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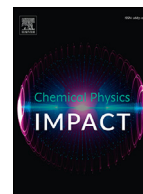
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Electronic transitions of tetrathiafulvalene oriented in polyethylene film. Near and vacuum UV synchrotron radiation polarization spectroscopy

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ABSTRACT

The electronic spectrum of tetrathiafulvalene (TTF) oriented in a polyethylene film is characterized experimentally using synchrotron radiation linear dichroism from the near-UV to the vacuum-UV region to 56,500 cm⁻¹ (177 nm). The non-planar TTF molecule is shown to have electronic transitions of significant intensity polarized along all three molecular symmetry axes. A procedure for processing linear dichroic data to obtain partial absorbance curves representing different polarization directions is exemplified. The overlapping contributions to eight individual spectral features are furthermore interpreted by the aid of time-dependent density functional theory using CAM-B3LYP/6-311++G(3df,3pd) with geometry optimized at the B3LYP / 6-311++G(3df,3pd) level within the C_{2v} point group. Additional calculations using larger basis sets as well as other long-range corrected functionals (LC- ω PBE and ω B97XD) yielded similar results. The planar conformer with D_{2h} symmetry is also considered and it is discussed that rapid equilibration via this transition state may contribute to the diffuse nature of some features of the electronic spectrum. The TTF molecule is a dynamic and 3-dimensional chromophore, and these characteristics may serve as a basis for understanding the optical properties of the numerous TTF-based materials finding applications in supramolecular chemistry, molecular electronics and beyond.

1. Introduction

The tetrathiafulvalene (TTF, [Scheme 1](#)) motif is renowned for its role in Bechgaard salts [1,2]. These are organic superconductors that rely on charge-transfer complexes comprised of a TTF derived radical cation and an anion, which in the solid state can display low-temperature superconductivity. TTF itself is non-aromatic and non-planar, its stable geometry being a boat-like conformation of C_{2v} symmetry. The compound has remarkable redox properties, and the aromatic radical cation and di-cation forms are readily obtained reversibly, the former being planar with D_{2h} symmetry, and the latter twisted along the central bond with D₂ symmetry. Prior to Bechgaard salts being characterized, numerous examples of conducting TTF materials were described and explored for their electrically conducting properties, see an overview by Martin [3]. TTF is also intrinsically connected with the term *molecular electronics* and with so-called Aviram–Ratner Rectifiers that were proposed in a seminal paper in 1974 [4]. Such compounds where a TTF donor is connected with an acceptor by a σ -bonded bridge have since been experimentally characterized; see for instance Ho et al. [5]. TTF has also had a prominent role in supramolecular chemistry and for construction of mechanically in-

terlocked molecules, electrochromic materials, molecular switches and machines, where functionality can be incorporated by virtue of the electron donor capability of TTF derivatives and their ability to engage in donor-acceptor complexes with electron acceptors [6–9].

The electronic structure of TTF has been investigated by several workers [10–17]. In this publication, we report the results of an experimental and theoretical study of the excited electronic states of TTF. The electronic absorption spectrum is investigated by Synchrotron Radiation Linear Dichroism (SRLD) spectroscopy in the range 56,500 – 20,000 cm⁻¹ (177 – 400 nm) on molecular samples partially aligned in stretched polyethylene (PE). LD spectroscopy on an ordered molecular assembly enables elucidation of otherwise unresolved spectral features and provides information on the moment directions of the observed transitions [18–23]. TTF turns out to be a truly three-dimensional chromophore, with overlapping contributions from intensity polarized along all three symmetry axes of the chromophore, a situation which complicates the interpretation of the LD spectra in terms of partial absorbance curves. We shall show that the construction of so-called reduced absorbance curves provides a useful representation of the experimental polarization spectra, revealing previously unrecognized features. The observed

Abbreviations: TTF, Tetrathiafulvalene; SRLD, Synchrotron Radiation Linear Dichroism; PE, Polyethylene.

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absorbance bands are compared with theoretical transitions predicted with Time Dependent Density Functional Theory (TD-DFT) [24–26] using different functionals and basis sets. Additional information is provided as Supplementary data, referred to in the ensuing text as S1 – S11.

2. Experimental

2.1. Materials

Tetrathiafulvalene (TTF) [31366-25-3] (97%) was obtained as a red solid from Sigma-Aldrich (Aldrich cat. no. 183180). Polyethylene films (PE) were pure low-density PE sheet material (Hinum Plast, DK-2670 Greve, Denmark). Chloroform was spectroscopic grade (Uvasol) CHCl_3 from Sigma-Aldrich.

2.2. Sample preparation

For UV measurements a PE sheet of approximately 100 μm thickness (prior to stretching) was soaked briefly in a chloroform solution containing TTF, while a reference sheet was soaked in pure chloroform. The chloroform was subsequently allowed to evaporate from the PE sheets in a fume hood. The film surfaces were cleaned with methanol to remove any crystalline deposits of TTF. The resulting sample thus consisted of TTF solubilized inside the PE sheets. For linear dichroism (LD) measurements, the polymer was stretched uniaxially approximately by 500% in an in-house constructed apparatus. All sample manipulations were performed at room temperature and ambient pressure. Additional information on stretched polyethylene samples can be found in the literature [18–23].

2.3. Synchrotron radiation UV linear dichroism

Synchrotron radiation LD spectra were measured at room temperature as previously described [27–34] on the UV beamline [35–37] at the storage ring ASTRID2 at the Centre for Storage Ring Facilities (ISA), Aarhus University, Denmark. The synchrotron beamline provides a much higher photon flux in the far UV spectral range compared to a conventional light source. This yields an improved signal to noise ratio, as well as extending the accessible wavenumber range for PE samples up to at least $56,000\text{ cm}^{-1}$. Data were recorded in the $500\text{ nm} - 177\text{ nm}$ ($\sim 56,500\text{ cm}^{-1}$) range with one point per nm. The baseline-corrected LD absorbance curves are denoted $E_U(\tilde{\nu})$ and $E_V(\tilde{\nu})$ and correspond to parallel and perpendicular polarization of the radiation with respect to the uniaxial stretching direction U of the polymer sample. To minimize problems due to evaporation of TTF from the PE sample during the measurements, the sample curves were recorded in the following sequence: first $E_V(\tilde{\nu})$, then $E_U(\tilde{\nu})$, and then again $E_V(\tilde{\nu})$, immediately after one another. For definition of the LD, the average of the two $E_V(\tilde{\nu})$ absorbance measurements was taken and compared with the intermediate $E_U(\tilde{\nu})$ spectrum. The resulting LD curves are shown in Fig. 1, top.

3. Density functional theoretical calculations

Quantum chemical calculations were performed with the GAUSSIAN09 [38] and GAUSSIAN16 [39] software packages. The ground state geometry of TTF was computed by using B3LYP [40,41] DFT and the 6-311++G(3df,3pd) basis set [38,39]. The molecule is predicted to have a C_{2v} symmetrical boat-shaped nuclear equilibrium configuration, consistent with the results of previous experimental and theoretical investigations [15–17,42–44]. The planar D_{2h} symmetrical configuration is predicted to be a transition structure, interrelating two equivalent boat-shaped structures; the electronic energy barrier is computed to be 0.08 kcal/mol. The computed nuclear coordinates and molecular energies for the C_{2v} and D_{2h} structures are provided as Supplementary data S1 and S2. Vertical electronic transitions from the ground state to the

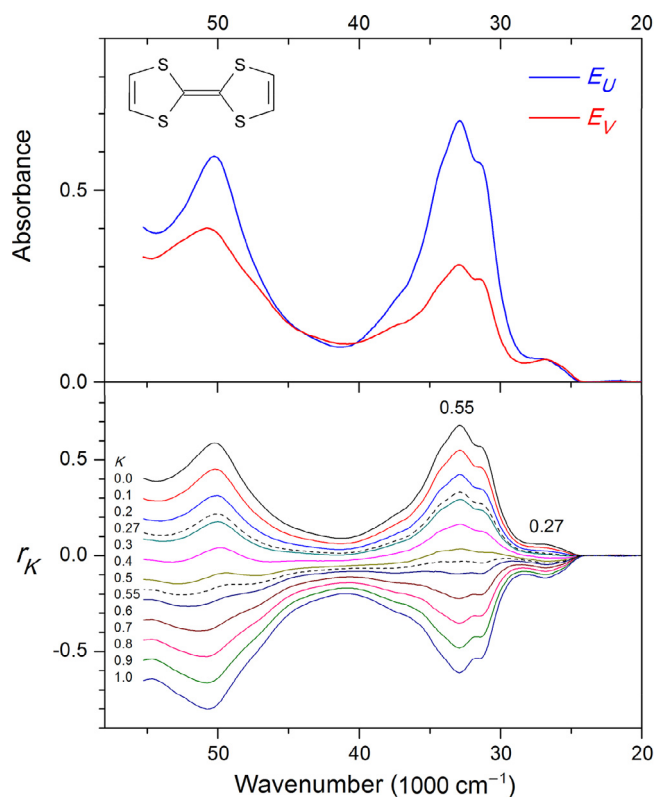


Fig. 1. Top: Experimental UV synchrotron radiation polarization spectra of TTF oriented in a polyethylene film. $E_U(\tilde{\nu})$ and $E_V(\tilde{\nu})$ denote absorbance measured with the beam polarization parallel and perpendicular to the stretching axis U of the sample. Bottom: Linear combinations $r_K(\tilde{\nu}) = (1 - K)E_U(\tilde{\nu}) - 2KE_V(\tilde{\nu})$ of the spectra, allowing assignment of K -values (see text).

50 lowest excited singlet states were computed with the TD-DFT procedure [24–26] using the long range-corrected functional CAM-B3LYP [45] and the 6-311++G(3df,3pd) basis set [38,39]. The main calculated transitions are listed in Table 1 and shown graphically in Fig. 2 (bottom); full listings are provided as Supplementary data S3 and S4. A constant value of 3000 cm^{-1} was subtracted from the computed wavenumbers to facilitate comparison of observed and predicted trends [32–34]. A comparison of transitions predicted for boat-shape and planar TTF is provided in S5, and results obtained with and without diffuse functions in the basis set are compared in S6. Some important orbitals are shown in Fig. 3. The TD-CAM-B3LYP calculations for boat-shape TTF were repeated with the larger basis sets AUG-cc-pVTZ and AUG-cc-pVQZ [46,47] and additional TD-DFT calculations were performed with the long-range corrected functionals LC- ω PBE [48,49] and ω B97XD [50], all yielding rather similar results (S7 – S11). Convolutions of the predicted transitions were performed by assigning a Gaussian function to each excitation wavenumber with an area proportional to the oscillator strength of that transition, using a constant width parameter, $\sigma = 1500\text{ cm}^{-1}$.

4. Results and discussion

4.1. Linear dichroism: orientation factors and partial absorbance curves

The observed LD absorption curves $E_U(\tilde{\nu})$ and $E_V(\tilde{\nu})$ for TTF partially aligned in stretched PE are shown in Fig. 1 (top). They are consistent with those measured in the Near-UV region ($40,000 - 20,000\text{ cm}^{-1}$) in a similar experiment by Gleiter et al. [12]. However, our analysis of the observed linear dichroism data differs considerably from that of Gleiter et al. Most significantly, in the present study TTF is recognized and treated explicitly as a three-dimensional chromophore.

Table 1

Observed features of the SRLD spectrum of tetrathiafulvalene (TTF) and electronic transitions predicted with TD-CAM-B3LYP.

Observed				C_{2v} boat-shape configuration ^a				D_{2h} planar configuration ^a			
	$\tilde{\nu}^b$	Abs ^c	Pol ^d	Term	$\tilde{\nu}^{b,e}$	f^f	Leading configurations ^g	Term	$\tilde{\nu}^{b,e}$	f^f	Leading configurations ^g
A	22.0	–	–	2 $^1A_1(z)$	21.0	$4 \cdot 10^{-4}$	78% (1,-1); 18% (1,-4)	1 $^1B_{1u}(z)$	20.1	$6 \cdot 10^{-4}$	80% (1,-1); 16% (1,-3)
B	26.7	0.13	x,z	1 $^1B_1(x)$	26.8	0.03	88% (1,-3)	1 $^1B_{3u}(x)$	27.7	0.05	97% (1,-4)
C	31.3	0.14	x,z	2 $^1B_1(x)$	31.4	0.03	48% (1,-5); 39% (1,-13)	2 $^1B_{1u}(z)$	31.6	0.02	64% (1,-3); 16% (1,-9)
				3 $^1A_1(z)$	32.2	0.02	63% (1,-4); 15% (1,-9)				
D	32.9	1.19	y	1 $^1B_2(y)$	30.4	0.09	30% (1,-2); 27% (1,-10)	1 $^1B_{2u}(y)$	32.3	0.39	98% (1,-6)
				2 $^1B_2(y)$	32.7	0.29	58% (1,-6); 27% (1,-10)				
E	38.8	0.24	x,z	4 $^1A_1(z)$	38.2	0.02	52% (1,-12); 25% (1,-9)	3 $^1B_{1u}(z)$	37.5	0.02	53% (1,-11); 27% (1,-9)
				5 $^1A_1(z)$	38.9	0.02	53% (1,-9); 36% (1,-12)	4 $^1B_{1u}(z)$	38.5	0.02	51% (1,-9); 38% (1,-11)
F	48 ^h	0.53	x,z	6 $^1B_1(x)$	47.7	0.06	88% (1,-17)	2 $^1B_{3u}(x)$	47.1	0.07	95% (1,-17)
				7 $^1B_1(x)$	50.0	0.07	44% (2,-7); 23% (2,-8)	3 $^1B_{3u}(x)$	50.4	0.09	78% (2,-8); 10% (3,-6)
G	50.0	0.78	y	6 $^1B_2(y)$	46.3	0.02	36% (1,-16); 33% (1,-19)	2 $^1B_{2u}(y)$	46.4	0.05	94% (1,-16)
				7 $^1B_2(y)$	47.4	0.03	32% (1,-19); 32% (1,-16)	3 $^1B_{2u}(y)$	52.1	0.15	72% (3,-4); 21% (4,-8)
H	52.6	0.91	x,z	9 $^1B_2(y)$	50.9	0.10	73% (3,-3); 13% (4,-7)				
				10 $^1B_1(x)$	53.9	0.10	51% (3,-6); 13% (2,-7)				

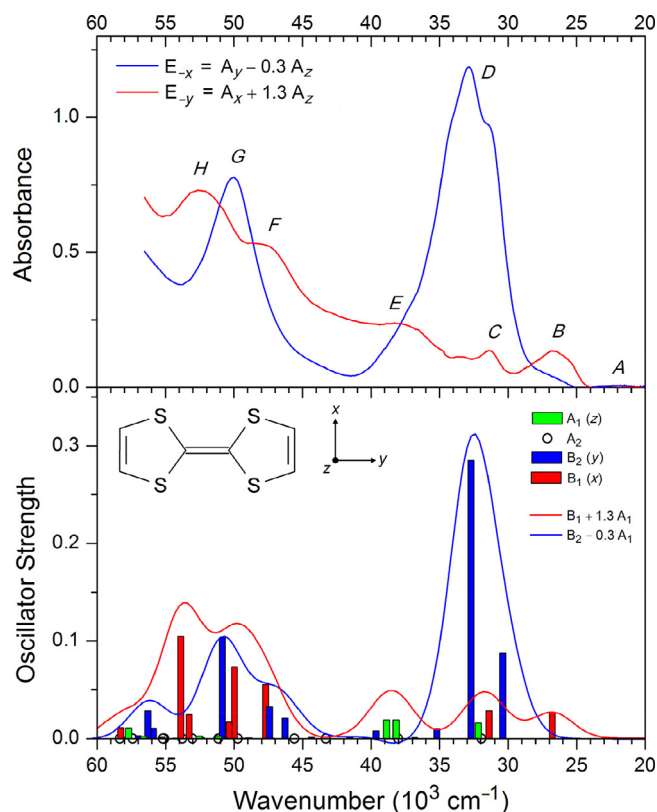
^a TD-CAM-B3LYP/6-311++G(3df,3pd)//B3LYP/6-311++G(3df,3pd). Most significant transitions only; full listing is provided as supplementary data.^b Peak wavenumber in 1000 cm^{-1} .^c Peak absorbance from the reduced absorbance curves $E_{-y} = A_x - 0.3A_z$ and $E_{-x} = A_y + 0.3A_z$ in Fig. 2.^d Polarization direction, see text.^e 3000 cm^{-1} have been subtracted from the calculated wavenumbers.^f Oscillator strength.^g The notation (i,-j) indicates a configuration generated by promotion of an electron from the i'th highest occupied to the j'th lowest unoccupied MO. Several important MOs are shown in Fig. 3.^h Broad shoulder.

Fig. 2. Top: Reduced UV absorbance curves $E_{-x}(\tilde{\nu}) = A_y(\tilde{\nu}) - 0.3 \cdot A_z(\tilde{\nu})$ and $E_{-y}(\tilde{\nu}) = A_x(\tilde{\nu}) + 1.3 \cdot A_z(\tilde{\nu})$ derived from the observed LD absorbance curves $E_U(\tilde{\nu})$ and $E_V(\tilde{\nu})$ according to Eqns. 5. Contributions from x-polarized transitions are absent in $E_{-x}(\tilde{\nu})$ and those from y-polarized transitions are absent in $E_{-y}(\tilde{\nu})$. Bottom: Graphical representation of electronic transitions predicted with TD-CAM-B3LYP for boat-shaped, C_{2v} symmetrical TTF (see Table 1). The Gaussian convolutions indicate linear combinations corresponding to the reduced absorbance curves $E_{-x}(\tilde{\nu})$ and $E_{-y}(\tilde{\nu})$.

Relative to absorbance spectroscopy on isotropic samples, the additional information that can be derived from the LD curves is represented by the orientation factors K_i for the moments of the observed transitions i [18–23]:

$$K_i = \langle \cos^2(\vec{M}_i, U) \rangle \quad (1)$$

Here (\vec{M}_i, U) is the angle of the transition moment vector \vec{M}_i of transition i with the uniaxial stretching direction U of the polymer. The pointed brackets indicate an average over all solute molecules in the light path. A large value of the orientation factor K_i indicates efficient alignment of the transition moment \vec{M}_i with the stretching direction U , and vice versa. The K_i values may be determined by the graphical TEM (Trial and Error Method) procedure [18,19] which involves formation of linear combinations of $E_U(\tilde{\nu})$ and $E_V(\tilde{\nu})$. Here we consider the reduced absorbance curves $r_K(\tilde{\nu})$ [51]:

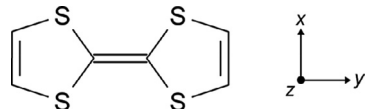
$$r_K(\tilde{\nu}) = (1 - K)E_U(\tilde{\nu}) - 2KE_V(\tilde{\nu}) \quad (2)$$

A family of curves $r_K(\tilde{\nu})$ for TTF is shown in Fig. 1 (bottom). A spectral feature due to transition i vanishes from the linear combination $r_K(\tilde{\nu})$ for $K = K_i$ and the K_i value may thus be determined by visual inspection. In the present case of molecular C_{2v} or D_{2h} symmetry, optically allowed transitions must be polarized along the three molecular symmetry axes x , y , and z , corresponding to transitions to excited states of B_1 , B_2 , and A_1 symmetry in the case of C_{2v} , or B_{3u} , B_{2u} , and B_{1u} symmetry in the case of D_{2h} . Hence, within experimental error, we should observe only three different K_i values equal to K_x , K_y , and K_z , the orientation factors for the three molecular axes. Moreover, the three characteristic values should add up to unity, $K_x + K_y + K_z = 1$.

The following orientation factors were determined in a previous IR-LD investigation of TTF aligned in stretched PE: $(K_x, K_y, K_z) = (0.31 \pm 0.02, 0.45 \pm 0.02, 0.23 \pm 0.02)$ [52]. In that study TTF was introduced into a thick, stretched PE sample by sublimation at 60 $^\circ\text{C}$ for nine days. A more efficient solute alignment is achieved in the present thin sheet sample, resulting in a different distribution of the K -values: Inspection of the $r_K(\tilde{\nu})$ curves in Fig. 1 (bottom) leads to $K = 0.27$ for the feature at 26700 cm^{-1} and $K = 0.55$ for the one at 32900 cm^{-1} . We assign these values to K_x and K_y , corresponding to “in-plane” short- and long axis-polarized transitions, respectively. We thus have

MO no.	Sym.	E (eV)		
-12	64	20 a_1	1.57	
-9	61	19 a_1	1.29	
-7	59	12 a_2	0.92	
-6	58	16 b_2	0.85	
-5	57	13 b_1	0.82	
-4	56	18 a_1	0.48	
-3	55	12 b_1	0.45	
-2	54	15 b_2	0.42	
-1	53	17 a_1	0.10	
<hr/>				
1	52	16 a_1	-6.05	
2	51	14 b_2	-8.08	
3	50	11 a_2	-9.23	

Fig. 3. Numbering, symmetry, and energy of molecular orbitals of boat-shape, C_{2v} symmetrical TTF predicted with CAM-B3LYP/6-311++G(3df,3pd) with indication of the orbital shape.



Scheme 1. Tetrathiafulvalene (TTF) and the applied coordinate system. For theoretical calculations both a planar (D_{2h}) and boat-shape (C_{2v}) configuration are considered.

$(K_x, K_y, K_z) = (0.27, 0.55, 0.18)$, where K_z is obtained from the relation $K_z = 1 - K_x - K_y$.

While determination of the K -values may be relatively straightforward, it is far more difficult to derive the partial absorbance curves $A_x(\bar{\nu})$, $A_y(\bar{\nu})$, and $A_z(\bar{\nu})$ corresponding to absorbance polarized along the three symmetry axes of the molecule. In general, the three partial absorbance curves cannot be determined from only two linearly independent spectra $E_{IJ}(\bar{\nu})$ and $E_V(\bar{\nu})$. We shall adopt the formalism outlined by Madsen et al. [51] and construct the pair of reduced absorbance curves

$E_{-x}(\bar{\nu})$ and $E_{-y}(\bar{\nu})$:

$$\begin{aligned} E_{-x}(\bar{\nu}) &= (K_y - K_x)^{-1} r_{K_x}(\bar{\nu}) \\ E_{-y}(\bar{\nu}) &= (K_x - K_y)^{-1} r_{K_y}(\bar{\nu}) \end{aligned} \quad (3)$$

Contributions from x -polarized transitions are absent in $E_{-x}(\bar{\nu})$ and those of y -polarized transitions are absent in $E_{-y}(\bar{\nu})$. The resulting curves produced with $(K_x, K_y) = (0.27, 0.55)$ are shown in Fig. 2 (top). They are related to the partial absorbance curves $A_x(\bar{\nu})$, $A_y(\bar{\nu})$, and $A_z(\bar{\nu})$ through the relations [51]:

$$\begin{aligned} E_{-x}(\bar{\nu}) &= A_y(\bar{\nu}) + \frac{K_z - K_x}{K_y - K_x} A_z(\bar{\nu}) \\ E_{-y}(\bar{\nu}) &= A_x(\bar{\nu}) + \frac{K_z - K_y}{K_x - K_y} A_z(\bar{\nu}) \end{aligned} \quad (4)$$

For many planar or nearly planar chromophores, “out-of-plane” polarized absorbance such as $A_z(\bar{\nu})$ can to a good approximation be set equal to zero in the near UV region, yielding directly $E_{-x}(\bar{\nu}) = A_y(\bar{\nu})$ and $E_{-y}(\bar{\nu}) = A_x(\bar{\nu})$. However, this is not possible with TTF where the three partial absorbance curves all contribute significantly to the observed spectrum (see below). TTF can thus be characterized as a “three-dimensional” chromophore. With $(K_x, K_y, K_z) = (0.27, 0.55, 0.18)$ we obtain:

$$\begin{aligned} E_{-x}(\bar{\nu}) &= A_y(\bar{\nu}) - 0.3 \cdot A_z(\bar{\nu}) \\ E_{-y}(\bar{\nu}) &= A_x(\bar{\nu}) + 1.3 \cdot A_z(\bar{\nu}) \end{aligned} \quad (5)$$

As discussed in the following, $E_{-x}(\bar{\nu})$ and $E_{-y}(\bar{\nu})$ provide a useful representation of the observed polarization data for TTF.

4.2. Electronic transitions

The reduced absorbance curves $E_{-x}(\bar{\nu})$ and $E_{-y}(\bar{\nu})$ are shown in Fig. 2 (top) with indication of prominent features A to H. As explained above and indicated in Eqns. 5, the curves $E_{-x}(\bar{\nu})$ and $E_{-y}(\bar{\nu})$ contain linear combinations of the partial absorbance curves $A_x(\bar{\nu})$, $A_y(\bar{\nu})$, and $A_z(\bar{\nu})$. But for simplicity, features in $E_{-x}(\bar{\nu})$ are in the following described as “long axis-polarized” and those in $E_{-y}(\bar{\nu})$ as “short axis-polarized”. The bottom panel of Fig. 2 shows transitions predicted for the boat-shape C_{2v} symmetrical equilibrium geometry, as well as corresponding convoluted curves constructed to correspond to the reduced absorbance curves $E_{-x}(\bar{\nu})$ and $E_{-y}(\bar{\nu})$ according to Eqns. 5. The observed features and the suggested assignments to predicted electronic transitions are listed in Table 1.

The absorption spectrum of TTF starts with a weak transition A with a maximum at $22,000 \text{ cm}^{-1}$ (455 nm), responsible for the red color of the substance. The band is primarily long axis-polarized, but the observed polarization of this very weak absorbance is probably determined by intensity borrowed from stronger transitions at higher energy, such as those giving rise to the intense, long axis-polarized band D (see below). Band A must be assigned to the optically very weak 2^1A_1 state predicted at $21,000 \text{ cm}^{-1}$. This state is dominated by the HOMO-LUMO excitation involving promotion of an electron from $16a_1$ to $17a_1$ (Fig. 3). This is essentially a π - σ^* transition, although π and σ type contributions are more or less mixed in the boat-shape C_{2v} symmetrical equilibrium conformation. The present assignment of band A is consistent with previous assignments, such as those by Andreu et al. [15] and Pou-Amérgo et al. [16,17].

The relatively intense feature B observed at $26,700 \text{ cm}^{-1}$ (375 nm) is short axis-polarized. The feature overlaps the onset of the long axis-polarized band D and probably contains long axis-polarized contributions due to vibronic interaction with this strong band. Band B is easily assigned to the x -polarized electronic transition to the 1^1B_1 state predicted at $26,800 \text{ cm}^{-1}$. This is essentially a π - π^* transition involving promotion from $16a_1$ to $12b_1$ (Fig. 3). Again, this assignment is consistent with previous assignments [15–17].

The following feature C at $31,300 \text{ cm}^{-1}$ (320 nm) was not clearly observed in previous experimental studies, largely due to overlap with the strong absorbance D; it does not seem to have been discussed in detail

in previous literature. It is short axis-polarized and can be assigned to overlapping contributions from the states 2^1B_1 and 3^1A_1 predicted at 31,400 and 32,200 cm^{-1} , giving rise to *x*- and *z*-polarized intensity, respectively. The orbital origins of the computed transitions are complex, as indicated in Table 1. Wavenumber and intensity of the predicted 3^1A_1 state depend significantly on the inclusion of diffuse functions in the basis set (S6), indicating a substantial component of non-valence character. Pou-Amérgo and co-workers predicted Rydberg states from about 30,000 cm^{-1} and above, but with low oscillator strengths [16,17].

The strong, long axis-polarized feature *D* peaking at 32,900 cm^{-1} (304 nm) is the most intense absorption band in the investigated spectral region. It displays a prominent shoulder close to 31,500 cm^{-1} (317 nm). This composite band can be assigned to overlapping contributions from transitions to the 1^1B_2 and 2^1B_2 states computed at 30,400 and 32,700 cm^{-1} with oscillator strengths 0.09 and 0.29, respectively (Table 1). Pou-Amérgo et al. [17] calculated corresponding 1^1B_2 and 2^1B_2 states at 32,300 and 34,400 cm^{-1} with TD-B3P86/aug-cc-pVDZ.

The tail of band *D* overlaps the short axis-polarized feature *E* with a maximum at 38,800 cm^{-1} (258 nm). This absorbance has apparently not previously been discussed in any detail. According to the present theoretical results, the feature *E* can be assigned to the states 4^1A_1 and 5^1A_1 predicted at 38,200 and 38,900 cm^{-1} , giving rise to transitions polarized along the “out-of-plane” *z* axis. Prediction of the 4^1A_1 and 5^1A_1 states depend strongly on inclusion of diffuse functions in the basis set (S6), indicating that the states have significant non-valence character. The transitions are primarily due to promotions to the virtual orbitals $19a_1$ and $20a_1$ (−9 and −12 in Table 1) which have large *d* and *s* type Rydberg character, respectively, see Fig. 3. The predictions are supported by the results of calculations with larger basis sets and with other functionals (S7 – S11), although the computed relative optical intensities of the 4^1A_1 and 5^1A_1 states depend on the model.

The vacuum UV region exhibits overlapping long and short axis-polarized intense absorbance. Assignment of the observed features to the numerous transitions calculated in this region is necessarily tentative. The short axis-polarized absorbance is characterized by a very broad band with maximum *H* close to 53,900 cm^{-1} (186 nm) and a prominent shoulder *F* at 48,000 cm^{-1} (210 nm). This absorbance can be assigned to several states, such as the 6^1B_1 , 7^1B_1 , and 10^1B_1 states predicted at 47,700, 50,000, and 53,900 cm^{-1} (Table 1). The long axis-polarized absorbance *G* peaking at 50,000 cm^{-1} (200 nm) can be assigned to the 9^1B_1 state predicted at 50,900 cm^{-1} , with contributions also from the 6^1B_2 and 7^1B_2 states calculated at 46,300 and 47,400 cm^{-1} (Table 1). But it must be emphasized that diffuse functions in the basis set have a profound impact on the absorption profiles predicted in the vacuum UV region (S6), suggesting significant non-valence character of several transitions. The applied theoretical model is likely to be less accurate in this region.

In the preceding paragraphs, the observed absorption bands of TTF are discussed with reference to theoretical transitions calculated for the boat-shape C_{2v} symmetrical equilibrium nuclear configuration. Table 1 also lists the transitions calculated for the planar D_{2h} symmetrical molecular geometry, and a comparison of the computed spectra is provided in S5. It is apparent that the predicted spectra show obvious similarities, but also significant differences. In particular, the 1^1B_2 and 2^1B_1 states of boat-shape TTF predicted at 30,400 and 31,400 cm^{-1} correspond to optically forbidden states in the planar D_{2h} geometry.

5. Conclusions

Tetrathiafulvalene (TTF), a compound with a diverse field of applications in both molecular electronics and supramolecular chemistry, has been characterized in detail with respect to electronic states in the near- and vacuum-UV region using synchrotron radiation polarization spectroscopy. Interpretation of the experimental linear dichroism absorbance data show that TTF is a truly 3-dimensional chromophore with UV spectral contributions from electronic transitions polarized along all three

molecular axes. These findings may be of importance in functional applications relying on TTF-derived compounds e.g. in photoresponsive conducting materials [53]. The LD analysis allowed for resolution of eight distinct spectral features, several of which were overlapping and previously unrecognized. Theoretical calculations of electronic transitions for both the non-planar C_{2v} symmetrical equilibrium geometry and the planar D_{2h} geometry were performed using TD-DFT models. Considering the low barrier of the D_{2h} transition state, TTF must be considered a dynamic chromophore that likely undergoes rapid fluctuation, flipping between two C_{2v} conformations. Such behavior can most likely contribute to the diffuseness of the bands observed in the UV spectrum, and may also via consideration of vibronic coupling have implications for the molecular electronic properties of TTF-derived compounds, as discussed for certain salts [54]. We find in general that there is a good agreement between experimental transitions in the low-energy region $<40,000 \text{ cm}^{-1}$ ($>250 \text{ nm}$) to the results consistently obtained with a selection of different TD-DFT models and basis sets and a reasonable agreement in the high-energy region. However, the DFT calculations did show that diffuse basis set functions were essential for a reliable prediction of several transitions, perhaps due to their Rydberg-like characteristics. More advanced theoretical approaches are required for a more complete understanding of the electronic transitions, particularly concerning the high-energy region ($>40,000 \text{ cm}^{-1}$) with a proper treatment of Rydberg states in an approach that can also accommodate the dynamic nature of the chromophore.

Declaration of Competing Interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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Supplementary materials

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