Evidence for string-like behaviour in all-trans octatetraene.

Buma, W.J.; Zerbetto, F.

Published in:
Journal of the American Chemical Society

DOI:
10.1021/ja9612864

Citation for published version (APA):

General rights
It is not permitted to download or to forward/distribute the text or part of it without the consent of the author(s) and/or copyright holder(s), other than for strictly personal, individual use, unless the work is under an open content license (like Creative Commons).

Disclaimer/Complaints regulations
If you believe that digital publication of certain material infringes any of your rights or (privacy) interests, please let the Library know, stating your reasons. In case of a legitimate complaint, the Library will make the material inaccessible and/or remove it from the website. Please Ask the Library: https://uba.uva.nl/en/contact, or a letter to: Library of the University of Amsterdam, Secretariat, Singel 425, 1012 WP Amsterdam, The Netherlands. You will be contacted as soon as possible.
The versatile nature of polycenes, H(CH)_{n}H, makes them prototypes of biologically active molecules and of polyacetylene, a polymer of fundamental importance in materials science. In the polymer, electron transport has long been modeled in terms of solitons which appear in the dynamics of a linear string of bodies.\textsuperscript{1} In the pioneering model of polyacetylene,\textsuperscript{2} the string was described by π electrons that were treated as quantized, with a tight binding scheme, whereas the σ electrons and nuclei were simulated by classical harmonic oscillators. No allowance was made for potential energy functions of bending and out-of-plane motions or for the hybridization of the carbon atoms was made for potential energy functions of bending and out-of-plane motions or for the hybridization of the carbon atoms that forms angles of \( \sim 120^\circ \). Although the quasi-particles can appear in high-level calculations, the simplicity and success of the original model indisputably captures the fundamental aspects of the macroscopic phenomena, and the “experimental” detection of stringlike behavior in any polyene would sanction the generality of this ingenious scheme.

To detect the signature of stringlike behavior from experimental data, we selected all-trans-octatetraene, a highly studied polyene.\textsuperscript{3−7} For alternant hydrocarbons,\textsuperscript{8} such as octatetraene, a host of information can be obtained on the basis of pseudoparity considerations require that the vibronic interaction between electronic states of different pseudoparity be most effective for couplings \( \nu \) via bending vibrations.\textsuperscript{15} This requirement finds strong experimental support in the dipole-forbidden \( \nu_5(1 \text{A}_{g}) \) \( \rightarrow \nu_1(2 \text{A}_{g}) \) spectrum of octatetraene where the most intense band is associated with the lowest-frequency in-plane bending vibration of CCC character.\textsuperscript{4,6,7} This vibrational band owes its intensity to the coupling of \( \nu_4(S_1) \) with \( \nu_5(S_0) \).\textsuperscript{13} Because of this context, it is natural to focus on bending motions of CCC character. If octatetraene were linear, a degenerate counterpart would be associated with each in-plane CCC bending mode. This counterpart is an out-of-plane CCC motion in the real molecule. Stringlike behavior would consequently imply similar roles for

![Table](image)

\( \nu_{\alpha} \rightarrow 2.734(1) \)
\( \nu_{\beta} \rightarrow 0.416(1) \)
\( \nu_{\gamma} \rightarrow 0.480(1) \)
\( \nu_{\delta} \rightarrow 2.037(5) \)
\( \nu_{\epsilon} \rightarrow 2.770(13) \)
\( \nu_{\zeta} \rightarrow 3.293(1) \)

The couplings due to CCC bending vibrations are underlined. The numbers between brackets give the accuracy in the last digits of the calculated value. The intensities are given with respect to the intensity of \( \nu_{\zeta} \) which was taken as 100.0.

The coupling due to bending vibrations becomes indistinguishable when both the electronic states involved have the same symmetry. Thus, the out-of-plane vibrations are divided into \( \alpha \) and \( \beta \) symmetries and do not have the correct symmetry to mix the two states. But do they not? A combination of any two out-of-plane modes of different symmetry does indeed fulfill the symmetry requirements. Interestingly, if octatetraene becomes a string, the two electronic states still have different symmetries whereas only the \( \alpha \) mode, becomes the counterpart of the \( \beta \) in-plane mode. In the real molecule, the remaining \( \beta \) mode can be seen as a helping vibration whose function merely is to “dress” the molecular deformation of octatetraene with the proper symmetry.

To determine the presence of stringlike behavior in octatetraene, one must therefore compare the coupling between \( \nu_4(S_1) \) and \( \nu_5(S_0) \) induced by CCC bending vibrations of \( \beta \) symmetry and by the combination of \( \alpha \) and \( \beta \) CCC modes. Previously, we have employed quantum-chemical modeling to simulate the first-order vibronic activity in the \( S_1 \) \( (1 \text{A}_{g}) \) \( \rightarrow S_1 \) \( (2 \text{A}_{g}) \) excitation spectrum of all-trans-octatetraene.\textsuperscript{4,12} The calculated first-order vibronic couplings, are shown in Table 1. Notice that a two-state model gives excellent agreement with the full-scale calculations for the three CCC bending vibrations, \( \nu_{\alpha}, \nu_{\gamma}, \) and \( \nu_{\epsilon} \). For instance, for the induced transition moment of \( \nu_{\epsilon} \) it predicts an induced moment of 0.0913 \( e\alpha_0 \) versus 0.0851 \( e\alpha_0 \) obtained in our previous calculations.\textsuperscript{8} We can conclude that in case of the CCC bending modes the vibronically induced intensities are predominantly determined by the \( S_1−S_2 \) couplings, and that pseudoparity rules are almost perfectly obeyed.

The second-order couplings for combinations of out-of-plane modes are shown in Table 2. It is clear that the magnitudes of

\( \nu_{\epsilon} \rightarrow 2.770(13) \)
\( \nu_{\zeta} \rightarrow 3.293(1) \)

Evidence of Stringlike Behavior in all-trans-Octatetraene

Wybren Jan Buma*

Laboratory for Physical Chemistry
University of Amsterdam, Nieuwe Achtergracht 127
1018 WS Amsterdam, The Netherlands

Francesco Zerbetto*

Dipartimento di Chimica “G. Ciamician”
Universit`a degli Studi di Bologna, V. F. Selmi 2
40126 Bologna, Italy

Received April 18, 1996
Revised Manuscript Received June 28, 1996

The couplings due to CCC bending vibrations are underlined. The numbers in brackets give the accuracy of the last digits of the calculated value. Entries which have a numerical error larger than the value itself are indicated by #.

Table 3. Calculated Intensities of Second-Order Vibronic Coupling Induced $1\text{A}_g \rightarrow 2\text{B}_u$ Transitions

<table>
<thead>
<tr>
<th>$\nu_{25}$</th>
<th>$\nu_{24}$</th>
<th>$\nu_{23}$</th>
<th>$\nu_{22}$</th>
<th>$\nu_{21}$</th>
<th>$\nu_{20}$</th>
<th>$\nu_{19}$</th>
<th>$\nu_{18}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.2 (0.2)</td>
<td>2.4 (3.3)</td>
<td>0.1 (0.2)</td>
<td>5.4 (0.1)</td>
<td>0.3 (4.1)</td>
<td>4.1 (1.2)</td>
<td>3.1 (1.3)</td>
<td>0.1 (0.2)</td>
</tr>
<tr>
<td>0.4 (0.7)</td>
<td>0.7 (2.0)</td>
<td>2.7 (24.5)</td>
<td>45.7 (1.5)</td>
<td>0.5 (8.6)</td>
<td>0.4 (0.2)</td>
<td>0.8 (1.1)</td>
<td>0.0 (2.1)</td>
</tr>
<tr>
<td>1.0 (0.7)</td>
<td>0.1 (1.7)</td>
<td>4.8 (7.4)</td>
<td>519.2 (1.8)</td>
<td>1.8 (1.1)</td>
<td>2.2 (2.7)</td>
<td>1.5 (7.8)</td>
<td>0.4 (0.1)</td>
</tr>
<tr>
<td>2.6 (2.6)</td>
<td>1.4 (10.2)</td>
<td>0.3 (1.3)</td>
<td>7.0 (2.3)</td>
<td>17.0 (0.5)</td>
<td>2.1 (0.2)</td>
<td>0.3 (6.8)</td>
<td>0.4 (0.1)</td>
</tr>
<tr>
<td>3.9 (0.4)</td>
<td>0.0 (1.7)</td>
<td>3.1 (0.3)</td>
<td>5.8 (1.8)</td>
<td>12.2 (4.3)</td>
<td>5.0 (2.1)</td>
<td>3.5 (0.1)</td>
<td>1.1 (25.1)</td>
</tr>
<tr>
<td>2.0 (0.4)</td>
<td>0.4 (0.1)</td>
<td>1.0 (1.3)</td>
<td>0.6 (2.7)</td>
<td>3.9 (2.9)</td>
<td>0.4 (8.2)</td>
<td>0.1 (13.6)</td>
<td>37.5 (4.6)</td>
</tr>
<tr>
<td>0.1 (0.1)</td>
<td>13.9 (38.8)</td>
<td>12.9 (0.5)</td>
<td>1.8 (7.6)</td>
<td>129.5 (0.5)</td>
<td>34.9 (3.2)</td>
<td>13.8 (38.8)</td>
<td>1843.1 (15.8)</td>
</tr>
</tbody>
</table>

Intensities are given with respect to the calculated intensity of the $\nu_{46} (b_2)$ band taken as 100. The frequencies (in cm$^{-1}$) of the vibrations in the $2\text{A}_g$ state employed in the assignments are indicated with bold numbers and have been calculated in ref 4. The intensities without parentheses derive from a calculation in which Duschinsky mixing was taken into account; those given in parentheses represent intensities in the absence of Duschinsky mixing. In italics are given tentative assignments to bands observed in the excitation spectrum$^5$ together with the experimentally observed intensities, scaled$^4$ for the measured lifetime. Notice that the frequencies of the experimental bands are given with respect to the $\nu_{46} (b_2)$ vibronically induced origin in the one-photon excitation spectrum at 76 cm$^{-1}$ from the true 0–0 transition.$^6$