

Spectroscopic characterization of structural isomers of naphthalene: 1-Phenyl-1-butyne-3-ene

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ABSTRACT

Laser induced fluorescence (LIF), single vibronic level dispersed fluorescence (DFL) spectra, and high resolution rotationally resolved scans of the S_0 – S_1 transition of the $C_{10}H_8$ isomer 1-phenyl-1-butyne-3-ene have been recorded under jet-cooled conditions. The S_0 – S_1 origin of PAV at 34922 cm^{-1} is very weak. A vibronic band located 464.0 above the origin, assigned as 30^1_0 , dominates the LIF excitation spectrum, with intensity arising from vibronic coupling with the S_2 state. High resolution scans of the S_0 – S_1 origin and 30^1_0 vibronic bands determine that the former is a $65:35\text{ }a:b$ hybrid band, while 30^1_0 is a pure a -type band, confirming the role for vibronic coupling and identifying the coupled state as the S_2 state. DFL spectra of all vibronic bands in the first 800 cm^{-1} of the spectrum were recorded. A near-complete assignment of the vibronic structure in both S_0 and S_1 states is obtained. Herzberg–Teller vibronic coupling is carried by two vibrations, ν_{28} and ν_{30} , involving in-plane deformations of the vinylacetylene side chain, leading to Duschinsky mixing evident in the intensities of transitions in excitation and DFL spectra. Extensive Duschinsky mixing is also present among the lowest five out-of-plane vibrational modes, involving motion of the side chain. Comparison with the results of DFT B3LYP and TDDFT calculations with a $6\text{-}311+\text{G}(\text{d,p})$ basis set confirm and strengthen the assignments.

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1. Introduction

From combustion to planetary atmospheres, the formation and growth of polyaromatic hydrocarbons (PAHs) is of great interest. PAH formation during the combustion of fossil fuels is known to be a critical first step in the process of soot formation [1–4]. Recently, the Cassini orbiter has provided evidence of complex organic chemistry taking place in the atmosphere of Titan, Saturn's largest moon. Data from the Cassini Plasma Spectrometer (CAPS) shows intriguing peaks near the masses of naphthalene ($C_{10}H_8$, m/z 128) and anthracene ($C_{14}H_{10}$, m/z 178), the simplest PAHs [5]. The formation of these simple fused ring aromatics is postulated to be the first step in the formation of large organic compounds called "tholins" [5,6]. While it is tempting to assign species with $M = 128$ amu to naphthalene, it is important to keep in mind that there are many other $C_{10}H_8$ structural isomers possible, calling for the need for isomer-specific studies.

The chemistry of Titan's atmosphere is driven by solar radiation, with polyynes and aromatic hydrocarbons as important ultraviolet absorbers. Current photochemical models lack much in the way of structural details beyond formation of the first aromatic ring

[7,8]. It is therefore important to establish pathways that lead from benzene and its simple derivatives to naphthalene. Among the pathways worth exploring in some detail are those that involve formation of singly- or doubly-substituted aromatic derivatives, which themselves either photolyze or photoisomerize to naphthalene. As a precursor to photochemical studies, it is important first to characterize the spectroscopy of key aromatic derivatives that will act as intermediates in pathways to naphthalene. To that end, we have recently carried out systematic studies of the vibronic spectroscopy of a series of $C_{10}H_8$ isomers, including o -, m -, and p -ethynylstyrene and phenylvinylacetylene (PVA) [9–11].

In a previous benzene discharge study by Güthe et al., four unknown m/z 128 isomers were found [12]. While not identified in the study, it was confirmed that none of them were naphthalene. Later, studies by our group identified two of the species to be e - and z -phenylvinylacetylene [10,11]. These $C_{10}H_8$ species were also identified in a photochemistry experiment looking at the reaction of excited diacetylene ($C_4H_2^*$) with styrene [13]. We have recently reported in a preliminary way on the spectroscopy of 1-phenyl-1-butyne-3-ene (PAV) [14]. Here we provide a more detailed account of its vibronic spectroscopy, including high resolution studies with rotational resolution.

Structurally, 1-phenyl-1-butyne-3-ene, can be viewed as a close analog of PVA, differing in the ordering of the ethynyl and vinyl

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groups relative to the phenyl ring. To emphasize this reordering, we have labeled this molecule PAV. In much the same way that PVA was shown to have similar characteristics to styrene, it is expected that PAV will have many properties similar to that of phenylacetylene.

As a prototypical ethynylbenzene, phenylacetylene has received considerable attention over the years [15–20]. The inherent oscillator strength of the S_0 – S_1 transition of phenyl acetylene (PA) is very weak due to the near cancellation of the electronic transition dipole moment (TDM) contributions from the two orbital components involved in the transition [15]. As a result, the vibronic spectroscopy of PA is dominated by vibronic coupling. In particular, the strongest transition in the excitation spectrum of PA is a vibronic band 490 cm^{-1} to the blue of its S_0 – S_1 origin [15,17]. This band gains its intensity by Herzberg–Teller vibronic coupling to a higher electronic state (S_2) with large oscillator strength [19]. Other phenylacetylene derivatives have similar vibronic intensity patterns reflecting closely analogous effects [16,19]. In the case of PA, two separate vibrational modes are strongly involved in the coupling, leading to a mixing of the modes upon excitation [19]. This mode mixing, or Duschinsky mixing [21], can lead to a break down in the mirror symmetry generally seen between fluorescence excitation and dispersed fluorescence spectra [19]. It was shown by Small et al., that comparison of the intensities on the mixed modes in the ground and excited states can give insight on the relative directions of the TDM components induced by each normal mode [18]. Later work by Chang and co-workers proved that inclusion of vibronic coupling involving both totally symmetric and non-totally symmetric vibrations was essential to quantitative prediction of the vibronic spectrum of PA [22].

In this work, a detailed study of the jet-cooled vibronic and rovibronic spectroscopy of the S_0 – S_1 transition of PAV is presented. Using a combination of laser induced fluorescence (LIF), dispersed fluorescence (DFL), and high-resolution UV techniques, it is seen that the S_0 – S_1 transition has more in common with the corresponding transition in phenylacetylene than it does with PVA. In particular, the spectrum is dominated by Herzberg–Teller vibronic coupling involving in-plane modes that also show evidence for substantial Duschinsky mixing. As will be shown, the spectrum of PAV also provides a match with the unassigned transitions in the benzene discharge products observed by Güthe et al., furthering the assignment of unknown species in this mass channel [12].

2. Experimental and computational methods

The laser induced fluorescence (LIF) and dispersed fluorescence (DFL) spectra of PAV were carried out in the fluorescence chamber at Purdue described in detail elsewhere [23]. Briefly, the sample of PAV was entrained in helium at 3 bar and expanded through a $500\text{ }\mu\text{m}$ pulsed valve nozzle into vacuum. The doubled output from a Nd:YAG-pumped dye laser was used to excite the molecule. Fluorescence was then either directed into a photomultiplier tube for LIF, or directed into a 0.75 m monochromator and dispersed off a grating onto a charged couple device (CCD) camera for acquisition of DFL spectra.

High-resolution scans of several vibronic bands were carried out at the National Institute of Standards and Technology (NIST) using a setup that has been described previously [24]. Briefly, the sample was expanded into the vacuum chamber via a continuous quartz source with a $125\text{ }\mu\text{m}$ orifice diameter. Using argon at a backing pressure of 27 kPa (200 Torr), the sample of PAV was maintained at 60°C for the duration of the measurements. An Ar^+ -pumped cw ring dye laser using Rhodamine 590 laser dye was used to generate $\sim 250\text{ mW}$ of laser light near 565 and 573 nm . Approximately 10 mW of UV light was generated in an

external resonant cavity using a BBO crystal. The molecular beam was skimmed and interrogated by the laser 18 cm downstream. Fluorescence was collected using two spherical mirrors and detected using a PMT and computer-interfaced photon counter. This allowed for a Doppler-limited resolution of $21(1)\text{ MHz}$.

PAV was synthesized via a published procedure [25]. Cuprous iodide was added to a mixture of bis(triphenylphosphine) palladium dichloride and phenylacetylene in ethylamine under a nitrogen atmosphere. Vinylbromide was bubbled through the flask and the solution was stirred for 6 h at room temperature. The solvent, and unreacted starting material, was removed under reduced pressure and the remaining residue was extracted using a water/hexane extraction. GC/MS showed the final product to contain 95% 1-phenyl-1-butyne-3-ene with a 5% impurity of diphenyldiacetylene. The sample was purified using column chromatography.

The ground state geometries of PAV, PVA and PA were optimized using density functional theory (DFT) with a Becke3LYP [26,27] functional and 6-311+G(d,p) basis set. To obtain predictions for the TDM, time-dependent excited-state (TDDFT) optimizations were carried out at the same level of theory. To obtain accurate ordering of the excited states, CASSCF(10,10) optimizations [28] at 6-31G(d) level of theory were carried out. These calculations were performed using Gaussian 09 [29]. Simulations of the high resolution rotational structure of key bands in the spectrum were carried out with JB95 software [24]. All spectra were initially fit to an asymmetric rotor Hamiltonian (representation I') using a distributed parallel version of the genetic algorithm (GA) program [24] beginning with ground state rotational constants estimated from *ab initio* theory. Parameter uncertainties from linear least-squares fits of the bands (type A, $k = 1$) [33] were confirmed from comparisons with results from repeated GA runs on the same band.

3. Results and analysis

3.1. LIF excitation and high resolution UV spectroscopy

In previous work, we reported the mass-resolved resonant two-photon (R2PI) spectrum of PAV [14]. Ultraviolet holeburning was used to demonstrate that both the strong vibronic features starting at 35388 cm^{-1} and the weak features to the red were due to a single species in the expansion. As a result, we made an assignment of the S_0 – S_1 origin to the weak transition at 34924 cm^{-1} , while the intense transition at 35388 cm^{-1} ($+464\text{ cm}^{-1}$) was postulated to be a vibronic transition that gains its intensity through vibronic coupling to a higher electronic state.

Fig. 1 shows the first 800 cm^{-1} of the LIF excitation spectrum of PAV, which is nearly identical in form to the R2PI spectrum, indicating that the fluorescence and ionization quantum yields from the intermediate states vary in a similar way over this wavelength range.

In order to provide more definitive evidence for, and characterize in greater detail, the vibronic coupling present in PAV, high resolution spectra of key vibronic bands in the spectrum were recorded and fit using a custom software package, JB95 [24]. The best-fit parameters for each band are shown in Table 1. The S_0 – S_1 origin (Fig. 2a) was found to have a transition dipole moment of $\mu_a^2:\mu_b^2:\mu_c^2 = 65:35:0$. In contrast, the $+464\text{ cm}^{-1}$ vibronic band (Fig. 2b) was found to be entirely *a*-type, indicating a significant change in TDM direction brought about by vibronic coupling. The incomplete subtraction in the residual (bottom trace) is due to the perturbation of Q-branches from Coriolis coupling. Similar Coriolis perturbations are also seen in phenylacetylene and have recently been modeled in detail by Chang and coworkers [22]. From a structural viewpoint, the small (near zero) inertial defects

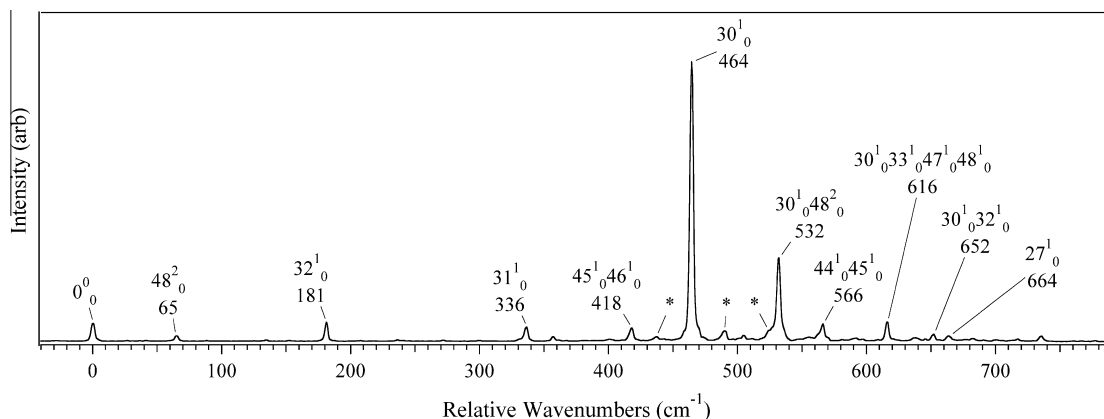


Fig. 1. LIF excitation spectrum of PAV with labeled vibronic transitions. The S_0 – S_1 origin of PAV is located at 34924 cm^{-1} . The peaks denoted with asterisks (*) are hot bands.

Table 1
Fitting parameters for fitting 0^0_0 and $+464\text{ cm}^{-1}$ bands of PAV.

Parameter ^a	0^0_0	$0^0_0 + 464\text{ cm}^{-1}$
A'' (MHz)	4958.16(3)	4958.16(3)
B'' (MHz)	573.59(1)	573.59(1)
C'' (MHz)	514.33(1)	514.33(1)
ΔA (MHz)	−180.34(3)	−185 (3)
ΔB (MHz)	−1.57(1)	−1.2(5)
ΔC (MHz)	−3.44(1)	−3.2(5)
$\Delta I''$	−0.606(3)	−0.606(3)
$\Delta I'$	0.351(1)	0.37(5)
$\mu_a:\mu_b:\mu_c$	65:35:0	100:0:0
T (K)	8(2)	9(3)

^a Uncertainties shown in parentheses refer to the last digits shown and are Type A, coverage factor $k = 1$ (1 std. dev.; Ref. [33]).

of the ground and excited states imply that PAV is planar in both states. This will have important implications when assigning vibronic transitions in the spectra below.

This change in direction of the transition dipole moment induced by vibronic coupling in PAV is similar to that observed in phenylacetylene. Ribblett et al. showed that the origin of phenylacetylene was purely b -type in nature while the HT band was found to be a -type [20]. The shift in the transition moment identifies the $+464\text{ cm}^{-1}$ band as one that gains its intensity via vibronic coupling, as anticipated. The direction of the TDM can also be used to identify the higher electronic state involved, as will be explored in more detail below.

3.2. Dispersed fluorescence

In seeking vibronic assignments for the observed transitions, dispersed fluorescence (DFL) spectra of several of the most intense bands of PAV were recorded. A total of ten vibronic bands (shown in Fig. 1) were examined. Assigned transitions are labeled using the Mulliken numbering scheme [30]. Frequency assignments were aided by comparison with DFT calculations (B3LYP/6-311+G(d,p)) and are summarized in Table 2. The peaks labeled with asterisks (*) in the excitation spectrum are hot bands from vibrationally excited molecules in the ground-state. These transitions were used in confirming ground-state assignments and assigning excited state frequencies, as will be detailed below.

Using the calculations and the results for phenylacetylene as a guide,[15] the $+464\text{ cm}^{-1}$ peak in the LIF excitation spectrum was tentatively assigned to the 30^0_1 transition, with ν_{30} an in-plane distortion of the vinylacetylene group. If this transition gains much of its intensity through vibronic coupling, it is expected that peaks

in the DFL spectra involving ν_{30} should reflect Herzberg–Teller selection rules of $\Delta\nu_{30} = \pm 1$. Furthermore, if vibronic coupling is also active in emission from the S_1 origin, one would anticipate strong emission via the 30^0_1 transition. Indeed, the S_1 origin DFL spectrum (Fig. 3a), has its dominant transition at -497 cm^{-1} . If this intensity was Franck–Condon in nature, then there should be a peak with large intensity at twice this frequency (-994 cm^{-1}) corresponding to the next member of the Franck–Condon progression. As there is not, this band is tentatively assigned as the 30^0_1 HT band corresponding to a $\Delta\nu = +1$ transition in the HT active mode. On this basis, we surmise that the inherent oscillator strength of the S_0 – S_1 transition is very weak, with the intensity present in the S_0 – S_1 origin mostly due to HT coupling to a $\nu' = 1$ level in the S_2 state.

The DFL spectrum of the 30^0_1 transition in the R2PI spectrum (Fig. 3b) confirms the HT nature of the band, with strong resonance fluorescence ($\Delta\nu_{30} = -1$) and a strong transition at -994 cm^{-1} (2×497 , $\Delta\nu_{30} = +1$). This reinforces the assignment of the -497 cm^{-1} band in the 0^0_0 DFL spectrum as 30^0_1 . As can be seen, a second strong transition (-628 cm^{-1}) appears in the 0^0_0 DFL spectrum shifted 131 cm^{-1} from 30^0_1 . Because of its large intensity, it must be involved in HT coupling, either as a combination band built off 30^0_1 , or as a second fundamental X^0_1 that is HT active.

If the band were built off of 30^0_1 , then, given its relative intensity, one should see a FC progression with overtones of the band at -759 , -890 and so on, which are not present. In addition, one would anticipate seeing the 131 cm^{-1} progression built off the resonance fluorescence, but this is not the case. We therefore assign the -628 cm^{-1} transition in Fig. 3a to the 28^0_1 fundamental, with ν_{28} a second HT active mode. The lack of a corresponding intense 28^1_0 transition in the excitation spectrum implies that Duschinsky mixing [21] is occurring, with ν_{30} in the excited state a linear combination of the ground state ν_{28} and ν_{30} modes. Small has worked out the implications of Duschinsky mixing of HT active modes, proving that HT activity involving more than one mode necessarily leads to Duschinsky mixing [18]. In PAV, the presence of strong 28^0_1 and 30^0_1 transitions in the S_1 origin DFL spectrum results from coupling of the S_1 origin to the ν_{30} level of S_2 , where ν'_{30} is defined as a mixture of ν'_{30} and ν''_{30} by the equation

$$\nu'_{30} = c|\nu''_{28} + d|\nu''_{30}, c^2 + d^2 = 1 \quad (1)$$

where c and d are the Duschinsky matrix coefficients. This Duschinsky mixing is also obvious in the 30^0_1 DFL spectrum (Fig. 3b), in which the 30^0_2 , 30^1_1 , and 30^0_1 triad are all observed (connected by red tie lines).

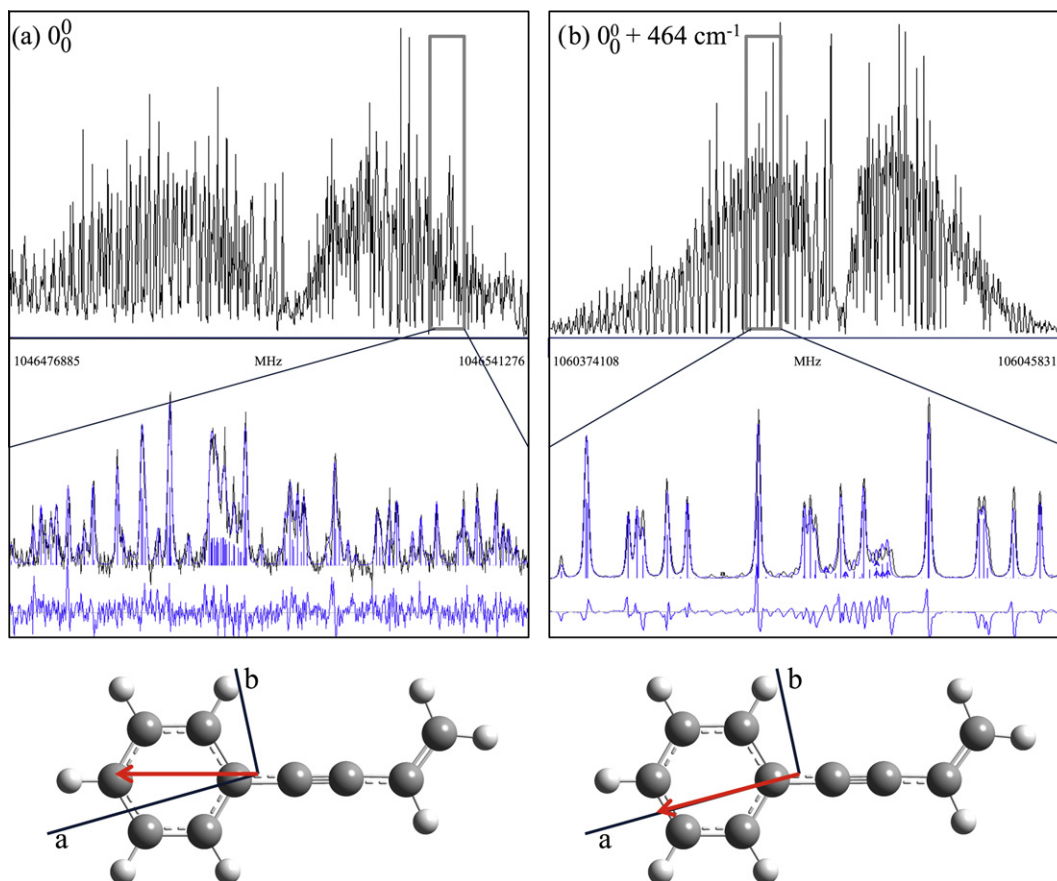


Fig. 2. High resolution LIF scans of the (a) S_0 - S_1 origin at 34924 cm^{-1} (34907.87 cm^{-1} in vacuum), and (b) the vibronic band at $+464\text{ cm}^{-1}$. The lower traces show expanded portions of the spectra together with the simulated spectra (blue, middle) and residuals (blue, lower). While the residuals of the weak origin band are small relative to the signal-to-noise, the large residuals of the strong $+464\text{ cm}^{-1}$ band are well in excess of predictions from a rigid rotor fit and reflect perturbations that depend on the rotational state indicative of Coriolis coupling. Even larger perturbations are found for the $+531\text{ cm}^{-1}$ band (not shown). The red arrows superimposed on the molecular structures give the direction of the transition dipole moment for each transition based on the fit. (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)

Table 2
Select low frequency modes^a of PAV in wavenumbers (cm^{-1}).

Mode	Symmetry	S_0 (Exp)	S_0 (DFT)	S_1 (Exp)	S_1 (TDDFT)
ν_{25}	A'	1008	1014		992
ν_{26}	A'	940	949		926
ν_{27}	A'	706	717		701
ν_{28}	A'	629	638		612
ν_{29}	A'	584	584		558
ν_{30}	A'	497	508	464	494
ν_{31}	A'	366	375	336	377
ν_{32}	A'	192	202	181	178
ν_{33}	A'	63	71	63	64
ν_{44}	A''	400	411	326	356
ν_{45}	A''	375	400	240	308
ν_{46}	A''	237	235	178	187
ν_{47}	A''	87	93	60	87
ν_{48}	A''	35	44	32	44

^a Calculated using DFT and TDDFT (B3LYP/6-311+G(d,p)) level of theory. All values are unscaled.

Once the dominant pattern of ν_{30} as a HT active mode and its Duschinsky mixing with ν_{28} are recognized, all other vibronic activity in these spectra can be understood in terms of normal FC activity built off the S_1 origin or these vibronic bands. For example, the combination bands $26^0_1 30^1_0$ and $25^0_1 30^1_0$ in the 30^1_0 DFL spectrum (Fig. 3b) are FC in nature, with intensities relative to the

resonance fluorescence peak similar to those in the 0^0_0 DFL spectrum (Fig. 3a).

From the small inertial defects determined in the high resolution scans, we have already surmised that PAV retains planarity in both the ground and excited states. As a result, only even overtones and combination bands of out-of-plane vibrations should appear in the spectrum. The lowest frequency out-of-plane mode, ν_{48} , has a calculated frequency of 44 cm^{-1} in both S_0 and S_1 (Table 2). Based on this, it is natural to assign the $0^0_0 + 64\text{ cm}^{-1}$ transition as 48^2_0 , leading to an initial prediction of $\nu'_{48} = 32\text{ cm}^{-1}$. In the 0^0_0 DFL spectrum (Fig. 3a), there are small transitions at -63 and -70 cm^{-1} that are candidates for $\nu'' = 2$ of ν_{48} . Fig. 3c presents an overview DFL spectrum of the $0^0_0 + 64\text{ cm}^{-1}$ transition that associates the excited state level at $+64\text{ cm}^{-1}$ with a level at 70 cm^{-1} in S_0 . The transition to this level is observed more easily in expanded form in Fig. 4b, leading to an assignment of ν_{48} as 35 cm^{-1} in S_0 and 32 cm^{-1} in S_1 . Given the low frequencies of ν_{48} and ν_{47} , hot band transitions are anticipated to involve population of $\nu'' = 1$ levels of these vibrations. As Fig. 4a shows, under lower backing pressure conditions, transitions located at -27 , $+25$ and $+63\text{ cm}^{-1}$ from the 30^1_0 transition grew in intensity relative to the 30^1_0 transition under warmer expansion conditions, identifying them as hot bands. In order to make firm assignments to the out-of-plane vibrations, we recorded DFL spectra of these transitions, which are shown in Fig. 4c–e, respectively.

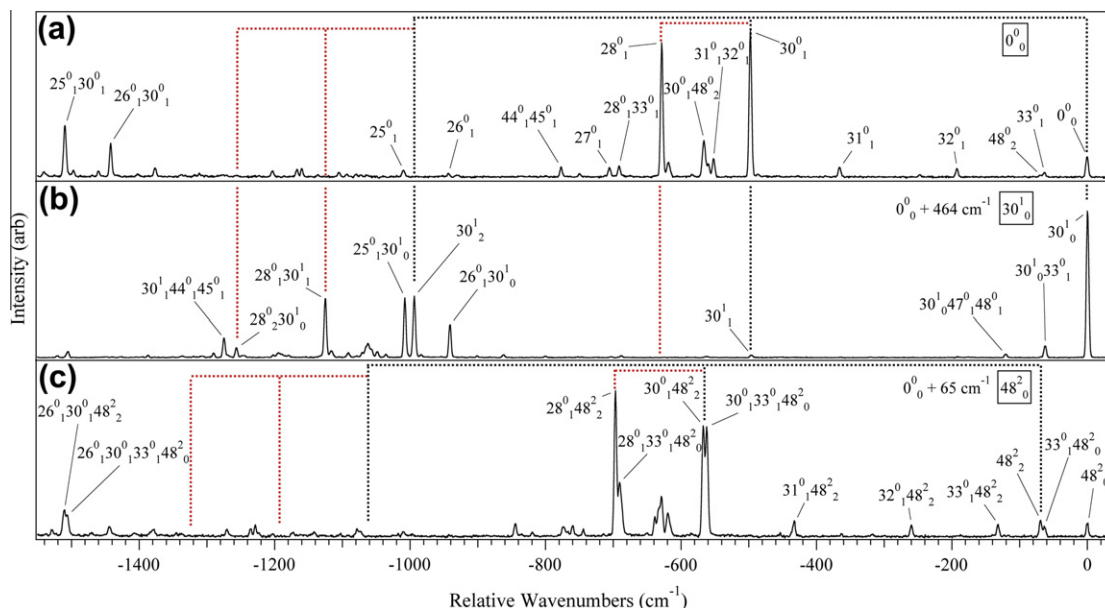


Fig. 3. DFL spectra of (a) the S_0 - S_1 origin, (b) 30^1_0 Herzberg-Teller vibronic band and (c) 48^2_0 out-of-plane overtone.

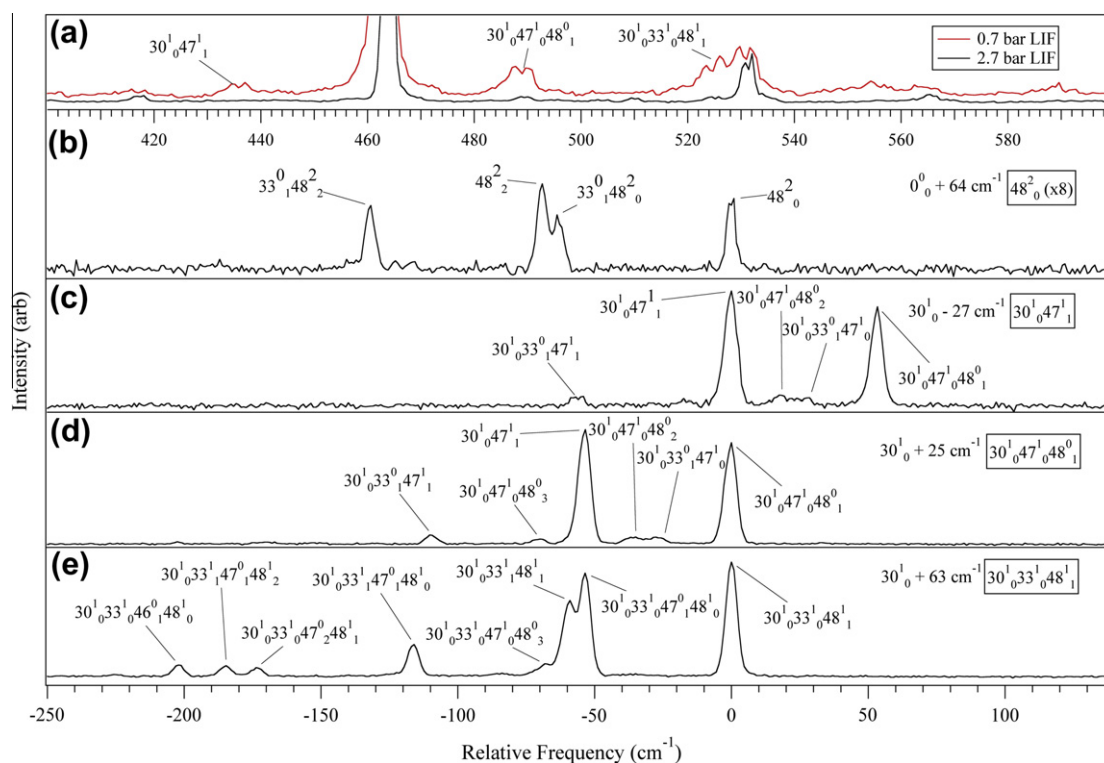


Fig. 4. (a) Comparison of the LIF of PAV near the 30^1_0 band using high backing pressure (black) and low backing pressure (red) showing the growth of hot bands. (b) Expanded view of the DFL spectrum of the 48^2_0 vibronic band. (c–e) DFL spectra arising from hotbands (c) $30^1_0 47^1_1$, (d) $30^1_0 47^1_0 48^0_1$, and (e) $30^1_0 33^1_0 48^1_1$. (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)

The DFL spectra for $30^1_0 - 27 \text{ cm}^{-1}$ and $30^1_0 + 25 \text{ cm}^{-1}$ (Fig. 4c and d) are identical in absolute frequency, indicating that they share the same excited state level, but come from different ground state levels. With this in mind, the observed frequency difference (52 cm^{-1}) in the excited state is the difference of the ground state frequencies, leading to an assignment of ν''_{47} as 87 cm^{-1} . Given that this 52 cm^{-1} is the same as the spacing between the two dominant features in the DFL spectra, it follows that $30^1_0 - 27 \text{ cm}^{-1}$ and the

$30^1_0 + 25 \text{ cm}^{-1}$ should be assigned as the $30^1_0 47^1_1$ and $30^1_0 47^1_0 48^0_1$ hot bands respectively. Furthermore, since $30^1_0 47^1_1$ is $\Delta v = 0$ in ν_{47} , it follows that ν'_{47} should be 27 cm^{-1} less than ν''_{47} . Thus, ν'_{47} has a frequency of 60 cm^{-1} . The large intensity of the cross sequence $30^1_0 47^1_0 48^0_1$ transition involving ν_{47} and ν_{48} indicates strong Duschinsky mixing involving these two vibrations, with the excited state vibrations near-equal mixes of the ground state normal modes. This is very similar to what is seen in PVA

in its lowest frequency modes,[10,11] as will be discussed in more detail below.

The DFL spectrum of the hot band at $30^1_0 + 63\text{ cm}^{-1}$ (Fig. 4e) also is remarkably similar in Franck–Condon activity to the spectrum above it. We assign the hot band responsible for this spectrum to the $30^1_0 33^1_0 48^1_1$ transition for the following reasons. First, while similar, the spectrum in Fig. 4e is not identical to that above it, indicating that the upper level is not the 47^1 level responsible for the other two hot bands. Second, given the extensive Duschinsky mixing involving ν_{47} and ν_{48} , the similar intensities of transitions to 48_1 and 47_1 levels in the ground state suggests the other Duschinsky mixed level (48^1) as the $47^1 48^m$ component of the upper state. Third, the strong new transition at -60 cm^{-1} in the DFL spectrum is at a frequency position associated with one quantum of ν_{33} , suggesting $30^1 48^1 33^1$ as the upper state responsible for the emission. With $\nu'_{48} - \nu''_{48} = -3\text{ cm}^{-1}$, ν'_{33} must be 63 cm^{-1} , remaining unchanged upon excitation. Finally, there is likely some contribution to this hot band from $30^1_0 48^3_1$, which should appear at $30^1_0 + 61\text{ cm}^{-1}$.

The assignments that arise from this hot band analysis confirm and strengthen the assignment of the 48^2_0 transition to the $0^0_0 + 64\text{ cm}^{-1}$ transition. They also provide additional spectroscopic evidence for the planarity of PAV in both S_0 and S_1 states, with strict adherence to $\Delta v = \text{even}$ transitions for out-of-plane modes. Furthermore, they have uncovered extensive Duschinsky mixing involving ν_{47} and ν_{48} between S_0 and S_1 states.

The assignment of subsequent bands in the excitation spectrum as either FC active transitions built off the S_0 – S_1 origin or combination bands built off the HT-active 30^1_0 transition can be accomplished by comparing their DFL spectra to those of the origin and 30^1 . Fig. 5b–d shows the DFL spectra of the low-frequency transitions (up to $+336\text{ cm}^{-1}$) that are built off the origin with no involvement of ν_{30} . In each case, just as with the 0^0_0 DFL spectrum above them, the two dominant transitions in the spectrum are separated from one another by 131 cm^{-1} , the splitting between one quantum of ν_{30} and one of ν_{28} . In all three spectra, a weak false ori-

gin is identifiable $497/628\text{ cm}^{-1}$ to the blue, identified by a tie line in the figure. In Fig. 5b, the position of the false origin (-70 cm^{-1}) is consistent with the first overtone of ν_{48} (Table 2), as has already been described. The corresponding false origins in Fig. 5c and d are assigned as 32^1_1 and 31^1_1 , respectively, with experimental positions within a few cm^{-1} of the calculated frequencies for these vibrations.

Fig. 6a and b shows DFL spectra from the $+418$ and $+566\text{ cm}^{-1}$ bands, respectively. The diagnostic vibrational bands are again present in the $+566\text{ cm}^{-1}$ spectrum. Tracing back to the false origin shows a triplet of peaks centered on the false origin. This triplet is strong evidence of Duschinsky mixing occurring between two out-of-plane modes. The outer two peaks are split by approximately 50 cm^{-1} , indicating their fundamentals should be split by 25 cm^{-1} . Guided by the calculations, these peaks were assigned as even overtones of ν_{44} and ν_{45} with fundamental frequencies of 400 and 375 cm^{-1} respectively. In this manner, the center peak at -775 cm^{-1} could be assigned as the $44,45_1$ combination band leading to the assignment of the $+566\text{ cm}^{-1}$ peak in the LIF excitation spectrum as $44^1_0 45^1_0$.

The DFL spectrum of the $+418\text{ cm}^{-1}$ band (Fig. 6a) is more difficult to assign. With two sets of strong transitions in the high frequency region and multiple peaks in the low frequency region, the peak was assigned assuming Duschinsky mixing is playing a critical role. All of the peaks between -400 and -800 cm^{-1} can be assigned as even combinations of out-of-plane modes, strengthening the argument for Duschinsky mixing. Tracking back from the intense bands, showed that combination bands involving combinations of ν_{44} , ν_{45} , and ν_{46} are the dominant modes involved in the transition with ν_{47} and ν_{48} playing small roles as well. Here we tentatively assign the vibronic band to be the $45^1_0 46^1_0$ vibronic band pending a more detailed analysis of the Duschinsky mixing like that carried out for PVA [10,11,31].

Fig. 7 compares the DFL spectra of several $30^1_0 X^n_m$ combination bands built off the 30^1_0 transition (Fig. 7a). All three of the displayed spectra share the characteristic $\Delta\nu_{30} = \pm 1$ transitions that

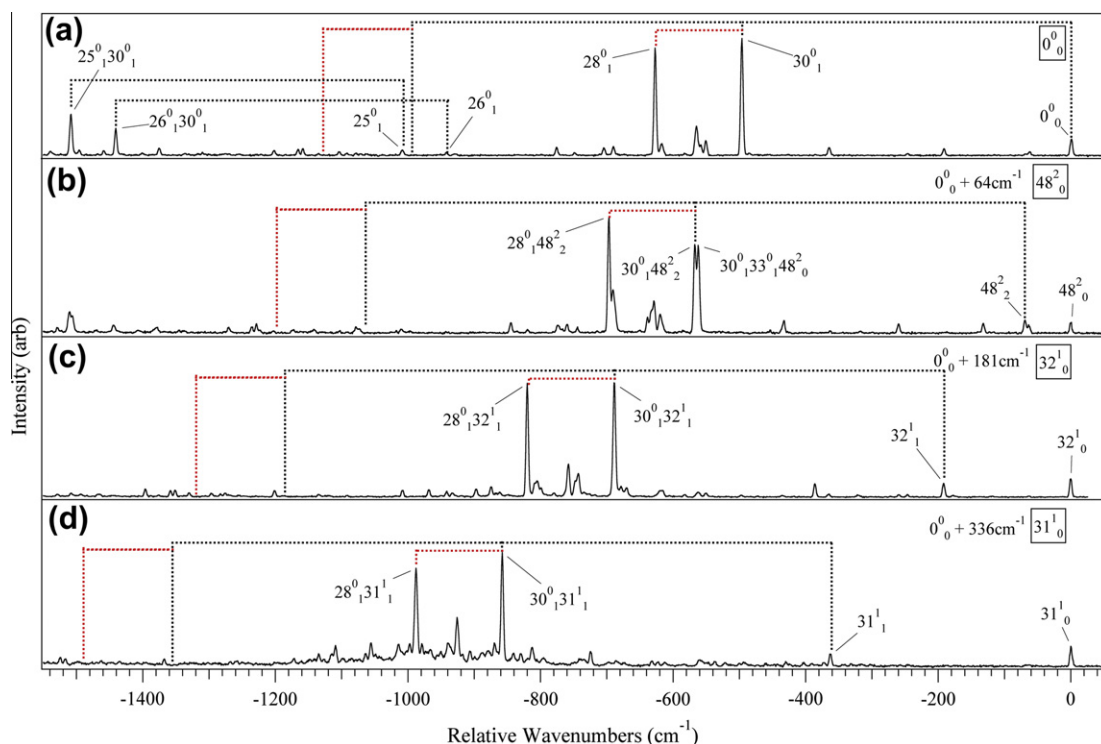
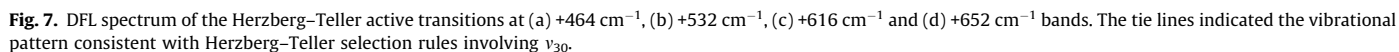
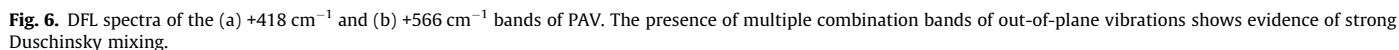


Fig. 5. DFL spectra of the (a) S_0 – S_1 origin, (b) $+64\text{ cm}^{-1}$, (c) $+181\text{ cm}^{-1}$ and (d) $+336\text{ cm}^{-1}$ bands. The tie lines indicated the vibrational pattern consistent with Franck–Condon bands built off the origin.



Finally, the transition at $+618\text{ cm}^{-1}$ (Fig. 7c) is readily identified as a $30^1_0X^0_0Y^0_mZ^0_p$ combination band involving 30^1_0 based on the $\Delta v_{30} = \pm 1$ selection rules, with an energy for the $X^nY^mZ^p$ level of $618 - 464 = 154\text{ cm}^{-1}$. It is assigned as $30^1_033^1_047^1_048^1_0$ based on the presence of a Duschinsky-mixed 47_n48_m triad with $n+m=2$ at -69 , -120 , and -172 cm^{-1} . No pure $n+m=2$ 47^n48^m combination is in the right wavenumber region, but the

Finally, despite excellent signal-to-noise in the excitation spectrum, it was not possible to identify the 28^1_0 transition, even after careful searches in the expected wavenumber region. We will consider this point further in the discussion section.

Because of the spectral similarities between PAV and phenylacetylene, it is worth considering a side-by-side comparison of the two. Fig. 8 shows a pictorial representation of the v_{30} normal

mode of PAV compared to the ν_{35} mode of phenylacetylene, the dominant HT mode in phenylacetylene [32]. In PAV, the mode consists primarily of an in-plane bending of the acetylenic moiety accompanied by a scissoring motion of the vinyl group, while in phenylacetylene, it is primarily the in-plane bending of the acetylenic group due to the lack of a heavy atom substituent at the terminal end. It is obvious from this comparison that the HT-active normal mode is very similar in the two molecules, both in its form and vibrational frequency (492 cm^{-1} in PA and 464 cm^{-1} in PAV in the excited state).

Previous work has shown that phenylacetylene has two modes participating in Herzberg–Teller coupling and that both can be observed in the excitation and the fluorescence spectra [15,16,19]. In PAV, the DFL spectra indicate that there are two modes participating in Herzberg–Teller coupling, ν_{30} and ν_{28} ; however, ν_{28} is not observable in the excitation spectrum. In his landmark paper in 1971, Small proved that when two vibrations of the same symmetry are vibronically coupled to the same higher state, they undergo Duschinsky mixing [18]. By comparing the ratio of the excited state intensities to the ratio of the ground state intensities, it is possible to determine the relative directions of each vibration's induced transition moment. In the case of PAV the ratios are

$$\frac{I(30_0^1)}{28_0^1} > 50 \frac{I(30_1^0)}{I(28_1^0)} \approx 1$$

so

$$\frac{I(30_0^1)}{28_0^1} > \frac{I(30_1^0)}{I(28_1^0)}$$

which implies that the induced transition moment vectors of the modes are antiparallel, enhancing the intensity in emission, but nearly canceling one component in excitation. Bacon et al. showed that this was also the case for phenylacetylene [16]. In a recent study by Chang and co-workers, the induced transition moment vectors of several transitions of phenylacetylene were calculated and used to simulate the excitation spectrum to a remarkably accurate degree [22].

To understand the nature of the HT coupling state, CASSCF(10,10) optimizations were carried out on the first two $\pi\pi^*$ -states of PAV to look at the nature of S_0 – S_n excitations. CASSCF was chosen over CIS or TDDFT methods because of known issues of state mis-ordering in phenylacetylene [33]. Oscillator strengths

and transition dipole moments (TDMs) are taken from TDDFT optimizations (B3LYP/6-311+G(d,p)). The phenylacetylene results (Fig. 9, left) very closely match those in other studies and are consistent with the observed data [17,33–35]. The S_2 state in PA carries large oscillator strength from S_0 , and is responsible for the observed vibronic coupling in the S_0 – S_1 spectrum of PA. In addition, the predicted TDM directions agree with those observed for the S_0 – S_1 origin and 35_1^0 transitions by Ribblett et al. [20] It is important to note that the S_0 – S_1 electronic transition in PA is allowed, but is very weak because the two electronic components nearly cancel in the transition, which is a roughly equal mix of HOMO–1 $\rightarrow$ LUMO and HOMO $\rightarrow$ LUMO+1 character.

The S_0 – S_1 transition of PAV is analogous to that of phenylacetylene with a similar HOMO–1 $\rightarrow$ LUMO and HOMO $\rightarrow$ LUMO+1 transition predicted (Fig. 9, middle). A striking difference between PAV and phenylacetylene is the direction of the S_0 – S_1 TDM. As can be seen, the predicted TDM of 65:35:0 for the PAV origin is in good agreement with the one determined from the high resolution scan (Table 1) while in phenylacetylene, the S_0 – S_1 transition is pure b -type [20]. This change in direction of the TDM is at least partially due to the breaking of the C_{2v} symmetry by addition of the vinyl group.

The TDM of the Herzberg–Teller band in both PAV and phenylacetylene is a pure a -type transition, both experimentally and in the calculations. In each case, the transitions are predicted to involve the promotion of an electron from the HOMO to LUMO orbitals with high oscillator strength. Thus, both the nature of the observed electronic transitions and the nature of the Herzberg–Teller vibronic modes in PAV are very similar to those in phenylacetylene.

It is worth noting that PAV also has a similar predicted nature for its low-lying singlet–singlet transitions to those in e -PVA (Fig. 9, middle and right) and z -PVA (not shown). In all cases, the lower energy state has smaller oscillator strength, but while the oscillator strength of PAV is only $3\times$ larger than phenylacetylene, PVA is over $50\times$ larger than PAV. This was born out by previous studies of the vibronic spectroscopy of z - and e -PVA that found vibronic activity that was primarily Franck–Condon in nature, with strong S_0 – S_1 origin bands followed by smaller vibronic bands [10,11]. In that work, it was noted that z -PVA shows evidence of weak HT coupling in one of its vibrational modes, but to a much lesser degree than in PAV or phenylacetylene [11]. In addition, in PVA the breakdown in mirror symmetry between the LIF and DFL spectra was shown to be the result of a state crossing to a dark $\pi\sigma^*$ state [10,11]. PAV showed no evidence of a similar crossing within the studied region. We surmise on this basis that the vibronic behavior of PVA shares more in common with styrene, while PAV is more closely related to phenylacetylene.

On the other hand, the form of the normal modes and their response to electronic excitation are quite similar in PVA and PAV. As shown above, PAV exhibits extensive Duschinsky mixing involving several of the low-frequency out-of-plane modes. In fact, taken as a whole, the current dataset provides evidence for Duschinsky mixing involving the lowest five out-of-plane modes (ν_{48} – ν_{44}). In a prior study specifically of Duschinsky mixing in PVA, it was shown that the lowest four modes (ν_{48} – ν_{45}) are involved in a four mode mixing [31]. In PVA, the abundant DFL combination band spectra were used to fit the data to a quantitative four-mode model of the Duschinsky mixing using a fitting routine developed expressly for the purpose [31]. Fig. 10 presents a comparison of the four lowest energy, out-of-plane, ground state normal modes (ν_{48} – ν_{45}) of PVA and PAV predicted by DFT (B3LYP/6-311+g(d,p)) calculations. It can clearly be seen that many of the modes are analogous to each other with minor differences arising from the reordering of the vinyl and ethynyl groups. A deeper understanding of these vibrations and the changes they undergo upon electronic excitation in PAV

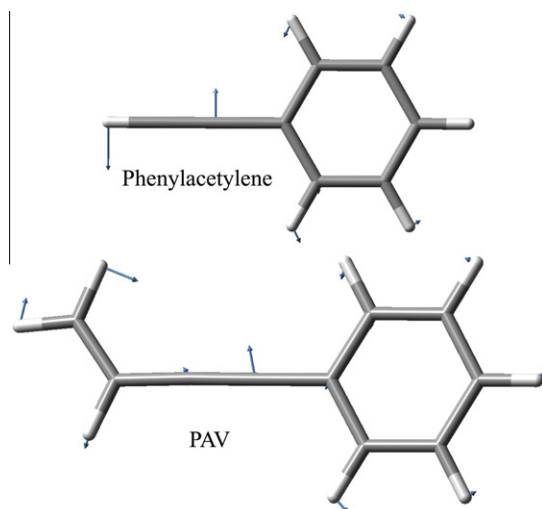


Fig. 8. Comparison of the dominant Herzberg–Teller modes of phenylacetylene (top) and PAV (bottom).

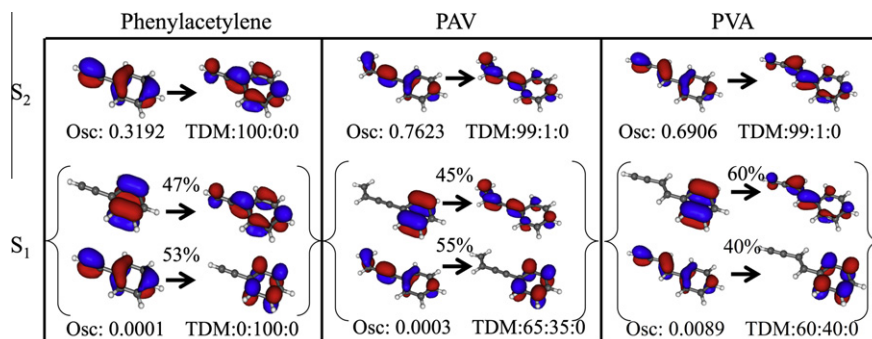


Fig. 9. A comparison of the first two allowed electronic transitions of phenylacetylene (left), PAV (middle), and *e*-PVA (right). Analogous comparisons can also be made for *z*-PVA (not shown). Orbitals with calculated using CASSCF(10,10) B3LYP/6-31G(d) while TDMs and oscillator strengths (Osc) were calculated using TDDFT B3LYP/6-311+G(d,p) methods.

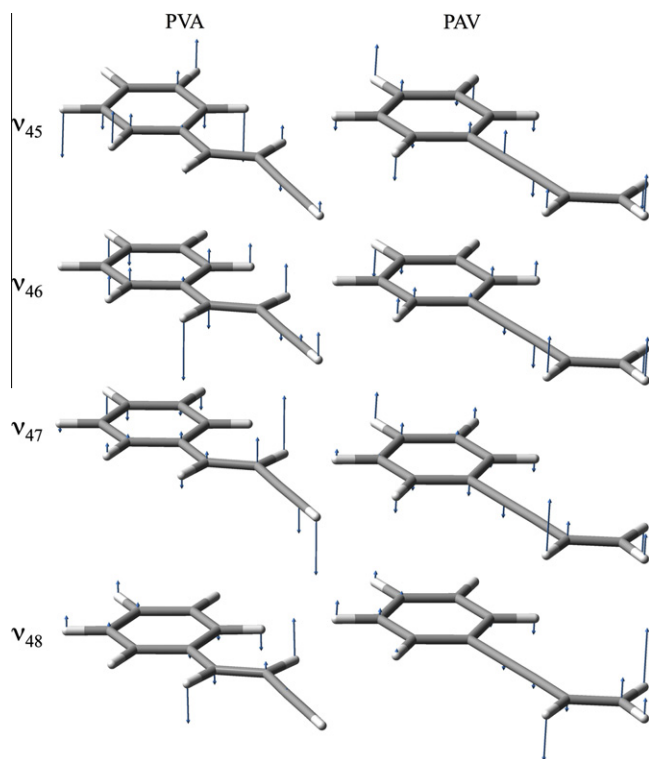


Fig. 10. Comparison of the ground state normal coordinates for modes ν_{45} – ν_{48} of PVA (left) and PAV (right) calculated using B3LYP/6-311+G(d,p) level of theory.

would benefit greatly from a similar analysis of the five-coordinate mixing. Such an analysis would benefit from characterization of other combination bands involving these modes, if they can be located in the spectrum.

5. Conclusions

The work carried out in this study has shown that extending the conjugation of phenylacetylene through the addition of a vinyl group to the acetylenic substituent, further strengthens the Herzberg–Teller vibronic coupling that is present in phenylacetylene. In the same way that PVA was shown to have many electronic and vibrational properties in common with styrene [10,11], PAV shares an even stronger spectroscopic resemblance to its prototype, phenylacetylene. PAV also exhibits strong Duschinsky mixing in its lowest out-of-plane vibrations much like that seen in PVA [10,11,31]. This study has provided a detailed spectroscopic

characterization of another $C_{10}H_8$ structural isomer, providing a foundation for future studies of its isomerization to form naphthalene, or its involvement in other pathways as an intermediate leading either toward or away from naphthalene. Indeed, a recent study in our group, has shown the formation of PVA, PAV and naphthalene upon the photoexcitation of the $C_{10}H_{10}$ compound benzylallene using 193 nm light [36].

Acknowledgments

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