Experimental determination of conjugation lengths in long polyene chains

Bryan E. Kohler

Chemistry Department, University of California, Riverside, California 92521

I. D. W. Samuel
Cavendish Laboratory, Madingley Road, Cambridge, CB3 OHE, United Kingdom

(Received 13 February 1995; accepted 11 July 1995)

Since the low energy absorption spectrum of a linear polyene is dominated by the strongly allowed $1^1A_g \rightarrow 1^1B_u$ transition ($S_0$ to $S_2$), it can be reconstructed for any chain length if the 0–0 band excitation energy, the band profile, and intensity are known. From this premise, this paper uses information developed in high resolution experiments on well-defined linear polyenes to extract the distribution of effective conjugation lengths from absorption spectra of solutions of long linear polyenes. These distributions are found to be dominated by short conjugation lengths. © 1995 American Institute of Physics.

I. INTRODUCTION

Linear polyenes may be specified by their chain length $N$, the number of conjugated double bonds (translational repeat units in the bond alternating polyene backbone) as indicated in the diagram below.

Knowledge of how the nonlinear optical response of a linear polyene depends on the number of conjugated double bonds is not only of fundamental importance, it is one of the key issues to be considered in designing new polymeric materials. While this dependence is open to experimental investigation, systematic studies have been inhibited by the lack of methods for synthesizing long polyene chains. This synthetic problem now appears to be well in hand, which has made possible the recent measurements of $\chi^2$ for a series of model polyene oligomers with up to 240 conjugated double bonds by Samuel et al. However, one problem remains. Even though chemical analysis leaves little doubt as to the number of repeat units in these long polyene chains, the conformations are not known and so neither is the distribution of effective conjugation lengths. This paper presents a method for estimating this distribution for a given polyene from the room temperature absorption spectrum. This method is then applied to the absorption spectra for polyenes with $N=28$, 39, 68, 88, 152, and 240 as measured by Samuel et al. A model for the distribution of conjugation lengths in long polyene chains that accounts for the distributions derived in this paper is presented in a second paper.

II. MODELING THE ABSORPTION SPECTRUM

Given a reference library of absorption spectra for planar all-trans linear polyenes, the decomposition of a measured absorption spectrum into an oligomer distribution would be straightforward, at least, in principle. Since the absorption spectrum of a linear polyene is dominated by the strongly allowed $1^1A_g \rightarrow 1^1B_u$ absorption ($S_0$ to $S_2$), knowledge of the dependence of this excitation energy on the number of double bonds in a planar all-trans linear polyene together with the band profile and intensity for this transition would allow the generation of this library. Two of the three things that are needed, $1^1A_g \rightarrow 1^1B_u$ excitation energies as a function of the number of conjugated double bonds and the absorption band profile for the $1^1A_g \rightarrow 1^1B_u$ transition, are well known from experiment. There is less information on the third, the intensity of the $1^1A_g \rightarrow 1^1B_u$ transition as a function of the number of double bonds, but this may be reasonably estimated using molecular orbital theory.

A. $1^1A_g \rightarrow 1^1B_u$ transition energy

Excitation energies for the 0–0 bands of the $1^1A_g \rightarrow 1^1B_u$ transitions of unsubstituted linear polyenes with from 3 to 8 double bonds in conjugation have been measured for these molecules substituted in low temperature n-alkane crystals: Reference 5 summarizes these data and gives the citations to the original reports. The fully resolved vibrational structure of both the $1^1A_g \rightarrow 2^1A_g$ and $1^1A_g \rightarrow 1^1B_u$ transitions make it clear that the observed spectra are those of a mixed molecular crystal where the linear polyene simply replaces n-alkane molecules in a fully ordered n-alkane crystal. Since it is known from x-ray crystallography that in an n-alkane crystal the molecules pack as planar all-trans chains, this must also be the conformation of the substituted linear polyene.

We have previously shown that the $1^1B_u$ 0–0 excitation energies are accurately reproduced by a simple model (Hückel theory with alternating resonance integrals—the Hückel Spectrum Simulator or HSS model). Since there is an analytical solution for the energy levels in this model, it is easy to calculate the 0–0 excitation energy of a planar all-trans polyene chain of any length. The fact that such a calculation really amounts to extrapolating experimentally measured energies with a quantitatively accurate and physically reasonable model gives us confidence in the calculated values. Further assurance may be derived by looking at the behavior of the model in the long chain limit.

The $1^1A_g \rightarrow 1^1B_u$ excitation energy in the long chain limit calculated by this model is 16 200 cm$^{-1}$ or 2.0 eV. This
is reasonably close to the value reported for the polyacetylene absorption band edge.

Since the simple HSS model not only accurately reproduces $1^1A_g \rightarrow 1^1B_u$ transition energies in $n$-alkane solution for planar all-trans linear polyenes with 3–8 double bonds in conjugation, but appears to behave reasonably in the long chain limit, it provides the library of 0–0 band excitation energy versus chain length. Representative values are summarized in Table I and are plotted in Fig. 1.

### B. $1^1A_g \rightarrow 1^1B_u$ transition intensity

Unfortunately, the chain-length dependence of the intensity of the $1^1A_g \rightarrow 1^1B_u$ transition is not as thoroughly understood as is the transition energy. This is primarily due to the difficulties of making quantitative measurements on the low temperature mixed crystals for which the geometry of the polyene chains is known to be trans-planar. Accordingly, we use theoretical values calculated with the simple model that accurately reproduces the excitation energies. It should be noted that although the $1^1A_g \rightarrow 1^1B_u$ transition dipole is proportional to the number of repeat units in the chain for the nonalternating chain, the increase of transition dipole with chain length is strongly suppressed by the alternation of resonance integrals that must be included to obtain the experimentally measured excitation energies. Representative values for the transition dipole moments calculated assuming a trans-planar geometry with all C=C bond lengths equal to 1.332 Å, all C–C bond lengths equal to 1.451 Å, and all C–C–C bond angles equal to 125° are given in Table I and plotted in Fig. 1.

### C. $1^1A_g \rightarrow 1^1B_u$ band profile

To simulate a spectrum, a delta function at the $1^1A_g \rightarrow 1^1B_u$ 0–0 excitation energy for a given chain length is convoluted with the appropriate absorption band profile weighted by the squared transition dipole times the probability of finding that chain length. Since the vibronic development of this transition is very similar for all chain lengths, any linear polyene $1^1A_g \rightarrow 1^1B_u$ absorption band shifted by its 0–0 excitation energy is a reasonable candidate for the band profile. The choice is an arbitrary one: we have elected to use the absorption spectrum for trans β-carotene in CS$_2$, shifted by 20 876 cm$^{-1}$ to lower energy. This spectrum is shown in Fig. 2.

There is a recursive element in this analysis since the room temperature absorption spectrum of β-carotene may itself be the superposition of contributions from different

### Table I. Representative $1^1A_g \rightarrow 1^1B_u$ excitation energies and transition dipoles obtained using the HSS model.

<table>
<thead>
<tr>
<th>Double bonds</th>
<th>$E(1^1B_u)/hc$ (cm$^{-1}$)</th>
<th>$\langle 1^1A_g \mu \rangle(1^1B_u)$ (Debye)</th>
</tr>
</thead>
<tbody>
<tr>
<td>2</td>
<td>47 630</td>
<td>5.160</td>
</tr>
<tr>
<td>3</td>
<td>37 740</td>
<td>6.876</td>
</tr>
<tr>
<td>4</td>
<td>32 180</td>
<td>8.381</td>
</tr>
<tr>
<td>6</td>
<td>26 240</td>
<td>10.873</td>
</tr>
<tr>
<td>8</td>
<td>23 190</td>
<td>12.819</td>
</tr>
<tr>
<td>10</td>
<td>21 380</td>
<td>14.351</td>
</tr>
<tr>
<td>15</td>
<td>19 080</td>
<td>16.957</td>
</tr>
<tr>
<td>20</td>
<td>18 040</td>
<td>18.509</td>
</tr>
<tr>
<td>50</td>
<td>16 580</td>
<td>21.336</td>
</tr>
<tr>
<td>100</td>
<td>16 300</td>
<td>22.022</td>
</tr>
</tbody>
</table>
III. ANALYSIS OF THE MEASURED SPECTRA

The algorithm for determining the chain length distribution from a measured absorption spectrum is straightforward. To calculate the absorption spectrum that corresponds to a given distribution, the band profile shown in Fig. 2 is shifted to the $1^1A_g$ to $1^1B_u$ transition energy for a chain with $N$ double bonds in conjugation, weighted by the probability for that chain length times the squared transition dipole, and accumulated. The probability amplitudes are adjusted to minimize the rms deviation between the calculated and measured spectra. To demonstrate this decomposition we have analyzed six absorption spectra measured for the samples for which Samuel et al.\textsuperscript{2,3} reported $\chi^3$ values. Three representative spectra are shown in Fig. 3.

It is informative to compare these measured absorption spectra to the absorption band profile shown in Fig. 2 shifted to the 0–0 energy obtained from the HSS model (ideal oligomer spectra). These ideal oligomer spectra are the spectra calculated by the means described in Sec. II when the distribution of conjugation lengths is taken to be a delta function at the molecular chain length. There are substantial differences: as is seen in Fig. 4 the measured spectra exhibit substantially less absorption to low energy and more absorption to high energy than is expected. This suggests that the distribution of conjugated chain lengths differs from the ideal situation where most of the molecules exist as fully conjugated chains. There must be significant contributions to the absorption spectrum from conjugation lengths that are shorter than the molecular chain lengths.

To model these absorption spectra we tried a number of forms for the conjugation length distribution: a single Gauss-

![FIG. 2. Linear polyene absorption profile (absorption spectrum of β-carotene in room temperature CS$_2$ solution shifted 20 876 cm$^{-1}$ to lower wave number).](image)

![FIG. 3. Absorption spectra for long polyenes (28, 68, and 240 double bonds) in room temperature THF solution as measured by Samuel et al. (Ref. 3).](image)
ian centered at the molecular chain length (that is, the maximum possible conjugation length), a single Gaussian centered at the chain length that minimized the squared deviations of the calculated and measured spectra, etc. We were somewhat surprised to find that distributions where probability increased with conjugation length gave spectra that differed qualitatively from the those measured, whereas distributions where probability decreased with conjugation length did much better. The best model by far contained two Gaussians centered at $N=2$, the shortest conjugation length considered

$$P(n) = \frac{e^{-(n-2)^2/\sigma_1^2} + A e^{-(n-2)^2/\sigma_2^2}}{\sum_{n=2}^{N} (e^{-(n-2)^2/\sigma_1^2} + A e^{-(n-2)^2/\sigma_2^2})}.$$  

In this model three parameters (two widths and the relative amplitude for the broader of the two Gaussians) were varied to obtain a best fit to the measured spectra. The distributions that gave the best fit to the measured spectra for three representative cases are shown in Fig. 5. The measured and simulated spectra are compared in Fig. 6. As is seen in Fig. 6, the resulting fits are almost perfect. The only apparent deviations are at short wavelengths and these derive entirely from the partially resolved vibrational structure in the reference spectrum.

Similar analyses on solution spectra for other molecular chain lengths ($N=39$, $N=88$, $N=152$) were also carried out with exactly analogous results. The chain length distribution parameters for all six cases are summarized in Table II.

**IV. CONCLUSIONS**

Absorption spectra measured for solutions of long model polyenes show significantly less intensity at long wavelengths and significantly more intensity at short wavelengths than would be predicted from what is known about ideal oligomer spectra. The conjugation-length dependence of the
energy and intensity of the $1^1A_g$ to $1^1B_u$ transition that has been developed in high resolution experiments on well-defined linear polyenes can be used to extract the distribution of effective conjugation lengths from the absorption spectra measured for solutions of long linear polyenes. These distributions are found to be dominated by short conjugation lengths, exactly as would be predicted if it is assumed that higher energy conformations where conjugation is broken—presumably by twisting about essential single bonds—exist.\(^4\) While a different extrapolation of the high resolution data on well-defined oligomers would change the distribution parameters, the qualitative form is dictated by the directly determined data on short chains. Of course, we have left open the question of the detailed structure and dynamics of these segmented conformers.

Given the fact that for $N \geq 4$ fluorescent yield increases with decreasing chain length, it might be imagined that excitation on the blue edge of the absorption band would result in emission from the short segments that dominate the conjugation length distribution. This would only be expected if these segments were isolated. Because they are linked together we expect that the transfer of excitation energy from short to longer segments will effectively quench the emission from the short segments. While we do not feel that we know enough about the detailed structure and dynamics of the conjugation breaks to speculate further on the fate of excitation after photon absorption, this is an issue that deserves serious attention.

When samples contain a broad distribution of effective conjugation lengths, experimentally determining the conjugation-length dependence of nonlinear optical response is difficult, but, at least in principle, it should still be possible. The determination of these distributions that is presented here is a first step in this more extensive analysis.

**ACKNOWLEDGMENTS**

Support from the National Science Foundation (Grant No. CHE-8803916 to B.E.K.) and Christ's College, Cambridge (research fellowship for I.D.W.S.) is gratefully acknowledged.


\(^3\)We are grateful to R. R. Schrock, R. J. Silbey, H. H. Fox, C. Dhenaut, I. Ledoux, and J. Zyss for making the measured absorption spectra available to us.

