

# Vibrational Spectroscopic Analysis of 1,3-Dianiline Squarate: Infrared, Normal Raman, Surface-Enhanced Raman Scattering, and Density Functional Theory Calculations

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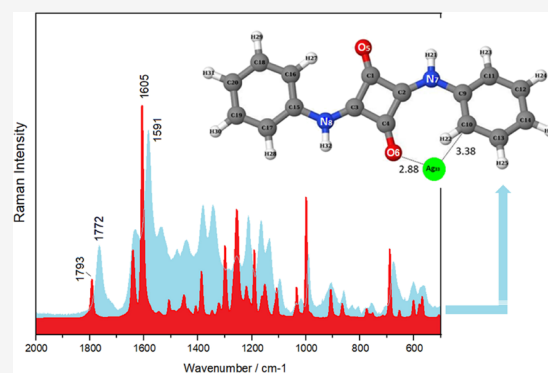
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**ABSTRACT:** 1,3-Dianiline squarate (DSQ) is an interesting squaraine frequently used as an intermediary reactant in organic synthesis aiming products 1,3-( $R_1R_2$ )-squarate type, as well as a building block of photoinitiators under visible light widely used in photopolymerization reactions. In this work, structural investigations of DSQ were performed using spectroscopic methods such as solid-state  $^{13}\text{C}$  nuclear magnetic resonance and several vibrational techniques. Therefore, a detailed vibrational spectroscopic analysis of DSQ was carried out by infrared, normal Raman, and surface-enhanced Raman scattering (SERS) combined with density functional theory calculations. SERS data suggest two preferential interactions between squaraine and the silver nanoparticle. It is proposed that squaraine is adsorbed mainly through a regular Ag–O interaction involving the carbonyl group; that connection impacts the oscillators around them and consequently their vibrational spectra. In addition, the silver atoms may perturb the DSQ planarity by interacting with the phenyl rings; they promote the molecule to adopt a non-planar tilted orientation on the metal nanoparticle surface.

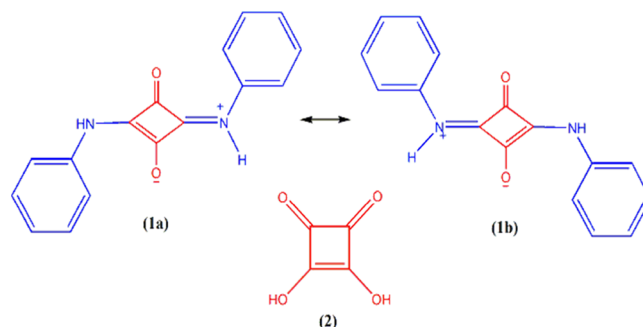


## 1. INTRODUCTION

Squaraine-based dyes are a class of organic compounds with diverse uses in different fields of science, from organic synthesis to modern applications, such as photodynamic therapy,<sup>1–3</sup> molecular sensors,<sup>4–9</sup> and imaging,<sup>1,8–10</sup> and as photoinitiators of polymerization reactions.<sup>11</sup> Several of these fascinating derivatives present important nitrogen-containing groups inserted in the ring, generating improved systems with new or upgraded properties. This is essentially due to their excellent thermal and photochemical stabilities,<sup>12</sup> besides their peculiar absorption and emission features.<sup>13–15</sup> Thus, many squaraine-based dyes have been extensively investigated and vibrational spectroscopies also emerge as a potential tool for their investigation together with other techniques such as fluorescence-based detection.<sup>1,8,16–19</sup> Such species are normally known as squaraine, squarylium, or squaramide compounds, and there are several derivatives available in the literature.<sup>19–21</sup>

1,3-Dianiline squarate (DSQ) or also called 1,3-bis(phenylamino)squaraine (1) is a symmetric molecule presenting a resonance stabilized structure (see Scheme 1). It is composed of a highly electron-deficient central core (from the oxocarbon squarate, SQ, 2), surrounded by two opposite “aniline” ligands, electron-rich donating species, forming a *trans*-zwitterionic structure with important spectroscopic

**Scheme 1. Chemical Structure of Zwitterionic Structures of DSQ: 1,3-Dianiline Squarate or *trans*-Bis(phenylamino)squaraine (1a/1b) and the Precursor Squaric Acid (2)**



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implications. SQ is powerful electrophilic species and reacts easily with aromatic amines yielding deeply colored condensation products.<sup>22,23</sup> DSQ has been commonly used as an intermediary reactant aiming to obtain 1,3-(R<sub>1</sub>R<sub>2</sub>)-squatrate derivatives.<sup>24–28</sup> However, its specific potential applications have been underexplored despite some studies dating back to 1975, possibly due to its solubility issues.<sup>29,30</sup> There are not many studies available in the literature about its physical–chemical properties, and only a few characterization data can be found.<sup>24,25,31</sup>

Although the practical uses of DSQ and DSQ-based dyes have been sparse, in the last few years, there has been increasing attention to their applications as photosensitizers.<sup>11,32,33</sup> Due to their strong light absorption in the blue region, these squaraines have been used as visible light photoinitiators in photopolymerization reactions.<sup>11,32</sup> Compared with some commercially available photoinitiators, DSQ-based systems can lead to better polymerization efficiencies.<sup>32,33</sup> In this regard, Kabatc et al. have demonstrated that the photo-excited squaraine might act both as an electron donor or acceptor, simply changing the co-initiator.<sup>33</sup> Other optical spectroscopic properties of DSQ-based dyes were recently found by Vega et al. and ensure further potential applications.<sup>34</sup> In their work, it was observed that the monoanion of 1,3-bis(4-cyanophenylamino) squaraine shows intense fluorescence in the presence of silver ions. Here, we aim to study the adsorption of DSQ on silver nanoparticles. To the best of our knowledge, this is the first study that explores such species both experimental and theoretically by using a combination of surface-enhanced Raman scattering (SERS) and density functional theory (DFT) calculations. SERS is a highly selective and sensitive spectroscopic technique suitable to study the molecule on an extraordinary scale, making it possible to get convenient information, such as the molecule interactions and/or orientation on the nanoparticle surfaces.<sup>35,36</sup> SERS studies of some oxocarbons, pseudo-oxocarbons, and squaraine derivatives have been widely carried out before; for example, Stokes et al. studied the SERS properties of several squaraine dyes and showed that they are excellent SERS reporters in the red and near-infrared spectral region.<sup>37–43</sup> SERS of squaraines has also found important applications in studies related to cancer diagnosis and imaging,<sup>9,43</sup> which makes this study an important complement to understanding their chemical behavior.

## 2. MATERIALS AND METHODS

**2.1. Synthesis.** All chemical reagents were of analytical grade, obtained from commercial suppliers, and used as received. Aniline was previously bi-distilled and squaric acid (SQ) was used without pretreatment, both chemicals from Sigma-Aldrich (Merck). DSQ was synthesized according to adaptations in the methodology available in the literature.<sup>24,25,28,44,45</sup> *N,N*-Dimethylformamide (DMF) was predried with molecular sieves. Diamidation reaction was conducted under a boiling solvent point for 100 min; the mixture of 0.570 g (5 mmol) of SQ in 25 mL of DMF was added to 0.930 g (10 mmol) of aniline (molar ratio 1:2). After this period was added 15 mL of water at 5 °C to stop the process; the yellow product obtained was purified by washing with the following solvent gradients and temperatures (two times): water at 50 °C, acetonitrile, hot methanol (60 °C), acetone, and dichloromethane (25 °C). A second purification was necessary by adding DMF at 50 °C under stirring for 1 h. Yield 86%. Anal.

calc for C<sub>16</sub>H<sub>12</sub>O<sub>2</sub>N<sub>2</sub>.1DMF: C, 72.72; H, 4.58; N, 10.60%. Found: C, 69.52; H, 4.88; N, 11.42%. Solid <sup>13</sup>C nuclear magnetic resonance (NMR) (ppm): 260.2 (C1), 248.8 (C3), 241.0(C2), 238.7(C4), 177.5, 170.6(C9/C15), 167.9(C12/C13), 140.7(C18/C19/C20), 121.7(C16/C17), 129.5(C14), 119.2(C10/C11), 40.9, 37.9.

**2.2. Colloid Preparation.** The silver colloid was prepared according to Creighton's chemical reduction method.<sup>46</sup> Briefly, 30 mL of sodium borohydride solution (2.0 mM) was placed in an ice bath under vigorous stirring, and then, 20 mL of AgNO<sub>3</sub> (1.0 mM) was added dropwise. The stock solution of 50 mM DSQ was prepared in dimethyl sulfoxide. For the SERS experiments, 5 μL of the stock solution of DSQ was added to 0.5 mL of the silver colloid. The final concentration of DSQ was 495 μM.

**2.3. Vibrational Techniques.** The SERS spectrum was recorded using a portable Raman spectrometer (Enwave Optronics, Inc.) with a 532 nm excitation wavelength, 20 mW laser power at the sample, and 20 s exposure time. The shown spectrum corresponds to the average of five spectral scans. The Fourier-transform Raman spectrum was obtained by using a Bruker MultiRAM instrument equipped with a Nd<sup>3+</sup>/YAG laser of 1064 nm wavelength. The final spectrum was obtained by accumulating 512 scans, with a 4 cm<sup>-1</sup> spectral resolution and 50 mW laser power. The infrared spectrum was obtained by using a Bruker Alpha FTIR spectrometer with a diamond ATR crystal using the accumulation of 128 spectral scans with 4 cm<sup>-1</sup> spectral resolution.

All calculations were performed on cluster GAUSS of INCT-FCx using the Gaussian 09 program.<sup>47</sup> The Raman activities and infrared (IR) intensities of DSQ and its silver complex (Ag–DSQ) in a vacuum were calculated by the following procedure: first, full geometry optimizations were performed using the CAM-B3LYP functional<sup>48</sup> with the basis set def2TZVP, and then, the vibrational wavenumbers, Raman activities, and IR intensities were obtained. The vibrational analysis confirmed the equilibrium geometries of all studied structures, and no imaginary wavenumbers were observed in the calculated spectra. The atomic charges calculated with CHELPG using the same level of QM calculation.<sup>49</sup>

**2.4. NMR Measurements.** NMR spectra were performed on a Bruker Avance III HD300 (7.04 T) spectrometer at 75 MHz for <sup>13</sup>C in which a 4 mm inverse probe head was installed (ZrO<sub>2</sub> MAS rotors with KeI-F caps). The chemical shift was referenced indirectly by using glycine as an external reference, and tetramethylsilane as the primary standard.

## 3. RESULTS AND DISCUSSION

The structure of DSQ is auxiliary, confirmed from its <sup>13</sup>C NMR spectrum as shown in Figure S1 of the Supplementary Material. Despite all the complexity of this system, there are 10 sets of carbon atoms present in the resonance spectrum. Four non-equivalent carbonyl carbons (C1 to C4) resonate up δ 230 ppm, all of them from the squaryl group; that is, important information once shows the diverse chemical environment of each SQ-carbon. That information is essential to evaluate the preferential interaction with other groups as will be discussed next. The carbons from the phenyl groups, despite similarities, show slight differences at resonance shifts due to the positive charge located preferentially at one nitrogen atom. This promotes different levels of charge delocalization around that specific phenyl-carbon, and then, we can verify some

equivalent resonance as C10 and C11 at  $\delta$  119 ppm. Other equivalent carbon resonance signals can be assigned as C16/C17 at  $\delta$  122 ppm; C18/C19 and C20 at  $\delta$  141 ppm; and C12/C13 at  $\delta$  168 ppm. In the region up to 235 ppm are the resonances of carbons from the squaryl carbons: C4, C2, C3, and C1 at  $\delta$  239, 241, 249, and 260 ppm, respectively. These carbons atoms are not in a similar chemical environment and, therefore, appear as different peaks with low intensity and are severely unshielded. Such species are strongly influenced by their position between the two opposite aniline groups, which will pull the electron density toward it and causes the deshielding of these nuclei.

The normal Raman and IR spectra of solid DSQ are shown in Figure 1. The calculated optimized structure of the isolated

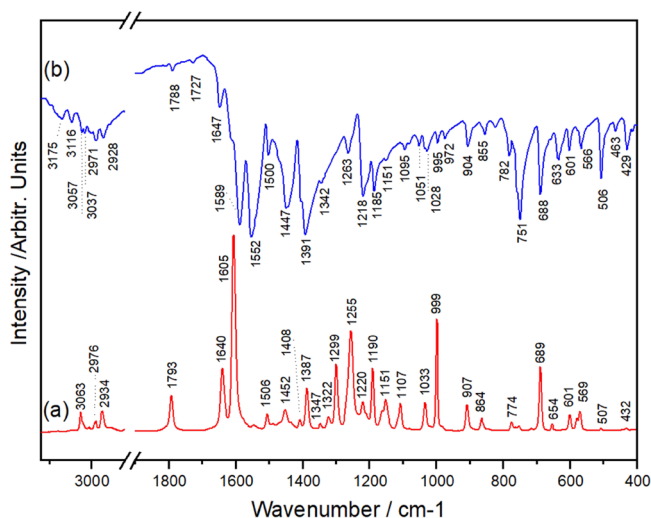


Figure 1. (a) Normal Raman and (b) IR spectra of solid DSQ.

DSQ is shown in Figure 2a, and the structural parameters can be found in Tables S1 and S2. Tables 1 and S3 list the experimental Raman and IR wavenumbers of solid DSQ, the

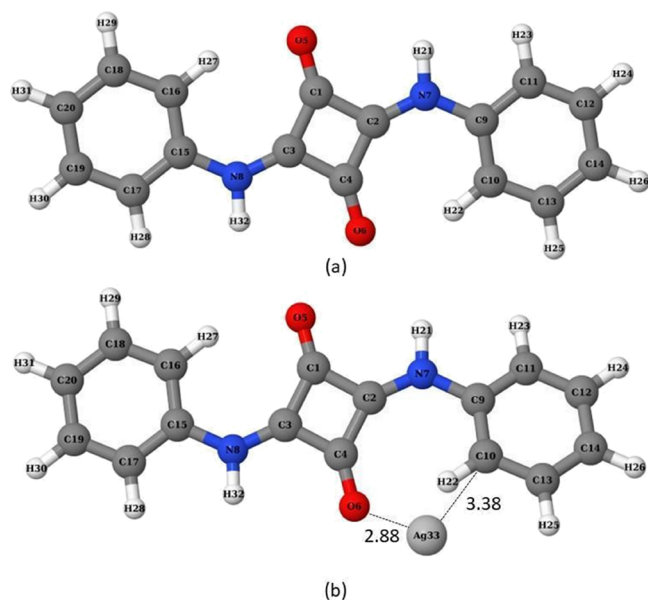


Figure 2. Optimized structures of (a) DSQ and (b) Ag-DSQ complex. The distances are in Å.

calculated wavenumbers, Raman activities, and IR intensities, as well as the corresponding vibrational mode assignments. The vibrational assignments were carried out based on the DFT calculations and in the literature data available for aniline and its derivatives.<sup>50,51</sup> We used as criteria for the vibrational assignment, the correlation between the calculated wavenumbers, Raman activity, and IR intensities with the observed spectra. There is in general an excellent agreement between the non-scale predicted wavenumbers with the experimental Raman and IR band positions. The major differences occur above  $1600\text{ cm}^{-1}$  where a theoretical scaling factor would improve the match between the experiment and calculation. There are some discrepancies in the calculated and experimental relative intensity. However, the predicted presence of Raman and IR active peaks in some specific spectral regions was useful for more reliable band assignments.

The most intense bands in the normal Raman spectrum of solid DSQ occur at  $689$ ,  $999$ ,  $1255$ , and  $1605\text{ cm}^{-1}$ . The Raman band detected at  $999\text{ cm}^{-1}$  is assigned to the phenyl ring breathing vibrations. The band at  $1255\text{ cm}^{-1}$  has a contribution from in-plane C–H bending, N–H bending, and C–N stretching modes. The strongest Raman band observed at  $1605\text{ cm}^{-1}$  is assigned to a mixture of in-plane phenyl ring stretching, C–H bending, and C–N stretching vibrations. The IR spectrum of solid DSQ matches well with the one previously reported by Gauger and Manecke.<sup>29</sup> The strongest bands are observed at  $688$ ,  $751$ ,  $1391$ ,  $1552$ , and  $1589\text{ cm}^{-1}$ ; the bands at  $751$  and  $1391\text{ cm}^{-1}$  are assigned to out-of-plane and in-plane C–H bending from phenyl groups, respectively. The band at  $751\text{ cm}^{-1}$  also has a contribution from N–H out-of-plane bending. The bands at  $1552$  and  $1589\text{ cm}^{-1}$  correspond to a combination of in-plane C–H and N–H bending movements.

The analysis of both the absorption and scattering spectra highlights the IR active band at  $1552\text{ cm}^{-1}$ ; as above-mentioned, it is assigned to the in-plane asymmetric vibrations of phenyl groups. Other peaks relatively strongest in the IR than in the Raman spectrum can be observed at  $751$ ,  $1391$ , and  $1447\text{ cm}^{-1}$ ; with exception of the first one (assigned to out-of-plane vibrations), the others are assigned to in-plane vibrations from phenyl ( $\delta\text{CH/NH}$ ) and squarate groups ( $\nu\text{CN}$ ). The strongest Raman bands can be found at  $999$  and  $1255\text{ cm}^{-1}$ ; both have the contribution of phenyl groups, the first mode contains the phenyl rings breathing, and the second vibration includes deformations of CH/NH, added to the CN stretching. The peak at  $1605\text{ cm}^{-1}$  also deserves to be highlighted once it is the most intense band in the spectrum and has the contribution of important groups from phenyl and SQ. It corresponds to CC phenyl, CO stretching, and  $\nu\text{C–N}$  where “C” is from SQ and “N” is from the aniline group. That could be considered a “marker band” once perturbations on this region must impact the energy mode, which could be considered a “key peak”.

Several other bands are also observed in the vibrational spectra of solid DSQ. The peak at  $1793\text{ cm}^{-1}$  in the normal Raman spectrum corresponds to a combination of C=O and C–N stretching vibrations. This is in agreement with the position of the carbonyl stretching vibration previously reported for the squarate dianion in solution and solid samples.<sup>52</sup> The corresponding band in the IR spectrum occurs at  $1788\text{ cm}^{-1}$ , but its intensity is relatively very weak.

The bands at  $429$  and  $506\text{ cm}^{-1}$  have a contribution from phenyl rings and C–H out-of-plane bending. The band at  $782$

**Table 1. Summary of Band Positions for Normal Raman and Infrared Spectra of DSQ (Solid) and SERS (495  $\mu\text{M}$ ) of DSQ; Calculated Data, Raman Activities, and IR Intensities of DSQ and the Ag-DSQ Complex<sup>a</sup>**

FT-Raman ( $\text{cm}^{-1}$ )	calculation DSQ			calculation Ag-DSQ					
	FT-IR ( $\text{cm}^{-1}$ )	$\text{cm}^{-1}$	Raman act. ( $\text{A}^2/\text{amu}$ )	IR int. ( $\text{km}/\text{mol}$ )	SERS ( $\text{cm}^{-1}$ )	$\text{cm}^{-1}$	Raman act. ( $\text{A}^2/\text{amu}$ )	IR int. ( $\text{km}/\text{mol}$ )	Ag-DSQ assignments
414 vw	414 vw	424.0	0	0	411 vw	422.7	0.1	0.0	$\omega\text{R}_1/\omega\text{R}_2/\omega\text{CH}(\text{R}_1,\text{R}_2)$
432 vw	429 m	424.1	0	0	442 vw	426.8	4.6	0.1	$\omega\text{R}_1/\omega\text{R}_2/\omega\text{CH}(\text{R}_1,\text{R}_2)$
507 vw	463 w	474.1	0	27.0		475.2	0.5	26.3	$\delta\text{R}_1/\delta\text{R}_2/\delta\text{CO}/\delta\text{CCN}$
569 w	506 s	522.8	3.9	0	514 vw sh	523.5	4.3	4.1	$\omega\text{R}_1/\omega\text{R}_2/\omega\text{CH}(\text{R}_1,\text{R}_2)$
	566 m	531.3	0	26.9		530.6	1.1	29.4	$\omega\text{R}_1/\omega\text{R}_2/\omega\text{CH}(\text{R}_1,\text{R}_2)$
601 w	601 m	545.0	3.7	0		557.9	28.5	4.8	$\omega\text{NH}/\omega\text{Sq}$
	633 m	618.5	0	13.8	612 w	619.8	0.87	11.2	$\delta\text{R}_1/\delta\text{R}_2/\delta\text{CNC}$
654 vw	688 s	629.7	35.4	0		631.8	28.7	0.0	$\delta\text{R}_1/\delta\text{R}_2$
689 s	751 s	640.3	0	0.3		641.9	0.4	0.2	$\delta\text{R}_1/\delta\text{R}_2$
	782 m	663.8	3.3	0	667 sh	666.8	4.7	1.1	$\delta\text{Sq}/\delta\text{R}_1/\delta\text{R}_2$
907 m	904 m	690.7	0.2	0	686 s	691.8	1.5	2.3	$\omega\text{Sq}/\omega\text{NH}$
	995 w	716.3	24.0	0	718 vw sh	718.1	17.0273	4.3	$\delta\text{Sq}/\delta\text{R}_1/\delta\text{R}_2$
1107 m	1028 m/ 1051 w	718.1	0	98.4	764 vw	721.8	2.0	54.3	$\omega\text{CH}(\text{R}_1,\text{R}_2)/\omega\text{NH}$
1151 m	1185 m	785.1	0	136.4		787.1	1.7	79.0	$\omega\text{CH}(\text{R}_2)$
1190 m	1218 s	918.1	39.5	0	917 m	920.7	33.1	0.2	$\delta\text{CCN}$
1220 m	1263 m	1026.4	0.4	2.0		1031.1	77.1	1.6	ring breathing (R2)
1255 s	1391 s	1068.1	101.3	0		1032.2	186.8	0.3	ring breathing (R1)
1299 m	1447 s	1070.7	0	0.9		1071.9	79.8	0.0	$\delta\text{CH}(\text{R}_1,\text{R}_2)$
1323 w/ 1346 vw	1500 m	1130.0	10.6	0		1074.6	1.6	0.2	$\delta\text{CH}(\text{R}_1,\text{R}_2)$
1387 s	1552 s	1179.5	63.0	0		1134.9	8.4	0.5	$\delta\text{CH}(\text{R}_1,\text{R}_2)$
1452 w	1589 s	1188.6	0	7.0		1184.7	27.6	54.5	$\delta\text{CH}(\text{R}_2)/\delta\text{NH}_2/\delta\text{Sq}$
1546 vw	1605 vs	1189	73.4	0		1196.6	1.66	1.9	$\delta\text{CH}(\text{R}_1,\text{R}_2)$
		1226.2	289.1	0		1196.9	51.2	0.8	$\delta\text{CH}(\text{R}_1,\text{R}_2)$
		1227.6	0	0.9		1231.8	141.5	0.8	$\delta\text{CH}(\text{R}_1)$
		1270.5	2501.0	0		1234.9	93.9	0.1	$\delta\text{CH}(\text{R}_2)$
		1281.5	0	51.0		1275.3	2137.4	0.5	$\delta\text{CH}(\text{R}_1,\text{R}_2)/\delta\text{NH}_1/\delta\text{NH}_2/\nu\text{CN}$
		1333.8	476.8	0		1285.9	68.8	47.0	$\delta\text{CH}(\text{R}_1,\text{R}_2)/\delta\text{NH}_1/\delta\text{NH}_2/\nu\text{CN}$
		1384.9	0	273.5		1335.1	352.8	2.3	$\delta\text{CH}(\text{R}_1)/\nu\text{R}_1$
		1387.5	96.1	0		1388.4	11.4	168.5	$\delta\text{CH}(\text{R}_1)$
		1429.0	0	2853.2		1392.9	64.8	71.9	$\delta\text{CH}(\text{R}_2)$
		1488.0	84.0	0		1431.4	2.4	2531.5	$\delta\text{NH}_1/\delta\text{NH}_2/\nu\text{CN}$
		1497.1	0	393.2		1490.4	75.9	3.2	$\delta\text{CH}(\text{R}_1,\text{R}_2)/\delta\text{NH}_1/\delta\text{NH}_2$
		1552.2	0	39.3		1501.5	5.7	429.4	$\delta\text{CH}(\text{R}_1,\text{R}_2)/\delta\text{NH}_1/\delta\text{NH}_2$
		1554.6	380.2	0		1558.4	22.5	21.8	$\delta\text{CH}(\text{R}_1,\text{R}_2)/\delta\text{NH}_1/\delta\text{NH}_2$
		1583.8	0	1635.2		1560.9	308.6	1.8	$\delta\text{CH}(\text{R}_1,\text{R}_2)$
		1661.5	554.9	0		1583.9	3.3	1482.9	$\delta\text{NH}_1/\delta\text{NH}_2/\delta\text{CH}(\text{R}_1,\text{R}_2)$
		1675.2	0	159.9		1591.9	522.2	119.2	$\delta\text{CH}(\text{R}_1,\text{R}_2)/\nu\text{R}_1/\nu\text{R}_2/\nu\text{CN}/\text{CO}$
						1676.0	13.3	152.9	$\delta\text{CH}(\text{R}_1,\text{R}_2)/\nu\text{R}_1/\nu\text{R}_2/\delta\text{NH}$

Table 1. continued

FT-Raman ( $\text{cm}^{-1}$ )	calculation DSQ			calculation Ag-DSQ					
	FT-IR ( $\text{cm}^{-1}$ )	$\text{cm}^{-1}$	Raman act. ( $\text{A}^+/\text{amu}$ )	IR int. ( $\text{km}/\text{mol}$ )	SERS ( $\text{cm}^{-1}$ )	$\text{cm}^{-1}$	Raman act. ( $\text{A}^+/\text{amu}$ )	IR int. ( $\text{km}/\text{mol}$ )	Ag-DSQ assignments
1640 s	-	1681.8	2542.1	0	1629/1646 s	1684.0	1635.4	14.9	$\delta\text{CH}(\text{R1},\text{R2})/\nu\text{R1}/\nu\text{R2}/\delta\text{NH}$
1793 s	1647 m	1682.4	0	40.0	1729 sh	1685.6	283.4	49.6	$\delta\text{CH}(\text{R1},\text{R2})/\nu\text{R1}/\nu\text{R2}/\delta\text{NH}$
2934 w	1727 vw	1721.1	0	1393.8	1772 s	1713.9	107.0	945.9	$\nu\text{CO}/\nu\text{CN}/\delta\text{NH}$
2976 w	1788 vw	1893.7	91.7	0	2925 m	1889.6	167.0	10.6	$\nu\text{CO}/\nu\text{CN}$
3063 w	2928 w	3182.2	52.0	2.4	3064 w	3184.1	36.1	6.0	$\nu\text{CH}(\text{R1})$
	2971 w	3182.3	15.9	7.8		3186.7	42.0	5.4	$\nu\text{CH}(\text{R2})$
	3116 w	3207.2	194.6	0		3210.9	82.0	7.2	$\nu\text{CH}(\text{R1})$
	3175 w	3219.0	1.1	35.1		3222.9	377.0	18.5	$\nu\text{CH}(\text{R2})$
		3565.5	0.2	145.4		3552.5	119.4	93.7	$\nu\text{NH}$

$\nu$ , stretching;  $\delta$ , in-plane bending;  $\omega$ , out-of-plane bending;  $\tau$ , twisting; Sq, squaryl ring; R1, phenyl ring 1; R2, phenyl ring 2; sh, shoulder; s, strong; m, medium; w, weak; v, very.

$\text{cm}^{-1}$  is assigned to C–H out-of-plane bending. The peak at  $688 \text{ cm}^{-1}$  is a combination of the squaryl and N–H out-of-plane bending. In the Raman spectrum, except for the band at  $689 \text{ cm}^{-1}$ , the other out-of-plane vibrations are weak.

The SERS spectrum of DSQ using silver nanoparticles is shown in Figures 3, S2, and S3. Table 1 summarizes the

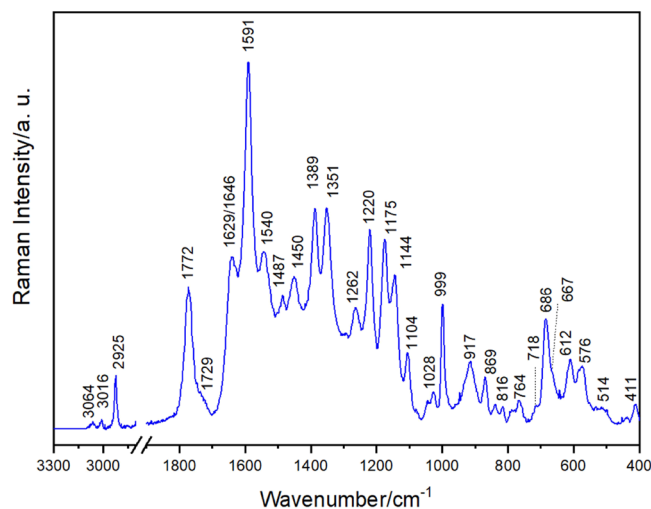


Figure 3. SERS spectrum of DSQ using 532 nm excitation.

wavenumbers of the observed bands, the calculated wavenumbers, Raman activities, and IR intensities, as well as the corresponding vibrational mode assignments obtained using the Ag(0)–DSQ model shown in Figure 2b. Other predicted data can be found in Tables S1 and S2. The SERS spectrum of DSQ is crowded in the spectral region from  $1000$  to  $1700 \text{ cm}^{-1}$  (Figure S2 shows the spectral deconvolution of the SERS spectrum). Though the number of active bands agrees well with those detected in the normal Raman spectrum of the solid sample, several differences are observed in their positions and relative intensities. Figure S3 shows the similarities between both normal Raman and SERS spectra of DSQ; the stronger band in the SERS spectrum at  $1591 \text{ cm}^{-1}$  corresponds to the stronger band of the solid but is shifted  $-14 \text{ cm}^{-1}$ ; as expected, this band is a good peak marker in the sense of monitoring the environment around the linked regions between SQ and aniline groups. Bands at  $1144$ ,  $1220$ ,  $1351$ ,  $1540$ , and  $1772 \text{ cm}^{-1}$  are remarkably enhanced in the SERS spectrum compared with the normal Raman of the solid, all of them assigned to in-plane vibrational movements.

The carbonyl stretching band at  $1793 \text{ cm}^{-1}$  in the solid sample shifts to  $1772 \text{ cm}^{-1}$  in the SERS spectrum. In previous work, the SERS spectrum of SQ has a very strong band at  $1772 \text{ cm}^{-1}$ .<sup>42</sup> It was suggested that the intensity enhancement of this mode is due to the adsorption of the oxocarbon on the nanoparticle surface through the carbonyl oxygen. Therefore, the presence of this strong band in the SERS spectrum of DSQ is an essential indicator of its adsorption, which may occur through one of the oxygen atoms. This interpretation is also supported by the optimized structure of the Ag(0)–DSQ complex since there is favorable coordination of the silver atom to one oxygen of the squaryl ring (see Figure 2b). As shown in Table S2, there are only small changes in the bond distances and angles in the presence of a silver atom. However, there is a slight lengthening of the  $\text{C}_4\text{--O}_6$  bond which may explain the

wavenumber downshift of the carbonyl stretching band in the SERS spectrum.

Only a few out-of-plane vibrations of DSQ are observed in the SERS spectrum at 411, 686, and 764  $\text{cm}^{-1}$ . The bands at 411 and 764  $\text{cm}^{-1}$ , which are very weak in the spectrum of the solid, are slightly enhanced in the SERS spectrum. The band at 411  $\text{cm}^{-1}$  is assigned to a combination of the phenyl ring and C–H out-of-plane bending. The peak at 764  $\text{cm}^{-1}$  is attributed to C–H out-of-plane bending and N–H out-of-plane bending. Qi et al. observed intensity enhancement of these bands in the SERS spectrum of aniline, suggesting that the molecule adopts a tilted orientation on the metal surface.<sup>50</sup> The observed strong SERS intensity of the 686  $\text{cm}^{-1}$  band, which has a contribution from squaryl out-of-plane bending, also indicates that the four-membered ring of DSQ may be tilted relative to the nanoparticle surface.

As seen in Figure 2b, the obtained minimum energy geometry of Ag(0)–DSQ is non-planar with the silver atom interacting with one oxygen. Using DFT calculations, Vega et al. also reported a non-planar structure for the complex of deprotonated 1,3-bis(4-cyanophenylamino) squaraine with two silver atoms.<sup>34</sup> It was shown that each silver atom interacts with one phenyl ring by an Ag(I)– $\pi$  interaction. The DFT calculation of Ag(0)–DSQ carried out here suggests a weak interaction of the Ag atom with one of the phenyl rings sufficiently to perturb the planarity of the DSQ. The calculation predicts a quasi-planar structure for DSQ, with torsion angles of  $\alpha$  ( $\text{C}_3\text{--N}_8\text{--C}_{15}\text{--C}_{16}$ ) =  $-0.002^\circ$  and  $\beta$  ( $\text{C}_2\text{--N}_7\text{--C}_9\text{--C}_{10}$ ) =  $-0.035^\circ$  (demonstrating coplanarity between the two phenyl rings and squaryl ring), and a nonplanar structure for the Ag(0)–DSQ complex with  $\alpha$  =  $0.103^\circ$  and  $\beta$  =  $-14.276^\circ$ . The band at 907  $\text{cm}^{-1}$  in the normal Raman spectrum, which is assigned to  $\text{C}_4\text{--C}_3\text{--N}_8$  and  $\text{C}_1\text{--C}_2\text{--N}_7$  in-plane bending motions, shifts to 917  $\text{cm}^{-1}$  in the SERS spectrum. The predicted change in the torsion angle  $\beta$  in the presence of the silver atom explains the experimental shift in the wavenumber of this band.

The interaction of the silver atom with DSQ may also be the origin of the shift of other bands with contribution from C–H vibrations.<sup>53</sup> For instance, the bands at 1151, 1190, 1255, and 1605  $\text{cm}^{-1}$  in the normal Raman spectrum shift to 1144, 1175, 1262, and 1591 in the SERS spectrum, respectively. The change in the torsion angle  $\beta$  may have also an influence on the shift of the bands at 1255 and 1605  $\text{cm}^{-1}$  which have the contribution of C–N stretching vibrations.

Despite DSQ derivative presenting as a very symmetrical system, NMR data preliminary showed us different carbons atoms from squaryl groups; thus, there were diverse chemical environments available for process adsorptions, but only one of them was favorable for it. Overall, the results obtained here suggest that DSQ is mainly adsorbed through one of the carbonyl groups and has a weak interaction with the silver nanoparticle. They also indicate that the molecule lost its planar structure in the presence of the nanoparticle and has a tilted configuration concerning the surface.

#### 4. CONCLUSIONS

In the present work, we have reported and characterized for the first time the normal Raman and SERS spectra of DSQ. The detailed comparison of these spectra suggests that DSQ has a tilted configuration correlated with the silver nanoparticle surface. From the experiments and the DFT calculations, it was revealed that surface adsorption may occur through the

interactions of a DSQ carbonyl group and a phenyl ring with the silver atoms. In addition, the presence of the nanoparticle (silver atom) promoted the loss of planarity of the DSQ structure. Taking into account the known use of squaraines and the results obtained here, it is expected that the interaction of the DSQ and DSQ-based dyes with plasmonic silver nanoparticles can open potential applications in several fields and particularly in nanoplasmonics.

#### ■ ASSOCIATED CONTENT

##### SI Supporting Information

The Supporting Information is available free of charge at <https://pubs.acs.org/doi/10.1021/acs.jpcc.2c07109>.

Solid-state  $^{13}\text{C}$  NMR spectrum of DSQ; deconvolution of the SERS spectrum of DSQ; Raman spectra; XYZ coordinates; data for the optimized geometries; and band positions for Normal Raman and infrared spectra (PDF)

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##### Notes

The authors declare no competing financial interest.

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