Real-time observation of multi-mode vibronic coherence in pentafluoropyridine

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The ultrafast dynamics of pentafluoropyridine in the 1^1B_2 ($\pi\pi^*$) electronic state excited at $\lambda_{\text{pump}} = 255$ nm is investigated by femtosecond time-resolved time-of-flight mass spectrometry and photoelectron imaging spectroscopy. A pronounced, long-lived, and complex periodic modulation of the transient ion yield signal with contributions by four distinct frequency components, 72 cm^{-1} , 144 cm^{-1} , 251 cm^{-1} , and 281 cm^{-1} , is observed for up to 9 ps. The recorded photoelectron images display a spectral band from the excited 1^1B_2 ($\pi\pi^*$) state only in the oscillation maxima; the signal is strongly reduced in the oscillation minima. Supported by electronic structure calculations at the RI-SCS-CC2 and XMCQDPT2 levels of theory, the oscillating components of the signal are identified as frequencies of b_1 symmetry coupling modes in a vibronic coherence of the 1^1B_2 ($\pi\pi^*$) and 1^1A_2 ($\pi\sigma^*$) electronic states. The optical excitation initiates regular and periodic wavepacket motion along those out-of-plane modes. In the distorted molecular structure, the initially excited state acquires substantial $\pi\sigma^*$ character that modulates the transition dipole moment for ionization and results in the observed oscillations. *Published by AIP Publishing.* [<http://dx.doi.org/10.1063/1.4983306>]

I. INTRODUCTION

The pronounced influence of $\pi\sigma^*$ electronic states on the photochemistry of heteroaromatic molecules has received considerable attention in the last decade. While $\pi\sigma^*$ excited states are usually dissociative, it could be shown that in many cases an energetically low-lying conical intersection with the S_0 ground electronic state enables an ultrafast radiationless internal conversion that strongly increases the photostability of the molecules.¹ In other cases, they can lead to ultrafast predissociation of initially excited $\pi\pi^*$ states.^{2–5}

Highly fluorinated benzene derivatives have recently moved into the foreground in this context for a different type of vibronic interaction of $\pi\pi^*$ with $\pi\sigma^*$ excited states.^{6–12} Upon substitution of hydrogen by fluorine atoms, the σ^* molecular orbitals (MOs) experience a substantial stabilization such that their energy gap above the lower π^* MOs is strongly reduced. The consequences of this so-called perfluoro-effect on the spectra of electronically excited states have been investigated for a range of molecules.^{7,8,13–15} The intense $\pi\pi^*$ electronic transitions continue to determine the observed UV absorption spectra,¹⁵ which tend to become broad and structureless, while the presence of the $\pi\sigma^*$ excited states can only indirectly be inferred. However, in the cases of penta- and hexafluorobenzene (PFB and HFB), for example, the vibronic interaction of the excited $\pi\pi^*$ with a neighboring $\pi\sigma^*$ state manifests itself in strongly red-shifted fluorescence emission bands with much lower quantum yields.^{7,15}

In recent femtosecond time-resolved studies, the dynamics after the excitation of the lowest $\pi\pi^*$ state in PFB and HFB have been investigated in more detail.^{8,9,12} In

particular, transient absorption studies in solution as well as time-of-flight (TOF) ion yield measurements in a molecular beam reported the observation of periodic and long-lived temporal amplitude oscillations. In our previous work on PFB,¹² where we observed an oscillation frequency of 78 cm^{-1} , we could show that the underlying physical mechanism is the breaking of the molecular symmetry due to an unusually strong vibronic coupling of the initially excited 1^1B_2 ($\pi\pi^*$) state with the energetically higher-lying, optically dark 1^1A_2 ($\pi\sigma^*$) state. The interaction is mediated by out-of-plane vibrations of b_1 symmetry. The adiabatic potential energy curves (PECs) along certain b_1 modes of the $\pi\pi^*$ state get distorted to symmetric double wells, in which the wavepacket excited by the pump laser pulse performs a regular, periodic motion. The electronic characters of the adiabatic $\pi\pi^*$ and $\pi\sigma^*$ excited states mix gradually during the out-of-plane vibration, where the largest $\pi\sigma^*$ contribution occurs at maximal displacements along the b_1 modes. Because ionization preferentially happens from the $\pi\pi^*$ configuration, the ionizing probe pulse effectively maps the wavepacket motion into the observed ion yield oscillation.

In this work, we present results of a femtosecond time-of-flight mass spectrometry (TOF-MS) and photoelectron imaging (PEI) study for the molecule pentafluoropyridine (PFPy) as an even more stunning case. The energetically lowest 1^1B_2 ($\pi\pi^*$) electronic state was excited with laser pulses at $\lambda_{\text{pump}} = 255$ nm and the ensuing dynamics were probed by multiphoton ionization at $\lambda_{\text{probe}} = 402$ nm. We observed the effects of a vibronic coherence with the 1^1A_2 ($\pi\sigma^*$) state by a complex modulation of the transient ion yield signal that is composed of oscillatory components of four distinct frequencies. The underlying mechanism is discussed in context with the PEI results and electronic structure calculations at the RI-SCS-CC2 and XMCQDPT2 levels of theory.

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II. EXPERIMENTAL AND COMPUTATIONAL METHODS

The experiments employed a femtosecond pump–probe setup with a home-built linear time-of-flight mass spectrometer (TOF-MS) and photoelectron imaging (PEI) spectrometer.¹² The 255 nm pump pulses with 30 fs duration were generated by frequency-doubling of the temporally compressed output of a non-collinear optical parametric amplifier (NOPA). The 402 nm (frequency-doubled Ti:Sa) probe pulses for multi-photon ionization had a duration of 90 fs. The pentafluoropyridine molecules (abcR GmbH, 99% purity), seeded in helium carrier gas at 2 bar backing pressure, entered the vacuum chamber in a pulsed and skimmed molecular beam, which was crossed by the co-propagating pump and probe beams between the repeller and extractor plates of a Wiley-McLaren electrode assembly. The obtained ions or electrons were detected on a micro-channel plate backed by a stainless-steel anode or a position-sensitive phosphor screen imaged by a CCD camera. The Abel inversion of the recorded photoelectron images was done using the pBASEX program.¹⁶ The images were calibrated by measurements of the $^2P_{3/2}$ and $^2P_{1/2}$ lines¹⁷ from the ionization of xenon in a multi-photon above-threshold ionization process with correction for the ponderomotive shift of the ionization energies caused by the intense electric field.¹⁸

The ground-state equilibrium structures of neutral (1^1A_1) and ionic (1^2A_2 , π^-) PFPy, which has C_{2v} symmetry in its ground state, were optimized computationally using second-order Møller-Plesset (MP2) perturbation theory under the resolution of the identity (RI) approximation and the spin-component scaling (SCS) modification (RI-SCS-MP2)^{19–23} with a def2-TZVPPD^{24–26} basis set. Vertical excitation energies (VEEs) and ionization energies (IEs) were calculated using the second-order approximate coupled cluster method in the same variant (RI-SCS-CC2)^{27–32} for four electronically excited $\pi\pi^*$ states (1^1B_2 , 2^1A_1 , 3^1A_1 , 2^1B_2), two $\pi\sigma^*$ states (1^1A_2 , 2^1B_1), two $n\pi^*$ states (1^1B_1 , 2^1A_2), and the cationic 1^2B_1 (π^-) and 1^2A_1 (n^-) states. The equilibrium structures for the neutral 1^1B_2 ($\pi\pi^*$) state and the cationic 1^2B_1 (π^-) state were optimized using the same method. The nature of the stationary points obtained from the structure optimizations was checked by Hessian diagonalizations. The second derivatives of the energy were computed as finite differences of the first derivatives because analytic second derivatives are not available at the CC2 level of theory. All above-mentioned calculations were carried out using the Turbomole 7.0 program package.^{33,34} Moreover, the VEEs of the neutral excited states were also calculated by applying the extended multi-configuration quasi-degenerate second-order perturbation theory (XMCQDPT2) method³⁵ to the complete active space self-consistent field (CASSCF) wavefunctions with an active space of eight electrons in nine orbitals, including the nitrogen n orbital, the three highest occupied π orbitals, the three lowest unoccupied π^* orbitals, and two σ^* orbitals, using the aug-cc-pVDZ basis set³⁶ and the Firefly QC package³⁷ which is partially based on the GAMESS (US)³⁸ code. As expected, the π and π^* orbitals are delocalized over the molecular frame, while the σ^* orbitals are located on specific C–F bonds and show substantial 3s Rydberg character. State-averaging over

the twelve lowest CASSCF states was found necessary as the CASSCF method gave a wrong ordering of the excited states.

III. RESULTS

A. UV absorption spectrum and calculated electronically excited states

The gas-phase UV absorption spectrum of PFPy is depicted in Figure 1. The spectrum shows a broad band with an absorption maximum at $\lambda = 254$ nm without a resolved vibrational structure. A second absorption band begins to rise at $\lambda < 220$ nm. The respective assignments are found from the quantum chemical calculations. The computed VEEs of the lowest eight electronically excited states are listed in Table I. In the order of increasing energy given by the CC2 method, we have the 1^1B_2 ($\pi\pi^*$), 1^1A_2 ($\pi\sigma^*$), 2^1A_1 ($\pi\pi^*$), 1^1B_1 ($n\pi^*$), 2^1B_1 ($\pi\sigma^*$), 2^1A_2 ($n\pi^*$), 3^1A_1 ($\pi\pi^*$), and 2^1B_2 ($\pi\pi^*$) states. The CC2 and XMCQDPT2 calculations give results in good agreement with each other, although the energetic order differs for a few of the higher-lying states.

The VEE of the 1^1B_2 ($\pi\pi^*$) state is calculated to be 5.10 eV (CC2) or 4.89 eV (XMCQDPT2), in excellent agreement with the experimentally observed absorption maximum at $\lambda = 254$ nm (4.88 eV). In our previous work on PFB,¹² we already observed that the CC2 method places the VEE for this transition slightly too high compared to the experimental result. While the structure optimization in the electronic ground state yields a planar geometry (Figure 2(a)), the molecule acquires a strong out-of-plane distortion in the first excited state (Figure 2(b)). The N atom is displaced out of the plane defined by the four carbon atoms on the side of the ring by 1.5° and the C and F atoms opposing the N atom by 2.5° and 35° , respectively. The other four F atoms are displaced by about 5° in the opposite direction. This structural deformation corresponds to nuclear motion along normal modes of b_1 symmetry, as will be discussed in Section IV B. (Although the relaxed structures have C_s symmetry, we continue to employ C_{2v} symmetry labels here and in the following as is

FIG. 1. Gas phase UV absorption spectrum of PFPy ($p = 0.75$ mbar). The absorption maximum of the 1^1B_2 ($\pi\pi^*$) excited state peaks at $\lambda = 254$ nm. The band at $\lambda < 220$ nm was assigned to the 2^1A_1 ($\pi\pi^*$) state.

TABLE I. Calculated vertical (VEE) and adiabatic (AEE) transition energies (in eV) from the S_0 (1^1A_1) electronic ground state to the lowest eight valence excited states of the neutral PFPy molecule, to the electronic ground state of the ion, and to the lowest two excited states of the ion. The calculated oscillator strengths are given in parentheses next to the RI-SCS-CC2 energies. Experimental values are given for comparison where available.

State	RI-SCS-CC2 VEE	XMCQDPT2 VEE	RI-SCS-CC2 AEE	Experimental VEE/AEE
1^1B_2 ($\pi\pi^*$)	5.10 (0.056)	4.89	4.41	4.88 ^a /4.60 ^a
1^1A_2 ($\pi\sigma^*$)	6.35 (0.000)	6.23	...	...
2^1A_1 ($\pi\pi^*$)	6.64 (0.015)	6.46	...	-/5.90 ^a
1^1B_1 ($n\pi^*$)	6.71 (0.003)	6.35	...	...
2^1B_1 ($\pi\sigma^*$)	7.23 (0.012)	7.22	...	-/6.12 ^a
2^1A_2 ($n\pi^*$)	7.30 (0.000)	6.95	...	...
3^1A_1 ($\pi\pi^*$)	7.59 (0.549)	7.11	...	-/6.57 ^a
2^1B_2 ($\pi\pi^*$)	7.68 (0.487)	7.05	...	...
1^2A_2 (π^{-1})	10.28	...	10.00	10.27 ^b /10.08 ^b
1^2B_1 (π^{-1})	11.53	...	11.27	11.37 ^b /11.17 ^b
1^2A_1 (n^{-1})	12.20	...	...	12.08 ^b /11.84 ^c

^aThis work.

^bBrundle *et al.* (Ref. 14).

^cUtsunomiya *et al.* (Ref. 40).

customary for other C_{2v} molecules with quasi-planar out-of-plane distorted excited electronic state structures.³⁹⁾

The adiabatic excitation energy (AEE) of the 1^1B_2 state, which is a good estimate for the excitation energy of the 0–0 transition from the S_0 ground state, amounts to 4.41 eV at the CC2 level of theory. We observed a similarly pronounced energetic stabilization of an out-of-plane deformed structure for the excited state of PFB.¹²

Although we do not expect energetically higher-lying electronic states to be excited by single-photon absorption of our 255 nm pump pulses, their VEEs and electronic characters were calculated to investigate possible vibronic couplings with the 1^1B_2 ($\pi\pi^*$) state. Moreover, some of those states act as resonant intermediates in the multi-photon probe process. The second $\pi\pi^*$ transition, which leads to the 2^1A_1 state, is computed with a VEE of 6.64 eV (CC2) or 6.46 eV (XMCQDPT2). With an oscillator strength of $f = 0.015$, this transition is likely responsible for the observed UV absorption band at $\lambda < 220$ nm (see Figure 1). Higher states of $\pi\pi^*$ character are 3^1A_1 and 2^1B_2 with calculated VEEs of 7.59 eV and 7.68 eV (CC2) or 7.11 eV and 7.05 eV (XMCQDPT2). Both have very large oscillator strengths of $f \sim 0.5$ and are therefore likely to be resonant intermediate states in the multi-photon ionization process.

The symmetry-forbidden transition to the 1^1A_2 ($\pi\sigma^*$) state is calculated to have a VEE of 6.35 eV (CC2) or 6.23 eV (XMCQDPT2). Both calculated values are in good agreement with each other. The computed excitation energies for the 2^1B_1 state reached by the second $\pi\sigma^*$ transition agree with each other as well. As will be discussed in Section IV B, for symmetry reasons only the 1^1A_2 state can vibronically couple to the 1^1B_2 ($\pi\pi^*$) state via b_1 vibrational modes. The VEE for the 1^1B_1 ($n\pi^*$) state is calculated to be at 6.71 eV or 6.35 eV and for the 2^1A_2 ($n\pi^*$) state at 7.30 eV or 6.95 eV, respectively. Here, the computational methods disagree with each other, as the CC2 method systematically places the $n\pi^*$ transitions at

FIG. 2. RI-SCS-CC2-optimized molecular equilibrium structures (a) in the electronic ground state and (b) in the excited 1^1B_2 ($\pi\pi^*$) state of PFPy. ((c)–(g)) Displacement vectors of the calculated harmonic vibrational normal modes $v_{18} - v_{14}$ of b_1 symmetry in the order of increasing frequency.

higher energies than the XMCQDPT2 method. However, the dynamics in the excited 1^1B_2 ($\pi\pi^*$) state are not expected to be influenced by the 2^1A_2 ($n\pi^*$) state through b_1 modes, although coupling would be allowed by symmetry (see Section IV B).

The electronic structure of the cation was investigated at the CC2 level of theory to aid the assignment of the PE spectra. The vertical and adiabatic ionization energies for the cationic 1^2A_2 (π^{-1}), 1^2B_1 (π^{-1}), and 1^2A_1 (n^{-1}) states are in excellent agreement with the experimental values determined by Brundle *et al.*¹⁴ and Utsunomiya *et al.*⁴⁰ (cf. Table I). The third cationic excited state 2^2B_1 (π^{-1}) with an experimentally determined adiabatic IE of 13.46 eV⁴⁰ is not reached energetically in our experiment and is therefore not considered any further. The results of the structure optimizations show that the molecule retains a planar geometry in the cationic ground and first excited states with only minor structural differences compared to the neutral ground state.

B. Time-resolved time-of-flight mass spectrometry

The recorded time-resolved parent ion yield signal of PFPy is shown in Figure 3(a). The initial spike around $\Delta t = 0$ ps is followed by a pronounced and long-lived periodic modulation of the signal amplitude. The oscillatory behavior can

FIG. 3. (a) Recorded transient PFPy parent ion yield signal as function of pump-probe delay time after excitation at $\lambda_{\text{pump}} = 255$ nm. (b) TOF mass spectrum of PFPy resulting from the multi-photon ionization at $\lambda_{\text{probe}} = 402$ nm. As can be seen, the spectrum shows virtually no fragmentation. (c) Repeated measurements shown on an enlarged time scale up to $\Delta t = 4$ ps. The vertically displaced curves represent separate measurements recorded on different days to highlight the reproducibility of the modulation pattern.

be observed for up to ~ 9 ps after the excitation. Subsequently, the ion yield signal decays exponentially within about 200 ps. A zoomed-in plot of the oscillating part is depicted in Figure 3(c). The maxima have a temporal spacing of about 0.47 ps, and each of them displays a sub-structure of up to three further local maxima within the first ~ 3.5 ps. To ensure that this complex signal modulation is not an effect of experimental noise, the measurements were repeated on several different days. The respective results are shown by the vertically displaced curves in Figure 3(c). As can be seen, the modulation pattern of the ion yield signal is reproducible to a remarkable degree. We emphasize that the TOF mass spectrum of PFPy using multi-photon ionization at 402 nm, which is shown in Figure 3(b), exhibits no evidence for the dissociation or fragmentation of the excited molecules or ions within our experimental detection sensitivity. Thus, the eventual temporal decay of the PFPy parent ion yield signal in Figure 3(a), which is observed on a time scale of ~ 40 ps, has to be ascribed to nonadiabatic electronic deactivation from the excited 1^1B_2 ($\pi\pi^*$) state to the S_0 ground state.

The molecular frequencies encoded in the oscillating signal were found by a Fourier transform (FT) analysis. To this end, we first subtracted from the data points the initial spike

FIG. 4. (a) Least-squares fit of a biexponentially decaying model function (solid red line) to the transient PFPy ion yield data points (connected circles). (b) Fourier transform of the remaining oscillatory signal shown in the inset (c) after subtraction of the biexponential model decay function. The FT analysis identifies four frequencies at 72 cm^{-1} (I), 144 cm^{-1} (II), 251 cm^{-1} (III), and 281 cm^{-1} (IV).

around time zero and the slowly decaying component of the signal. As shown in Figure 4(a), both could be nicely modeled by least-squares fitting using a biexponential decay function convoluted with a Gaussian representing the instrument response function (IRF). The resulting best fit is indicated by the solid red line in Figure 4(a). The subtraction of this curve from the experimental ion yield data points gave the oscillatory part of the signal depicted in Figure 4(c). The resulting Fourier transform is given in Figure 4(b). Four spectral components, corresponding to frequencies of 72 cm^{-1} (I), 144 cm^{-1} (II), 251 cm^{-1} (III), and 281 cm^{-1} (IV), are readily distinguished. The value of frequency II looks like the second harmonic of frequency I. This assumption will be substantiated in Section IV B.

C. Time-resolved photoelectron imaging

Time-resolved PE images were recorded using one-photon excitation from the pump pulse and at least two photons from the ionizing probe pulse at temporal delay times corresponding to the first, second, and third maxima of the oscillating ion yield signal, as well as the first and second minima. The resulting raw images together with their Abel-inverted images are shown in Figure 5. A probe-only image using four-photon

FIG. 5. Recorded photoelectron images (left) and corresponding meridional slices through the recovered three-dimensional photoelectron distributions (right). (a) PE image by four-photon ionization using the probe laser pulse at $\lambda_{\text{probe}} = 402$ nm only. ((b)–(f)) Transient PE images recorded using both pump and probe laser pulses at delay times corresponding to the first few maxima and minima of the transient ion yield signal.

ionization with the 402 nm laser pulses recorded for comparison is reproduced in Figure 5(a). Four distinct rings can be identified in the probe-only image, whereas the pump-and-probe time-resolved images at the oscillation maxima (Figures 5(b), 5(d), and 5(f)) only show three rings. Moreover, the middle ring appears to vanish when going from an oscillation maximum to the minimum (Figures 5(c) and 5(e)).

FIG. 6. Probe-only photoelectron spectrum resulting from four-photon ionization at $\lambda_{\text{probe}} = 402$ nm. The maximal available energy in this process is indicated by the dashed vertical line. Four peaking bands can be distinguished, which are centered at (a) 0.72 eV, (b) 1.15 eV, (c) 1.60 eV, and (d) 2.00 eV.

The photoelectron spectra associated with those images are shown in Figure 6 (probe-only) and Figure 7 (pump-and-probe time-resolved). The dashed vertical lines denote the maximal available PE kinetic energy

$$E_{\text{avl}} = \hbar (n \times \omega_{\text{pump}} + m \times \omega_{\text{probe}}) - IE$$

that a photoelectron can gain after an n -photon pump and m -photon probe process with a given adiabatic molecular ionization energy IE . If a higher ionic state with a larger IE is

FIG. 7. Time-resolved photoelectron spectra after excitation at $\lambda_{\text{pump}} = 255$ nm and multi-photon ionization at $\lambda_{\text{probe}} = 402$ nm. The dashed vertical line marks the maximal available photoelectron energy $E_{\text{avl}}^{1+2'}$ in the $1 + 2'$ ionization scheme. The spectra were recorded at delay times corresponding to the first, second, and third maxima ($\Delta t = 0.04$, 0.42 , and 0.84 ps) and the first and second minima ($\Delta t = 0.26$ and 0.70 ps) of the transient ion yield signal (shown above the spectra for orientation with color-coded arrows indicating the delay times). Note that the spectrum at $\Delta t = 0.04$ ps (gray curve) has been multiplied by a factor of 0.5. At delay times corresponding to the maxima, three distinct bands can be distinguished, which are centered at (a) 0.70 eV, (b) 1.10 eV, and (c) 1.60 eV (see the text). In the oscillation minima, the signal amplitude over the entire spectral range is strongly reduced and band (b) appears to be missing.

accessed, the available kinetic energy will decrease accordingly. In the probe-only experiment, this energy amounts to $E_{\text{avl}}^{4'} = 2.27$ eV for four-photon ionization, whereas $E_{\text{avl}}^{1+2'} = 0.96$ eV in the time-resolved experiments with the desired $1 + 2'$ (one-photon pump, two-photon probe) process. The probe-only spectrum (Figure 6) exhibits four distinct PE bands, which are centered at (a) 0.72 eV, (b) 1.15 eV, (c) 1.60 eV, and (d) 2.00 eV. The PE bands in the pump-and-probe time-resolved PE spectra (Figure 7) are centered at virtually identical energies within experimental errors (± 0.05 eV) of (a) 0.70 eV, (b) 1.10 eV, and (c) 1.60 eV. No peak is observed around 2.00 eV, which is the position of band (d) in Figure 6. Band (b) at 1.10 eV corresponds to the middle ring in the PE images that is missing at pump-probe delay times corresponding to oscillation minima.

IV. DISCUSSION

A. Assignment of the photoelectron spectra

As found from the excited electronic state calculations (cf. Table I), three energetically close-lying ionic states are accessible from ground-state PFPy by our pump-and-probe scheme: $1^2A_2 (\pi^-)$, $1^2B_1 (\pi^-)$, and $1^2A_1 (n^-)$. Several arguments allow us to identify those states in our photoelectron spectra. In particular, the specific ionic state that is reached in a two-color multi-photon ionization process is often determined by a specific molecular orbital that gives the largest contribution to the resonant intermediate excited state accessed by the pump pulse.^{41,42} For the assignment of the observed PE bands, it is therefore useful to consider the electron configurations of the involved states in some detail.

Following our CC2 and XMCQDPT2 calculations, the $1^1B_2 (\pi\pi^*)$, $1^1A_2 (\pi\sigma^*)$, and $2^1A_1 (\pi\pi^*)$ excited states all have the largest contribution from the excitation of an electron from the $3a_2 (\pi)$ orbital. The ionization of the PFPy molecule from either of those excited states will therefore likely lead to the $1^2A_2 (\pi^-)$ ionic state. This is the ground (i.e., D_0) state of the PFPy^+ ion. Conversely, the higher-lying $2^1B_1 (\pi\sigma^*)$, $3^1A_1 (\pi\pi^*)$, and $2^1B_2 (\pi\pi^*)$ electronic states have the largest contribution from the excitation of an electron from the $5b_1 (\pi)$ orbital. Their ionization is thus expected to reach the first excited $1^2B_1 (\pi^-)$ state of PFPy^+ . By the same token, ionization from one of the 1^1B_1 or $2^1A_2 (n\pi^*)$ excited states should lead to the ion in the $1^2A_1 (n^-)$ excited state. The electronic excitation and ionization processes that lead to the observed structure of the PE spectra are summarized in the ionization scheme in Figure 8 and will be detailed in the following.

Keeping the above-mentioned ionization correlations in mind, PE band (a) in the time-resolved spectra in Figure 7 can be unambiguously assigned to ionization from $1^1B_2 (\pi\pi^*)$ to $1^2A_2 (\pi^-)$. It is the only signal below $E_{\text{avl}}^{1+2'}$ and has a very large amplitude due to the resonant excitation in the $1 + 2'$ process (cf. Figure 8(a)). From its spectral position, we estimate the AEE of the $1^1B_2 (\pi\pi^*)$ state to be 4.60 eV. As this band (a) is also present in the probe-only PE spectrum (Figure 6), the $1^1B_2 (\pi\pi^*)$ state appears to be excited by the probe pulses alone as well. Since the energy of $\hbar\omega = 3.08$ eV of a single probe photon is not sufficient, we propose that a two-photon

FIG. 8. Pump-probe scheme in the photoelectron imaging experiment showing the excitation of PFPy with one pump photon at $\lambda_{\text{pump}} = 255$ nm (blue arrows) and the multi-photon ionization at $\lambda_{\text{probe}} = 402$ nm (red arrows) to different ionic states. (a) Excitation of the two lowest $\pi\pi^*$ states 1^1B_2 and 2^1A_1 followed by two-photon ionization to the ionic ground state $1^2A_2 (\pi^-)$, leading to the observed PE bands (a) and (d). (b) Proposed multi-photon excitation of the higher-lying $\pi\pi^*$ states 3^1A_1 and 2^1B_2 and of the $2^1B_1 (\pi\sigma^*)$ state followed by ionization to the first excited $1^2B_1 (\pi^-)$ ionic state, resulting in PE bands (b) and (c). The resulting photoelectron kinetic energies are given vertically above the arrows.

absorption with a total energy of $\hbar\omega = 6.17$ eV (corresponding to $\lambda = 201$ nm, cf. Figure 1) does in fact excite the $2^1A_1 (\pi\pi^*)$ state. To understand how this transition leads to a simultaneous excitation of the $1^1B_2 (\pi\pi^*)$ state, we turn to our computational results and compare those to the structurally related, but highly symmetric, benzene molecule (D_{6h} point group). Both the CC2 and XMCQDPT2 methods reveal that the $2^1A_1 (\pi\pi^*)$ state has major contributions from the $3a_2 \rightarrow 4a_2$ and $5b_1 \rightarrow 6b_1$ electronic transitions, while the $1^1B_2 (\pi\pi^*)$ state is established mostly by the $3a_2 \rightarrow 6b_1$ and $5b_1 \rightarrow 4a_2$ transitions. The occupied $3a_2$ and $5b_1$ π orbitals emerge from the twofold degenerate e_{1g} highest occupied molecular orbital (HOMO) of benzene, while the $4a_2$ and $6b_1$ π^* orbitals correspond to the e_{2u} lowest unoccupied molecular orbital (LUMO). In benzene, transitions between those orbitals are responsible for the 1^1B_{2u} , 1^1B_{1u} , and 1^1E_{1u} excited states, of which the first two correspond to the 1^1B_2 and $2^1A_1 (\pi\pi^*)$ states of PFPy, where the degeneracy of the MOs is lifted due to the reduction to C_{2v} symmetry. We therefore assume that the excitation of 2^1A_1 can be followed by an ultrafast internal conversion to 1^1B_2 . Estimating the AEE of the $2^1A_1 (\pi\pi^*)$ state to be around 5.90 eV, which corresponds to the right shoulder of the absorption band at $\lambda \sim 210$ nm in the UV absorption spectrum (Figure 1), a PE band after two-photon ionization to the ionic ground

state would be expected at around 2.00 eV (cf. Figure 8(a)). This corresponds exactly to the position of PE band (d) in the probe-only PE spectrum in Figure 6, thereby suggesting that our above assumptions are correct. Band (d) is missing in the time-resolved PE spectrum in Figure 7 because the subsequent absorption of one (time-delayed) probe photon after the absorption of one pump photon excites states of far higher energy than $2\ ^1A_1$ ($\pi\pi^*$) (cf. Figure 8), giving rise to bands (b) and (c), instead.

PE bands (b) and (c) are present in both the probe-only and the pump-and-probe time-resolved PE spectra and are therefore likely caused by the ionization of very high-lying excited electronic states. Those states can be excited by a combination of three probe photons or by one pump plus one probe photon and are subsequently ionized by two additional probe photons (i.e., reached by $3' + 2'$ or $1 + 1' + 2'$ ionization, see Figure 8(b)). Their assignment to the emitting electronic states is not straightforward, as the corresponding total photon energies available for the excitation of $\hbar\omega = 9.25$ eV ($3' + 2'$ process) and $\hbar\omega = 7.95$ eV ($1 + 1' + 2'$ process) allow for excitation to all electronic states considered in our quantum chemical calculations (cf. Table I). While PE band (b) has a sharp peak in the probe-only PE spectrum, it displays a partially resolved vibrational structure in the pump-and-probe time-resolved PE spectra. The latter is likely connected to the excitation of a larger number of vibrational modes by the spectrally broad pump pulse. PE band (c), on the other hand, has a similar spectral shape in both PE spectra. Moreover, PE band (b) vanishes at delay times corresponding to oscillation minima in the time-resolved PE spectra, while band (c) retains its amplitude in relation to (a). These observations suggest that the electronic characters of the excited states responsible for bands (b) and (c) differ from each other. It seems likely that at least one of the PE bands is due to the excitation of either the $3\ ^1A_1$ ($\pi\pi^*$) or the $2\ ^1B_2$ ($\pi\pi^*$) state because the corresponding transitions have large calculated oscillator strengths ($f = 0.487 - 0.549$). The allowed transition to the $2\ ^1B_1$ ($\pi\sigma^*$) state with $f = 0.012$ might also be excited in the multi-photon process. Presuming an ionization of those states to the first excited $1\ ^2B_1$ (π^{-1}) ionic state (see the ionization correlations discussed above and Figure 8(b)), adiabatic electronic excitation energies of 6.12 eV and 6.57 eV can be calculated from the PE band energies of 1.15 eV (b) and 1.60 eV (c). The excitation energy difference of 0.45 eV is in good agreement with the difference of the calculated CC2 VEEs for the $1\ ^1B_1$ ($\pi\sigma^*$) and $3\ ^1A_1$ or $2\ ^1B_2$ ($\pi\pi^*$) states of 0.36–0.45 eV. The VEEs obtained with the XMCQDPT2 method, on the other hand, predict a smaller energetic difference. Therefore, the assignments of PE bands (b) and (c) remain somewhat speculative within our present scope.

B. Periodic oscillations of the transient ion yield signal

The periodic modulation of the PFPy ion yield signal (Figure 3) is similar in principle to that in our previous work on the PFB molecule.¹² However, the detection of four distinct frequency components in the case of PFPy clearly stands out. The two energetically lowest excited states of both PFPy and PFB are $1\ ^1B_2$ ($\pi\pi^*$) and $1\ ^1A_2$ ($\pi\sigma^*$) at the Franck-Condon (FC) structure, with a difference in their VEEs of slightly

more than 1 eV at the CC2 and XMCQDPT2 levels of theory. Vibronic coupling between those states can be mediated by vibrational modes of b_1 symmetry, which are out-of-plane deformation modes. In our previous study, we calculated the diabatic and adiabatic PECs along the six b_1 normal mode coordinates $Q_{20} - Q_{15}$ of PFB (numbered according to the Mulliken notation) using the XMCQDPT2 method. The results showed that, while the diabatic PECs of the first excited $\pi\pi^*$ state all have their minima at the planar FC structure, the adiabatic PECs exhibit symmetric double wells along the Q_{20} , Q_{18} , Q_{17} , and Q_{16} coordinates with minima at out-of-plane distorted structures. A symmetry-breaking pseudo-Jahn–Teller (PJT) effect⁴³ is caused by strong vibronic couplings between the $1\ ^1B_2$ ($\pi\pi^*$) and $1\ ^1A_2$ ($\pi\sigma^*$) states by those b_1 modes. The result is a repulsion between the first and second adiabatic PECs that, for the Q_{20} , Q_{18} , Q_{17} , and Q_{16} coordinates of PFB, is strong enough to stabilize an out-of-plane distorted molecular geometry of the $1\ ^1B_2$ ($\pi\pi^*$) state. Subsequent quantum dynamics simulations based on a vibronic coupling model Hamiltonian^{44,45} parametrized from the results of the XMCQDPT2 calculations indeed showed that the $\pi\pi^*$ excited PFB molecule performs a long-lived regular periodic motion mainly along Q_{20} , while little oscillatory motion could be observed along other coordinates.¹² The nuclear motion along the b_1 coordinates in the adiabatic picture is associated with a mixing of the $\pi\pi^*$ and $\pi\sigma^*$ electronic characters of the first and second excited states. This mixing is mirrored by the calculated time-dependent diabatic excited-state populations of the $\pi\pi^*$ and $\pi\sigma^*$ states, which accordingly show large amplitude oscillations with opposite phases. The frequency and damping time of the calculated oscillating state populations is in good agreement with the experimentally observed transient ion yield oscillation.¹²

Considering the distinct similarity of the experimental results, the computed electronic excited-state structure, and the molecular equilibrium structure in the first excited $1\ ^1B_2$ ($\pi\pi^*$) state of PFPy in comparison to PFB, the physical mechanisms at the origin of the observed oscillations in the PFPy molecule are assumed to be analogous to those in PFB. As we already noted above, PFPy exhibits an out-of-plane distorted molecular structure in the relaxed first excited state. The distortion corresponds to displacements along normal modes of b_1 symmetry. The respective displacement vectors are visualized in Figures 2(c)–2(g). Therefore, the adiabatic PECs of PFPy along at least some of the b_1 normal mode coordinates should exhibit similar symmetric double-well shapes induced by $1\ ^1B_2$ ($\pi\pi^*$) to $1\ ^1A_2$ ($\pi\sigma^*$) vibronic coupling as found in PFB. Notable effects caused by coupling of the $1\ ^1B_2$ ($\pi\pi^*$) to the $2\ ^1A_2$ ($n\pi^*$) state, which does not exist in PFB, are assumed to be small due to the large energetic distance of more than 2 eV. Furthermore, we do not expect $n\pi^*$ excitation to cause a drastic out-of-plane deformation as calculated for the $\pi\pi^*$ state because the involved MOs are located on the aromatic ring, in contrast to the σ^* MO that is located on the C–F bond.

The calculated harmonic frequencies for the b_1 vibrational modes of PFPy in the ground state and in the first excited state at the CC2 level of theory are compiled in Table II. As can be seen, the frequencies for the ground state are in

TABLE II. Calculated harmonic vibrational frequencies of the b_1 normal modes (numbered according to the Mulliken notation) in cm^{-1} in the electronic ground state and the first excited 1^1B_2 ($\pi\pi^*$) state at the RI-SCS-CC2 level of theory.

No.	1^1A_1 (gs) expt. ^a	1^1A_1 (gs) calc. ^b	1^1B_2 ($\pi\pi^*$) calc. ^b
14	736	746	677
15	620	635	537
16	353	357	264
17	224	219	158
18	174	160	78

^aExperimental values for the ground state taken from Ref. 48.

^bThis work.

excellent agreement with experimental values. The frequencies in the first excited state are substantially lower, especially considering the three lowest-frequency modes $\nu_{18} - \nu_{16}$. These frequencies were calculated as finite differences of the first derivatives of the electronic potential energy in the harmonic approximation (cf. Section II). In a highly anharmonic potential, as is the case for the double-well adiabatic PECs, knowledge of the exact curvatures of the potential combined with numerical diagonalization of the corresponding Hamiltonian would be required to gain the physically correct vibrational frequencies. Nonetheless, the low frequency values are fully compatible with the assumed strong vibronic coupling with the 1^1A_2 ($\pi\sigma^*$) excited state.

The FT analysis of the oscillating experimental ion yield signal gave three distinct frequency components of 72 cm^{-1} (I), 251 cm^{-1} (III), and 281 cm^{-1} (IV). Thus, based on the present computational results and the parallels to the results for PFB, we tentatively assign our experimentally observed modulation frequencies to wavepacket motion along the Q_{18} , Q_{17} , and Q_{16} coordinates of PFPy in the first excited state. The 144 cm^{-1} frequency component (II) appears to us to correspond to the second harmonic of frequency I. We note that an appearance of the second harmonic frequency is not unexpected at all, as the solution of the equation of motion for a vibrational wavepacket in an anharmonic double-well potential is well known to lead to additional oscillatory terms with higher multiples of the fundamental frequency.^{46,47} We emphasize, however, that we cannot rule out the alternative of a possible correspondence of the 144 cm^{-1} frequency component to ν_{17} . Clearly, the calculated harmonic vibrational frequencies can only be taken as a zero-order guide for a comparison, so we cannot expect quantitative agreement. Evidently, however, the pump pulse excites a vibrational wavepacket that periodically oscillates in the anharmonic PECs of the b_1 modes. When the wavepacket executes its out-of-plane distortion by moving from the FC region to the outer turning points of the double-well potential curves of the 1^1B_2 adiabatic state, the electronic wavefunction acquires a pronounced $\pi\sigma^*$ character. The $\pi\pi^*$ character is recovered when the wavepacket returns to the FC structure. This motion is periodically repeated until dephasing of the various components of the wavepacket occurs. The mixing of the $\pi\pi^*$ and $\pi\sigma^*$ characters affects the electronic transition moment for photoionization, as the ionization occurs preferably from the $\pi\pi^*$ electronic configuration. Therefore, the observed experimentally long-lived ion yield oscillations provide a direct

mapping of the wavepacket motion in the first excited adiabatic state and of the associated strongly coupled electron-nuclear dynamics.

The appearance of the second harmonic of the 72 cm^{-1} frequency indicates that, similar to PFB, wavepacket motion along the lowest-frequency mode ν_{18} has the largest contribution to the observed behavior. This is also reflected by its amplitude in the Fourier-transformed transient ion yield signal. On the other hand, the simultaneous presence of the higher oscillation frequencies III and IV indicates that, contrary to our results on PFB, regular oscillatory motion takes place involving higher vibrational modes as well. Moreover, the employed laser pulse parameters are expected to have a pronounced effect on the observable experimental signal. The photon energy and spectral bandwidth of the pump pulses determine the composition of the excited wavepacket from vibrational eigenstates, and the temporal duration of the probe pulses determines whether the induced dynamics can actually be experimentally resolved at all. For a systematic study on the influence of these parameters, improvements of our laser-optical setup are required. Also, detailed calculations of the diabatic and adiabatic PECs along the b_1 coupling modes of PFPy and the frequencies in the double-well PECs are currently underway in our group, and subsequent quantum dynamics simulations to this end are in preparation. However, the complexity of the calculations is raised substantially compared to PFB due to the presence of the energetically close 2^1A_2 ($n\pi^*$) state.

V. CONCLUSIONS

In the present paper, we reported on a pronounced vibronic coherence between the 1^1B_2 ($\pi\pi^*$) and 1^1A_2 ($\pi\sigma^*$) electronic states of pentafluoropyridine after femtosecond laser excitation with 30 fs pump pulses centered at $\lambda = 255\text{ nm}$. The recorded transient PFPy⁺ ion yield signal, generated by multi-photon ionization with probe laser pulses at $\lambda = 402\text{ nm}$, exhibits a complex long-lived oscillatory behavior for about 9 ps. A Fourier analysis revealed that the oscillations are composed of four distinct frequency components of 72 cm^{-1} , 144 cm^{-1} , 251 cm^{-1} , and 281 cm^{-1} . Photoelectron images were recorded at temporal delay times corresponding to the first three maxima and the first two minima of the ion yield signal. The associated PE spectra revealed only one transition from the 1^1B_2 ($\pi\pi^*$) state by the desired $1 + 2'$ ionization process. Additional bands were attributed to energetically higher-lying, resonant intermediate electronic states accessed in the multi-photon probe process.

RI-SCS-CC2 and XMCQDPT2 calculations showed that the two lowest excited states of PFPy are 1^1B_2 ($\pi\pi^*$) and 1^1A_2 ($\pi\sigma^*$). The $\pi\pi^*$ state has an out-of-plane distorted equilibrium structure that corresponds to a displacement along normal coordinates of b_1 symmetry. The energetic stabilization of this symmetry-broken structure is a consequence of the pseudo-Jahn–Teller effect between the $\pi\pi^*$ and $\pi\sigma^*$ excited states induced by the b_1 vibrations. The adiabatic electronic potential energy curves along the coupling modes acquire pronounced anharmonic, and, in fact, for at least some of the modes, double-well character. The spectrally broad pump

pulse excites localized wavepacket motion along the coupling modes which leads to a periodic mixing of the $\pi\pi^*$ character of the initially excited state with the $\pi\sigma^*$ character of the optically dark second excited state. The associated modulation of the transition moment for photoionization enables a direct mapping of the wavepacket motion into the transient ion yield signal by the probe laser pulse, which mirrors the electronic coherence driven by the molecular vibrations. Three modulation frequencies were tentatively assigned to wavepacket motion along the Q_{18} , Q_{17} , and Q_{16} normal coordinates and one to the overtone along the Q_{18} coordinate. Our ability to observe the higher-frequency Q_{15} and Q_{14} coupling modes is currently limited by the spectral width of our pump pulses and the duration of our probe pulses. Any improvement of our setup in this respect would allow us to gain even deeper insight into the vibrational modes that are involved in the vibronic ${}^1B_2(\pi\pi^*) - {}^1A_2(\pi\sigma^*)$ coupling in perfluorinated aromatics.

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