REPORT DOCUMENTATION P

AD-A255 477

0188 (2)

1. AGENCY USE ONLY (Leave blank)

2. REPORT DATE 24 June 1992

Final Report, 19 Mar 90 - 18 Mar 92

4. TITLE AND SUBTITLE
Preliminary investigations of Metal liquid-like films
and coatings derived from them

5. FUNDING NUMBERS
DAAL03-90-G-0060

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8. PERFORMING ORGANIZATION REPORT NUMBER

9. SPONSORING/MONITORING AGENCY NAME(S) AND ADDRESS(ES)
U. S. Army Research Office
P. O. Box 12211
Research Triangle Park, NC 27709-2211

10. SPONSORING/MONITORING AGENCY REPORT NUMBER
ARO 27759.2-CH

11. SUPPLEMENTARY NOTES
The view, opinions and/or findings contained in this report are those of the author(s) and should not be construed as an official Department of the Army position, policy, or decision, unless so designated by other documentation.

12a. DISTRIBUTION/AVAILABILITY STATEMENT
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12b. DISTRIBUTION CODE

13. ABSTRACT *(Maximum 200 words)*

Metal liquid-like films consist of a layer of metal deposited between two immiscible liquids. The films are glossy, and have rheological properties similar to a liquid, but are not conductive. We have carried out studies on these films under high pressure, to alter their structure, and after the film has dried, to study their use as coatings. Pressure does not severely alter the form of the MELLF, though temperature and pressure may combine to affect their long term stability. Coatings on silica gels successfully maintain the properties of reflectivity and non-conductivity; spectra indicate no change in the chemical properties occurred. Further work will include long term stability measurements and more work on the coating procedures.

92

92-20802

14. SUBJECT TERMS

15. NUMBER OF PAGES
13 w/cover page

16. PRICE CODE

17. SECURITY CLASSIFICATION OF REPORT	18. SECURITY CLASSIFICATION OF THIS PAGE	19. SECURITY CLASSIFICATION OF ABSTRACT	20. LIMITATION OF ABSTRACT
UNCLASSIFIED	UNCLASSIFIED	UNCLASSIFIED	UL

Metal liquid-like films: Effect of pressure and drying

Final Report

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Proposal Number 27759-CH
Funding Number DAAL03-90-G-0060

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A. Statement of the problem studied

Metal liquid-like films (MELLFs) consist of a film of metal (i.e., silver) deposited between two immiscible liquids.[1] MELLFs have unique properties with intriguing possibilities for novel applications, most notably in catalysis and coatings technology. The liquid films are glossy, and have rheological properties similar to liquids, but do not conduct electricity. When dried, MELLFs produce glossy or matte films, neither of which conduct, depending upon the preparation.

MELLFs apparently consist of a dense, interfacial suspension of colloidal particles stabilized by surfactants or metal complexes.[1] One objective is to understand the chemistry and structure of MELLFs by observing their response to pressures up to 5 kbars, and from 5 to 75 °C. This perturbs the interface, especially the environment of adsorbed species, without altering the chemical composition. Surface enhanced Raman spectroscopy is used to observe changes in the adsorbed species. We recently began probing particle size variation via UV-visible spectroscopy, but this work is incomplete.

We are simultaneously using MELLFs to generate coatings on glass slides, silica gels and porous glass, with analysis by SEM and Raman spectroscopy.[2] Coatings on glass slides are neither conductive or glossy. The silica gel samples retain both the non-conductive and glossy nature of liquid phase MELLFs. Raman shows the nature of the film is not changed on the gel. SEM photos indicate the preparatory methods affect the micro-structure of the dried films. Finally, we expose silver island films[3] to the MELLF aqueous phase for comparison.

We prepare MELLFs using Efrima's methods.[1] Glass containers coated with a 4% dichlorodimethylsilane in chloroform solution were partially filled with dichloromethane. The aqueous phase, consisting of ammoniacal 0.05 M $AgNO_3$, 0.1% w/w anisic acid and 0.03% w/w FC-143 (an anionic perfluorocarbon surfactant produced by 3M), was then added. One drop of a 0.5% w/w hydrazine sulphate solution was added per ml of aqueous phase to initiate reduction.

B. Summary of Most Important Results

i. High pressure results

The MELLF aqueous phase contains ammonia at high pH. Basic ammonia corroded our copper and lead pressure sealing gaskets, especially under high pressure. After many attempts to overcome this problem, we isolated the MELLF from the pressure cell by placing saran wrap over the glass insert; the plastic stretched, allowing pressure transfer to the MELLF. This problem consumed many months; the high pressure results reported were acquired very recently as the system became reliable.[4]

There are three main Raman peaks reported by Efrima,[5] due to the carbonyl mode of the anisic acid (1600 cm^{-1}), the vibration of the aromatic ring (1150 cm^{-1}), and a vibration of the surfactant (1050 cm^{-1}). Additional modes due to the organic were also seen. Observation of signal at 1050 cm^{-1} in solutions with no surfactant led us believe the assignment of the mode at 1050 cm^{-1} should be to the vibration of nitrate ions. We replaced the aqueous phase with water, and recorded Raman spectra. The 1050 cm^{-1} signal lost intensity as the dilution proceeded, while the 1600 cm^{-1} mode did not. Unfortunately, this reassignment means less information can be obtained about MELLFs than hoped.[6]

Figures 1-4 show the effect of pressure on the frequency of each Raman vibration.[4] The subplots represent a constant temperature; no shift is seen as the temperature varies. In all cases, the modes shift to higher energies under pressure, indicating an increase in repulsive interactions. The shift in the anisic acid (AA) mode, which comes from the carbonyl adsorbed directly to the silver, implies that AA is pushed down onto the silver colloid, or solvent is forced into the space between adjacent AA molecules. The former is more likely, as the solvent would need to penetrate far to cause such a shift. We note preliminary results using $CHCl_3$ do not show this increase with pressure; we are presently checking this.

We conclude from the plots that neither pressure nor temperature over the ranges studied drastically alter the structure of the MELLF. No sudden frequency shifts, or sudden intensity changes, are observed.

ii. Dried MELLF films

Our goal was to dry MELLFs while retaining the defining properties, principally, high reflectivity and non-conductivity.[2] The top surface of a silver MELLF is 40-50% reflective while the underside is dark. The reflective top surface and non-conductivity of the MELLF should be retained if MELLFs can be lowered onto and accommodated by a rough or porous surface, resulting in films which match the natural state of the silver MELLF. Our initial attempts involving filtration or evaporation onto paper and sintered glass yielded dull, powdery coatings. Much greater success was achieved with silica gel substrates, prepared by the sol-gel process.[7] The gel, whose pores were filled with the organic solvent, acted as a stationary organic phase. The MELLF particles were trapped on the gels, after which the remaining organic drained away. This yielded dry gels with a shiny, non-conductive MELLF film on them.

When placed atop the organic phase, the gel disc remained whole, but floated. The disc cracked severely when the aqueous phase was added. Immediately after reduction, brown "fingers" formed inside the gel. We next weighed down the gel to prevent flotation. The gel did not crack as severely, but the precipitate formed during reduction dirtied the disc. We modified our procedure by inserting the gel only after reduction was complete. This greatly reduced the amount of debris on the gels, and the gels did not severely crack.

We now use a teflon block, with a sliding dam separating two compartments. MELLFs are prepared in one side, while a gel soaks in the organic in the other. The dam is raised and the weighted gel is slid under the MELLF. After the shiny interface contacts the gel, the aqueous phase is siphoned off. The gel has only minor cracks.

For comparison, silver island films were formed on frosted glass slides following the procedure of Cotton and Ni.[3] The coated slides were exposed to the aqueous phase, allowing material to adsorb under the same conditions as present in MELLFs.

As noted above, evaporation of a MELLF onto glass leaves a non-reflective, non-conductive, dull gray coating littered with crystalline residue. Washing of a coated slide with water reveals a dull gray (non-reflective), non-conductive coating. SEM photos of washed slides show the coating is inhomogeneous. On unwashed slides, large crystals appear, which overlap and curl upwards from the surface. EDAX spectra showed the crystals contain silver, probably from $AgNO_3$ precipitated as the aqueous phase becomes saturated during evaporation; their removal by washing supports this explanation.

MELLFs apparently consist of closely packed spheres; like an inverted pile of marbles, they are smooth at the interface, but rough on the bottom.[1,8] The inhomogeneous, non-reflective coating results from discontinuous drying. In the last stages of drying, small bubbles of the organic are present. The MELLF is stable only over the organic, so the MELLF congregates around the organic droplets. This leaves silver aggregates piled randomly on one another, and uncoated regions where the organic dries away first. The resulting film is visibly inhomogeneous.

Raman spectra of dried MELLFs contain peaks similar to those reported by Efrima for the native silver MELLF.[5] Peaks assigned to anisic acid adsorbed to the silver cores, at 1608 cm^{-1} and 1143 cm^{-1}, are visible in both the washed and unwashed samples. The washed coating also exhibits small peaks at 1259 cm^{-1} and 1387 cm^{-1}, assigned to the silver salt of anisic acid, and a very weak signal at 1042 cm^{-1}, due to the nitrate. The crystalline debris on the unwashed slide apparently interferes with the Raman spectra. Apparently, evaporation does not chemically alter the MELLF.

We are able to produce highly reflective, non-conductive MELLF coatings on silica gel discs. Before coating, the silica gel is rough, full of ridges and craters. The coated gel is covered with a granular MELLF made up of spherical particles approximately 150-300 nm in diameter. The particles resemble a pile of marbles, closely packed and fairly level at the top layer, resulting in the high reflectivity. As noted by Efrima,[1] as evaporation proceeds over glass, the silver cores aggregate to form larger particles. The organic in the pores of the gel mimics the bulk organic until the MELLF is immobilized on the gel surface, which prevents agglomeration. The particles on the surface thus closely resemble the native colloid. They are closely packed, resulting in high reflectivity; however, the silver cores are not in contact, as indicated by the non-conductivity of the coating. Raman spectra of these gels confirm the presence of anisic acid adsorbed to the silver. Peaks were noted at 1607 cm^{-1} and 1143 cm^{-1} corresponding to those reported by Efrima.[5]

A shiny coating results when the MELLF solution evaporates slowly, over several days. Rapid evaporation typically produces a non-reflective coating. The exact relationship between evaporation time and surface structure of the coating is not clear, but speed of evaporation does play a role in determining the reflectivity. The coated gel samples are originally non-conductive. Some samples became conductive after long ageing periods (several weeks). Whether this is due to contraction of the gel network forcing the silver cores together, or a change in the coating itself, is under investigation.

A highly reflective coating results when the teflon block described above is used. SEM on these gels reveals an unusual pattern repeating over the surface. The pattern, shown in Figure 5a of reference 2, consists of a group of circles connected by spindly filaments radiating out from a central hub. Each circle has a dendritic structure, with the filaments being most prominent near the hub. The hubs have holes near their center, and have a different surface morphology than the surrounding circles. The hubs appear to be over dark areas of the gel, which resemble large pores. The surface of the circles (but not the hubs) has a granular appearance. These patterns probably result from the drainage of the organic during the drying process. Over most of the surface, the drying proceeds evenly; however, near these large pores, the drying is enhanced as the organic flows down the pore. The MELLF material is stretched by the relatively rapid outflow of the organic, leaving material behind, like soapy water flowing down a drain. The filaments result from material (MELLF particles) deposited during the latter stages of this flow. The hub becomes congested with sediment, giving it a different appearance.

A small amount of material floating atop the aqueous phase, may be generated by inserting and then quickly withdrawing a glass rod into a MELLF. We captured this floating material on glass at the top surface after a thin layer of material had been produced. The resulting pile of overlaying crystals were not as substantial as on the evaporated glass, but were similar in shape. They were non-reflective and non-conductive. The Raman spectra showed the characteristic peaks for anisic acid.

MELLF coatings result from the adhesion of MELLF particles, with the anisic acid and surfactant present, to the surface. Silver can also be coated onto glass slides using the silver island film (SIFs) procedure.[5] Pyridine and other substrates have been adsorbed onto these for use in SERS experiments. We exposed SIFs to the unreacted aqueous phase of a MELLF, expecting the molecules which adsorb to silver colloids in MELLFs to adsorb onto the silver island film. SIFs are non-conductive, before and after soaking in the MELLF aqueous phase. Raman spectra of the soaked samples contain signals indicative of adsorbed anisic acid and strong signals due to the adsorbed FC-143, the surfactant used in the MELLFs. This combination of observations confirms the peak assignments of Efrima,[5] who reported silver - anisic acid salts having Raman signals at

862, 1149, 1267, 1390 and 1604 cm^{-1}. Soaked SIF samples exhibit Raman signals at 848, 1145, 1178, 1260, 1390, 1514, 1574, 1603 and 1652 cm^{-1}. The Raman peak at 1044 cm^{-1}, due to the adsorbed surfactant FC-143, is much stronger than observed for any of the MELLF samples. This may be due to preferential adsorption of the surfactant (relative to anisic acid) by the SIFs.

C. List of all publications and technical reports

Bradley, M., Krech, J. H., Lorenc, C. Coatings of Metal Liquid-like films on porous silica gel substrates. *Journal of Colloid and Interface Science*, in press.
Bradley, M., Krech, J. H., Efrima, S. Effect of high pressure on Metal Liquid-like films. In preparation.

D. List of all participating scientific personnel

Bradley, Michael S.	Primary investigator, Assistant Professor of Chemistry.
Krech, John H.	Graduate student (Ph.D. anticipated Fall 1993, with this work representing the main focus of his project).
Lorenc, Carol	Undergraduate student (B.S. anticipated Spring 1993, with a senior thesis presented on her work on this project).

Figure Captions

1. Plots of the effect of high pressure on the 1600 cm^{-1} Raman mode (carbonyl mode of adsorbed anisic acid) of a MELLF. Each subplot represents a constant temperature, as listed.

2. Same as Figure 1, for the 1150 cm^{-1} Raman mode (aromatic ring vibration of the adsorbed anisic acid) of a MELLF.

3. Same as Figure 1, for the 1050 cm^{-1} Raman mode (dissolved nitrate, according to our assignment) of a MELLF.

4. Same as Figure 1, for the 700 cm^{-1} Raman mode (vibration of the organic solvent, $CHCl_2$) of a MELLF.

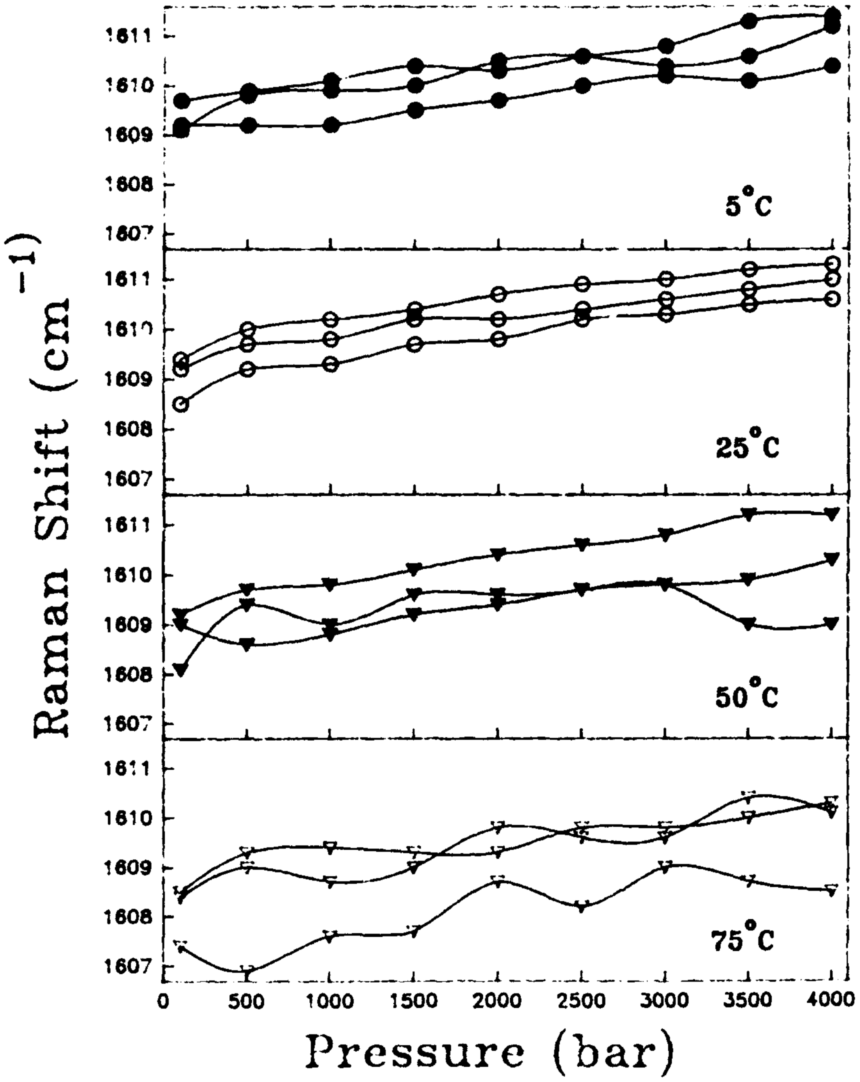

Figure 1.

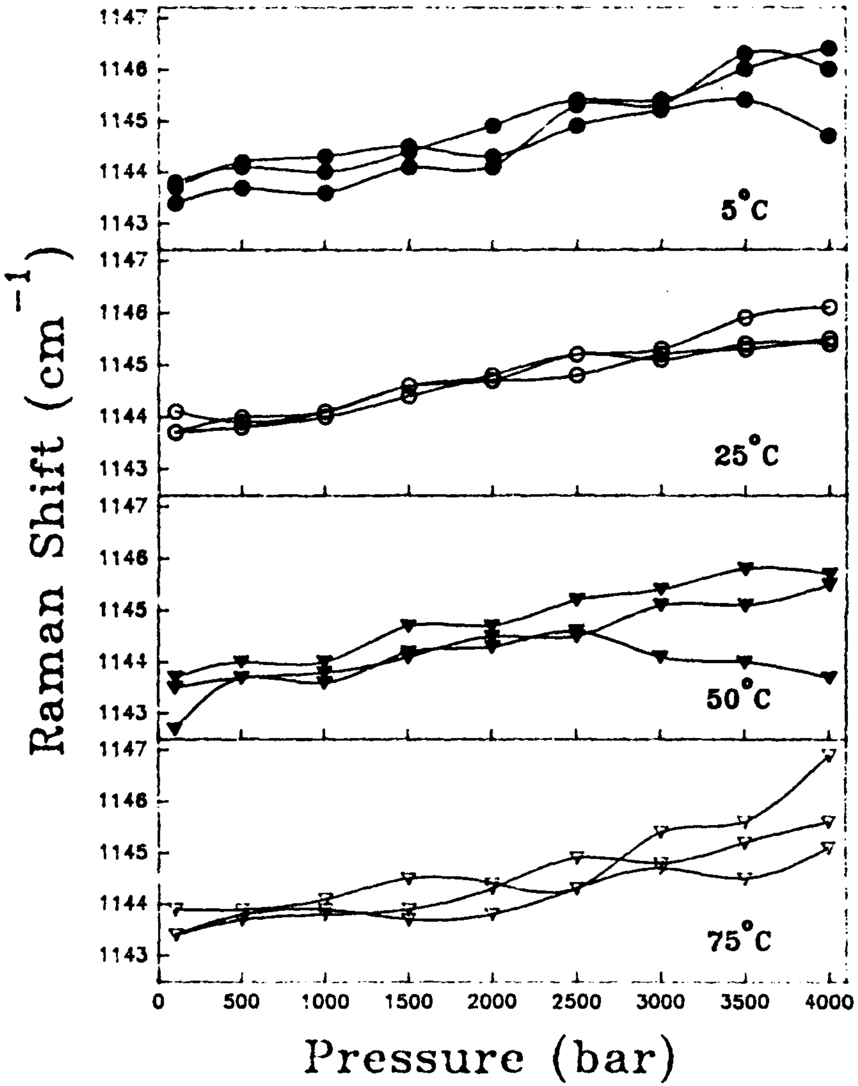

Figure 2.

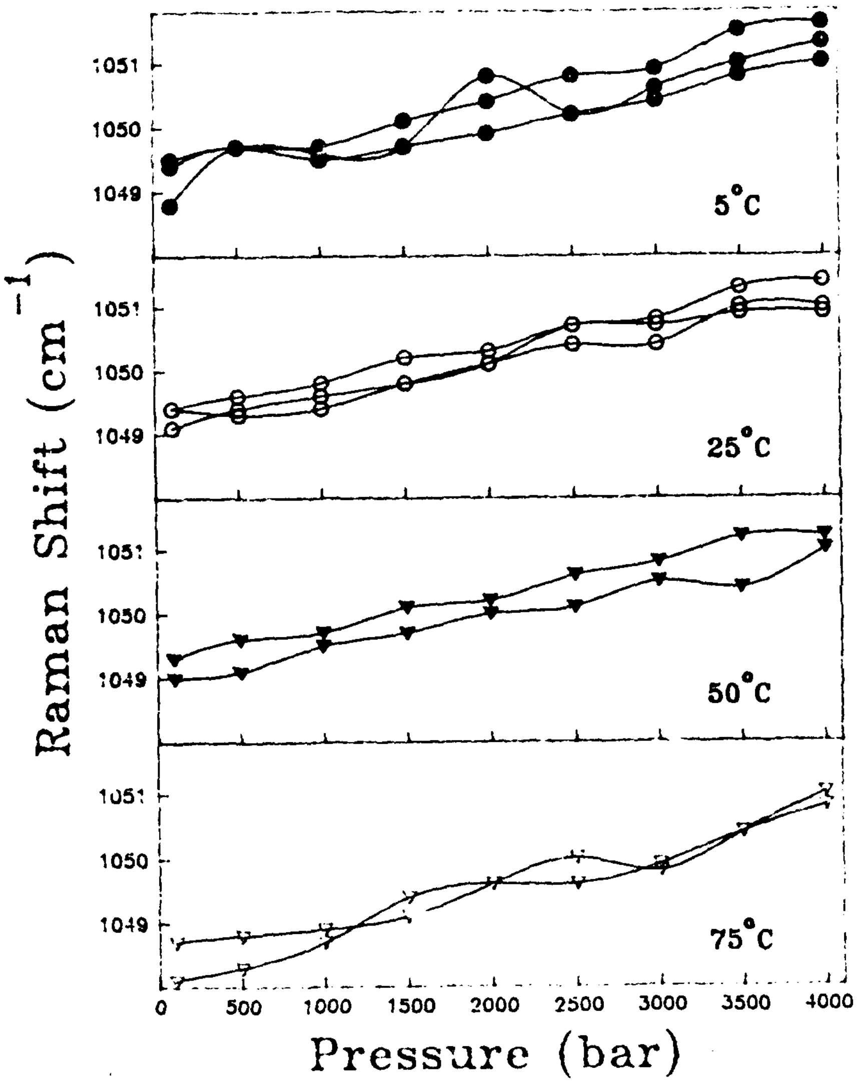

Figure 3.

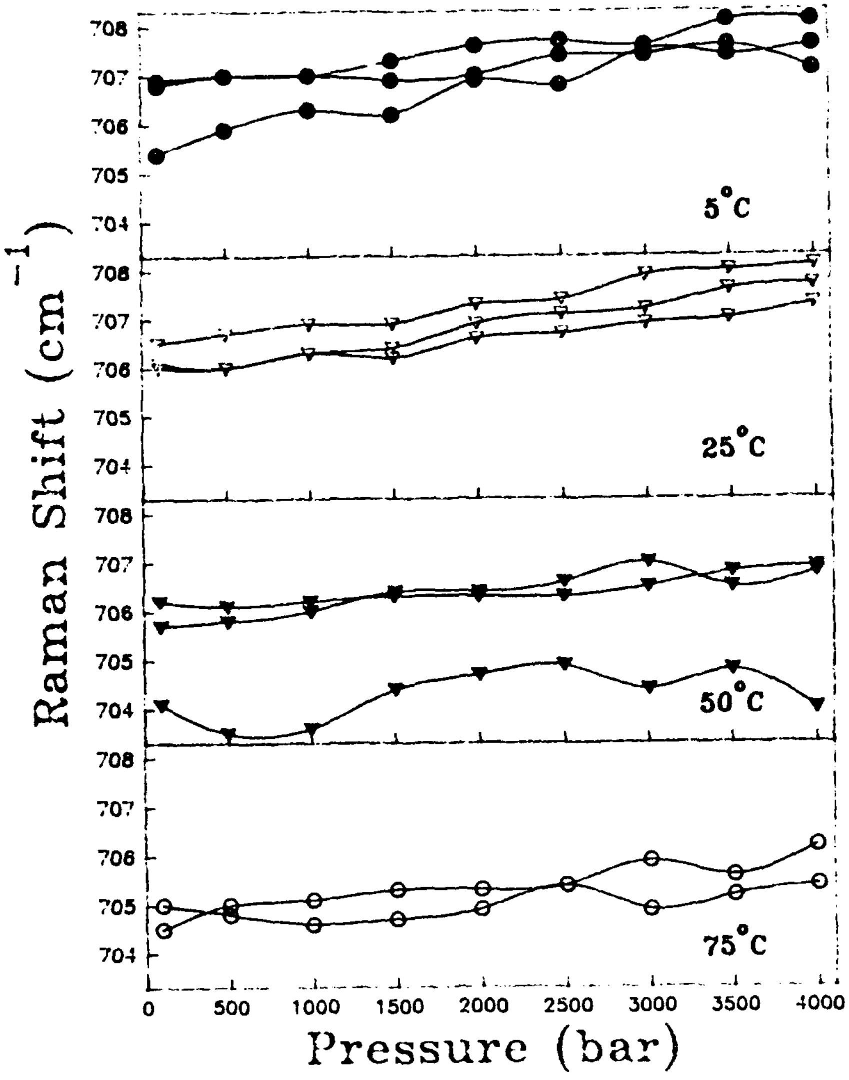

Figure 4.

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