

Identification and Characterization of Volatile Organic Compounds of Fresh Plant Using Headspace Combined with Surface-Enhanced Raman Scattering

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Abstract

The spectra of volatiles of fresh garlic, Chinese chive and scallion plants were successfully recorded by headspace combined with surface-enhanced Raman scattering using the portable Raman spectrometer. For garlic: high intensity bands are present in 1622, 1397, 1287, 1182, 711, 569, 461 cm^{-1} and low intensity bands are present in 1017, 979, 918, 307 cm^{-1} . For Chinese chives: the high intensity band is present in 672 cm^{-1} and low intensity bands are present in 1618, 1396, 1289, 1185, 575, 412, 274 cm^{-1} . For scallion high intensity bands are present in 699, 1023 cm^{-1} and low intensity bands are present in 369, 887, 1084, 1314 cm^{-1} . The main volatiles of fresh garlic, Chinese chive and scallion are diallyl disulfide, allyl methyl sulfide and 1-propanethiol respectively. As the bulk concentration changes, different conformers are absorbed on silver.

Keywords: Fresh alliums species; Headspace; SERS; Calculation; Volatile

Introduction

In the last few years, the investigations of volatile organic compounds of Allium species by means of GC-MS, gas chromatography-mass spectrometry and HPLC, High-performance liquid chromatography have attracted attention [1-4]. However, these methods have some serious draw backs, including labour intensive sample pretreatment and extractions; they are also expensive and not currently portable. In several studies it has been shown that, besides the above methods usually applied, the chemical compositions of various essential oils can also be determined by vibrational spectroscopic methods such as IR, NIR and Raman spectroscopies [5-8]. It should be noted that the term "essential oil" relates to the method of preparation, namely the distillation of plant material at atmospheric pressure. However, changes in the composition of the oil may be observed during the distillation process as a result of elevated temperature and the hydrolysis reaction in the acidic solution [9-11]. The direct analysis of volatile organic compounds of fresh plants without sample preparation would hence be very desirable. Headspace volatile analysis is a good alternative technique because it is simple, rapid, inexpensive, and does not consume solvents. As well, sample manipulation is reduced. But headspace volatiles are normally present at low concentrations. They should therefore be determined by use of sensitive analytical techniques. Surface-enhanced Raman scattering (SERS), resulting in strongly increased Raman signals from molecules attached to or adjacent to nanometre structures [12] is a good alternative for trace analysis techniques. From an analytical point of view, SERS provides spectral fingerprint capability at trace concentration level, which is achieved by only a few analytical techniques [13]. Garlic (*Allium sativum* Linnaeus), Chinese chives (*Allium tuberosum* L.) and scallion (*Allium fistulosum*) were used as our samples. To our knowledge, there has been no previous analysis of these plants using SERS. In this paper, microwave heating method was utilized to obtain Ag colloids [14]. The SERS spectra of volatile of fresh garlic, garlic chives and scallion were investigated and calculations were performed. The calculated result from gaussian 03 was compared with the experimental ones.

Experiment

Preparation of Ag colloids

Ag colloids were prepared by reduction of AgNO_3 with sodium citrate. An AgNO_3 solution (0.001 M) of 250 ml was mixed with a sodium citrate solution (1%) of 8 ml. Then the mixture was heated up for 30 min by using a microwave oven. Ag colloids of a gray color were obtained as a homogeneous solution [14].

Materials

All reference standards were of analytical grade and were purchased from J&K Scientific Ltd. The SERS of liquid state reference standards each was obtained by mixing 20 ml reference standards with 1.5 ml of Ag colloids. The SERS of gas state reference standards each was obtained as follows: 1ml reference standard was placed in the headspace vial (volume: 250 ml) and sealed; After 5 minutes 30 ml of gas were drawn from the vial with a syringe and were injected very slowly into 1.5 ml of Ag colloids for this experiment. Garlic, Chinese chives and scallion were obtained from a local market and chopped into pieces 2-3 mm long. Then 13.00 gram of each was placed in the headspace vial (volume: 250 ml) and sealed; they are then well shaken to ensure their volatility. No further sample preparation was used. After 5 minutes, 30 ml of gas was drawn from the vial with a syringe and were injected very slowly into 1.5 ml of Ag colloids for test.

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Instrumentation

The Raman and SERS spectra were recorded on a portable Raman spectrometer (R-3000TM, Ocean Optics Co., USA) with an excitation wavelength of 785 nm from an air-cooled diode laser.

Results and Discussion

Garlic

The SERS spectrum of garlic volatile is shown in Figure 1(a). It can be seen that several of high intensity bands are present in 1622, 1397, 1287, 1182, 711, 569, 461 cm^{-1} . Low intensity bands are present in 1017, 979, 918, 307 cm^{-1} . The most important precursor of garlic flavor is allicin (2-propene-1-sulfinothioic acid S-2-propenyl ester, Diallyl thiosulfinate). Allicin is not a stable compound and readily degrades to form secondary products: a variety of sulfides, which contribute to the characteristic flavor and taste of garlic [15,16]. Diallyl disulfide was found to be the predominant flavor components of garlic samples.

¹⁵ Thus, the SERS spectrum of garlic volatile may come from diallyl

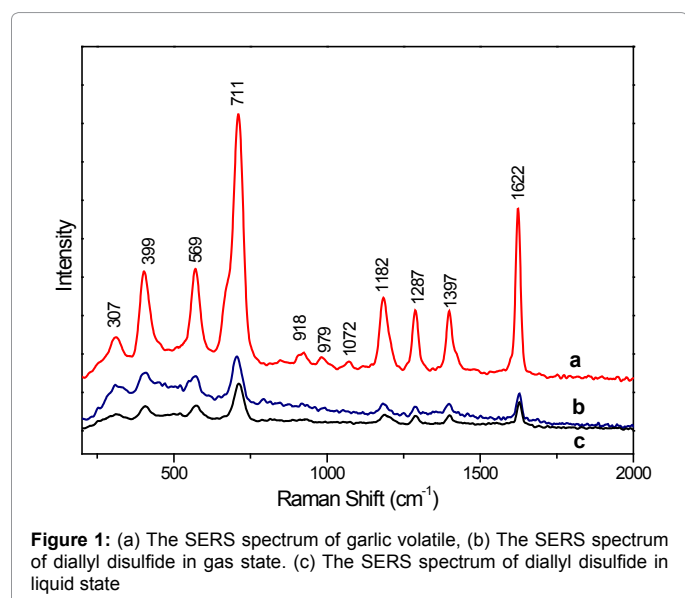


Figure 1: (a) The SERS spectrum of garlic volatile, (b) The SERS spectrum of diallyl disulfide in gas state. (c) The SERS spectrum of diallyl disulfide in liquid state

disulfide. The SERS spectra of gas and liquid sample of diallyl disulfide are shown in Figures 1b,1c. Comparing Figure 1a with Figures 1b,1c almost all peaks from Figure 1a have corresponding peaks from Figures 1b, 1c. Thus, the conclusion can be made that garlic volatile on the silver surface were identified as diallyl disulfide (Table 1).

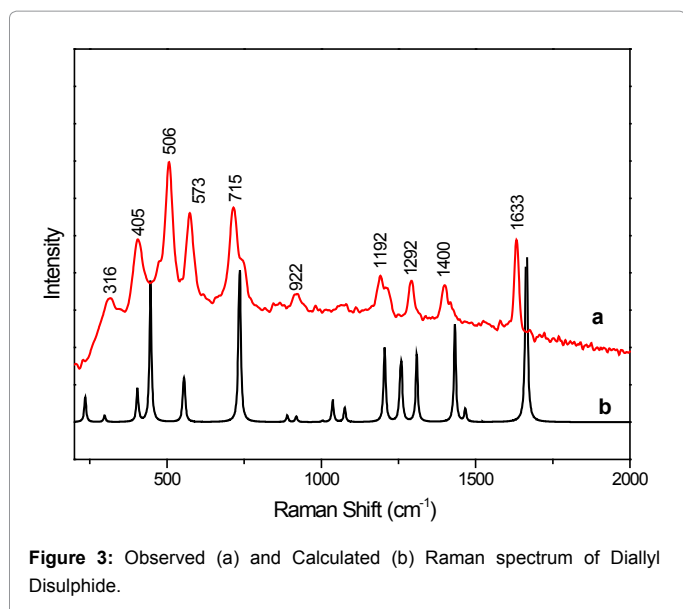
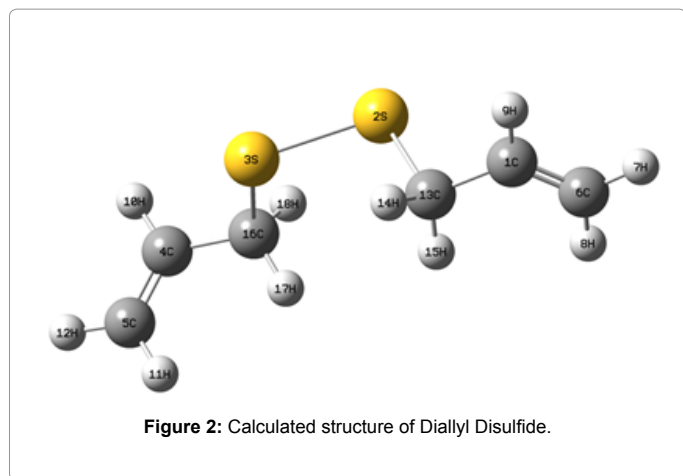
The structure of diallyl disulfide is shown in Figure 2. The density functional theory (DFT) calculation of diallyl disulfide's Raman spectrum matches well with the experiment result (Figures 3a,3b). Although the peak locations of RHF/6-31G level are not exactly predicted for all Raman but the band positions and the intensity pattern are similar. So the RHF/6-31G is a very useful method for the assignment of the Raman spectrum. The dominant assignment for diallyl disulfide including computational and experimental results is given in Table 1. It can be seen from Figures 1b,1c that the SERS spectra of diallyl disulfide are considerably different from the ordinary Raman spectrum of the molecule (Figure 3a). The coincidence of the two SERS spectra demonstrates that S-S bond scission in diallyl disulfide occurs on the silver surface, and the resulting diallylthio group attaches to silver via its sulfur atom. The absence in the SERS spectrum of the S-S stretching 506 cm^{-1} which is present in the ordinary Raman spectrum is clear evidence supporting the S-S cleavage of this molecule on silver. A similar conclusion was drawn from the SERS investigation of dimethyl disulfide [17].

Chinese chives

The SERS spectrum of Chinese chives volatile is shown in Figure 4a. It can be seen that the high intensity band is present in 672 cm^{-1} . Low intensity bands are present in 1618, 1396, 1289, 1185, 575, 412, 274 cm^{-1} . Allyl methyl trisulfide, diallyl trisulfide, dimethyl trisulfide, allyl disulfide, allyl methyl disulfide, dimethyl disulfide, diallyl sulfide and allyl methyl sulfide were identified from Chinese chive essential oil. Five of these sulfur volatiles (allyl methyl sulfide, allyl disulfide, allyl methyl disulfide, dimethyl disulfide, dimethyl trisulfide) were also found in the headspace of crushed Chinese chive leaf samples [18]. The SERS spectra of gas and liquid sample of allyl methyl sulfide are shown in Figures 4b,4c. Comparing Figure 4a with Figures 4b,4c almost all peaks from Figure 4a have corresponding peaks from Figures 4b,4c. Thus, the conclusion can be made that Chinese chive volatile on silver surface was identified as allyl methyl sulfide (Table 2).

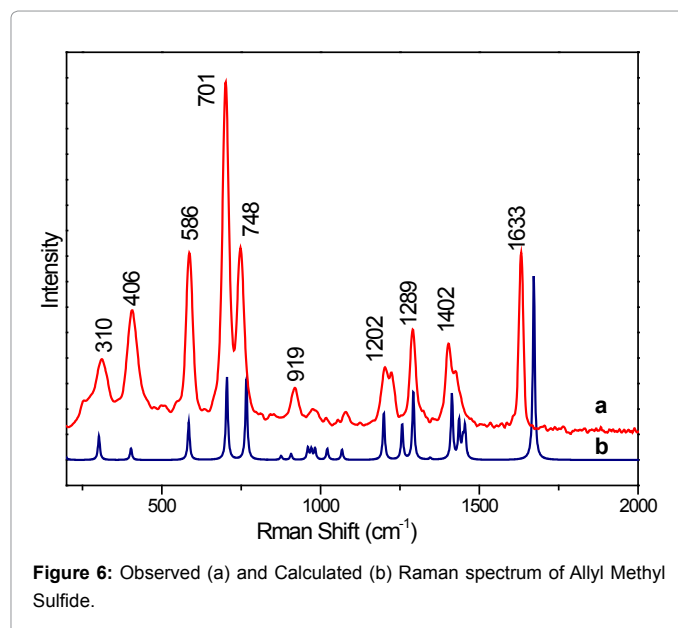
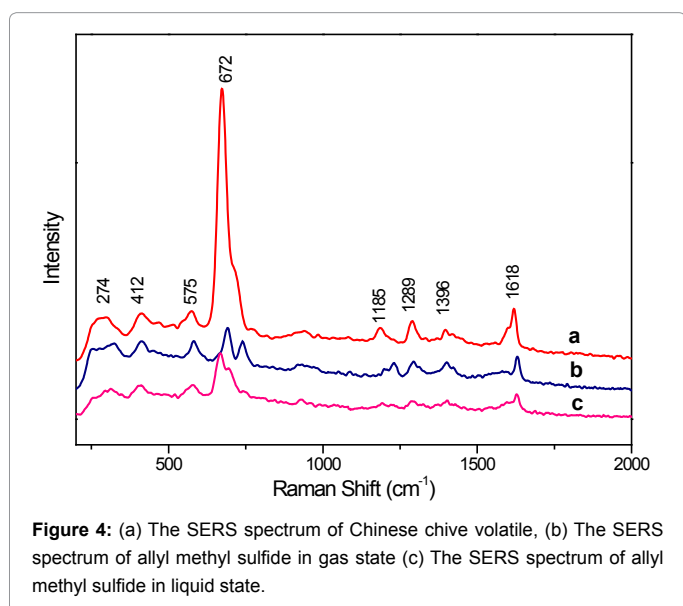
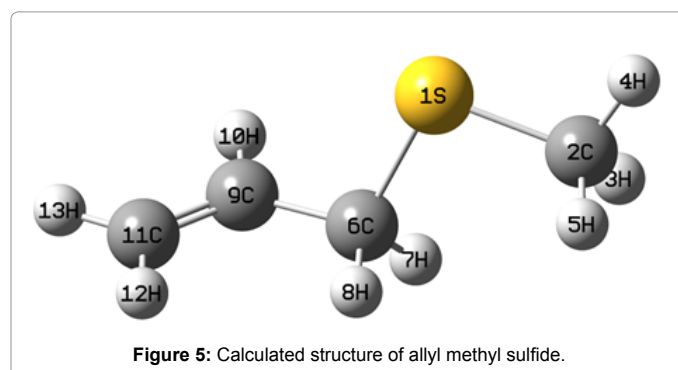
Calculation	Raman Activity	NR (experiment)	SERS (gas)	SERS (liquid)	SERS (volatile of garlic form)	Assignment
157	13.7527					C-S-S deformation
235	17.6321					C1-H, C4-H, C5-H, C6-H bending
297	3.3560	316	308	311	307	C1-H, C4-H, C5-H, C6-H bending
404	23.5794	405	407	406	399	C6=C1-C13, C16-C4=C5 deformation
446	105.2454	506				S2-S3 stretching
555	23.2117	573	571	573	569	S3- C16, S2- C13 and S3-S2 stretching, C5-H ₂ , C6-H ₂ twisting
736	91.7303	715	705	711	711	S3- C16, S2- C13 stretching C5-H ₂ , C6-H ₂ , twisting
889	5.5307					C-H rocking
918	2.2878	922			918	C4-C16, C1-C13 stretching, CH ₂ wagging
1037	5.1471				979	C1-H9, C6-H7, C4-H18, C5-H12 bending
1076	11.3605				1072	C(13,16)H ₂ twisting
1205	37.8646	1192	1183	1188	1182	C(13,16)H ₂ twisting
1259	43.4005	1292	1288	1298	1287	C(13,16)H ₂ wagging
1309	33.1564					C4-H, C5-H, C1-H, C6-H rocking
1433	49.4170					C5-H ₂ , C6-H ₂ scissoring
1468	3.4354	1400	1398	1400	1397	C13-H ₂ , C16-H ₂ scissoring
1667	201.6596	1633	1628	1628	1622	C1=C6, C4=C5 stretching

Table 1: Assignments of Theoretical Wave Number Values (scaling factor 0.8929) to Experimental Bands in the Raman of diallyl disulfide.



The structure of allyl methyl sulfide is shown in Figure 5. The density functional theory (DFT) calculation of allyl methyl sulfide's Raman spectrum matches well with the experiment result (Figure 6). Although the peak locations of HF/6-311G (d, p) level are not predicted exactly for all SERS, but the band positions and the intensity pattern are similar. So the HF /6-311G (d, p) are a very useful method for the assignment of the Raman spectrum. The dominant assignment for allyl methyl sulfide is given in Table 2. From Table 2, high intensity bands 672 cm^{-1} in SERS spectrum of Chinese chive is assigned to C-S stretching. There is a decrease of 29 cm^{-1} compared with Raman (701 cm^{-1}). This suggested that allyl methyl sulfide is adsorbed on Ag surface via C-S. This is further evidenced by the observation of the C-S-C scissoring vibration at about 274 cm^{-1} ; it shows a decrease of 36 cm^{-1} compared with Raman (310 cm^{-1}).

As is evident from Figure 4, some features in the SERS spectra of gas state allyl methyl sulfide, liquid state allyl methyl sulfide and Chinese chive volatile differ dramatically. In particular, one band such as the 1S-6C stretching vibration at about 739 cm^{-1} (Figure 4b) is not present in its liquid state or in Chinese chive volatile (Figures 4a,4c), and the band 1S-2C stretching centered at around 691 cm^{-1} decreased 24 cm^{-1} and 19 cm^{-1} in its liquid and in Chinese chive volatile. These changes in the band seem to occur with different bulk concentrations as different conformers are absorbed in the surface. A similar conclusion was



drawn from the SERS study of 1-propanethiol [19] and 1-butanethiol [20].

Scallion

The SERS spectrum of scallion volatile is shown in Figure 7a. It

can be seen that high intensity bands are present in 699 and 1023 cm^{-1} . Low intensity bands are present in 369, 887, 1084, 1314 cm^{-1} . The SERS spectrum of scallion is very different from Chinese chive and garlic. The SERS spectra of gas and liquid sample of 1-propanethiol are shown in Figures 7b,7c. Comparing Figure 7a with Figure 7c almost all peaks

Calculation	Raman Activity	NR	SERS (gas)	SERS (liquid)	SERS (volatile of Chinese chive form)	Assignment
302	6.2498	310	327	313	274	6C-1S-2C scissoring, 11CH ₂ twisting, 9C-10H bending
402	3.0867	406	411	404	412	11CH ₂ =9C-6C bending
585	10.5955	586	581	577	575	11CH ₂ twisting, 9C-10H in-plane bending, 1S-6C stretching
705	23.8293	701	691	667	672	1S-2C stretching
765	23.6953	748	739			1S-6C stretching, 11CH ₂ twisting
876	1.2256					6CH ₂ wagging
907	1.8171	919	918	928	910	11CH ₂ wagging, 9C-6C stretching
960	3.6514					2CH ₂ out-plane bending
970	3.1421					11CH ₂ bending (down)
983	3.3885				983	2CH ₂ bending (down)
1021	3.4182	1020				9C-10H out-plane bending, 11CH ₂ twisting
1067	3.1797		1087			6CH ₂ twisting, 9C-10H bending
1199	15.2036	1202	1198	1191	1185	6CH ₂ twisting
1257	11.5576		1229			6CH ₂ , 9C-10H bending
1293	22.7778	1289	1294	1287	1289	9C-10H, 11C-12H bending
1345	0.6354					2CH ₃ umbrella
1413	22.5144	1402	1401	1402	1396	11CH ₂ scissoring, 9C-10H bending
1436	12.8914					2C-(3,5)H ₂ twisting, 2C-4H stretching
1449	5.9285					2C-(3,5)H ₂ scissoring 2C-4H bending (up)
1454	10.6668					6C-H ₂ scissoring
1671	67.8280	1633	1629	1627	1618	11C=9C stretching

Table 2: Assignments of Theoretical Wave Number Values (scaling factor 0.9040) to Experimental Bands in the Raman of allyl methyl sulfide.

Calculation	Raman Activity	NR	SERS (gas)	SERS (liquid)	SERS (volatile of scallion form)	Conformer	Assignment
291	1.0138	288				G	1CH ₃ twisting (5,6) CH ₂ twisting, 11S-12H bending
399	1.0312	359	368	369	371	T	1C-5C-8C bending
634	20.8671	644				G	8C-11S stretching, 5CH ₂ wagging
			699	699	697	T	8C-11S stretching
712	1.2830	723				G	11S-12H bending, (8, 9)CH ₂ wagging
795	5.3812	801				G	1CH ₃ , (5,8) CH ₂ wagging, 11S-12H bending
850	8.0578	872				G	1C-5C-8C stretching
			889	888	888	T	CH ₂ rocking
917	4.0690						11S-12H bending, 8CH ₂ twisting, 1CH ₃ wagging
1016	5.0862	1029	1022	1023	1022	T	5C-8C stretching
1065	2.5424					G	5CH ₂ twisting, 1CH ₃ wagging
1092	2.7549	1104		1090	1088	T,G	1CH ₃ wagging, 11S-12H bending, (5, 8) C-H bending
1223	4.6034	1210			1217	T,G	8CH ₂ twisting, 5C-6H bending
1263	9.8347	1250					5CH ₂ twisting, 8C-9H bending
1315	1.8054	1293					5CH ₂ twisting, 8CH ₂ wagging
1354	0.7383	1330			1322	T,G	5CH ₂ wagging, 1CH ₃ umbrella
1393	0.8632						1CH ₃ umbrella, 5CH ₂ wagging
1437	14.2164						8CH ₂ scissoring
1449	15.9339	1442			1440	T,G	5CH ₂ scissoring
1459	4.5614				1453	T,G	1C-(2,3)H ₂ twisting, 5CH ₂ scissoring
1468	4.7926						1C-H bending

Table 3: Assignments of Theoretical Wave Number Values (scaling factor 0.9040) to Experimental Bands in the Raman of 1-Propanethiolate.

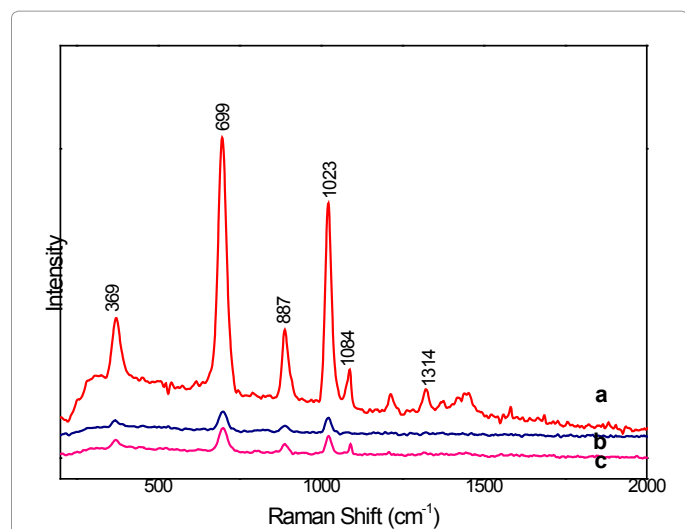


Figure 7: (a) The SERS spectrum of scallion volatile. (b) The SERS spectrum of 1-propanethiol in gas state (c) The SERS spectrum of 1-propanethiol in liquid state.

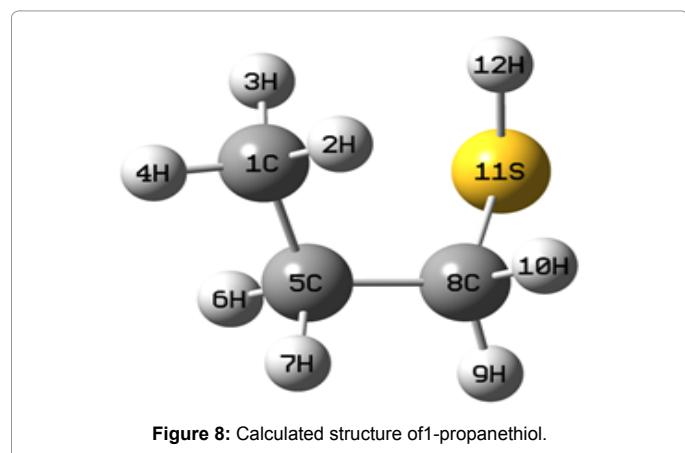


Figure 8: Calculated structure of 1-propanethiol.

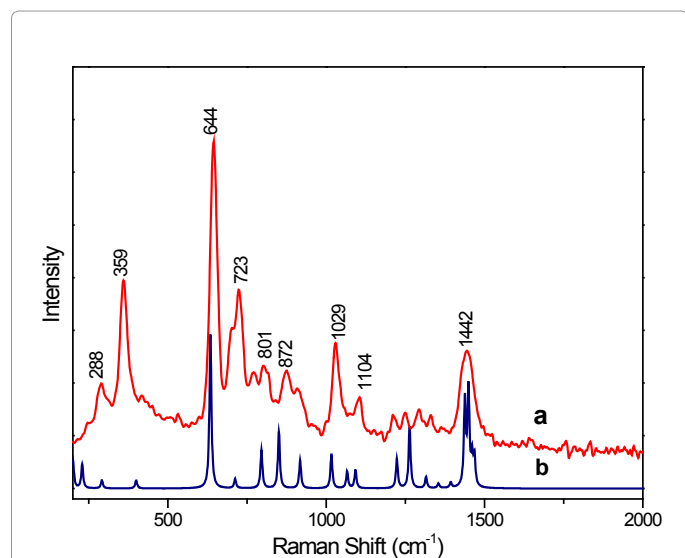


Figure 9: Observed (a) and Calculated (b) Raman spectrum of 1-propanethiol.

from Figure 7a have corresponding peaks from Figure 7c. Thus, the conclusion can be made that scallion volatile on silver surface was identified as 1-propanethiol (Table 3).

The structure of 1-propanethiol is shown in Figure 8. The density functional theory (DFT) calculation of 1-propanethiol's Raman spectrum matches well with the experiment result (Figure 9). Although the peak locations of HF/6-311G (d, p) level are not predicted exactly for all SERS, the band positions and the intensity pattern are similar. So the HF /6-311G (d, p) are a very useful method for the assignment of the SERS spectrum. The dominant assignment for 1-propanethiol is given in Table 3. The SERS of 1-propanethiol has been investigated by Myung Soo Kim, et al. [19]. The vibrational spectra and the stable conformers of 1-propanethiol have been investigated by Torgrimssen, et al. [21]. According to their study, the conformers and some dominant assignment for 1-propanethiol is also given in Table 3. The bands in 288, 644, 723, 801 cm^{-1} corresponding to the C-C-S deformation (G), C-S stretching (G), S-H bending (G) and C- S-H deformation (G) of 1-propanethiol respectively is not present in its SERS. High intensity bands in 699 cm^{-1} corresponding to the C-S stretching (T) appear in all SERS spectra. It seems that the 1-propanethiol is absorbed to Ag colloids surface via "trans" conformer.

Conclusions

The fresh garlic, Chinese chive and scallion volatile in the headspace are diallyl disulfide, allyl methyl sulfide and 1-propanethiol respectively, which provide the highest affinity to bind to silver. The presented results illustrate that combining headspace with SERS is a powerful tool for identifying Allium volatiles. The volatile can be detected in fresh Allium directly and quickly without extraction.

Acknowledgements

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