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Xiaodong Li, Yanyan Zhang, Ling Wang, Hao Zhang, Junfeng Wu, Hongjun Chen, Rui Su, Can Li, Jiandong Hu, "SERS of diazinon: a experimental and computational study," Proc. SPIE 12349, International Conference on Agri-Photonics and Smart Agricultural Sensing Technologies (ICASAST 2022), 123490K (18 October 2022); doi: 10.1117/12.2657234

**SPIE.**

Event: International Conference on Agri-Photonics and Smart Agricultural Sensing Technologies (ICASAST 2022), 2022, Zhengzhou, China

# SERS of Diazinon: A Experimental and Computational Study

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## ABSTRACT

Diazinon is a highly efficient, highly toxic, low residual organophosphorus pesticide used widely in rice, vegetables, and corn crops. Conventional methods for diazinon detection are limited by expensive instruments and tedious sample pre-treatment methods, so a new method for rapid, simple, and reliable trace pesticide residues is needed to ensure the safety of crop products. In this paper, silver nanoparticles were synthesized as active substrates using a reduction technique for SERS signal enhancement. The SERS spectra of diazinon were collected over a wide range of concentrations. The characteristic peaks at 1642  $\text{cm}^{-1}$  and 1351  $\text{cm}^{-1}$  were selected for quantitative analysis, and their coefficient of determination ( $R^2$ ) were 0.9929 and 0.9951, respectively. In addition, the molecular structure of diazinon was simulated for the first time, and the vibrational modes corresponding to the characteristic spectra of diazinon were calculated with good agreement using the density flooding theory B3LY P/6-31+G (d, p). These results indicate that the application of SERS to diazinon detection is feasible and has broad application prospects.

**Keywords:** Diazinon, SERS, DFT

## 1. INTRODUCTION

There is an urgent need to address the safety problems caused by pesticide residues in food. Organophosphorus (OP) pesticides are among the most widely used and play an important role in protecting against plant diseases and insect pests and ensuring increased quality and quantity of products to meet the high demands for food [1]. Many studies and reports worldwide have demonstrated the impact of OP pesticides on human health through food contamination [2-3]. Diazinon, O, O-diethyl O-(2-isopropyl-6-methylpyrimidin-4-ylphosphorothioate) (IUPAC), is a highly toxic OP insecticide extensively used in crops such as rice, vegetables, and corn, as well as for the in-house control of cockroaches and ants [4]. Diazinon is reported to enter the human and animal body mainly through the diet, after which it will be converted into a more toxic compound, called diazoxon [5]. In recent years, some researchers have found that high diazinon levels in food exceed the maximum residual amount (MRL) [6-7]. Thus, conducting studies on the detection of diazinon is of great significance to reduce the risks caused by them to humans.

Currently, some classical analytical methods such as high-performance liquid chromatography [8], gas chromatography-mass spectrometry (GC-MS) [9], and liquid chromatography-mass spectrometry [10] were used to analyze OP pesticide residue in food. However, these methods are time-consuming and require expensive equipment, well-trained personnel, and a complex pretreatment methodology. For this reason, researchers have begun to develop new and faster detection methods. Surface-enhanced Raman scattering (SERS), which combines Raman spectroscopy with nanotechnology, has increasingly become a popular and promising detection technique. SERS is not only fast and water-resistant but also has a significantly enhanced Raman signal; hence, it can detect trace substances with much higher sensitivity [11]. Density generalized theory (DFT) is a quantum mechanical method to study the electronic structure of multi-electron systems and is widely used in calculations of solid-state physics, theoretical simulations of analytical structures and properties, and spectral analysis. In recent years, there have been more and more reports on the use of DFT theory to optimize the structure of molecules to study molecular spectra.

In this study, SERS spectra of diazinon concentrations in the range of (0.1-10  $\mu\text{g/mL}$ ) were obtained using simple and easily synthesized silver nanoparticles as signal enhancement substrates and operated with spectral pre-processing

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*The authors are thankful to the National Natural Science Foundation of China (grant number: 32071890).*

International Conference on Agri-Photonics and Smart Agricultural Sensing Technologies (ICASAST 2022),  
edited by Jiandong Hu, Proc. of SPIE Vol. 12349, 123490K · © 2022 SPIE  
0277-786X · doi: 10.1117/12.2657234

Proc. of SPIE Vol. 12349 123490K-1

software for baseline removal and noise. The characteristic peaks at  $1642\text{cm}^{-1}$  and  $1351\text{cm}^{-1}$  were selected for quantitative analysis. Meanwhile, the molecular structure of diazinon was simulated and the vibrational modes corresponding to the characteristic spectral bands of diazinon were calculated using the B3LYP/6-31+G (d, p) of density functional theory. These works will promote the application of the SERS technique in pesticide diazinon residues.

## 2. THE EXPERIMENT PART

### 2.1 Material

Silver nitrate, hydroxylamine hydrochloride, sodium hydroxide, acetone, and diazinon standard solution  $100\ \mu\text{g/mL}$ . Before the experiment, all glassware was soaked overnight in royal water [HCL:  $\text{HNO}_3 = 3:1$  (V/V)], ultrasonically cleaned, and repeatedly washed with ultrapure water.

### 2.2 Preparation of Ag nanoparticles

The silver nanoparticles were obtained by taking  $45\ \text{mL}$  of  $1.11 \times 10^{-3}\text{M}$   $\text{AgNO}_3$  solution in a  $100$  round bottom beaker and adding a mixture of  $2.5\ \text{mL}$   $0.06\text{M}$  hydroxylamine hydrochloride and  $2.25\ \text{mL}$   $0.1\text{M}$  sodium hydroxide under magnetic stirring and continuing the reaction for  $15\ \text{min}$  and then stopping the reaction.

### 2.3 SERS measurements and spectra data preprocessing

The standard sample of diazinon was diluted to different concentrations with acetone, and then silver nanoparticles were evenly mixed with the diazinon solution for SERS detection. SERS measurements were performed using a confocal Raman microscope system (Pioneer Technology Co., Ltd., Beijing). During spectrum acquisition, a  $532\ \text{nm}$  laser was used as the excitation source, the laser was focused on a  $100 \times$  objective lens, the scanning range was  $800 \sim 1800\ \text{cm}^{-1}$ , and the integration time was  $5\ \text{s}$ . The SERS spectral signal was collected by LIBS software, and the Vancouver Raman Algorithm was used for pre-processing.

### 2.4 Calculation of diazinon using the density functional

The optimal molecular structures of diazinon were determined and computed using Gaussian 09 and Gauss View 5.0 software at the level of the B3LYP/6-31+G (d, p) group of DFT, and the calculated findings were compared to the experimentally observed spectra.

## 3. RESULTS AND DISCUSSION

### 3.1 The geometric configuration of diazinon molecules

The diazinon molecule comprises phosphorothioate, and computations revealed that no imaginary frequencies exist, indicating that the optimized diazinon chemical structure is stable. The atomic marks on the right side of Figure 1 depict the structure of the optimized diazinon molecule. As shown in Figure 1, the diazinon molecule consists of a series of groups consisting of, among others,  $-\text{S}=\text{P}-$ ,  $-\text{C}-\text{O}-\text{P}-$ ,  $-\text{C}-\text{C}-$ , and  $-\text{C}-\text{H}$ .

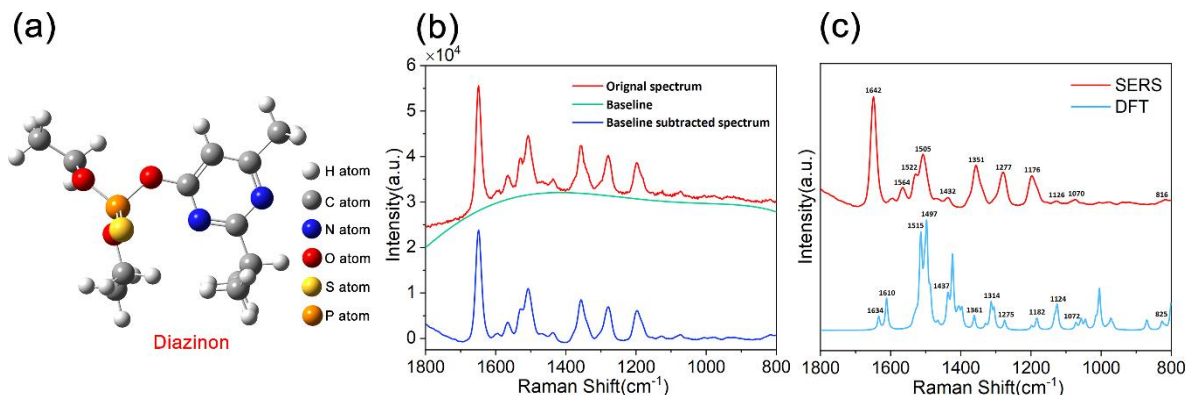


Figure 1 (a) Optimized molecular of diazinon, (b) shows the software processed SERS spectra, and (c) shows the processed SERS spectra and DFT calculated Raman spectra

### 3.2 Preprocessing for SERS spectra

SERS signal acquisition results inevitably degrade data quality and present poorly due to noise and fluorescence factors. This interference information often comes from a variety of factors, SERS spectral acquisition process noise mainly from the instrumentation factors, environmental stray light changes, and the undulation of the sample surface. At the same time, there is generally no strong fluorescence effect in the sample, but if the sample is mixed with a very low concentration of fluorescent impurities, it will also produce a very strong fluorescent background, and with the accumulation of integration time, the fluorescence effect of the object surface being excited will also be enhanced, and even the intensity is close to or exceeds the SERS spectral intensity. We used Vancouver Raman Algorithm software to process the collected SERS spectra, and the results are shown in Figure 2.

### 3.3 Vibrational assignments of SERS spectra

The experimental Raman spectra at 100  $\mu\text{g/mL}$  and the theoretically computed spectra of the diazinon molecule are shown in Figure 1. The experimental Raman spectrum has typical peaks at 1642 $\text{cm}^{-1}$ , 1564 $\text{cm}^{-1}$ , 1522 $\text{cm}^{-1}$ , 1505 $\text{cm}^{-1}$ , 1432 $\text{cm}^{-1}$ , 1351 $\text{cm}^{-1}$ , 1277 $\text{cm}^{-1}$ , 1176 $\text{cm}^{-1}$ , 1070 $\text{cm}^{-1}$ , and 816 $\text{cm}^{-1}$ , as seen in the image. The theoretically computed peaks are somewhat skewed, and the wavenumber deviation is roughly 10 $\text{cm}^{-1}$ , thus identifying typical peaks will not be a problem. Furthermore, only SERS can detect the distinctive peak at 1564 $\text{cm}^{-1}$ , and only DFT can calculate the Raman peaks at 1314 $\text{cm}^{-1}$ . This is because theoretical calculations are based on the vibrational modes of the molecules in the ideal state, ignoring the influence of the solvent-diazinon molecule contact, but the SERS experiment includes the effect of the solvent-diazinon molecule interaction. The Raman characteristic peaks produced from the tests significantly differed from the theoretically expected spectra due to the interaction between diazinon and solvent molecules.

The distinctive peaks of spectra are varied for various functional groups. Table 1 shows the spectral band allocations of diazinon's primary distinctive peaks. The P=S vibration is responsible for the Raman peak of diazinon at 816  $\text{cm}^{-1}$ , while the P-O vibration in the P-O-C structure (1070  $\text{cm}^{-1}$ ), the C-C vibration in the isopropyl structure (1126  $\text{cm}^{-1}$ ), the deformation of the benzene ring (1277  $\text{cm}^{-1}$  and 1642  $\text{cm}^{-1}$ ), the C-H oscillation in the -P-C-C structure (1176  $\text{cm}^{-1}$ , 1432  $\text{cm}^{-1}$ , 1505  $\text{cm}^{-1}$  and 1522  $\text{cm}^{-1}$ ).

Table.1 Band assignments for major peaks of diazinon (vibration w: wagging  $\delta$ : deformation)

Calculated by DFT( $\text{cm}^{-1}$ )	Experimental SERS( $\text{cm}^{-1}$ )	Vibrational Mode Assignment
825	816	$\nu$ (P = S)
1072	1070	$\nu$ (P-O-C)+ $\nu$ (C-C)
1124	1126	$\nu$ (C-C)
1182	1176	w(C-H)
1275	1277	$\delta$ ring
1314	-	w(C-H)
1361	1351	w(C-H)
1437	1432	w(C-H)
1497	1505	w(C-H)
1515	1522	w(C-H)
-	1564	-
1634	1642	$\delta$ ring

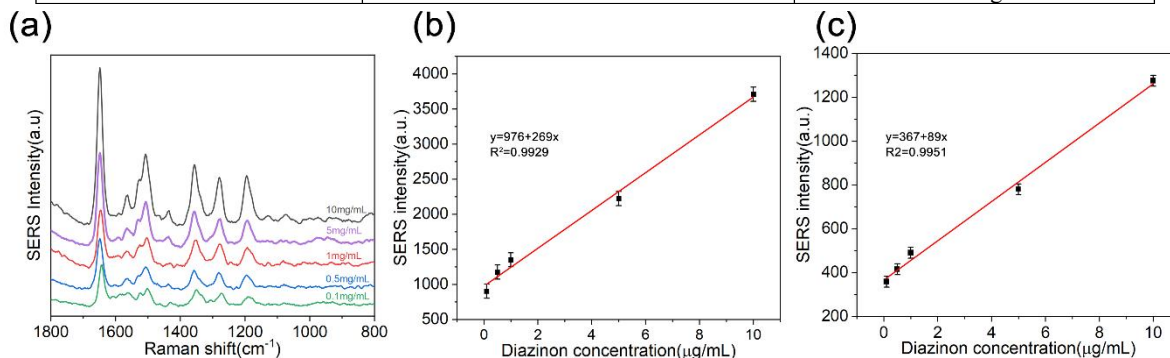


Figure 2 (a) shows the SERS spectra of five different concentrations of diazinon solutions, (b) shows the quantification of the characteristic peak at 1642 $\text{cm}^{-1}$ , and (c) shows the quantification of the characteristic peak at 1351 $\text{cm}^{-1}$

### 3.4 The quantitative analysis of diazinon

Figure 2 presents the experimentally obtained SERS spectra for five different concentrations of diazinon solutions (10, 5, 1, 0.5, and 0.1  $\mu\text{g/mL}$ ). We see that as concentration increases, the intensity of the peaks increases proportionally, thus demonstrating the potential of quantitative sensing in a wide range. Diazinon was selected for quantitative analysis at 1642  $\text{cm}^{-1}$  and 1351  $\text{cm}^{-1}$  characteristic peaks, and the standard curves established are shown in Figure 2. The linear equations are  $y=976+269x$  and  $y=367+89x$  with the coefficient of determination ( $R^2$ ) of 0.9929 and 0.9951.

## 4. CONCLUSION

This paper takes the organophosphorus pesticide diazinon as the research object and focuses on the confirmation of its Raman spectral peak vibration mode and SERS quantitative analysis, which is a powerful supplement to the existing research system of organophosphorus pesticide trace detection problems, and to a certain extent, makes up for the shortage of existing rapid and trace detection of diazinon. Firstly, the results show that the feasibility of SERS application for quantitative detection of diazinon is very high, and there is a good linear relationship between concentration and SERS intensity. Secondly, DFT was used for the calculation of diazinon Raman molecules, and the vibrational modes of diazinon Raman spectral peaks were confirmed with good agreement. Finally, there are certain shortcomings in this study, and the main variables are: on the one hand, although the silver nano-enhancement effect is very good, the stability is poor, and this may lead to the problem of mismatching the standard curve established between the detection signal and the concentration, which in turn leads to some deviations in the regression prediction results. On the other hand, the diazinon solution detected in this study did not involve real samples and failed to show the feasibility in real samples. Therefore, further investigation of diazinon detection in real samples with stability-enhanced substrates is urgently needed to ensure that SERS can be practically used for diazinon residue detection in food.

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