

Experimental and theoretical study of infrared active phonons in heavily doped K_xp -terphenyl

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We present an experimental and theoretical study of the infrared-active phonon modes of heavily potassium (K) doped p -terphenyl, a material of great current interest due to reports of high-temperature superconductivity. First, we show that the phonon features in the fingerprint region of the midinfrared domain can be well reproduced through the density functional theory (DFT) quantum-chemical simulations. Compelling evidence for a distorted organic molecular framework is obtained here from the emergence of up to three absorption bands that are predicted to be infrared (IR)-inactive under idealized D_{2h} planar symmetry and a systematic softening of specific vibrational modes. Computational models of twisted conformers exhibiting reduced D_2 or C_{2h} symmetry are shown to successfully reproduce the activation of these silent modes and the redshifting shown by others. Second, we present an analysis of the lineshape of the experimental IR-phonon modes in a wide temperature range from 6 to 300 K. We show that several of the IR phonons have a strongly asymmetric shape that is indicative of a Fano-like interaction with the doped charge carriers. Notably, we find that the phonon asymmetries, and the corresponding Fano parameters, undergo anomalous changes around 100 K that are reminiscent of a charge localization transition around 90 K that has been previously reported from a corresponding study of the low-energy electronic response.

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I. INTRODUCTION

Alkali metal-doped carbon-based materials have obtained significant attention due to their intriguing electronic and vibrational properties. Doping with potassium can render them metallic and even superconductivity with rather sizeable transition temperatures has been reported already more than three decades, e.g., for K_3C_{60} with $T_c = 18$ K [1]. At present, the commonly accepted record value for an organic superconductor is held by Cs_3C_{60} with $T_c = 38$ K under high pressure [2]. For these alkali-metal-doped fullerenes, it is widely assumed that the threefold degeneracy of the lowest unoccupied molecular orbital plays an important role in the superconductivity, via an enhancement of the electron-phonon coupling by

the Jahn-Teller effect [3]. Nevertheless, electron correlation effects appear to be also relevant, since at ambient pressure Cs_3C_{60} turns out to be Mott insulator [4].

In 2010, superconductivity was reported for the first time in a polycyclic aromatic hydrocarbon, namely, in picene ($C_{22}H_{14}$) doped with potassium [5,6], which has a surprisingly large critical temperature of $T_c = 18$ K. Since then, several related organic materials have been found to become superconducting upon doping, notably phenanthrene ($C_{14}H_{10}$) with $T_c = 5$ K [7], dibenzopentacene ($C_{30}H_{18}$) with $T_c = 33$ K [8], and pentacene ($C_{22}H_{14}$) with $T_c = 4.5$ K [9].

More recently, potassium-doped *para*-terphenyl (K_xp -terphenyl) has obtained a great deal of attention, since it has been reported that it might be a high-temperature organic superconductor with a transition temperature of up to $T_c \sim 120$ K for a nominal composition of $K_3 p$ -terphenyl [10–12]. The evidence for superconductivity is mainly based on magnetic susceptibility data; these data reveal the onset of a weak diamagnetic signal below 120 K that has been interpreted in terms of a superconducting phase with a small volume fraction on the order of a few percent. The weak diamagnetic signal has been confirmed by an independent group based on a magnetization study of polycrystalline $K_3 p$ -terphenyl

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samples that were synthesized under high-pressure conditions [13]. Signatures of a high- T_c superconducting phase, possibly with a rather small volume fraction, have also been reported from electrical transport measurements [14]. Moreover, evidence for possible high-temperature superconductivity has been reported from an angle-resolved photoemission spectroscopy (ARPES) study of a *p*-terphenyl crystal with a heavily K-doped surface layer, for which a gaplike feature with a magnitude of about 12 meV was observed in the electronic excitation spectrum below about 120 K [15]. A gaplike feature of about 11 meV has also been seen in a scanning tunneling spectroscopy study that sets in below about 50 K. However, it has been argued that this gap feature might not arise from superconductivity, since the spectra did not show any coherence peaks and they remained unaffected by a large magnetic field [16].

Pristine *p*-terphenyl is a wide-gap semiconductor with a bandgap of about 3.5 eV [17]. The K doping gives rise to a transfer of electrons from the K cations to the *p*-terphenyl molecules and results in a reduction of the band gap and eventually a conducting state. How exactly this closing of the band gap happens and a conducting state emerges remains a matter of debate.

Zhong *et al.* have performed calculations of the evolution of the band structure of K_x *p*-terphenyl as a function of the potassium content, which suggest that a finite density at the Fermi level and thus a metallic state occurs for all doping levels ranging from $K = 1$ to $K = 3$. They also suggested that the heavily doped K_3 *p*-terphenyl samples are the most likely candidates to host high T_c superconductivity. This hypothesis has been supported by the work of Mazziotti *et al.* [18].

Nevertheless, it remains disputed whether in these highly K-doped samples the potassium is homogeneously distributed. Accordingly, the superconducting phase might have a different K-content or even originate from clusters or filaments of K-rich material for which the composition is presently unknown, as discussed, e.g., in Refs. [19–21].

To shed more light on the low-energy electronic and lattice dynamical properties, we have performed an infrared ellipsometry study of a heavily doped K_x *p*-phenyl sample with a nominal doping level of $x = 3$. A twin sample has been studied with electric transport measurements, which revealed anomalous changes of the dc resistivity below about 90 K. The analysis of the low-energy electronic response in the infrared range for temperatures ranging from 6 to 300 K has already been reported in Ref. [22]. It has revealed an anomalous redistribution of low-energy spectral weight that occurs below about 90 K and is characteristic of a weak localization of the charge carriers rather than of a superconducting transition. The possibility that these anomalous changes of the low-energy response might be caused by plasmonic effects due to a filamentary superconducting phase could, however, not be entirely excluded.

Here, we report the corresponding analysis of the infrared active phonon modes of the same heavily K_3 -doped *p*-terphenyl sample for which the electronic response was reported in Ref. [22]. We find that some of the phonons exhibit a strongly asymmetric lineshape, which is indicative of a sizeable electron-phonon coupling and/or a spatial variation of the distortion of the *p*-terphenyl molecules. For several of these

phonon modes, we furthermore observe that their asymmetries undergo sudden changes around 100 K. We therefore argue that this coincidence of the changes of the electronic and lattice dynamics around 90–100 K is suggestive of a combined structural and electronic transition that reduces the intermolecular mobility of the doped charge carriers. Moreover, we compare the experimental data with density functional theory (DFT) calculations of the infrared (IR)-active phonon modes of heavily K-doped *p*-terphenyl. We find that a reasonably good agreement of the eigenfrequencies and intensities of the phonons can be obtained by assuming a distorted, nonplanar structure of the *p*-terphenyl molecules, which involves a rotation angle of the benzene rings of about 40°–45°.

The paper is structured as follows. In Sec. II, we discuss the experimental details of the sample growth and characterization, and the ellipsometry technique. Subsequently, we present in Sec. III the measured room-temperature spectra for a nominal K_3 *p*-terphenyl sample and compare it with those of bare *p*-terphenyl. We also discuss the fitting of the phonon modes with an asymmetric Lorentz oscillator model. Section IV contains a detailed description of the DFT-based calculations of the phonon modes for the case of di-anion molecules. It reveals that a good agreement with the experimental phonon spectrum of the nominal K_3 sample can be obtained by considering a distorted, nonplanar structure of the doped *p*-terphenyl molecules. In Sec. V, we present the temperature dependence of the experimental spectra and their best fits, which reveal for several of the phonon modes rather sudden changes of the asymmetry parameter around 100 K. Finally, in Sec. VI, we summarize our findings and discuss their implications.

II. EXPERIMENT

A polycrystalline sample of highly potassium-doped *p*-terphenyl with a nominal composition of K_3 *p*-terphenyl has been synthesized following the procedure described in Ref. [14]. For comparison, we also prepared a sample of the undoped *p*-terphenyl. For the optical measurements, we pressed pellets with a diameter of 12 mm and a thickness of about 1 mm that were prepared and subsequently handled under dry and inert Ar gas atmosphere. For this purpose, we constructed an optical cell that allows to keep the sample under Ar atmosphere while it is mounted inside the He-flow cryostat of our infrared ellipsometer. A detailed description of the optical cell and the ellipsometry setup is given in Refs. [22,23]. The ellipsometric spectra have been recorded at an angle of incidence of $\phi = 75^\circ$ at different temperatures from 6 to 300 K. For the far-infrared range from 50 to 700 cm^{-1} , we used a rotating analyzer setup with polarizers made from wire grids evaporated on thin polyethylene foil. The midinfrared range from about 600 to 5000 cm^{-1} was measured with a rotating compensator based on a ZnSe prism and wire grid polarizers on KRS-5 substrates. A He-cooled bolometer was used as a detector for the entire spectral range.

III. ANALYSIS OF THE ROOM-TEMPERATURE PHONON SPECTRA

Figure 1(a) displays the spectra of the real part of the optical conductivity at 300 K for the polycrystalline

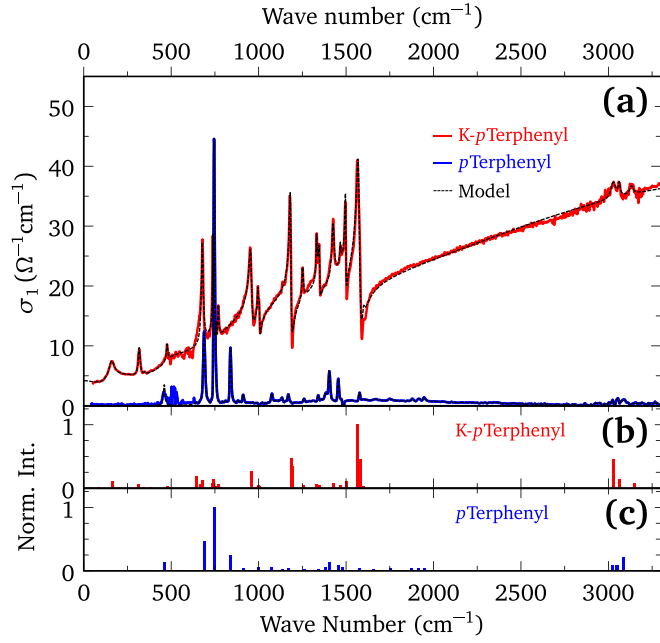


FIG. 1. (a) Comparison of the optical conductivity spectra at 300 K of polycrystalline samples of pristine *p*-terphenyl (blue) and nominal K₃*p*-terphenyl (red). The black dotted line shows the best fit with the Drude-Lorentz model of Eq. (1). The scale bars in panels (b) and (c) indicate the obtained values of the frequency and the relative intensity (normalized to that of the strongest mode) of the phonon modes of K₃*p*-terphenyl and pristine *p*-terphenyl, respectively.

samples of pristine *p*-terphenyl (blue symbols) and nominal K₃ *p*-terphenyl (red symbols). The black lines show the best fit using the following so-called Drude-Lorentz model that is widely used for fitting the infrared electronic and lattice response of solid state materials [24,25]:

$$\varepsilon(\omega) = \varepsilon^{el}(\omega) + \sum_{i=1}^N S_i \frac{\omega^2 - i\omega\sigma_i}{\omega^2 - \omega_i^2 - i\omega\Gamma_i} + \varepsilon_{\infty}. \quad (1)$$

The first term describes the electronic response of the free and weakly bound electrons as well as the interband transitions. As discussed in detail in Ref. [22], this electronic response has been described with a sum of a weak Drude term and several broad Lorentz oscillators. The second term consists of a sum of asymmetric Lorentz oscillators that account for the much narrower lineshapes of the IR-active phonons that are the main target of this manuscript. Here, $S_i = \Delta\varepsilon$ is the oscillator strength, ω_i the frequency, and Γ_i the linewidth of the *i*th Lorentz oscillator. The parameter σ_i determines the asymmetry of the phonon lineshape. Technically, it describes a mixing of the real and imaginary parts of the dielectric function that allows to reproduce the distorted lineshape of a Lorentzian peak in a Kramers-Kronig consistent manner and independent of a particular physical model. Like the more commonly used Fano function [26–31], it allows to describe the asymmetry of a phonon mode that arises from its interaction with a broader electronic background. The modulus of the σ parameter accounts for the strength of the asymmetry of the phonon mode. A positive (negative) sign implies that the phonon is interacting with a broad electronic mode that is

centered on its low-frequency (high-frequency) side. Likewise, contributions to the asymmetry can arise from a mixing of anharmonic phonon modes [32] or from a spatially inhomogeneous distribution of the phonon eigenfrequencies, e.g., due to a local variation of the K concentration and the subsequent doping level of the molecules. Finally, the third term contains the high-frequency dielectric constant ε_{∞} that accounts for the offset of ε_1 due to the interband transitions at energies well above the experimental range.

The parameters for the best fit of the IR-active phonon modes of the pristine *p*-terphenyl and K₃*p*-terphenyl using Eq. (1) are listed in Table I. This table also shows an assignment of the phonons according to their different types of ionic displacement patterns that have been adopted from Ref. [34] and from the DFT calculations presented in Sec. IV. Moreover, Figs. 1(b) and 1(c) show scale bar plots that visualize the eigenfrequencies and the normalized intensities (for each compound with respect to the strongest mode) of pristine *p*-terphenyl and nominal K₃*p*-terphenyl, respectively.

It is evident from Fig. 1 and Table I that the K substitution gives rise to pronounced changes of the IR-active phonon modes. For example, the spectrum of the nominal K₃*p*-terphenyl sample reveals two pronounced low-energy phonons at 161 and 317 cm^{-1} that are absent, or at least orders of magnitude weaker, in pristine *p*-terphenyl. For the latter, the lowest phonon mode is resolved at 460 cm^{-1} . These modes are of a ring deformation type and thus involve a distortion of the benzene rings that acquires a large dipole moment via the modulation of the doped electrons on the π orbitals.

The phonon modes above 500 cm^{-1} also exhibit some pronounced doping-induced changes. For the K₃*p*-terphenyl sample, several of these modes have a strongly enhanced oscillator strength and a more strongly asymmetric shape than those of the pristine *p*-terphenyl. These features are signatures of the doped π electrons and their coupling to the intramolecular phonon modes, which modulate their spatial distribution and mobility. The details of the displacement patterns of these phonon modes and their interaction with the itinerant and weakly bound charge carriers are discussed in Sec. IV, based on a comparison with DFT calculations.

IV. DFT CALCULATIONS OF THE IR-ACTIVE PHONON MODES OF DI-ANIONIC K₂ (*p*-TERPHENYL)

In an attempt to describe what we think is a distorted molecular geometry in the raw material, we have carried out DFT calculations using Gaussian 16 of *p*-terphenyl dianion while constraining the tilt angle between the rings. We think this nonentirely relaxed structure may be the concomitant result of a solid state synthesis, in which potassium (K) intercalation of pristine *p*-terphenyl crystals occurs but thermal energy is not enough to relax the entire reticular structure. Unfortunately, adequate ways to purify or crystallize these types of sensitive materials are lacking, and stronger thermal treatments lead to sample destruction.

We have focused on the 600–1700 cm^{-1} region in our simulation, which covers the aromatic fingerprint region. It includes the aromatic C–C stretching region, the C–H in-plane bending, and the C–H out-of-plane bending region. In

TABLE I. Best fit parameters, using Eq. (1), for the experimental phonon modes of pristine *p*-terphenyl (left column) and nominal K3*p*-terphenyl (center column). Units are cm^{-1} for ω_i (eigenfrequency), ω_{pi} (plasma frequency), Γ_i (linewidth), and σ_i (asymmetry). The left-hand column indicates the displacement type of the phonon modes according to Ref. [33].

Measured	(K ₀)			Measured	(K ₃)			Mode assignment
ω_p	ω_{pi}	Γ_i	σ_i	ω_p	ω_{pi}	Γ_i	σ_i	
				83	17	8.5		Ring deform
				166.5	85	20		Ring deform
				252.7	40	68.5		Ring deform
				317.1	60	8.5		Ring deform
				346.9	18	10.5		Ring deform
				381.47	17	8.4		Ring deform
460	52	12.75		475.8	39	5.5		Ring deform
689	100	12.89	−132	680.11	114	12	−220.8	Ring deform
745	148	7.79	34	738.305	81.6	4.6	−208.2	C–H op bend
				756.5	31.2	5.92	237.937	C–H op bend
				769.8	48	5.43		C–H op bend
838	73	8.75						C–H op bend
910	37	12.4						C–H op bend
				956.26	99.4	18.44	−1148.12	C–H op bend
				961.75	37.67	6.04		C–H ip bend
				996.47	47	6.39	−214.17	C–H op bend
1006	39	76.72	1867.12	1006.38	24.7	4.85	−2233.5	C–H ip bend
1169	23	7.1		1185.22	91	11.33	−2141.93	C–H ip bend
1253	27	24.1	923.22	1253.81	57	8.38		C–H ip bend
				1333.04	59	6.29	−603.8	C–C stretch
1340	25	9.1						C–H ip bend
				1349.31	47.7	6.8	−2108.8	C–C stretch
				1426.85	89	11.9	−200	C–C stretch
1385	30	13.2						C–H op bend
1404	58	79.58	−3728.3					C–C stretch
1455	49	8.62						C–C stretch
				1470.27	32.68	8.35	−1036.1	C–C stretch
1488	20	7.48	2032.02					C–C stretch
				1501.24	49	6.61	−4647.2	C–C stretch
1577	29	8.52		1567.76	88.6	12.48	−1245.7	C–C stretch
				1583.2	35.5	17.27	−29 994.2	C–C stretch
				1597.5	48.2	14.61	−135.1	C–C stretch
3022	17	8.45						C–H stretch
				3030.1	74	38.3		C–C stretch
3053	18	9.68		3064.6	41	15		C–H stretch
3085	29	24.45						C–H stretch
				3148.23	31	32.6		C–H stretch

p-terphenyl, as well as with other aromatic hydrocarbons, the C–C/C–C stretching and in-plane C–H bending modes have frequencies close enough to produce normal modes of mixed character. When these modes are transformed as the same irreducible representation under the point group of the molecule and their atomic displacements are mechanically coupled (that is, the C–H bending occurs in phase with adjacent C–C stretching), they mix producing hybrid vibrational normal modes, usually in the 1 600–1 000 cm^{-1} range. Many of the bands that display mixed stretching/bending character described below are of this type. All these medium-frequency modes are, in principle, accurately modeled in a molecular type of calculation and are a powerful tool for identifying structural and electronic effects.

The assignment of the experimental spectrum was made by examining the molecular vibrational modes of the

different calculated conformations of the di-anions of *p*-terphenyl followed by regression analysis against the experimental spectrum. At the bottom of Fig. 3, the experimental spectrum at 6 and 300 K is reported (14 molecular modes at 6 K are 680.1, 738.3, 756.5, 769.8, 956.6, 996.6, 1186.2, 1253.8, 1334.6, 1349.7, 1426.9, 1470.3, 1501.2, and 1568.3 cm^{-1}) and (14 molecular modes at 300 K are 680.6, 738.8, 756.9 756.9 or 756.5, 769, 955.8, 995.2, 1185.1, 1250.9, 1333.6, 1347.3, 1427.7, 1470.5, 1498.4, and 1566.1 cm^{-1}) indicated by vertical blue bars.

We have set the dihedral angles as Fig. 2 shows between the rings to specific values starting from flat ($\varphi_1 = \varphi_2 = 0^\circ$ D_{2h} symmetry) to tilted (D_2 symmetric $\varphi_1 = \varphi_2 = 20^\circ$ – 60° at 5° increases) to perpendicular ($\varphi_1 = \varphi_2 = 90^\circ$, again D_{2h}), as well as other less symmetric options ($\varphi_1 = 0^\circ$, $\varphi_2 = 20^\circ$ – 60° , C_2). The potential distortion resulting from these geometric

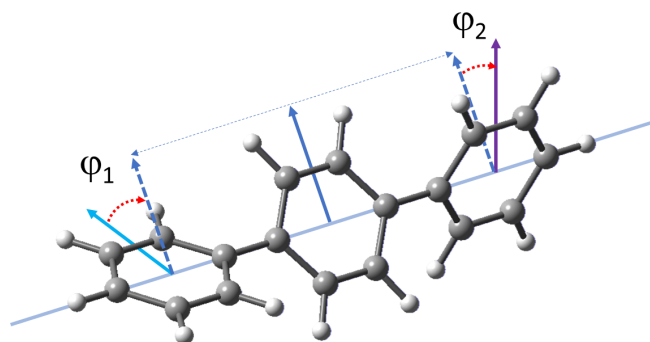


FIG. 2. Definition of torsional coordinates φ_1 and φ_2 .

constraints applied during optimization has been assessed and no significant detrimental effects have been observed. The reason is that none of the normal modes in the studied spectral region involve these φ_1 or φ_2 torsional coordinates, so we can assert that torsional modes are decoupled from mid-IR/fingerprint vibrations. Indeed, purely torsional normal modes $\varphi_1 + \varphi_2$ and $\varphi_1 - \varphi_2$ leading to D_2 and C_{2h} deformations from flat D_{2h} geometry, respectively, occur as very low frequency modes expected around 55 and 40 cm^{-1} (outside the experimentally measured range).

The best fitting was obtained for $\varphi_1 = \varphi_2 = 40^\circ\text{--}45^\circ$ (D_2 symmetry). They are shown in red and blue, respectively, in Fig. 3 along with a representative set of other calculated conformations. The actual IR-active modes and calculated spectrum for a representative p -terphenyl²⁻ of D_2 symmetry is shown in Fig. 4 against the experimental spectrum. In Fig. 3, at the bottom, the experimental spectrum at 300 K is reported (14 molecular modes at 680.1, 738.3, 756.5, 769.8, 956.6, 996.6, 1186.2, 1253.8, 1334.6, 1349.7, 1426.9, 1470.3, 1501.2, and 1568.3 cm^{-1}), indicated by vertical blue bars. Next immediately above is the calculated flat D_{2h} p -terphenyl di-anion. On top of it, an array of calculated spectra of p -terphenyl di-anion with tilted D_2 symmetry at different torsion angles followed by two more spectra of tilted C_{2h} symmetry.

Interestingly, the calculated spectra display fewer active peaks than the experimental one. Some symmetry IR-silent modes in the flat D_{2h} geometry (e.g., a B_{2g} related to P_5 at 757.0 cm^{-1} , a B_{1g} related to P_6 at 769.8 cm^{-1} , and a B_{3g} mode related to P_{12} at 1349.7 cm^{-1}) become IR active when the molecule adopts a lower D_2 tilted symmetry conformation, transforming into IR-active modes B_2 , B_1 , and B_3 , respectively. Also, for a number of modes, the effect of an increasingly tilted conformation shifts their frequency, either softening (P_{15} , P_{13} , P_{12} , P_{11} , P_{10} , P_9 , P_8 , P_5 , P_4) or leaving it nearly unchanged (P_{16} , P_{14} , P_7 , P_6 , P_3). This is another insightful parameter that we have taken into account for the fitting of the experimental spectrum and final conclusions. We also evaluated the potential steric hindrance effects of the ortho-hydrogens between adjacent rings in their motion along the corresponding vibrational coordinate, which could be alleviated by moving from flat D_{2h} to twisted conformations.

In the following, we describe the details of the 14 peaks included in the studied range, according to our assignment to a tilted p -terphenyl di-anion of D_2 symmetry. For further

insights into this discussion, we have also tracked back the equivalent mode of the corresponding flat D_{2h} molecule.

Peak P_3 . Table II(a)(b) shows the phonon 680.1 cm^{-1} . Two very close active IR modes may form this signal. The main one belongs to low- to mid-frequency aromatic C flexion (skeletal deformations). It is dominated by an antisymmetric in-plane flexing deformations of the carbon atoms mainly of the terminal phenyls. The C atoms at the periphery follow small in-plane displacements, consistent with the skeletal ring deformation. It has only moderate IR intensity reflecting a dipole moment change along the long molecular axis, activated by the asymmetric stretching (B_1 type in the D_2 geometry and B_{1u} type in D_{2h} geometry). This mode frequency is rather invariant to changes in the dihedral tilt of the rings (φ_1 , φ_2). Also, motion through this mode is not expected to display steric hindrance effects between the ortho-hydrogens of adjacent rings as they always move in the same direction.

Peak P_4 . Table II(c)(d) shows the phonon 738.3 cm^{-1} in the region of out-of-plane C–H wagging modes, this time of all three phenyl rings in phase. This mode is best described as a global, symmetric hydrogen out-of-plane wagging. The carbon atoms bonded to these hydrogen's show minor complementary motion, reinforcing the wag but not contributing significantly. All the hydrogen atoms swing collectively in phase above and below the ring plane. This results in significant dipole moment generation along the shortest molecular axis, in accordance with B_3/B_{3u} symmetry for the D_2/D_{2h} molecule. This mode is also indicative of torsional distortion (φ_1 , φ_2). The frequency diminishes going from planar to twisted configurations. Motion through this mode does not exhibit steric hindrance effects between the ortho-hydrogens of adjacent rings.

Peak P_5 . As Table II(e)(f) shows the phonons located at 756.5 cm^{-1} , also in the region of out-of-plane C–H wagging modes, this is a small peak yet significant. Again, the assigned vibrational mode is only IR active if the molecule adopts a nonplanar geometry, making its presence a clear indicator of structural distortion. This mode can be described as an asymmetric out-of-plane wagging of hydrogen atoms: Half of them oscillate above and below the ring planes, while the other half do so in an out-of-phase manner. This dynamics results in a modest dipole moment along the second longest molecular axis (red arrow), consistent with a B_2 symmetry mode under D_2 molecular symmetry. The carbon atoms bonded to these hydrogens show a minor complementary motion, contributing subtly to the overall vibration. This mode is also sensitive to torsional distortion (φ_1 , φ_2), and it does not induce steric hindrance between ortho-hydrogens of adjacent rings. When the molecule adopts a flat D_{2h} geometry, this vibration transforms into a similar but silent B_{2g} mode, in which the dipole moment generated by the C–H wagging in both sides of the molecules cancel each other out. It is therefore a hallmark of symmetry breaking or departure from perfect planarity.

Peak P_6 . For the phonon 769.8 cm^{-1} as Table II(g)(h) displays, it is in the region of out-of-plane C–H deformations, which comes along with a concomitant small C–C deformations toward pyramidalization in a wagging mode. The H atoms follow this out-of-plane deformation behaving like a wagging motion with opposite phases on both edges of the molecule. This results in a dipole moment oscillation along

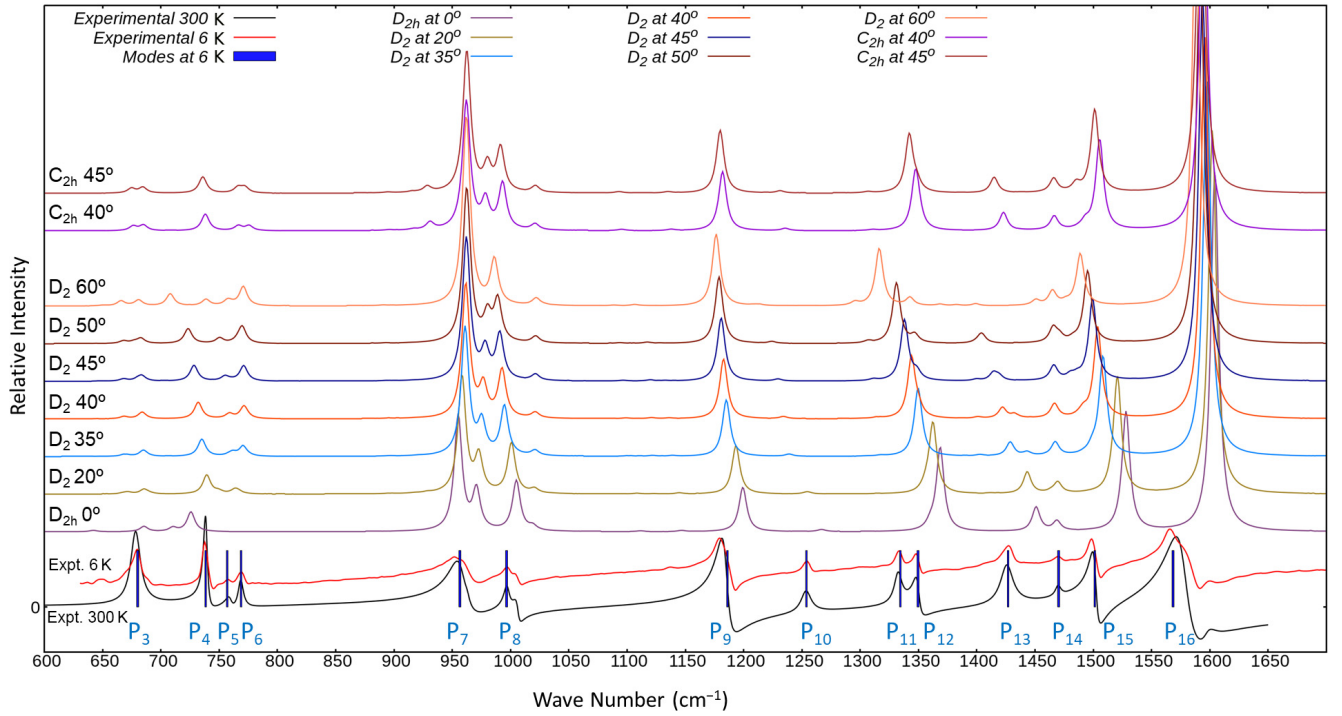


FIG. 3. Simulated phonon spectra for di-anion *p*-terphenyl as a function of molecular distortion angle, ranging from flat D_{2h} geometry $\varphi_1 = \varphi_2 = 0^\circ$ in violet, to tilted D_2 symmetry at different angles $\varphi_1 = \varphi_2 = 20^\circ$ in olive, 35° in light-blue, 40° in light-red, 45° in blue, 50° in orange-red, and 60° in coral. The two spectra on top correspond to tilted C_{2h} symmetry $\varphi_2 = 0^\circ = 40^\circ$ in violet and 45° in brown. For comparison, the experimental spectra of nominal K3*p*-terphenyl at 300 K (black) and 6 K (red) are shown at the bottom, with frequencies marked by vertical blue bars.

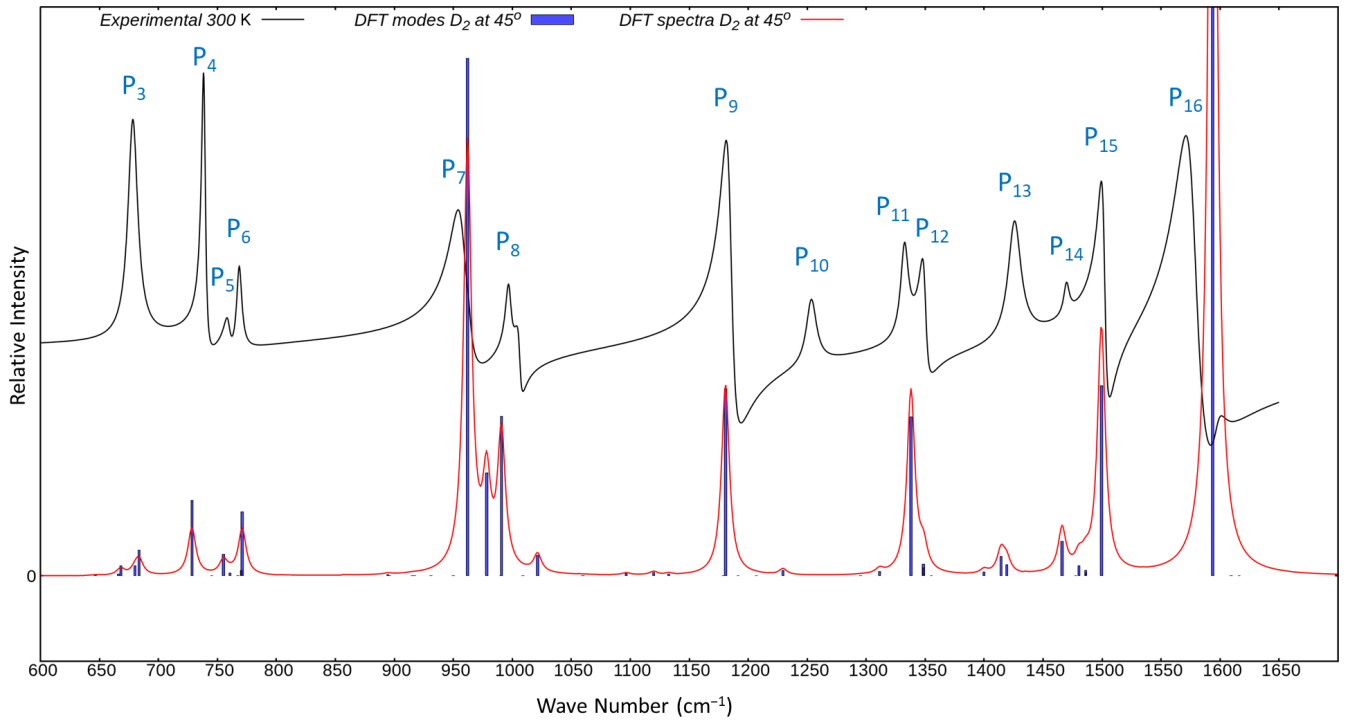


FIG. 4. Comparison of the experimental phonon spectrum for the nominal K3*p*-terphenyl sample (black line) with that of the best matching simulated phonon spectrum (red line) of di-anionic *p*-terphenyl with a D_2 molecular symmetry and $\varphi_1 = \varphi_2 = 45^\circ$ tilt. A similarly good agreement has been obtained for $\varphi_1 = \varphi_2 = 40^\circ$. The position and weight of the calculated phonon modes are indicated by the blue bars.

TABLE II. Ionic displacement patterns of the vibrational modes in the midinfrared region for D_2 -symmetry (left-hand-side column) and D_{2h} symmetry (right-hand-side column). The mode numbering $\mathbf{P}_x$ is according to the assignment shown in Fig. 3.

D_2		Wave Number ν^-	D_{2h}	
(a) B_1		$\mathbf{P}_3$ 680.1 cm^{-1}	(b) B_{1u}	
(c) B_3		$\mathbf{P}_4$ 738.3 cm^{-1}	(d) B_3	
(e) B_2		$\mathbf{P}_5$ 756.5 cm^{-1}	(f) B_{2g}	
(g) B_1		$\mathbf{P}_6$ 769.8 cm^{-1}	(h) B_{1g}	
(i) B_1		$\mathbf{P}_7$ 956.6 cm^{-1}	(j) B_{1u}	
(k) B_1		$\mathbf{P}_8$ 996.6 cm^{-1}	(l) B_{1u}	
(m) B_1		$\mathbf{P}_9$ 1186.2 cm^{-1}	(n) B_{1u}	
(o) B_2		$\mathbf{P}_{10}$ 1253.8 cm^{-1}	(p) B_{2u}	
(q) B_1		$\mathbf{P}_{11}$ 1334.6 cm^{-1}	(r) B_{1u}	
(s) B_3		$\mathbf{P}_{12}$ 1349.7 cm^{-1}	(t) B_{3g}	
(u) B_2		$\mathbf{P}_{12}$ 1349.7 cm^{-1}	(v) B_{3u}	
(w) B_2		$\mathbf{P}_{13}$ 1426.9 cm^{-1}	(x) B_{2u}	
(y) B_1		$\mathbf{P}_{14}$ 1470.3 cm^{-1}	(z) B_{1u}	
(α) B_1		$\mathbf{P}_{15}$ 1501.2 cm^{-1}	(β) B_{1u}	
(γ) B_1		$\mathbf{P}_{16}$ 1568.3 cm^{-1}	(δ) B_{1u}	

the longest molecular axis, in accordance with B_1 symmetry for the D_2 molecule. Interestingly, the lack of inversion symmetry in D_2 makes this vibration IR active, while it transforms into an analogous but silent B_{1g} mode in D_{2h} symmetry, without significant changes in frequency. This mode remains quite insensitive to changes in the dihedral tilt (φ_1 , φ_2). It is another hallmark of a distorted molecular geometry. Also, this mode does not show substantial changes in the steric hindrance between ortho-hydrogens of adjacent rings in their motion.

Peak P_7 . Table II(i)(j) is highly IR active at 956.6 cm^{-1} and very interesting mode best characterized as an in-plane skeletal deformation (or breathing) that involves strong asymmetric C stretching distortion within the outer phenyl rings with some C–H bending coupling. The carbon atoms at alternating positions on the rings undergo coordinate stretching and compression, preserving an overall antisymmetric displacement pattern consistent with a B_1/B_{1u} mode for the D_2/D_{2h} point groups, respectively. Notably, although this mode induces a significant dipole moment change along the long molecular axis, it remains insensitive to dihedral tilt (φ_1 , φ_2) as can be seen in Fig. 3. This mode should show little steric hindrance effects of ortho-hydrogens between adjacent rings in their motion along the vibrational coordinate.

Peak P_8 . The phonon at 996.6 cm^{-1} as Table II(k)(l) shows is another strong IR-active mode showing an in-plane skeletal ring deformation, characterized by asymmetric contraction/expansion of terminal rings and concomitant connected hydrogen atoms motion, notably affecting the dipole moment along the long molecular axis.

One side ring expands while the opposite contracts, creating a net oscillation along the main axis. The central ring acts as a nodal region, merely connecting both movements with little participation. Hydrogens in the outer rings coherently bend with their bonded C atoms significantly contributing to the dipole moment change. The overall motion is assigned to a typical IR active B_1/B_{1u} mode for the D_2/D_{2h} geometries, respectively. This mode is also indicative of torsional distortion (φ_1 , φ_2) due to a frequency softening from planar to twisted configurations.

Peak P_9 . Table II(m)(n) displays a strong IR-active mode 1186.2 cm^{-1} showing a very small carbon framework stretching contribution coordinated with a large peripheral hydrogen bending motion. Hydrogens on the outer rings exhibit strong in-plane scissoring motion. The combined vibration displays a push-pull dynamic: C–H scissoring in one terminal ring is out of phase in the opposite ring, creating an effective oscillating dipole along the long molecular axis that contributes significantly to a strong IR intensity. This hydrogen displacement depicts the asymmetry of the mode, aligning with a typical IR active B_1/B_{1u} mode for the D_2/D_{2h} geometries, respectively. The central phenylene ring shows only minor deformations, mostly acting as a coupling platform. This mode is also a spectroscopic marker of torsional distortion (φ_1 , φ_2) and can distinguish twisted (both D_2 or C_{2h}) versus planar (D_{2h}) configurations of p -terphenyl di-anion due to both a frequency softening and an increase of the intensity.

Peak P_{10} . Table II(o)(p) displays a low-intensity peak 1253.8 cm^{-1} assigned to a mode whose frequency is interestingly quite sensitive to the dihedral twist ($\varphi_1 = \varphi_2$ in D_2 symmetry). Its dynamics shows a concerted in-plane C–C

stretching deformation and connected hydrogen atom bending across all three phenyl rings but in the direction of the second longest axis, therefore consistent with B_2/B_{2u} asymmetric modes in D_2/D_{2h} geometries, respectively. There is a considerable softening of the mode frequency as ϕ increases in going from flat D_{2h} to twisted D_2 symmetries. There are no other concurrent vibrational active modes near this frequency, so its location can be safely considered a marker of out-of-plane geometry distortion from D_{2h} to D_2 or C_{2h} geometries. Hydrogens—especially those in orthopositions—show large in-plane bending, contributing significantly to the dipole moment change, but also imparting severe steric hindrance effects against other ortho-hydrogens of adjacent rings in their motion.

Peak P_{11} . The phonon at 1334.6 cm^{-1} , as Table II(q)(r) shows that it is very close to the former peak and with substantially increased intensity, this mode is a C–C stretching particularly involving the central phenyl ring instead and its connecting bonds to the outer rings, along with some C–H in-plane bending coupled with these ring deformations. At the central ring, vibration consists of an asymmetric stretching between para-carbon atoms and the connected outer phenyl rings. With many similarities in its dynamics to the Peak P_{15} , it is like that one also enhanced by di-anion charge delocalization and very sensitive to the dihedral twisting tilt (φ_1 , φ_2) of the molecule, which affects its full conjugation. Its symmetry is also analogous, B_1/B_{1u} types in D_2/D_{2h} symmetries, respectively, and has a substantial dipole moment change along the long molecular axis. There are severe steric hindrance effects of the ortho-hydrogens between adjacent rings in their motion along this vibrational coordinate.

Peak P_{12} . As Tables II(s)(t) and II(u)(v) shows that this vibrational feature at phonon 1349.7 cm^{-1} is a key diagnostic indicator of planarity in the p -terphenyl di-anion. It exemplifies another vibrational mode in the medium-to-high frequency range resulting of the strong coupling of aromatic C = C stretching with in-plane C–H bending of peripheral hydrogen atoms. Both terminal phenyl rings undergo in-plane out-of-phase stretching of alternating C–C bonds coordinated with C–H bending, while the central ring remains nearly static. Symmetry analysis assigns it to a B_3 irreducible representation for the D_2 symmetry conformation with significant IR activity and dipole change along the shortest axis direction (red arrow facing the observer). Interestingly, at the D_{2h} geometry this mode is assigned to a B_{3g} irreducible representation rendering the mode IR inactive for the flat molecule. Its detection serves as another hallmark of symmetry breaking from perfect planarity (D_{2h}) to lower symmetry (D_2 in this case). This mode is also highly effective in identifying deviations from planarity, as it hardens quickly in going from D_2 to flat D_{2h} geometry.

The *in-phase* variant of this vibration [Table II(u)(v)] shown below may also be a contributing part of Peak P_{12} , as it has nearly degenerated energy and similar intensity, but only for the tilted D_2 geometry that corresponds to a B_2 irreducible representation. For the flat D_{2h} molecule, although equally IR active, the corresponding B_{2u} mode also hardens quickly and falls off relatively far from this region.

Peak P_{13} . The phonon at 1426.9 cm^{-1} is a medium-low intensity asymmetric C=C stretching mode as Table II(w)(x)

shows, it is coupled with substantial peripheral hydrogen atom motion but involving mainly the terminal rings. This time the change in dipole moment is in the direction of the second longest axis (B_2/B_{2u} asymmetric modes in D_2/D_{2h} geometries, respectively) (red arrows). The motion is dominated by terminal phenyl rings. The imposed twist (dihedral $\varphi_1 = \varphi_2$ in D_2 symmetry) disrupts conjugation and causes loss of delocalized electronic motion. This dihedral twist does soften the frequency very significantly. Introducing asymmetry also entails an intensity deenhancement due to a decreased participation of hydrogen atoms in dipole-generating motion. Hydrogens—especially those in orthopositions—show noticeable in-plane rocking, contributing significantly to the dipole moment change. This mode is also highly diagnostic for conjugation perturbation and H-coupled deformation. It shows severe steric hindrance effects of ortho-hydrogens between adjacent rings in their motion along this vibrational coordinate.

Peak P_{14} . As Table II(y)(z) shows, phonon at 1470.3 cm^{-1} corresponds to a low-intensity medium-high frequency vibration with substantial peripheral hydrogen atom motion coupled to a minor, less perceptible aromatic C–C stretching. Moving in phase, all three rings exhibit a coordinated but subtle intraring C–C bond stretching that goes along with a concomitant, large in-plane rocking of the peripheral hydrogen atoms compensating the movement. This affords again an overall B_1/B_{1u} mode in D_2/D_{2h} symmetries, respectively. One noticeable feature of this mode is that its frequency remains essentially unchanged in going from flat D_{2h} to tilted D_2 geometries, indicating that the dihedral twist has very little electronic effect on this vibrational frequency. However, the IR intensity slightly increases toward the twisted D_2 structure. This reduced symmetry apparently allows for more dipole coupling along the main axis. This intensity boost in D_2 geometry may help distinguish twisted versus planar structures.

Peak P_{15} . Table II(α)(β) displays phonon's mode at 1501.2 cm^{-1} , this peak is a distinctive feature of the doped material and a key signature of the spectrum since the vibration of analogous symmetry of the undoped hydrocarbon is found at a lower energy (1481 cm^{-1}). This remarkable effect indicates a bond-order increase upon electron doping. It is the consequence of the strengthening of the interring bonds by adopting a quinoidlike structure along the long molecular axis direction, in comparison with the neutral hydrocarbon of benzenoid structure, so it is strongly coupled with the delocalized electronic structure of the di-anion. As a consequence, this mode is very sensitive to the dihedral angle (φ_1, φ_2) hardening toward the flat D_{2h} geometry (which is the absolute minimal energy conformation of the isolated molecule) and softening as the dihedral angle between rings increases in D_2 geometries due to electronic delocalization impairment. It involves a strong asymmetric interring C–C stretching, specifically between the central and terminal phenyl rings. In this mode, the interring carbon atoms lying on the main axis oscillate with opposite phases especially across the central ring, a motion involving the longitudinal elongation and contraction of these bonds consistent with B_{1u}/B_1 modes in D_{2h}/D_2 symmetries, respectively, and a large dipole moment change along the long molecular axis. Hydrogen atoms in the periphery move slightly to accommodate the deformation of

the ring skeleton. The motion reflects the delocalized nature of the π system and is highly sensitive to molecular planarity and indicative of quinoidal distortions in charged aromatic systems. It also shows severe steric hindrance effects of ortho-hydrogens between adjacent rings in their motion along this vibrational coordinate.

Peak P_{16} . Table II(γ)(δ), the phonon located at 1568.3 cm^{-1} is the most IR intense band on the spectrum, making it a key spectral signature. It corresponds to a high intensity C–C stretching localized mainly across the outer two benzene rings along the longitudinal molecular axis (long-axis) direction. Both rings alternate vibrating at an asymmetric pace (B_{1u}/B_1 symmetries in D_{2h}/D_2 point groups). Hydrogen atoms on the periphery undergo minor displacements, largely compensatory and following the motion of the bonded carbons. This motion involves a strong change of dipole moment along the main axis during the vibration (red arrow), partially enhanced by the delocalized electronic structure of the di-anion. The vibration of analogous symmetry in the neutral hydrocarbon in the solid state (1577 cm^{-1}) has indeed a much lower intensity. The mode frequency is sensitive only to a limited extent to molecular planarity, as can be seen in Fig. 4.

A. Anharmonic correction of stretching modes

To refine the IR characterization, those modes with larger C–C or C–C stretching component, for example P_{16} and P_{15} with the highest frequencies of the studied region, were recalculated using anharmonic vibrational analysis on the unconstrained *p*-terphenyl dianion. Stretching modes exhibit the greatest numerical red shift among other vibrational types when moving from harmonic to anharmonic frequencies. This effect arises because the potential-energy curve for bond stretching is highly asymmetric (a Morse potential): compressing the bond incurs a steep, high-energy repulsion, whereas stretching it gradually flattens the curve as the bond nears dissociation, deviating significantly from an idealized harmonic parabola. In contrast, bending vibrations occur in a much more symmetrical potential well. Upon anharmonic vibrational calculation, there is a substantial redshift in the stretching vibration modes assigned to P_{16} and P_{15} , fitting now much better to the experimental data. Figure 5 reflects these facts.

B. Comparison with Raman spectroscopy

The infrared-active phonon modes proved to be more sensitive to molecular geometric distortions than the corresponding Raman modes. Although earlier Raman simulations by some of the authors—performed at a lower level of theory for the planar D_{2h} geometry—did perform well in simulating the experimental spectra [35], it has been found that the Raman spectra simulated for the twisted D_2 conformations match the experimental data just as well when performed with the tools used in this work. Former DFT studies of isolated *p*-terphenyl di-anion, all of them with D_{2h} geometry, are described in Refs. [34,36].

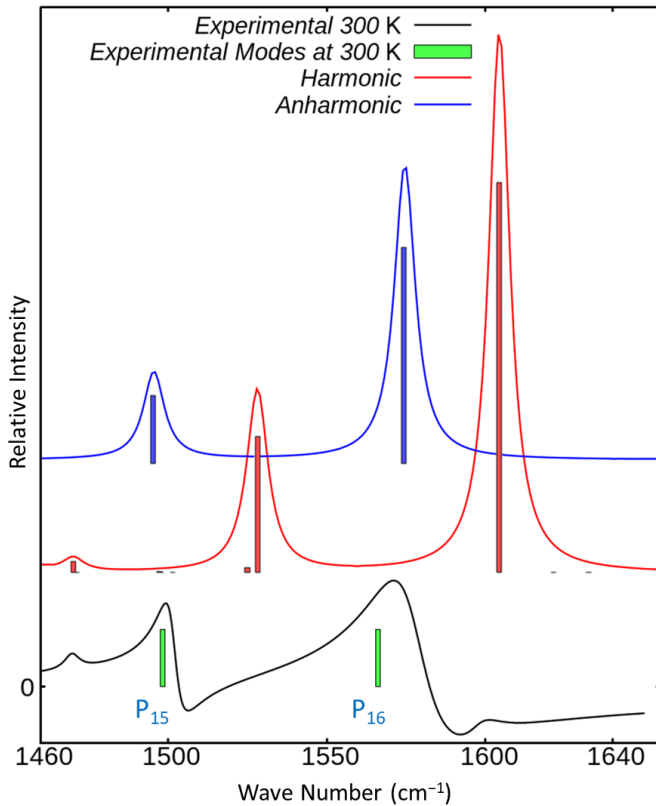


FIG. 5. Effect of anharmonic corrections on the principal stretching modes P16 and P15. Shown is the comparison of the calculated anharmonic spectrum and modes (blue), and the harmonic spectrum and modes (red). The experimental spectrum at 300 K (black) and the modes (green bars).

V. TEMPERATURE DEPENDENCE OF THE IR-PHONONS OF $K_x(p\text{-TERPHENYL})$

In the following, we present the temperature dependence of the IR phonon modes of the nominal $K_3p\text{-terphenyl}$ sample. Figure 6 (a) displays the temperature evolution of the IR-active phonon modes of the nominal $K_3p\text{-terphenyl}$ sample in terms of the conductivity spectra in the frequency range from 50 to 1700 cm^{-1} and at temperatures between 6 and 300 K. The spectra are interrupted between about 500 and 600 cm^{-1} , where the intensity is strongly suppressed by the two-phonon absorption in the Si windows of the optical cell. The strongest modes outside this missing range, for which reliable fits have been obtained with the function given in Eq. (1), are labeled in the order of their increasing eigenfrequency values using the notation P_1 – P_{16} as defined in the previous section. The modes with symmetric lineshapes are marked with open diamonds and the asymmetric modes with an asterisk symbol.

Figures 6(b) and 6(c) display the temperature evolution of the obtained best-fit parameters of the phonon modes P_1 – P_{16} . The left panels show the eigenfrequency and the scattering rate, and the right panels show the corresponding oscillator strength and asymmetry parameter. For the modes $P_1, P_2, P_6, P_7, P_8, P_9, P_{10}, P_{15}$, these fit parameters evolve gradually as a function of temperature and do not exhibit any clear anomalies. For the modes $P_3, P_4, P_7, P_{11}, P_{13}, P_{12}, P_{14}, P_{16}$, however, it is evident that some of the fit parameters exhibit

rather sudden changes around 100 K. These anomalies are most pronounced for the asymmetry parameter, which accounts for the strength of the interaction of these phonons with the underlying low-energy electronic excitations. Note that additional contributions to the asymmetry of the phonon modes may arise from anharmonicity effects or from an inhomogeneous spatial distribution of the potassium ions. This raises the question as to what distinguishes the phonons with a strong anomaly of the asymmetry parameter around 100 K from those without such an anomaly? It appears that the decisive factor is not the overall magnitude of the asymmetry parameter. For example, the asymmetry parameters of the modes P_9 – P_{16} are very large, but they hardly change as a function of temperature. Moreover, for all the asymmetric modes (marked by asterisk symbols in Fig. 6), except for the very weak P_5 mode, the asymmetry parameter tends to have a negative value. In the framework of the Fano model, this reflects the circumstance that the underlying electronic excitations are centered on the high-frequency side of these phonon modes. Such a trend is indeed evident from the infrared spectra in Fig. 1, for which the electronic conductivity increases toward high frequencies well beyond the phonon range. The analysis of the electronic conductivity in Ref. [22] has indeed identified a broad maximum around 4000 cm^{-1} . Moreover, it revealed an anomaly around 90 K in the temperature dependence of the electronic excitations well below 4000 cm^{-1} , in particular, a redistribution of spectral weight from a weak Drude peak at the origin to a mode around 160 cm^{-1} (or 20 meV) [22] that is characteristic of a weak charge localization effect. Since the spectral weight of these low-energy bands depends on the intermolecular and/or the intramolecular mobility of the doped charge carriers, it is quite natural to assume that the anomalous changes of the low-energy electronic response around 90 K and that of the Fano parameter of some of the IR-active phonon modes around 100 K are related phenomena. Based on the present data and analysis, we cannot come up with a conclusive interpretation of the structural changes that underlie this weak charge localization phenomenon. We can only speculate that it involves changes of the lattice sites and the spatial distribution of the potassium ions. It is also possible that a subtle change in the distortion of the individual molecules contributes to the charge localization phenomenon. A twisting transition of the individual molecules is indeed well known for plain $p\text{-terphenyl}$, where it occurs around 195 K and has been directly observed with x-ray diffraction [37]. For the plain $p\text{-terphenyl}$, however, this twisting transition does not give rise to strong phonon anomalies since it lacks π electrons.

VI. DISCUSSION AND OUTLOOK

Our combined experimental and theoretical study of the infrared-active phonon modes in heavily K-doped $p\text{-terphenyl}$ has revealed several interesting features. From the experimental spectra, we have obtained evidence for a rather strong interaction of the phonon modes with the doped charge carriers that manifests itself via an enhanced intensity and a strong asymmetry of several of the phonon modes, as compared to the phonon of pristine $p\text{-terphenyl}$. In particular, the appearance of several low-frequency modes that are absent in the

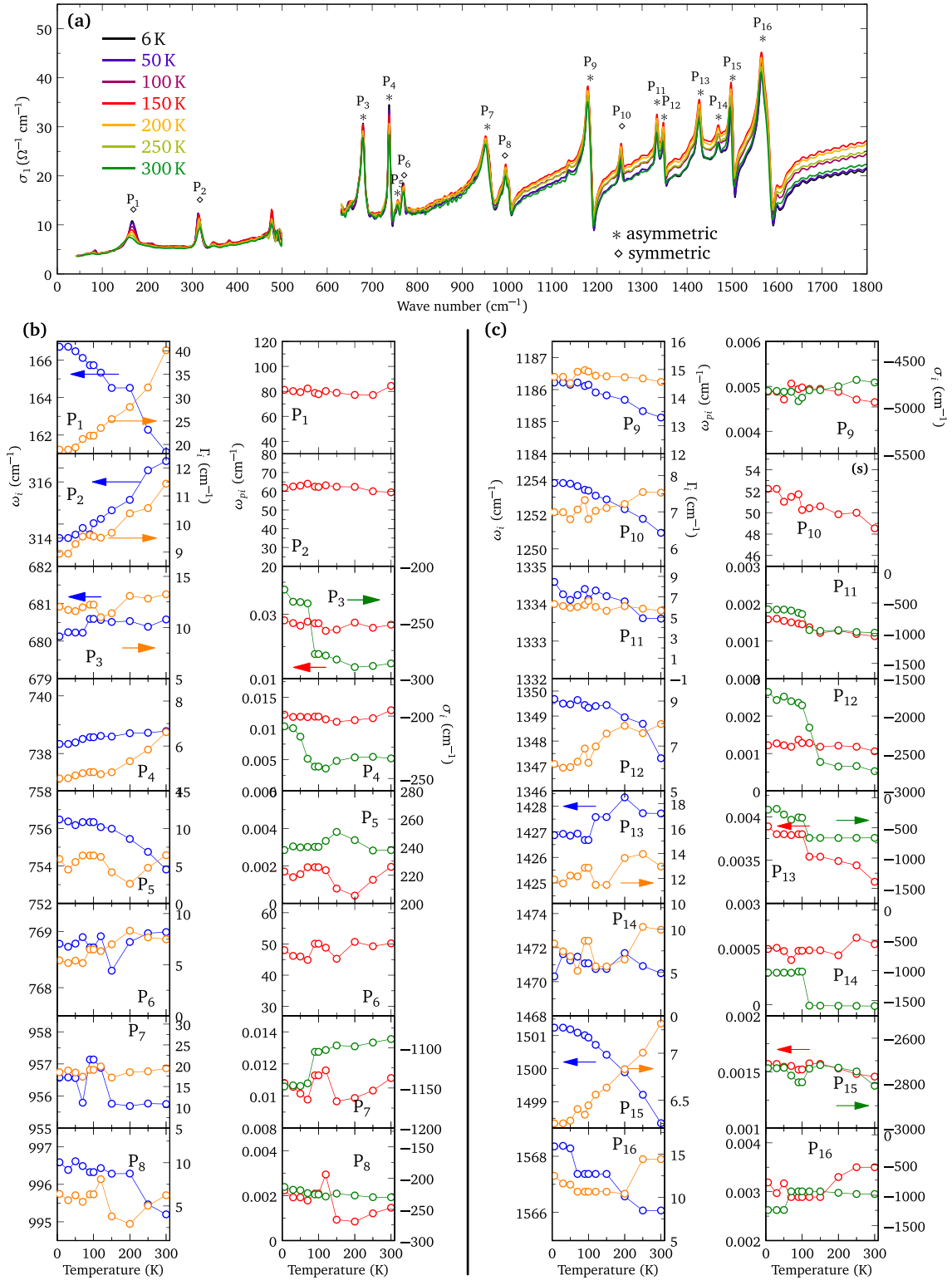


FIG. 6. Panel (a) displays the temperature-dependent spectra of the optical conductivity of K_3p -terphenyl from 50 to 1700 cm^{-1} . The missing data between 500 and 620 cm^{-1} are due to the two-phonon absorption in the Si windows of the optical cell. The phonons, which have been successfully fitted with asymmetric Lorentzian functions as detailed in Eq. (1), are denoted as P1–P16 in the order of their increasing frequencies. Panels (b) and (c) show the temperature dependence of the obtained best-fit parameters for the frequency (blue dots), scattering rate (orange dots), oscillator strength, and the asymmetry parameter of the modes P1–P16.

TABLE III. Energy of (*p*-terphenyl)^{2−} at the given conformations (B3LYP/Def2-QZVPP).

Symmetry	φ_1 (deg)	φ_2 (deg)	Energy (hartree)
D_{2h}	0	0	694.560 941
D_2	2.27	2.27	694.560 954
D_2	10	10	694.560 269
D_2	15	15	694.558 927
D_2	20	20	694.556 783
D_2	25	25	694.553 773
D_2	30	30	694.549 851
D_2	35	35	694.544 989
D_2	40	40	694.539 280
D_2	45	45	694.532 844
D_2	50	50	694.525 786
D_2	60	60	694.510 641
C_{2h}	40	−40	694.540 239
C_{2h}	45	−45	694.533 585
C_2	0	40	694.550 666
C_2	0	45	694.547 507
D_{2h}	90	90	694.497 302

pristine sample provides evidence for structural distortions and charge transfer due to potassium doping.

The DFT-quantum chemical simulations of the phonon modes in the fingerprint region in the midinfrared domain (from 650 to 4000 cm^{−1}) of the di-anionic compound and their comparison with the experimental phonon spectra have provided compelling evidence of a distorted organic molecular framework. This conclusion has been based on the emergence of up to three absorption bands that are predicted to be IR-inactive under idealized D_{2h} planar symmetry, alongside a systematic softening of several specific vibrational modes. Computational models of twisted conformers exhibiting reduced D_2 or C_{2h} symmetry have successfully reproduced the activation of these silent modes and the redshifting shown by others, confirming a departure from planarity of the *p*-terphenyl^{2−} conforming the bulk material. This nonplanar structure seems to result from an incomplete structural relaxation during the solid-state synthesis at rather low temperature, where potassium (K) intercalation of pristine *p*-terphenyl occurs, while the thermal energy is not sufficient to relax the entire reticular structure.

This experimental study has been complemented with DFT-quantum chemical simulations of the phonon modes in the fingerprint region (from 600 to 1700 cm^{−1}) in the midinfrared domain of the di-anionic compound. The comparison of the theoretical and experimental phonon spectra provided compelling evidence of a distorted organic molecular framework. This conclusion has been based on the emergence of up to three absorption bands that are predicted to be IR-inactive under idealized D_{2h} planar symmetry, alongside a systematic softening of several specific vibrational modes. Computational models of twisted conformers exhibiting reduced D_2 or C_{2h} symmetry have successfully reproduced the activation of these silent modes and the redshifting shown by others, confirming a departure from planarity of the *p*-terphenyl^{2−} units conforming the bulk material. This nonplanar structure seems to result from an incomplete structural relaxation

during the solid-state synthesis at rather low temperature where potassium (K) intercalation of pristine *p*-terphenyl occurs, while the thermal energy is not sufficient to relax the entire reticular structure.

The experimental spectra have also been analyzed with respect to the temperature dependence of the phonon parameters. This has revealed intriguing anomalies around 100 K in the asymmetry parameters of several of the IR-active phonons that are suggestive of sudden changes of a Fano-type interaction between the phonon modes and the doped charge carriers. Notably, these changes of the phonon response around 100 K occur close to a previously reported charge-localization transition in the low-energy electron response around 90 K [22]. This coincidence implies that the combined changes of the lowenergy electronic and lattice responses are caused by a structural transition that triggers a localization of some of the charge carriers. The underlying structural changes may be rather subtle and, e.g., involve changes in the position of the K ions, which affect the intermolecular mobility of the doped charge carriers. In addition, there may be changes to the nonplanar structure of the individual molecules that reduce the intramolecular mobility of the charge carriers, which delocalize via the pi bonds of the benzene rings. To clarify the nature of the structural changes underlying this charge localization, additional studies will be required on samples with a well-controlled and homogenous K content. In particular, corresponding studies of the temperature-dependent IR response of K₂*p*-terphenyl samples, which are insulators and thus lack mobile charge carriers, will be very instructive.

Irrespective of these open questions, we emphasize that the combined changes to the electronic and lattice dynamics of the heavily doped K₃*p*-terphenyl sample cannot be accounted for in terms of a superconducting transition. Whereas the previously reported, relatively subtle changes of the low-energy electronic response might have been explained in terms of plasmonic effects from a filamentary superconducting phase (see Ref. [22]), the phonon anomalies reported here are bulk-like phenomena that can hardly be caused by a small minority phase. Our analysis of the combined electronic and lattice infrared response thus provides consistent evidence of a charge localization transition around 100 K that occurs in a similar temperature range as the previously reported superconducting transition [11]. This raises the question whether the small changes to the magnetic susceptibility [13] and the energy gap observed in the ARPES data of Ref. [15] might be related to a charge localization rather than to a superconducting transition. Note that a previous scanning tunneling microscopy study has revealed a gap feature in the low-energy electronic response with a magnitude of 11 meV and an onset temperature of about 50 K that appears to be unrelated to superconductivity, since it lacks the coherence peaks and remains unaffected by high magnetic fields [16].

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DATA AVAILABILITY

The data that support the findings of this article are available from the authors upon reasonable request.

APPENDIX A: CALCULATION DETAILS

The electronic structure and vibrational properties of the *p*-terphenyl di-anion C₁₈H₁₄^{2−} were investigated using DFT. Given the system’s di-anionic nature and the delicate balance between planar and twisted conformations, particular care was taken in selecting the exchange-correlation functional and basis set to ensure accurate geometry optimizations and vibrational frequency predictions. All geometry optimizations were carried out using tight convergence criteria (Opt = Tight) in combination with an ultrafine integration grid (Int = UltraFine) in Gaussian 16. These settings were chosen to ensure highly precise optimized geometries, which are essential for accurate vibrational frequency calculations and for resolving small energy differences. The tight convergence thresholds applied to gradients and displacements guarantee that the molecular structures are very close to true minima on the potential energy surface. Tight optimization is defined by four criteria (in atomic units): maximum force ≤ 0.000015 hartree/bohr; rms force ≤ 0.000010 hartree/bohr; maximum displacement ≤ 0.000060 bohr; and rms displacement ≤ 0.000040 bohr. Additionally, the ultrafine grid enhances the numerical integration of the exchange-correlation functional, reducing noise in the computed force constants. Under these conditions, and for all the molecular conformations calculated in this work, the predicted energy change in the final optimization steps consistently ranged between 10^{−10} and 10^{−13} hartree, confirming excellent convergence and numerical stability across all systems studied.

1. Functional and basis set selection

Calculations were performed using the B3LYP functional [38,39], which provided the best agreement with experimental IR spectra among the tested methods (M06, ωB97XD). A range of basis sets was evaluated, including Pople-style [e.g., 6-311 + G(d, p)], Dunning’s correlation-consistent sets (cc-pVDZ, cc-pVTZ), and the Karlsruhe Def2 series (Def2-SVPP, Def2-TZVPP, and Def2-QZVPP), and their

	1 B3	2 B2	3 A
Frequencies	37.7245	57.7362	58.3774
Red. masses	5.2853	4.9462	3.6024
Frc consts	0.0044	0.0097	0.0072
IR Inten	0.0242	0.1696	0.0000
Raman Activ	2.6957	0.2963	197.0900
Depolar (P)	0.7500	0.7500	0.2893
Depolar (U)	0.8571	0.8571	0.4487
	4 B1	5 B3	6 B2
Frequencies	98.8184	106.5306	107.4828
Red. masses	3.5419	4.3354	4.9435
Frc consts	0.0204	0.0290	0.0336
IR Inten	59.5403	0.1434	0.0284
Raman Activ	1.8798	64.9541	0.7919
Depolar (P)	0.7500	0.7500	0.7500
Depolar (U)	0.8571	0.8571	0.8571
	7 B3	8 B2	9 A
Frequencies	202.5358	205.5363	208.1385
Red. masses	4.2606	4.3566	6.6893
Frc consts	0.1030	0.1084	0.1707
IR Inten	0.0478	5.2901	0.0000
Raman Activ	13.3886	301.3035	184.3586
Depolar (P)	0.7500	0.7500	0.4225
Depolar (U)	0.8571	0.8571	0.5941
	10 B3	11 B2	12 B1
Frequencies	260.6919	390.1864	396.8483
Red. masses	3.3565	4.5204	6.2115
Frc consts	0.1344	0.4055	0.5764
IR Inten	0.0654	1.6338	36.5651
Raman Activ	329.4249	7.3597	1.8874
Depolar (P)	0.7500	0.7500	0.7500
Depolar (U)	0.8571	0.8571	0.8571
	13 B3	14 B2	15 A
Frequencies	425.4587	429.7191	436.5229
Red. masses	2.0194	2.4471	3.2887
Frc consts	0.2154	0.2662	0.3692
IR Inten	40.1892	56.3181	0.0000
Raman Activ	34.0814	65.7939	32.5851
Depolar (P)	0.7500	0.7500	0.5845
Depolar (U)	0.8571	0.8571	0.7378
	16 B1	17 A	18 B3
Frequencies	439.1500	449.4650	478.7092
Red. masses	3.2806	3.4219	3.1513
Frc consts	0.3728	0.4073	0.4255
IR Inten	47.0550	0.0000	11.1177
Raman Activ	6.8975	1782.3730	54.0142
Depolar (P)	0.7500	0.2418	0.7500
Depolar (U)	0.8571	0.3894	0.8571

	19 B2	20 B3	21 A		37 B3	38 B2	39 A
Frequencies	502.9154	509.0246	593.7754	Frequencies	895.9487	915.1172	916.2264
Red. masses	1.4540	1.5042	7.4022	Red. masses	1.2034	1.2320	1.3436
Frc consts	0.2167	0.2296	1.5377	Frc consts	0.5692	0.6079	0.6646
IR Inten	10.6836	42.9548	0.0000	IR Inten	0.0041	0.9324	0.0000
Raman Activ	982.0489	16.8302	89.4423	Raman Activ	195.0205	39.3842	2.3079
Depolar (P)	0.7500	0.7500	0.1604	Depolar (P)	0.7500	0.7500	0.3403
Depolar (U)	0.8571	0.8571	0.2765	Depolar (U)	0.8571	0.8571	0.5078
	22 B3	23 B2	24 B3		40 B1	41 A	42 A
Frequencies	624.1803	627.7811	646.5368	Frequencies	917.4526	931.3433	950.2747
Red. masses	6.4294	6.0922	6.1902	Red. masses	1.3020	1.3627	4.0513
Frc consts	1.4758	1.4146	1.5245	Frc consts	0.6457	0.6964	2.1555
IR Inten	0.0286	0.1177	1.4504	IR Inten	0.4420	0.0000	0.0000
Raman Activ	8.5739	1.9250	0.1831	Raman Activ	0.1935	27.8094	154.6509
Depolar (P)	0.7500	0.7500	0.7500	Depolar (P)	0.7500	0.3291	0.3888
Depolar (U)	0.8571	0.8571	0.8571	Depolar (U)	0.8571	0.4952	0.5599
	25 B3	26 B2	27 B2		43 B1	44 B1	45 A
Frequencies	666.2829	668.2549	680.2037	Frequencies	962.1054	978.2786	990.7631
Red. masses	3.0148	3.9746	2.7499	Red. masses	4.8240	2.8157	2.3421
Frc consts	0.7885	1.0458	0.7496	Frc consts	2.6309	1.5877	1.3546
IR Inten	2.3007	14.9127	14.8930	IR Inten	1096.3118	221.3451	0.0000
Raman Activ	24.2464	42.3646	22.8427	Raman Activ	0.7118	0.0055	3259.1680
Depolar (P)	0.7500	0.7500	0.7500	Depolar (P)	0.7500	0.7500	0.3310
Depolar (U)	0.8571	0.8571	0.8571	Depolar (U)	0.8571	0.8571	0.4973
	28 B1	29 B3	30 A		46 B1	47 A	48 B1
Frequencies	683.6994	728.4291	745.2406	Frequencies	990.8269	1009.2091	1021.4072
Red. masses	5.6056	1.4407	6.0246	Red. masses	2.2027	6.1029	6.1603
Frc consts	1.5438	0.4504	1.9714	Frc consts	1.2741	3.6623	3.7866
IR Inten	38.6849	121.4635	0.0000	IR Inten	347.7952	0.0000	46.4673
Raman Activ	8.6761	5.2100	452.7941	Raman Activ	2.7421	9.8850	0.0586
Depolar (P)	0.7500	0.7500	0.4025	Depolar (P)	0.7500	0.3068	0.7500
Depolar (U)	0.8571	0.8571	0.5740	Depolar (U)	0.8571	0.4696	0.8571
	31 B2	32 B1	33 A		49 B3	50 B2	51 B2
Frequencies	755.1166	760.7353	767.4175	Frequencies	1059.8875	1060.2966	1096.5982
Red. masses	2.0458	1.2577	1.2548	Red. masses	1.6822	1.7238	1.7904
Frc consts	0.6873	0.4288	0.4354	Frc consts	1.1134	1.1418	1.2685
IR Inten	36.0197	4.7260	0.0000	IR Inten	0.2121	0.2592	5.2229
Raman Activ	23.7920	4.8713	262.1109	Raman Activ	78.0086	93.5985	3.0779
Depolar (P)	0.7500	0.7500	0.2425	Depolar (P)	0.7500	0.7500	0.7500
Depolar (U)	0.8571	0.8571	0.3903	Depolar (U)	0.8571	0.8571	0.8571
	34 B3	35 B1	36 B2		52 B3	53 B2	54 A
Frequencies	770.3938	771.1081	894.4189	Frequencies	1119.8931	1132.6190	1178.8118
Red. masses	1.9252	1.2656	1.1957	Red. masses	1.4214	1.2099	1.1456
Frc consts	0.6732	0.4434	0.5636	Frc consts	1.0503	0.9144	0.9379
IR Inten	9.2391	108.9481	2.9671	IR Inten	8.2711	4.0127	0.0000
Raman Activ	104.9232	0.4572	3.2646	Raman Activ	325.5074	17.2507	996.3049
Depolar (P)	0.7500	0.7500	0.7500	Depolar (P)	0.7500	0.7500	0.3139
Depolar (U)	0.8571	0.8571	0.8571	Depolar (U)	0.8571	0.8571	0.4779

	55 B1	56 A	57 B3
Frequencies	1180.7285	1191.5038	1206.9801
Red. masses	1.1536	1.1172	1.9353
Frc consts	0.9476	0.9345	1.6612
IR Inten	486.8066	0.0000	0.7669
Raman Activ	0.4411	1504.8476	158.8162
Depolar (P)	0.7500	0.2869	0.7500
Depolar (U)	0.8571	0.4458	0.8571
	58 B2	59 B3	60 B2
Frequencies	1229.4854	1295.2361	1311.4358
Red. masses	1.7915	2.3331	3.8565
Frc consts	1.5956	2.3061	3.9079
IR Inten	14.9926	0.4986	12.3981
Raman Activ	23.2279	22.3605	9.8011
Depolar (P)	0.7500	0.7500	0.7500
Depolar (U)	0.8571	0.8571	0.8571
	61 B1	62 B3	63 B2
Frequencies	1337.9926	1348.6162	1348.6964
Red. masses	2.6305	2.1120	1.9548
Frc consts	2.7746	2.2632	2.0949
IR Inten	468.5275	34.5573	24.0447
Raman Activ	0.8833	94.9956	139.9889
Depolar (P)	0.7500	0.7500	0.7500
Depolar (U)	0.8571	0.8571	0.8571
	64 A	65 B3	66 B2
Frequencies	1355.3545	1399.8930	1414.3398
Red. masses	4.5629	1.9161	2.6728
Frc consts	4.9385	2.2123	3.1501
IR Inten	0.0000	11.7106	60.5048
Raman Activ	3573.0401	248.2276	127.5573
Depolar (P)	0.3277	0.7500	0.7500
Depolar (U)	0.4936	0.8571	0.8571
	67 B3	68 B1	69 A
Frequencies	1419.1062	1466.1019	1477.7870
Red. masses	2.7416	1.7832	2.1073
Frc consts	3.2530	2.2583	2.7114
IR Inten	35.0196	111.9478	0.0000
Raman Activ	0.1998	0.0009	9067.5520
Depolar (P)	0.7500	0.7500	0.3096
Depolar (U)	0.8571	0.8571	0.4728
	70 B2	71 B3	72 B2
Frequencies	1480.3210	1486.0282	1486.0723
Red. masses	4.6427	2.6987	2.8039
Frc consts	5.9942	3.5113	3.6483
IR Inten	33.1600	9.9649	17.7610
Raman Activ	1.8024	43.3494	214.7061
Depolar (P)	0.7500	0.7500	0.7500
Depolar (U)	0.8571	0.8571	0.8571

	73 B1	74 B1	75 A
Frequencies	1499.4082	1593.7899	1609.6554
Red. masses	2.6951	5.2989	5.6459
Frc consts	3.5699	7.9305	8.6188
IR Inten	627.8308	2982.9890	0.0000
Raman Activ	0.4404	45.9490	10598.2317
Depolar (P)	0.7500	0.7500	0.2146
Depolar (U)	0.8571	0.8571	0.3534
	76 A	77 B1	78 A
Frequencies	1616.2995	3075.4223	3075.9540
Red. masses	5.7971	1.0827	1.0826
Frc consts	8.9229	6.0334	6.0352
IR Inten	0.0000	278.8239	0.0000
Raman Activ	2000.7469	355.3478	707.7240
Depolar (P)	0.0900	0.7500	0.0050
Depolar (U)	0.1651	0.8571	0.0100
	79 B3	80 B2	81 B3
Frequencies	3076.5977	3076.6316	3092.1776
Red. masses	1.0850	1.0851	1.0820
Frc consts	6.0508	6.0513	6.0957
IR Inten	124.3175	124.8480	2.2257
Raman Activ	2268.0122	1882.0781	1.4755
Depolar (P)	0.7500	0.7500	0.7500
Depolar (U)	0.8571	0.8571	0.8571
	82 B1	83 B2	84 A
Frequencies	3093.9054	3117.3619	3121.7560
Red. masses	1.0827	1.0921	1.0916
Frc consts	6.1063	6.2532	6.2675
IR Inten	0.0021	84.6143	0.0000
Raman Activ	0.4075	35.9668	172.7536
Depolar (P)	0.7500	0.7500	0.6504
Depolar (U)	0.8571	0.8571	0.7882
	85 B3	86 B2	87 B1
Frequencies	3130.3001	3130.5877	3131.2146
Red. masses	1.0893	1.0892	1.0880
Frc consts	6.2887	6.2895	6.2852
IR Inten	116.8128	133.5020	5.5011
Raman Activ	379.2934	381.0003	189.3728
Depolar (P)	0.7500	0.7500	0.7500
Depolar (U)	0.8571	0.8571	0.8571
	88 A	89 B1	90 A
Frequencies	3132.4245	3147.0569	3147.3368
Red. masses	1.0884	1.0928	1.0925
Frc consts	6.2921	6.3766	6.3760
IR Inten	0.0000	243.9565	0.0000
Raman Activ	223.3604	218.0590	2486.3508
Depolar (P)	0.2804	0.7500	0.1705
Depolar (U)	0.4380	0.8571	0.2913

diffuse-augmented variants. Although diffuse functions are often recommended for anionic systems to capture delocalized electron density, they were found to introduce numerical instabilities or artifactual shifts in vibrational frequency calculations. This observation aligns with previous reports on the limitations of overly diffuse basis sets in vibrational analyses. Their absence can be effectively compensated by employing a large, flexible basis set such as Def2-QZVPP [40], which inherently captures diffuse character while maintaining numerical stability in vibrational analyses. The B3LYP/Def2-QZVPP combination—featuring a quadruple-zeta basis with double polarization but no explicit diffuse functions—yielded the most reliable vibrational spectra. The inherent flexibility of Def2-QZVPP (four zeta functions for valence orbitals and multiple polarization functions) effectively captured the di-anion’s electron distribution, rendering additional diffuse functions unnecessary. Notably, no scaling factors were required for the vibrational frequencies obtained with this method.

2. Conformational sensitivity and basis set performance

The *p*-terphenyl di-anion exhibits subtle energy differences between planar and twisted conformations, which are highly sensitive to the level of theory. The Def2-QZVPP basis set proved particularly effective in resolving these differences due to high-angular-momentum polarization functions (e.g., *f* orbitals on carbon), essential for modeling torsional barriers in polyaromatic systems [40]. Geometry optimizations were performed with tight convergence criteria, followed by harmonic frequency calculations to confirm true minima (no imaginary frequencies) and simulate IR spectra. The B3LYP/Def2-QZVPP method consistently reproduced experimental band positions and intensities, indicating accurate treatment of both electronic structure and vibrational coupling.

3. Constrained optimization and symmetry considerations

To explore the potential energy surface, selected optimizations were carried out with torsional constraints on the inter-ring dihedral angles (φ_1 and φ_2), enforcing D_{2h} , D_2 , or C_2 symmetry. In the absence of any constraint, the fully optimized structure is a nearly flat conformation

($\varphi_1 = \varphi_2 = 2.27^\circ$) closely approximating D_{2h} symmetry consistent with an optimal delocalization of the anionic charge through the π system but slightly counterbalanced to minimize steric effects of the ortho-hydrogens. All constrained structures converged to true minima, confirmed by the absence of imaginary frequencies. As expected, constrained conformers exhibited slightly higher energies, reflecting the balance between steric repulsion and π conjugation. Table III summarizes the energy of some optimized geometries along with the imposed dihedral constraint.

Anharmonic vibrational frequency calculations were carried out in Gaussian16 using the second-order vibrational perturbation theory (VPT2) approach at the same theory level (B3LYP/Def2QZVPP) to correct the harmonic frequencies of the specific modes for anharmonicity [41].

APPENDIX B: CALCULATED HARMONIC VIBRATIONAL MODES

The calculated harmonic vibrational modes displayed in Fig. 4 for *p*-terphenyl^{2−} (B3LYP/def2QZVPP) follow. They correspond to the molecule of D_2 symmetry and $\varphi_1 = \varphi_2 = 45^\circ$ as geometric constraints. All 90 harmonic modes are given. Output from Gaussian calculation: mode number, symmetry, harmonic frequencies (cm^{-1}), reduced masses (a_μ), force constants ($\text{mdyn}/\text{\AA}$), IR intensities (km/mole), Raman scattering activities ($\text{\AA}^4/a_\mu$), and depolarization ratios for plane and unpolarized incident light.

APPENDIX C: CALCULATED ANHARMONIC VIBRATIONAL MODES

From Fig. 5: *p*-terphenyl^{2−} (B3LYP/def2QZVPP). Anharmonic vibrational modes at the stationary point corresponding to the absolute minimum, no geometric constraints. Anharmonic data for the relevant modes 73 and 74 assigned to P_{15} and P_{16} , respectively, are given:

Mode	Harmonic freq.	Anharmonic freq.	Diff.
No. (assigned peak)	(cm^{-1})	(cm^{-1})	(cm^{-1})
74 (P_{16})	1604.32	1574.58	−29.74
73 (P_{15})	1528.23	1495.61	−32.63

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