We report the first measurements of anti-Stokes Raman scattering in trans polyacetylene. The lineshapes are quite consistent with a disorder model in which the variation is attributed, for instance, to a disorder-induced distribution of conjugation lengths. The results suggest that the recently proposed hot luminescence model makes no significant contribution to the variation in the Raman lineshape with incident photon energy.

IT HAS BEEN KNOWN for some time that the Raman lineshape in trans polyacetylene varies dramatically with excitation wavelength [1–4]. This is especially true of the two vibrational modes at $v_1 = 1070 \text{ cm}^{-1}$ and $v_2 = 1460 \text{ cm}^{-1}$ which have mixed single and double bond character and both of which are strongly coupled to the main electronic excitation band. With excitation near the absorption edge ($\sim 12000 \text{ cm}^{-1}$) a relatively narrow line is obtained for both these modes [5]. Excitation at higher energies, well into the absorption band, yields a sideband on the high frequency side of these Raman bands, which shifts to still higher frequencies as the excitation energy is increased. The initial explanation [2–4] put forward for this phenomenon, the disorder model, was that trans polyacetylene (PA) is composed of a distribution of conjugation lengths, i.e., the length over which conjugation is maintained without disruption by a chemical or structural defect. This explanation, which has important implications for all aspects of the electronic characterization of polyacetylene, has been questioned in recent work suggesting that hot luminescence in long chains is primarily responsible for this phenomenon [1].

In this paper we present for the first time results on anti-Stokes Raman scattering in trans PA. These data suggest that hot luminescence as described by Mele [1] makes no significant contribution to the Raman profiles. Our results are completely consistent with the disorder model and further emphasize the important role played by disorder in trans PA [6–8].

The electronic properties of trans PA, and other conjugated systems, extrapolate to those of the finite chain polymer with roughly a reciprocal chain length dependence, due to the increased delocalization of the $\pi$ electron density with increasing chain length. The optical absorption frequency varies with conjugation length, $n$, approximately as $[9–10]$

$$\omega(n) = 12000 + 70000/n \text{ cm}^{-1}. \quad (1)$$

The Raman frequencies, designated $v_1$ and $v_2$ respectively, follow a similar empirical relationship. For example in the $v_2$ case which has been most extensively studied, the variation is approximately [3]

$$v_2(n) = 1460 + 700/n \text{ cm}^{-1}. \quad (2)$$

In the disorder model, there is a distribution of conjugation lengths extending down to very small values of $n$. When the excitation frequency is near the absorption maximum for a segment of length $n$, the Raman profile will have an enhanced contribution from that segment due to the resonance Raman effect. In other words, that segment has been photoselected [9]. This basic model yields a fairly good (semi-quantitative) description of the Raman profiles and their variation with excitation frequency [2, 3]. To obtain a better fit to the experimental data other workers have used a $1/n^2$ dependence for long conjugation segments and a $1/n$ dependence for short segments [4]. A generalized version of the disorder model has been described by Vardeny et al. [11]. They show that a distribution in electron–phonon coupling
constants with normal Raman scattering processes (i.e., no hot luminescence) yields a reasonable fit to the Raman and infrared data, but do not discuss the physical origin of this distribution. We believe the physical origin of the disorder is most likely to be a distribution of conjugation lengths, this being most clearly the case with excitation below 600 nm [5]. In any case since the model of Vardeny et al. [11] deals with normal Raman processes, it is for our purposes indistinguishable from that based on a specific conjugation length distribution.

Mele [1] has suggested an alternative model to explain the Raman profiles which does not require disorder. Trans PA is assumed to consist only of very long conjugation length molecules; however the initially prepared wavepacket of the excited state is assumed to evolve prior to emission. This evolution results in an excitation energy dependent broadening of the lineshape. Thus the broadening is assigned to hot luminescence, not a Raman process. This model yields Raman profiles which agree qualitatively with experiment. Recently employing excitation profiles at various Raman frequencies, Lauchlan et al. [12] have lent their support to the hot luminescence (HL) model and have criticized the disorder model [13].

A qualitative illustration of the two competing models is shown in Fig. 1. For the disorder model, the process is just normal Raman scattering. Disorder produces a dispersion in the electronic and vibrational states, with photoselection via the resonance Raman effect enhancing the contribution on those states near the excitation frequency of the incident laser (ωs). In the HL model for the Stokes case, two processes can be described which could yield scattered photons near (but removed from) the Raman line. If the energy relaxation involves excitation of low frequency lattice modes (vL), we have case a in the figure. This process, discussed here by us but not considered by Mele, could yield the observed Stokes lineshape when vL is on the order of the observed Raman linewidth (about 100 cm⁻¹). In the second case, which has been treated in Mele’s simulation [1] of the scattering process, the wavepacket evolution on the excited potential surface involves excitation of the vibrational mode vL. Mele assumes that vL has a similar dispersion to that calculated for the ground state v1. In this case, emission is back to the ground state and the observed Raman lineshape is attributed to a combination of the normal Raman process with a sideband to lower energies determined by the vL - v1 difference.

Consider now the anti-Stokes Raman experiment. In the disorder model, the outgoing photon is ω' = ωs + v1, as illustrated in Fig. 1. Thus the anti-Stokes spectrum will be the mirror image of the Stokes spectrum. In the HL case, anti-Stokes scattering yields photons at ω' = ωs + v1 - vL in case a or ω' = ωs + v1 - vL in case b.

The latter, considered in detail by Mele, will not yield any intensity near the anti-Stokes line. Case a in the HL model could yield appreciable intensity near the normal anti-Stokes line, but not with a mirror image relationship to the Stokes line.

There is an additional relaxation process which will yield anti-Stokes intensity, labeled c in the figure. Energetically this process is the opposite to that considered explicitly by Mele, in that a phonon is absorbed prior to emission, yielding an emitted photon at ω' = ωs - v1 and ω' = ωs + v1 - vL. In case c, the anti-Stokes emission occurs after phonon absorption in the excited state so that ω' = ωs + v1.

Fig. 1. Schematic diagram for Stokes and anti-Stokes scattering. At the top, the normal Raman processes are shown as they would be applied in the disorder model. For the hot luminescence process, case a represents energy relaxation via low frequency lattice modes so that ω' = ωs - vL and ω' = ωs + v1 - vL. In case b, the process considered explicitly by Mele [1], the energy relaxation is via excitation of vL so that ω' = ωs - vL and ω' = ωs + v1 - vL. In case c, the anti-Stokes emission occurs after phonon absorption in the excited state so that ω' = ωs + v1.
thermal equilibrium, so that the S/AS ratio would now be given by \( \exp\left(-2\frac{\hbar v^2}{kT}\right) \) since the emitting state for the Stokes process has energy \( \omega_a - v_1^* \) while that for the anti-Stokes process is \( \omega_a + v_1^* \). Thus the S/AS ratio for the case of a thermalized distribution in the HL model would be \( \sim 3 \times 10^4 \). The rate of vibrational relaxation which produces thermal equilibrium thus determines the S/AS ratio in the HL model. Vibrational relaxation processes are known to be fast (subpicosecond) in large organic molecules in condensed phases at the high temperatures of our experiments [15]. Moreover, the width of our lines imply that the experiment is sensitive to times on the picosecond scale. Thus the experiment should be in the intermediate time regime where the populations of the relevant states will be affected by relaxation processes; therefore, the S/AS ratio (in the HL model) is predicted to be intermediate between \( \exp\left(-\frac{\hbar v^2}{kT}\right) \) and \( \exp\left(-2\frac{\hbar v^2}{kT}\right) \).

*Trans* PA was obtained by dopant-induced isomerization of *cis*-rich PA films of approximately 100 \( \mu \)m thickness. This process has been shown to yield higher quality *trans* PA films than thermal isomerization [8]. Raman spectra were recorded in front surface scattering geometry with a Spectra Physics model 166 Argon ion laser and a Spex 1402 double monochromator. Since all experiments were carried out at room temperature, laser power was kept below 10 mW to avoid damage to the sample. A single scan was sufficient for a good signal-to-noise ratio in the Stokes mode; in the anti-Stokes mode typically 50 scans were averaged. We chose \( v_1 \) for this investigation, since the intensity of the anti-Stokes emission is reduced by a Boltzmann factor, \( \exp\left(-\frac{\hbar v_1^*}{kT}\right) \), compared to the Stokes emission. For \( v_1 \), this translates to a factor of about 170 at 1065 cm\(^{-1}\). (For \( v_2 \), the factor would be about 1200.) We observe a Stokes/anti-Stokes ratio of about 200, as expected for normal Raman scattering and not nearly large enough for the relaxation-dominated HL model to be important.

Care must be taken in selecting the excitation frequency in the anti-Stokes experiment (\( \omega_a \)) for comparison to the Raman lineshape obtained in a Stokes experiment at \( \omega_s \) [16]. Within the disorder model we want to maintain at least approximately the same resonance conditions with the \( n \) distribution. Resonance effects will be important at both the excitation frequency and the scattered frequency, \( \omega_a \) and \( \omega_a - v_1 \) for the Stokes experiment and \( \omega_a \) and \( \omega_a + v_1 \) for the anti-Stokes experiment. Therefore, we expect resonance effects of the lineshapes to be roughly the same if we choose \( \omega_a - \omega_a \sim v_1 \). For cases \( a \) and \( b \) in the HL model, we want the state prepared by the excitation beam to be at the same energy in the Stokes and anti-Stokes experiments [1]; since excitation is from a vibrationally hot ground state (see Fig. 1), this is again best achieved with

\[ \omega_a - \omega_a \sim v_1. \]

With the Argon laser lines available to us, this excitation condition is approximately met with \( \omega_a \) at 488.0 nm and \( \omega_a \) at 514.5 nm (\( \omega_a - \omega_a = 1055 \) cm\(^{-1}\)) and with \( \omega_a \) at 476.5 nm (\( \omega_a - \omega_a = 852 \) cm\(^{-1}\)). These excitation conditions are used in the experiments described here and provide a straightforward comparison of the models without the complications of absorption, reflection, and resonance corrections.

Results are shown in Figs. 2 and 3 along with the anti-Stokes spectra predicted with the disorder model. We have not generated the theoretical curves from first principles, but have instead generated the theoretical expectation for the anti-Stokes spectrum based on the lineshape of the experimentally observed Stokes spectrum. As pointed out above, the disorder model predicts that the anti-Stokes lineshape (due to the disorder-induced dispersion in \( v_1 \) values) should be the mirror image of the Stokes lineshape, and the theoretical curves have been constructed accordingly for the figures.

A detailed calculation of the anti-Stokes spectrum in the HL model requires more than knowledge of the
Fig. 3. Same as Fig. 2, except the Stokes incident frequency is 21840 cm$^{-1}$ (457.9 nm) and the anti-Stokes incident frequency is 20990 cm$^{-1}$ (476.5 nm).

Stokes spectrum. Nevertheless, a useful qualitative picture can be obtained. The HL model assumes that the initially absorbed photon excites the molecule electronically, but leaves the vibrational state unchanged. In case $a$, this vibrational state then relaxes and due to the electron–phonon coupling, scatters the electron from state to state while losing energy to the lattice. In case $b$, the state relaxes by emitting a $\nu_1^e$ phonon and fluoresces to return to the ground state (Fig. 1). Clearly, the initially prepared vibrational state will differ in the anti-Stokes experiment from the Stokes experiment, since in the former case the initially prepared state has one quantum of ground state vibrational energy. In addition, there will be a distribution of vibrational states in the anti-Stokes experiment due to the large density-of-states of excited vibrational levels. All of these factors make the anti-Stokes spectrum difficult to calculate in the HL model. However, it is clear that independent of the initial state, cases $a$ and $b$ in the HL model predict relaxation of the population so that the outgoing photons will be largely of lower energy than those from the unrelaxed molecules. For case $a$ in Fig. 1, the qualitative prediction in the HL model would be that the hot luminescence would appear as a sideband on the low energy side of the anti-Stokes line, whereas the experiment yields a sideband on the high energy side. For case $b$ described by Mele [1], no sideband is expected, whereas the experiment yields a sideband very similar to that observed in the Stokes mode.

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REFERENCES
13. We do not accept the arguments of [12] for several reasons: (1) In his thesis Imhoff [14] has pointed out the problems associated with the correction of Raman spectra for the optical constants of (CH)x. The main argument in [12], the flatness of the 1510 cm⁻¹ excitation profile, appears to be an artifact of the adopted correction procedure. The complex morphology of the sample, the correct specular reflectance [7] and the presence of diffuse scattering [18] all have to be taken into account to arrive at reliable excitation profiles. (2) The failure to extend the measurements to high frequencies where short chains make their maximum contribution seriously compromises the conclusions of [12]. (3) The complications introduced into excitation profiles at different Raman frequencies ("sliced" profiles) by large intrinsic linewidths are neglected. These large linewidths lead to overlapping contributions at any given Raman frequency from various species (chain lengths) within the inhomogeneous distribution. For example, the Raman linewidth is about 25 cm⁻¹ with red excitation (long chains only) and only about 70 cm⁻¹ with blue excitation (see Figs. 2–3).
17. Note also that if we make a Boltzmann correction to the anti-Stokes spectra, the agreement with the disorder model is improved. For example, the intensity at 1110 cm⁻¹ would be increased by about 25% with respect to that at 1065 cm⁻¹ by this correction.