Momentum-Dependent Excitations in β-Carotene, a Finite-Size System between Molecules and Polymers

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Electron-energy-loss spectroscopy has been used to study momentum-dependent excitations of π electrons in β-carotene. These investigations illustrate that the orbital levels of π electrons in finite polyenes and other conjugated oligomers can be mapped out. It turns out that the electronic structure of the π electrons can be described in terms of a quasi band structure with a finite number of momentum values. The results are compared with theoretical calculations based on an effective Su-Schrieffer-Heeger Hamiltonian.

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The electronic structure of finite-size systems such as clusters has been the subject of a large number of recent studies.[1] A transition from continuous bands into discrete levels is expected when going from solids to atoms. With photoemission the density of occupied states could be studied as a function of cluster size.[2] However, the wave-vector dependence of these states could not be investigated by angular-resolved photoemission since for these measurements the clusters should be oriented. Momentum-dependent excitations in potassium clusters have been studied by means of electron-energy-loss spectroscopy.[3] The focus of these studies has been collective excitations such as volume and surface plasmons. Discrete levels could not be resolved by single-particle excitations due to the relatively large size of the clusters (~ 1000 atoms).

Alternatively, for the investigation of the electronic structure of finite-size systems one can use conjugated oligomers, e.g., polyenes. These systems can be prepared well oriented and with a definite length. The interaction between the polyenes is negligibly small compared to the level spacing. Therefore, these systems are extremely well suited to study the momentum dependence of excitations in finite-size systems.

In addition, conjugated polyenes have attracted a good deal of attention during the last 50 years because they were important in the development of molecular-orbital theory for π-electron systems.[4–6] Furthermore, they bridge the gap between short molecules and polymers like, e.g., *trans*-polyacetylene (PA). The latter is in the doped form the prototype of the conducting polymers,[6–8] which were the focus of strong research activities during the last twelve years. Although numerous experimental and theoretical investigations have been performed on conjugated oligomers and polymers, the electronic structure of these systems is by no means clear. There is a considerable debate on the importance of electron-electron interaction for the size of the gap[5,6] in the undoped systems, the detailed form of defects created upon doping is still discussed, and the metallic state which is formed at high dopant concentration is still not completely understood.

In this Letter we report on investigations of the electronic structure of β-carotene which with respect to the π-electron structure is a polyene with 22 C atoms. Compared to *trans*-PA there is no occupied π band and no unoccupied π^* band but there are eleven occupied π and eleven unoccupied π^* levels. In *trans*-PA the dispersion of the π bands could be studied by momentum-dependent interband transitions using electron-energy-loss spectroscopy (EELS).[9] The finite-size system β-carotene, located between molecules and the polymeric solid, offers the possibility to study the level spacing by measuring momentum-dependent transitions between discrete π and π^* levels. In optical spectroscopy where the momentum transfer is almost zero, most of the π-π^* transitions are not allowed or are strongly suppressed by small matrix elements. Therefore, only the transition from the highest occupied to the lowest unoccupied molecular orbital is prominent. A detailed mapping of the various orbital states is not possible. In EELS, however, transitions with variable momentum transfer can be induced. Therefore, it should be possible to map out molecular-orbital states. This study describes the first use of EELS in this field. It turns out that the electronic structure of π electrons in finite polyenes or other oligomers can qualitatively be described by a quasi band structure in which the π bands of the polymers with an infinite number of k values are transformed into discrete π levels having discrete k values separated by $k_0 = 2\pi/(N+1)a$, where N is the number of C atoms in the chain and a is the mean distance between two C atoms. The width of these levels with respect to momentum should be about 2π divided by the effective length of the π system, yielding a value close to k_0.

For these investigations, it is advantageous to use oriented samples because then a definite momentum transfer parallel to the polyene chains can be selected.

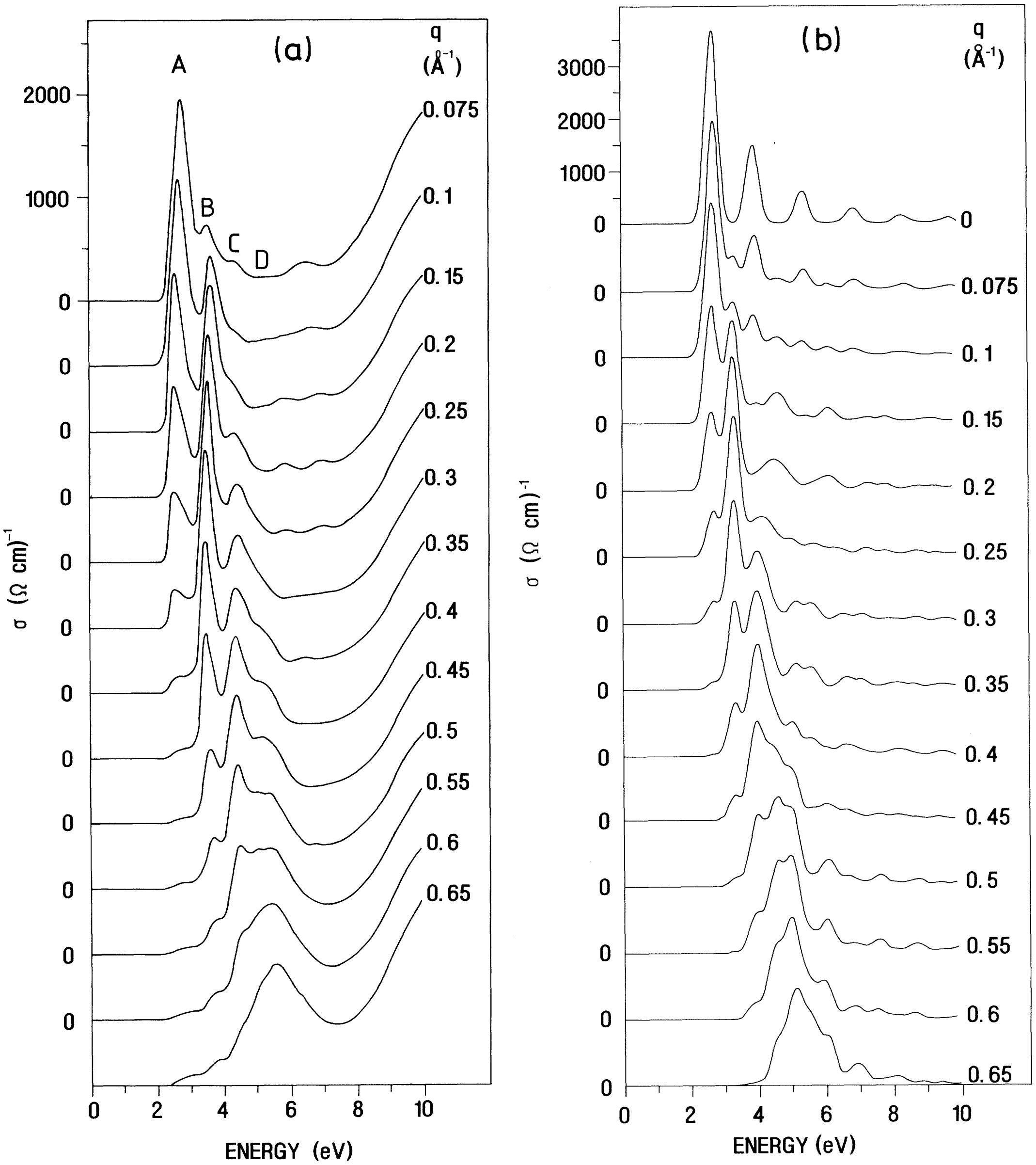

FIG. 1. Momentum-dependent optical conductivity of β-carotene. (a) Experimental data derived from EELS measurements. (b) Theoretical data.

Therefore, we used β-carotene single crystals with a thickness of about 1000 Å. They were grown by the addition of methanol to a hot benzene solution.[10] EELS spectra were measured in transmission using a 170-keV spectrometer.[11] The energy and momentum resolution was chosen to be 0.18 eV and 0.04 Å^{-1}, respectively. In all data shown here, the momentum transfer **q** was set parallel to the **b** axis of the β-carotene crystal. Since the angle between the **b** axis and the two nonparallel polyene chains per unit cell is 32.7°, this results for both chains in the same reduced momentum transfer $q_{\parallel}$ parallel to the chain axis. Using the refractive index from optical data,[10] the absolute size of the loss function for small q was determined. For higher momentum transfer a sum rule on $\omega \operatorname{Im}[-1/\varepsilon(q,\omega)]$ was used.[12] Then, the optical conductivity was calculated by a Kramers-Kronig analysis. The data for various momentum transfers are shown in Fig. 1(a). They can be described by several lines due to transitions between occupied π states and unoccupied π^* states. The energy of these lines and their assignment to particular transitions is given in Table I.

The experimental data can be explained by transitions from the eleven occupied π levels $(11,\ldots,1)$ to the eleven unoccupied π^* levels $(1^*,\ldots,11^*)$. Starting from an infinite polyene, a picture may be applied where

TABLE I. Excitations energies of π-π^* transitions measured by EELS ($E_{\mathrm{expt}}^{\mathrm{EELS}}$) and optical spectroscopy $E_{\mathrm{expt}}^{\mathrm{opt}}$. For comparison, theoretical values E_{theor} for the individual transitions and mean values $\bar{E}_{\mathrm{theor}}$ are presented. All values are given in eV.

		k_0	$E_{\mathrm{expt}}^{\mathrm{EELS}}$	$E_{\mathrm{expt}}^{\mathrm{opt}}$	E_{theor}	$\bar{E}_{\mathrm{theor}}$
A	1-1*	0	2.6	2.6	2.74	2.74
B	1-2*	1	3.5		3.37	3.36
	2-1*	1			3.34	
C	1-3*	2	4.3	4.3	4.26	4.05
	3-1*	2			3.92	
	2-2*	0,2			3.98	
D	1-4*	3	4.9		5.12	4.78
	2-3*	3			4.87	
	4-1*	3			4.56	
	3-2*	3			4.55	

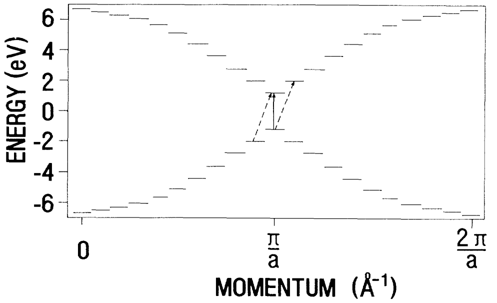

FIG. 2. Quasi band structure for the π electrons in β-carotene. The vertical 1-1* transition and the nonvertical 2-1* and 1-2* transitions are shown.

these levels are lined up on a curve similar to that of π and π^* bands in *trans*-PA (see Fig. 2). Since in the finite systems the momentum is no longer a good quantum number, these levels have a finite width. For small q only vertical transitions, i.e., 1-1*, 2-2*, etc., are allowed as in optical spectroscopy. Therefore, the optical conductivity for $q = 0.075$ Å^{-1} is dominated by the 1-1* transition [line *A* in Fig. 1(a)] traditionally called the $1\,{}^1A_g$-$1\,{}^1B_u$ transition. Excitations of triplet states are not allowed since in high-energy EELS exchange effects can be neglected. This is different from low-energy EELS where excitations into triplets states could be observed.[4] At finite momentum transfer nonvertical transitions occur: 1-2* and 2-1* transitions (line *B*) are prominent for $q_\parallel = k_0$, 3-1*, 1-3*, and 2-2* transitions (line *C*) for $q_\parallel = 2k_0$, etc.

In order to obtain some qualitative insight into the involved physics, the optical conductivity $\sigma(\mathbf{q},\omega)$ was calculated for a 22-membered chain within an *effective* Su-Schrieffer-Heeger model[13] using the current operator representation of Ref. 14. The calculations were extended by next-nearest-neighbor hopping terms and diagonal terms to model the electron-repelling effect of the methyl groups and the end rings.[15] The method to obtain self-consistently the eigenvalues, the wave functions, and the relative displacements of the C atoms is described in Ref. 16. The model parameters have been adjusted to the positions and widths of the first three experimentally observed peaks. For the nearest-neighbor hopping integral $t_0 = 3.5$ eV has been obtained, in qualitative agreement with a value $t_0 = 3.2$ eV derived from EELS measurements on *trans*-PA (without taking into account local-field effects)[9] but slightly larger than the frequently used value $t_0 = 2.5$-3 eV. A value of $t_0 = 3.5$ eV has also been used to describe recent optical data on *trans*-PA.[17] A possible $\sim 10\%$ increase of t_0 for β-carotene compared to the "infinite" chain *trans*-PA is expected to be mainly caused by side groups and end rings and to a lesser extent by finite-size effects. For the next-nearest-neighbor hopping term $t_2 = -0.1t_0$ was assumed.[18] A nearest-neighbor electron-phonon coupling constant $\alpha_1 = 8.85$ eV/Å and a spring constant due to σ electrons $K = 65$ eV/Å^2 were used. The next-nearest-neighbor electron-phonon coupling constant α_2 was chosen $\alpha_2 = 0.1\alpha_1$, and the diagonal term to model the influence of methyl groups was chosen $\varepsilon_n = 0.2t_0$.[15]

Thus, the e-e interactions resulting in a large gap in polyenes have been simulated as usual by a large value of α_1. As was noted in Ref. 14, the expression for the optical conductivity is insensitive to the presence of such terms in the electronic part of the Hamiltonian H_{el}, since $[c_n^\dagger c_n, H_{\mathrm{el}}] = 0$. Furthermore, for weak on-site Coulomb energy U the eigenvalues of extended states are shifted nearly by the same value resulting in unchanged transition energies (in first order of $U/4t_0$).[6] The theoretical results for the transition energies in undoped β-carotene are compared in Table I with the experimental values.

In Fig. 1(b) we show the calculated optical conductivity as a function of momentum transfer. In order to take into account finite experimental resolution, lifetime broadening, and vibronic excitations, the data were broadened with a Gaussian having a width of 0.45 eV. There is qualitative agreement between the experimental and the theoretical curves. In Fig. 3 the momentum dependence of the intensity of the individual lines of the experimental and the calculated optical conductivity is shown. In the calculated curves all lines with a similar momentum dependence were summed up (see also Table I). For line *A* there is excellent agreement between theory and experiment; in particular, the full width at half maximum is in both cases $\Delta q_\parallel = 0.30$ Å^{-1}. Generally, the maxima of lines *B*, *C*, and *D* appear at slightly lower momentum compared to the theoretical values and the experimental width is larger than the theoretical value. For example, for line *B*, the theoretical values for the maximum and the width is $q_\parallel = 0.2$ Å^{-1} and $\Delta q_\parallel = 0.22$ Å^{-1}, respectively, while the experimental values are $q_\parallel \sim 0.18$ Å^{-1} and $\Delta q_\parallel = 0.30$ Å^{-1}. In addition, there is also a deviation in the shape of the curve *B* between theory and experiment. The reason for the deviations are not clear at present. They may be caused by correlation effects or by an incorrect normalization of

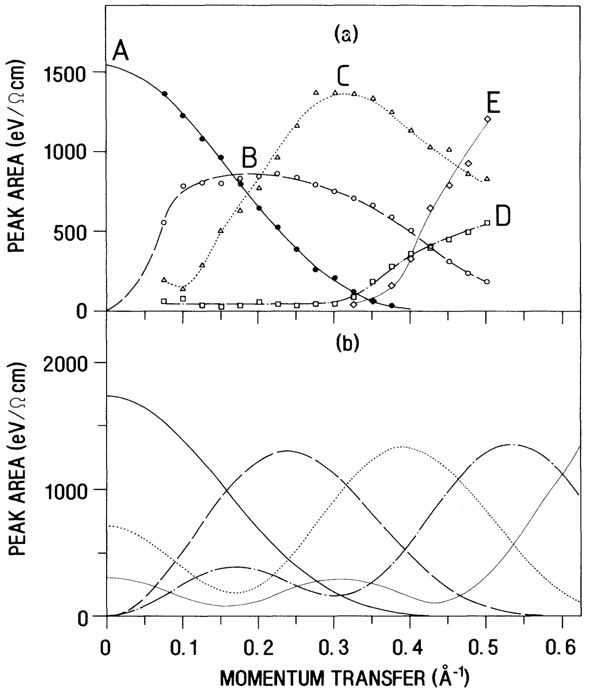

FIG. 3. Intensity of the various lines detected in the optical conductivity as a function of momentum transfer **q** parallel to the **b** axis. (a) Experimental data and (b) theoretical values.

the loss function at higher momentum transfer. The intensities of lines *C* and *D* are superpositions of lines with $q_{\|}=2k_0$ and $3k_0$ and therefore cannot be compared directly with the calculated intensities shown in Fig. 3(b).

The results given above demonstrate that the discrete levels of the π electrons of oligomers can be investigated by momentum-dependent EELS measurements. In the future, this method can be used to study changes of these levels due to different structures, by adding various substituents or by changing heteroatoms. The most interesting field will be momentum-dependent measurements on transitions related to defect states formed upon doping where the character and the spatial extension of these defects (solitons, polarons) can be studied.[19] Recent measurements on I-doped β-carotene will be published elsewhere.[20] Finally, we point out that the above method can be used for polycrystalline samples, too, since the π-π^* transitions are strongly enhanced only for **q** parallel to the chain axis. For example, recently well-resolved lines changing their intensity as a function of momentum transfer could be resolved in hexathiophene oligomers.

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