Allene and pentatetraene cations as models for intramolecular charge transfer: Vibronic coupling Hamiltonian and conical intersections

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We consider the vibronic coupling effects involving cationic states with degenerate components that can be represented as charge localized at either end of the short cumulene molecules allene and pentatetraene. Our aim is to simulate dynamically the charge transfer process when one component is artificially depopulated. We model the Jahn–Teller vibronic interaction within these states as well as their pseudo-Jahn–Teller coupling with some neighboring states. For the manifold of these states, we have calculated cross sections of the *ab initio* adiabatic potential energy surfaces along *all* nuclear degrees of freedom, including points at large distances from the equilibrium to increase the physical significance of our model. *Ab initio* calculations for the cationic states of allene and pentatetraene were based on the fourth-order Møller–Plesset method and the outer valence Green’s function method. In some cases we had to go beyond this method and use the more involved third-order algebraic diagrammatic construction method to include intersections with *satellite states*. The parameters for a five-state, all-mode diabatic vibronic coupling model Hamiltonian were least-square fitted to these potentials. The coupling parameters for the diabatic model Hamiltonian are such that, in comparison to allene, an enhanced preference for indirect charge transfer is predicted for pentatetraene. © 2005 American Institute of Physics. [DOI: 10.1063/1.1867433]

I. INTRODUCTION

The vibrational energy level structure of various ionized and neutral molecules has been studied by valence photoelectron spectroscopy.1–6 Photoelectron transitions generally occur to more than one final electronic state. These are often coupled through the nuclear motion, an effect known as vibronic coupling. Whenever strong vibronic interactions are present, the Born–Oppenheimer approximation breaks down, i.e., the nuclear motion cannot be considered on one electronic potential energy surface (PES) alone. Instead, nuclear motion has to be monitored simultaneously on all surfaces that participate in the coupling.

The photoionization spectrum bears the signature of the vibronic coupling, more so if a conical intersection7–10 is involved, where the coupling between states is particularly important.11 This field of research has received increasing attention over recent years.12–17 A particular class of conical intersections is formed by the Jahn–Teller (JT) systems.18,19 In these, the electronic degeneracy enforced by symmetry is unstable with respect to nuclear distortions. Systems in which interactions between a degenerate and a nondegenerate state exist that lift the degeneracy are labeled pseudo-Jahn–Teller (PJT) systems.11,20

In this paper, we will consider the vibronic coupling effects involving cationic states with degenerate components that can be represented as charge localized at either end of the short cumulene molecules allene (C₃H₄) and pentatetraene (C₄H₂). Extending previous theoretical studies of allene,21–23 we model the JT vibronic interaction within these states as well as their PJT coupling with some neighboring states. For the manifold of these states, we have calculated cross sections of the *ab initio* adiabatic PESs. A comparison between the vibronic coupling model Hamiltonians of these states and the dynamical behavior of these two molecules shall serve to formulate heuristic rules for the changes in the PESs and coupling strengths when the carbon chain is extended.

The vibronic coupling in the intervening cumulene, butatriene (C₄H₄), has also been studied previously.24 This molecule, however, has D₂ₙ symmetry rather than the D₂ₕ symmetry of allene and pentatetraene. As a result the states of this molecule are not readily comparable with those considered here.

The ground and excited state of the allene cation and the ground and *first two* excited states of the pentatetraene cation are of the 2E type, i.e., \( \tilde{X}^2E \) and \( \tilde{A}^2E \) in allene and \( \tilde{X}^2E \), \( \tilde{A}^2E \), and \( \tilde{B}^2E \) in pentatetraene. These states are each orbitally degenerate at the \( D_2 \) symmetry equilibrium geometry of the neutral molecule. The JT effect in the highest occupied molecular orbital (HOMO)-ionized \( \tilde{X}^2E \) electronic manifolds of allene and pentatetraene was first theoretically inves-
tigated in Ref. 25, where the impact of \( E \times B \) JT coupling was identified and dynamical calculations were performed to predict photoelectron spectra for these states that compared well to experimental results.\(^{26}\) \( E \times B \) is a relatively rare form of JT coupling in which the orbital degeneracy is lifted by a nondegenerate pair of vibrations.

We label the main cationic states of the molecules as \( \tilde{X}, \tilde{A}, \tilde{B}, \) etc., while satellite states (which may be energetically between main states) are given the labels \( \tilde{S}_1, \tilde{S}_2, \) etc. Here we are interested in the states \( \tilde{A}^2E \) in allene and \( \tilde{B}^2E \) in pentatetraene. The hole charge is localized at one end of the molecule in the components of these states. We are aiming to use the model Hamiltonians constructed in dynamical calculations in which one component of these states is artificially depopulated. These simulations will serve as models for intramolecular charge transfer. We will therefore refer to these states as charge transfer states in the following. Ultrafast charge transfer and, more specifically, electron transfer processes between molecular systems play an important role in biological and biochemical systems.\(^{27-29}\) They have also been studied as candidates for future molecular computational devices experimentally\(^{30-36}\) as well as theoretically,\(^{37-40}\) forming an active field of current research.

In the photoelectron spectrum of allene, a sharp peak ascribed to the \( \tilde{X}^2E \) manifold and a broader structure assigned to the interacting \( \tilde{A}^2E/\tilde{B}^2B_2/\tilde{C}^2A_1 \) states exist. In the gap between these two structures, a feature is found that is assigned to a satellite state \( \tilde{S}_1 \) by Baltzer \textit{et al.} This view is contested by Bawagan \textit{et al.}\(^{41}\) who assert that interaction between \( \tilde{X}^2E \) and \( \tilde{S}_1 \) plays a significant role in its formation.\(^{42}\) Although this may be the case, we are concerned with states that are energetically above and separated from these states, so that we did not include them in our considerations explicitly in order to arrive at a model that can be parametrized and on which dynamics can be performed with justifiable effort.

This means that we consider the \( \tilde{X}^2E/\tilde{S}_1 \) and \( \tilde{A}^2E/\tilde{B}^2B_2/\tilde{C}^2A_1 \) bands as separate (as was done in previous studies\(^{31,22,43}\)). Note that the effect of other states coupling to the explicitly included states is taken into account to the extent that it influences their shapes, as this is what is fitted.

The spectral band in the energy range we are interested in has a number of well-resolved peaks at lower energies and an unstructured region at higher energies.\(^{41,44,45}\) The loss of structure is ascribed to the strong vibronic interaction between the electronic states.\(^{45}\)

The JT effect in the \( \tilde{A}^2E \) electronic manifold of allene has been investigated by Woywod and Domecke\(^{43}\) using a two-state, four-mode model. They managed to reproduce most of the low-energy part of the spectrum. According to the coupling parameters extracted from their model, they assigned the low-energy structures to progressions along the H-C-H bending vibrational normal modes \( \nu_2 \in A_1 \) and \( \nu_7 \in B_2 \). However, this assignment required a considerable empirical adjustment of the linear vibronic coupling constants of these modes. In their experimental publication, Yang \textit{et al.}\(^{44}\) had assigned the same structure to progressions along the \( \nu_2 \) and \( \nu_7 \) normal modes.

This model was extended by Mahapatra \textit{et al.} to a three-state, ten-mode\(^{21}\) and a three-state, all-mode\(^ {22}\) model. In these publications, the interplay between JT and PJT effects (the latter involving the \( \tilde{B}^2B_2 \) state above the \( \tilde{A}^2E \) state) was demonstrated and it was ascertained that, additionally to \( \nu_2 \) and \( \nu_7 \), the \( \nu_3 \in A_1 \) has to be taken into account to explain features of the photoelectron spectrum. After minor adjustments to some parameters of the model Hamiltonian, a good agreement with the experimental photoelectron spectrum by Baltzer \textit{et al.}\(^ {45}\) was achieved.

Experimental data at the desired resolution is presently unavailable for the pentatetraene bands of interest. We will thus develop a model Hamiltonian for allene exclusively from \textit{ab initio} data so that a fully analogous fitting process can be performed for pentatetraene, giving models suitable for a meaningful comparison.

Mahapatra \textit{et al.} parametrized their vibronic coupling Hamiltonian using finite-difference derivatives of calculated PESs at the equilibrium geometry of the molecule. Instead of evaluating the calculated PESs exclusively near the equilibrium geometry, in a study on the photoelectron spectrum of butatriene, Cattarius \textit{et al.}\(^ {24}\) used a least-square fitting procedure for the parameters of the vibronic coupling Hamiltonian. This extended fit approach takes the overall shape of the PESs better into account and led to reproducible parameters which model the surfaces to a good accuracy away from the equilibrium geometry. In the present article we set out to use this extended fit approach to construct model Hamiltonians for the states of interest in allene and pentatetraene. The \textit{ab initio} PESs were calculated using outer valence Green’s function method (OVGF) and, where necessary, the compatible third-order algebraic diagrammatic construction (ADC(3)) method.

Allene and pentatetraene have 15 and 21 degrees of freedom, respectively. We present here model Hamiltonians taking all degrees of freedom into account. The results of wave-packet propagation simulations with these Hamiltonians will be presented in a forthcoming publication. The Hamiltonians alone express many properties of the molecules and are therefore of their own interest. They will be discussed in detail in this article.

Section II discusses the basic properties of the vibronic coupling Hamiltonian and the method used to parametrize it according to the data from \textit{ab initio} calculations. Sections III and IV describe the PESs calculated and model Hamiltonians extracted for allene and pentatetraene, respectively. Section V contains a comparison and discussion of the results for the two molecules.

II. THEORETICAL BACKGROUND

A. The vibronic coupling Hamiltonian

The states representable as localized at either end of the molecules discussed in this work are the \( \tilde{A}^2E \) state of allene and the \( \tilde{B}^2E \) state of pentatetraene. Neighboring states at
higher ionization energies are a $^{2}B_{2}$ and a $^{2}A_{1}$ state in each molecule. The calculated ionization energies of these states are listed in Tables I and V. These tables also feature additional states which are needed for fitting the $^{2}E$ surfaces. These are denoted $S$ for satellite. Their properties are detailed in the appropriate sections for allene and pentatetraene.

The coupling between the states selected and the vibrational modes is modeled by the bilinear model vibronic coupling Hamiltonian

$$\hat{H} = \hat{H}_0 + (e_{ij})_{i,j=1,...,5}. \quad (1)$$

Here $\hat{H}_0 = \hat{T}_n + V_0$ is a harmonic oscillator plus quartic correction Hamiltonian modeling the neutral ground state of the molecule. $I$ denotes the $5 \times 5$ unit matrix. The square matrix $(e_{ij})_{i,j=1,...,5}$ is the coupling matrix. The 15 vibrational modes of allene have the irreducible representations

$$\Gamma = 3A_1 + B_1 + 3B_2 + 4E. \quad (2)$$

The corresponding 21 normal modes of pentatetraene are

$$\Gamma = 4A_1 + B_1 + 4B_2 + 6E. \quad (3)$$

Thus

$$\hat{T}_n = \sum_{\nu \in A_1,B_1,B_2} \frac{\omega_{\nu}}{2} \frac{\partial^2}{\partial Q_{\nu}^2} + \sum_{\nu \in E} \frac{\omega_{\nu}}{2} \left( \frac{\partial^2}{\partial Q_{\nu x}^2} + \frac{\partial^2}{\partial Q_{\nu y}^2} \right), \quad (4)$$

$$V_0 = \sum_{\nu \in A_1,B_1,B_2} \frac{\omega_{\nu}}{2} Q_{\nu}^2 + \sum_{\nu \in E} \frac{\omega_{\nu}}{2} (Q_{\nu x}^2 + Q_{\nu y}^2)$$

$$+ \sum_{\nu \in A_1,B_1,B_2} \frac{g_{\nu}}{4!} Q_{\nu}^4 + \sum_{\nu \in E} \frac{g_{\nu}}{4!} (Q_{\nu x}^4 + Q_{\nu y}^4). \quad (5)$$

$Q_{\alpha}$ denotes the mass-frequency scaled coordinate of the degree of freedom $\alpha$. $\omega_{\nu}$ are the harmonic angular frequencies of the normal modes and $g_{\nu}$ are quartic terms accounting for anharmonicities in the ground state potential of the neutral molecule due to the use of rectilinear coordinates, as discussed below.

The elements $e_{ij}$ of the coupling matrix are expanded in a Taylor series up to second order with additional fourth-order diagonal elements. Using selection rules derived from symmetry considerations, they can be parametrized as follows:

$$e_{11} = E_{1}^{(1)} + \sum_{\nu \in A_1,B_2} \kappa_{\nu}^{(1)} Q_{\nu} + \frac{1}{2} \sum_{i,j} \gamma_{ij}^{(1)} Q_{i} Q_{j} + \frac{1}{4!} \sum_{i} e_{i}^{(1)} Q_{i}^4, \quad (6)$$

$$e_{22} = E_{2}^{(2)} + \sum_{\nu \in A_1,B_2} \kappa_{\nu}^{(2)} Q_{\nu} + \frac{1}{2} \sum_{i,j} \gamma_{ij}^{(2)} Q_{i} Q_{j} + \frac{1}{4!} \sum_{i} e_{i}^{(2)} Q_{i}^4, \quad (7)$$

$$e_{kk>1} = E_{k}^{(4)} + \sum_{\nu \in A_1} \kappa_{\nu}^{(4)} Q_{\nu} + \frac{1}{2} \sum_{i,j} \gamma_{ij}^{(4)} Q_{i} Q_{j} + \frac{1}{4!} \sum_{i} e_{i}^{(4)} Q_{i}^4, \quad (8)$$

$$e_{12} = e_{21} = \sum_{\nu \in B_1} \lambda_{\nu}^{(12)} Q_{\nu} \quad (9)$$

$$e_{13} = e_{31} = \sum_{\nu \in E^{(b)}} \lambda_{\nu}^{(13)} Q_{\nu}, \quad e_{23} = e_{32} = \sum_{\nu \in E^{(a)}} \lambda_{\nu}^{(13)} Q_{\nu}, \quad (10)$$

$$e_{14} = e_{41} = \sum_{\nu \in E^{(b)}} \lambda_{\nu}^{(14)} Q_{\nu}, \quad e_{24} = e_{42} = \sum_{\nu \in E^{(a)}} \lambda_{\nu}^{(14)} Q_{\nu}, \quad (11)$$

$$e_{15} = e_{51} = \sum_{\nu \in E^{(b)}} \lambda_{\nu}^{(15)} Q_{\nu}, \quad e_{25} = e_{52} = \sum_{\nu \in E^{(a)}} \lambda_{\nu}^{(15)} Q_{\nu}, \quad (12)$$

$$e_{34} = e_{43} = \sum_{\nu \in B_2} \lambda_{\nu}^{(34)} Q_{\nu}. \quad (13)$$

where $\kappa_{\nu}^{(1)} = \kappa_{\nu}^{(1)}$ for $\nu \in A_1$, $\kappa_{\nu}^{(2)} = -\kappa_{\nu}^{(1)}$ for $\nu \in B_2$, $\gamma_{ij}^{(1)} = \gamma_{ij}^{(1)}$ for $\nu_i, \nu_j$ of the same symmetry, $\gamma_{ij}^{(2)} = -\gamma_{ij}^{(1)}$ for $\nu_i, \nu_j$ of the same symmetry, $\gamma_{ij}^{(2)}$ are the linear JT and PJT coupling constants between the states $k$ and $l$ for the mode $i$, $\gamma_{ij}^{(4)}$ are the intrastate bilinear coupling constants, and $\gamma_{ij}^{(4)}$ are the intrastate quartic coupling constants.

Relations of the form $\nu \in \Gamma$ have to be understood as “the $i$th mode is of symmetry $\Gamma$.” $Q_{ix}$ and $Q_{iy}$ denote the x and y components of the degenerate vibrational E modes. $E^{(a)}$ and $E^{(A)}$ distinguish the E modes according to the symmetry of the component of the E state in $C_4$ that is lowest energetically away from the equilibrium. Allene and pentatetraene each have one mode where this component is A', while in all other E modes it is A. This distinction is discussed in more detail below.

The coefficients $\gamma_{ij}^{(k)}$ specify a frequency change due to coupling in state $k$ and mode $i$ while the $\gamma_{ij}^{(k)}$ specify a change in the corresponding quartic coefficient.

As will be detailed in Sec. III below, the fitting process yielded zero quartic corrections $e_{i}^{(k)}$, $k=1, 2$. The other $e_{i}^{(k)}$, $k=3, 4, 5$ are only small corrections, so the quartic terms in the model Hamiltonian are mainly due to anharmonicities present in the ground state potential rather than coupling. This means that first-order coupling terms dominate the coupling process in allene and pentatetraene.

Higher order coupling constants (for example, bilinear off-diagonal or general quadrilinear) were not used to parametrize the vibronic coupling Hamiltonian. We will demon-
strate that the fit achieved with the model Hamiltonian of Eqs. (6)–(13) is already satisfactory, supporting the notion that the vibronic coupling Hamiltonian Taylor expanded to a certain order represents a good approximation to the physical circumstances.

Note that all coupling parameters involving the fourth and fifth state, \(k=4,5\), are additional to the ones used by Mahapatra et al.\textsuperscript{21–23} for allene, as there exclusively the states \(A^2E\) and \(B^2B_2\) were taken into account. The newly introduced states mainly serve to better fit the topology of the \(A^2E\) and \(B^2B_2\) states. They are thus representatives for a multitude of states coupling with these.

The linear coefficients \(\kappa_i\) and \(\lambda_i\) can only be nonzero if, at the equilibrium geometry \(Q=0\), the cross product of the representations of the involved electronic states \(\alpha\) and \(\beta\) and the mode \(\nu_i\) contains the totally symmetric representation, i.e.,

\[
\Gamma_{\alpha} \times \Gamma_{\nu_i} \times \Gamma_{\beta} \supseteq A_1.
\]  

(15)

Analogous relations hold for the bilinear coefficients \(\gamma_{ij}\).

The mechanism of vibronic coupling is the same in both molecules: The symmetric direct product of the \(E\) representation in \(D_{2d}\) decomposes as

\[
E \times E = A_1 + B_1 + B_2.
\]  

(16)

While totally symmetric modes of representation \(A_1\) cannot lift the degeneracy of the \(^2E\) electronic manifold, the \(B_1\) and \(B_2\) modes can, i.e., they display \(E \otimes B\) Jahn–Teller activity in the charge-localized state. The \(B_1\) modes can thus be regarded as “coupling” modes and the \(B_2\) modes as “tuning” modes.\textsuperscript{11} Although in an \(E \otimes B\) Jahn–Teller system these labels are arbitrary, they are convenient for allene and pentatetraene, as these molecules each have only one \(B_1\) mode.

**B. Ab initio calculations**

Geometry optimization and vibrational normal mode calculations in the neutral ground state were performed at the fourth-order Möller–Plesset perturbation theory (MP4) level employing the 6-311G\(^d\) Gaussian basis set.\textsuperscript{46} The dimensionless normal coordinates \(Q\) are obtained from the mass-weighted normal coordinates by multiplication with the square root of the angular frequency \(\sqrt{\omega_i}\).\textsuperscript{48} Subsequently, points of the neutral ground state along the rectilinear normal mode coordinates of both molecules were calculated with the same method.

To gauge their accuracy, the MP4 ground state energies were checked against results of coupled cluster singles and doubles with triple excitation correction\textsuperscript{48} calculations, which is regarded as one of the most accurate in quantum chemistry today. The differences in energy to the MP4 results were of the order of 0.01 eV, i.e., the MP4 results are highly accurate.

In previous work,\textsuperscript{21–23,25,43} all coefficients not excluded by symmetry were set to the corresponding first or second derivatives of the adiabatic potentials or differences thereof at the equilibrium geometry \(Q=0\), e.g., for \(\nu_i \in A_1\)

\[
\kappa_i = \frac{1}{2} \left. \left( \frac{\partial^2 \mathcal{E}}{\partial Q_i^2} \right) \right|_{Q=0}.
\]  

(17)

Afterwards, some of these values were adjusted in order to better approximate the experimental photoelectron spectrum.

We would like to extend this model, which is accurate near the neutral ground state equilibrium, to coordinates \textit{away} from the equilibrium geometry. A corresponding model will also be presented for pentatetraene and its parameters compared to those determined for allene.

In order to do this, we have calculated cross sections of the adiabatic PESs along the rectilinear normal coordinates of the molecules. Generally speaking, it would be desirable to use normal mode coordinates at every point away from the equilibrium rather than rectilinear coordinates. However, this would complicate the kinetic energy operator considerably, making dynamical simulations involving all normal modes computationally unviable. Since the dynamics and the charge transfer process simulated by the artificial depopulation of one component of the charge transfer state are dominated by the conical intersection, this is not so serious an approximation as it may seem.

In order to allow a meaningful comparison between the molecules, we have not adjusted the parameters to fit any experimental results but instead rely fully on the parameters derived from the \textit{ab initio} results. A comparison with the experimental photoelectron spectrum for allene shall serve merely to gauge the physical relevance of the model. Details of the fit procedure will become apparent as we describe the \textit{ab initio} data and the fitting in the following sections.

For the calculation of the cationic PESs, we have used the \textit{ab initio} OVGF method (Refs. 49 and 50) as implemented in the \textsc{gaussian} 98 program package.\textsuperscript{46} This method is based on the ionization of a single valence electron from its Hartree–Fock orbital and determines the ionization energy by a Green’s function approach. The ionization energy is then added to the MP4 ground state energy at each data point to construct the cationic PESs.

For some of the normal modes of \(E\) symmetry, we had to go beyond OVGF and use the more involved but more precise ADC(3) method (Ref. 51) to gain more appropriate results. This method takes two–hole–one–particle states explicitly into account for the purpose of subsequent Green’s function calculations which means that the basis from which states can be constructed by linear combination is hugely increased. \textit{Satellite states} can be detected with ADC(3) which do not constitute ionization from a single electronic orbital but consist of a linear combination of several electronic configurations, many of which are two–hole–one–particle. In regions where interaction with satellite states is weak, ADC(3) reproduces the results of OVGF. It is therefore readily used as natural extension to OVGF. In cases where satellite states play a minor role, the OVGF data can then be retained in order to save numerical effort.
III. FIVE-STATE, ALL-MODE MODEL VIBRONIC COUPLING HAMILTONIAN FOR ALLENE

When taking the topology of the potential surfaces away from the equilibrium configuration of the neutral molecule into account, anharmonicities even in the ground state potential become visible. These are mainly due to the use of rectangular coordinates which are not strictly normal modes at geometries away from the equilibrium, particularly for normal modes with rotational character.

Figure 1 shows data points from our \textit{ab initio} MP4 calculations of the ground state potential along the in-plane tail wag mode \( \nu_{11}(E) \) (see Fig. 2) of allene. The harmonic potential predicted by the normal mode frequency is shown in Fig. 1(a) and a fit using an additional fourth-order term [with coefficient \( \xi_{11} \) in Eq. (5)] is shown in Fig. 1(b). It is obvious from the figure that the fourth-order term accurately describes the deviation from the harmonic model. The correction of the ground state PES via \( \xi_i \) is performed correspondingly along all normal modes.

During the fitting along other normal modes it turned out that the fourth-order constant \( \xi_i \) extracted from a fit of the ground state usually sufficed to yield a good first-order fit for the cationic states. Quartic corrections \( \kappa_{ij}^{(4)} \) were needed only for some modes \( i \) and there only for \( k=3, 4, 5 \). This means the vibronic coupling Hamiltonian is almost linear, as the dominating fourth-order corrections appear in the model ground state potential \( V_0 \) in Eq. (5) rather than in the coupling terms, Eqs. (6)–(13).

Table I shows the OVGF and ADC(3) energies above the neutral ground state equilibrium geometry (in eV) of the states of interest for allene. They are between 15 eV and 17.7 eV. It can be seen that the results agree quite well qualitatively. The \( E \) and the \( B_2 \) state are slightly further apart from each other in the ADC(3) result. The ADC(3) energies are used to fit the Hamiltonian as they derive from a higher level method.

For the purpose of least-square fitting the vibronic coupling model Hamiltonian to the \textit{ab initio} data, we have used and extended the program package VCHAM that had been used to fit a model potential for butatriene by Cattarius \textit{et al.}.\textsuperscript{24} This program starts from an initial guess for the diabatic Hamiltonian of the form Eqs. (6)–(13) and least square optimizes its parameters by a standard conjugate gradient method.\textsuperscript{52} The least-square deviation from the \textit{ab initio} data is calculated by numerical matrix diagonalization of the diabatic model Hamiltonian at every geometry where an \textit{ab initio} data point is given.

We have extended VCHAM to allow it to handle an arbitrary number of electronic states (versus two states in butatriene) and fourth-order coefficients in the Hamiltonian. Also, we have introduced constrained optimization in order to force certain relationships between coefficients fitted. This is important to guarantee that the symmetry relations noted underneath Eq. (13) are satisfied.

Figure 2 shows a selection of the PESs of allene along some normal modes.\textsuperscript{53} We have also calculated potential energy points where the molecule is distorted along the action of two normal modes, one of \( A_1 \) and one of \( B_2 \) symmetry. These lines were fitted using the bilinear coefficients \( \gamma_{ij}^{(2)} \).

The PESs along the totally symmetric \( A_1 \) modes \( \nu_1, \ldots, \nu_5 \) exemplified in the upper row of Fig. 2 are symmetric functions of the normal coordinate. The regions where the discrepancy between the present harmonic plus fourth-order model becomes noticeable is vibrationally inaccessible for the wave packet placed initially at the ground state equilibrium, so we can continue using this model (note energy scale). The mode shown in the second row of Fig. 2 is the coupling mode \( \nu_4(B_1) \) (the twisting mode). Here, the resulting adiabatic PESs are symmetric functions of the normal coordinate.

The third row of Fig. 2 exemplifies the PESs along the tuning modes \( \nu_5, \nu_7(B_2) \) which are symmetric with respect to the equilibrium geometry. Due to linear coupling between the \( B_2 \) state and the \( A_1 \) state has to be parametrized as well as the intrastate linear coupling parameters \( \kappa_{ij}^{(1)} \) of the \( E \) state manifold.

The last row of Fig. 2 exemplifies a PJT active \( E \) mode. In the calculation of the cationic states using the OVGF method, complications arose that are discussed in the following paragraphs. Alternative data sets were therefore used to fit these potential energy curves as described below.

The inconsistencies become apparent in Fig. 3, where the OVGF results of the adiabatic potential energy lines of the \( E \) and \( B_2 \) states along the mode \( \nu_{11}(E) \) are presented. The distortion of the molecule along an \( E \) mode breaks almost all molecular symmetries, leaving only the mirror symmetry, in this case in the plane of the tail wag, i.e., the molecule has \( C_s \) symmetry when moving along an \( E \) normal mode. In Fig. 3 it can be seen that along \( \nu_{11}(E) \) the upper branch of the electronic \( E \) state manifold assumes \( A'' \) symmetry. The \( B_2 \) state has \( A' \) symmetry in \( C_s \). The main problem is that the crossover of the state symmetries does not coincide with the
crossover of OVGF energies as it should do. Near the crossing, the OVGF energy values are also visibly distorted.

An additional complication is found along the \( n_{10} \) mode which is an out-of-plane H–C–H bending tail wag. Here, the electronic \( E \) state manifold splits in such a way that the component of symmetry \( A_9 \) in \( C_s \) has lower energy than the \( A_8 \) component. This anomalous behavior is denoted by the superscript \( A_9 \), \( n_{10} E \) in Eqs. (6)–(13). The other \( E \) modes are denoted \( E A_8 \). Due to symmetry, this suggests coupling with one or several higher lying state(s) of the same symmetry, i.e., \( A' \). However, our OVGF calculations yielded only states of \( A' \) symmetry above the \( E \) electronic state.

These problems indicate that for modes of \( E \) symmetry

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<th>Displacement Diagram</th>
<th>Adiabatic Potential</th>
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FIG. 2. Some normal modes of allene. Mode labels with symmetry, displacement diagrams illustrating the mode and adiabatic energies derived from vibronic coupling model Hamiltonian (lines) with \textit{ab initio} data points (filled circles). From top to bottom are exemplified a totally symmetric mode, the coupling mode, a tuning mode, and a pseudo-Jahn–Teller active mode.

TABLE I. OVGF and ADC(3) energies above the neutral ground state equilibrium geometry (in eV) of the states of interest for allene. It can be seen that the \( E \) and the \( B_2 \) state are further apart from each other in the ADC(3) result. The ADC(3) energies are used to fit the Hamiltonian as they are more accurate.

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<th>OVGF energy</th>
<th>ADC(3) energy</th>
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<td>( \tilde{S}_{1E} )</td>
<td>( \cdots )</td>
<td>13.96</td>
<td>15.04</td>
</tr>
<tr>
<td>( \tilde{A}^3 E )</td>
<td>1.2</td>
<td>15.04</td>
<td>15.08</td>
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<tr>
<td>( \tilde{S}_{E} )</td>
<td>( \cdots )</td>
<td>16.81</td>
<td>16.81</td>
</tr>
<tr>
<td>( \tilde{B}^2 B_2 )</td>
<td>3</td>
<td>15.46</td>
<td>15.42</td>
</tr>
<tr>
<td>( \tilde{A}^2 A_1 )</td>
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<td>17.47</td>
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<tr>
<td>( \tilde{S}_{E} )</td>
<td>5</td>
<td>( \cdots )</td>
<td>17.69</td>
</tr>
</tbody>
</table>
the OVGF method does not capture all states coupling to the charge transfer states of interest. It is well known that OVGF becomes unsuitable as a computational tool once satellite states are close by and interact with the main states. Hence we decided to repeat the potential surface calculations along the low-frequency \( E \) modes (where distortions were apparent) using the ADC(3) method. This method takes two-hole–one-particle states into account explicitly. Satellite states are now detected which are not represented by an ionization from a single electronic orbital but by a linear combination of several electronic excitations, many of which are two-hole–one-particle. One of these satellite states is selected as representative and used to fit the topology of the charge transfer states. This is the state denoted \( S, k=5 \) in Eqs. (6)–(13). It has the required symmetry \( A' \) in \( C_s \) that is needed to model coupling with the charge transfer \( E \) state manifold along the \( \nu_{0}(E) \) mode. As the main cationic states are already labeled \( \tilde{X}, \tilde{A}, \tilde{B}, \tilde{C} \), and so forth, we will label the satellite states \( \tilde{S}_1, \tilde{S}_2, \tilde{S}_3 \), and so on. In this notation, the satellite state selected is \( S=\tilde{S}_1(E) \) and as such degenerate. However, as it is used as a representative for the purpose of fitting only, this degeneracy is ignored.

In order to demonstrate that the use of ADC(3) resolves the problems described above, Fig. 4 shows the results of the ADC(3) calculations for points along some low-frequency \( E \) modes of allene.

Along the \( \nu_d \) mode, it can be seen that the PESs from OVGF [Fig. 4(a)] approximate the ADC(3) PESs presented alongside it [in Fig. 4(b)] very well. The solid lines drawn in Fig. 4(b) are the fit lines according to the OVGF data, shifted to the ADC(3) energies at the equilibrium coordinate. It is remarkable that the fit appears better compared to the higher accuracy ADC(3) results, particularly at the minima of the \( A' \) branch of the \( \tilde{A}^2 E \) state, although this fit was made using the OVGF data. This supports the view that the linear vibronic coupling model Hamiltonian is a good approximation to the physically relevant situation. Note that the \( A_1 \) state is used only to fit the charge transfer states, so its crossing with a satellite is ignored.

The ADC(3) results shown in Fig. 4(c) (along the \( \nu_{10} \) mode) demonstrate a more complex situation with satellite states of \( A' \) symmetry (black symbols) crossing through the \( B_2 \) state and the upper branch of the \( E \) state in the region outside 3.8 normal coordinate units from \( Q=0 \) and around 16.5 eV. As before, the crossing points lie at a considerable vibrational energy relative to the energy at equilibrium geometry (about 1.5 eV above the \( E \) state energy at the equilibrium), so for the purpose of wave-packet dynamic simulations, this additional state can be ignored.

The data points seen below the \( \tilde{A}^2 E \) state and crossing with it belong to the satellite of \( E \) symmetry that cannot interact along the \( \nu_{0} \) mode by symmetry, as in \( C_s \) (where the mode itself is always \( A' \)).

\[
A''\times A'\times A' \not= A'.
\] (19)

Other modes (to be thought of as running into the paper plane) may, however, lift the degeneracy and couple the states. Whether this happens is difficult to ascertain from the present data.

Coupling effects, if present, appear to be weak, however, since the shape of the PESs can be fitted so well with the present model Hamiltonian along the cuts through the equilibrium coordinate along the other modes. (If strong coupling was present, it should be seen along the other modes as these run parallel to lines imagined into the paper plane at a crossing point.)

The ADC(3) results shown in Fig. 4(d) (along the \( \nu_{11} \) mode) demonstrate that satellite states of \( A' \) symmetry cross through the \( B_2 \) state and the upper branch of the \( E \) state in the region at 4.2 normal coordinate units from \( Q=0 \) and around 15.5 eV. However, the crossing point lies at about 0.5 eV above the energy at the equilibrium of the charge transfer \( E \) state of interest. For the purpose of wave-packet dynamic simulations that this work aims for, this additional state can be ignored. A complete model should of course take it into account. This crossing explains the aberrant behavior of the OVGF result as seen in Fig. 3. The ADC(3) results show no such inconsistencies, so fitting can proceed on the five-state model using the ADC(3) data.

Concluding this analysis, it has become clear that ADC(3) data needed to be used to fit the low-frequency \( E \) modes. The action of the linear coupling parameters \( \lambda^{(\nu)}_i \) is best seen in the shape of the \( B_2 \) state along \( \nu_6(E^{A'}) \) (this state is bent upwards due to coupling with the \( E \) manifold) and in the PES of the satellite state along \( \nu_{0}(E^{A''}) \) (where the \( S \) state at the top is bent upwards).

The \( S \) state, \( k=5 \), was fitted only along \( \nu_{10} \) and \( \nu_{11} \), as it was represented by the harmonic model along all other modes. Along \( \nu_{1}(E^{A'}) \), the PES of \( S \) is bent downwards, most likely due to coupling with states lying higher up in energy. Fitting this state according to the vibronic coupling paradigm would necessitate involving these higher states and probably even higher ones coupling to them and so on. This is neither feasible nor necessary, as satellite states generally

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**FIG. 3.** Inconsistencies in the main state PESs along the tail-wag mode \( \nu_1(E) \) in allene, as calculated with OVGF. The filled dots mark energies of states of \( A' \) symmetry in \( C_s \); the open dots mark energies of states of \( A'' \) symmetry. It can be seen that the crossing points of the energies and of the symmetries of the upper branch of the \( \tilde{A}^2 E \) state and the \( \tilde{B}^2 B_1 \) state do not coincide as they should. The energy values are visibly distorted near the crossing. The problem is resolved by noting that a satellite state interacts with the main states in the region where inconsistencies arise. Such satellite states can be accounted for using the ADC(3) method (see text, Sec. III).
have diminished transition matrix elements with the neutral ground state and therefore can be ignored as an initial state for the purpose of wave-packet dynamic simulations. The satellite state modeled only plays a role due to its coupling with the \( E \) state. It is therefore sufficient to fit its shape in order to reproduce the right recurrence behavior in the dynamics. This was done by means of the quadratic and fourth-order coefficients \( \gamma_{ij}^{(5)} \) and \( \delta_{ij}^{(5)} \).

In regions where satellite states do not interact with the main states, OVGF results approximate well the corresponding ADC(3) results by construction. Hence, the potential surfaces calculated with OVGF were used for the purpose of fitting the vibronic coupling Hamiltonian along these normal modes. For the high-frequency \( E \) modes, the distortion due to satellite states was also negligible so that OVGF data could be used for those as well, saving computational effort. All in all, this means that we have relied on a mixed data set consisting of OVGF results along the nondegenerate modes and ADC(3) results along the pseudo-Jahn–Teller active \( E \) modes. ADC(3) naturally extends the corresponding OVGF results, so this mixed approach is consistent.

Table II shows an overview of the on-diagonal linear and quadratic parameters for allene, alongside a comparison of the normal mode frequencies from this work (\( \omega_{\text{theor}} \)) and from experimental work (\( \omega_{\text{expt}} \), from Ref. 54). Table III shows the linear off-diagonal (\( \lambda_{ij}^{(op)} \)) and the on-diagonal bilinear (but not quadratic) coupling coefficients (\( \gamma_{ij}^{(o)} \)), with the corresponding values from the previous model shown for comparison.

Table IV shows the quartic coefficients of the model Hamiltonian. Note that \( \varepsilon_{ij}^{(1)} = \varepsilon_{ij}^{(2)} = 0 \), and the other \( \varepsilon_{ij}^{(k)} \) are only small corrections. This means that the quartic shapes of cation PESs are mainly due to anharmonicities present in the ground state and first-order coupling terms dominate the coupling process in this model Hamiltonian.

The most important coefficients mediating the coupling between the diabatic electronic states are the off-diagonal coupling coefficients \( \lambda_{ij}^{(4)} \). A comparison of the values in Table III shows that the newly fitted coupling coefficient \( \lambda_{11}^{(12)} \) mediating the direct coupling within the charge transfer manifold of the \( E \) state differs by about 11% to the previous studies, while the coefficients \( \lambda_{11}^{(13)} \) mediating the coupling to the \( B_2 \) state (where present in the previous studies)
TABLE II. Linear and quadratic on-diagonal coefficients of model Hamiltonian for allene (all values in eV). Note that parameters for state 1 are related to those for state 1 by the relations listed below Eq. (13) and parameters not shown are zero.

<table>
<thead>
<tr>
<th>$i$</th>
<th>Sym</th>
<th>$\kappa^{(1)}_i$</th>
<th>$\kappa^{(3)}_i$</th>
<th>$\eta^{(4)}_i$</th>
<th>$\gamma^{(1)}_{ii}$</th>
<th>$\gamma^{(3)}_{ii}$</th>
<th>$\gamma^{(4)}_{ii}$</th>
<th>$\gamma^{(5)}_{ii}$</th>
<th>$\omega_{\text{th}}$</th>
<th>$\omega_{\text{expt.}}$</th>
</tr>
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<tbody>
<tr>
<td>1</td>
<td>$A_1$</td>
<td>-0.4471</td>
<td>-0.2762</td>
<td>-0.4491</td>
<td>0.0251</td>
<td>-0.0029</td>
<td>0.0166</td>
<td>0.3937</td>
<td>0.3945</td>
<td></td>
</tr>
<tr>
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</tr>
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<td>-0.0077</td>
<td>-0.0206</td>
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<td>$B_2$</td>
<td>0.3364</td>
<td>0.0440</td>
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<td>-0.0020</td>
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<td>0.1782</td>
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<td>$B_2$</td>
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<td>$B_2$</td>
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<td>$E$</td>
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<td>$E$</td>
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<td>0.0446</td>
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</tr>
</tbody>
</table>

*Reference 22.

TABLE III. Off-diagonal linear ($\lambda_{ij}^{(ab)}$) and on-diagonal bilinear ($\gamma_{ij}^{(ab)}$) coefficients of model Hamiltonian for allene compared to corresponding values by Mahapatra et al. (Ref. 22). All values are in eV. Note that coupling along the mode $v_10$ between states 1 and 5 in Ref. 22 is replaced in this work by coupling between states 1 and 5. Where corresponding parameters were fitted in Ref. 22, they agree qualitatively with those from the present work. Note also that $\gamma$ parameters with exchanged indices are related to those shown by the relations listed below Eq. (13) and that parameters not shown are zero.

<table>
<thead>
<tr>
<th>$i$</th>
<th>$\alpha$</th>
<th>$\beta$</th>
<th>$\lambda_{ij}^{(a)\alpha}$</th>
<th>$\lambda_{ij}^{(b)\beta}$</th>
<th>$i$</th>
<th>$j$</th>
<th>$\alpha$</th>
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<td>7</td>
<td>3</td>
<td>0.0641</td>
<td></td>
</tr>
</tbody>
</table>

*This work.

*Reference 22.

Differ by about 11%–14%. This qualitative agreement is reassuring, as the experimental photoelectron spectrum was reproduced very well by the model Hamiltonian due to Mahapatra et al.\textsuperscript{21–23}

The most important differences between the two models come about by the inclusion of the $A_1$ state $k=4$ and the $A^\pi$ state $k=5$. Coupling along $v_10$ between the $E$ manifold and the $B_3$ state through a coupling coefficient $\lambda_{10}^{(13)}$ is not present in the new model, as it turns out to be symmetry forbidden as discussed above. Instead, a coupling coefficient $\lambda_{10}^{(15)}$ mediating coupling between the $E$ manifold and the $A^\pi$ state was parametrized. Note that this parameter has a larger magnitude compared to the other $\lambda_{i}^{(k\ell)}$. This is due to the larger energy difference between the $E$ state and the $A^\pi$ state at the equilibrium geometry, necessitating a larger coupling parameter to effect a comparable change in the adiabatic $E$ state.

The newly introduced coupling parameters $\lambda_{10}^{(34)}$ mediating coupling between the $B_2$ state and the $A_1$ state are of the same order of magnitude as the parameters $\lambda_{1}^{(13)}$. This means that they are necessary to take into account and may offer a new pathway for charge transfer between the localized electronic states.

**IV. FIVE-STATE, ALL-MODE MODEL VIBRONIC COUPLING HAMILTONIAN FOR PENTATETRAENE**

The overall qualitative features of the PESs of the charge transfer states $\tilde{B}^2E$ and associated states $\tilde{C}^2B_1$ and $\tilde{D}^2A_1$ of the pentatetraene cation are very similar to the corresponding ones in allene. As in allene, exactly one mode exists that exhibits anomalous down bending of the $A^\pi$ component of the $E$ state manifold. It is $v_{12}(E^\pi)$. All other $E$ modes, of which there are six in pentatetraene (four in allene), are $E^a\pi)$. As before, we solved the problem of the $E^a\pi$ mode and spurious crossings of the PESs by recalculating the relevant PESs along the low-frequency $E$ modes with ADC(3). The satellite state selected to fit via coupling the $A^\pi$ component of the $E$ manifold along $v_{12}(E^\pi)$ is at the energy of the $S^\pi_{13}(E)$ state (above which many satellite states exist). As before, this state is used merely to provide an additional degree of freedom for the fitting procedure rather than being of interest itself.

Table \textsuperscript{V} shows the OVGF and ADC(3) energies above the neutral ground state equilibrium geometry (in eV) of the states of interest for pentatetraene. It can be seen that the $E$ and the $B_2$ state are this time closer to each other in the
TABLE IV. Quartic on-diagonal coefficients of model Hamiltonian for allene (all values in eV). Note that parameters not shown are zero, particularly \( e_{i}^{(3)} = e_{i}^{(5)} = 0 \).

<table>
<thead>
<tr>
<th>( i )</th>
<th>Sym</th>
<th>( \xi_i )</th>
<th>( e_{i}^{(3)} )</th>
<th>( e_{i}^{(4)} )</th>
<th>( e_{i}^{(5)} )</th>
</tr>
</thead>
<tbody>
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<td>0.031 87</td>
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<tr>
<td>2</td>
<td>( A_1 )</td>
<td></td>
<td></td>
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</tr>
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<td>3</td>
<td>( A_1 )</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>4</td>
<td>( B_1 )</td>
<td>0.018 00</td>
<td></td>
<td></td>
<td>(-0.018 00)</td>
</tr>
<tr>
<td>5</td>
<td>( B_2 )</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>6</td>
<td>( B_2 )</td>
<td></td>
<td></td>
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<td></td>
</tr>
<tr>
<td>7</td>
<td>( B_2 )</td>
<td>0.002 64</td>
<td>0.010 36</td>
<td>0.010 36</td>
<td></td>
</tr>
<tr>
<td>8</td>
<td>( E )</td>
<td>0.050 00</td>
<td></td>
<td>(-0.050 00)</td>
<td>(-0.050 00)</td>
</tr>
<tr>
<td>9</td>
<td>( E )</td>
<td>0.006 50</td>
<td></td>
<td>(-0.006 50)</td>
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</tr>
<tr>
<td>10</td>
<td>( E )</td>
<td>0.024 00</td>
<td></td>
<td>(-0.010 00)</td>
<td>(-0.002 00)</td>
</tr>
<tr>
<td>11</td>
<td>( E )</td>
<td>0.015 50</td>
<td></td>
<td></td>
<td>0.006 80</td>
</tr>
</tbody>
</table>

ADC(3) result, unlike for allene, where the correction was in the other direction. The ADC(3) energies are used to fit the Hamiltonian as they are more accurate. The states of interest are between 15 and 18.4 eV.

As for allene, we present a selection of the normal modes with the fitted vibronic coupling Hamiltonian results in Fig. 5. The first row exemplifies a totally symmetric mode and the coupling mode which are mostly fitted as for allene. The anharmonicity of the PES functions along the totally symmetric modes is most pronounced along the \( \nu_1 \) mode. The regions of large discrepancy to the present model Hamiltonian are inaccessible by a vibrational wave packet but the fit can be improved by adding cubic terms \( \frac{1}{2} \xi_i^{(1)} \xi_i^{(1)} \) to the diagonal Hamiltonian matrix elements \( e_{kk} \) in Eqs. (6)–(8). This approach necessitates changing all other model parameters for this mode accordingly and introduces spurious maxima in the PESs which are, however, kept at vibrationally inaccessible energies due to the balancing action of fourth-order terms. The fit using cubic terms is shown in the top right panel of Fig. 5.

A quantitatively more appropriate model for the PESs along the \( A_1 \) modes would use Morse-type potentials but the polynomial fit is satisfactory and has the advantage of being within the Taylor expansion paradigm.

The last two rows of Fig. 5 exemplify degenerate \( E \) modes. As for allene, an \( E^{(3)} \) mode exists and spurious OVGF results are seen along the low-frequency modes. As before, this is analyzed by comparing to ADC(3) results.

OVGF and ADC(3) results for two low-frequency modes of pentatetraene are compared in Fig. 6. The OVGF result shown along the \( \nu_{12}(E) \) mode in Fig. 6(a) approximates the main states from the ADC(3) result [Fig. 6(b)]. The OVGF results are used for the purpose of fitting the model Hamiltonian. The successful fit along the \( \nu_{12}(E) \) mode in allene based on OVGF data and confirmed by the ADC(3) results that was presented in the preceding section serves as motivation for this approach.

The overall qualitative shapes agree in both results, although the upper branch of the \( \tilde{B}^2E \) state is predicted to be steeper in OVGF (and actually crosses the \( \tilde{C}^2B_2 \) state further away from \( Q=0 \)). The crossing in OVGF has no repercussion on the fitted coupling constants. It can be seen in Fig. 6(b) that satellite states of \( E \) symmetry (marked by “sat E”) cross into the \( \tilde{B}^2E \) state from below. These crossings potentially complicate the interaction in pentatetraene. In the interest of obtaining a computationally viable model and for comparability with allene, we decided to omit this interaction in our model and leave its detailed analysis for the future.

It can be seen in Fig. 6(d) that a satellite state crosses the \( \tilde{C}^2B_2 \) state at around 4 U removed from the equilibrium. However, the \( \tilde{C}^2B_2 \) state is included primarily as representative for a larger number of states of the corresponding symmetry to aid the fit of the charge transfer states and so this crossing is ignored. The data points seen around the \( \tilde{B}^2E \) state belong to satellite states of \( E \) symmetry. Although they
do visibly cross with the state of interest, they are not allowed to interact with it by symmetry [Eq. (19)]. As before, coupling into the paper plane cannot be excluded but is likely to be weak.

Tables VI and VII show the parameters for the vibronic coupling model Hamiltonian for pentatetraene. Parameters from a fit along $\nu_1$ involving cubic fitting parameters are presented in Table VIII. On-diagonal bilinear coupling terms that are not quadratic, i.e., mediate coupling depending on two different normal mode coordinates were not fit, as their influence on the potential surfaces in pentatetraene is marginal. (These coefficients were already small—of the order of 0.01 eV—in allene, as witnessed by Table III.)

It can be seen that the $S$ adiabatic state along the $\nu_{12}(E^{(A''})$ mode seen in Fig. 5 is upward bent with respect to the harmonic model due to fitting the down bent of lower branch of the $E$ state. No corresponding data points are shown for this state, however, as it is placed at a region populated by many satellite states and selected merely to aid the fitting of the charge transfer $E$ state.

Due to the large number of states crossing into the states
considered in this energy region, it is very likely that more states should be taken into account for a complete description of the system. However, this is outside the scope of this work. Since we are interested in a good model for the \( B^2E \) and \( C^2B_2 \) states relevant for charge transfer and the \( S \) state was introduced only to aid this fit, this is acceptable.

V. COMPARISON OF THE TWO MODELS AND DISCUSSION

As the energy spacing between the charge transfer states and the states coupling most strongly to them is similar in the allene and pentatetraene cations (Tables I and V), a comparison of the expected coupling strengths can be made by means of the off-diagonal linear coupling constants (Tables III and VII).

It can immediately be seen that the \( E \) manifold JT intrastate coupling constant which mediates direct coupling between the charge transfer states is, at \( \lambda_{5}^{(12)} = 0.0251 \) eV in pentatetraene, only 37% of the corresponding value in allene (0.0917 eV). This was expected due to the increased length of the pentatetraene molecule compared to allene.

The other off-diagonal PJT coupling constants of pentatetraene involving the \( E \) state, \( \lambda_{i}^{(11)}, \ell = 3,\ldots,5 \), which mediate indirect coupling between the charge transfer states are of a very similar order to the corresponding values in allene. On top of this, there are six \( E \) modes present in pentatetraene along which such activity is present, i.e., two more than in allene. This means that the preference for indirect coupling between the charge transfer states via other electronic states should be at least twice as strong in pentatetraene as in allene.

A factor that should greatly influence the time-dependent populations of the diabatic electronic states is the vibronic coupling between the \( B_2 \) and \( A_1 \) states along \( B_2 \) normal modes which has previously not been considered due to the absence of the \( A_1 \) state from other models. This coupling process transfers the wave function from the \( B_2 \) to the \( A_1 \) state, where coupling to the \( E \) state manifold is overall slightly weaker. This process should therefore slightly diminish the preference for the indirect charge transfer expected from the coupling constants of the form \( \lambda_{i}^{(1)} \), \( \ell = 3,\ldots,5 \) alone.

The number of \( B_2 \) modes in pentatetraene is 4, one more
than in allene. The $\lambda_{1}^{(34)}$ coupling constants are roughly 0.2, 0.1, 0.36, and 0.08 eV (see Table VII for accurate numbers). In allene, the corresponding numbers are roughly 0.2, 0.25, and 0.23 eV. This means that two of the coupling constants are much smaller in pentatetraene while one is much larger. Overall, the coupling between the $B_2$ and $A_1$ states should be slightly stronger in pentatetraene.

This slightly stronger adverse effect on the PJT coupling in pentatetraene should not, however, fully quench the large increase in preference for PJT coupling over JT coupling. The photoelectron spectrum of pentatetraene should, due to the larger PJT coupling, be less structured than that of allene.

Overall, the number of satellite states found in the ADC(3) calculations for pentatetraene is much larger than that in allene. This means that the errors introduced by selecting only five states to model the charge transfer process is more severe for pentatetraene. This is demonstrated in Fig. 6(b), where a number of satellite states crosses into the $E$ state manifold from below. The density of satellite states at higher energies is immense but their interaction with the charge transfer state is modeled by only the one $S$ state. Currently, these effects have to be ignored in the interest of computational viability. This means that the need for future improvements of the presented model is more pressing for pentatetraene than for allene.

The results of the MCTDH wave-packet dynamics along with a detailed analysis of the evolution of the diabatic state populations will be published in a forthcoming publication.

### VI. CONCLUSION

We have performed ab initio OVGF calculations of the charge transfer states and states interacting with them for the linear carbohydrate molecules allene and pentatetraene. Along the low-frequency $E$ modes a satellite state interacts with the main states and hence we had to go beyond OVGF and use the more involved ADC(3) method which takes satellite states into account.

<table>
<thead>
<tr>
<th>$i$</th>
<th>Sym</th>
<th>$\kappa_{i}^{(1)}$</th>
<th>$\kappa_{i}^{(3)}$</th>
<th>$\kappa_{i}^{(4)}$</th>
<th>$\gamma_{i}^{(1)}$</th>
<th>$\gamma_{i}^{(3)}$</th>
<th>$\gamma_{i}^{(4)}$</th>
<th>$\gamma_{i}^{(5)}$</th>
<th>$\omega$</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>$A_1$</td>
<td>-0.3780</td>
<td>-0.2440</td>
<td>-0.2440</td>
<td>0.001</td>
<td>-0.00094</td>
<td>-0.00096</td>
<td>-0.00076</td>
<td>0.3921</td>
</tr>
<tr>
<td>2</td>
<td>$A_1$</td>
<td>-0.1411</td>
<td>-0.2266</td>
<td>-0.2656</td>
<td>0.001</td>
<td>-0.0128</td>
<td>-0.0106</td>
<td>0.0014</td>
<td>0.2387</td>
</tr>
<tr>
<td>3</td>
<td>$A_1$</td>
<td>-0.2907</td>
<td>0.3658</td>
<td>-0.0464</td>
<td>-0.0199</td>
<td>-0.0225</td>
<td>0.1801</td>
<td></td>
<td></td>
</tr>
<tr>
<td>4</td>
<td>$A_1$</td>
<td>-0.0989</td>
<td>-0.0739</td>
<td>-0.0268</td>
<td>-0.0080</td>
<td>-0.0128</td>
<td>-0.0106</td>
<td>0.0914</td>
<td></td>
</tr>
<tr>
<td>5</td>
<td>$B_1$</td>
<td>-0.0276</td>
<td>-0.0429</td>
<td>-0.0665</td>
<td>0.001</td>
<td>-0.0103</td>
<td>-0.0417</td>
<td>0.1634</td>
<td></td>
</tr>
<tr>
<td>6</td>
<td>$B_2$</td>
<td>0.3384</td>
<td>0.0033</td>
<td>0.0031</td>
<td>-0.0269</td>
<td>0.3920</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>7</td>
<td>$B_2$</td>
<td>0.0750</td>
<td>-0.0234</td>
<td>0.0513</td>
<td>-0.0248</td>
<td>0.2731</td>
<td></td>
<td></td>
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</tr>
<tr>
<td>8</td>
<td>$B_2$</td>
<td>0.1887</td>
<td>0.3370</td>
<td>-0.0476</td>
<td>-0.0290</td>
<td>-0.0319</td>
<td>0.1873</td>
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<tr>
<td>9</td>
<td>$B_2$</td>
<td>0.2806</td>
<td>-0.0191</td>
<td>-0.1024</td>
<td>0.0542</td>
<td>0.4054</td>
<td>0.4033</td>
<td></td>
<td></td>
</tr>
<tr>
<td>10</td>
<td>$E$</td>
<td>-0.0086</td>
<td>-0.1303</td>
<td>0.0279</td>
<td>-0.0053</td>
<td>0.1253</td>
<td></td>
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</tr>
<tr>
<td>11</td>
<td>$E$</td>
<td>0.0100</td>
<td></td>
<td></td>
<td></td>
<td>0.1016</td>
<td></td>
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<td></td>
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<tr>
<td>12</td>
<td>$E$</td>
<td>0.0107</td>
<td>-0.0178</td>
<td>0.0670</td>
<td></td>
<td>0.0543</td>
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<tr>
<td>13</td>
<td>$E$</td>
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<td>-0.0662</td>
<td>0.0875</td>
<td>0.0367</td>
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<tr>
<td>14</td>
<td>$E$</td>
<td>-0.0350</td>
<td>-0.0339</td>
<td>-0.0192</td>
<td>0.1300</td>
<td>0.0188</td>
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</tr>
</tbody>
</table>

TABLE VII. Off-diagonal linear ($\lambda_{i}^{(ab)}$) and on-diagonal quartic ($\xi_{i}^{(ab)}$) coefficients of model Hamiltonian for pentatetraene (all values in eV). Note that parameters for state 2 are related to those for state 1 by the relations listed below Eq. (13) and that parameters not shown are zero, particularly $\lambda_{i}^{(34)}=\lambda_{i}^{(12)}=0$. 

<table>
<thead>
<tr>
<th>$i$</th>
<th>$\alpha$</th>
<th>$\beta$</th>
<th>$\lambda_{i}^{(ab)}$</th>
<th>$\xi_{i}^{(ab)}$</th>
<th>$\xi_{i}^{(1)}$</th>
<th>$\xi_{i}^{(3)}$</th>
<th>$\xi_{i}^{(4)}$</th>
<th>$\xi_{i}^{(5)}$</th>
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<tbody>
<tr>
<td>5</td>
<td>1</td>
<td>2</td>
<td>0.0251</td>
<td>1 $A_1$</td>
<td>0.001</td>
<td>-0.00094</td>
<td>-0.00096</td>
<td>-0.00076</td>
</tr>
<tr>
<td>10</td>
<td>1</td>
<td>3</td>
<td>0.2921</td>
<td>2 $A_1$</td>
<td>0.001</td>
<td>0.01828</td>
<td>0.00564</td>
<td>-0.01828</td>
</tr>
<tr>
<td>11</td>
<td>1</td>
<td>3</td>
<td>0.2311</td>
<td>3 $A_1$</td>
<td>0.001</td>
<td>-0.01136</td>
<td>-0.03483</td>
<td>-0.01145</td>
</tr>
<tr>
<td>15</td>
<td>1</td>
<td>3</td>
<td>0.0681</td>
<td>4 $A_1$</td>
<td>0.001</td>
<td>0.00156</td>
<td>-0.02610</td>
<td>-0.01145</td>
</tr>
<tr>
<td>10</td>
<td>1</td>
<td>4</td>
<td>0.2261</td>
<td>5 $B_1$</td>
<td>0.001</td>
<td>0.00564</td>
<td>-0.01828</td>
<td>-0.01145</td>
</tr>
<tr>
<td>11</td>
<td>1</td>
<td>4</td>
<td>0.0326</td>
<td>6 $B_2$</td>
<td>0.001</td>
<td>-0.01136</td>
<td>-0.03483</td>
<td>-0.01145</td>
</tr>
<tr>
<td>13</td>
<td>1</td>
<td>4</td>
<td>0.0808</td>
<td>7 $B_2$</td>
<td>0.001</td>
<td>-0.02610</td>
<td>-0.01145</td>
<td>-0.01145</td>
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<tr>
<td>14</td>
<td>1</td>
<td>4</td>
<td>0.2224</td>
<td>8 $B_2$</td>
<td>0.001</td>
<td>-0.01136</td>
<td>-0.03483</td>
<td>-0.01145</td>
</tr>
<tr>
<td>12</td>
<td>1</td>
<td>5</td>
<td>0.7000</td>
<td>9 $B_2$</td>
<td>0.001</td>
<td>-0.01136</td>
<td>-0.03483</td>
<td>-0.01145</td>
</tr>
<tr>
<td>6</td>
<td>3</td>
<td>4</td>
<td>0.1823</td>
<td>10 $E$</td>
<td>0.0850</td>
<td>0.03087</td>
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<td>-0.08604</td>
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<tr>
<td>7</td>
<td>3</td>
<td>4</td>
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<td>0.00666</td>
<td>0.02430</td>
<td>-0.02023</td>
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</tr>
<tr>
<td>8</td>
<td>3</td>
<td>4</td>
<td>0.3620</td>
<td>12 $E$</td>
<td>0.0380</td>
<td>-0.03600</td>
<td>-0.00826</td>
<td>-0.01732</td>
</tr>
<tr>
<td>9</td>
<td>3</td>
<td>4</td>
<td>0.0761</td>
<td>13 $E$</td>
<td>0.00751</td>
<td>-0.00525</td>
<td>-0.00199</td>
<td>-0.00726</td>
</tr>
<tr>
<td>14</td>
<td>1</td>
<td>4</td>
<td>0.0270</td>
<td>14 $E$</td>
<td>0.02700</td>
<td>-0.01643</td>
<td>-0.00936</td>
<td>-0.02767</td>
</tr>
<tr>
<td>15</td>
<td>1</td>
<td>4</td>
<td>0.0180</td>
<td>15 $E$</td>
<td>0.01800</td>
<td>-0.00329</td>
<td>-0.00249</td>
<td>-0.01732</td>
</tr>
</tbody>
</table>
We have least-square fitted the data to a linear vibronic coupling Hamiltonian, Eq. (13), using the fitting program VCHAM.\textsuperscript{24} Compared to previous work,\textsuperscript{21–23} the model Hamiltonian was extended by fourth-order terms mainly to and between the $B_2$ states and the $E$ states coupling with the $A_1$ states. Extended by fourth-order terms mainly to and between the $B_2$ states and the $E$ states, the Hamiltonian was fitted to the adiabatic PESs calculated for allene and pentatetraene. The resulting photoelectron spectrum should have less pronounced features. We will present an evaluation of these predictions against the results of wave-packet dynamics simulations of the allene and pentatetraene cations in a forthcoming publication.

**ACKNOWLEDGMENTS**

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**TABLE VIII.** Fitting parameters along the $\nu_4$ mode for pentatetraene from a fit involving third-order coupling terms (all values in eV). This fit is shown in the top right panel of Fig. 5. The parameters changed with respect to the first two tables in Tables VI and VII and are marked with a tilde. Note that the cubic terms are offset with quartic terms to avoid potential maxima in the region of interest. Note also that $\tilde{\kappa}_1^{(1)} = \tilde{\kappa}_1^{(2)}$, $\eta_1^{(1)} = \eta_1^{(2)}$, and $\tilde{\kappa}_1^{(1)} = \tilde{\kappa}_1^{(2)}$.

<table>
<thead>
<tr>
<th>$\tilde{\kappa}_1^{(1)}$</th>
<th>$\tilde{\kappa}_1^{(3)}$</th>
<th>$\tilde{\kappa}_1^{(4)}$</th>
<th>$\eta_1^{(1)}$</th>
<th>$\eta_1^{(3)}$</th>
<th>$\eta_1^{(4)}$</th>
<th>$\tilde{\kappa}_1^{(1)}$</th>
<th>$\tilde{\kappa}_1^{(3)}$</th>
<th>$\tilde{\kappa}_1^{(4)}$</th>
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</thead>
<tbody>
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<td>-0.315</td>
<td>-0.114</td>
<td>-0.189</td>
<td>-0.1276</td>
<td>-0.1522</td>
<td>-0.1345</td>
<td>0.030 95</td>
<td>0.029 95</td>
<td>0.021 64</td>
</tr>
</tbody>
</table>

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\textsuperscript{6}Faraday Discuss. 115, 1 (2000).
\textsuperscript{7}E. Teller, J. Phys. Chem. 41, 109 (1937).
42 Note that in Ref. 41 satellites are not counted separately, so that they denote these states as \( \tilde{A} \) and \( \tilde{A} \). Accordingly, the state \( \tilde{A} \) discussed in our article is designated as \( \tilde{B} \) in Ref. 41 and so on.
53 See EPAPS Document No. E-JCPSA6-122-304513 for an overview of all modes of allene and pentatetraene which may serve as a companion for the interested reader to illustrate statements made in the text. A direct link to this document may be found in the online article’s HTML reference section. The document may also be reached via the EPAPS homepage (http://www.aip.org/pubservs/epaps.html) or from ftp.aip.org in the directory /epaps/. See the EPAPS homepage for more information.