate the radius of gyration, as another approach for estimating particle's size. Results of different defined values, the radius of gyration, approximate coherence length are estimated and decision on the size of molecule is made. These analyses will provide us some neat picture of different definitions of size of nano-systems, which lacks clearance in the literature.

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### چکیده

تکنیک پراش اشعه X به دلیل تواناییش در به تصویر کشیدن مدل اتمی ملکولها برترین روش در میان روشهای گوناگون مشخصه‌یابی ملکولهاست. در این مقاله، داده‌های پراش اشعه X را تحلیل می‌کنیم، که از واحدهای مجزای یک ملکول جدیداً سنتز شده با فرمول شیمیایی  $C_{52}H_{60}N_4S_8Zn_2$  به دست آمده است، تا بتوانیم قابلیت این تکنیک را در تعیین سایز نانو ذرات نشان دهیم. ابتدا، نظم درون ملکولی را توضیح می‌دهیم و نوع این نظم را در ساختار مزبور تعیین می‌کنیم. سپس، سایز نانو ذره را تعریف می‌کنیم و نشان خواهیم داد که تعاریف گوناگونی برای این سایز وجود دارد که الزاماً منحصر به فرد و یکسان نیستند. این تعاریف مبتنی بر همدوسی و همبستگی و جز اینهاست. هر مقداری که از یک تعریف معین به حاصل می‌آید، تفسیری دارد که بیان خواهد شد. از تحلیل تابع دبای (DFA) استفاده خواهیم کرد تا شعاع ژیراسیون ملکول و طول همدوسی را تقریب بزنیم. این تحلیلها شناختی از تعاریف گوناگون سایز نانوذرات به ما می‌دهد که معمولاً در متون رایج علمی به خوبی تشریح نشده است.

### اطلاعات مقاله

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## 1 Introduction

Molecules having tens of atoms, without the crystallinity strength to form crystal units, can't be captured by PDFs of XRD libraries and there needs some more elaborate methods for their characterization [1]. There are some points, however, for particle's size determination to add. First, if the nano-particle is not characterized crystallographically (as such in some rod shape, long axis crystalline nano-particles) we will have no chance to clearly decide which of different definitions for particle's size, for example obtained from Scherrer formula for different Bragg peaks, will give the correct answer. On the other hand, most nano-systems have a plenty of allotropes mixed with pretty various morphologies that make the analysis difficult [2].

Also, some molecules don't crystallize during long terms and retain their non-crystalline state over time. In these cases, we must define clearly the approach for particle's size determination, especially type of temporal and spatial averaging, at first step. The range of ability of wave-length for size determination should be discussed, and then, the coherence length and its meaning should be clarified. In fact, the relationship between these quantities and intra-molecular interactions is critical for overcoming the nano-challenge [3,4].

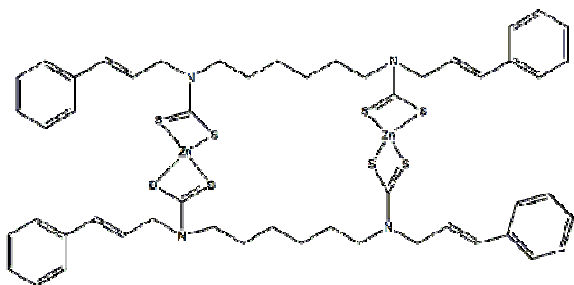
Addition to Scherrer formula and Hall-Williamson analysis, Debye function analysis (DFA) simulation of discrete molecule is useful for proposing the mean parameters of plausible asymmetric units [5]. With the idea of Debye, which resembles the output of total scattering intensity from the particle, we can visualize some averaged local structure of atomic model. Theoretically, the XRD diffraction curves are not something so different from rescaled Debye function (DF) [6,7]. DF is a generalized version of structure factor  $S(\mathbf{q})$ , which is measured in scattering experiments from material structures, directly. X-ray diffraction from any phases of matter depicts interesting curves [8], however, Debye function carries the general scattering features for a general structure with random orientation.

As a primary benefit, the range of order in the system can be observed qualitatively from a quick look at the Debye function curve. Also and interestingly, the scattering picture of Debye can be used to provide comparative information, especially to attack the radius of gyration problem of micro-molecules, which is one of the most challenging problems in determining the structure of nano-systems [9]. Even, DFA is able to justify the plausible geometrical structure and its attributed atomic model, quantitatively; (DFA is a powerful tool for real space visualization of particle structure. This potential application is not discussed here.) Same models and techniques were utilized recently to characterize the molecular magnet, along with the successful simulation of the molecule first-principally [10,11]. For a brief theoretical discussion of quantities and the procedure of characterization from the X-ray diffraction pattern see [10].

In this work, different approaches for size determination of micro-molecules are investigated. The results of such analysis is applied on  $C_{52}H_{60}N_4S_8Zn_2$ , which recently has been synthesized and will reported elsewhere [12]. The range of parameters measurable with the wavelength of X-ray used is discussed and coherence and correlation length in the molecule under question is determined. DFA analysis on the size of micro-molecule  $C_{52}H_{60}N_4S_8Zn_2$  is done. The method employs the technique in isotropic situations, in which the X-ray intensity depends upon the magnitude of wave vector  $k$  only.

## 2 Molecule

The molecule having chemical formula  $C_{52}H_{60}N_4S_8Zn_2$  was synthesized recently [12]. This molecule has two Zn nucleus, eight S atoms, and many others. The molecule doesn't form crystalline matter over long periods, so we resort to Debye function analysis (DFA) for its characterization. The constituents of the molecule surround the Zn atom, in a layered sheet, as shown in Fig. 1.

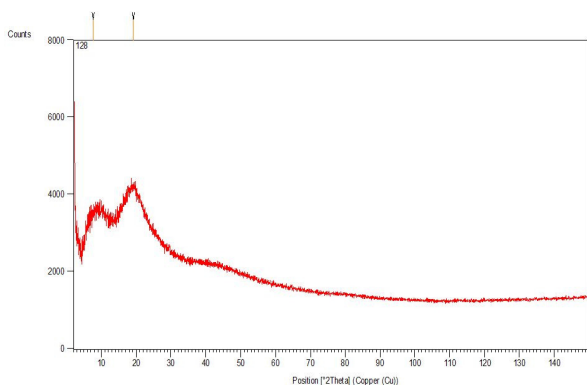


**Fig. 1.** Molecular shape of the micro-molecule of chemical formula  $C_{52}H_{60}N_4S_8Zn_2$ , predicted from chemical data via procedure of synthesis [12].

This structure is proposed also, as the most plausible molecular structure, which is verified by some other indirect techniques [12].

### 3 Experiment

DFA is applied to the results of the X-ray diffraction from  $C_{52}H_{60}N_4S_8Zn_2$  in solid phase. Firstly, I report the experimental pattern of XRD (Fig. 2).



**Fig. 2.** Experimental X-ray intensities diffracted from  $C_{52}H_{60}N_4S_8Zn_2$ .

#### a. The experimental X-ray scattering parameters

The data were collected using X-ray diffraction experiment set in  $\theta - \theta$  geometrical configuration with the scan time of 29.0700s and step of  $0.0260^\circ$ . The wavelength of X-ray was chosen about  $\lambda = 1.54060\text{\AA}$  (Cu-K $\alpha$ ) and the data were collected by Debye-Scherrer camera. The software Xpert was used to eliminate undesired intensities of radiation by forward-backward Fourier transform.

The total scattering data are collected by Diffractometer System= XPERT-PRO, with Goniometer=PW3050/60 $\theta/\theta$  configuration. Minimum step size was  $2\theta = 0.001$ , minimum step size  $2w = 0.001$ , and sample stage=Reflection-Transmission spinner PW3064/60; finally minimum step size  $\Phi = 0.1$ . The experiment was done in KEFA Company. Fine Calibration Offsets for  $2\theta = 0.605^\circ$ . The data were collected from  $\theta = 1.51013028000000E + 0000^\circ$  to  $\theta = 1.49970130280000E + 0002^\circ$ .

Table 1 summarizes some useful details.

**Table 1.** The parameters of XRD experiment done on powder of molecule  $C_{52}H_{60}N_4S_8Zn_2$ .

Comments	Creation date=2015-04-21 11:29:23 AM
	Goniometer=PW3050/60 ( $\theta/\theta$ )
	Minimum step size $2\theta$ :0.001
	Reflection-Transmission Spinner PW3064/60
	Diffractometer system=XPERT- PRO
	Fine Calibration Offset for $2\theta = 0.605$ deg
Start Position [2Th.]	1.5101
End Position [2Th.]	149.9701
Step Size [2Th.]	0.0260
Scan Step Time [s]	43.0950
Scan Type	Continuous
Temperature [Celsius]	25.00
Anode Material	Cu
K-Alpha1 [\AA]	1.54060
K-Alpha2 [\AA]	1.54443
K-Beta [\AA]	1.39225

### 4 Analysis of results

#### a. DFA analysis on a system without any preferred orientation

Debye function (DF) analysis on a sample without any preferred orientation in an ideal case provides many useful and reliable information in amorphous or nano-particle systems. Therefore, the methodology of DFA is utilized mainly for structure determination or analysis when there exists short correlation, which is the case in

our sample. The reason for this type of conclusion is as follows (section [4b]).

### b. Short- versus long-range order in the molecule

X-ray diffraction diagram from  $C_{52}H_{60}N_4S_8Zn_2$  in powder form (Fig. 2), which is known as Debye function curve, is the only basic data obtained from XRD experiment. The first observed qualitative behavior of the diffracted beam seen in the graph implies to intramolecular order [13].

Range of order at a glance can be deduced qualitatively from the dominant peaks and valleys of the diagram in Fig. 2. In crystalline materials, the peaks exist non-decreasingly even to large diffraction angles. However, the molecule under question doesn't crystallize at long term periods. As shown in Fig. 2, characteristic peaks do not mostly exist till  $2\theta \cong 45^\circ$ . This means that the interaction in asymmetric unit of molecule plays a central role mostly at medium (nearly short) range distances, i.e. there exist medium (nearly short) range order in the system.

The interaction of molecules in solid phase is of question, but it can be neglected where the intramolecular coherence of units is greater than the intermolecular one. Therefore, every molecule can be considered as a separate and nearly free structure, and can be modeled by a discrete geometrical object. This approximate scheme is very important for calculating or attributing the experimental data to any single structure and for developing simple models, too. In conclusion, the mean parameter of nano-system may be attributed to a single free isotropic geometrical object, unless the types of calculation or relevance interactions are clearly stated.

### c. Size of micro-molecule

Many further progress in the field of device fabrication depends critically on characterization of the mean parameters of a collection of single molecules in physical/chemical medium, of which worth mentioning

is size of the molecule. We refer to it onwards, as mean diameter of molecule (MDM). For example, effective length of medium,  $L = N \times 2l$ , is constructed from the queue of  $N$  molecules, where  $D = 2l$  is its MDM [5].

However, determination of the size of nano-system is one of the most challenging problems. There are many major fundamental quandaries, related to the exact definition and appropriate deciding for the proper technique for this type of characterization. For example, Scherrer formula is applicable only to spherical objects, and for other shapes, the meaning of the determined parameter must be emphasized. The particle's size obtainable from TEM and XRD experiments are not equal; why is there this difference? For non-spherical particles, any experimentally obtainable MDM may show specific feature of the particle. In this subsection, some vastly used methods of particle's size determination are utilized and an interpretation of different estimated parameters will be addressed.

The MDM method may be replaced by analytical expressions for coherence length dampening effects on the simple geometries [2, 14]. The molecule at hand, however, has a more elaborate structure (nearly a tetragonal shape), which can't be replaced by simple shapes of spherical geometries. So, the MDM of the molecule should be inferred from rough experimental data [5]. We estimate MDM of the molecule  $C_{52}H_{60}N_4S_8Zn_2$  with the following methods and compare the results.

#### i. Size of micro-molecules obtainable from these types of measurements

First, we provide a range, in which characteristic lengths are relied. The maximum representative angle of coherence in XRD diagram is about  $\theta_{max} \cong 45^\circ$ , corresponding to  $q_{max} = 2k\sin\theta_{max} \cong 6.1281 \times 10^{10}m^{-1}$ . The scattering vector plays a central role in all diffraction experiments. The inverse of the maximum scattering vector  $q_{max}^{-1}$  is equal to 1.634nm. If we attribute this obtained value for distance corresponding

to  $q_{max}$ , MDM of molecule is something measurable if about  $D \cong 1.634\text{nm}$ .

The coherence length of the molecule, if considered as range of interaction, may be larger than  $D$ ; we notice that the low-angle region of the scattering data provides the data about larger portions of the molecule, whereas at high-angle the measurements of smaller intra-molecular parts of the molecule can be made [15].

Therefore, for this technique of estimation of measurement ability, it is appropriate to consider the smallest peak (other than interpolated zero angle) for our crude estimate of MDM. The first peak occurs at  $\theta \cong 10^\circ$ , then  $q_{max} \cong 0.5348 \times 10^{10} m^{-1}$ . So, the maximum range of intra-molecular interaction between portions of molecule is  $r_{max} \cong 18.7\text{nm}$ . This large value demonstrates high extension of the molecule, which was not unexpected. But, this value is one order of magnitude greater than the previous estimated value of  $D \cong 1.634\text{nm}$ . Each of these results shows the behavior of one portion of the molecule, which is not exactly matched to its MDM, but it, demonstrates that this technique is capable of determining the size of molecule's having  $D$  about these values.

So, we choose DF analysis (For a detailed discussion of the mean diameter of molecule (MDM) Ref. [5]), vide infra.

### ii. Size of micro-molecule

Two previous estimations of order of micro-molecular size can be deepened via more scrupulous consideration of measurement data. In X-ray scattering measurements, the scattering function  $I(\theta)$  contains valuable information to be extracted. The low-angle region, which is the main region in the scattering data (Fig. 2), contains the latent information about the size of the micro-molecule.

1. Coherence length between a pair, inferred from the degree of correlation between nearest neighbors, is approximately  $1/\text{FWHM}$ , which is calculated about  $4.747\text{\AA}$ .

2. With the technique of radius of gyration, which is known from elementary texts in analytical mechanics, the size of molecule is obtained without any need to model the geometrical shape of the molecule.

As DF presents, the scattering function, *i. e.* the intensity  $I$  re-scaled by non-diffracted intensity  $I_0$ , reads

$$S(q) = \frac{1}{N^2} \sum_{i,j=1}^N \frac{\sin(qr_{ij})}{qr_{ij}}. \quad (1)$$

When, the radius of gyration,  $R_G$ , of the molecule is comparable with the light wave-length, which is the case in our experiment, then the scattering function can be expanded as

$$S(q) = 1 - \frac{q^2}{3!N^2} \sum_{i,j=1}^N r_{ij}^2 = 1 - \frac{q^2}{3} R_G. \quad (2)$$

We ascribe the size of molecule  $D$ , via a simple geometrical consideration formulating the radius of gyration of molecule, to  $R_G$  [15]. Therefore, the overall diameter of molecule is obtained from the slope of scattering function versus  $q^2$ . As can be seen from the figure,  $D$  is estimated as  $\cong 2.1\text{\AA}$ , since the origin is a representative of the point from which the probability of existing another electron is calculated. Fortunately, this type of analysis is independent of the geometrical shape of molecule.

3. Scherrer formula is applicable to nearly spherical particles (it is applicable only to exactly spherical objects). This technique relates the size of the micro-system to the broadening of diffraction peak, and reads

$$D = \frac{0.9\lambda}{\beta \cos\theta}, \quad (3)$$

where,  $b$  is the broadening at half maximum (FWHM).

Another point to be mentioned for Scherrer formula is that  $D$  is the mean size of the particle and may be equal or smaller than the size of nano-system. For our case, the Scherrer particle size is obtained as  $D \cong 1.67\text{nm}$ .

4. Hall-Williamson technique is familiar for any novice in the field of nano-particle's size characterization. The equation reads [16]

$$\beta \cos \theta = \frac{K\lambda}{D} + 4\epsilon \sin \theta. \quad (4)$$

Some softwares, such as Fullprof generates plot Williamson-Hall curves and estimates the values (size, strain etc). We use the raw formula and determine size of micro-molecule as  $\cong 2.1\text{\AA}$ . Stick in mind that the H-W method isn't reliable for characterizing sub-nano scaled particles, since the method suffers from major aberrations in XRD instruments.

## 5 Conclusions

In the present work, the XRD-DFA analysis of the micro-molecule having chemical formula  $C_{52}H_{60}N_4S_8Zn_2$  was performed and intra-molecular order was specified. The method employed here investigates various definitions applicable for size determination of a micro-molecule. There are some various techniques, each of which suffers from pitfalls due to incompleteness of particles, lack spherical geometry and/or errors in XRD instruments. For example, Debye-Scherrer or incomplete Bragg peak analysis, since their power in determining the size of nano-particles is limited by lack of crystallinity in non-crystalline systems (*e.g.* in micro-molecules). Also, Hall-Williamson methodology isn't reliable for characterization the diameter of molecule in sub-nano scale.

Techniques of coherence and correlation length determination are applied. Then, methods of radius of gyration, Scherrer and Hall-Williamson are employed. Mean diameter of molecule (MDM) of the nano-system is estimated by any method, and selected bond lengths were given.

OPEN PROBLEMS: 1. A crude MDM is inferable from the diagram of DF (Fig. 2), such that the extreme limit of attributed coherence length in Fourier transformed X-ray

diagram, is ascribed to MDM. 2. The method of Warren-Averbach is applied [17].

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