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A Brillouin light scattering study of the λ transition in liquid sulphur

F. SCARPONI^{†*}, D. FIORETTO^{†*}, L. CRAPANZANO[‡], G. MONACO[‡]

[†]Dipartimento di fisica, Università di Perugia, Via Pascoli, I-06102 Perugia, Italy.

^{*}INFM CRS-SOFT c/o Università di Roma "La Sapienza", P. A. Moro 2, I-00185 Roma, Italy.

[‡]European Synchrotron Radiation Facility, B.P. 220, F-38043 Grenoble Cedex, France.

The dynamics of liquid sulphur has been investigated in the temperature region corresponding to the so-called λ transition by means of Brillouin Light Scattering. Results of this work, together with ultrasonic spectroscopy and inelastic X-ray scattering results in literature, indicate that the main structural relaxation is slightly affected by the transition and suggest the dramatic increase of shear viscosity to be related to the onset of a low frequency additional relaxation. Such a feature is commonly found in rubber-like materials and can be related to the polymerization of sulphur molecules across the transition.

Keywords : Sulphur; Lambda transition; Brillouin light scattering; Living polymerization

**corresponding author :*

Email: scarponi@fisica.unipg.it -Tel-Fax: +39 075 5852767

1. Introduction

Sulphur is one of the more common chemical elements on the earth, well known since the most ancient times due to its abundance (it is often found in large natural repositories near active volcanoes), its penetrating smell and its flammability. At ambient temperature and pressure sulphur is a pale yellow solid; it melts at about 393 K to form a low viscosity liquid and becomes vapour at 717 K. Starting from a temperature T_λ of about 433 K, liquid sulphur undergoes a complex chemical and physical transformation, commonly known as λ transition.

The best known feature of the λ transition is the enormous increase in shear viscosity [1] immediately above T_λ , from values in the order of 10^{-2} Pa·s to a maximum, slightly lower than 10^2 Pa·s, at about 458 K; at higher temperatures the viscosity decreases smoothly and reverts to low values over 600 K. Remarkable modifications during the λ transition concern also the specific heat [2], the index of refraction [3] and the optical absorption [4]. The density of liquid sulphur [5] and ultrasonic sound speed [6-9] have also been measured in the λ transition region and appear to be comparatively less sensitive to the phenomenon.

The physical modifications described so far can all be related to the living polymerization [10] of sulphur molecules which takes place spontaneously in the λ transition region. In the solid and in the ordinary liquid phase (below T_λ) sulphur is composed by crown shaped S_8 molecules; near and above the threshold temperature, these cyclic units tend to open and to chain. A dynamical equilibrium thus establishes among closed rings, open rings and chains of different length; large chains can eventually close, becoming polymer rings, while unstable linear allotropes of sulphur have also been detected [11,12] in small amounts. The phenomenon is fully reversible and controlled by thermodynamic parameters, mainly by the temperature.

The experimental determination of the mass fraction of polymer in liquid sulphur has been performed using chemical dissolution methods [13] or Raman spectroscopy [14], while estimates of the average chain length have been produced by means of ESR [15] or from magnetic susceptibility measurements [16]. A deeper knowledge of the chain length distribution has been so far prevented by the difficulty in discriminating experimental contributions from sulphur chains of different lengths.

During the λ transition, the polymer mass fraction grows up to 0.55, while the average chain length is almost always above 10^3 atoms and can be as large as 10^6 . While it is well established in general [17] that an increase of shear viscosity can stem from variations in polymer content and chain length, a detailed picture of the dynamics in liquid sulphur and its evolution across the λ transition is still missing.

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3 The simplest hypothesis one can make on the dynamics of a liquid is to consider the structural
4 relaxation to be the only active one. In the case of sulphur, if we make such an assumption, we
5 should relate directly the change in viscosity to a variation of the structural relaxation time. If the
6 well known Maxwell relation $\eta = G_{\infty} \cdot \tau_s$ holds while viscosity increases during the λ transition, being
7 τ_s the main structural relaxation time and G_{∞} the limiting high frequency shear modulus, we should
8 expect τ_s to vary by 4 orders of magnitude as viscosity does. This would imply a noticeable shift of
9 the relaxation time, from the ps range (typical value for a low viscosity liquid) to the ns range.
10

11 Such a dramatic change in the structural relaxation time would lead to an enormous increase in
12 damping and dispersion of acoustic modes in the GHz frequency range, commonly accessed by
13 Brillouin light scattering (BLS) spectroscopy. The BLS study of liquid sulphur in the λ transition
14 region reported thereafter is thus expected to provide valuable information on the structural
15 dynamics in liquid sulphur. The results of this work will be discussed together with ultrasonic
16 spectroscopy (US) data available in literature [6-9], reporting values of the sound speed in the 0.5-
17 150 MHz frequency region, and recent inelastic X-ray scattering (IXS) results [18], accessing the
18 collective dynamics of liquid sulphur in the THz range.
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31 32 **2. Experimental details**

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35 Sulphur of 99.999% purity was purchased from Sigma-Aldrich chemicals and physically purified
36 by boiling under low pressure (~2 mbar) dry nitrogen in a glass test tube (inner diameter 10 mm).
37 The tube was then flame sealed and inserted in the copper sample holder of an experimental
38 chamber. Care was taken to avoid overheating and contamination during preparation; the sample
39 was kept skew during the solidification, to deposit sulphur on the tube walls and prevent explosion
40 of the tube due to thermal expansion of the polycrystalline solid at melting.
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46 During the measurements the temperature was monitored through a 100 Ω platinum resistance
47 sensor and controlled by a PID feedback loop. Using this setup we were able to reduce thermal
48 fluctuations within $5 \cdot 10^{-2}$ K around the selected temperature, in the range between room
49 temperature and about 570 K. Two optical paths were selectable, allowing back scattering and a
50 90° scattering configuration.
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55 [Insert figure 1 about here]

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57 The light source used was a Coherent Innova 300 Ar⁺ laser, tuned on a single line of the 514.5 nm
58 mode, vertically polarized with respect to the scattering plane; the light scattered from the sample
59 was analysed by means of a Sandercock type 3+3 pass tandem interferometer, with a typical
60 contrast higher than 10^9 and a finesse of ~100.

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3 During the λ transition, power absorption greatly increases in the higher part of the optical spectrum
4 [4]: a very low incident light intensity must be adopted in order to avoid local heating of the sample.
5 We performed tests to check the power dependence of the gathered spectra; neutral density filter
6 were then employed to keep the effective power on the sample below 0.7 mW. This value of
7 incident power was found low enough to give no sensible power dependence of results. The back
8 scattering measurements were taken without any polarization analyser (VU configuration); some of
9 the measurements carried out in 90° scattering geometry were performed inserting a dichroic sheet
10 polarizer between the sample and the interferometer, to select the horizontally polarized scattered
11 light contribution (VH configuration) .
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21 3. Results and discussion

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24 Brillouin light scattering spectra were collected in back scattering geometry at temperatures
25 between the melting point and 530 K; a subset of the data is shown in figure 1. In all the spectra, the
26 Brillouin doublet due to longitudinal modes propagating in the fluid is well visible at frequencies
27 around 10 GHz. After each change in temperature, various measurements were taken in succession
28 and compared each other to ensure full chemical and thermal equilibrium had been reached in the
29 sample.
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35 [Insert figure 2 about here]

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37 The characteristic frequency Ω and half width Γ of the longitudinal acoustic modes was determined
38 by fitting the Brillouin peaks region to a damped harmonic oscillator (DHO) model function :

$$39 I(q, \omega) = \frac{1}{\pi} \frac{\Gamma \Omega^2}{(\omega^2 - \Omega^2)^2 + (\Gamma \omega)^2}$$

40
41 convoluted with the instrumental function. Exchanged momentum (q) values were calculated
42 keeping into account the thermal variation of index of refraction [3] through the relationship $q =$
43 $2nK_i \sin \theta/2$, where K_i is the incident light wave number $K_i = 2\pi/\lambda$. The same values were used to
44 get estimates of real part (M') and imaginary part (M'') of the longitudinal elastic modulus M ,
45 through the relations :
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$$54 M'(\Omega) = \frac{\Omega^2 \rho}{q^2}$$

$$55 M''(\Omega) = \frac{\Gamma \Omega \rho}{q^2}$$

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57 where the mass density ρ is from ref. [5]. The longitudinal sound speed c in the GHz frequency
58 region can be calculated from M' values using the relation $M' = c^2 \cdot \rho$. The values obtained are shown
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3 in figure 2 (top graph), compared with estimates of the same physical observable at ultrasonic
4 frequencies [6-9] and with the limiting high frequency (THz region) values recently obtained by
5 means of IXS [18].
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8 A BLS investigation on liquid sulphur was performed in the past [19], using He-Ne laser light and a
9 spectroscopic instrumentation quite similar to our one. In this work, the purification of the sample
10 was very accurate and the red light source was chosen to avoid local heating effects. Nonetheless,
11 the authors adopted a complex model for data analysis, obtaining an anomalous scatter of the fitting
12 parameters and being, for their own admission, unable of drawing significant conclusions about the
13 physical interpretation of the parameters. Moreover, since the exchanged momentum is different
14 from our one, a comparison with our results would be cumbersome and would take us far from the
15 main topic of this work. The present work investigates sulphur in a wider temperature range than
16 [19], obtaining a smoother and clearer dataset, which allows us to draw specific conclusions.
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19 A strong relaxation is clearly present in longitudinal modulus between the GHz frequency range
20 and the THz range, at temperatures both below and above the λ transition threshold. Such a big
21 variation can be ascribed to the main structural relaxation: its substantial independence from
22 temperature indicates a weak correlation between the big change in viscosity across the λ transition
23 and the main structural relaxation. This thesis is confirmed also by the behaviour of the imaginary
24 part of the modulus (figure 2, bottom), proportional to acoustic absorption, which *decreases* exactly
25 in the temperature region of larger viscosity, where we should expect a slowing down of the main
26 structural relaxation time and an increase in sound absorption. On this basis, we believe also that the
27 low frequency tail of the structural relaxation is responsible for the variation in sound speed
28 between the ultrasonic regime and the Brillouin frequency range.
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31 During the measurements, we also performed a series of 90° depolarized (VH configuration)
32 scattering observation in the highest viscosity temperature range, looking for signs of transverse
33 modes propagating in the sample but, also in this case, no evidence of a structural slowing down
34 was found.
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37 The single relaxation model is evidently inadequate to describe the dynamics of liquid sulphur
38 during the λ transition. The main structural relaxation time appears unchanged by the transition, so
39 an additional relaxation must be hypothesized [18], contributing to viscosity as an additional term in
40 the Maxwell relation :
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42

$$\eta = \tau_s (G_\infty - G_{\infty 1}) + \tau_r G_{\infty 1}$$

43 The relaxation time τ_r and unrelaxed shear modulus $G_{\infty 1}$ of this additional relaxation can now be
44 roughly guessed. Rheometric measurements on quick quenched semi polymeric sulphur samples
45 [20] indicate (low temperature trend) a value of G_∞ of about 10^{10} Pa, while suggesting (high
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3 temperature trend) a superior limit for $G_{\infty 1}$ of about 10^6 Pa. Assuming these values, we can
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5 consider $G_{\infty 1}$ to be very small when compared to G_{∞} . If the main structural relaxation time τ_s
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7 remains in the ps scale during the λ transition, the first contribution to viscosity will be always in
8
9 the order of 10^{-2} Pa·s and the large part of the viscosity in the same temperature region must be
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11 provided by the second term. Given the value of $G_{\infty 1}$, τ_r should be at least larger than 10^{-4} s to
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13 obtain a viscosity of 100 Pa·s during the transition [18].

14
15 The existence of very low frequency relaxations is typical of concentrated solutions of linear
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17 uncross linked polymers [17] and is due to entanglement coupling between chains in the melt. The
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19 onset of an entanglement related relaxation at low frequencies usually leads to rubber-like elastic
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21 behaviour and would be sound for sulphur, given the high average weight of the polymer chains
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23 produced in the region of larger increase of the viscosity.

24 25 **4. Conclusions**

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28 Brillouin light scattering measurements were performed in liquid sulphur in the λ transition region.
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30 The experimental results confirm the hypothesis [18] that the large increase in shear viscosity
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32 during the transition does not correspond to a slowing down of the main structural relaxation, but
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34 rather to the onset of an additional very low frequency relaxation, to be found below 10 kHz. Such a
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36 feature should be related to the increasing polymer mass fraction in the melt, and specifically to
37
38 entanglement coupling between sulphur polymer chains. Ultrasonic works in literature were all
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40 performed at frequencies higher than 500 kHz, thus being unable to reveal the existence of this
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42 relaxation, exploring partially relaxed regimes and finding apparent violations of hydrodynamic
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44 predictions [9]. An experimental effort is currently in progress, in collaboration with dr. Tullio
45
46 Scopigno (CRS-SOFT Rome, IT) and dr. Spyros Yannopoulos (FORTH/ICE-HT Patras, GR), to
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48 directly observe the timescale where the low frequency relaxation should be located.
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References

- [1] R.F. Bacon, and R. Fanelli, J. Am. Chem. Soc. **65**, 639 (1943).
- [2] E.D. West, J. Am. Chem. Soc. **81**, 29 (1959).
- [3] A. Donaldson and A.D. Caplin, 1985, Phyl. Mag. B **52**, n. 2, 185.
- [4] S. Hosokawa, T. Matsuoka and K. Tamura, J. Phys. Cond. Matt. **6**, 5273 (1994).
- [5] A.M. Kellas, J. Chem. Soc. **113**, 903 (1918).
- [6] M.B. Gitis and I.G. Mikhailov, Sov. Phys. Acoust. **13**, no. 2, 251 (1967).
- [7] D.L. Timrot, M.A. Sredniskaya and T.D. Chkhikvadze, Dokl. Akad. Nauk. SSSR **279**, 617 (1984).
- [8] V.F. Kozhevnikov, J.M. Viner and P.C. Taylor, Phys. Rev. B **64**, 214109 (2001).
- [9] V.F. Kozhevnikov, W.B. Payne, J.K. Olson, C.L. McDonald and C.E. Inglefield, J. Chem. Phys. **121**, no. 15, 7379 (2004).
- [10] S.C. Greer, Adv. Chem. Phys. **XCIV**, 261 (1996).
- [11] R. Steudel, Top. Curr. Chem. **230**, 81 (2003).
- [12] R. Steudel, Top. Curr. Chem. **231**, 31 (2003).
- [13] J.C. Koh and W. Klement Jr., J. Phys. Chem. **74**, 4280 (1970).
- [14] A.G. Kalampounias, K.S. Andrikopoulos and S.N. Yannopoulos, 2003, J. Chem. Phys. **118**, n. 18, 8460 (2003).
- [15] D.M. Gardner and G.K. Fraenkel, J. Am. Chem. Soc. **78**, 3279 (1956).
- [16] J.A. Poulis and W. Derbyshire, Trans. Faraday Soc. **59**, 559 (1963).
- [17] J.D. Ferry, *Viscoelastic properties of polymers* (John Wiley & Sons, New York, 1980).
- [18] G. Monaco, L. Crapanzano, R. Bellissent, W. Crichton, D. Fioretto, M. Mezouar, F. Scarponi, and R. Verbeni, Phys. Rev. Lett. **95**, 255502 (2005).
- [19] A.D. Alvarenga, M. Grimsditch, S. Susman and S.C. Rowland, J. Phys. Chem. **100**, 11456 (1996).
- [20] A.V. Tobolsky, W. MacKnight, R.B. Beevers and V.D. Gupta, 1980, Polymer **4**, 423 (1980).

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4 **Figure captions**
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10 **Figure.1 :**

11 Brillouin light scattering spectra taken in back scattering configuration at various temperatures.
12 Original points have been stacked multiplying for an arbitrary factor to allow easier comparison of
13 spectral features.
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20 **Figure.2 :**

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22 Results for the real part of the longitudinal elastic modulus in liquid sulphur from BLS
23 measurements are reported in the top graph, compared with literature data from recent inelastic X-
24 ray scattering measurements [18] and various ultrasonic works in literature [6-9]. The imaginary
25 part of the longitudinal elastic modulus is shown in the bottom graph.
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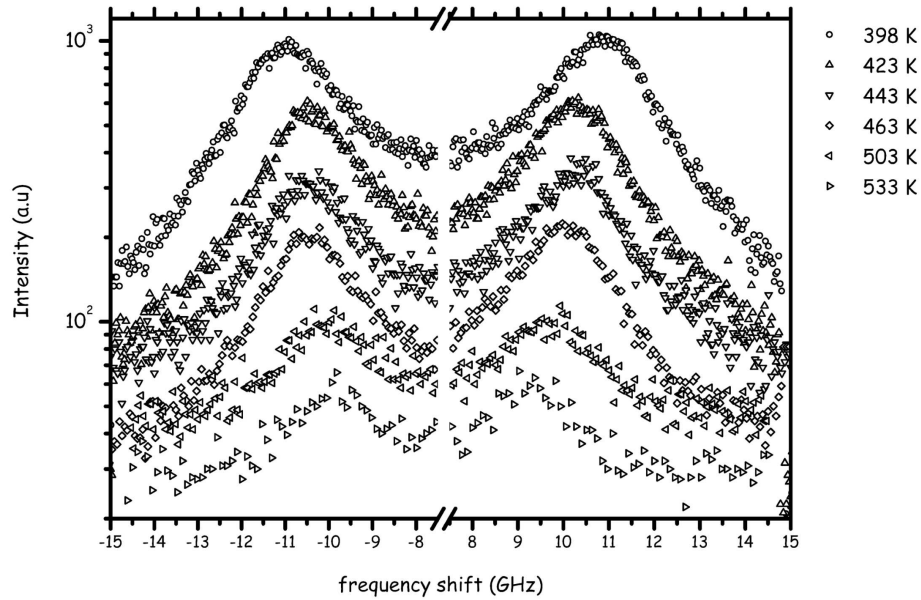


Figure 1
149x104mm (400 x 400 DPI)

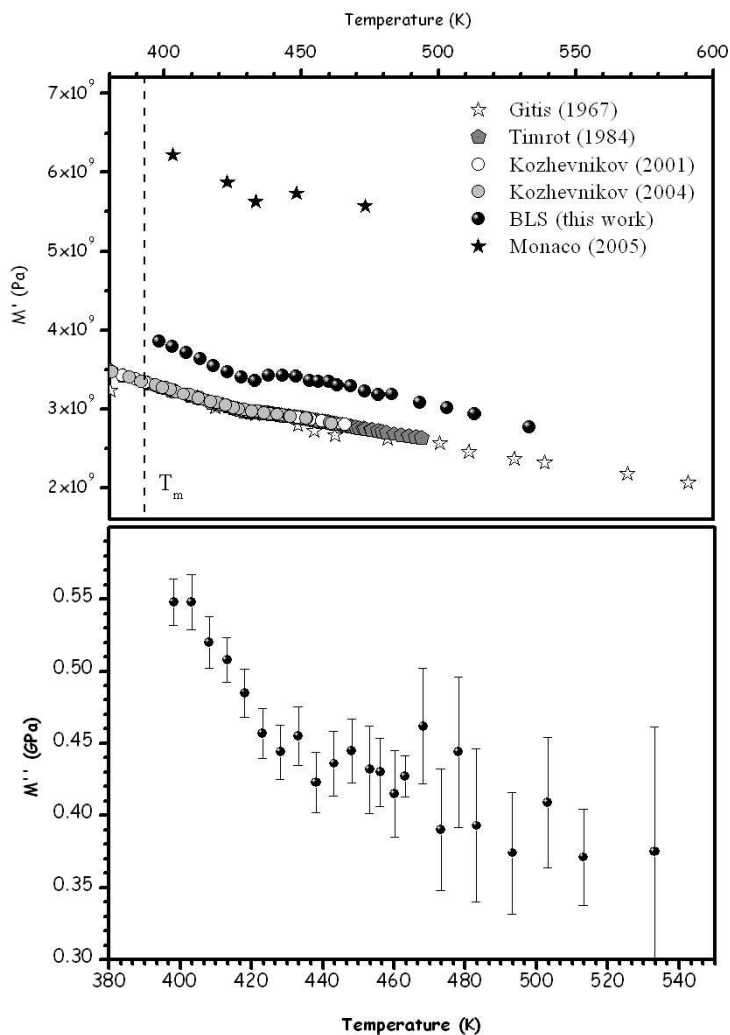
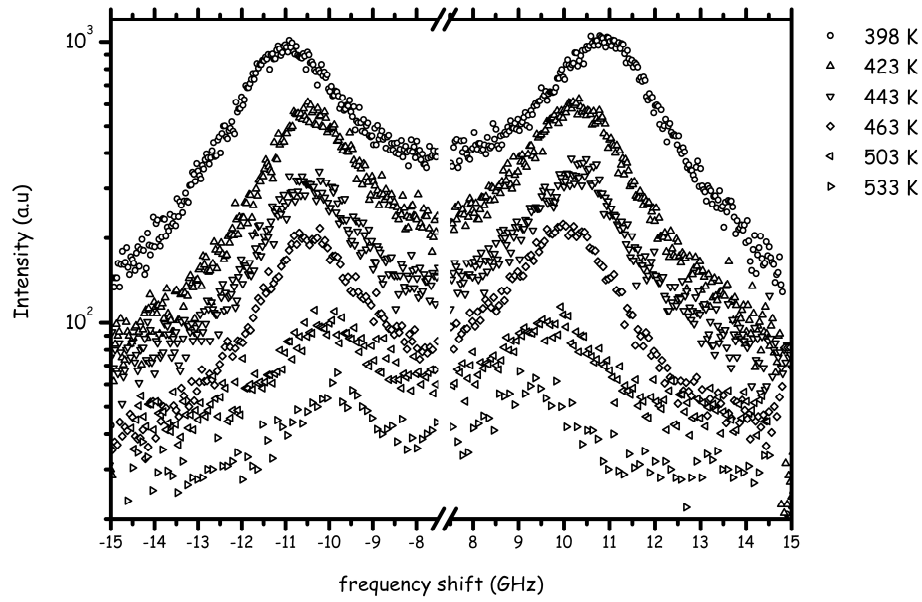


Figure 2
402x463mm (72 x 72 DPI)

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