Electron-flux infrared response to varying π-bond topology in charged aromatic monomers

Héctor Álvaro Galué1, Jos Oomens1,2, Wybren Jan Buma1 & Britta Redlich2

The interaction of delocalized π-electrons with molecular vibrations is key to charge transport processes in π-conjugated organic materials based on aromatic monomers. Yet the role that specific aromatic motifs play on charge transfer is poorly understood. Here we show that the molecular edge topology in charged catacondensed aromatic hydrocarbons influences the Herzberg-Teller coupling of π-electrons with molecular vibrations. To this end, we probe the radical cations of picene and pentacene with benchmark armchair- and zigzag-edges using infrared multiple-photon dissociation action spectroscopy and interpret the recorded spectra via quantum-chemical calculations. We demonstrate that infrared bands preserve information on the dipolar π-electron-flux mode enhancement, which is governed by the dynamical evolution of vibronically mixed and correlated one-electron configuration states. Our results reveal that in picene a stronger charge π-flux is generated than in pentacene, which could justify the differences of electronic properties of armchair- versus zigzag-type families of technologically relevant organic molecules.
A challenge in the innovation of molecular organic electronics is to understand the fundamental physical principles controlling charge transport\cite{1,2}. Significant efforts have focused on acene\cite{3} aromatic hydrocarbons consisting of fused benzenoid rings arranged in centrosymmetric linear structures. Acenes are key monomeric building blocks for designing prototypical organic solids as the number of rings defines the electronic band structure\cite{3} via the extent of molecular π-conjugation or delocalization (in which overlapping \(p_z\) atomic orbitals interconnect electrons across rings). Another approach to organic electronics is offered by phenacenes\cite{4,5} which are non-centrosymmetric versions of acenes consisting of rings fused in angular-oriented structures. Illustrative examples in the case of molecular crystal structures based on acenes and phenacenes show diverse electronic properties\cite{3,4} ranging from semiconducting to metallic and even superconducting. In particular, pentacene of five linearly fused rings, is a common active compound used in field-effect semiconductors\cite{6}. The semiconducting phenacene counterpart of pentacene is picene, which exhibits important differences in charge mobility and chemical stability\cite{7,8,10,11,12,13}. A more intriguing distinction between the two monomers is the reported superconductivity of metal-doped picene solids, which is absent in pentacene analogues\cite{9,11,13,14,15}. While the crystal configuration (for example, lattice, doping, chemical-group functionalization) and operational conditions govern the conductivity in the above examples, one can expect that the intrinsic picene and pentacene molecular structures play a decisive role as well.

Presently, a molecular-level picture reconciling the differences in electronic properties is lacking. Yet, a recognizable influential factor on these properties is the vibronic coupling of molecular vibrations with π-electron molecular orbitals\cite{12,14,15,16,17,18,19,20} inherent to the π-bond-edge topology\cite{19}. To gain insight in the role of this topology in picene and pentacene vibronic behaviours, we probe here their monomeric structures in the positive charge state (picene\(^+\), pentacene\(^+\)) using infrared multiple-photon dissociation action spectroscopy\cite{20,21}. This spin-doublet cationic state, featuring an unpaired electron in the highest-occupied molecular orbital, vibronically couples with electronic states of the proper symmetry. In our experiments we isolate gas-phase cations in an ion trap and probe them with infrared photons from the Dutch free-electron laser (FEL) for infrared experiments. By means of resonant multiple-photon vibrational excitation, we record photodissociation spectra as we tune the FEL photon energy. This high-sensitivity technique helps us circumvent the issue of undetectable direct absorptions of the low-density ion samples that result from electrostatic repulsion. Although quantification of action spectra can be non-trivial due to the multiple-photon dissociation dynamics\cite{20,21,22,23,24,25,26,27,28}, the central thesis here is the isomeric correspondence between picene and pentacene in which multiple-photon dissociation channels have spectral responses affected by alike intrinsic kinetics. Thus, in this case, action spectra of two species can be compared quantitatively provided that the spectra are measured under similar experimental settings.

The spectra of both cationic systems show substantial infrared activity in the 1,100–1,600 cm\(^{-1}\) range, which we ascribe to electronic density oscillations during antisymmetric C=C stretch vibrational excitation. The driving vibronic mechanism\cite{23,24,25,26} arises in the molecular dipole moment (\(\mu\)) derivative along the nuclear normal-coordinate \(Q_k\) of the infrared intensity (ref. 27) \(I_k = \frac{8\pi \hbar^2 N \hbar^2 \Delta \hbar}{3h_0} |V_0|^2 \langle \mu | \partial^2 \mu/\partial Q_k \partial Q_j | \psi_0 \rangle^2 \), where the vibrational wavefunctions \(V_0\) and \(V_1\) characterize the fundamental harmonic dipole transition (1 – 0) of \(v_1\)th mode. The second term of the molecular dipole \(\dot{\mu} = \mu_{\nu}(R) + (\nabla \times (\vec{\psi}_g(\vec{r}),\vec{R}))\) (\(-e\vec{r})\langle \psi_g(\vec{r}),\vec{R})\)) is the non-classical dipolar part of ground-state electrons described by the Born–Oppenheimer wavefunction \(\Psi_{\nu}(\vec{r})\) and \(R\) being the electronic and nuclear coordinates, and \(\dot{Q}_k\) being the nuclei dipole. By equating a first-order expansion of \(\Psi_{\nu}\) with respect to nuclear normal coordinates \(Q\) (Supplementary Note 1) into \(\mu\) we write \(\dot{\mu}/\partial Q_k\) as a sum of two sources of infrared activity\cite{24,25,26,27,28,29,30}

\[
\frac{\partial \mu}{\partial Q_k} = \frac{\partial}{\partial Q_k} \left[ N + \langle \psi_0 | - e \vec{r} | \psi_0 \rangle \right] + 2 \sum_{\xi=1}^{2} \frac{\langle \psi_0 | \{ \partial H/\partial Q_k \} | \psi_\xi \rangle}{E_\xi - E_0} \langle \psi_0 \ | \ \vec{r} \ | \psi_\xi \rangle, \tag{1}
\]

where single (one-electron) configuration wavefunctions \(\psi_{\alpha} \) (evaluated at equilibrium nuclear positions) and energies \(E_{\alpha} \) correspond to ground \((\alpha)\) and excited \((\xi)\) adiabatic states \((\xi)\). The matrix elements \(\langle \psi_\alpha | \{ \partial H/\partial Q_k \} | \psi_\xi \rangle \) and \(\langle \psi_\alpha \ | \ \vec{r} \ | \psi_\xi \rangle \) are the Herzberg–Teller vibronic coupling strength and electronic transition, respectively, and \(H\) is the electronic Hamiltonian. The first static-charge term arises from oscillating nuclei and nuclei-fixed electrons, while the second charge-flux term of oscillating non-fixed electrons is the vibronically active contribution of low-lying electronic excited states mixing into the ground state.

We show that the vibronic contribution to the picene\(^+\) infrared spectrum can be twice as large as in the pentacene \(^+\) spectrum, which is attributed to stronger dipole π-electron fluxes in the former system. Quantum-chemical calculations support this conclusion but also reveal that electronic correlation is essential to describe the intense C=C stretch π-flux modes of picene\(^+\). Whereas the multiple-photon dynamics impedes extracting absolute magnitudes of the underlying π-fluxes in picene\(^+\) and pentacene\(^+\), by virtue of comparing their multiple-photon dissociation yields we are able to discern molecular charge-flux effects (driven by vibronic coupling) on the resultant action spectra. We show that within the used FEL settings, the recorded action bands scale quasi-linearly with FEL average power and are satisfactorily described under the harmonic approximation as corroborated by quantum-chemical theory (apart from the anharmonic band broadenings inherent to the multiple-photon excitation process). We assert that the ability of picene to enable a significant dipolar π-flux charge separation, as manifested in the infrared action bands, is a general characteristic of aromatic motifs with armchair-edge topology. The fundamental distinction found here between picene and pentacene provides a dynamical charge-flux—structure relation useful to rationalize charge transport phenomena in π-conjugated organic materials built from aromatic structures.

Results

Molecular structures. We first examine the structural edge topology\cite{2,22} (Fig. 1a) in terms of π-electron delocalization. With zigzag edges, pentacene has only one resonant ring sextet of interconnected π-electrons\cite{33}, while the other 16 non-sextet π-electrons tend to stay within bonds. Conversely, the picene armchair edges enable three π-sextets to resonate into adjacent rings\cite{33}, and this fact fosters an aromatic system in which delocalization extends over the entire structure. This justifies the higher stability of neutral picene over pentacene by 0.68 eV calculated by density functional theory (B3LYP/6-311G**). The degree of π-delocalization is then inherently different in both systems as reflected in the π-electron spin-orbital wavefunctions. Figure 1b shows the energetic orderings with different spacing of frontier molecular π spin-orbitals. The orderings define the electronic configurations of cationic spin-doublet ground states \(D_{\alpha}\) \(2B_1\) and \(2B_2\) of picene\(^+\) and pentacene\(^+\), respectively, and
of low-lying excited states accessible via $\pi \to \pi^*$ excitations (Supplementary Tables 1 and 2). Experimentally, we produce pentacene and picene radical cations ($\text{C}_2\text{H}_14^+$) by non-resonant two-photon ionization$^{34}$ of the neutral precursors at 193 nm (Figs 2c and 3) resulting from averaging various dissociation yield functions $\beta(\lambda)$ retrieved from the product ion signals recorded along FEL photon energy (Methods). The final average of both systems is corrected for FEL power variation and normalized to 1. The two spectra include a low-energy range extending down to 400 cm$^{-1}$. The power correction normalizes the band intensities from different spectral scans as measured in independent FEL-ion-trap experimental sessions. The precision in our measurements is discussed below for a data set sample of single scans (Supplementary Fig. 2). Apart from the large random noise component and slight variations in band broadening, each single spectrum in the sample exhibits similar infrared absorption features as confirmed by the partial spectra averages featuring reduced random noise level (Supplementary Figs 3 and 4 with band characterizations in Supplementary Tables 3–6).

The statistical random noise in each one-scan spectrum produces somewhat diverse baselines upon dividing by the FEL power curve (hence, averaging usually precedes the power correction). Also, the high noise in each spectrum impedes performing the spectral deconvolution curve fitting since the parameter initialization (based on the initial guess of band peak positions) fails. We thus obtain the frequency ($\tilde{\nu}_{\text{exp}}$) and intensity ($\beta$) band values manually. Despite the inaccuracy added by this human factor, the statistics from the data sample provides a notion of the precision between measurements. The $\tilde{\nu}_{\text{exp}}$ (and $\beta$) band characterizations are $a_1$: 1,567 ± 19 cm$^{-1}$ (0.50 ± 0.10), $a_2$: 1,512 ± 17 cm$^{-1}$ (0.73 ± 0.09), $b_1$: 1,338 ± 10 cm$^{-1}$ (0.61 ± 0.05), $b_2$: 1,328 ± 10 cm$^{-1}$ (0.60 ± 0.05).
by the intermediate B structure does not influence the spectra. That the two product ions (both exhibit same spectral features) arise from the same parent; hence, the possible event of sequential photon absorption.

**Figure 2 | Laser photoexcitation dynamics and multiple-photon dissociation action spectra.** (a) Schematic of adiabatic electronic potentials involved in ultraviolet and infrared photo-excitation leading respectively to charged D0-state aromatic monomers and vibrational infrared action spectra. The spin-doublet excited state D1 closest to the ground state D0 is defined by the singly excited configuration ψ(4A2→4b) for picene+ and ψ(2A2→3b0) for pentacene+. (Supplementary Tables 1 and 2). The y-axis equilibrium electronic energy (Ε) shows the corresponding ground-state molecular terms. (b) Typical mass analysis upon ultraviolet photoionization and infrared FEL macropulse irradiation. The ionization energies of picene and pentacene are 7.5 and 6.6 eV, respectively, and the excess of vibrational excitation determined by the Franck–Condon overlaps of neutral- and cationic-state vibrational wavefunctions partially evolves as C2H2-loss dissociation (Methods). (c) Infrared action spectra (β(λ)) retrieved from C20H12+ (m/z 252) and C15H8+ (m/z 226) ion signals recorded continuously along tuned FEL photon energy (action bands characterized in Table 1). (d) Proposed scheme of multiple-photon induced dissociation kinetics along the potential energy reaction profile (reaction coordinate from left to right) connecting the reactant C20H12+ parent ion (as transition state) with C2H2-loss product ion (A), the intermediate isomerization product ion (B), and the C2H2-loss product ion (C2H4). The energy barriers E1, Eiso, and E2 correspond to first C2H2-loss (1), isomerization and second C2H2-loss (2) reactions. Figure 6 confirms that the two product ions (both exhibit some spectral features) arise from the same parent; hence, the possible event of sequential photon absorption by the intermediate B structure does not influence the spectra.

| b: 1,281 ± 9 cm−1 (0.75 ± 0.05), b: 1,212 ± 8 cm−1 (0.62 ± 0.04), and c: 1,141 ± 10 cm−1 (0.56 ± 0.07) for picene+; and a: 1,448 ± 16 cm−1 (0.45 ± 0.06), b: 1,313 ± 9 cm−1 (0.78 ± 0.09), c: 1,176 ± 7 cm−1 (0.77 ± 0.09), e: 911 ± 7 cm−1 (0.47 ± 0.05), and f: 737 ± 4 cm−1 (0.43 ± 0.04) for pentacene+. These values are in fair agreement with the values determined via the more rigorous deconvolution procedure applied on sample averages (B2B3 and A for picene+; D1D3D5 and D6D7 for pentacene+) featuring a reduced noise (Supplementary Tables 3–6), and with the values of the full data set average (Fig. 3). We establish that the vexp and β band fluctuations are due to typical random changes during experiments rather than to systematic instrumental biases or uncharacterized molecular processes during ion trapping. Finally, note that averaging over the full data set reduces the noise component more than when averaging over partial data sets. Thus, the larger random errors in the partial spectra are reflected in the spectral curve fittings characterizing the measured bands. For picene+ b band, the vexp and β average values between B2B3 and A data samples are 1,279.5 ± 0.1 and 0.87. These values represent a deviation of 0.20 and 6.5% relative to final values (Table 1) and accounts in part for the higher random error of partial spectra. From D1D3D5 and D6D7 data samples of pentacene+, the vexp (and β) average is 1,317.5 cm−1 (0.89) and represents a random error deviation of 0.11% (53%).

**Harmonic analysis.** Although the multiple-photon excitation relies on the anharmonic character of IVR coupled modes, which could induce noticeable nonlinear effects, there are examples such as the naphthyl+ action spectrum8,39 confirming the quasi-resonant harmonic description of adiabatic molecular potentials probed by multiple-photon action spectroscopy37,40. Here, the bands observed in the action spectra are summarized in Table 1 with their spectral deconvolutions and harmonic mode assignments (from Supplementary Tables 7–16) based on the B3LYP vibrational analysis of Fig. 3. Both cations feature a very intense high-energy 1,600–1,100 cm−1 region of a, b and c bands, and a relatively weak mid-energy 1,100–700 cm−1 region of d, e and f bands. The band decompositions in Fig. 3a,f reveal the extent to which individual normal modes contribute to action bands. The mean value of absolute shifts between action and harmonic band frequencies is 1.43 ± 0.9% in picene+ and 1.19 ± 0.79% in pentacene+. The larger total shift in picene+ reflects the contribution of the C2H2-loss dissociation channel (larger than in pentacene+) for which high activation energy brings larger anharmonic shifts20 (vide infra).

Despite the higher symmetry in pentacene+, its action spectrum reveals more spectral congestion than picene+ action spectrum as confirmed by its bigger number of fitted peak components (Fig. 3a,f). The high-energy region of b2u–symmetry modes in picene+ and b2u–symmetry modes in pentacene+ comprises, respectively, 92% and 88% of the total infrared activity (Supplementary Table 17). Generally, b2 and b3u modes involve C=C stretching motions antisymmetric with respect to the molecular xz plane, and are susceptible to vibronic couplings with low-lying π-orbitals. The band decompositions show that the intense vibronically active modes v78 and v84 in picene+ are responsible of bands a and b (see Fig. 3a,e), whereas the strongest mode v85 in pentacene+ generates band b (Fig. 3f).
Theoretical linear harmonic spectra (generated by convoluting scaled normal modes with a Lorentzian 30 cm
picene
bending modes
systems, results from photoexcitation at out-of-plane C–H
character, arises from two and one C–H oscillators at the three
respectively, for picene
and pentacene
, in 9 and 11 Lorentzian band peaks (each correspond to a lower case letter), which cumulative peak spectral
curve is depicted in black. In Table 1 resultant peaks are summarized and sequentially numbered from \( a \) to \( f \) in correspondence with action band features. Theoretical linear harmonic spectra (generated by convoluting scaled normal modes with a Lorentzian 30 cm
function) are based on ROHF (b, picene
and g, pentacene
) and B88, BLYP and B3LYP density functionals (see Methods, mode assignations in Supplementary Tables 7–16 where B is B88) for c–e, picene
and h–j, pentacene
.

**Figure 3 | Harmonic mode analysis as a function of electronic correlation.** The resultant final action spectra (grey) converted to spatial frequency wavenumbers (cm
) of (a) picene
 and (f) pentacene
. The spectral deconvolution band fitting based on the Levenberg-Marquardt algorithm results, respectively, for picene
 and pentacene
, in 9 and 11 Lorentzian band peaks (each correspond to a lower case letter), which cumulative peak spectral curve is depicted in black. In Table 1 resultant peaks are summarized and sequentially numbered from \( a \) to \( f \) in correspondence with action band features.

As seen later, the relatively high intensities of \( f \) and \( e \) bands (see \( \beta/I_{\text{cal}} \) ratios, Table 1) arise equally in picene
 and pentacene
 from an increased ion production through the C2H2-loss dissociation channel at these low excitation energies.

**Electronic correlation.** The dipolar charge redistribution along any vibration in both monomers is governed by the molecular electronic wavefunction \( \Psi_h \) having a well-defined ground-state configuration (Supplementary Tables 1 and 2). Within the so-called crude adiabatic approximation\(^{24} \) this ground-state configuration is defined at the equilibrium position \( Q_{h0} \) and is assumed to be independent of nuclear coordinates. For some modes, however, a proper description of \( \Psi_h \) requires other configurations describing low-lying excited states to be incorporated. Its dynamical evolution along a relevant normal coordinate \( Q_h \) is thus better described by the correlated configuration interaction of ground and excited configurations belonging, in this case, to a spin-doublet electronic manifold. Here we study the role of this electronic correlation on infrared mode activities of both spin-doublet monomers by applying three density-functional theory methods that gradually increase the level of electronic exchange-correlation (Fig. 3): B88→BLYP→B3LYP. Also, we applied the mean-field method ROHF that does not include correlated dynamics.
The comparison between experimental and theoretical spectra show that the mean-field theory diverges more severely in picene\(^+\), particularly in the C–C stretch high-energy region, suggesting the need for electron correlated dynamics to properly describe its modes. This suggests that picene\(^+\) wavefunction readily interacts with certain excited electronic configurations during C–C stretch nuclear displacements, described in this case by \(\mathbf{b}_2\)-symmetry normal modes, which is a clear sign of vibronic activity (see next section). The \(\mathbf{b}_2\)-mode \(v_{85}\) exhibits for instance an unusual mean-field intensity of ca. 4,000 km mol\(^{-1}\) (Fig. 3b) since the ROHF method is unable to simulate the effective intramolecular electric field responsible for the generated dipole derivative. However, the density functional rectify the odd intensities as corroborated by the experimental spectrum. Despite not including explicit vibronic treatments, their better performance is explained by the fact that density functionals implement local and non-local exchange-correlation interactions based on the single-valued electronic density\(^{42,43}\). In this sense, including gradient-density corrections (which account for density fluctuations emerging from low-lying excited configurations) further rectify the C–C stretch band pattern in agreement with the measured relative strengths of picene\(^+\) bands \(a\) and \(b\), for example, B88→B3LYP (Fig. 3c,e). For pentacene\(^+\), the spectroscopic comparisons suggest an evolution of its wavefunction \(\Psi_g\) along normal modes that roughly can be described by a single configuration; yet, some degree of correlated configuration interaction is required to reproduce the intensities of high-energy \(b_{2u}\) modes.

For the out-of-plane C–H bending modes of the mid-energy region, all methods predict similar infrared activities except for some mode frequency shifts. The mean-field intensities of modes carrying \(e\) and \(f\) bands are 61 and 110 km mol\(^{-1}\) for \(v_{85}\) and \(v_{87}\) in pentacene\(^+\), and 68 and 112 km mol\(^{-1}\) for \(v_{85}\) and \(v_{89}\) in picene\(^+\). These intensities agree with B3LYP intensities (Table 1), showing that out-of-plane infrared-active modes are invariant to the level of theory.

Vibronically driven \(\pi\)-fluxes. The previous section shows that electron–electron correlated interactions are required for a proper description of dipole derivatives for C–C stretch \(b_{2u}\)-modes of picene\(^+\), and to a certain extent, also for C–C stretch \(b_{2u}\)-modes of pentacene\(^+\). Such electronic correlation manifests itself in equation (1) as non-negligible vibronic matrix elements that represent a configuration-interaction expansion of excited-to-ground state mixing coefficients. Together with the electronic matrix term, they comprise the vibronic dipolar term enabling molecular \(\pi\)-electron fluxes. To elucidate the physics of dipolar \(\pi\)-fluxes we first analyse the symmetry properties of both matrix elements.

### Table 1 | Infrared multiple-photon action bands of picene\(^+\) and pentacene\(^+\).

<table>
<thead>
<tr>
<th>Band</th>
<th>(\tilde{v}_{\text{exp}})</th>
<th>(\beta)</th>
<th>Peak</th>
<th>(\tilde{v}_c)</th>
<th>(\epsilon)</th>
<th>(w)</th>
<th>(A)</th>
<th>(h)</th>
<th>(\tilde{v}_{\text{cal}})</th>
<th>(l_{\text{cal}})</th>
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<tr>
<td>(a)</td>
<td>1,513</td>
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<td>1</td>
<td>1,591</td>
<td>9.35</td>
<td>199</td>
<td>19.01</td>
<td>105</td>
<td>19.44</td>
<td>0.34</td>
<td>1573</td>
<td>0.31</td>
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<tr>
<td>(a)</td>
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<td>5</td>
<td>1,312</td>
<td>0.97</td>
<td>73</td>
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<td>0.36</td>
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<tr>
<td>(d)</td>
<td>1,271</td>
<td>0.26</td>
<td>7</td>
<td>1,013</td>
<td>24.21</td>
<td>18.21</td>
<td>60</td>
<td>6.14</td>
<td>0.19</td>
<td>796</td>
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<td>(e)</td>
<td>823</td>
<td>0.23</td>
<td>8</td>
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<td>1.81</td>
<td>67</td>
<td>7.25</td>
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<tr>
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<td>0.36</td>
<td>41</td>
<td>2</td>
<td>11</td>
<td>0.56</td>
<td>0.17</td>
<td>745</td>
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For pentacene\(^+\):

<table>
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<tr>
<th>Band</th>
<th>(\tilde{v}_{\text{exp}})</th>
<th>(\beta)</th>
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<th>(\tilde{v}_c)</th>
<th>(\epsilon)</th>
<th>(w)</th>
<th>(A)</th>
<th>(h)</th>
<th>(\tilde{v}_{\text{cal}})</th>
<th>(l_{\text{cal}})</th>
<th>(\tilde{v}<em>{\text{exp}}/\tilde{v}</em>{\text{cal}} - 1)</th>
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The \(\Psi_g\) wavefunction along normal modes that roughly can be described by a single configuration; yet, some degree of correlated configuration interaction is required to reproduce the intensities of high-energy \(b_{2u}\) modes.

For the out-of-plane C–H bending modes of the mid-energy region, all methods predict similar infrared activities except for some mode frequency shifts. The mean-field intensities of modes carrying \(e\) and \(f\) bands are 61 and 110 km mol\(^{-1}\) for \(v_{85}\) and \(v_{87}\) in pentacene\(^+\), and 68 and 112 km mol\(^{-1}\) for \(v_{85}\) and \(v_{89}\) in picene\(^+\). These intensities agree with B3LYP intensities (Table 1), showing that out-of-plane infrared-active modes are invariant to the level of theory.
pentacene oscillates between extreme values (\(|pentacene\)) one-carbon density centers determine, respectively, the bonding and anti-bonding electronic characters of the excited spatial redistributions. Molecular side features an accumulation (scaling by a factor of 4) of bonding during the vibronic mixing of \(C^+2^-2^--\) induced by mode destabilizing (–) character of the two-carbon density centers (+) relationships reflect the bond stabilizing (\(+\)) wavefunctions along FEL photon energy (Fig. 6), suggesting that \(C_2H_2\) and \(C_4H_4\) are preserved in each system and then renormalize the spectra sample from the final average of Fig. 3. Note that the infrared-strength ratio of \(C_2H_2\) and \(C_4H_4\) is 0.52/0.94 \(\beta_{\text{obs}}[\text{pentacene}^+]\) (Table 1). We have used the mid-energy band \(f\) since in both systems this band is carried by intrinsically equivalent out-of-plane C–H bending modes. Solving for \(\beta_{\text{obs}}[\text{pentacene}^+]\) results in 2.15 \(\beta_{\text{obs}}[\text{pentacene}^+]\), which remarkably agrees with the strength ratio \(I_{\text{obs}}/I_{\text{C2H2}}\) and thus, confirms the twofold increase of \(\pi\)-flux strength in \(\text{pentacene}^+\).

Degree of non-linearity in action spectra. The above analysis shows that relative intensities of action bands \(f\) and \(b\) can be described under the linear-absorption harmonic approximation. However, we have mentioned that action spectra are inherently susceptible to nonlinearities as introduced by the multiple-photon dissociation (Fig. 2b,d). Moreover, relative intensities are based on dissociation yield functions that have been power-corrected and normalized, and these procedures could have brought an accidental agreement to the harmonic ratio \(I_{\text{obs}}/I_{\text{C2H2}}\). Therefore, to estimate the extent of these effects, we compare spectra from control measurements at high-energy FEL macropulses with a spectra sample from the final average of Fig. 3. Note that the spectra retrieved from the control measurements are not part of the final average.

We first compare in Fig. 6 the \(C_2H_2\) and \(C_4H_4\) loss ion signals of \(\text{pentacene}^+\) recorded at 0 and 3 dB FEL power levels (signal and band characterizations in Supplementary Tables 18–20). The signal ratio \(C_2H_2\)-loss/\(C_4H_4\)-loss is found approximately constant along FEL photon energy (Fig. 6), suggesting that \(C_2H_2\) and \(C_4H_4\) loss rates evolve in quasi-linear proportion to each other. On
attenuation (3 dB), the mean value of the hence (quasi-)constant ratio of 1.73 changes to 2.52 always in favour of C₂H₂ loss. It is clear that at reduced macropulse energies, the energized molecular ion population reaches a lower average internal energy (E). This leads to a lower dissociation rate and eventually shuts down dissociation into the C₂H₂-loss channel with higher activation energy (that is, the inequality E₁ – E₂ < E₂ is fulfilled, see Fig. 2d). At the lowest FEL photon energies (ca. <900 cm⁻¹) the ratio deviates from linearity towards C₂H₂ loss. For instance at the peak of band f, the ratio drops from 2.37 to 3.28 (Supplementary Table 20). Here the production of C₄H₄-loss ions drops as much as 38% while for C₂H₂-loss it drops only 14%. Comparing with band e, C₂H₂ and C₄H₄ losses decline by 30% and 45%, respectively. Despite the uneven variations between channels at band f, Fig. 6 does suggest that the dissociation yield decreases linearly on attenuation, revealing the determining role of C₂H₂-loss in the action spectra.

Whereas multiple-photon excitation with lower-energy macropulses decreases the C₂H₂ and C₄H₄ loss ion productions at f, e and a bands (an exception is band e C₂H₂-loss, which retains the 0 dB signal), the C₂H₂ loss increases 17% at band b. This 17% increment is close to the observed 14% decrement of C₄H₄ loss (also at band b) suggesting linearly inverted dissociation kinetics between channels. Specifically for pentacene⁺, we observe that C₄H₄ loss marginally varies on FEL irradiation along the tuned range, which correlates with the relatively lower oven temperatures set for sublimation. This shows that most energized pentacene⁺ ions have an average internal energy just above the C₄H₄-loss activation energy (Fig. 2d). Because C₂H₂-loss steers the multiple-photon dissociation kinetics in both systems, their dissociation yields along excitation have a strong C₂H₂-loss signal component, from which nonlinear effects are recognized to be much smaller than the inherent differences between the two molecular systems.

**Power dependence of action band intensities.** To test whether nonlinear effects on band intensities are negligible, we retrieve the spectra from the ion signals of Fig. 6 (Fig. 7a,b; band decompositions in Supplementary Tables 21 and 22). The resultant yield functions β*(v) are not normalized nor corrected for FEL power variations (as a function of excitation energy) to perform absolute comparisons between band intensities at 0 and 3 dB power levels. Table 2 lists four bands with their frequency peak, CPm, and m constant and exponent factors). As seen in Fig. 6 for band f, a twofold power reduction (corresponding to a macropulse energy change from 42 to 20.8 mJ) brings a linear twofold yield change, that is, m = 1. For bands a and e the variations are nearly linear (m ≈ 0.8). For band b we find a non-linear behaviour (m = 0.1) as expected from the reversed 17% increasing signal behaviour of C₂H₂-loss as we reduce the macropulse energy (Fig. 6).
Comparing the absolute band yields of picene$^+$ with those of pentacene$^+$ (Fig. 7c, Supplementary Table 23) measured at the lower FEL power values reveals a reasonable agreement (compare Fig. 7b,c). The pentacene$^+ f$ yield intensity (0.00894) recorded at 26 mJ (260 mW) linearly scales to 0.0072 at 20.8 mJ in fair agreement with picene$^+ f$ yield 0.0077 recorded at 20.8 mJ (Table 2). This resemblance confirms the equal theoretical infrared strengths of their photoexcited modes ($\nu_{\text{S9}}$ in picene$^+$ and $\nu_{\text{P9}}$ in pentacene$^+$). For band c, we expect some deviation given the difference in excitation energies between picene$^+$ and pentacene$^+$ for this band (frequency deviation of $\Delta\nu_{\text{exp}}(e) = 10\%$ from Table 1), which suggests somewhat different anharmonic couplings. Indeed, at 19.3 mJ the pentacene$^+ e$ yield (measured at 23.9 mJ) scales to 0.0060 whereas the picene$^+ e$ yield is 0.0071 (Table 2).

For band b, the similar excitation energies required in both parent ions ($\Delta\nu_{\text{exp}}(b) = 2.8\%$) suggest that absolute yields could be comparable at the lower FEL power values (Fig. 7b,c). The b yields are 0.0125 and 0.0153 recorded at 17.8 and 9.9 mJ for pentacene$^+$ and picene$^+$, respectively. For pentacene$^+$, the b
yield at 9.9 mJ linearly scales to 0.00695. This lower pentacene $^+$ intensity does reflect the theoretical strength of the photoexcited mode ($v_{b3}$) carrying this band relative to the one of picene $^+$ ($v_{b5}$) that is as twice as intense (that is, $I_{b5}/I_{b3} = 2.06$). Indeed, the ratio between absolute yields at 9.9 mJ is 2.2, which represents an accuracy error relative to the calculated $I_{b5}/I_{b3}$ ratio of 6.8%.

Finally, note that the random noise in band $b$ intensities leads to standard deviation percentages of about ±6% (picene $^+$) and ±11% (pentacene $^+$) (Supplementary Fig. 2). These deviations are the largest attained in our experiments since they correspond to a smaller representative data sample spectrum (of which noise component is evidently higher than in the full data sample average of Fig. 3. The random noise influences the accuracy of the spectral deconvolution fittings characterizing the experimental band intensities. Let us now use these deviations to investigate the ratio error in the case of the absolute intensities $I_{b5}^*$ reported above. The pentacene $^+$ $I_{b5}^*$ intensity is 0.0125 ± 0.00138, and the lower and upper $I_{b5}^*$ bounds linearly scaled to 9.9 mJ are 0.0062 and 0.0077 leading to ratio bounds relative to picene $^+$ ($I_{b5}^* = 0.0153$) of 1.98 and 2.47. For picene $^+$, we determine the ratio bounds relative to pentacene $^+$ at 17.8 mJ ($I_{b5}^* = 0.0125$) as 2.07 and 2.33. We thus establish that even at these limits the statistical error in our measurements justifies the band $b$ ratio as also confirmed by its agreement with the theoretical value.

Discussion
We have deduced the relative strength between vibronic $\pi$-flux contributions to modes $v_{b4}$ and $v_{b5}$ generating the action band $b$ of picene $^+$ and pentacene $^+$, respectively. Within our FEL macropulse settings, the picene $^+$ -to-pentacene $^+$ $b$ band ratio is satisfactorily explained under the harmonic approximation which predicts an intensity ratio $I_{b4}/I_{b5}$ of 2.06 (at B3LYP/6-311G** level of theory). This means that a harmonic Hamiltonian can describe the molecular potential along action $b$ band vibrations. One last question relates to the effects of spectral convolution on band intensities. On the basis of the heights ($h$) of deconvoluted peaks for $f$ and $b$ bands, we estimate an experimental band ratio of 2.41 (where we subtracted the 0.035 offset for pentacene $^+$ peaks, see Table 1). This value deviates by 12% from the first value obtained from relative intensities in Fig. 3. The better agreement in the first estimation could be due to an error cancelation on averaging over the full data set, but also, it could reflect the absolute intensity difference of picene $^+$ (0.00777) and pentacene $^+$ (0.0072) $f$ bands. Nonetheless, the fair agreement between action and harmonic band intensity ratios ratifies the twofold $\pi$-flux increase in picene $^+$ compared with pentacene $^+$.

From our studies a picture emerges in which picene is able to generate a higher degree of dipolar charge separation along its monomeric structure than pentacene. We have argued that this is a direct consequence of the spatial dynamical evolution (via the adiabatic vibronic operator (\(\partial H/\partial q_0\))) of mixed armchair-edge type electronic wavefunctions typical of angular-orientated aromatic structures. These armchair-edge wavefunctions are intrinsically strongly correlated. Thus, in the case of superconducting molecular crystals based on picene and related monomers9,12, this evidence implies that both electron–phonon and electron–electron interactions could be at the origin of electron pairing. This work allows us to also envision the exploration of picene-like motifs in heterojunctions49 or supramolecular nano-assemblies45 of these devices, whose operation is triggered by photon-induced charge separation. Finally, note in equation (1) that larger vibronic couplings along modes of armchair-type monomers relative to zigzag-type monomers may not always translate in larger dipolar charge-flux contributions to the infrared spectra in the former class, since the vibronic coupling strength is weighted by the electronic transition matrix element. In conclusion, our results show that infrared multiple-photon action spectroscopy can deliver significant information on intramolecular charge dynamics when applied to charged molecular species with similar dissociation kinetics and vibrational resonances.

Methods
Free-Electron Laser for Infrared eXperiments FELIX. In our experiments, FELIX delivered typically 7 µs long macropulses every 100 ms with transform-limited bandwidth of about 1% of the central $\lambda$ tuned in steps of 0.02 or 0.04 µm. Each macropulse consisted of 1 ps long micropulses at 1 GHz. A typical average energy at 13 µm was 42 mJ per macropulse, which delivers a fluence of 5.3J cm$^{-2}$ in the center of the ion trap on a spot of 1-mm diameter. Nowadays, FELIX is located at Radboud University in Nijmegen (The Netherlands).

Infrared multiple-photon dissociation action spectroscopy. Action spectra are recorded with a Paul-type ion trap mass-spectrometer (Jordan TOF Products, Inc.) attached to a FELIX beamline20-23. The ion trap built into a high vacuum chamber is made of a toroidal inner ring electrode of $2 \, \text{cm}$ inner diameter interposed between two hyperbolic endcap electrodes. The trap is biased at +1 000 VDC, setting a potential difference relative to a 60-cm length time-of-flight (TOF) mass spectrometer used for mass-to-charge (m/z) ion detection. Cations (m/z 278) of pentacene and picene are produced by 193 nm ultrafast photoinionization of gas-phase neutral molecules effused to the inner trap volume upon sublimation of solid samples (99.9% picene, TCI Europe; 99% pentacene, Sigma-Aldrich) with a built-in oven at temperatures as high as 280 °C. The ultraviolet source is a 5-ns pulsed excimer laser (PSX-501 Neweks Ltd.) adjusted to a typical energy of 1.6 mJ per pulse and power density in the trap of $3 \times 10^8 \, \text{W/cm}^2$. For TOF mass analysis, axial extraction is achieved by switching off the RF voltage while applying a ~250 VDC pulse to the endcap (with a 3 mm hole) closest to the TOF-tube. Ultraviolet photo-induced product ions below $m/z$ 278 are ejected before FEL irradiation by a brief (2 ms) RF amplitude increase. After a few milliseconds after isolation of an ensemble of picene $^+$ (or pentacene $^+$) ions, FEL on-resonance irradiation at fundamental vibrational transitions induces multiple-photon dissociation. Two spherical mirrors (gold coated) are used to enhance the FEL fluence. A FEL-triggered delay generator (SRS-DG520) controls the 10 Hz experimental sequence. The recorded ion signals of parent and multiple-photon product ions are amplified and digitized (Acquisir). The pressure values in the high vacuum chamber were typically in the $10^{-6}$–10$^{-7}$ mbar range. We estimate the dissociation yield, $b(I)$ or

Table 2 | Absolute dissociation yield band intensities versus FEL average power.

| Infrared band | $I_{b5}$ (cm$^{-1}$) | P (mW) | $I_{b5}$* | $I_{b5}$% | $I_{b5}/I_{b5}$* | $I_{b5}/I_{b5}$% | $I_{b5}/I_{b5}$ | $m$ | C
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<td>a</td>
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<td>0.0063</td>
<td>0.20</td>
<td>1.91</td>
<td>1.64</td>
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<tr>
<td></td>
<td>1,492</td>
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<td>0.0103</td>
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<td>99</td>
<td>0.0153</td>
<td>0.99</td>
<td>2.01</td>
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<td>e</td>
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<td>193</td>
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<td>1.76</td>
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<td>0.0155</td>
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Infrared band characteristics of action spectra of Fig. 7a,b. The column headings are action band label (Infrared band), action band peak frequency ($I_{b5}$), FEL average power ($P$), or macropulse energy ($P^*$/Hz, in mJ), absolute dissociation yield intensity ($I_{b5}$), band peak frequency shift deviation ($\Delta I_{b5}$), FEL average power ratio ($P_{b5}/P_{b5}$), yield ratio ($I_{b5}/I_{b5}$), and constant (C) factors. Given the large frequency deviation between high- and low-power band peaks ($\Delta I_{b5}/I_{b5}$), the lower-power band characterization is done at $P_{b5}/P_{b5}$ = 2 (1.91). The $b$ value thus differs from the one reported in Supplementary Table 22.
Quantum chemical calculations. We obtained optimized electronic structures and harmonic vibrational mode frequencies using \textit{ab initio} Hartree–Fock theory as the spin-restricted open-shell ROHF method\textsuperscript{45}, and the local spin-density approximation (LSDA) plus a variety of exchange-correlation gradient-corrected functionals. These are the LSDA gradient-corrected exchange-only Becke-1988 functional\textsuperscript{43} (B88), the Becke-1988 method plus the gradient-corrected correlation LYP functional\textsuperscript{42} (BLYP), and the hybrid 3-parameter functional that includes generalized exchange-correlation gradient corrections and some degree of exact Hartee–Fock exchange energy\textsuperscript{47} (B3LYP). The atomic-orbital basis set used is a split-valence triple-\(\zeta\) Gaussian-type 6-311G with \(d\) and \(p\) polarization functions. The excited-state calculations were done at the B3LYP level after transposing the relevant spin-orbitals involved in the excitations. To reduce computational cost we used the smaller set 6-31G\textit{d}(\(p\)). All reported harmonic spectra were generated by convoluting normal modes with a Lorentzian with ultraviolet absorption spectra in the catacondensed series.

Data availability. The data supporting the findings of this study are available within the article, Supplementary Information, and if applicable, from the corresponding author on request.

References
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Author contributions
B.R. supervised, maintained and operated FELIX, and assisted in FELIX-ion-trap experiments. W.J.B. performed the calculations and analysis. J.O. supervised the research, performed analysis, and assisted in FELIX-ion-trap experiments. H.A.G. conceived the study, performed the FELIX-ion-trap experiments, calculations and analysis, and wrote the manuscript with inputs of W.J.B. and J.O.

Additional information
Supplementary Information accompanies this paper at http://www.nature.com/naturecommunications

Competing financial interests: The authors declare no competing financial interests.

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