Journal of Undergraduate Chemistry Research, **2021**, 20(1), 1

RAMAN SPECTROSCOPIC CHARACTERIZATION OF AN IONIC LIQUID (1-BUTYL-3-METHYLIMIDAZOLIUM THIOCYANATE)

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Abstract

Ionic liquids are a class of purely ionic, salt-like materials that are liquid at unusually low temperatures. These materials manifest physiochemical behaviors quite unlike water or organic solvents. They possess high ionic conductivity, high ion concentrations, and excellent oxidative stability, making them ideal materials for demanding applications at elevated temperatures. Ionic liquids have many applications, such as powerful solvents, electrolytes (electrically conducting fluids), and power sources (batteries, capacitors, and fuel cells). In this study, the Raman spectra of 1-butyl-3-methylimidazolium thiocyanate or [BMIM][SCN] were obtained using a confocal dispersive Raman spectrometer and a handheld Raman spectrometer, and peaks were assigned to the corresponding vibrational mode. The assignment of peaks was made possible by correlating the experimental results with ab initio calculations.

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Keywords: ionic liquid, Raman, 1-butyl-3-methylimidazolium thiocyanate, ab initio

Introduction

Ionic liquids (ILs) are among the most exciting and successful materials developed. Since 1992 when the air and water stable ILs were first reported by Wilkes and Zawrotko,[1] ILs have been studied in the last 30 years for various scientific and applicative issues.[2] They are defined as salts with a melting point below the boiling temperature of water (100 °C).[3] Unlike other liquids like water, which is made mainly of electrically neutral molecules, ionic liquids are made of ions and ion pairs. Ionic liquids have many different properties, such as electrical conductivity, powerful solvents, highly viscous with low vapor pressure, and good thermal stability.[3-6] Many classes of chemical reactions like Friedel-Crafts reactions and Diels-Alder reactions can be performed using ionic liquids.[7] Because of their different properties, ionic liquids are attracting attention in many different fields.

In this study, the ionic liquid being examined is 1-butyl-3-methylimidazolium thiocyanate or [BMIM][SCN] (Figure 1). This ionic liquid was chosen since it has been used in various applications. For instance, [BMIM][SCN] was used to separate cyclohexane from benzene[8], propylene from propane[9], and n-heptane from toluene[10]. It has also been used to extract alcohols from n-heptane [11], in the extractive desulfurization of liquid fuel (specifically the removal of dibenzothiophene) [12], in the pretreatment and fractionation of lignocellulosic biomass in wheat straw[13] and as epoxy crosslinkers and graphite nanoplatelets dispersants [14]. Lately, this ionic liquid has been utilized in studies involving biomolecules. The thermal and conformational stability of insulin in the presence of [BMIM][SCN] was reported in one study [15]. Another study looked at the effect of the ionic liquid on the suppression of bovine insulin amyloid formation [16]. A similar study was also conducted wherein several proteins such as cytochrome c, myoglobin, lysozyme, ribonuclease A, and beta-lactoglobulin were used [17].

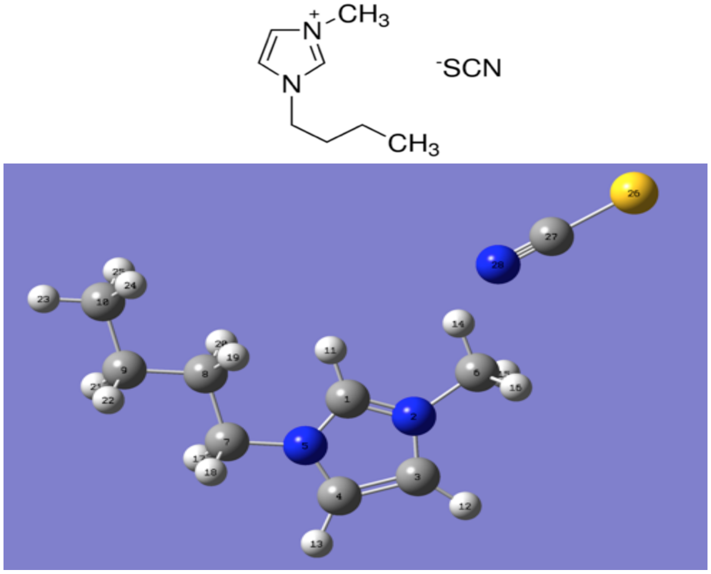

Figure 1. Structure of 1-butyl-3-methylimidazolium thiocyanate or [BMIM]$^+$[SCN]$^-$ used in this study. The figure in the lower part is the optimized structure obtained from theoretical calculations

Raman spectroscopy is a non-destructive method that measures the vibrational modes of a sample. A spectrum consists of a wavelength distribution of peaks corresponding to molecular vibrations specific to the sample being analyzed [5]. It complements with the other vibrational method, infrared (IR), which is more popular and more established than Raman. The IR method usually depends on the dipole moment of the molecule, while Raman is based on changes in the molecule's polarizability. The IR method is limited by some problems; foremost of them is the broadband peak given by a hydroxy group, of which Raman can be used instead for samples containing water. Raman, on the other hand, is limited by the sample's strong fluorescence, of which the IR method can be used instead.

Numerous vibrational studies using Raman and IR were performed on imidazolium-based ionic liquids. Among these is the study comparing the monocationic and dicationic imidazolium ionic liquids where it was also reported that there are more active modes in Raman compared to IR [18]. Several follow-up studies looked at the effect of the nature of the anion on three dicationic ionic liquids and the effect of cation alkyl chain length on two new dicationic ionic liquids[19-20]. There is also a study that revisited the vibrational assignments of imidazolium-based ionic liquids [21].

Most of the studies for the ionic sample ([BMIM][SCN]) were focused on the thiocyanate group region. One study looks at the Raman band shape of the cyano stretching modes on four cyanate-anions that include [BMIM][SCN] [22]. Another study characterized the surface of the ionic liquid at the gas-liquid interface using sum frequency generation spectroscopy [23].

A complete Raman spectrum scan has yet to be reported. This study aims to look at the Raman spectra of [BMIM][SCN] in different regions and assigned the vibrational mode responsible for the peaks. Simultaneously, theoretical calculations were performed to correlate the experimental results and aid in peak assignments. Results from this study can add basic knowledge regarding the behavior of ionic liquids when put in different enrironment (i.e. different solvent and pH effects).

Experimental Methods

The ionic liquid [BMIM][SCN] was purchased from Sigma Aldrich. The Raman spectra of the pure ionic liquid were obtained using a Jasco NRS-3100 confocal dispersive Raman spectrometer (Easton, MD). This was performed by placing 30 uL of the ionic liquid on quartz cuvet where Raman scattering was induced by a 12 mW 488 nm laser and collected on a thermoelectrically cooled CCD detector. Reproducibility in the band position measurements was better than ± 1 cm^{-1} based on the sample to sample variations. All Raman spectra were obtained at room temperature.

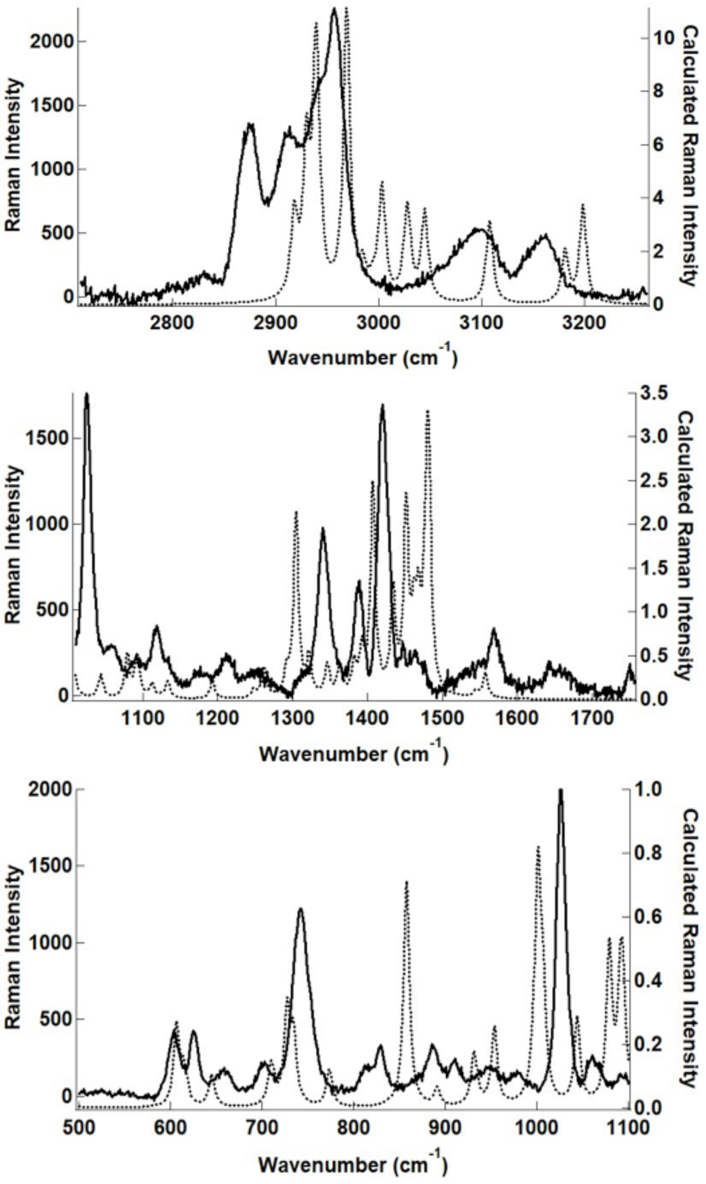

Figure 2. Raman spectra of the ionic liquid in the 400-3400 cm^{-1} region. Calculated Raman spectra are dotted lines.

In addition, the Raman spectra of the sample were also obtained using a portable handheld Raman spectrometer. With a run lasting for 5 minutes, the laser of a MiniRam Raman spectrometer (Model BTR111-785) from B&W Tek, Inc. (Newark DE, USA) was focused on the amber vial containing the ionic liquid sample. An excitation wavelength of 785 nm was used to obtain spectra ranging from 495 to 3150 cm^{-1}. The following parameters in the portable Raman spectrometer were set and used: laser power of 50 (425 mW), an integration time of 500 s, and an average of 100 with a multiplier of 5.

Computational studies were performed to aid in the peak assignments to help analyze the Raman spectra. Geometry optimization was initially performed, followed by vibrational frequencies determination. All calculations were executed on Gaussian 09W software[24] and carried out using density functional theory (DFT) approximation implementing the Becke's three-parameter exchange function combined with the Lee, Yang, and Parr correlation function (or B3LYP)[25] with a basis set of 631G(d). GaussView05[26] was used in preparing the input file and analyzing the calculations. The resulting calculated spectrum was adjusted with the Wong factor (multiplying the obtained frequencies with 0.9612)[27] and compared with the experimental spectrum.

Results and Discussion

Frequency		
Experimental*	Calculated**	Assignment
3175	3198	υ (C-H)
3100	3106	CH_3(N)NCH str
2975	2969	$v_{as}(CH_3)$
2914	2935	$v_{as}(CH_2)$
2850	2918	$v_s(CH_2)$
2058 (2049)	2064	CN
1642	1556	ring mode
1566	1546	v(N=C, C=C)
1420 (1404)	1451	$\delta(CH_2)$
1389	1392	$\delta(CH_2)$
1340	1346	CH_3(N)CN str
1211	1193	$\delta(CH_2)$
1119	1113	$\delta(CH_3)$
1025 (1010)	1002	ring mode
911	932	CCH bend
885	891	NC(H)N bend/CCH bend
830	858	NC(H)N bend/CCH bend
813	802	v(N-C)
743 (729)	738	$\omega(CH_2)$ rocking; S-C
703	711	$\omega(CH_2)$
659	645	CH_2(N)/CH_3(N)CN str
625	615	$\omega(CH_2)$
604	607	ω(N-H)/$v_{ip}(N\text{-}CH_3)$

Table 1. Peak assignment of 1-butyl-3-methylimidazolium thiocyanate. *Peaks obtained using confocal dispersive Raman spectrometer while those from portable Raan spectrometer are denoted in parenthesis. **Calculated peaks were obtained using the Wong scale factor [27].

The Raman spectra of the [BMIM][SCN] ionic liquid in different regions is seen in Figure 2. Table 1 also shows the peaks observed in the Raman spectra with the assigned vibrational modes. From 2800-3300 cm^{-1} region, five peaks can be observed (3175, 3100, 2975, 2914 and 2850 cm^{-1}). The vibrational modes of this spectral region can be assigned to an alkyl C-H stretch. Although the two highest broad peaks can be assigned to C-H stretching, it is possible that a ring NC(H)NCH stretching can be assigned to one of them, as reported in one study. The peak at 2975 can be assigned to CH_3 asymmetric stretching, while 2914 and 2850 are characteristic of CH_2 asymmetric and symmetric stretching modes. These peaks were assigned based on theoretical calculations, which correlate well with the experimental results (Figure 2). The Raman spectra in this region matched the one reported in one study [23].

Figure 2 also shows the spectral region 1000-1700 cm^{-1}, where different vibrational modes can be observed. Among these are the ring stretch modes and aliphatic CH bending modes. The peak at 1645 and 1566 cm^{-1} can be assigned to the C=C and C=N ring stretching modes. Since the ring is affected, the CH, CH_2, and CH_3 attach to the ring also exhibited in-plane bending, as observed in theoretical simulation. In-plane CH_2 and CH_3 bending can be assigned to the peak at 1420 cm^{-1}, while in-plane CH_2 bending can be assigned at 1389. Wagging of CH_2 can also be observed in the alkyl end of BMIM cation, and this can be exhibited in this region. The peak at 1340 cm^{-1} can be due to the C-N stretching with CH_2 scissoring. In addition, the C-H in the methyl group was found to have in-plane bending. The peaks at 1211 and 1119 cm^{-1} can be assigned to CH_2 and CH_3 in-plane bending and C-C stretching. Lastly, the peak at 1023 cm^{-1} can be due to the in-plane bending of CH (N) and ring C-N interaction and the -C=C- modes.

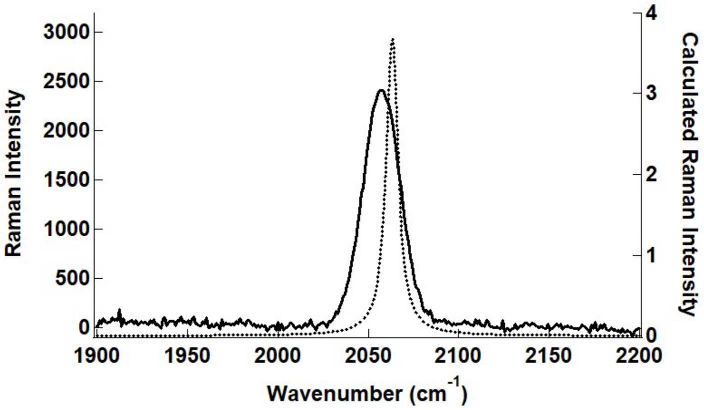

Figure 3. Raman spectra of [BMIM][SCN] at 2000 cm^{-1} region. Calculated Raman spectra are dotted lines.

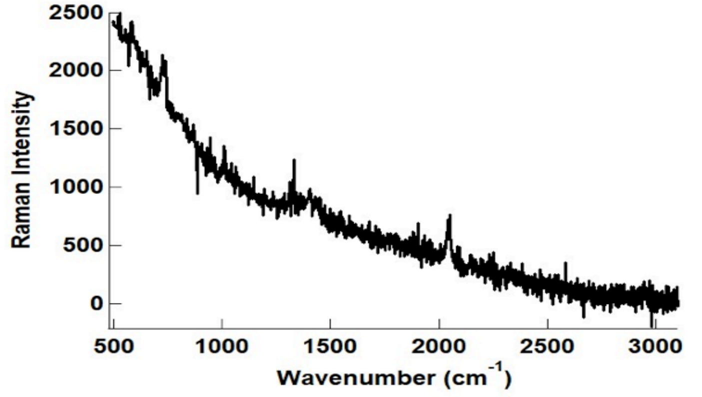

Figure 4. Raman spectra obtained using a portable Raman spectrometer.

The peaks at less than 1000 cm^{-1} are usually assigned to out of plane bending of the different functional groups. The major peak found in this region is that at 742 cm^{-1} that can be assigned to out of plane ring bending and the C-S stretching. The peaks at 596 and 625 cm^{-1} pertains to out of plane ring bending. It has been reported that $[BMIM]^+$ has a peak at 624 cm^{-1} that can be assigned to a mixture of out-of-plane ring bending and in-phase CH_2(N) and CH_3(N) CN stretching vibrations [22].

In addition, we look at the peak at 2056 cm^{-1} that can be assigned to the cyano mode or specifically thiocyanate group (Figure 3). This region is unique since the other functional groups are not present. The cyano mode observed at 2056 cm^{-1} in experimental data matched with the peak at 2065 cm^{-1} observed in theoretical calculations. The cyano functional group is the most studied region, and the peak is close to the thiocyanate region of 2135-2170 cm^{-1}. The peak observed is close to those reported at 2054 cm^{-1} [1, 22].

Lastly, the Raman spectrum of the ionic liquid obtained using a handheld Raman spectrometer can be seen in Figure 4. The signal to noise observed in the portable Raman spectrometer is not as good as seen in the confocal dispersive Raman spectrometer. However, some peaks can be observed close to the one observed in the benchtop Raman spectrometer. Among these are peaks observed at 729, 1010, 1404, and 2049 cm^{-1}, which are among the strongest peaks (743, 1025, 1420, and 2058 cm^{-1}) in the benchtop Raman spectrometer. With these results, Raman spectroscopy can be a good method to determine the behavior of ionic liquids especially those with cyano functional groups since this is a unique region where changes in the environment can result in shifts of peak [29].

Conclusion

The complete Raman spectra of 1-butyl-3-methylimidazolium thiocyanate or [BMIM][SCN] obtained using a confocal dispersive Raman spectrometer, and a portable Raman spectrometer was reported. Although weaker signals can be observed in the portable instrument, the main peaks observed matched in both instruments. Theoretical calculations of the same compound were utilized to aid in the assignment of peaks. The peaks of the major functional groups, such as the thiocyanate, showed agreement between the experimental and theoretical results.

Acknowledgments

We would like to thank Dr. Ruel Z. B. Desamero of York College for the use of the confocal dispersive Raman spectrometer.

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