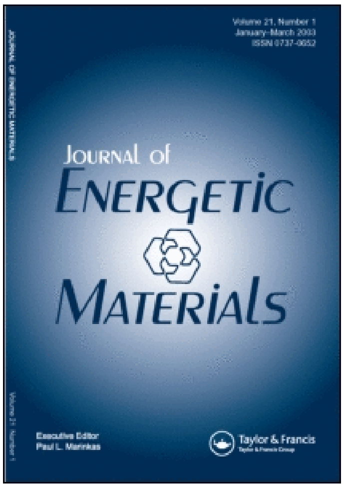

Journal of Energetic Materials
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713770432

Optical and Raman studies of explosives under varying pressure and temperature

C. M. Pereira[a]; M. M. Chaudhri[a]
[a] Cavendish Laboratory, Cambridge, England

To cite this Article Pereira, C. M. and Chaudhri, M. M.(1989) 'Optical and Raman studies of explosives under varying pressure and temperature', Journal of Energetic Materials, 7: 4, 297 — 322

To link to this Article: DOI: 10.1080/07370658908014901

URL: http://dx.doi.org/10.1080/07370658908014901

OPTICAL AND RAMAN STUDIES OF EXPLOSIVES UNDER VARYING PRESSURE AND TEMPERATURE

C.M. Pereira and M.M.Chaudhri
Cavendish Laboratory, Madingley Road, Cambridge, CB3 0HE, England

Recent studies of the effect of pressure and temperature on the optical and Raman spectra of the azides of potassium, thallium, silver and lead have been made using a diamond anvil cell, helium low temperature cryostat and high temperature furnace. With increasing temperature or decreasing pressure potassium azide was found to show stiffening of the lattice modes. Thallium azide however, shows both pressure and temperature induced phase changes which lead to a doubling of the unit cell in the c direction. Silver azide does not show any phase change with temperature although some of its Raman modes stiffen and some soften with temperature. Optical absorption at low temperatures in silver azide show strong excitonic features near the band edge and with pressure the crystals are found to darken irreversibly. Some recent results on the Raman and optical spectra of pure and sensitised nitromethane are also reported.

INTRODUCTION

A study has been made of the optical absorption and Raman phonon spectra of various explosive and explosive related materials. In particular single and polycrystalline samples of potassium, thallium and silver azides and pure and sensitised nitromethane have been studied.

Of particular interest in the study of the metal azides is why small differences in their crystallographic structures can cause large differences in their relative stabilities[1,2].

Nitromethane (CH_3NO_2), a liquid at room temperature and pressure is a relatively simple explosive and has been extensively studied for many years as a model for predicting the behaviour of more complex molecules. One characteristic of nitromethane is that the addition of small amounts (~5 to 10% by weight) of an amine such as diethylamine (DEA) or diethylenetriamine (DETA) can greatly enhance its shock sensitivity[3,4]. Cook[4] has recently reported that in a gap test the thickness of the barrier for a 50% probability of initiation of detonation increases from ~15mm for pure nitromethane to ~55mm for nitromethane sensitised with 5 to 25% DETA.

EXPERIMENTAL PROCEDURE

The optical absorption spectra of both the solid and liquid explosive samples were measured using a Perkin Elmer Lambda 9 UV-NIR spectrophotometer running in the transmission mode.

The Raman spectra were obtained on either a Coderg T800 triple grating high resolution spectrometer or a Dilor Omar 98 multichannel spectrometer with an Ar^+ laser tuned to 5145Å (above the absorption edges for the azides). For the metal azides, laser powers of less than 5mW were used to avoid sample decomposition and only unpolarised Raman spectra were obtained because of the small sizes of the single crystal samples.

The Raman spectra taken from nitromethane were found to be insensitive to laser intensities so that intensities of up to 200mW could be used to obtain good quality Raman spectra. However, when nitromethane was sensitised by the addition of a small amount of diethylenetriamine (DETA), it was found that these samples decomposed and changed colour after about one hour so that for consistency freshly mixed samples were used for each run.

Samples were either mounted in a continuous flow low temperature He cryostat (to 4K), a high temperature furnace (to 600K) or a high pressure diamond anvil cell (to 50kbar).

RESULTS AND DISCUSSION

Metal Azides

At pressures above 4 kbar AgN_3 was found to darken irreversibly so that accurate transmission measurements could not be obtained. It is suggested here that this darkening is due to partial decomposition of the samples leading to the precipitation of metallic silver. Measurements from X-ray diffraction photographs of samples before and after pressurising give similar lattice parameters indicating that the bulk of the silver azide does not undergo a permanent phase change with pressure. Preliminary X-ray diffraction studies made under hydrostatic pressure in a diamond anvil cell suggest a possible reversible phase change at 4kbars, although the nature of this change has not yet been fully determined. Electrical conductivity measurements on pressed powder pellets of silver azide under pressure[5] do not show any evidence of a phase transition at low pressure, suggesting that if silver is precipitated, the number of silver atoms are too few to cause a change in the electrical conductivity

Figure 1 shows the change in the optical absorption spectra of AgN_3 as a function of temperature. At low temperatures three bands at 3.44, 3.46 and 3.51eV are seen which are found to sharpen and shift to higher energy as the temperature is lowered.

Previously, Deb and Yoffe[6] had reported two very weak bands at 3.44 and 3.46eV. These were explained, following the initial work of McLaren and Rogers[7], as Wannier type excitons with n=3 and 4. This interpretation has been disputed by Gora et al.[8] who argued on the absence of n=1 and 2 excitons. From our results the measured bands do not fit the $E_n \propto 1/n^2$ relationship expected for Wannier type excitons and the energies of the bands are also too low to be excited states of the cation or anion[9]. In conclusion, the nature of the exciton bands is still unresolved.

By comparison β-$Pb(N_3)_2$ is found to remains clear under increasing pressure up to 40kbar and the band edge shifts linearly with a gradient of -5.9×10^4 eV $kbar^{-1}$ as shown in figure 2. In our samples no excitonic features were resolved near the absorption band edge. On very thin polycrystalline films, a sharp band at 3.3eV has been reported[10]. This shifts by 4×10^{-3}eV $kbar^{-1}$ and has been attributed to an exciton.

Raman Spectra

Unpolarised Raman spectra were obtained from potassium, thallium and silver azides under conditions of varying pressure or temperature. With laser intensities of over 5mW the Raman spectra of both AgN_3 and TlN_3 were found to change with time as the samples decomposed. As the wavelength of the argon ion laser used (514.5nm) was above the crystals absorption band edges (typically ~360nm) it is probable that sample decomposition initially takes place due to absorption by impurities within the crystals.

Potassium azide, with one of the simplest azide structures has been well characterised using Raman spectroscopy[11,12]. It has a tetragonal unit cell (D^{18}_{4h}). Group theory predicts 5 Raman active modes in total, 2 internal modes associated with the azide group (A_{1g},B_{2g}) and 3 external metal-metal (E^1g) and azide-azide modes (B_{1g},$E^2{}_g$). Under increasing temperature, up to its melting point (623 K), or with decreasing pressure the potassium azide phonons behave in an expected way with the modes softening, figure 3 and figure 4 respectively, with the temperature dependencies of the internal modes given in Table 1.

TABLE 1

Rate of Change in Internal Mode Frequencies in potassium azide with Pressure and Temperature. The $E^1{}_g$ mode is a cation lattice mode and the $E^2{}_g$ and B_{1g} modes azide libration modes (not resolved with temperature).

Mode	R.T. Freq. cm^{-1}	Temp. Dep cm^{-1}/K	Pressure Dep. $cm^{-1}/kbar$
$E^1{}_g$	105.7	-0.014	0.023
$E^2{}_g$	146.5	-0.091	1.506
B_{1g}	153.1		1.441

At R.T. TlN_3 has the tetragonal crystallographic structure of potassium azide so that a similar Raman spectrum is seen. Below 240K there is a phase change to lower symmetry phase with an orthorhombic unit cell ($D^{20}{}_{2h}$). This is accompanied by a doubling of the unit cell from two to four formula units[13]. Figure 5 shows the change in the Raman spectrum of the external modes and figure 6 the change in the internal modes.

Correlation between the zone centre phonons in the R.T. and L.T. phases, Figure 7, show that the original room temperature phonons are still Raman active in the L.T. phase. This can be seen in the Raman spectrum covering the external modes, Figure 5, where although the the original room temperature Raman modes split they do not vanish. The internal modes, Figure 6, are not greatly affected by the phase change although these also split by the doubling of the unit cell in the *c* direction below the transition temperature. The Raman spectra suggests that the phase change in thallium azide occurs in two stages, the first stage being a rotation of the azide groups in the *a* and *b* planes, giving rise to the shifting of the Raman modes associated with the external azide modes and then a subsequent doubling of the unit cell in the *c* direction which gives rise to the splitting of both the new external modes and the original internal azide moves. Preliminary pressure Raman studies on thallium azide up to 45kbar also show a structural phase change starting at low pressures (~5kbar). Here there also appears to be a doubling of the unit cell in the *c* axis similar to that found at L.T. phase.

Silver azide is similar crystallographically to potassium azide. However because the neighbouring azide ions which lie above each other in the *c* direction are not at right angles, as they are in potassium azide but are slightly distorted, the lengths of the *a* and *b* axes are different. This lowers the crystal symmetry to orthorhombic, D^{26}_{2h}[14]. The change in azide-azide angle is thought to arise from a small degree of covalent bonding between the metal and azide ions in the layer perpendicular to the *c* direction so that a layer type structure in the *b* direction is formed. Correlation between the potassium azide and AgN_3 crystal symmetries predict that the potassium azide E (doubly degenerate) modes split in the AgN_3 structure as shown in figure 8. There are now nine Raman active modes; 2 internal (A_g, B_{2g}) and 7 external $(A_g + 3B_{1g} + B_{2g} + 2B_{3g})$. In our samples seven Raman modes were seen and their frequencies measured; five external (figure 9) and two internal (figure 10). These were assigned by correlation between the AgN_3 and potassium azide zone centre modes and their temperature dispersion measured, Table 2 and figure 11 (external modes) and figure 12 (internal modes)

TABLE 2

Frequencies of the Raman Active Phonons Measured in Silver Azide.

Frequency		Temp. Dep	Assignment
70K	R.T.	$\Delta f/\Delta T (x10^{-2})$	
65	56	-4.7	B^1_{3g}
77.5	76.5	-0.52	B^1_{2g}
149	160	4.1	A_g
209	189.5	-7.3	B^2_{3g}
226	230	2.3	B^2_{2g}
1248	1245(250K)	-2.352	v_2 (comb.)
339	1334	-2.096	A_g

The directions of the shifts of the lattice modes suggest that, somewhat unusually ,the crystal lattice tends towards a higher symmetry phase on cooling. Although the azide rocking modes,B^2_{2g} B^2_{3g}, (which are derived from the single doubly degenerate E_g mode in the potassium azide structure), tend to converge at low temperature suggesting the formation of a tetragonal potassium azide like lattice. The A^1_{1g} mode however, does not converge to the same frequency as in potassium azide but remains at a lower frequency as seen in thallous azide. On cooling the dominant effect is the anharmonic interaction between the π-orbitals of the stacked azide groups which stop the angle between them, in the *b* direction, from reducing as the lattice contracts.

Nitromethane

Why sensitization occurs with the addition of an amine is not well understood. An explanation based on a chemical type sensitisation has been has been proposed by Engleke[3]. This is supported by Cook[4] who has conjectured that the sensitization is neither physical nor mechanical. His high-speed framing photographs show that the fast reaction initiates at 'hot spots' which are also seen away from the barrier/explosive border.

According to Engleke, the addition of DETA produces 'aci-ions', figure 13, which are responsible for causing the sensitizing of the nitromethane. The formation of the aci ions have also been seen by NMR in UV irridiated nitromethane[15]. In nitromethane at high pressure it is thought that they are responsible for an increase in the reaction rate and the subsequent generation of heat.

It has been predicted[16] that the presence of the aci ions can be detected by UV absorption and Raman spectroscopy. Engleke has calculated a UV aci-ion absorption band at ~233nm, and a Raman active phonon mode at ~3336cm^{-1}[16].

Because nitromethane absorbs strongly in the near UV a solution of a few percent of nitromethane in methanol was investigated. This is found to have a strong absorption band centered at 210nm and pure DETA diluted in methanol shows a strong band at 215nm. A mixture of DETA and nitromethane in methanol show a band at 205nm suggesting some chemical change to the system although no new band near the aci ion predicted frequency was seen. Under pressure pure nitromethane in the diamond anvil cell shows a strong absorption edge at 325nm and it is found to freeze at 14kbars without a large shift in absorption band.

Raman studies were made both pure and sensitised nitromethane (DEA and DETA), figure 14. Near the predicted frequency for the aci-ion pure nitromethane does not have any Raman bands. DETA however shows a Raman band at 3296cm^{-1}. In a mixture of a few percent of DETA in nitromethane a band appears at 3315cm^{-1}, figure 14. This band is within 20cm^{-1} of the predicted aci-ion frequency and may be due to the formation of the aci-ion. The Raman spectrum arising from the nitromethane does not appear to change when a small amount of DETA is added. After about 24hours the nitromethane/DETA mixture appears to decompose, changing colour and separating out into a mixture of a light brown liquid and a rather denser dark brown liquid. The increase in shock sensitivity seen in nitromethane/DETA mixtures is also reported as being reduced after about 24 hours. However, the band is still seen in the shifted position in sensitised samples over 24 hours old. In a mixture of nitromethane and DEA a similar Raman band is measured at 3310cm^{-1} but the position of this band is not significantly different from that seen in pure DEA (3312cm^{-1}) to be conclusive.

SUMMARY AND CONCLUSIONS

The experiments have shown that although the monovalent metal azides studied have similar crystal structures there are large differences in their relative temperature and pressure stabilities.

Potassium azide has a tetragonal unit cell (*a* = *b*) and is non-explosive. It is the most ionic of the metal azides studied with the angles between the stacked azide ions being 90° and showed no structural phase transitions in the temperature and pressure ranges investigated. Thallium azide is less ionic and has the same tetragonal space group as potassium azide at room tempeture. However, it is found to explode when heated or shocked mechanically. At low temperature (240K) and high pressure (11kbar) thallium azide was found to show structural phase transitions. These transitions appear to involve slight rotation of the stacked azide groups in the *a*-*b* plane which results in a reduction in the crystal symmetry to orthorhombic. Silver azide, which is the least ionic of the azides studied, is also the most explosive. Here the stacked azide ions are rotated, in the *a*-*b* plane, from their potassium azide tetragonal position at room temperature. There is also evidence[17] of some extra bonding, covalent in nature, between the silver atoms and the azide end nitrogen atoms (N_{111}) in the *b* direction forming a 'layer' type structure. This bonding has been attributed to hybridisation between the outer filled metal d_{xy}, d_{yz} orbitals and the N_{111} p_y orbitals. Although it does not show a structural phase transition at low temperature, the temperature dependent Raman spectrum suggests that the azide ions rotate, as seen in thallous azide, causing the orthorhombic structure to tend towards the tetragonal potassium azide type structure at low temperature. It is suggested that the tetragonal stucture is never actually reached at low temperature because of the extra metal-azide bonding and because the radii of the silver ions are too large to allow the azide ions to rotate freely without a large increase in the unit cell dimensions.

The Raman studies of nitromethane/DETA mixtures indicate some chemical activity leading to a band at 3315cm^{-1} without affecting the original nitromethane bands. Whether this band is due to the formation of an aci-ion is still unclear although it is near the predicted frequency. The UV absorption studies have not yet shown evidence of any chemical change.

ACKNOWLEDGEMENTS

We would like to thank Dr. W.Y. Liang and Dr. A.D. Yoffe for their helpful comments and suggestions and the S.E.R.C., M.O.D.Procurement Executitive and U.S. Government for their support.

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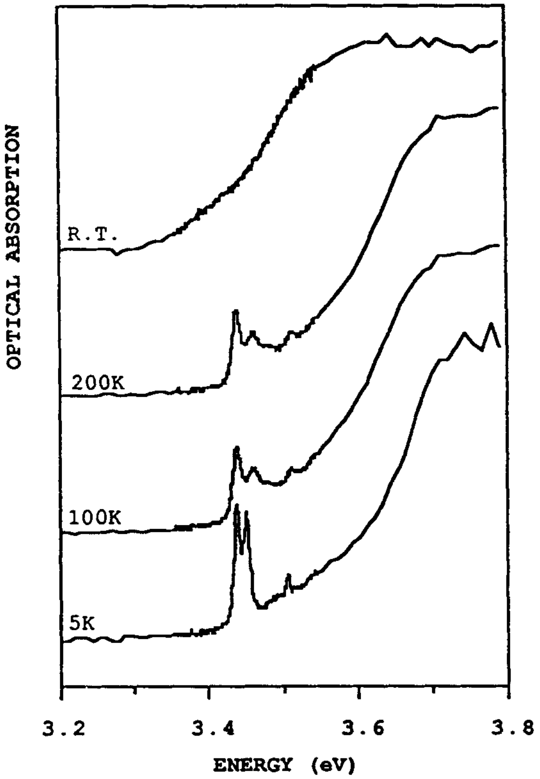


FIGURE 1
Change in the optical absorption of a single crystal of silver azide with temperature.

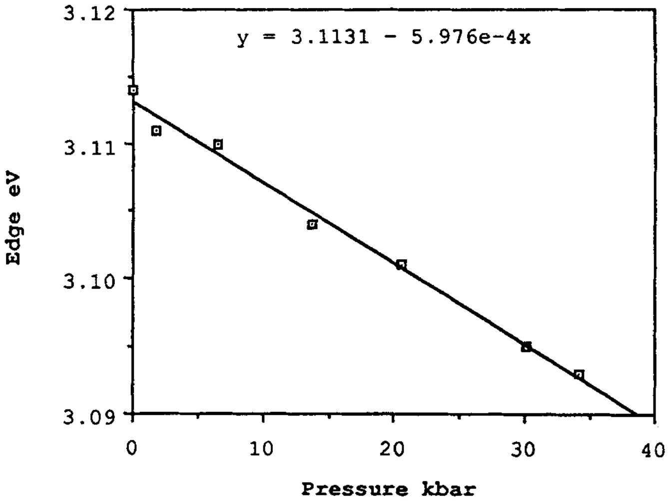


FIGURE 2
Shift of the absorption band edge with pressure in ß-Lead Azide

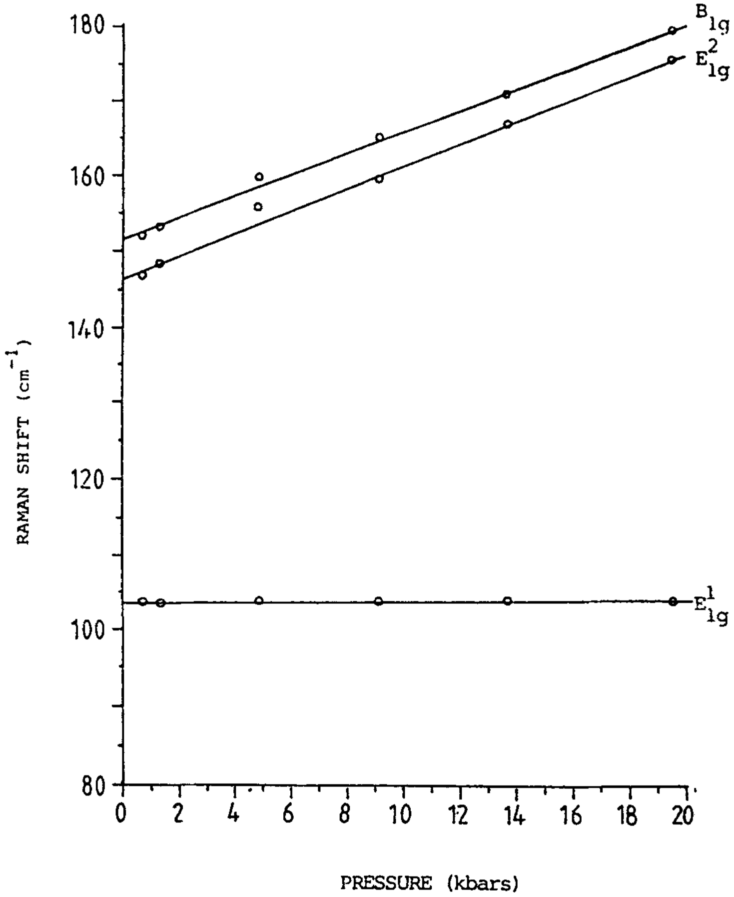


FIGURE 3
Temperature dependence of the external Raman active modes of potassium azide

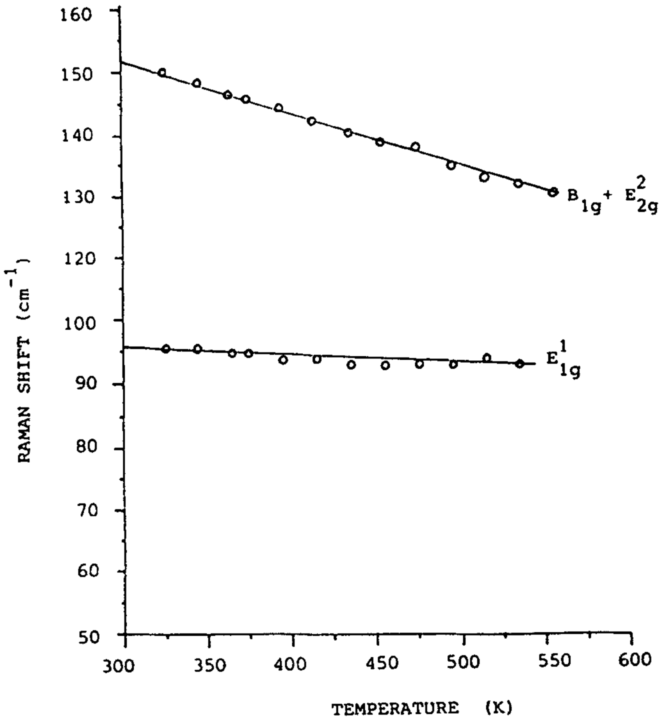


FIGURE 4
Pressure dependence of the external Raman active modes of potassium azide. Here the two azide libration modes are not resolved

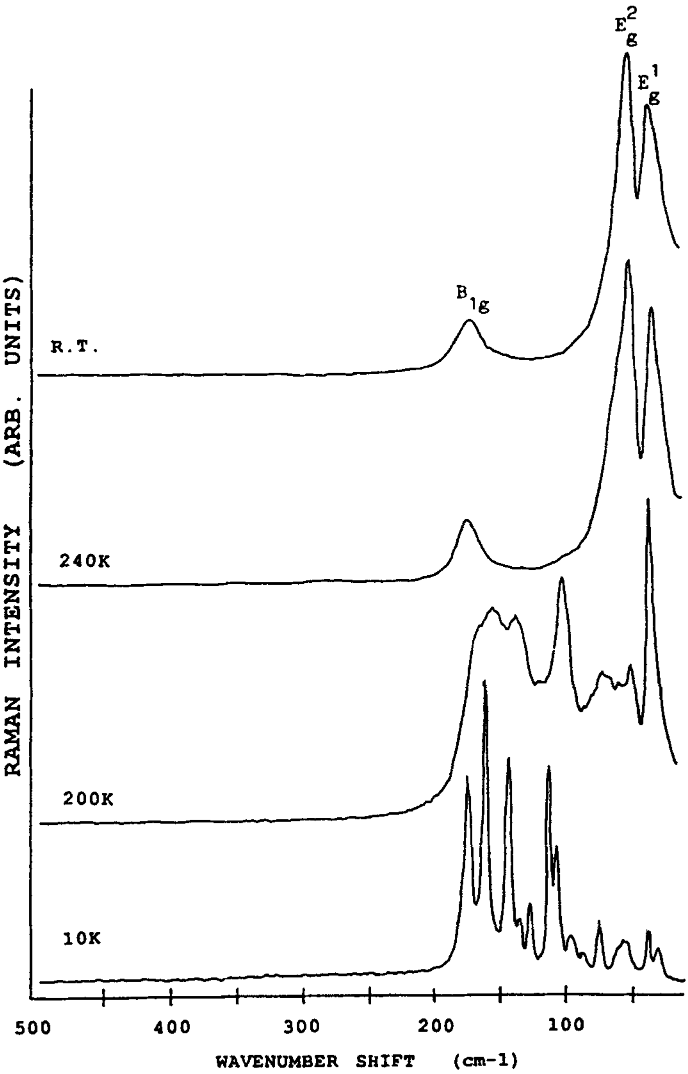


FIGURE 5
Raman spectra of the external modes of Thallous Azide as a function of temperature

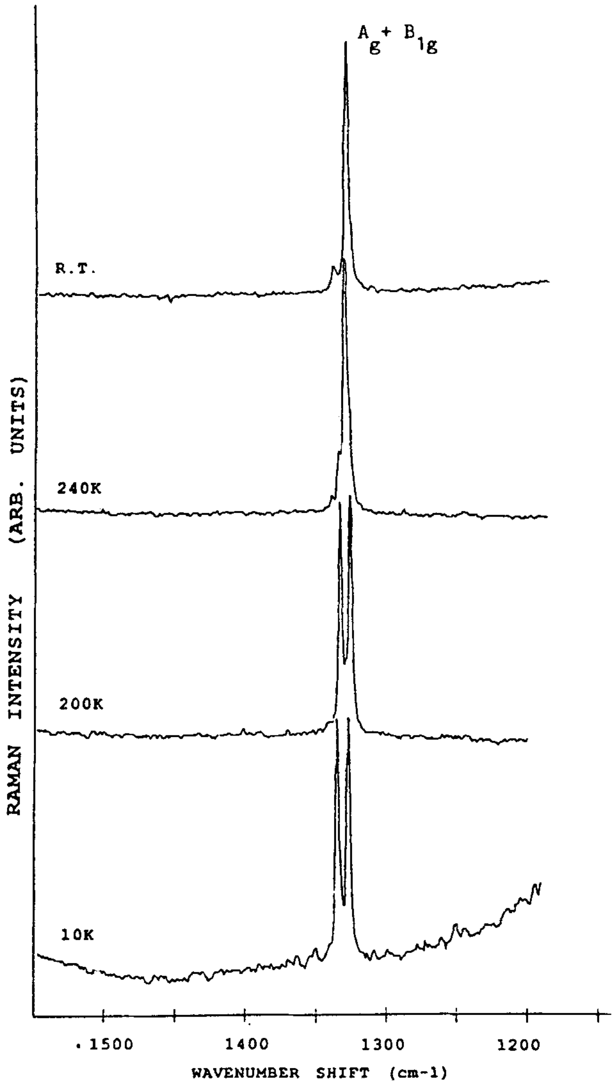


FIGURE 6
Raman spectra of the internal modes of Thallous Azide as a function of temperature

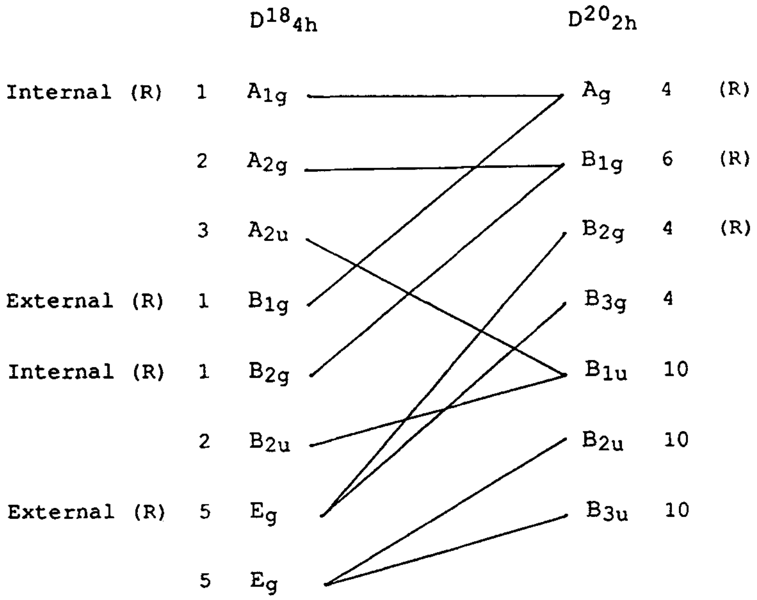


FIGURE 7
Correlation between the zone centre phonons in the R.T. (D^{18}_{4h}) and L.T. (D^{20}_{2h}) phases of Thallous azide. (R) denotes Raman activity.

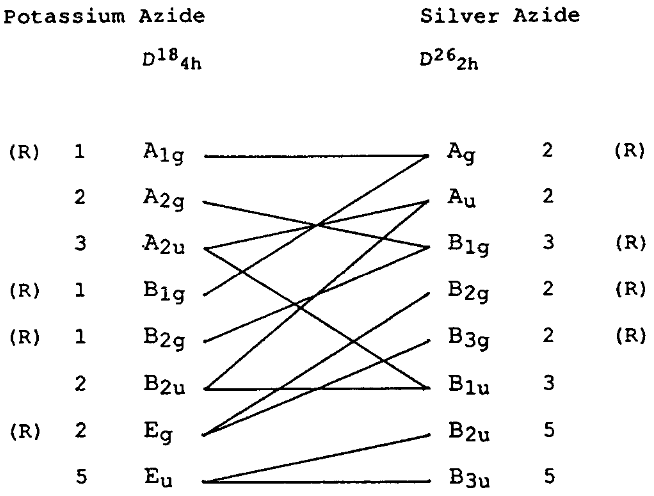


FIGURE 8
Correlation between the zone centre phonons in the potassium azide (D^{18}_{4h}) and silver azide (D^{26}_{2h}). (R) denotes Raman activity.

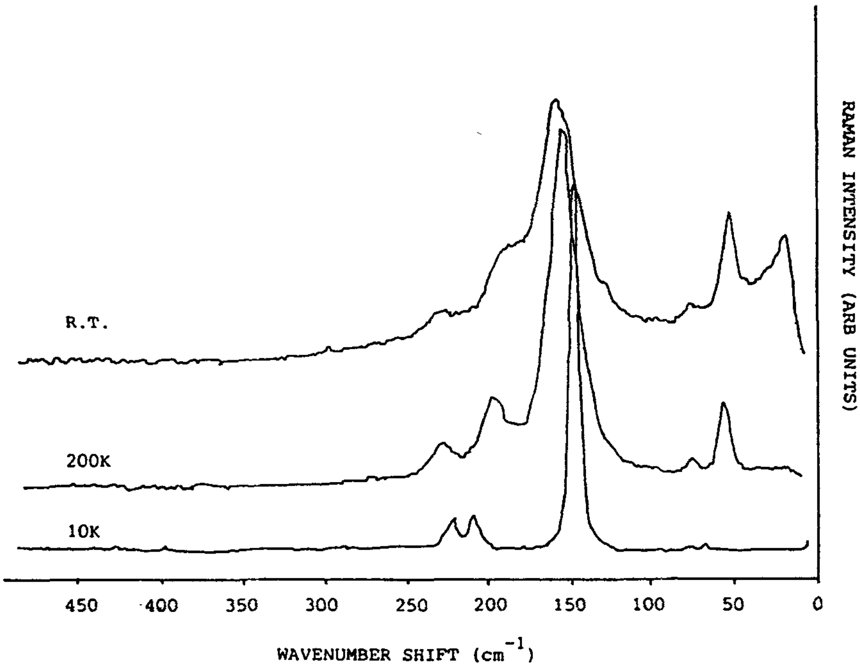


FIGURE 9
Raman spectra of the external modes of Silver Azide as a function of temperature

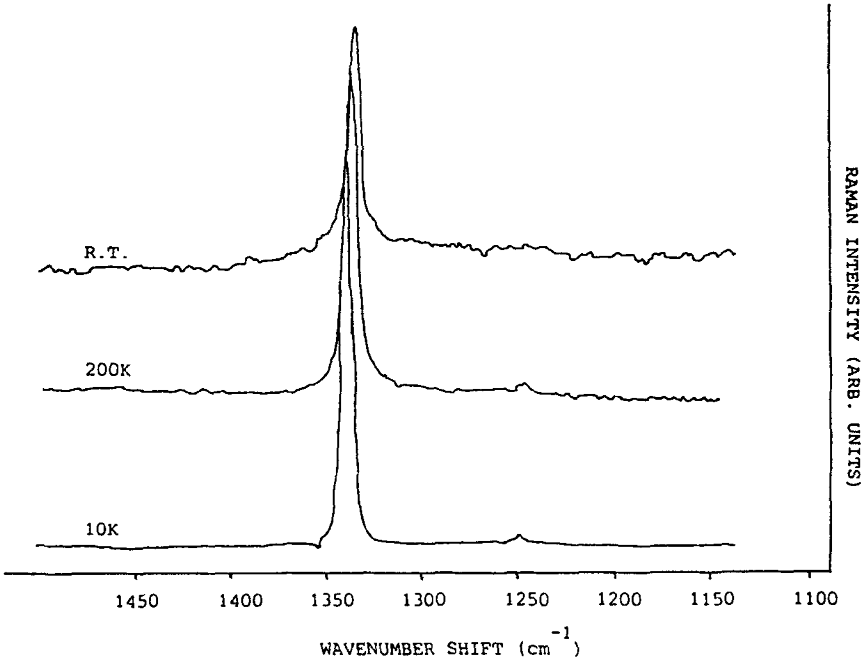


FIGURE 10
Raman spectra of the internal modes of Silver Azide as a function of temperature

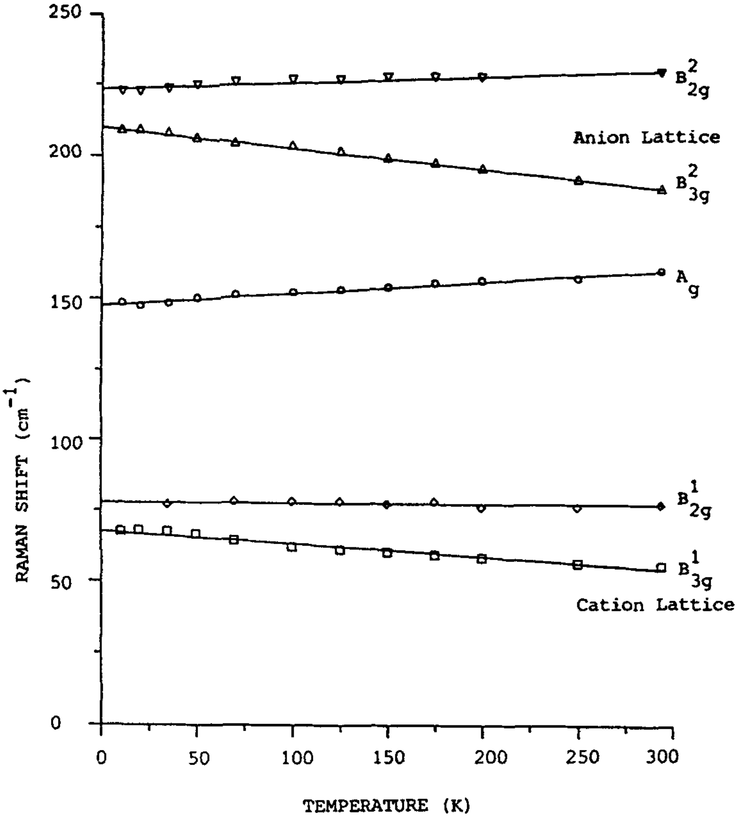


FIGURE 11
Temperature dependence of the external Raman active modes of silver azide

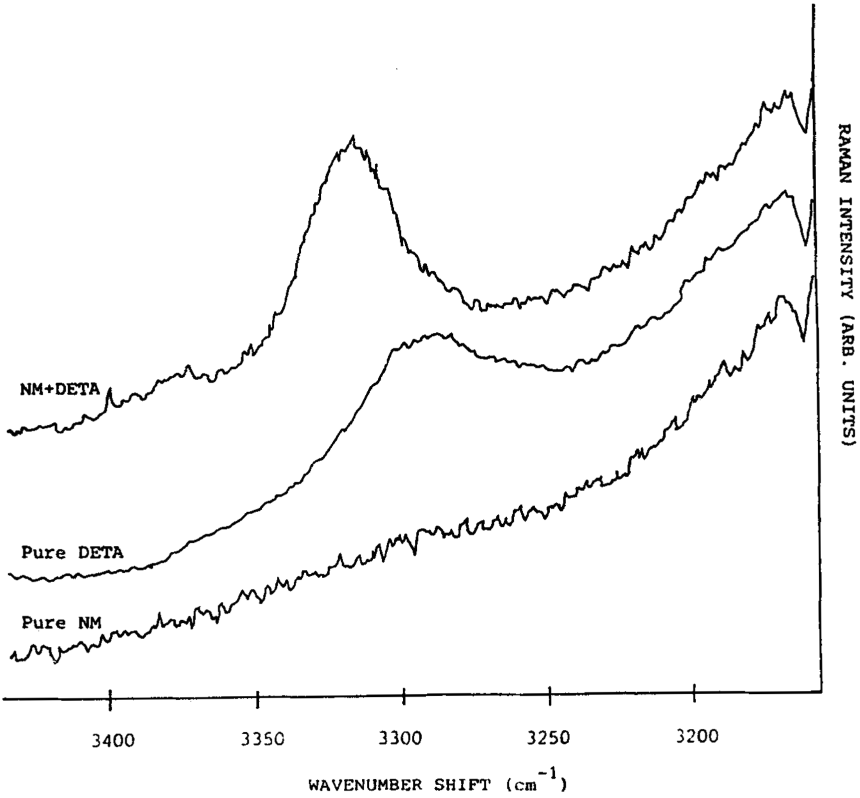


FIGURE 12
Temperature dependence of the internal Raman active modes of silver azide

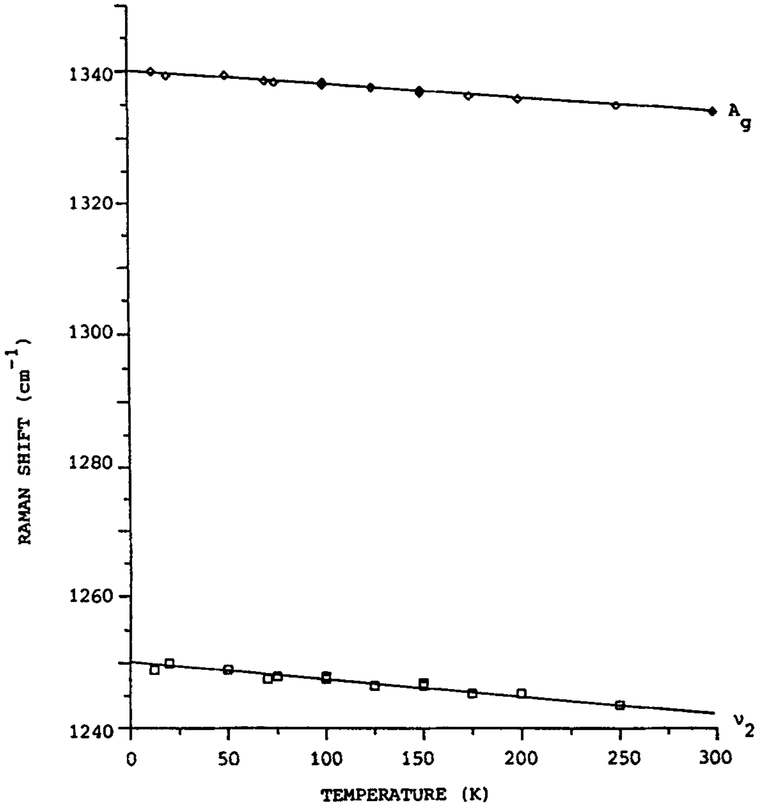
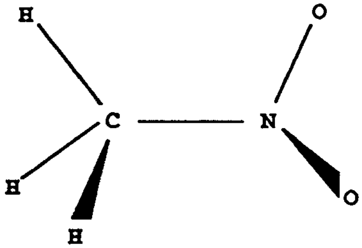


FIGURE 13
The 'normal' form of nitromethane (1) and the aci ion (2)



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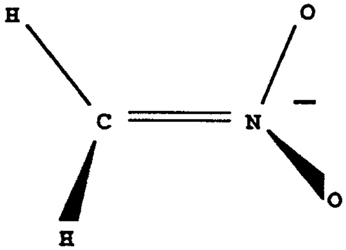

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FIGURE 14
Raman spectra of pure nitromethane, DETA and a mixture of 10% (approx) DETA in nitromethane