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# The hydrogen bonding in the Raman O-H stretching band of propylene glycol in nanometre confined space. Surface interactions and finite-size effects

V. CRUPI[1], F. LONGO[1], D. MAJOLINO[1], P. MIGLIARDO[1] and V. VENUTI[*1]

[1]Physics Department, University of Messina, S.ta Sperone 31, 98166 S. Agata, Messina, ITALY.

*Corresponding author: vvenuti@unime.it

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**Abstract**

The O-H stretching vibration of Propylene Glycol (PG) has been investigated by Raman spectroscopy in the -15°C ÷ +60°C temperature range, in the bulk state and confined to the ~ 26 Å pores of a controlled porous glass. By modifying (from hydrophilic to hydrophobic) the nature of the substrate we separated the surface-like and the finite-size contributions to the high-frequency vibrational dynamics of this glass-forming system. The spectra have been fitted by four Gaussian peaks associated with PG molecules exhibiting different H-binding states (i.e. non H-bonded, chain-end, and doubly bonded). The T-dependencies of the peak wavenumbers and relative areas of the resolved components furnished a quantitative description of the role played by polymer-surface interactions and topological effects on the connectivity distribution of confined PG molecules.

*Keywords:* Confined Propylene Glycol; Raman scattering, O-H stretching vibration

## 1. Introduction

The influence of spatial confinement on the behaviour of condensed matter has been a topic of current interest in the last decade [1], especially when addressed to explain the mechanism of glassy dynamics. The performed experiments [2-3], however, have often lead to contradictory results, explained in terms of a competitive balance between the architecture of the confining host and the interaction of the confined molecules with the internal surface [4]. It is commonly believed [1] that only surface interactions, that highly affect the interfacial layer causing the formation of H-bonds and physisorption, contribute to slow-down the relaxational motions with respect to the corresponding bulk systems, giving rise to a dramatic increase of the glass transition temperature $T_g$. On the contrary, geometrical restrictions, causing an increase in the "free volume" available for the molecules, are retained the only responsible of the revealed enhanced mobility of the inner part

of the liquid with respect to the bulk [5]. This last hypothesis can justify the decrease of the $T_g$ observed by several authors. It is then reasonable to hypothesize that the study of the physical properties of chemically different liquids in reliable model confining systems exhibiting hydrophilic or/and hydorphobic interactions can be a good way to discriminate between the reduced dimensionality and large interface effects.

Nanoporous sol-gel glasses have proven to be excellent media to obtain geometrically controlled confinements, thanks, in particular, to their narrow distribution of pore sizes and the highly interconnected network of the pores and the possibility to tune the interactions between the pore surfaces and the liquid confined within them.

Propylene Glycol (PG, $H[OCH(CH_3)CH_2]OH$) is a prototype molecular glassformer system widely used [6] in the description of the slowing-down of the molecular motions approaching the $T_g$.

Very recently we studied [7], by inelastic neutron scattering, the effects induced by surface interactions and geometrical restrictions on the density of vibrational states (VDOS) of PG in the bulk state and in the aforementioned GelSil glass with unmodified and modified inner surface. Low frequency collective *intermolecular* vibrational modes were revealed. The observation of the boson peak at ~ 64 $cm^{-1}$ allowed us to hypothesize a transition, induced by confinement, from *propagating* vibrations typical of a continuous medium to *quasilocalized* ones. In this respect, surface interactions are shown to play the main role. Bulk PG spectra evidenced non resolved vibrational peaks that support the existence of a complex network for liquid PG due to intra- and intermolecular H-bond. The evolution of the VDOS passing from the bulk to the confined state showed evident changes in the H-bonded PG scheme, assinged to interfacial and/or topological effects.

The work therein was undertaken to investigate the bonding properties of PG in the aforementioned nanoporous silica glass, by means of the analysis of the *intramolecular* vibrational dynamics. In this sense, a preliminary polarized Raman study of the complex O-H stretching vibrational band (3100 ÷ 3800 $cm^{-1}$) was already performed, versus temperature, on PG in the bulk phase and confined in GelSil with unmodified inner surface [8]. We found, as main result, that confinement tends to hinder the formation of more extended arrangements that are present in the bulk. Here, we went deep into this study, by measuring polarized Raman spectra in the 2700 ÷ 3800 $cm^{-1}$ region, in a wider temperature range (-15°C ÷ +60°C) and by varying the nature (hydrophilic or hydrophobic) of the inner surface of the glass. A model of decomposition of the O-H stretching band into the minimum number of components, corresponding to PG molecules with different types of H-bonding, has been employed in the analysis of the spectra. The data treatment and the analytical procedure used here have been refined with respect to the one used in Ref. [8]. In addition, the data collected for bulk PG and PG in unmodified GelSil, as far as the common temperatures are

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concerned, have been refitted at the light of the wider investigated T-range and, especially, taking into account the new information given by the spectra of PG in unmodified GelSil. These last are expected, and turned out, to be closer to the ones of bulk PG, since the modifications due to surface interactions are, in this case, removed. All these reasons can explain some discrepancies revealed with our previous data. The evolution of the main fitting parameters will furnish a quantitative picture of the differences in the connectivity pattern of bulk and confined PG, according to the hydrophilic/hydrophobic properties of the confining matrix.

## 2. Experimental set-up

PG, from Aldrich Chemical Company, has been the model system for this study. As confining host materials, controlled porous glasses GelSil with specific pore sizes of 26Å were used, purchased from GelTech Inc., USA. The glasses have narrow pore size distribution (5% standard deviation), pore volume fraction of 0.39, bulk density of 1.2 g/cm$^3$, and huge inner surface (609 m$^2$/g of the glass). The pores are higly-branched and connected in a fractal-like geometry. The internal glass surface contains a large concentration of silanol SiOH groups which can form H-bonds to the confined molecules. To modify the interaction of the PG molecules with the internal surface we used the same kind of GelSil glasses, still purchased from GelTech Inc., but with the internal surface of the pores modified by converting the hydrophilic SiOH groups to the hydrophobic trimethylsilyl $SiOCH_3$ groups. For the cleaning and filling procedure of the glasses the reader can refer to Ref. [4]. The Raman spectra were collected, in the -10°C÷+60°C range, by a high-resolution triple monochromator SPEX RAMALOG 5. The spectra were recorded in the 2700÷3800 cm$^{-1}$ range, so covering C-H (from ~ 2700 to ~ 3100 cm$^{-1}$) and O-H stretching (from ~3100 to ~3800 cm$^{-1}$) vibrations. We focused on the band-shape analysis of the highly polarized O-H Raman bands which were decomposed in Gaussian bands by a standard curve fitting procedure.

## 3. Results and discussion

As well known, Raman spectroscopy of the O-H stretching intramolecular band is a powerful tool to observe and study the H-bond [9]. In a general way, the revealed changes in its shape and position are indicative of variations in the relative populations of molecules having different H-bond mean coordination numbers. The evolving balance between these populations, that furnishes a quantitative description of the connective tissue of the investigated system, is here discussed in the case of PG, as a function of T. In particular, the study is addressed to clarify how the hydration of

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the active SiOH groups and confinement in nanosized domains influence the observed changes in the structure of confined PG with respect to the bulk phase. Figure 1(a-c) shows the experimental polarized O-H Raman spectra for bulk and confined PG at T = -10°C, +30°C, +60°C, as examples. For both bulk and confined PG, a low-frequency shift of the O-H stretching band maximum is observed when T is decreased, as expected. Again, we can state that confining PG in nanopores results in a band shift, compared to the bulk state, that is within the experimental error. Then, the same analysis can be applied for both bulk and confined system.

[Insert figure 1 about here]

A large number of vibrational spectroscopic studies of H-bonding in different substances have been published [10]. In all these studies, the interpretation is supported by the decomposition of the O-H stretching vibration into component sub-bands, ascribed to different types of H-bonded molecules, i.e., nonbonded, H-bonded nondonating or nonaccepting, and doubly bonded (molecules accepting two H-bonds at the same time). This approach has been followed also here. A problem which arises in the analysis of our spectra is the partial overlapping of the C-H and O-H stretching bands. The best way to overcome this difficulty, so separating the two bands and resolving the O-H stretching band into components, is to fit simultaneously the C-H and O-H stretching bands into four Gaussian components (eight components in total), with all the fitting parameters left free to vary upon iteration. Then, the contributions coming from the symmetric and antisymmetric methyl stretches have been subtracted from the total fits and more detailed fits have been performed just in the O-H stretching region. Figures 2-3 show the curve fitting results in the case of bulk PG, and PG confined in unmodified and modified GelSil, at T = -15°C and +40°C, as examples.

[Insert figure 2 about here]

[Insert figure 3 about here]

Even if the spectral decompostion procedures have no unique solution, we remark that the one we adopted uses the minimum number of parameters and, at the same time, it furnishes extremely good fits to the data. The best-fit is, in fact, characterized by $r^2 \sim 0.9999$ for all the investigated systems. On the other side, it is supported by the calculation of the second derivative profiles of the Raman spectra, reported in figure 4 for bulk PG at T = +50°C, as an example. As can be seen, four sub-minima are observed in the second derivative diagram indicating the presence of four sub-bands centred at $\omega_1 \sim 3240$ cm$^{-1}$, $\omega_2 \sim 3340$ cm$^{-1}$, $\omega_3 \sim 3450$ cm$^{-1}$, and $\omega_4 \sim 3600$ cm$^{-1}$.

[Insert figure 4 about here]

According to the literature, the sub-band $\omega_1$ is connected to OH oscillators involved in intramolecular H-bonds of closed monomeric structures. Going to higher frequencies, the sub-band $\omega_2$ is ascribed to molecules that donate and accept H-bonds, so giving rise to trimers and more

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extended structures. The component $\omega_3$ reflects the stretching mode of O-H oscillators of terminal PG molecules that donate, but do not accept, H-bonds. Finally, the highest energy sub-band, $\omega_4$, originates from the fundamental O-H stretching mode of isolated monomeric molecules and/or terminal groups that accept, but do not donate, H-bonds. We remark that the situation described by this picture is averaged over time and each molecule is expected to belong to the four different classes over several picoseconds. The main O-H stretching band fitting parameters, i.e. centre-frequencies and percentage intensities, for all the investigated samples are reported in table 1.

[Insert table 1 about here]

The peak wavenumbers express the strengths of the respective H-bonds and the variations in the average O···O distances in the corresponding H-bond scheme. The O-H stretching modes are, in fact, linked to the variety of O···O distances by [11]: $\omega(cm^{-1})=3592-304\cdot10^9[\exp(-R_{O\cdots O}/0.1321)]$, where $R_{O\cdots O}$ are the O···O distances in Angstrom units. By using the above relation, we evaluated the mean $\overline{R}_{O\cdots O_i}$ (i = 1, 2, 3, 4) distances corresponding to the mean peak wavenumber $\overline{\omega}_i$ (i = 1, 2, 3, 4) of each observed sub-band. They are reported in table 2.

[Insert table 2 about here]

The slight diminishing of the observed values passing from bulk to confined samples could indicate that, as a consequence of geometrical restrictions and surface interactions, a little bit more stable H-bonded structures are formed. The relative areas of the components are representative of the fractional population of H-bonded PG molecules assigned to each class. The dependencies of the percentage intensities of the resolved components $\omega_i$ (i = 1, 2, 3, 4) on T for PG in the bulk state and confined in unmodified and modified GelSil are reported in figure 5(a-d).

[Insert figure 5 about here]

First of all, for both bulk and confined PG, an increasing temperature causes the diminishing of the relative areas $I_1$ and $I_2$ favouring the increasing of $I_3$ and $I_4$. In terms of number of PG molecules belonging to the appropriate association state this means that the thermal motion is high enough to break the intramolecular H-bond of closed monomeric structures allowing them to open, and, on the other side, it contributes to destroy high-connectivity arrangements, favouring less coordinated structures, as expected. Let's compare now the behaviour of the relative areas passing from the bulk to the confined state in unmodified and modified GelSil. $I_1$ dramaticly reduces, with respect to the bulk, when PG is confined in GelSil with active inner surface. On the other side, its contribution strongly increases and becomes once again similar to the bulk state for PG entrapped in GelSil having inert inner surface. In terms of the population factor of the corresponding H-bonded structure, this means that, at a given T, surface interactions are almost the only responsible for the breaking of intramolecular H-bond of PG molecules arranged in closed monomeric bulk-like

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structures. Going on, $I_2$ strongly diminishes passing from bulk PG to PG confined in both unmodified and modified GelSil, and its values remain slightly higher in this last case with respect to the former. We want to underline that, in this case, this component can reflect bulk-like trimeric aggregates where PG molecules donate and accept H-bonds with other PG molecules, as well as, upon confinement, interfacial molecules, directly attached to the surface and connected to another (or more) PG molecule. These changes, then, indicate that the reduced dimensionality, together with the interconnected geometry of the pores, are the main effects that tend to destroy, when PG is confined, this long-distance aggregates. The further diminishing of $I_2$ in the case of PG confined in unmodified GelSil can be explained by saying that surface interactions will also contribute to hinder the formation of extended arrangements. On the contrary, the percentage areas $I_3$ and $I_4$ are observed to increase passing from the bulk to the confined state, and in a relevant way for PG in unmodified GelSil. We remark that, as far as the species associated to $I_3$ are concerned, they can be dimeric intermolecular structures involving two PG molecules and/or PG molecules H-bonded to the surface but no connected to any other molecule. $I_4$ is finally representative of "free" O-H oscillators belonging to both bulk and interfacial PG molecules. So, this trend gives clear evidence of how confinement contributes in favouring low-connectivity, open arrangements, with the main role played by the H-bond of the silanol surface groups with the liquid PG.

## 4. Conclusions

Raman scattering investigations have been carried out to explore, as a function of temperature, the conformations of propylene glycol (PG) molecules, in the bulk state and in 26 Å diameter pores of a sol-gel silica glass, GelSil. PG in GelSil exhibits different spectral characteristics than bulk PG, due to confinement in nanosized domains and H-bond surface interactions. Their interplay has been accounted by a comparison of the vibrational dynamics of the system in contact with an active (for H-bond interaction) or non-active interface of the glass. The analysis of the O-H stretching band by decomposition into components turned out to be a very sensitive method for the study of structural changes in the H-bonded aggregates, because of the strong influence of the sub-band parameters by the temperature and the hydrophilic/hydrophobic character of the inner surface of the glass. Hence, we can conclude: 1) Surface interactions turned out to be the only responsible for the breaking, upon confinement, of closed-ring H-bonded intramolecular PG species. 2) The spatial limitations imposed by the pores, together with their higly-branched interconnection, seemed to have the most prominent role in the observed reduction, upon confinement, of the doubly bonded supramolecular PG structures. 3) The diminishing of the population factors of the aforementioned closed and long-

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distance arrangements is compensated by the revealed enhancement, mainly connected to interfacial phenomena, of PG molecules with low-connectivity states, i.e. H-bonded non accepting and nonbonded. Finally, the evaluation of the O···O distances associated to the multiplicity of H-bonded schemes allowed us to hypothesize an increased stability of the corresponding structures, because of both the interaction between surface and PG molecules as well as the limiting pores size.

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| T (°C) | $\omega_1$ ($cm^{-1}$) | $I_1$ (%) | $\omega_2$ ($cm^{-1}$) | $I_2$ (%) | $\omega_3$ ($cm^{-1}$) | $I_3$ (%) | $\omega_4$ ($cm^{-1}$) | $I_4$ (%) |
|---|---|---|---|---|---|---|---|---|
| ***Bulk PG*** | | | | | | | | |
| -15 | 3260.8 | 40.8 | 3355.4 | 29.6 | 3466.8 | 28.6 | 3640.6 | 1.0 |
| -10 | 3247.6 | 40.4 | 3384.7 | 29.4 | 3462.3 | 29.1 | 3641.0 | 1.1 |
| 0 | 3251.1 | 40.0 | 3350.8 | 27.1 | 3457.9 | 29.4 | 3559.6 | 3.5 |
| +10 | 3249.8 | 34.9 | 3362.3 | 26.8 | 3448.9 | 33.9 | 3549.8 | 4.3 |
| +20 | 3224.7 | 27.1 | 3318.2 | 20.6 | 3430.6 | 48.8 | 3585.9 | 3.5 |
| +30 | 3228.4 | 24.7 | 3324.5 | 19.1 | 3441.8 | 54.1 | 3604.8 | 2.1 |
| +40 | 3241.4 | 25.9 | 3342.0 | 22.4 | 3444.0 | 43.1 | 3571.6 | 8.6 |
| +50 | 3246.3 | 24.0 | 3341.3 | 22.6 | 3447.3 | 46.0 | 3566.5 | 7.4 |
| +60 | 3223.0 | 11.5 | 3310.4 | 23.8 | 3431.1 | 52.8 | 3557.1 | 11.9 |
| ***PG in unmodified GelSil*** | | | | | | | | |
| -15 | 3217.4 | 30.5 | 3309.4 | 15.3 | 3430.9 | 38.7 | 3520.0 | 15.5 |
| -10 | 3189.3 | 18.7 | 3280.7 | 15.8 | 3420.3 | 45.3 | 3514.9 | 20.2 |
| 0 | 3183.8 | 9.6 | 3278.5 | 16.4 | 3397.3 | 52.8 | 3481.9 | 21.2 |
| +10 | 3218.5 | 9.6 | 3279.0 | 14.2 | 3395.7 | 53.0 | 3516.4 | 23.2 |
| +20 | 3180.3 | 9.7 | 3275.3 | 16.4 | 3393.6 | 53.2 | 3497.3 | 20.7 |
| +30 | 3199.1 | 8.6 | 3268.3 | 12.1 | 3403.8 | 60.1 | 3513.7 | 19.2 |
| +40 | 3213.6 | 8.9 | 3288.2 | 13.0 | 3403.9 | 59.2 | 3517.5 | 18.9 |
| +50 | 3209.5 | 7.7 | 3284.5 | 9.2 | 3422.8 | 60.9 | 3516.8 | 22.2 |
| +60 | 3182.4 | 6.9 | 3255.0 | 7.4 | 3405.4 | 60.7 | 3521.6 | 25.0 |
| ***PG in modified GelSil*** | | | | | | | | |
| -15 | 3277.8 | 49.4 | 3346.2 | 19.6 | 3452.5 | 26.5 | 3533.6 | 4.5 |
| -10 | 3245.3 | 39.9 | 3340.2 | 22.8 | 3429.6 | 34.3 | 3520.8 | 3.0 |
| 0 | 3268.7 | 41.1 | 3342.9 | 18.7 | 3411.6 | 33.4 | 3483.8 | 6.8 |
| +10 | 3237.5 | 32.8 | 3345.7 | 20.0 | 3379.6 | 40.1 | 3488.2 | 7.1 |
| +20 | 3220.5 | 29.7 | 3281.0 | 16.0 | 3372.4 | 48.1 | 3504.6 | 6.2 |
| +30 | 3231.7 | 22.8 | 3303.8 | 15.4 | 3405.5 | 55.8 | 3494.1 | 6.0 |
| +40 | 3198.6 | 26.4 | 3285.3 | 17.0 | 3411.9 | 45.5 | 3498.7 | 11.1 |
| +50 | 3241.1 | 23.7 | 3302.7 | 15.2 | 3406.4 | 51.4 | 3493.4 | 9.7 |
| +60 | 3214.9 | 17.8 | 3276.4 | 11.1 | 3416.9 | 58.3 | 3484.8 | 12.8 |

**Table 1** – O-H band best-fit results for bulk and confined PG.

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| $\bar{\omega}_1$ (cm$^{-1}$) | $\bar{R}_{O\cdots O_1}$ (Å) | $\bar{\omega}_2$ (cm$^{-1}$) | $\bar{R}_{O\cdots O_2}$ (Å) | $\bar{\omega}_3$ (cm$^{-1}$) | $\bar{R}_{O\cdots O_3}$ (Å) | $\bar{\omega}_4$ (cm$^{-1}$) | $\bar{R}_{O\cdots O_4}$ (Å) |
|---|---|---|---|---|---|---|---|
| ***Bulk PG*** | | | | | | | |
| 3241.4 | 2.719 | 3343.3 | 2.764 | 3447.8 | 2.836 | 3586.3 | 3.263 |
| ***PG in unmodified GelSil*** | | | | | | | |
| 3199.2 | 2.704 | 3279.9 | 2.734 | 3408.2 | 2.804 | 3511.1 | 2.912 |
| ***PG in modified GelSil*** | | | | | | | |
| 3241.4 | 2.719 | 3313.8 | 2.749 | 3409.6 | 2.805 | 3500.2 | 2.896 |

**Table 2** – Mean centre-frequencies of the observed sub-bands for bulk and confined PG, and corresponding O···O distances. See text for details.

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**Figure captions**

**Figure 1** – Experimental Raman spectra in the C-H and O-H stretching region for bulk PG (a) and PG confined in unmodified (b) and modified (c) GelSil at T = -10°C, +30°C, +60°C.

**Figure 2** – Decomposition of the O-H stretching band into four Gaussian functions for bulk PG (a) and PG confined in unmodified (b) and modified (c) GelSil at T = -15°C.

**Figure 3** – Decomposition of the O-H stretching band into four Gaussian functions for bulk PG (a) and PG confined in unmodified (b) and modified (c) GelSil at T = +40°C.

**Figure 4** – Second derivative profile of the Raman spectra in the O-H stretching region for bulk PG at T = +50°C.

**Figure 5** – Evolution, as a function of T, of the relative intensities $I_i$ (i = 1, 2, 3, 4) passing from bulk PG to PG confined in unmodified and modified GelSil.

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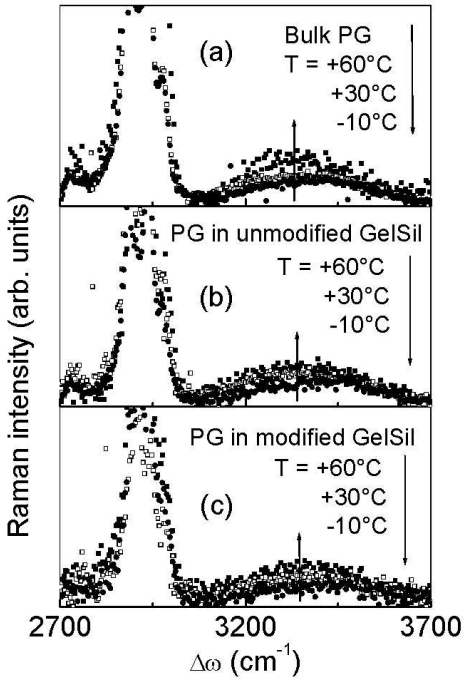


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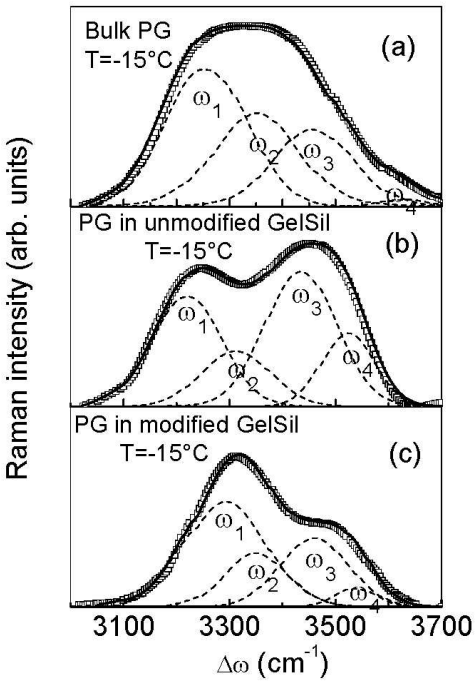


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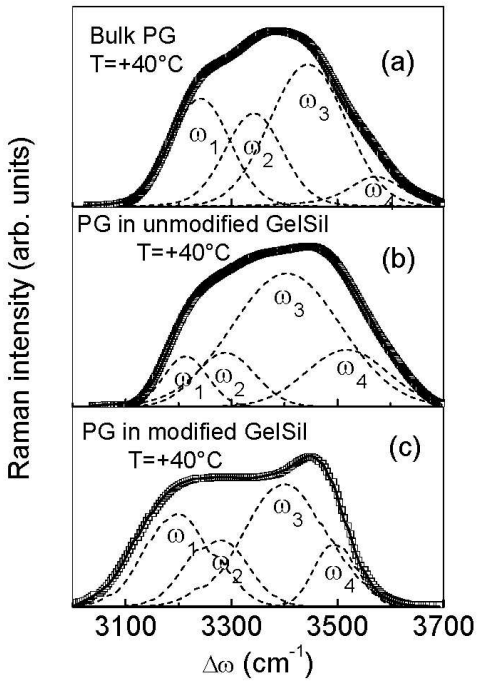


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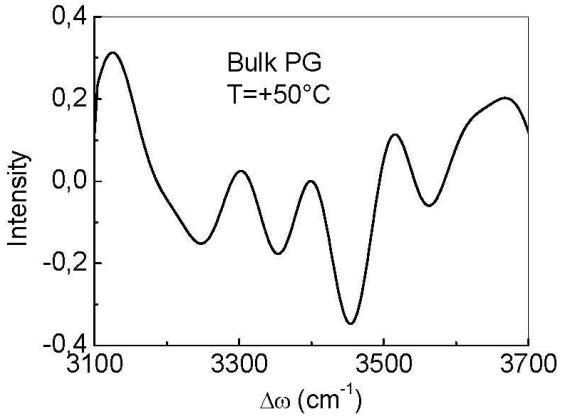


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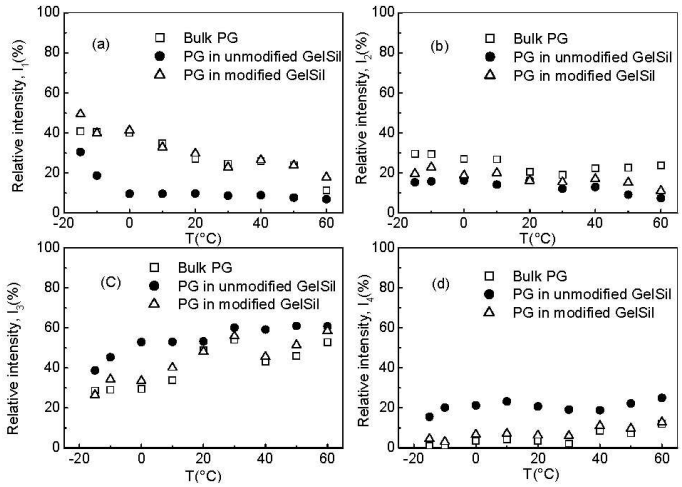


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