

Vibrational excitations of As_2O_3 . I. Disordered phases

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Raman, depolarization, and infrared spectra of the glass, liquid, and gaseous disordered phases of As_2O_3 have been studied at temperatures between 4.5 and 1200 K. Spectra recorded at temperatures in the range of the glass-liquid transition indicate that the microstructures of the glass and liquid are quite similar near T_g and can best be characterized as distorted layerlike remnants of the monoclinic crystalline phase, claudetite. Our results have been contrasted to corresponding results for As_2S_3 and As_2Se_3 and have been compared with the predictions of current models of the structure of As_2X_3 -type glasses. The observed spectra are most compatible with the composite model which combines aspects of the layer and molecular models. No evidence is found to support the conjecture of Taylor, Bishop, and Mitchell that for layer-type As_2X_3 glasses a characteristic temperature T_s exists such that $T_s > T_g$ and the layers catastrophically disintegrate at temperatures $T > T_s$. The temperature dependence of the Raman shift, full width at half-maximum ($\Gamma_{1/2}$), and integrated intensity of the 376-cm^{-1} band associated with the symmetric stretching mode of the As-O-As linkage have been studied as have the shifts with temperature of other prominent spectral features. We find that the glass transition temperature can be accurately determined from a plot of $\ln\Gamma_{1/2}$ vs $\ln(1000/T)$ and that above T_g $\Gamma_{1/2}(376\text{ cm}^{-1}) \propto T^{1/2}$. The temperature dependence of the ν_1 and ν_3 modes of the AsO_3 pyramidal unit indicates that the apex angle decreases with increasing temperature. The low-frequency ($8\text{--}30\text{ cm}^{-1}$) region of the Raman spectrum of vitreous As_2O_3 has been carefully studied at 11.4 K. From the reduced Raman spectrum of the low-frequency region it is found that the product of the frequency-dependent coupling coefficient $C(\omega)$ and the density of vibrational states $g(\omega)$ varies as $\omega^{2.5}$.

I. INTRODUCTION

There is considerable interest among solid-state physicists and physical chemists in the macroscopic and microscopic physical properties of bulk glasses. This interest is a manifestation of the fact that those amorphous solids which are preparable in bulk form constitute a bridge between the solid and liquid states of matter. Naturally, those chemical compounds which can be prepared in the crystalline, glassy, liquid, and gaseous states are of particular interest. One such compound is As_2O_3 . Accordingly, we report here and in the following paper the results of Raman, depolarization, and infrared spectroscopic studies of the disordered phases (glass, liquid, and gas) and crystalline phases (arsenolite and claudetite), respectively, of As_2O_3 . A preliminary report on the low-temperature Raman and depolarization spectra of vitreous As_2O_3 has appeared elsewhere.¹

While the liquid phase of As_2O_3 has not been previously studied the glassy,² crystalline,^{2,3} and gaseous^{3,4} forms of As_2O_3 have been the subjects of previous spectroscopic investigations. Most recently Bertoluzza *et al.*² have attempted to ascertain the microstructural features of the glassy phase by comparing the frequencies of several of the spectroscopic features of the glass with those of the two crystalline forms. Such comparisons, which incidentally are a noteworthy characteristic

of much of the previous work, are as we shall show, quite oversimplified especially since Bertoluzza *et al.* did not examine the depolarization spectra of the glass. Depolarization spectra are in fact more sensitive to the local microstructure of molecular amorphous solids than are the Raman spectra.^{1,5} The room-temperature Raman spectra of vitreous As_2O_3 reported by Bertoluzza *et al.*² exhibit an intense background extending from the laser line out to $\sim 100\text{ cm}^{-1}$. This background, which is undoubtedly due to parasitic scattering of the incident laser radiation, obscures the region below 100 cm^{-1} which contains important information on the low-frequency density of states and on the frequency dependence of the coupling coefficients involved in the light-scattering process. The spectra which we will report here extend down to $\sim 8\text{ cm}^{-1}$ and do not suffer from the above described limitations.

Both Beattie *et al.*³ and Brumbach and Rosenblatt⁴ have reported the Raman spectra of gaseous As_2O_3 which occur in the dimer form As_4O_6 . Because the results of these authors differ we have carefully reexamined the spectra of gaseous As_2O_3 .

Though we have examined the gaseous, liquid, and glass phases of As_2O_3 , we will concentrate in this paper on the glass-liquid transition. It has been generally recognized that the formation of a glass from a liquid is associated with diminishing

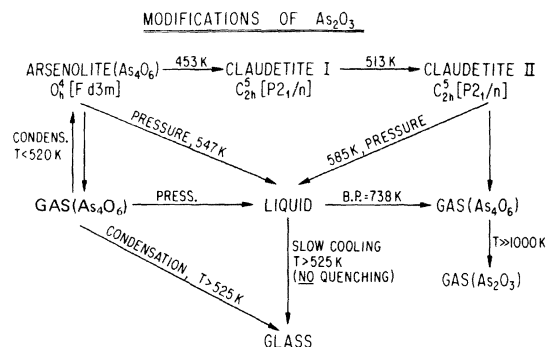


FIG. 1. Modifications of As_2O_3 including the space group symmetries of the crystalline phases.

fluidity. At a certain temperature the high-viscosity liquid becomes "rigid" thus yielding the vitreous state which in principle maintains its volume energy and liquid structure. The decrease in viscosity with increase in temperature of a glass-forming liquid has been attributed to both a breaking of the chemical bonds in order to permit flow units to migrate and to an increase of the available space in which the clusters can move. The stronger the bands to be broken, the larger the clusters which can move and the higher the viscosity.

To date there have been few detailed spectroscopic studies characterizing the possible structural differences between the vitreous and liquid states of glass-forming systems. Taylor *et al.* used infrared spectroscopy to study As_2Se_3 and $Tl_2Se \cdot As_2Te_3$ at temperatures up to 675 °K,⁶ while Finkman *et al.* studied the Raman spectra of As_2Se_3 in the temperature range 300–1040 K.⁷ Also the high-viscosity liquid of B_2O_3 has been studied using the Raman technique. Because the structures of As_2O_3 , As_2S_3 , and As_2Se_3 are quite similar in each of the phases they exhibit we will contrast our results with those of Taylor *et al.*⁶ and Finkman *et al.*⁷ It is worth noting at the outset however, that the interpretation of the As_2O_3 spectra is much simplified vis à vis the spectra of As_2Se_3 and As_2S_3 . The atomic masses of S and Se are high relative to O while the Raman and infrared bands of glasses and liquids are relatively broad. Thus the spectra of the As_2X_3 , $X = S, Se$ glasses and liquids are condensed in the region below 350 cm^{-1} ; independent determination of the position and polarization characteristics of many of the bands predicted to occur in these semiconducting materials is difficult if not impossible. In contrast, the spectra of vitreous and liquid As_2O_3 are spread beyond 600 cm^{-1} and provide for a more accurate determination of band characteristics.

II. EXPERIMENTAL DETAILS

A. Sample preparation

The many modifications of As_2O_3 ,⁹ and the space-group symmetries of the crystalline phases,¹⁰ are catalogued in Fig. 1. Also indicated in Fig. 1 by arrows are the pathways through which one particular phase can be transformed into another. For instance, arsenolite, the molecular crystal form, irreversibly transforms to claudetite I when heated to 453 K but reversibly transforms to As_4O_6 vapor at higher temperatures.

The starting material for the preparation of all forms of arsenic oxide was purchased from Baker Chemical Co., as an analytical reagent. Two different purification procedures were used: (a) The As_2O_3 from the bottle was either recrystallized twice from water solution yielding large ($\sim 1\text{ mm}$) crystals of arsenolite, or (b) the As_2O_3 was sublimed in closed quartz tubes and condensed as glass at temperatures between 200 and 250 °C. Samples of the glass were also prepared by melting and slow cooling of the recrystallized arsenolite. The Raman spectra of the glass samples prepared by either method were identical.

B. Apparatus

Each of the Raman spectra reported in this paper were recorded using the right-angle transmission scattering geometry. Either an Ar^+ or Kr^+ ion laser was used to excite the spectrum; the scattered radiation was dispersed by a Jarrel-Ash 25–100 double monochromator and detected by a cooled ($\approx -30\text{ }^\circ\text{C}$) ITT model FW 130 phototube coupled to a photon counting system. The depolarization spectra $\rho(\omega)$ reported here were computed from the ratio

$$\rho(\omega) = I_{HV}(\omega) / I_{VV}(\omega), \quad (1)$$

where the notation used in Eq. (1) is by now standardized.⁵

Low-temperature spectra of vitreous As_2O_3 were obtained from a $2 \times 3 \times 5\text{-mm}^3$ dislocation free parallelepiped which was polished with Linde polishing compound in "nujol" oil and mounted in a throttling-type optical cryostat manufactured by Andonian Associates, Waltham, Mass. Because of the low thermal conductivity of As_2O_3 , it is not feasible to use cold-finger-type cryostats if accurate low-temperature measurements are to be made. The throttling cryostat mentioned above has the advantage that the sample and thermometer (GaAs diode model TG 100 manufactured by Lakeshore Cryotronics Inc., Eden, N. Y.) are both in contact with cold helium gas. At 11.4 K peak signals of 4000 counts/sec were obtained with a spectral slit width of 3 cm^{-1} and 500 mW of incident laser power at 5145 \AA .

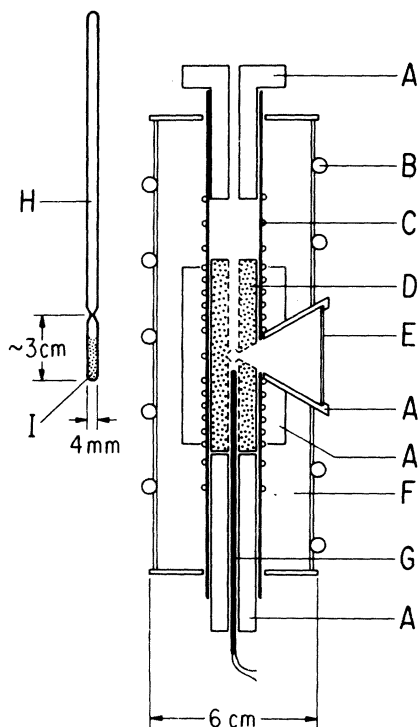


FIG. 2. Cut-away view of the high-temperature optical furnace and optical sample cell with manipulation rod. The materials used in construction of the furnace are designated as follows: A, lavite; B, copper tubing; C, kanthal wire; D, silver block; E, fused quartz window; F, insulating material, G, Pt-Pt-13%-Rh thermocouple; H, fused quartz manipulation rod; I, sample in optical cell.

To obtain high-temperature (up to 1200 K) spectra of the glass, liquid, and gas, a Kanthal wire water-cooled optical furnace was constructed. A cross-sectional view of the furnace is shown in Fig. 2. A metal block (silver block for $T < 1100$ K) inside the furnace minimized the temperature gradients to ± 2 K along the 3-cm optical cell (see description below). The temperature of the furnace was controlled with the use of a constant-voltage transformer and a Pt-Pt-13%-Rh thermocouple. The incident laser light passed perpendicular to the plane of Fig. 2 through the 4-mm hole in the center of the furnace and the scattered radiation was collected through the conical opening and window E of Fig. 2. With this furnace design, a collection aperture of $f/1.2$ was achieved.

The optical cells used for the study of the glass and the liquid at high temperatures were constructed from clear fused quartz tubing which was connected to a quartz manipulation rod. For a typical experiment an approximately 6-cm-long quartz tube was sealed at one end and was carefully cleaned and degassed in vacuum at ~ 1000 K. Crystals of arsenolite or chunks of vitreous As_2O_3 were placed in the tube, which was subsequently

evacuated and sealed. The sealed cell of approximate length 3 cm was connected to the manipulation rod and was placed in the furnace which had been preheated to a temperature above the melting point of arsenolite. Once initial optical alignment of the furnace with the cell in place was achieved, the apparatus remained undisturbed for the duration of a given set of temperature-dependent studies. On occasion, upon lowering the cell temperature below 430 K, the glass transition temperature of As_2O_3 ,¹¹ the quartz cell shattered.

To obtain the spectrum of gaseous As_4O_6 a cylindrical quartz tube of dimension 10 mm o. d. \times 3 cm long with a wall thickness of 1 mm was used. Prewighed amounts of As_2O_3 were transferred into a dry and degassed cell of known volume. The cell was then sealed under a vacuum of $\sim 10^{-6}$ Torr, attached to a manipulation rod, and placed into the optical furnace. The metal block D had been removed from the furnace and; consequently, higher-temperature gradients which increase with temperature were present. At 1200 K, the temperature variation along the ± 1.5 cm from the optical centerline of the furnace was ± 20 K.

The ir measurements reported here were made with a Digilab Fourier-transform spectrophotometer. Sample pellets of vitreous As_2O_3 were made using both KBr and CsBr. "Mull" samples of nujol oil and vitreous As_2O_3 were used to study the region below 200 cm^{-1} .

III. RESULTS AND DISCUSSION

A. Vitreous As_2O_3 , 11–300 K

In Fig. 3 is shown the low-temperature Stokes-anti-Stokes Raman spectra of vitreous As_2O_3 re-

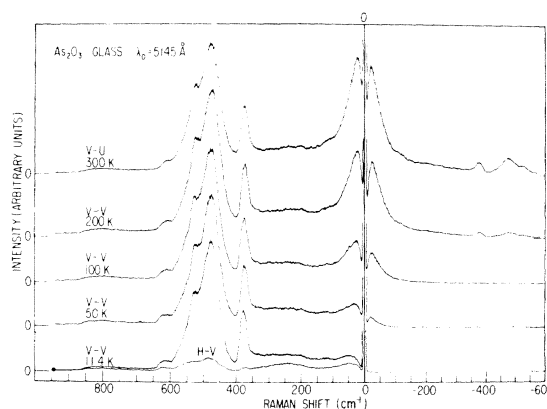


FIG. 3. Temperature dependence of the Stokes and anti-Stokes Raman spectrum of vitreous As_2O_3 in the range $11.4 < T < 300$ K. Polarization designations are given relative to the scattering plane by V—vertical, H—Horizontal, U—unanalyzed. Note that the abscissa of this spectrum and of all other Raman and depolarization spectra reported in this paper is linear in wavelength rather than wave number. The spectra were recorded with a spectral slit width of 3 cm^{-1} .

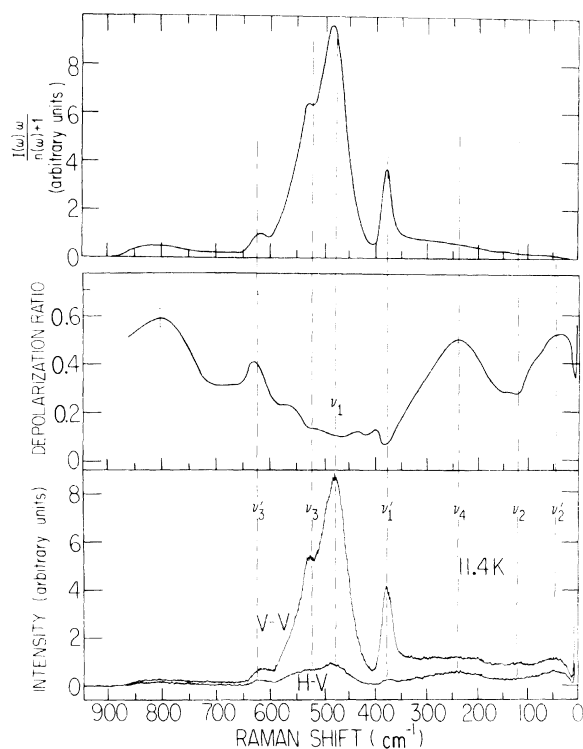


FIG. 4. Reduced Raman spectrum (top), depolarization spectrum (middle), and polarized Raman spectra (bottom) of vitreous As_2O_3 at 11.4 K. The spectra were excited with the 5145-Å line of an argon ion laser. The hatched vertical lines correspond to the frequencies of vibrational excitation calculated from a valence force field structural model for As_2O_3 [see Ref. 1 and Table I].

corded over the temperature range $11.4 \leq T \leq 300$ K. As expected the Boson peaks at $\approx \pm 50 \text{ cm}^{-1}$ which are characteristic of all glasses¹² are highly

temperature dependent especially in the anti-Stokes region. The spectra of Fig. 3 are quite similar in the range $\Delta\nu \geq +100 \text{ cm}^{-1}$, the only notable temperature dependence being a slight sharpening of some of the observable structure with decreasing temperature. It is clear from Fig. 3 that all of the spectral features observed including the broad band at $\sim 800 \text{ cm}^{-1}$ arise from a first-order Raman-scattering process.

In Fig. 4 we show respectively the reduced Raman spectra for the VV configuration, the depolarization spectrum and the 11.4-K Raman spectra from which the former were computed. The reduced Raman spectrum¹³ $R_{VV}(\omega)$ of Fig. 4(a) is computed from

$$R_{VV}(\omega) = \frac{\omega}{(\omega_0 - \omega)^4 [n(\omega) + 1]} I_{VV}(\omega), \quad (2)$$

where ω is the Raman shift, ω_0 is the frequency of the incident laser photon, and $n(\omega)$ is the temperature-dependent Bose-Einstein occupation number. The hatched vertical lines in Fig. 4 represent the frequencies of the vibrational excitations of vitreous As_2O_3 calculated from a valence force field molecular model as described previously.¹ Those bands designated ν'_i , $i = 1 \dots 3$ are modes of the As_2O "water" molecule while those designated ν_i , $i = 1 \dots 4$ are modes of the AsO_3 pyramidal unit. For completeness and for the purpose of reference in what follows we include here Table I of Ref. 1 summarizing the aforementioned calculation.

To further support the interpretation of the Raman spectrum of vitreous As_2O_3 given in Ref. 1 we show in Fig. 5 the room-temperature infrared transmission spectrum of vitreous As_2O_3 . The positions and polarization character of the room-tem-

TABLE I. Fundamental modes of vitreous As_2O_3 .

Band no.	Frequency (cm^{-1})	Polarization relative to lower frequency band	Assignment for AsO_3 "pyramidal" C_{3v} molecules, O-As-O band angle 114°		Assignment for As_2O "water" C_{2v} molecules, As-O-As band angle 125°		Intermolecular modes
			$k_1 = 2.061 \times 10^5$	$k_6/l^2 = 1.98 \times 10^4$	$k'_1 = k_1$	$k'_6/l^2 = k_1 \times 10^{-2}$	
I	~ 50	dp			56	ν'_2 ; $A_1(\text{p})$	
II	~ 125	p	144	$\nu_2, A_1(\text{p})$			
III	~ 250	dp	258	$\nu_4, E(\text{dp})$			
IV	370	p			376	ν'_1 ; $A_1(\text{p})$	
V	480	p	477	$\nu_1, A_1(\text{p})$			
VI	~ 525	dp	537	$\nu_3, E(\text{dp})$			
VII	(570) ^a	dp					$A'(\text{dp})$ or $A''(\text{dp})$ of C_s point group
VIII	~ 625	dp			627	ν'_3 ; $B_2(\text{dp})$	
IX	~ 800	dp					As_4 linkage

^aShoulder.

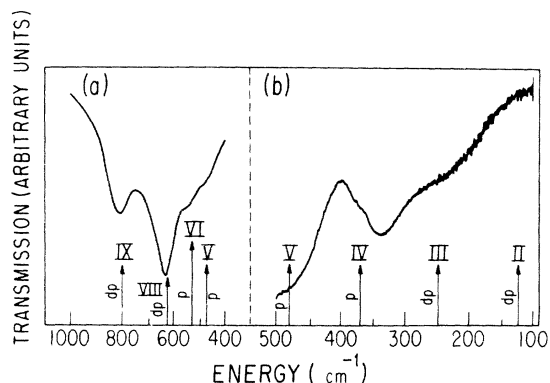


FIG. 5. Infrared transmission spectra of vitreous As_2O_3 recorded at 300 K. The positions and polarization characteristics (p=polarized, dp=depolarized) of the features observed in the Raman spectrum are indicated by vertical arrows and by Raman numerals that correspond to the band assignments of Table I.

perature Raman bands of vitreous As_2O_3 are indicated by vertical lines in Fig. 5 and by the symbols p and dp of Table I. As expected polarized Raman modes are invariably strong in the Raman spectrum and weak in the infrared spectra, while depolarized Raman modes exhibit strong infrared absorption bands and low Raman intensity.¹⁴ The infrared band at 255 cm^{-1} in Fig. 5 does not exhibit a companion band in the Raman spectrum, and its origin is to date unaccounted for by the molecular model.

Over the frequency range $0 \leq \omega \leq 50\text{ cm}^{-1}$ one expects

$$R_{\nu\nu}(\omega) = C_A(\omega)g(\omega), \quad (3)$$

where $C_A(\omega)$ is the coupling coefficient for scattering from acoustic modes and $g(\omega)$ is the density of vibrational states. In Fig. 6 we have plotted $R_{\nu\nu}(\omega)$ vs $\ln\omega$, $0 < \omega \leq 50\text{ cm}^{-1}$. Notice that the slope of the curve in Fig. 6 is 2.5. This indicates that $C_A(\omega)g(\omega) \propto \omega^{2.5}$. We expect $g(\omega)$ to be Debye like, i. e., $g(\omega) \propto \omega^2$ in the low-frequency region. If $g(\omega)$ does indeed vary as ω^2 , then $C_A(\omega) \propto \omega^{1/2}$ for $8\text{ cm}^{-1} \leq \omega \leq 50\text{ cm}^{-1}$. Thus $C(0) = 0$, as expected on theoretical grounds if the extrapolation of the $\omega^{1/2}$ behavior to frequencies lower than 8 cm^{-1} is valid.

B. Gaseous As_4O_6 , 800–1200 K

Gaseous arsenic oxide is known to be composed of As_4O_6 dimers.^{15,16} The four arsenic atoms form a tetrahedron and are bridged with oxygen atoms which are disposed on the corners of an octahedron. The point group symmetry of the molecule is T_d , thus the 24 vibrational modes can be group theoretically specified as follows³:

$$\Gamma_{\text{mol}} = 2A_1 + 2E + 2T_1 + 4T_2.$$

Of these modes the A_1 and E vibrations are Raman active, the T_1 vibration is infrared active, and the T_2 vibrations are simultaneously Raman and infrared active. We have measured the Raman spectra of As_4O_6 vapor at temperatures in the range 800–1200 K. The results of some of these measurements are shown in Fig. 7. Optical cells with pressures ranging from 0.2 to 1.5 atm at 1000 K were used. The position and polarization characteristics of all bands above 120 cm^{-1} measured by us are in essential agreement with the Raman spectra previously reported by Brumbach and Rosenblatt⁴ and Beattie *et al.*,³ whose measurements were in agreement above 120 cm^{-1} . However, in the region below 120 cm^{-1} Beattie *et al.* found a band at 99 cm^{-1} which was depolarized and was assigned to a T_2 vibration. In contrast, Brumbach and Rosenblatt found no bands below 185 cm^{-1} . We have therefore extensively studied the region below 120 cm^{-1} and have established that at all temperatures and pressures no Raman bands are present in this range. The 60-cm^{-1} band that appears in the 920-K spectrum of Fig. 7 is an instrumental artifact. Thus our results confirm the measurements of Brumbach *et al.* In Table II we compare our Raman measurements with those of Brumbach *et al.* and Beattie *et al.*

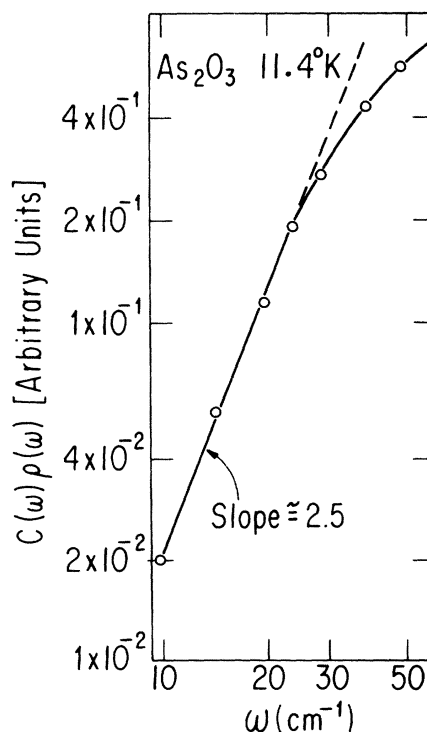


FIG. 6. Frequency dependence of the product of the Raman coupling coefficient and the low-frequency vibrational density of state of vitreous As_2O_3 .

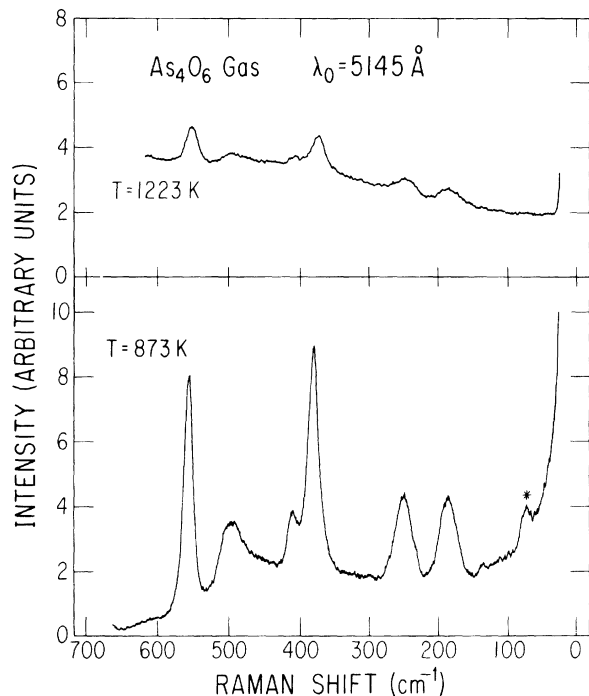


FIG. 7. Raman spectra of gaseous As_4O_6 . The asterisk in the lower figure indicates an experimental artifact. The spectra were recorded with a photon counting detection system and a spectral slit width of 8.5 cm^{-1} .

Early work on As_4O_6 vapors showed that the As_4O_6 dimers dissociate into As_2O_3 monomers at temperatures near 1050 K.¹⁷ We have attempted to study the fundamental modes of the monomer by studying the gaseous spectrum up to 1200 K. As can be seen from Fig. 7, the As_4O_6 bands appear to broaden and decrease in amplitude with increasing temperature but no new bands developed at high temperature. Moreover, no changes in the relative intensities of the bands are apparent. Clearly, at the highest temperatures we were able to achieve, the relative concentration of the monomer As_2O_3 was below a detectable value and probably less than 1%.

C. Glass-liquid transition 300–1120 K

Arsenic trioxide is the insulating member of the As_2X_3 , $X = \text{O}, \text{S}, \text{Se}, \text{Te}$ system of which the other members form semiconducting amorphous forms. The different compounds of the As_2X_3 system have remarkable structural similarities in the different forms they acquire. Most noteworthy is the fact that each compound acquires a layer crystalline form of C_{2h}^5 space-group symmetry, each acquires an As_4X_6 dimeric gaseous molecular form, and with the exception of the telluride, each forms a stable bulk glass.

This short-range order in the viscous liquid

forms of As_2X_3 , $X = \text{O}, \text{S}, \text{Se}, \text{Te}$ leads to the creation of structural units the vibrational states of which can be associated with the high-frequency ($\omega > 50 \text{ cm}^{-1}$) bands of the Raman spectrum. As in the case of molecular vitreous materials, both intramolecular and intermolecular vibrational states are present in the spectrum of the liquid. The presence of such intense high-frequency modes indicates that the structural relaxation time in the liquid is much longer than the time for vibration and that the bonding involved is partially covalent.

The low-frequency Raman spectra of simple liquids composed of spherical molecules exhibit the well-known polarized (VV) Rayleigh wing, while liquids of nonspherical molecules also yield a depolarized (HV) Rayleigh wing.¹⁸ Collision induced deformation of spherical molecule liquids can also yield a depolarized Rayleigh wing spectrum.¹⁹ There is evidence that the Rayleigh wing of viscous liquids which can extend to several hundred wave numbers contains a contribution from first-order phonon scattering processes associated with intermolecular vibrational states.⁸ Nevertheless, the translational and rotational diffusion contributions to the Rayleigh wing are not harmonic in character. Therefore the reduced Raman spectrum of the viscous liquid *cannot* simply be obtained by applying the formula in Eq. (2) to the spectrum of the liquid unless the contribution from collisional processes can first be subtracted from the total spectrum.

In Fig. 8 we show the temperature dependence of the Stokes Raman spectra of vitreous and liquid As_2O_3 over the range $300 \leq T \leq 1100 \text{ K}$. With the exception of the 300-K trace, the spectra were recorded consecutively in an undisturbed experimental configuration and can thus be compared directly. The low-frequency spectra at room temperature and below the glass transition temperature ($T_g = 430 \text{ K}$) are quite similar to the spectra of Fig. 3. Above T_g the Boson peak disappears and the Rayleigh wings become quite prominent.

There is very little change in either the position or polarization character of the high-frequency high-temperature Raman spectra as the transition

TABLE II. Assignments of the As_4O_6 gas raman-active vibrations.

Mode	Beattie (Ref. 3)	Brumbach (Ref. 4)	This work
T_2	:99 ^a		
E	184	185	185
T_2	253	253	253
A_1	381	381	381
E	(409)	409	409
T_2	492	496	496
A_1	560	555	556

^aBand not found in this work and Ref. 4.

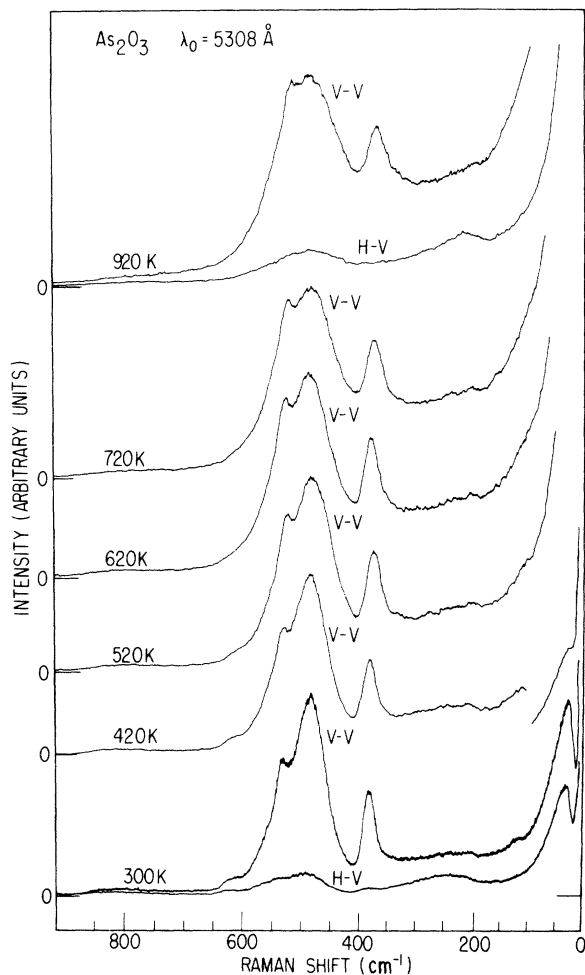


FIG. 8. Polarized Raman spectra of As_2O_3 above and below the glass transition temperature of 430 K recorded with a spectral slit width of 3 cm^{-1} .

is made from the vitreous to the liquid state. Thus as in the case of As_2S_3 ,⁷ the structures of glassy and liquid As_2O_3 are apparently quite similar. Consequently, structural models which have been successfully applied to the glass are probably equally valid for the liquid at temperatures near T_g .

The activation energy associated with the integrated intensity of the mode at 376 cm^{-1} can be obtained from the plot of $\ln R_{VV}(\omega)$ vs $1000/T$ as shown in Fig. 9. The slope of the line in Fig. 9 is equal to E_a/kT , where E_a is the activation energy. To obtain the integrated intensity we estimated the shape of the background upon which the 376-cm^{-1} line was superposed. While such an estimate yielded integrated intensities accurate to $\sim 10\%$ for the 376-cm^{-1} mode a corresponding estimate for other bands in the spectrum was precluded by the wing background.

In Fig. 10 we have plotted $\ln(\Gamma_{1/2}/1.634)$ vs

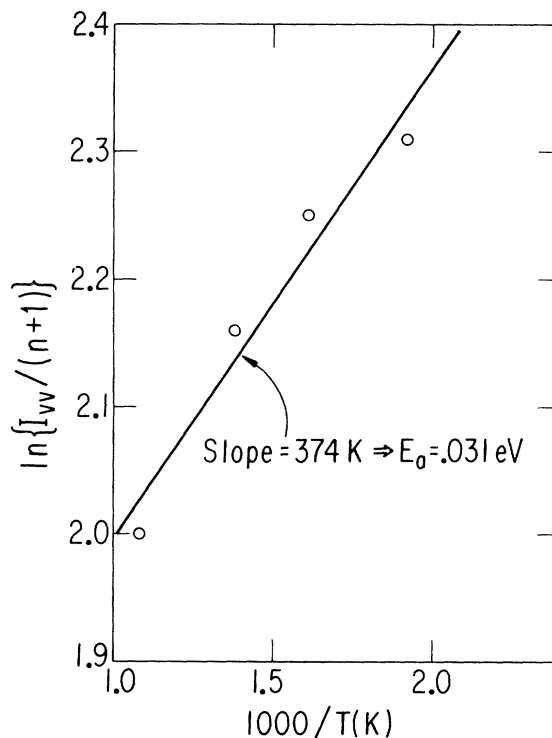


FIG. 9. Temperature dependence of the relative reduced VV Raman intensity of the 376 cm^{-1} band. The line is a least-squares fit to the data. The intensity is proportional to $e^{E_a/kT}$, where E_a is the activation energy and is equal to 0.031 eV .

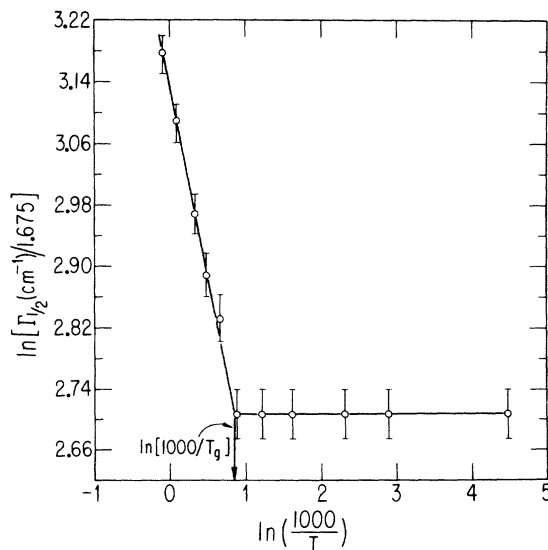


FIG. 10. Temperature dependence of the full width at half-maximum of the 376-cm^{-1} bond. The slope of the line for $T > T_g$ is $\frac{1}{2}$. The observed linewidth in millimeters converted to cm^{-1} by dividing by 1.675 as indicated in the abscissa.

$\ln(1000/T)$ for the 376-cm⁻¹ band over a temperature range spanning the glassy and liquid states. Here $\Gamma_{1/2}$ is the full width at half-maximum of the band. As can be seen from Fig. 10 the temperature dependence of the half-width in question is

$$\begin{aligned} \Gamma_{1/2}(T) &= 25 \text{ cm}^{-1}, & T \leq T_g - \epsilon, \\ \Gamma_{1/2}(T) &= 1.214 T^{1/2} \text{ cm}^{-1}, & T \geq T_g + \epsilon, \end{aligned} \quad (4)$$

where ϵ is a small but as yet undetermined temperature. Our inclusion of the value ϵ in Eq. (4) indicates that we do not think that $\Gamma_{1/2}$ for the 376-cm⁻¹ band is truly discontinuous at T_g . It is remarkable that the extrapolated \ln - \ln plot straight-line temperature dependences of $\Gamma_{1/2}$ for the glass and liquid states intersect at a value of $(\ln 1000/T)$ corresponding to a temperature of 429 °K which is (to within experimental error) equal to the glass transition temperature.

Qualitatively one expects that anharmonic effects will engender an increase in the linewidth of a given band with increasing temperature. This is especially true in the liquid state and at temperatures for which $kT \geq h\omega$, where, in the case of interest, the inequality occurs at a value of T given by $T = h\omega/k = 376 \text{ cm}^{-1}/k = 564 \text{ K}$ and well below the 920-K maximum temperature at which liquid As₂O₃ was studied. The $T^{1/2}$ dependence of $\Gamma_{1/2}$ suggests that the bandwidth is associated with the root-mean-square amplitude of the normal coordinate of the ν'_1 vibrational mode (see Table I). While the root-mean-square amplitude is temperature dependent, the As-O-As equilibrium bond angle is temperature independent for reasons which will be enumerated shortly.

Upon considering Fig. 9 again one notices additional temperature-dependent changes in the spectra that occur only in the liquid state. In Fig. 11 are plotted the temperature dependences of the peak positions of the ν_1 , ν_3 , and ν'_1 bands of the liquid. The ν_1 and ν_3 frequencies do shift somewhat towards each other with an increase in temperature, whereas the ν'_1 band position is temperature independent. In contrast the positions of corresponding bands of vitreous As₂O₃ are temperature independent over the range $4.2 \leq T \leq 420 \text{ K}$ as can be seen also from Fig. 11.

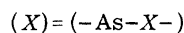
To explain the results of Figs. 8–11 we must employ a model that relates the microstructural features of glassy As₂O₃ to those of the liquid phase as manifested through the optical spectra. There currently exist three related structural models of bulk As₂X₃ type glasses:

(i) Lucovsky-Martin model²⁰—in this model the basic structural units are AsX₃ pyramids and As₂X bridging “water” molecules. The vibrational modes and symmetries of the optical spectra are deduced by applying valence force field calcu-

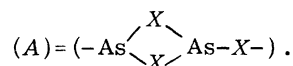
lations to the structural units which are (in the lowest approximation) treated as uncoupled.

(ii) Layer model^{8,21}—in this model proposed by Taylor *et al.* the basic structural units are distorted layers similar to but not as spatially extended as the layers which characterize the monoclinic crystalline forms. Such layers are of course built up from the AsX₃ and As₂X units of the Lucovsky-Martin model.

(iii) Composite model⁷—Finkman *et al.* have proposed a structural model for the glass and liquids which incorporates features of both the Lucovsky-Martin model and the layer model. In particular, they have suggested that both (X) and (A) structural units are present simultaneously in the disordered phases where



and



The layers of the layer modes are composed of only (X) units while the (A) units form disordered chainlike structures. There is evidence from work on vitreous As₂O₃ that (A) units exist in that material.¹

In support of the layer model, Taylor *et al.* have reported infrared studies of the glass liquid transition in As₂Se₃ and Tl₂Se · As₂Se₃.⁶ They find that certain modes at 189 and 246 cm⁻¹ which they associate with intralayer vibrations persist in Tl₂Se · As₂Se₃ to a temperature T_s significantly above T_g but these modes catastrophically attenuate at temperatures $T > T_s$. Moreover Taylor *et al.* suggest that all As₂X₃ type glasses exhibit a characteristic temperature T_s at which the layers dis-

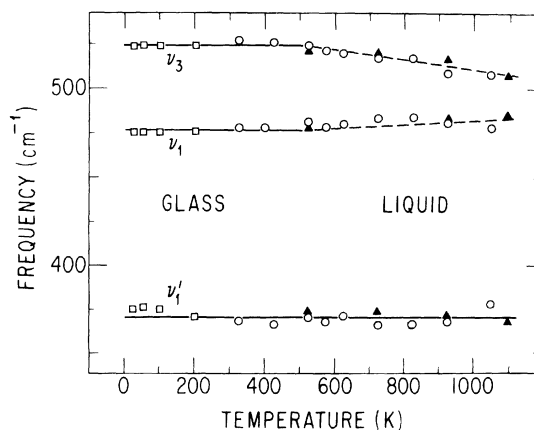


FIG. 11. Temperature dependence of the frequencies of the ν_3 , ν_1 , and ν'_1 bands of vitreous and liquid As₂O₃ (see text and Table I for explanation of band labels). (□): From data presented in Fig. 3; (○): From data presented in Fig. 8; (▲): From data not presented here.

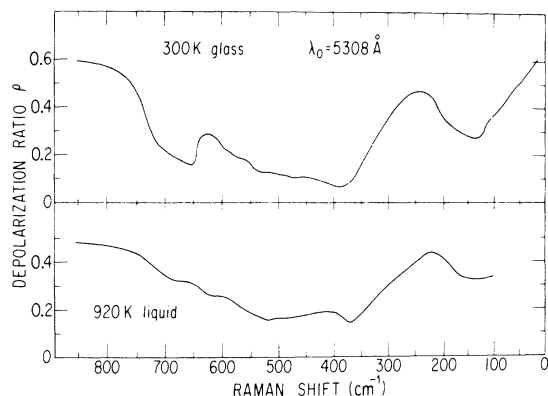


FIG. 12. Depolarization spectra of vitreous and liquid As_2O_3 .

integrate while at T_g the drop in viscosity of these materials can be attributed to the severing of interlayer bonds. The temperature T_g is approximately the temperature at which $10^3 \leq \eta \leq 10^4$ P, where η is the viscosity.⁶

The results of Figs. 8 and 9 are definitely incompatible with the layer model of Taylor *et al.* with respect to the presence of a characteristic temperature T_g . As can be seen from Fig. 8, virtually all of the prominent bands in the Raman spectrum of liquid As_2O_3 persist up to a temperature of 1100 K even though the value of T_g deduced from viscosity data²² should lie in the range $625 < T_g < 725$ K. Moreover, as can be seen from Fig. 12, the depolarization spectrum of the liquid at 920 K is quite similar in shape to that recorded at 300 K. The above results indicate that the structures of the glass at 300 K and the liquid at $T = 920$ K $\sim 1.5T_g$ are quite similar: there is no evidence of layer disintegration of the type suggested by Taylor *et al.*^{6,21} Our results are in agreement with those of Finkman *et al.*⁷ who observed the persistence of all prominent Raman bands in As_2S_3 up to 1040 K.

The modes at 189 and 246 cm^{-1} that characterize the onset of T_g in $\text{Tl}_2\text{Se} \cdot \text{AsSe}_3$ are well split in frequency from the 237- cm^{-1} mode of As_2Se_3 with which they have been associated. Thus those modes are inherent to the alloy. It is possible that at the temperature T_g a microscopic liquid-liquid phase separation occurs in vitreous $\text{Tl}_2\text{Se} \cdot \text{As}_2\text{Se}_3$ and that this phase separation, not the disintegration of the layers, causes the disappearance of the 189- and 246- cm^{-1} alloy modes. Such a hypothesis is compatible with the result that the widths of the above mentioned lines are temperature independent above T_g . In contrast, if the layers were indeed disintegrating at T_g one would expect the linewidths of the intralayer vibrations to be temperature dependent at temperatures $T \leq T_g$. In any case the T_g phenomena reported for TlSe_2

$\cdot \text{As}_2\text{Se}_3$ is apparently unique to that substance and not a general property of bulk As_2X_3 -type glasses.

While we cannot support the " T_g " aspect of the layer model we find that the layer and Lucovsky-Martin models are more similar than dissimilar. For instance, what minimum number of strongly coupled molecular units constitute a layer and what minimum coupling must obtain before the AsX_3 units from which the layers are constructed can be treated as molecular? Such questions represent differences in degree, not in kind.

Let us now turn again to the data of Figs. 8 and 11. We have been unable to distinguish experimentally whether the shifts of ν_1 and ν_3 with temperature are real or result only from the thermal broadening and overlap of two bands the peak positions of which are temperature independent. Nevertheless, a real shift in the positions of ν_1 and ν_3 is quite consistent with the composite model of Finkman *et al.*, as we now show.

Recent thermodynamic data on a series of metal halides^{23,24} (MX_2 : $M = \text{Mn, Zn, } \dots$; $X = \text{Cl, Br}$) have indicated that an increase in temperature enhances the covalency between nearest neighbors ($M-X$), while the interactions responsible for network-type structures are weakened. For liquid As_2O_3 , this would imply stronger k_1 (or k'_1) and $k_2 = k'_2/l^2$ but weaker k'_2/l^2 force constants (see Table I for force-constant labeling). For fixed angles α and β , where α is the apex angle of the AsX_3 unit and β is the As-X-As bond angle, and for fixed k_1/k_2 ratios, we have calculated the ν_i and ν'_i frequencies of the AsX_3 and As_2X units as a function of the stretching force constant k_1 . The results of that calculation indicate that all of the ν_i and ν'_i frequencies increase with increasing $k_1 (= k'_1)$. This result is incompatible with Fig. 11. However, assuming no dramatic force-constant changes we have also calculated the frequencies ν'_i and ν_i for various molecular angles α and β . The dependence of ν_i , $i = 1 \dots 4$ on the bond angle α and of ν_1 , $i = 1 \dots 3$ on β are shown in Fig. 13. (See also Fig. 2 of Ref. 1.) An increase in the bond angle α with increasing temperature would result in a displacement of ν_1 and ν_3 , in which the difference $|\nu_3 - \nu_1|$ increased with temperature. This result is opposite to the behavior exhibited in Fig. 11. It is however possible that the temperature increase leads to a breaking of the network-type structure and to more "closed" cluster units in which the bond angles are smaller. This phenomena is illustrated in Fig. 14 in which we show a two-dimensional network. The breaking of the As-O bonds at the points intersected by the dashed lines yields As and O atoms which will tend to maintain their valencies by forming bonds with near neighbors. This process will generate more compact cluster units.

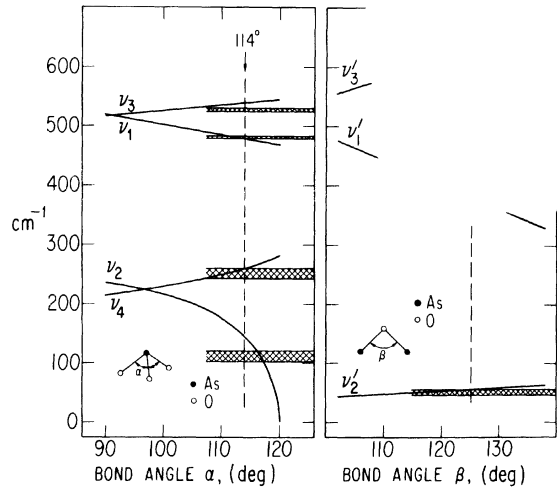


FIG. 13. Frequency dependence of the normal modes of the As_2O_3 pyramidal units as a function of apex angle α with fixed force constants k_1 and k_6/l^2 as given in Table I (left-hand side of figure) and the frequency dependence of the normal modes of the $\text{As}-\text{O}-\text{As}$ "water molecule" as a function of the bridging band angle β for fixed force constants $k'_1 = k_1$ and $k'_6 = k_1 \times 10^{-2}$ as given in Table I (right-hand side of figure). The solid curves represent calculated frequencies. The horizontal hatched regions indicated experimentally measured values and their uncertainties.

For As_2O_3 , the smallest and most stable high-temperature unit is undoubtedly the As_4O_6 molecule which forms in the gas phase and in arsenolite crystals. In the liquid near T_g , the angles α and β are very close to those found in the glass, i. e., $\alpha \approx 114^\circ$ and $\beta \approx 125^\circ$. In addition, the $\text{As}-\text{O}-\text{As}$ angle β is the same in the gas,^{15,16} liquid,¹ claudetite,⁹ and arsenolite⁹ phases or $\beta = 125^\circ \pm 3^\circ$. Therefore we assume that temperature-dependent structural changes in the liquid do not affect β . In particular, as the bonds of (X) units of the composite model break and heal into (A) units, the 376-cm^{-1} band associated with the ν'_1 water molecule vibration remains constant in frequency because the angle β is constant. In contrast the pyramidal angle α is larger in the glass and liquid¹

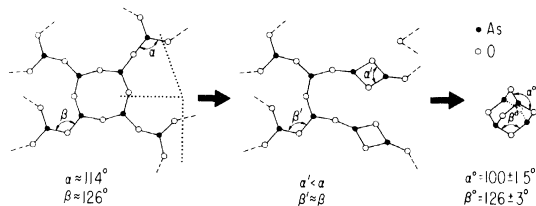


FIG. 14. Two-dimensional diagrammatic representation of bonding changes with temperature as vitreous As_2O_3 is heated through the glass transition temperature. The dotted lines indicate bonds which are broken.

(114°) than in the gas and crystalline phases (100°). In the hypothetical case of a superheated liquid the molecular units will tend to be the same as those of the undercooled gas, i. e., As_4O_6 molecules for which $\alpha = 100^\circ$. In other words, as the layer network of (X) units break up and transforms to (A) units the pyramidal angle α decreases, whereas the water type bond angle β remains constant. This process gives a reasonable explanation for both the temperature shifts of the ν_1 and ν_3 modes and the stability of the ν'_1 mode.

IV. CONCLUSIONS

Clearly the structural model most compatible with our Raman and infrared results for As_2O_3 is the composite model. In particular, we note that the Rayleigh wing spectrum of the liquid is highly depolarized, as can be seen from Fig. 8. Thus the structural units in the glass and liquid are optically highly anisotropic and very likely layerlike. In fact the Rayleigh spectrum (specifically its frequency and wave-vector dependence) of the liquid near T_g contains significant but as yet untapped information on the size and shape of the structural units from which the glass and liquid are constructed. For this reason we plan an extensive study of the Rayleigh spectra of bulk As_2X_3 -type glasses and liquids.

A note of caution is in order with respect to the interpretation of structural features from viscosity data. For instance, Taylor *et al.*⁶ reference the viscosity studies of Nemilov²⁵ as evidence for the layer like two-dimensional structures in vitreous As_2Se_3 . Yet Nemilov concludes from his viscosity measurements that As_2Se_3 is a three-dimensional network glass while As_2S_3 is a two-dimensional type. This discrepancy may be a manifestation of the extent of the layer units and of a reduced anisotropy in the correlation range for As_2Se_3 caused by severe warping of the layer units.

We noted in the introduction that there has been a tendency in the literature to associate the structure of the glass phase of a substance with the structure of a given crystalline phase by comparing only the positions of the bands in the respective optical spectra. We will show in the following paper that such a comparison is not sufficient for As_2O_3 . The prominent bands of *both* arsenolite and claudetite overlap the bands of vitreous As_2O_3 . However we shall show in the following paper that the band polarization characteristics of the glass are compatible with those of claudetite but are incompatible with arsenolite. This result is to be expected since the glass contains layerlike structural units very similar to the layers that characterize the structure of claudetite.

Finally, the glass transition temperature of As_2O_3 can be determined relatively accurately ($\pm 2\%$)

from the temperature dependence of the linewidth of the As_2O_3 symmetric stretching vibration. It would be interesting to see if the glass transition temperatures of other layer like glasses can be

similarly determined.

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