Vibronic bands in the HOMO-LUMO excitation of linear polyyne molecules

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Abstract. Hydrogen-capped linear carbon chain molecules, namely polyyne \( \text{H}(\text{C}≡\text{C})_n\text{H} \) \((n\geq2)\), give rise to three excited states in the HOMO-LUMO excitation. Electric dipole transition from the ground state is fully allowed to one of the three excited states, while forbidden for the other two low-lying excited states. In addition to the strong absorption bands in the UV for the allowed transition, the molecules exhibit weak absorption and emission bands in the near UV and visible wavelength regions. The weak features are the vibronic bands in the forbidden transition. In this article, symmetry considerations are presented for the optical transitions in the centrosymmetric linear polyyne molecule. The argument includes Herzberg-Teller expansion for the state mixing induced by nuclear displacements along the normal coordinate of the molecule, intensity borrowing from fully allowed transitions, and inducing vibrational modes excited in the vibronic transition. The vibronic coupling considered here includes off-diagonal matrix elements for second derivatives along the normal coordinate. The vibronic selection rule for the forbidden transition is derived and associated with the transition moment with respect to the molecular axis. Experimental approaches are proposed for the assignment of the observed vibronic bands.

1. Introduction
Vibronic interaction creates finest fingerprints in the electronic spectra of polyatomic molecules. A symmetry forbidden transition becomes weakly allowed by the mixing of states due to the vibronic coupling, resulting in the intensity borrowing from fully allowed transitions. A noticeable example is found for the \( \tilde{A} \rightarrow \tilde{X} \) transition in benzene, for which some absorption bands are observed around 260 nm [1].

Here, we discuss a series of linear hydrocarbon molecules consisting of a conjugated sp-carbon chain terminated by a hydrogen atom at each end. The centrosymmetric linear molecules, namely polyyne \( \text{H}(\text{C}≡\text{C})_n\text{H} \) \((n\geq2)\), can be produced experimentally by laser ablation of carbon particles in organic solvents [2, 3]. The series of polyyne molecules exhibits a systematic trend in the UV absorption spectra, shifting to longer wavelengths according to the molecular size \( n \) [4]. In addition to the strong absorption bands in the UV, weak absorption features have been identified in the near UV region [5]. These features are associated with intrinsically forbidden, but vibronically allowed transitions in the molecule [6].
2. The HOMO-LUMO excitation in linear polyynes molecules

The ground state electron configuration in the polyyne molecule is such that doubly degenerate π orbitals constitute a ladder of orbital energy levels in which the gerade and ungerade orbitals appear alternately above and below the HOMO-LUMO gap, e.g., ... for C10H2 and ... for C12H2. Non-degenerate σg and σu orbitals locate upper and lower sections of the π orbitals. Since the neutral polyyne molecule has a closed shell electronic structure, its ground state is totally symmetric, Σg+. The HOMO-LUMO excitation gives rise to three excited states, πu ® πg = Σu+ + Σu- + Δu, for both series of C4m+2H2 (πu for HOMO) and C4mH2 (πg for HOMO). Electric dipole transition from the ground state is fully allowed to the Σu+ state, while forbidden to the low-lying Σu- or Δu state.

Figure 1. (a) Electron configurations for the ground state (left panel) and excited states stemming from the HOMO-LUMO excitation (right panel) in the linear polyyne molecule, C4m+2H2, in D∞h point group symmetry. Four singly excited electron configurations in the πu–πg transition, ϕx-x, ϕy-y, ϕx+y, and ϕy-x, constitute an orthogonal set of linear combinations for three symmetry species, πu ® πg = Σu+ + Σu- + Δu. (b) Configurations for single-electron excitations providing various excited states as represented for C6H2. Among the states from a πu–πg excitation for the HOMO-LUMO excitation, Σu- and Δu come close in energy, while Σu+ occupies always the upper most energy level. (c) Calculated transition energies for C10H2 (TDDFT). The first allowed transition, Σu+ ® Σg+, has an oscillator strength of f = 5.8.

Figure 1(a) illustrates the electron configuration for the ground state (left panel) and those for
singly excited states stemming from the HOMO-LUMO excitation. Since HOMO and LUMO are doubly degenerate, there are four possible electron configurations within the spin-singlet manifold. In the $D_{xh}$ point group symmetry, the four configurations are classified into three symmetry species, $\Sigma^+_u$, $\Sigma^-_u$, and $\Delta_u$. Each of these states are represented by a linear combination of the singly excited configurations. The $\Sigma^+_u$ state contains excitations of an electron between $\pi$ orbitals in the same direction, while the $\Sigma^-_u$ state contains excitations between $\pi$ orbitals perpendicular to each other. The doubly degenerate $\Delta_u$ state includes both the parallel and perpendicular excitations.

Figure 1(b) depicts some single electron excitations, using a schematic orbital energy diagram for $C_6H_2$. The left column illustrates the HOMO-LUMO excitation, generating three symmetry species, $\Sigma^+_u$, $\Sigma^-_u$, and $\Delta_u$. The second column shows the electron excitation from HOMO to LUMO+1. Since the two orbitals have the same parity, $u$, the resulting three excited states have gerade symmetry, $\Sigma^+_g$, $\Sigma^-_g$, and $\Delta_g$. The excitation from a lower occupied level is also possible, e.g., from HOMO−1 to LUMO+1 as in the third column. With this higher energy excitation, another set of excited states including the same symmetry species as the HOMO-LUMO excitation is generated. In the fourth column in Fig. 1(b), the excitation from HOMO ($\pi_u$) to an upper lying $\sigma_g$ orbital gives rise to a $\Pi_u$ state.

Figure 1(c) plots the transition energy for singly excited states in $C_{10}H_2$ (TDDFT). The spin-singlet excited states are the consequence of the state mixing within the same symmetry species. The three excited states consisting mostly of the HOMO-LUMO excitation are the lowest two excited states, $\Sigma^+_u$ and $\Delta_u$, and an upper lying excited state, $\Sigma^+_g$. The $\Sigma^+_g$ state is the lowest energy excited state among those to which the optical transition from the ground state is fully allowed, namely the first allowed transition. The $\Pi_u$ state to which the electric dipole transition is also allowed from the ground state (see the fourth column in Fig. 2(b)), has much higher transition energy (~14 eV by the TDDFT calculation and not shown in Fig. 1(c)) than that for $\Sigma^+_u$ (~6 eV by TDDFT). In Fig. 2(c), it is noticeable that multiple states are locating in-between the lowest two excited states, $\Sigma^-_u$ and $\Delta_u$, and the upper $\Sigma^+_u$ state. These states stem from the electron configurations with higher transition energies (see the second and third column in Fig. 1(b)). Among the excited states stemming from the excitation between a pair of degenerate orbitals, the state for the optically allowed transition, in this case the $\Sigma^+_u$ state, is always the highest in its transition energy [7]. Therefore, several states from higher energy excitations are located below the $\Sigma^+_u$ state.

The electric dipoles, $ex$, $ey$, and $ez$, have irreducible representations, $\pi_u$, $\pi_u$, and $\sigma_g^+$, respectively. Therefore, the transition moment for $\Sigma^+_u\rightarrow\Sigma^+_g$ is parallel to the molecular axis $z$, while the transition moments in $(x, y)$ for $\Pi_u\rightarrow\Sigma^+_g$ are perpendicular to the molecular axis $z$.

3. Observations and conjectures

In a linear molecule in $D_{xh}$, the optical transition from the ground state, $\Sigma^+_u$, to an excited state other than $\Sigma^+_g$ or $\Pi_u$ is forbidden by the orbital symmetry, e.g., $\Delta_u\rightarrow/\rightarrow\Sigma^+_g$ or $\Sigma^-_u\rightarrow/\rightarrow\Sigma^+_g$. This selection rule strictly applies to the vibrational 0–0 band. The origin band is not observed for the forbidden transition. The missing origin in the optical spectra poses a difficulty for the assignment of the spectral features. However, in some cases, transitions are weakly allowed by the electric dipole mechanism when accompanied by activation or deactivation in a specific vibrational mode.

Haink and Jungen analyzed UV absorption spectra for diacetylene, $C_4H_2$, and triacetylene, $C_6H_2$, in the gas phase. The missing origin was located at 258 cm$^{-1}$ below the prominent band in the electronic transitions, $\Delta_u\rightarrow\Sigma^+_g$ and $\Sigma^-_u\rightarrow\Sigma^+_g$. The observed band was associated with an excitation of the $\pi_g$ vibrational mode [8]. Ding et al. observed resonant two photon ionization spectra for the series of polyynes, $C_{2n}H_2$ of $n=3$–7, in the gas phase. The vibronic selection rule for the forbidden transitions, $\Delta_u\rightarrow\Sigma^+_g$ and $\Sigma^-_u\rightarrow\Sigma^+_g$, was mentioned based on the
Herzberg-Teller coupling [6]. During Raman spectroscopy for the polyyne molecules C_{2n}H_2 of n=5–9 in solutions [9], new optical emission band systems were observed in the near UV and visible wavelength regions. The emission spectra systematically shifted to longer wavelengths with the increasing molecular size n [10].

Figure 2. Vibronic bands in the absorption and emission spectra for the forbidden transition, \( \Delta_u \leftrightarrow \Sigma_g^+ \), in the polyyne molecules (a) C_{12}H_2 and (b) C_{14}H_2 in hexane. For the emission spectra, the excitation wavelength was tuned for the allowed transition, \( \Sigma_u^+ \leftrightarrow \Sigma_g^+ \), in the UV [10].

Figure 2 shows the absorption and laser induced optical emission spectra for (a) C_{12}H_2 and (b) C_{14}H_2 in hexane [10]. The vibrational progression is noted in the absorption and emission spectra, showing a characteristic vibrational frequency, 1800–2100 cm\(^{-1}\), for the totally symmetric \( \sigma_g \) stretching vibrational mode of sp-carbon chains. The absorption and emission spectra constitute a mirror image. The missing origin between the absorption and emission features is a promise of the forbidden transition in the molecule. The lowest energy band in the absorption and the highest energy band in the emission are largely separated by 2975 and 2817 cm\(^{-1}\) for these polyynes. If the pair of the absorption and emission bands belong to the same electronic transition, and if the spectral shift due to stabilization by the solvent molecules, so called a Stokes shift, is not so large, the missing origin should locate in the middle of the two bands. In this case, such a low frequency \( \pi_g \) mode at \( \omega_c=258 \text{ cm}^{-1} \) can not explain for the location of the missing origin.

4. Vibronic interactions in the symmetry forbidden transition
The aim of this article is to provide symmetry considerations on the vibronic selection rule for the forbidden transition in the linear polyyne molecule. In the following sections, the theory of vibronic transitions is summarized and applied to the polyyne molecule in \( D_{\infty h} \) point group symmetry. Vibronic transition mechanisms are based on the state mixing induced by symmetry lowering due to nuclear displacements along the normal coordinate for a vibrational mode. Intensity borrowing is expected for the forbidden transition when an excited state connected to the initial or the final state by an allowed transition is involved in the mixed states. Vibrational modes that activate the optical transition, namely inducing modes, depend on the state symmetries. The number of necessary vibrational quanta for an inducing mode is associated with the transition moment of allowed transitions in the intensity borrowing. The vibronic selection rule is deduced for a specific case of the \( \Delta_u \leftrightarrow \Sigma_g^+ \) transition.
5. The theory of vibronic transitions

5.1. Vibronic interactions in the Hamiltonian

Nuclear displacements in a molecule from their equilibrium geometry at a high symmetry cause perturbation, $H'$, in the Hamiltonian, $H$. The unperturbed Hamiltonian, $H_0$, is constructed for the equilibrium geometry [11]. The perturbation under the distortion, $H'$, can be expressed by a series of Taylor expansion around the equilibrium geometry by the displacements along the normal coordinates, $Q_k$ and $Q_l$, for the $k$th and $l$th vibrational modes, respectively.

$$H = H_0 + H',$$

$$H' = \sum_k \left( \frac{\partial H}{\partial Q_k} \right)_0 Q_k + \sum_{k,l} \frac{1}{2} \left( \frac{\partial^2 H}{\partial Q_k \partial Q_l} \right)_0 Q_k Q_l + H.O.$$  

Here, we take both the linear and quadratic terms in order to consider all possible allowed transitions in the intensity borrowing within the first order perturbation.

5.2. The Herzberg-Teller expansion

Using the linear and quadratic terms in Eqn. (2), the wavefunction for an electronic state is represented by a linear combination of unperturbed wavefunctions, $\phi^{(0)}_m(q,0)$, at the equilibrium geometry, $Q=0$. The wavefunction, $\phi^{(0)}_m$, is intrinsically a complex number thus contains a phase factor. For our purpose of symmetry considerations, only the real part is presented in the following discussion.

$$\phi^{(1)}_n(q,Q) = \frac{\left( \frac{\partial H}{\partial Q_k} \right)_0}{E_n - E_m} \phi^{(0)}_m(Q_k) \phi^{(0)}_n + \sum_{k,l} \frac{1}{2} \left( \frac{\partial^2 H}{\partial Q_k \partial Q_l} \right)_0 Q_k Q_l \phi^{(0)}_m(q,0).$$

The electronic wavefunction, $\phi^{(1)}_n(q,Q)$, as a function of the electron coordinates, $q$, under the nuclear displacements, $Q$, is represented by a linear combination of unperturbed wavefunctions, $\phi^{(0)}_m(q,0)$, at the equilibrium geometry, $Q=0$. The wavefunction, $\phi^{(0)}_m$, is intrinsically a complex number thus contains a phase factor. For our purpose of symmetry considerations, only the real part is presented in the following discussion.

5.3. The Born-Oppenheimer approximation

The vibronic wavefunction, $\psi_n(q,Q)$, in the $n$th electronic state is represented by a product of the electronic wavefunction, $\phi^{(1)}_n(q,Q)$ in Eqn. (3), and the vibrational wavefunction, $\chi_v(Q)$, with vibrational quantum numbers, $v$ [13, 14, 15].

$$\psi_n(q,Q) = \phi^{(1)}_n(q,Q)\chi_v(Q).$$

For an excited state, $e$, with vibrational quantum numbers, $v'$, the vibronic wavefunction is

$$\psi_e = \phi^{(0)}_e\chi_{v'} + \sum_{m \neq e} \sum_k \frac{\langle \phi^{(0)}_m | \left( \frac{\partial H}{\partial Q_k} \right)_0 | \phi^{(0)}_e \rangle Q_k}{E_e - E_m} \phi^{(0)}_m(Q_k) \chi_v \chi_{v'},$$

and for the ground state, $g$, with vibrational quantum numbers, $v''$, it is

$$\psi_g = \phi^{(0)}_g\chi_{v''} + \sum_{m \neq g} \sum_k \frac{\langle \phi^{(0)}_m | \left( \frac{\partial H}{\partial Q_k} \right)_0 | \phi^{(0)}_g \rangle Q_k}{E_g - E_m} \phi^{(0)}_m(Q_k) \chi_v \chi_{v''},$$

where the nuclear displacements, $Q_k$ and $Q_l$, are eligible for escaping the integral over the electron coordinates.
5.4. Transition moments
For the electric dipole, $\mu_\rho = e\rho (\rho = x, y, z)$, $\mu = ex + ey + ez$, the transition moment between the ground state and an excited state is represented as

$$\langle \mu \rangle = \langle \psi_g | e\rho | \psi_e \rangle \quad \Rightarrow \quad \langle \mu \rangle = \langle \mu_x \rangle + \langle \mu_y \rangle + \langle \mu_z \rangle. \quad (7)$$

The integral is taken over all the electron coordinates, $q$, and the nuclear coordinates, $Q$. The oscillator strength, $f$, is proportional to the square of the transition moment and the transition energy, $f \propto \Delta E |\langle \mu \rangle|^2$.

5.5. Allowed and forbidden transitions
Using the wavefunctions for the ground and excited states in Eqn. (5) and (6), the matrix element for the transition moment, $h_{ij}$, is calculated as

$$h_{ij} = \langle \phi^{(0)}_g | \mu | \phi^{(0)}_e \rangle \langle \chi_{\nu'} | \chi_{\nu} \rangle \quad \Rightarrow \quad h_{ij} = \sum_{m \neq e} \langle \phi^{(0)}_g | \mu | \phi^{(0)}_e \rangle \sum_k \left( \frac{\partial H}{\partial Q_k} \right)_0 \phi^{(0)}_m \langle \chi_{\nu'} | Q_k | \chi_{\nu} \rangle \langle \chi_{\nu'} | Q_k | \chi_{\nu} \rangle + \sum_{k,l} \left( \frac{\partial^2 H}{\partial Q_k \partial Q_l} \right)_0 \phi^{(0)}_m \langle \chi_{\nu'} | Q_k Q_l | \chi_{\nu} \rangle \langle \chi_{\nu'} | Q_k Q_l | \chi_{\nu} \rangle.$$

(9)

When the 0th order integral, $\langle \phi^{(0)}_g | \mu | \phi^{(0)}_e \rangle$, is not zero, the first term predominates the transition moment, $\langle \mu \rangle$. The relevant transition is designated as allowed or a dipole allowed transition. On the other hand, when the integral, $\langle \phi^{(0)}_g | \mu | \phi^{(0)}_e \rangle$, vanishes, the relevant electronic transition is designated as forbidden or a symmetry forbidden transition. In this case, however, having non-vanishing matrix elements in the latter four terms in Eqn. (9), transitions between particular pairs of vibronic states can have non-zero contributions to the transition moment. The selection rule for the vibronic bands in the forbidden transition can be obtained by looking for such contributions.

5.6. Franck-Condon integrals
For the allowed transition in the first term in Eqn. (9), the integral for vibrational wavefunctions, $\langle \chi_{\nu'} | \chi_{\nu} \rangle$, is represented explicitly as

$$\langle \chi_{\nu'} | \chi_{\nu} \rangle = \prod_j v'_{j} v_j. \quad (10)$$

The magnitude of this integral is approximated using a harmonic oscillator for each vibrational mode in the lower and upper electronic states. For the $j$th mode, the harmonic oscillator in the lower state, $|v'_j\rangle$, is located at the equilibrium geometry, $Q=0$, while that in the upper state,
|v''_j\rangle$, at the potential minimum in the excited state. The Franck-Condon integral, \langle v''_j|v'_j\rangle, can be calculated separately for each vibrational mode.

In the allowed transition, vibronic patterns are totally governed by the Franck-Condon factors, $|\langle v''_j|v'_j\rangle|^2$. Among all the possible combinations of vibrational energy levels, some contribute significantly to the vibronic pattern. For an extreme case in which the potential surfaces in the upper and lower electronic states are similar and both harmonic, the Franck-Condon factors, $|\langle v''_j|v'_j\rangle|^2$, are unity only for the case of $v''_j = v'_j$, providing contributions only from 0–0, 1–1, … transitions in all the vibrational modes.

Concerning the vibronic bands in the forbidden transition, four vibronic terms in Eqn. (9) are relevant, in which the nuclear displacements, $Q_k$ and $Q_l$, are involved in the integral over the nuclear coordinates, $Q$, as

\[
\langle \chi_{v'''}|Q_k|\chi_{v''}\rangle = \langle v''_k|Q_k|v'_k\rangle \prod_{j \neq k} \langle v''_j|v'_j\rangle, \quad (11)
\]

\[
\langle \chi_{v'''}|Q_k Q_l|\chi_{v''}\rangle = \langle v''_k|Q_k|v'_k\rangle \langle v''_l|Q_l|v'_l\rangle \prod_{j \neq k,l} \langle v''_j|v'_j\rangle, \quad (12)
\]

where the subscripts, $k$, $l$, and $j$, specify the normal modes. Note that the quadratic term in Eqn. (12) includes two cases, the diagonal term, $k = l$, for the overtone and the off-diagonal term, $k \neq l$, for the combination.

\[
\langle \chi_{v'''}|Q'_k Q'_l|\chi_{v''}\rangle = \langle v''_k|Q'_k Q'_l|v'_k\rangle \prod_{j \neq k,l} \langle v''_j|v'_j\rangle, \quad \text{overtone}
\]

\[
\langle \chi_{v'''}|Q_k Q_l|\chi_{v''}\rangle = \langle v''_k|Q_k|v'_k\rangle \langle v''_l|Q_l|v'_l\rangle \prod_{j \neq k,l} \langle v''_j|v'_j\rangle. \quad \text{combination}
\]

The number of vibrational modes in the centrosymmetric linear polyene molecule, $\text{H(C}≡\text{C)}_n\text{H}$, is $3N - 5 = 6n + 1$. They are classified into four symmetry species, $\sigma_g$, $\sigma_u$, $\pi_g$, and $\pi_u$. For $\sigma_g$ ($\sigma_u$), only $\sigma^+_g$ ($\sigma^+_u$) modes exist and there is no $\sigma^-_g$ ($\sigma^-_u$) mode. The $\sigma_g$ ($\sigma_u$) modes correspond to the symmetric (anti-symmetric) stretching vibrations with nuclear displacements along the molecular axis, $z$. The $\pi_g$ ($\pi_u$) modes correspond to the trans-bending (cis-bending) vibrations with nuclear displacements perpendicular to the molecular axis, $(x, y)$. The numbers of vibrational modes are $n + 1$, $n$, $n$, and $n$ for the $\sigma_g$, $\sigma_u$, $\pi_g$, and $\pi_u$ modes, respectively. Note that each of the $\pi_g$ and $\pi_u$ modes is doubly degenerate according to the degeneracy in the coordinates perpendicular to the molecular axis, $(x, y)$.

Concerning the trans-bending mode of $\pi_g$ symmetry in $D_{\infty h}$, the degeneracy is lifted by the nuclear displacements along the $\pi_g$ normal coordinate to lower the symmetry into $a_g$ and $b_g$ in $C_{2h}$. For the $a_g$ and $b_g$ modes, the planes of nuclear motions are perpendicular to each other. This applies also to the cis-bending $\pi_u$ mode. For a doubly degenerate $\pi_g$ mode, the quadratic vibronic coupling in Eqn. (12) is associated with an overtone, $\pi^2_g$, for the case of $a^2_g$ or $b^2_g$, or a combination, $\pi_g \pi^+_g$, for the case of $a_g b_g$. This is important for considerations on the vibronic coupling in the $\Sigma^-_u$ → $\Sigma^+_g$ and $\Delta_u$ → $\Sigma^+_g$ forbidden transitions.

### 6. Symmetry considerations on the transition moment
#### 6.1. The intensity borrowing

For large contributions to the transition moments in Eqn. (9), $\langle \phi_g^{(0)}|\mu|\phi_m^{(0)}\rangle$ and $\langle \phi_m^{(0)}|\mu|\phi_e^{(0)}\rangle$, must be large. The former is associated with the dipole allowed transition from the ground state such as $\Sigma^-_u$ → $\Sigma^+_g$ and $\Pi_u$ → $\Sigma^+_g$. The latter for the transition between excited states also contributes significantly. The vibronic transition becomes allowed with the aid of the transition moment in the allowed transitions, thus the mechanism is called intensity borrowing.
In the following discussion, we restrict our attention to a specific case for the \( \Delta_u \leftrightarrow \Sigma_g^+ \) transition in the linear polyyne molecule. The allowed transitions to be considered are those connecting either the initial or final state to another. Possible intermediate states are \( \Pi_u \) and \( \Sigma_u^+ \) for the allowed transitions connected with the ground state, \( \Sigma_g^+ \), while \( \Pi_g \) and \( \Delta_g \) for the allowed transitions connected with the excited state, \( \Delta_u \). The latter two are rationalized by the direct products, \( \Pi_g \otimes \Delta_u = \Pi_u \oplus \Phi_u \) and \( \Delta_g \otimes \Delta_u = \Sigma_u^+ \oplus \Sigma_u^- \oplus \Gamma_u \). Each of the direct products includes, at least, one representation corresponding to the electric dipoles, \( \Pi_u \) for \( (x, y) \) and \( \Sigma_u^+ \) for \( z \). These four transitions are classified by their transition moments, \( (x, y) \) and \( z \), and associated with the linear and quadratic terms in the vibronic coupling, respectively. The important vibronic terms in the \( \Delta_u \leftrightarrow \Sigma_g^+ \) transition are represented explicitly as

\[
\langle \mu \rangle = \langle \Sigma_g^+ | \chi_{\nu'} \mu | \chi_{\nu'} \rangle | \Delta_u \rangle
\]

\[
= \sum_k \langle \Sigma_g^+ | e \chi | \Pi_u \rangle \left( \frac{\partial H}{\partial Q_k} \right)_0 | \Delta_u \rangle \langle v''_k | Q_k | v'_k \rangle \prod_{j \neq k} \langle v''_j | v'_j \rangle
\]

\[+ \sum_k \langle \Pi_g | e \chi | \Delta_u \rangle \left( \frac{\partial H}{\partial Q_k} \right)_0 | \Pi_g \rangle \langle v''_k | Q_k | v'_k \rangle \prod_{j \neq k} \langle v''_j | v'_j \rangle
\]

\[+ \sum_{k,l} \langle \Sigma_g^+ | e \chi | \Sigma_u^+ \rangle \left( \frac{\partial H}{\partial Q_k} \right)_0 | \Delta_u \rangle \langle v''_k | Q_k | v'_k \rangle \langle v''_l | Q_l | v'_l \rangle \prod_{j \neq k,l} \langle v''_j | v'_j \rangle
\]

\[+ \sum_{k,l} \langle \Delta_g | e \chi | \Delta_u \rangle \left( \frac{\partial H}{\partial Q_k} \right)_0 | \Delta_g \rangle \langle v''_k | Q_k | v'_k \rangle \langle v''_l | Q_l | v'_l \rangle \prod_{j \neq k,l} \langle v''_j | v'_j \rangle.
\] (13)

6.2. Inducing modes

Once the intermediate state symmetry is determined from considerations on the intensity borrowing, the next step is to find vibrational modes, \( Q_k \) and \( Q_l \), which provide non-zero contributions to the vibronic coupling, \( \langle \Pi_u | (\partial H/\partial Q_k) | \Delta_u \rangle \) and \( \langle \Sigma_g^+ | \frac{1}{2} (\partial H/\partial Q_k \partial Q_l) | \Delta_u \rangle \). Since the unperturbed Hamiltonian, \( H_0 \), is totally symmetric, its derivatives with respect to \( Q_k \) and \( Q_k Q_l \) have the same symmetry as the relevant vibrational mode symmetry, \( \Gamma(Q_k) \) and \( \Gamma(Q_k) \otimes \Gamma(Q_l) \). For non-vanishing contributions, the direct product of the vibrational species and the two electronic species must contain a totally symmetric species. In other words, the symmetry species of the derivative must be the same as one of the symmetry species in the direct product of the two electronic states.

The linear molecule in \( D_{\infty h} \) has four fundamental species in the vibrational modes, \( \sigma_u^+, \sigma_g^+, \pi_u \), and \( \pi_u \). For the vibronic coupling, \( \langle \Pi_u | (\partial H/\partial Q_k) | \Delta_u \rangle \), the symmetry species for the electronic part is \( \Pi_u \otimes \Delta_u = \Pi_u \oplus \Phi_u \). Then, the vibrational mode of interest should be \( \pi_u \). Concerning the quadratic coupling, \( \langle \Sigma_u^+ | \frac{1}{2} (\partial H/\partial Q_k \partial Q_l) | \Delta_u \rangle \), the symmetry species for the electronic part is \( \Sigma_u^+ \otimes \Delta_u = \Delta_g \). The vibrational \( \delta_g \) species is produced by an overtone or a combination of \( \pi_g \) modes, \( \pi_g \otimes \pi_g = \sigma_g^+ (\oplus \sigma_g^+) \otimes \delta_g \). Also, by an overtone or a combination of \( \pi_u \) modes, \( \pi_u \otimes \pi_u \), the vibrational \( \delta_g \) species can be produced.

6.3. The vibronic selection rule in the \( \Delta_u \leftrightarrow \Sigma_g^+ \) transition

Suppose that a single \( \pi_g \) mode among the \( n \) \( \pi_g \) modes is the inducing mode which is responsible for the main spectral features in the vibronic transition. In the summation over all the vibrational modes, \( Q_k \) and \( Q_l \), in Eqn. (14), most terms other than those for the inducing mode, \( Q_k = Q_l = \pi_g \),
are eliminated for their null contribution.

\[
\langle \mu \rangle = \langle \sum_g^+ | e x + e y | \Pi_u \rangle \left\langle \frac{\Pi_u \left( \frac{\partial H}{\partial Q_{\pi_g}} \right)_0 | \Delta_u \rangle}{E(\Delta_u) - E(\Pi_u)} \langle \sum_g^+ | \Pi_g \right\rangle \prod_{j \neq \pi_g} \langle \nu''_g | \nu'_j \rangle \\
+ \langle \Pi_g | e x + e y | \Delta_u \rangle \left\langle \sum_g^+ \left( \frac{\partial H}{\partial Q_{\pi_g}} \right)_0 | \Pi_g \right\rangle \prod_{j \neq \pi_g} \langle \nu''_g | \nu'_j \rangle \\
+ \langle \Delta_g | e z | \Delta_u \rangle \left\langle \sum_u^+ \left( \frac{\partial^2 H}{\partial Q_{\pi_g}^2} \right)_0 | \Delta_g \right\rangle \prod_{j \neq \pi_g} \langle \nu''_g | \nu'_j \rangle. \quad (15)
\]

We further focus on a specific case of the emission from the vibrationally ground state, \( v'_j = 0 \) for all the \( 3N - 5 \) modes, in the upper electronic state, \( \Delta_u \), to multiple vibrational levels, \( \nu''_g \), in the lower electronic ground state, \( \Sigma^+_g \). Among the considerable number of Franck-Condon integrals, most are zero except for transitions to the \( \nu''_g = 0 \) level. An exceptional case for the HOMO-LUMO excitation in the polyyne molecule is a series of transitions for the CC stretching \( \sigma_g \) mode, providing the vibrational progression in \( \nu''_g \).

Harmonic oscillator considerations on the inducing \( \pi_g \) mode provide the vibronic selection rule, \( \Delta v_{\pi_g} = \pm 1 \) for the linear coupling associated with the transition moment in \((x,y)\) and \( \Delta v_{\pi_g} = \pm 2 \) for the quadratic coupling associated with the transition moment in \( z \). In the case of the emission from the vibrational \( v'' = 0 \) level in the excited \( \Delta_u \) state, the formula in Eqn. (15) is simplified as follows, including the vibrational progression for \( \nu''_g = 0 - 4 \).

\[
\mu_{x,y} = \left[ \left\langle \sum_g^+ | e x + e y | \Pi_u \right\rangle \left\langle \frac{\Pi_u \left( \frac{\partial H}{\partial Q_{\pi_g}} \right)_0 | \Delta_u \rangle}{E(\Delta_u) - E(\Pi_u)} + \left\langle \Pi_g | e x + e y | \Delta_u \right\rangle \left\langle \frac{\Pi_g \left( \frac{\partial H}{\partial Q_{\pi_g}} \right)_0 | \Pi_g \rangle}{E(\Pi_g) - E(\Sigma^+_g)} \right\rangle \right] \langle \nu_{\pi_g} \left| 0 \right\rangle \langle \nu''_{\pi_g} \left| 0 \right\rangle, \quad (16)
\]

\[
\mu_z = \left[ \left\langle \sum_g^+ | e z | \Sigma_u^+ \right\rangle \left\langle \Sigma_u^+ \left( \frac{\partial^2 H}{\partial Q_{\pi_g}^2} \right)_0 | \Delta_u \rangle}{E(\Delta_u) - E(\Sigma^+_u)} + \left\langle \Delta_g | e z | \Delta_u \right\rangle \left\langle \Delta_u \left( \frac{\partial^2 H}{\partial Q_{\pi_g}^2} \right)_0 | \Delta_g \rangle}{E(\Delta_g) - E(\Sigma^+_g)} \right\rangle \langle \nu_{\pi_g} \left| 0 \right\rangle \langle \nu''_{\pi_g} \left| 0 \right\rangle. \quad (17)
\]

7. Determining factors for the transition intensity
Figure 3 summarizes the mechanisms for the vibronic bands in the optical \((a)\) absorption and \((b)\) emission in the forbidden transition, \( \Delta_u \rightarrow \Sigma^+_g \), in the centrosymmetric polyyne molecule. Each of the four intermediate states is connected both to the initial and final states by a dipole allowed transition in one side and by a vibronic coupling in the other. In the vibronic coupling, one (two) vibrational quantum (quanta) is (are) excited in the inducing mode. The appearance of spectral features is a matter of relative amplitudes between the terms in Eqn. (15). The factors which determine the magnitude of the vibronic term in Eqn. (15) are examined in the following.

7.1. Strengths in the vibronic coupling
The primarily important factor is the vibronic coupling in the form of \( \langle \phi^{(0)}_m \left| \frac{\partial H}{\partial Q_k} \right| \phi^{(0)}_n \rangle \) or \( \langle \phi^{(0)}_m \left| \frac{1}{2} \left( \frac{\partial H}{\partial Q_k} \partial Q_l \right) \right| \phi^{(0)}_n \rangle \). The former is an off-diagonal matrix element for the first derivative. Similar coupling appears in considerations on the pseudo Jahn-Teller effects [16]. The latter
is an off-diagonal matrix element for the second derivative. This is beyond the conventional matrix elements in considerations on symmetry breaking systems. Calculations of these vibronic coupling matrix elements are the subject in theoretical developments in the future. It is our belief that the magnitude of the quadratic coupling, \(\langle \phi_m^{(0)} | \frac{1}{2} (\partial^2 H/\partial Q_k^2) | \phi_n^{(0)} \rangle \langle v_k' | Q_k' | v_k' \rangle\), can be comparable to the linear coupling, \(\langle \phi_m^{(0)} | (\partial H/\partial Q_k) | \phi_n^{(0)} \rangle \langle v_k' | Q_k' | v_k' \rangle\).

7.2. Transition moments in the allowed transition
For the intensity borrowing, transition moments in the allowed transition are important. In the polyyne molecule, oscillator strengths for \(\Sigma_u^+ \rightarrow \Sigma_g^+\) transitions are concentrated to the first allowed transition in the UV, \(\sim 5\) eV. This is regarded as the plasmon excitation with \(f_z = 5.8\) (TDDFT for C\(_{10}\)H\(_2\)) and with an absorption coefficient \(\epsilon \sim 2 \times 10^6\) L mol\(^{-1}\) cm\(^{-1}\) [4]. The \(\Pi_u \rightarrow \Sigma_g^+\) transition has been suggested to locate in the vacuum UV region, \(\sim 8\) eV, close to the
ionization threshold [5], with \( f_x + f_y = 2.3 \) (TDDFT for \( C_{10}H_2 \)). Although any allowed transition involving the \( \Delta_u \) state has not been observed, their oscillator strengths should be comparable to the other allowed transitions. Note that the relation between the transition moment and the oscillator strength is \( |\mu_{mn}|^2 \propto f_{mn}/\Delta E_{mn} \), where \( \Delta E_{mn} \) denotes the transition energy.

7.3. Energy denominators
The perturbation coefficient includes a denominator by the energy difference between electronic states connected by the vibronic coupling. As is seen in Figure 3, the magnitude of the denominator for the quadratic term, \( |E(\Delta_u) - E(\Sigma_g^+)\) is small. Thus, substantial contributions are expected by the intensity borrowing from the \( \Sigma_v^+ \rightarrow \Sigma_g^+ \) transition. Terms with denominators of \( |E(\Delta_u) - E(\Sigma_u^+)\) and \( |E(\Delta_u) - E(\Pi_u)\) may also contribute to some extent. The magnitude of the denominator, \( |E(\Pi_u) - E(\Sigma_g^+)\), is the largest, thus probably having a less contribution. Excited states for which the transition energies have been experimentally determined are the \( \Sigma_u^+ \) and \( \Delta_u \) states. Therefore, the comparison between the four denominators remains an estimate.

7.4. Vibrational off-diagonal elements associated with the inducing mode
Equation (15) contains three types of integrals for the vibrational wavefunctions in the forms of \( \langle v''_k | Q_k | v'_j \rangle \), \( \langle v''_k | Q_k^2 | v'_j \rangle \), and \( \langle v''_k | v'_j \rangle \), where \( k \) represents the inducing mode and \( j \) the other modes. The former two are associated with the linear and quadratic vibronic couplings. When the scaling factors in \( Q_k \) and \( Q_k^2 \) are normalized or cancelled by the factors in the vibronic coupling derivatives, all the vibrational integrals are counted as order unity. With a simple estimation based on the harmonic oscillator approximation, the integrals with unitary amplitudes are those for \( \Delta v_k = \pm 1 \) and \( \pm 2 \) for the linear and quadratic integrals, respectively. For polyne molecules, the inducing mode is a trans-bending \( \pi_g \) mode as discussed in Section 6.2 and 6.3 [5, 6, 8, 10, 17]. The importance of the quadratic term has been emphasized first with the observation of the pair of absorption and emission spectra in the forbidden transition [10].

7.5. Franck-Condon factors – the vibrational progression
Among the three types of vibrational integrals, the latter one, \( \langle v''_k | v'_j \rangle \), is the Franck-Condon integral. In the harmonic oscillator approximation, the integrals for \( \Delta v_j = 0 \) have an unitary amplitude. However, it is the electronic transition, thus the difference in the molecular geometry between the upper and lower electronic states causes the vibrational progression in some vibrational modes. Actually, for the \( \Sigma_v^+ \rightarrow \Sigma_g^+ \) allowed transition, the vibrational progression is conspicuous for the symmetric stretching \( \sigma_g \) mode with an increment of \( \sim 2000 \text{ cm}^{-1} \) [4, 9]. Also, for the vibronic spectra in the \( \Delta_u \rightarrow \Sigma_g^+ \) forbidden transition in Fig. 2(a) and (b) [6, 8, 10], the vibrational progression in the same \( \sigma_g \) mode is discernible.

7.6. Possible interference effects between the terms
Finally, it should be emphasized again that the transition intensity is proportional to the square of the transition moment and that the phase factor has not been considered in the present article. Interference effects may occur when the squared sum of the elementary transition moments are calculated explicitly. Some vibronic features can be pronounced and some can be diminished. Here, we just mention about the possibility for the interference effects. This may force some modifications to our description on the intensity for the vibronic bands in the forbidden transition.

8. The selection rule and the transition moment
Our considerations on the vibronic transition in the centrosymmetric linear polyne molecule complete when both the linear and quadratic vibronic couplings are included. The linear term is
associated with the transition of the single quantum excitation in the inducing vibrational mode with an intensity borrowing from the allowed transitions with a transition moment perpendicular to the molecular axis, \((x, y)\). On the other hand, the quadratic term is associated with the transition of the double quanta excitation in the inducing vibrational mode with an intensity borrowing from the allowed transitions with a transition moment in parallel with the molecular axis, \(z\). From the symmetry considerations on the inducing mode in Section 6, the selection rule for the vibronic bands in the \(\Delta_u \rightarrow \Sigma_g^+\) transition is established.

The remaining questions are (1) which \(\pi_g\) mode among the \(n\ \pi_g\) modes is really the inducing mode, (2) where the missing origin is located, and (3) which vibronic term is dominating in the observed vibronic bands. For answering these questions, the vibronic considerations presented in this article constitute a milestone casting a light for the direction in the future. First, the direct comparison in the absorption and emission spectra provides information on the vibrational frequency for the inducing mode as well as for the location of the missing origin [10]. Second, the direction of the transition moment is a key feature in the vibronic transition. Since the transition moment is related to the vibronic selection rule, the correlation between the transition intensity and the polarization of a linearly polarized light should be an interesting issue for understanding the mechanisms in the vibronic transition.

9. The experimental approach

Experimental approaches based on the idea presented above are under way in our group. Molecular crystals containing a trace amount of highly oriented polyyne molecules are the subject for absorption spectroscopy using a linearly polarized light. The allowed transition, \(\Sigma_u^+ \rightarrow \Sigma_g^+\), is known to have the transition moment in parallel with the molecular axis, thus the absorption should be strong when polarization of the incident light gets along the line of the molecular axis in the crystal. If the absorption intensity for the vibronic bands in the forbidden transition follows the intensity for those in the allowed transition upon rotation of the polarization of light, the vibronic bands must have the transition moment in the same direction as the allowed transition. In this case, the vibronic bands should be induced by the excitation of an overtone in the \(\pi_g\) mode. Therefore, the missing origin should be separated from the observed vibronic band by twice the frequency of the inducing \(\pi_g\) mode. If the absorption intensities in the allowed and forbidden transitions show anti-correlation upon rotation of the polarization of light, the vibronic bands in the forbidden transition must be associated with the single quantum excitation in the inducing \(\pi_g\) mode with the transition moment perpendicular to the molecular axis.

One of the critical issues for such experiments is to prepare an appropriate single crystal in which the linear polyyne molecules are highly oriented. Transparency down to shorter wavelengths, \(\sim 220\) nm, is also a necessary condition. We are trying to prepare such a crystalline form of molecular solids in which the size-selected polyyne molecules are embedded. Preparation of the size-selected polyynes as well as cyanopolyynes is in progress in our laboratory [18]. Very recently, we found that polyyne molecules form a relatively stable molecular complex with iodine molecules in non-polar solvents. For the polyyne-iodine complex, the vibronic bands in the forbidden transition were dramatically intensified in the absorption spectra [19, 20]. With the experiments in solutions and solids as well as in the gas phase, information is available for further understanding of the mechanisms for the vibronic transition in the linear polyyne molecules.

10. Conclusions

Based on the Herzberg-Teller coupling for the intensity borrowing, the optical selection rule was derived for the vibronic bands in the symmetry forbidden transition, \(\Delta_u \rightarrow \Sigma_g^+\), in the linear polyyne molecules, \(C_{2n}H_{2n}\), in \(D_{n\chi h}\) point group symmetry. In addition to the linear vibronic coupling by the first derivative, the quadratic vibronic coupling by the second derivative was
taken into account. The quadratic coupling is associated with the vibronic transition having
the transition moment in parallel with the molecular axis in the linear polyyne molecule. It
is induced by the excitation of an overtone in the vibrational $\pi_g$ mode, for which the intensity
borrowing from the fully allowed transition, $\Sigma_u^+ \leftrightarrow \Sigma_g^+$, is expected.

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