

Raman Under Liquid Nitrogen (RUN)

R N Compton^{*1} and N I Hammer²

¹ Departments of Physics and Chemistry, University of Tennessee, Knoxville, TN 37996, USA

² Department of Chemistry and Biochemistry, University of Mississippi, PO Box 1848, University, MS 38677, USA

E-mail: rcompton@utk.edu

Abstract. The recording of Raman spectra for many molecules in air at room temperature is difficult or impossible as a result of sample degradation which is due to a combination of laser heating and oxidation. Often nitrogen gas is applied over the sample in an attempt to reduce oxidation. Also, the samples are sometimes cooled to reduce ro-vibrational “hot bands” and enhance the spectra. We have found great utility in recording Raman spectroscopy of samples *under* liquid nitrogen, a technique we call RUN. The RUN spectra show much higher resolution as a result of ro-vibrational cooling and in some cases cooling produces only the lowest energy conformer of the molecular ensemble further simplifying the spectra. A very sharp Raman peak at 2327.0 cm⁻¹, due to liquid nitrogen, also serves as a convenient wavelength calibration. We also demonstrate the ability to clearly delineate the lattice modes for naphthalene and benzene crystals.

1. Introduction

The Raman effect was first described in 1928 by Sir Chandrasekhara Venkata Raman and Kariamanickam Krishnan which resulted in the Nobel Prize in Physics for Raman only two years later. Since that time Raman spectroscopy, when combined with computations, has become a powerful method for determining molecular structure and for examining intermolecular reactions and molecular dynamics in the condensed phase. Raman and infra-red (IR) spectroscopy provide complementary information on molecular vibrations and in cases of high molecular symmetry (e.g., I_h, O_h, etc.) the two methods are “mutually exclusive”, i.e., vibrational modes are either Raman active or IR active but not both. The selection rules for the interaction of light and matter predict that asymmetric vibrations are excited in IR absorption and symmetric vibrations are active in Raman scattering. Together these two complimentary methods of molecular spectroscopy have been essential techniques for understanding the structure of inorganic and organic molecules since the 1930's. When proper attention is addressed to removing the strong Rayleigh line, as well as laser scattered light near the laser line, Raman spectroscopy has also contributed greatly to the understanding of low frequency molecular vibrations as well as lattice modes in solids.

Raman spectroscopy has also proven to be a useful tool for the analysis of biological systems such as conformational changes of peptides and proteins in aqueous solutions. Likewise nucleic acids and polynucleotides have been studied. A general comparison of Raman and IR spectroscopy can be

^{*}To whom any correspondence should be addressed.



found in the books by Ingle and Crouch [1] and by Nakamoto [2]. An excellent introduction to Raman spectroscopy can be found in the general education article by Tobias [3]. Other sources for elementary discussions of Raman spectroscopy can be found in the books by Engel [4], Struve [5], Steinfeld [6] and Harris and Bertolucci [7] among others cited therein.

In 2004 we introduced an exceedingly simple method of recording Raman spectra at 77 K by submerging the sample under liquid nitrogen [8]. We named this method Raman Under Nitrogen or RUN. This study presented the first high resolution Raman spectra for the extremely air sensitive uranocene molecule as well as for other air sensitive metallocenes. In addition to RUN we have found that surface-enhanced Raman spectroscopy (SERS) under liquid nitrogen can be greatly enhanced as a result of the increased dielectric properties of the liquid nitrogen over that of air [9]. This technique is called SERS under nitrogen or SERSUN.

In this article we further describe RUN and present Raman spectra and analysis for the C_{60} fullerene molecule and the $C_{60}Br_{24}$ fullerene derivative. In addition we demonstrate the utility of examining the lattice modes of benzene and naphthalene crystals under liquid nitrogen.

2. Experimental details

The experimental arrangement for recording Raman spectra for samples under liquid nitrogen is exceedingly simple as illustrated in Figure 1 below. The outer container for the liquid nitrogen consists of Styrofoam packing container. The inner container is a Styrofoam coffee cup supported by three toothpicks from the outer container. A few holes are placed in the coffee cup in order for the liquid nitrogen to flow between the two Styrofoam containers. The inner Styrofoam cup reduces the amount of surface rippling due to boil off, vibrations and refilling to keep the level constant. The sample holder is a stainless steel block containing indentations to hold the liquid or solid samples. Sometimes it is necessary to place a screen grid over the solid sample to prevent the sample from floating to the surface of the liquid nitrogen. In most cases the boiling off of the liquid nitrogen prevents fogging of the lens in the Raman apparatus by “pushing” the water vapor in the room away from the lens.

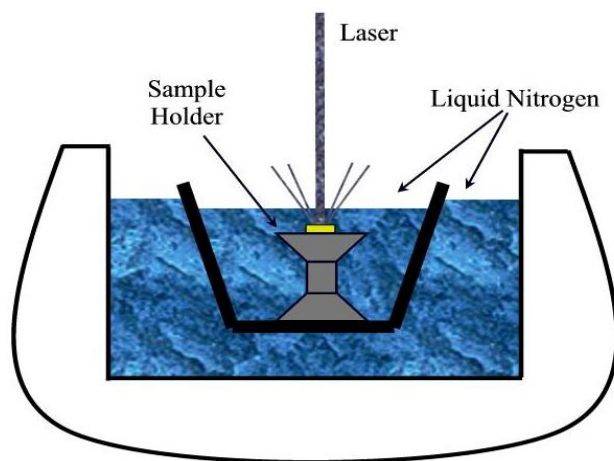


Figure 1. Set-up of the Raman Under Nitrogen (RUN) Spectroscopy experiment.

In the experiments reported herein two different Raman spectrometers were used: (1). At the University of Tennessee the Raman spectra were recorded using a Dilor XY 800 Raman spectrometer. Laser excitation was obtained using a Lexel, Inc. 3500 argon ion laser (5145 Å) and a Coherent Innova 300 krypton ion laser (6764 Å). Raman spectra were taken through Olympus confocal optics in a micro-Raman configuration utilizing a double fore-monochromator coupled to a liquid nitrogen

cooled Spectrum One CCD and (2) At the University of Mississippi Raman spectra was recorded using a Labview-controlled Jobin-Yvon Ramanor HG2-S Raman spectrometer employing a 90° scattering geometry relative to the incident laser. The spectrometer is equipped with a double grating (2000 grooves/mm) monochromator and a photomultiplier tube detector. The 514.5 nm laser line of a Spectra Physics Stabilite 2018 Ar^+/Kr^+ laser was used as the Raman excitation source.

The surrounding liquid nitrogen provides a narrow wavelength calibration. For example, the Raman spectrum of the liquid nitrogen shows two narrow features one at 2328.4 cm^{-1} and a weaker peak at 2290.2 cm^{-1} which are due to $^{14}\text{N}_2$ and $^{14}\text{N}^{15}\text{N}$, respectively as shown in Figure 2. The Raman spectra for liquid nitrogen have been well characterized and more accurate values for the N_2 Raman lines are 2327.0 cm^{-1} and 2288.8 cm^{-1} (see reference [10]). The liquid nitrogen vibration is only red-shifted by $\sim 3.4\text{ cm}^{-1}$ from the gas-phase value [11]. These peaks are always present and serve to provide a convenient wavelength calibration for the spectrum. The width of the $^{14}\text{N}_2$ peak can also be used to provide an estimate the resolution of the apparatus. These lines are very narrow and the positions of the peaks are sensitive to the atmospheric pressure. The presence of liquid oxygen is also seen as a peak at $\sim 1552\text{ cm}^{-1}$.

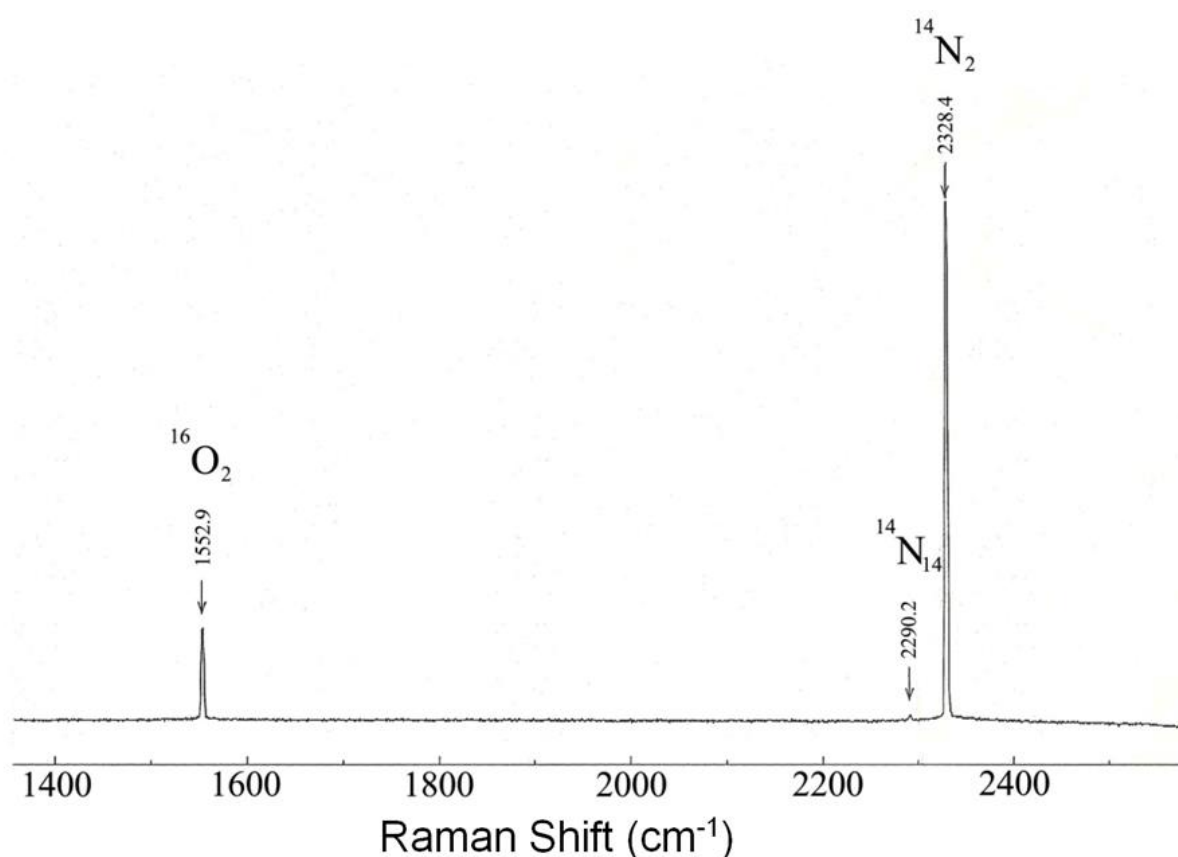


Figure 2. Raman spectrum of liquid nitrogen with the presence of some dissolved oxygen. Oxygen is generally not present in “fresh” samples of liquid nitrogen.

3. Examples of RUN spectra

The spectra to be presented are representative of that for over 150 samples studied over the years. We will discuss results for a few of these below. One of the first molecules to be studied by Sir Chandrasekhara Raman was tetrachlorobenzene, CCl_4 . Figure 3 shows a room temperature spectrum for CCl_4 taken at UM together with a simulated calculation of the symmetric stretch ν_1 vibration.

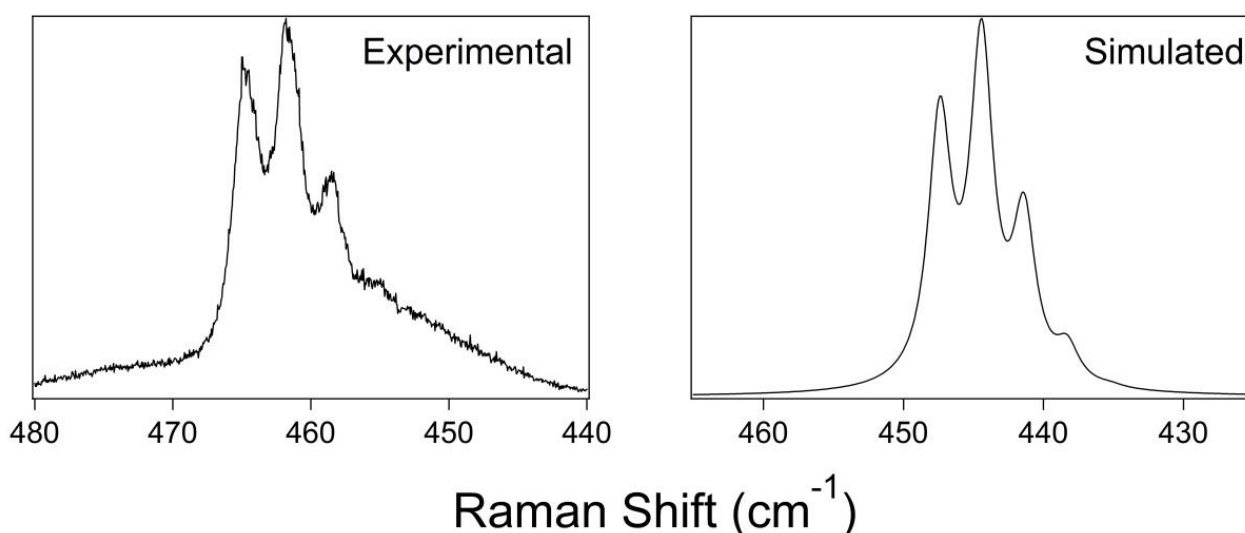


Figure 3. Room temperature Raman spectrum of carbon tetrachloride's symmetric stretch, ν_1 compared to an *ab initio* simulation.

This spectrum is clearly degraded by ro-vibrational contributions along with "hot bands". Figure 4 below shows the same vibrational frequency, ν_1 , under RUN conditions. In this example, ro-vibrational cooling allows for the individual isotopic contributions of the symmetric stretch, ν_1 , to be resolved. Comparison of the results from RUN and room temperature is dramatic. Other spectra of CCl_4 have been able to resolve the ^{13}C contributions to CCl_4 showing up between the Cl vibrations.

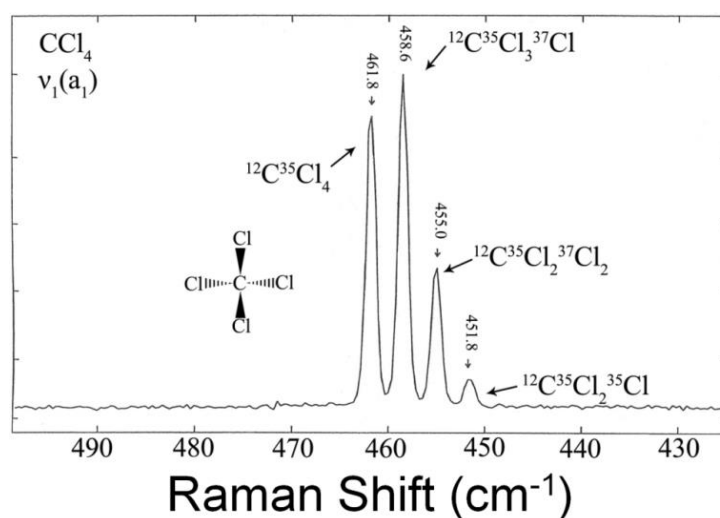


Figure 4. High resolution spectrum of carbon tetrachloride.

A full Raman spectrum of the C_{60} fullerene molecule is shown in Figure 5 below. In this study the C_{60} is dissolved in CS_2 . Figure 5 shows the ten first order Raman lines for C_{60} are seen to be in reasonable accord ($\pm 3 \text{ cm}^{-1}$) with the two A_g and eight H_g allowed Raman vibrational energies. A complete compilation of the vibrational frequencies for C_{60} has been tabulated by Dresselhaus et al. [12]. The spectra in Figure 6 agree with previous results however, the spectra seem to be more narrow than previous data. Run spectra for C_{70} and C_{84} show similar resolution and simplicity. Below we discuss RUN spectra for a fullerene derivative, $C_{60}Br_{24}$.

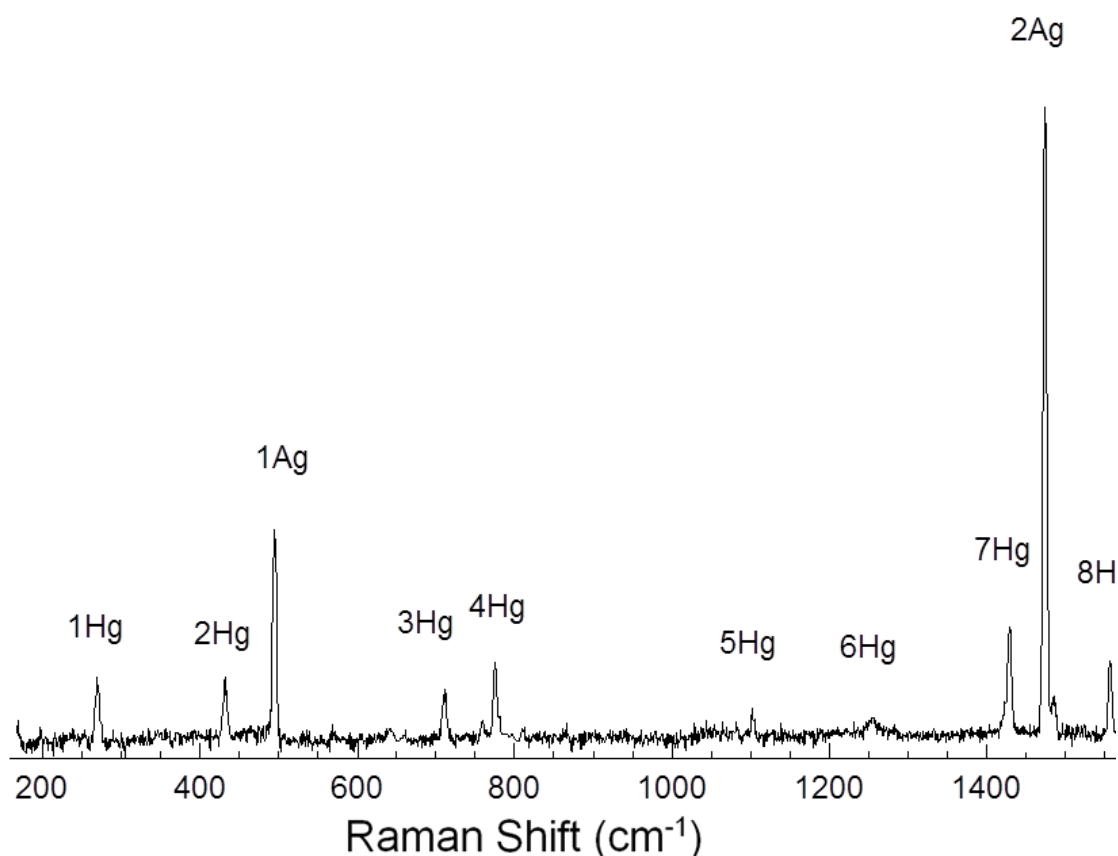


Figure 5. RUN spectrum of C_{60} dissolved in carbon disulfide.
The CS_2 Raman spectrum has been removed.

In 1992, Tebbe et al.[13] reported the synthesis and single-crystal X-ray structure of $C_{60}Br_{24}$ exhibiting T_h symmetry. Raman spectroscopy is also used to examine the structure of solid $C_{60}Br_{24}$ prepared by reactions between C_{60} and liquid bromine in the presence of an ion wire. Raman spectra recorded for $C_{60}Br_{24}$ under liquid nitrogen (RUN) reveals all of the allowed Raman active bands to be in good agreement with those calculated from density functional theory. An unexplained peak at 311 cm^{-1} is attributed to interstitial bromine molecules as previously suggested. The fundamental vibration for the bromine molecule is 323 cm^{-1} (see Reference [14]).

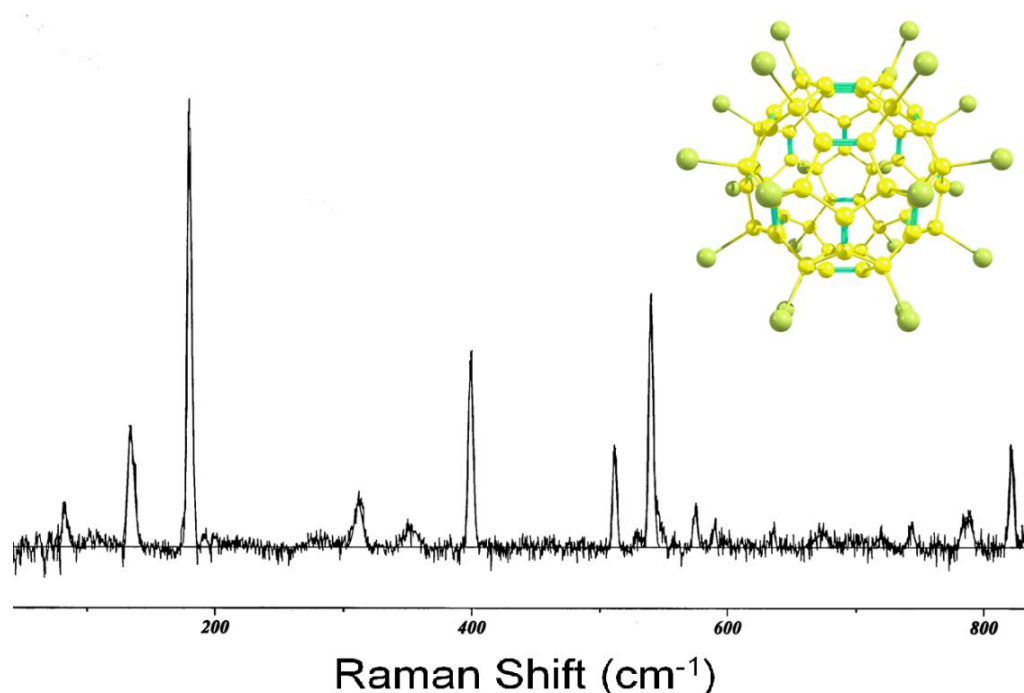


Figure 6. RUN spectrum of $C_{60}Br_{24}$.

Raman Under Nitrogen can also provide another method to examine the lattice modes of molecular crystals at liquid nitrogen temperature. We use RUN of benzene and naphthalene as examples of this application when Raman scattering near the Rayleigh line is possible. Figures 7 and 8 show RUN spectra of benzene and naphthalene, respectively. In both cases, low energy modes are sharpened by the reduction in temperature and collapse into the lowest rotational states. Fig. 9 shows a comparison of the low energy modes of naphthalene at room temperature and under liquid nitrogen.

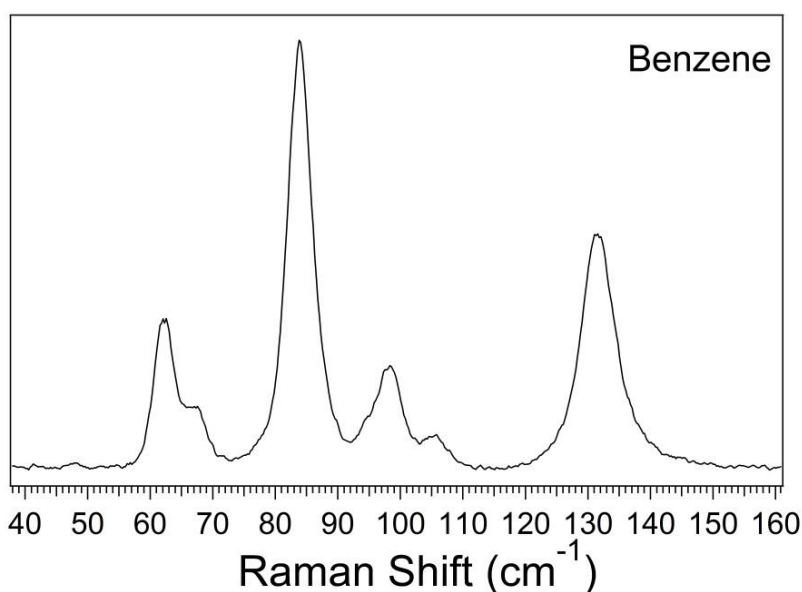


Figure 7. RUN spectrum of benzene in the low energy region of the spectrum recorded at UM. Lattice modes involving motions between benzene molecules are evident.

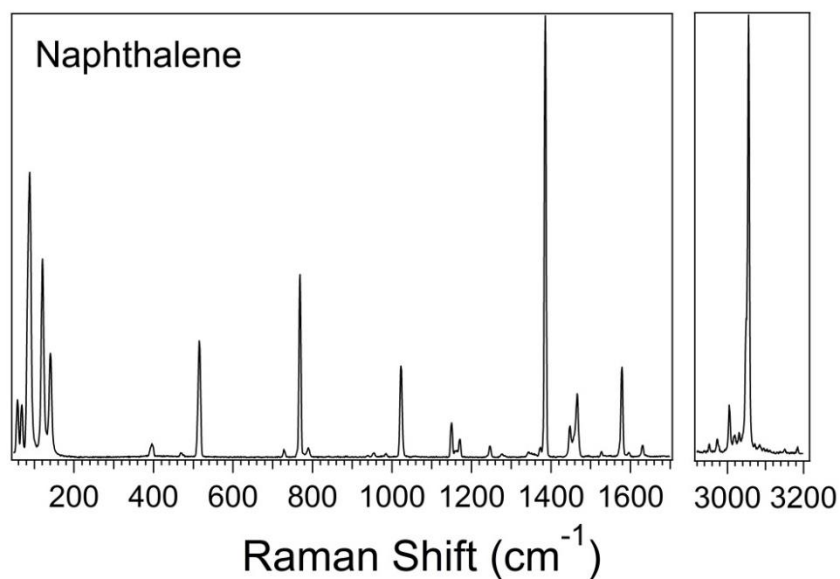


Figure 8. RUN spectrum of naphthalene recorded at UM.

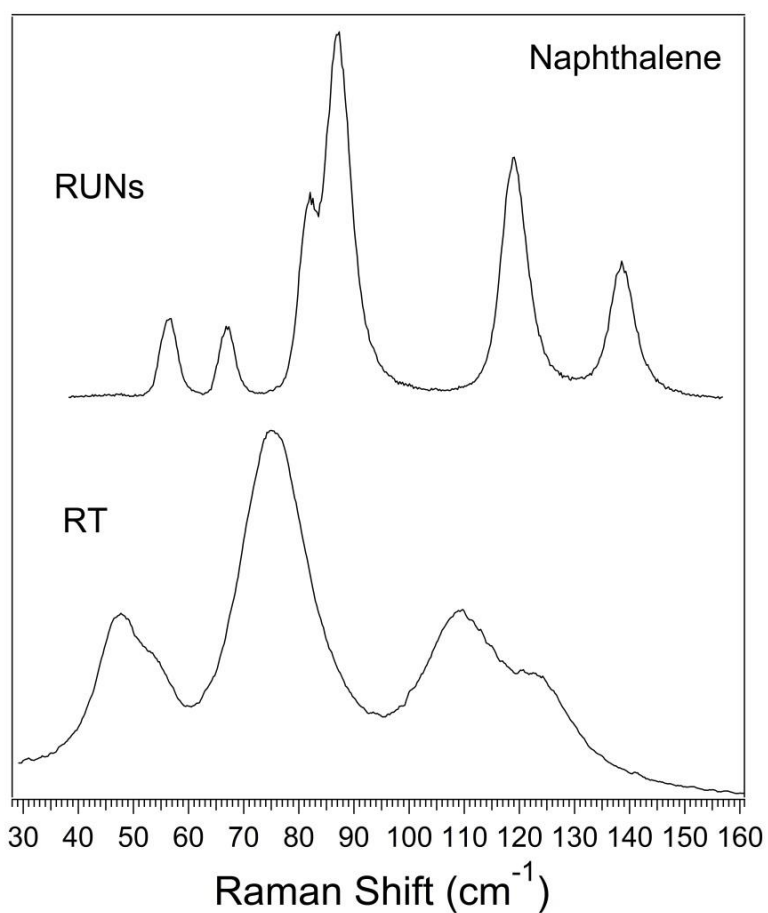


Figure 9. Room temperature Raman spectrum vs RUN spectrum of naphthalene in the low energy region. Normal modes are observed to blue shift and sharpen under liquid nitrogen.

The low energy modes of benzene [15] and naphthalene [16] have been studied in detail previously. Normal modes in this region are observed to blue shift and sharpen under liquid nitrogen. The use of RUN offers key advantages in systems such as these, including polycyclic aromatic hydrocarbons (PAHs). These include: (1) the ability to exclude atmospheric oxygen and water from the sample as the molecules start to interact in the crystalline phase and (2) the ability to study small shifts in vibrational frequencies due to the effects of noncovalent interactions. The latter feature is afforded by the sharper linewidth observed in RUN spectra.

Acknowledgements

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