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Internal rotation in Jahn-Teller coupled systems: The Ethene and Allene Cations

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Abstract

The electronic ground state of singly-charged cations of the cumulene family ($\text{H}_2\text{CC}_n\text{CH}_2$, $n = 0, 1, \dots$) is doubly degenerate at the D_{2d} geometry and is subject to an $\text{E} \otimes \text{b}$ or $\text{E} \otimes (\text{b}_1 \oplus \text{b}_2)$ Jahn-Teller effect. One of the Jahn-Teller active modes is the torsion, i.e. the disrotatory motion of the two terminal CH_2 entities. The 2π periodicity of the torsional motion and the presence of maxima in the potential energy path along the torsional coordinate at planar geometries poses problems in the usual treatment of the Jahn-Teller effect of these cations, which relies on a Taylor expansion of the potential energy surfaces at the point of electronic degeneracy (D_{2d}). A vibronic Hamiltonian has been derived to treat the $\text{E} \otimes \text{b}$ and $\text{E} \otimes (\text{b}_1 \oplus \text{b}_2)$ Jahn-Teller effects in molecules in which one of the Jahn-Teller active modes is the torsion or an internal rotation. The potential energy surfaces are expressed using Fourier series instead of Taylor series which enables a joint treatment of the Jahn-Teller effect and of hindered internal rotations. The resulting Hamiltonian has been used to predict the vibronic energy level structure of C_2H_4^+ and C_3H_4^+ and intensity distributions in the photoelectron spectra of C_2H_4 and C_3H_4 . In particular, splittings arise from tunneling through the potential energy barrier at the D_{2h} geometry. The predictions are compared with available spectroscopic data.

1 Introduction

The Jahn-Teller (JT) effect in doubly-degenerate electronic states (E) of polyatomic molecules has been investigated extensively theoretically and experimentally (see Refs. [1, 2, 3, 4] and references therein). Most treatments focused on the $E \otimes e$ JT effect and on the rovibronic energy level structures of prototypical molecular systems including H_3 [5, 6], Li_3 [7], Na_3 [8], CH_3O [9, 10], cyclopentadienyl [11, 12], $C_6H_6^+$ [13, 14, 15] and $C_5H_5^+$ [16, 17]. The vibronic coupling of a doubly-degenerate electronic state mediated by nondegenerate vibrational modes, i. e., the $E \otimes (b_1 \oplus b_2)$ or $E \otimes b$ JT effects apparent in molecules with a four-fold symmetry axis, has received less attention, maybe because it is considered to be the simplest [3].

We present here a modified Hamiltonian for the $E \otimes (b_1 \oplus b_2)$ JT effect which enables a joint treatment of the JT effect and hindered internal rotations with special attention to the torsional motion of the terminal CH_2 entities in the cations of the cumulene family ($H_2CC_nCH_2^+$, $n = 0, 1, \dots$). These cations, and the photoelectron spectra of the corresponding neutral molecules are prototypical systems for the treatment of vibronic coupling in polyatomic molecules. Successive refinements of vibronic coupling models by including (i) an increasing number of coupled electronic states, (ii) an increasing number of nuclear displacement coordinates, and (iii) an increasing number of terms in the Taylor series used to approximate the potential energy functions of the coupled electronic states have led to a detailed understanding of the He I photoelectron spectra of ethene [18, 19, 20], allene [21, 22, 23, 24, 25, 26, 27], and butatriene [28], and to a global and coherent description of the associated vibronic structure and dynamics. In our recent studies of the pulsed-field-ionization zero-kinetic-energy PFI-ZEKE photoelectron spectra of C_2H_4 [29] and C_3H_4 [30], we have observed spectral structures resulting from the tunneling along the torsional motion through the potential barrier located at the planar (D_{2h}) structure. These tunneling splittings are small and hardly observable by He I photoelectron spectroscopy. The corresponding large amplitude motion is difficult to describe accurately by standard vibronic coupling models, because its treatment necessitates a good description of the potential energy functions over the full range of torsional angles. The present ar-

article presents a conceptual framework that may be helpful in future treatments of large amplitude periodic motions in Jahn-Teller coupled systems. The vibronic coupling model is intentionally kept very simple and focusses on the torsional motion. It is not meant to substitute, by rather to complement, the vibronic coupling models mentioned above and used to describe the molecular cations of the cumulene family.

The $E \otimes e$ and $E \otimes (b_1 \oplus b_2)$ JT Hamiltonians are usually derived using normal coordinates q_i of symmetry Γ_{q_i} that couple the two components k and l of a doubly-degenerate electronic state of symmetry $\Gamma_{k(l)}$ if they fulfill the symmetry condition [1, 2, 3, 31]:

$$\Gamma_k \otimes \Gamma_{q_i} \otimes \Gamma_l \supseteq \Gamma_{\text{tot. sym.}}, \quad (1)$$

where $\Gamma_{\text{tot. sym.}}$ is the totally symmetric representation of the symmetry group under consideration. In first approximation, the Hamiltonian describing the JT effect can be expressed as:

$$\mathbf{H}/hc = E_0 \mathbf{1} + \underbrace{\left(\hat{T}_n(q) + \frac{1}{2} \sum_i^{3N-6} \tilde{\nu}_i q_i^2 \right) \mathbf{1}}_{\mathbf{H}_{\text{h.o.}}} + \underbrace{\begin{pmatrix} k_a q_a & k_b q_b \\ k_b q_b & -k_a q_a \end{pmatrix}}_{\mathbf{H}_{\text{JT}}}, \quad (2)$$

where $\hat{T}_n$ is the nuclear kinetic energy operator, k_i is the linear JT coupling constant of the normal mode ν_i and $\tilde{\nu}_i$ the harmonic wave number (all constants, including E_0 , and operators are given in units of cm^{-1}). q_i are the dimensionless normal coordinates. In Eq. (2), the diagonal terms of the Hamiltonian are approximated as sums of shifted harmonic oscillators for the individual displacements. $\mathbf{H}$ is therefore only valid for small displacements from the reference geometry q_0 which is usually taken as the highest-symmetry (D_{2d}) point, where the electronic state is degenerate.

Fig. 1 schematically depicts the potential energy surfaces along the two JT-active modes q_a and q_b obtained from the diagonalization of $\mathbf{H}_{\text{JT}}$ in Eq. (2). If the JT-active modes are degenerate (i. e., $q_a = q_b$ and $k_a = k_b$), the JT effect is labeled $E \otimes e$ and results in the potential energy surfaces depicted in Fig. 1 (a). If the JT-active modes are nondegenerate (i. e., $q_a \neq q_b$ and $k_a \neq k_b$), the JT effect is designated $E \otimes (b_1 \oplus b_2)$ and the

corresponding potential energy surfaces are depicted in Fig. 1 (b). At the reference geometry q_0 , the two potential sheets touch and form a conical intersection. In the case of the $E \otimes e$ JT effect, neglecting higher-order JT coupling terms, an equipotential energy path around the conical intersection results and gives rise to a geometric phase manifested in a pseudorotational motion around the conical intersection described by half-integer quantum numbers [5, 8]. In the $E \otimes (b_1 \oplus b_2)$ JT effect, the cut along the JT-active modes also reveals a potential energy surface with a conical intersection at the reference geometry q_0 , but the minimum energy path around the conical intersection has two minima and two saddle points at $q_a = 0$ and $q_b = 0$, respectively (or vice versa), because the harmonic wave numbers and coupling constants of the JT-active modes of b_1 and b_2 symmetry are different. Symmetry considerations predict the absence of tunneling through the saddle points because the degeneracy of the vibronic energy levels is not lifted by the JT interaction [3, 32].

However, if one of the JT-active modes is periodic, as is always the case in the cumulene family, the potential energy surface should reflect this periodicity which cannot be achieved with the Hamiltonian in Eq. (2). This was recognized by Merer and Schoonveld [33] who treated the vibrational structures of the 1744 Å Rydberg transitions of C_2H_4 and C_2D_4 using a one-dimensional torsional potential which included a crossing at the electronically degenerate point of D_{2d} symmetry following an earlier treatment by Hougen [32]. Merer and Watson [34] later presented a group theoretical analysis of internal rotation in ethylene-like molecules and derived qualitatively a potential energy path along the torsional mode (see their Fig. 3) which correctly describes the curve crossing at the point of D_{2d} symmetry. Ethene and ethene-like molecules are subject to the $E \otimes b$ JT effect. To our knowledge, no attempt has been made to generalize this treatment of the torsional motion to JT problems including more than one mode, and the present article aims at filling this gap. We note that Takahashi and Kikuchi [35] have reported calculations of the potential energy surfaces of the lowest two electronic states of $C_2H_4^+$ close to the D_{2d} conical intersection, and found that the stabilization energy along the two b_2 modes is much smaller (less than 100 cm^{-1}) than along the torsional mode (b_2), so that their effects are not expected to be significant at the low energies of interest for this study. A

one-mode treatment appears adequate at low energies as will be shown in Section 4.1.

In our recent studies of the PFI-ZEKE photoelectron spectra of C_2H_4 and C_3H_4 mentioned above, we have come to the conclusion that a full treatment of the rovibrational energy level structure of the cations at low energies must not only include the curve crossing (or conical intersection in C_3H_4^+) at D_{2d} geometry (which could be adequately described by Eq. (2)) but also the tunneling motion through the potential energy barrier along the torsional mode at the D_{2h} symmetry point. The need to extend the JT treatment over the full range of torsional angles and to unite it with existing models of hindered internal rotation [36] led us to derive a Hamiltonian that can treat the JT effect, the hindered internal rotation and their interaction with each other explicitly using a Hamiltonian of the form of Eq. (2), but using Fourier series rather than Taylor series for the torsional mode. This treatment, initially developed to understand the PFI-ZEKE photoelectron spectrum of allene, is, however, more general and can be applied to any molecule undergoing an $\text{E} \otimes \text{b}$ or $\text{E} \otimes (\text{b}_1 \oplus \text{b}_2)$ JT distortion involving a torsional mode. The advantages of representing the torsional mode as Fourier series have been previously exploited by Cattarius et al. [28] in their extensive vibronic coupling treatment of the butatriene cation, however, using an expansion around the D_{2h} reference structure and without utilizing the JT nature of the problem.

2 The $\text{E} \otimes (\text{b}_1 \oplus \text{b}_2)$ vibronic JT Hamiltonian in the basis of a hindered internal rotor

The present approach is related in spirit to that presented in Refs. [34, 37] and was developed to describe the $\text{E} \otimes (\text{b}_1 \oplus \text{b}_2)$ JT interaction as it occurs, for instance, in the allene cation in its doubly-degenerate $\tilde{\text{X}}^+ {}^2\text{E}$ electronic ground state. In the following, the entity that comprises the internal rotor is called 'top', whereas the rest of the molecule is referred to as the 'frame', following the convention of Ref. [36].

The potential energy operator along the internal rotation coordinate τ is expanded in

a Fourier series [38]:

$$V(r, \tau) = V(r, \tau^0) + V_1 \cos(\tau) + V_2 \cos(2\tau) + \dots, \quad (3)$$

where V_i represent expansion coefficients, and $i = 1, 2, \dots, n$ is an integer number. τ stands for the dihedral angle between the top and the frame as defined in Fig. 2 (a) with the example of allene or ethene. Only those terms of the Fourier series in Eq. (3) need to be retained which are invariant under the 180° rotation around the C_2 symmetry axis of the CH_2 top, i. e., all terms with i being an integer multiple of 2, so that Eq. (3) becomes:

$$V(r, \tau) = V(r, \tau^0) + V_2 \cos(2\tau) + V_4 \cos(4\tau) + \dots \quad (4)$$

Expanding the potential terms in Eq. (4) in Taylor series around the reference geometry, which we take at the torsional angle $\tau^0 = 2\pi/4$, the potential function reduces, for small values of τ , to that of a harmonic oscillator:

$$V(r, \tau) = V(r, \tau^0) + V_2(-1 + 2(\tau - \tau^0)^2 + \dots) + \dots \quad (5)$$

When $\tau^0 = \pi/2$, which represents the most symmetric staggered configuration, the odd members of the Taylor series vanish.

Fig. 2 (c) depicts a cumulene (C_nH_4) in a Newman-projection with the molecule-fixed z_m and Z'' axes pointing out of the page. The H atoms are labeled 1, 2, 3 and 4 and the molecule-fixed (x_m, y_m, z_m) and the transformed space-fixed (X'', Y'', Z'') axis systems are also indicated as defined in Fig. 3.2 of Ref. [39]. The third Euler angle χ is defined as in Ref. [40] and is adequate to describe a rotational motion for which the Z'' - and z_m axes remain co-linear; χ then represents the angle between the molecule-fixed x_m axis and the transformed space-fixed X'' axis. The torsional angle τ is the dihedral angle between the H_1CH_2 and H_3CH_4 planes.

Because the top cannot be distinguished from the frame in a molecule with two coaxial equivalent rotors, Watson *et al.* [37] treat the two CH_2 entities as rotating independently of each other about the Z'' axis, with two sets of rotational coordinates (ϕ, θ, χ_1) and

(ϕ, θ, χ_2) . χ_1 (χ_2) is then defined as the angle between the H_1CH_2 (H_3CH_4) entity and the space-fixed X'' axis as depicted in Fig. 2 (c). (θ, ϕ) are the polar coordinates of the $\text{C}=\text{C}_n=\text{C}$ axis, or, equivalently, the first two Euler angles. The rotation-torsion wave function ψ_{rt} is thus

$$\psi_{\text{rt}} = \frac{1}{2\pi} S_{Nm}(\theta, \phi) \exp(ik_1\chi_1) \exp(ik_2\chi_2), \quad (6)$$

where $S_{Nm}(\theta, \phi)$ describes the rotation of the z_m axis in the space-fixed frame. N is the quantum number associated with the total angular momentum excluding spin. Its projection onto the space-fixed Z axis is labeled by the quantum number m . Because of the 2π periodicity of the rotational functions, $k_{1(2)}$ is an integer quantum number associated with the projection of the angular momentum of the internal rotation of the H_1CH_2 (H_3CH_4) entity onto the molecule-fixed quantization axis and runs from $-\infty$ to ∞ . It is convenient to use the coordinates χ and γ to separate the internal rotation from the overall rotation (see Refs. [41, 37] for a detailed discussion of this coordinate transformation):

$$\gamma = \frac{1}{2}(\chi_1 - \chi_2) \mod 2\pi \quad (7)$$

and

$$\chi = \frac{1}{2}(\chi_1 + \chi_2) \mod 2\pi, \quad (8)$$

so that ψ_{rt} becomes

$$\psi_{\text{rt}} = \frac{1}{2\pi} S_{Nm}(\phi, \theta) \exp(ik_\gamma\gamma) \exp(ik_a\chi), \quad (9)$$

where k_γ is the quantum number of the torsional motion and k_a the projection of the rotational angular momentum onto the z_m axis. By comparison of Eq. (6) with Eqs. (7)-(9), k_γ and k_a can be expressed as [37]

$$k_a = k_1 + k_2, \quad k_\gamma = k_1 - k_2. \quad (10)$$

From Eq. (10), it is obvious that the restriction

$$|k_a - k_\gamma| = \text{even} \quad (11)$$

applies. Because the inertial tensor of allene has off-diagonal elements in the treatment of the hindered internal rotation when the dihedral angle τ is used [38], the half-dihedral angle $\gamma = \frac{1}{2}\tau$ is used here, so that a diagonal inertial tensor is obtained. γ is the angle between the plane of each CH_2 entity and the $x_m z_m$ -plane, so that (x_m, y_m, z_m) remain the principal inertial axes for all values of γ , i. e., x_m and y_m are fixed so as to always bisect the dihedral angle τ , as indicated in Fig. 2 (a).

Figs. 3 (a) and (b) depict schematic representations of a cut through the potential energy surfaces along the torsional normal coordinates defined as γ and τ , respectively. As can be seen in Fig. 3 (a), changing γ to $\gamma + \pi$ corresponds to a rotation of the molecule about the Z'' axis by π . However, Eq. (11) imposes a restriction on possible values of k_γ . As pointed out in Refs. [42, 34], if the rotor and top are equivalent and coaxial, an ambiguity in the symmetry species arises because of the indistinguishability of the top from the frame, which necessitates the introduction of extended molecular symmetry groups (here indicated by the superscript (2)). The extended molecular symmetry group relevant to allene with internal rotation is $G_{16}^{(2)}$ and is reproduced from Ref. [34] in Table 1.

With the transformation from τ to $\gamma = \tau/2$, Eq. (4) becomes

$$V(r, \gamma) = V(r, \gamma^0 = \frac{\pi}{4}) + V_2 \cos(4\gamma) + V_4 \cos(8\gamma) + \dots + V_{2n} \cos(4n\gamma). \quad (12)$$

The partially filled electronically degenerate orbital of the $\tilde{X}^+ {}^2\text{E}$ state of the allene cation in its D_{2d} geometric configuration transforms in the $G_{16}^{(2)}$ extended molecular symmetry group as $E_g \oplus E_u \oplus E^+ \oplus E^-$ (see backward correlation in Table 1). The ground electronic state of the cation is labeled $\tilde{X}^+ {}^2\text{E}^+$ to stress that the overall wave function is single-valued (E_g and E_u wave functions would be double-valued) [34]. The JT-active modes are determined as

$$E_g \otimes E_g = E_u \otimes E_u = (A_{1g}^+ \oplus A_{2g}^- \oplus B_{1g}^+ \oplus B_{2g}^-) \quad (13)$$

$$E^+ \otimes E^+ = E^- \otimes E^- = (A_{1g}^+ \oplus A_{2u}^+ \oplus B_{1g}^+ \oplus B_{2u}^+). \quad (14)$$

Since $\cos(2\gamma)$ transforms as B_{1g}^+ , this term can couple the two doubly-degenerate components of the $\tilde{X}^+$ cationic ground state of allene. The leading term of the Taylor expansion of $\cos(2\gamma)$ around $\gamma^0 = \pi/4$

$$\cos(2\gamma) = -2(\gamma - \gamma^0) + \frac{4}{3}(\gamma - \gamma^0)^3 + \dots \quad (15)$$

is analogous to the linear JT coupling term in Eq. (2). This and the fact that the torsional mode ν_4 transforms as B_{1g}^+ in $G_{16}^{(2)}$ leads to the conclusion that $\cos(2\gamma)$ is the linear JT coupling operator if the JT-active mode is expressed in the basis of a hindered internal rotor. The term $\cos(4\gamma)$ is totally symmetric (of A_{1g}^+ symmetry) and must therefore remain on the diagonal like the harmonic terms in Eq. (2). The asymmetric C=C=C stretching mode (ν_6 in allene) transforms as B_{2u}^+ and is therefore also JT-active. In analogy to Eq. (2), the vibronic Hamiltonian can now be re-written in terms of γ as

$$\begin{aligned} \mathbf{H}/hc = & E'_0 \mathbf{1} + \underbrace{(\hat{T}_\gamma(\gamma) + V_2(1 + \cos(4\gamma)) + V_4(1 + \cos(8\gamma)))}_{\mathbf{H}_{\text{tors}}} \mathbf{1} \\ & + \underbrace{\left(\hat{T}_n(q) + \frac{1}{2} \sum_i^{3N-7} \tilde{\nu}_i q_i^2 \right)}_{\mathbf{H}_{\text{h.o.}}} \mathbf{1} + \underbrace{\begin{pmatrix} k_6 q_6 & V_1 \cos(2\gamma) \\ V_1 \cos(2\gamma) & -k_6 q_6 \end{pmatrix}}_{\mathbf{H}_{\text{JT}}}. \end{aligned} \quad (16)$$

In Eq. (16), $\hat{T}_\gamma(\gamma)$ is the kinetic energy operator (expressed in units of cm^{-1}) of the hindered internal rotation:

$$\hat{T}_\gamma(\gamma) = -A \frac{\partial^2}{\partial \gamma^2} = A \frac{\hat{J}_\gamma^2}{\hbar^2}, \quad (17)$$

where A (in units of cm^{-1}) is the rotational constant of the entire molecule about the a axis [34]. In Eq. (16), $E'_0 = E_0 - V_2 - V_4$, so that the conical intersection is at E_0 . Omitting the kinetic energy operators, the Hamiltonian in Eq. (16) can easily be diagonalized, yielding the JT-coupled potential energy hypersurfaces, of which the cut along the plane spanned by $q_4 = \gamma$ and q_6 is displayed in Fig. 4 for $V_4 = 0$. The values for k_6 and $\tilde{\nu}_6$ were chosen such that $\frac{k_6^2}{2\tilde{\nu}_6} < \frac{V_1^2}{8V_2}$ so that the relative energetic positions of the stationary points are similar to those determined by *ab initio* quantum chemistry for the allene cation [22]. The ratio $\frac{V_1}{V_2}$ was chosen somewhat arbitrarily to be equal to two. The

potential energy surface along $q_b = \gamma$ and $q_a = q_6$ exhibits the same general features as Fig. 1 (b) obtained from the Hamiltonian in the harmonic oscillator basis in Eq. (2) which has two minima of D_2 geometry along the torsional coordinate γ at $q_6 = 0$ and two saddle points along the asymmetric stretch normal coordinate q_6 at $\gamma = \frac{\pi}{4}$. However, there are now two more saddle points of D_{2h} geometry at $\gamma = \pi$ and $\gamma = 0$, where the two CH_2 entities are coplanar. The Hamiltonian in Eq. (16) is also valid for the $\tilde{X}^+ {}^2\text{E}$ ground state of C_2H_4^+ , if $\gamma_0 = \pi/4$ is taken as the reference geometry.

3 Vibronic structure and intensity calculations

In order to calculate the energy level structure of allene or ethene, the Hamiltonian $\mathbf{H}$ in Eq. (16) is expressed in a basis of rotation-torsion-vibronic wave functions. The rotation-torsion-vibronic wave function ψ_{rtve} can be constructed as a product of the torsion-rotation wave function in Eq. (9), harmonic oscillator wave functions of the remaining $3N - 7$ normal coordinates $\Phi_{\text{vib}}(q_1, q_2, \dots, q_{3N-7})$ and the electronic wave function $\Phi_{\text{elec}}(\Lambda)$, where the quantum number associated with the projection of the electronic angular momentum onto the principal axis is Λ and takes the values ± 1 for a doubly-degenerate electronic state. The internal wave function, neglecting nuclear and electron spins, can then be expressed as

$$\begin{aligned} \psi_{\text{rtve}} &= \frac{1}{2\pi} \underbrace{S_{Nm}(\theta, \phi) \exp(ik_a\chi)}_{\Phi_{\text{rot}}} \underbrace{\exp(ik_\gamma\gamma)}_{\Phi_{\text{tors}}} \Phi_{\text{vib}}(q_1, q_2, \dots, q_{3N-7}) \Phi_{\text{elec}}(\Lambda) \\ &= |N, k_a, m; k_\gamma; v_{i=1, \dots, 3N-7}; \pm 1\rangle. \end{aligned} \quad (18)$$

The vibronic structure is calculated by setting $J = k_a = 0$. Restricting the treatment to the two JT active modes ($q_a = \nu_4$ and $q_b = \nu_6$ in the allene cation), the nonzero matrix elements for the rotationless Hamiltonian are found to be (compare also with Refs. [36]

and [40]):

$$\begin{aligned}
\langle N, k_a, m; k_\gamma; v_6; \pm 1 | \hat{H}_{\text{h.o.}} | N, k_a, m; k_\gamma; v_6; \pm 1 \rangle &= \tilde{\nu}_6(v_6 + \tfrac{1}{2}) \\
\langle N, k_a, m; k_\gamma; v_6; \pm 1 | k_6 q_6 | N, k_a, m; k_\gamma; v_6 + 1; \pm 1 \rangle &= k_6 \sqrt{v_6} \\
\langle N, k_a, m; k_\gamma; v_6; \pm 1 | k_6 q_6 | N, k_a, m; k_\gamma; v_6 - 1; \pm 1 \rangle &= k_6 \sqrt{v_6 + 1} \\
\langle N, k_a, m; k_\gamma; v_6; \pm 1 | V_2 \cos(4\gamma) | N, k_a, m; k_\gamma \pm 4; v_6; \pm 1 \rangle &= V_2/2 \\
\langle N, k_a, m; k_\gamma; v_6; \pm 1 | V_1 \cos(2\gamma) | N, k_a, m; k_\gamma \pm 2; v_6; \mp 1 \rangle &= V_1/2 \\
\langle N, k_a, m; k_\gamma; v_6; \pm 1 | -A \partial^2 / \partial \gamma^2 | N, k_a, m; k_\gamma; v_6; \pm 1 \rangle &= A k_\gamma^2.
\end{aligned} \tag{19}$$

Figs. 5 (a), (b) and (c) depict a correlation diagram where V_1 , V_2 and k_6 in Eqs. (16) and (19) are varied, respectively, and $\tilde{\nu}_6$ is kept fixed at 1911 cm^{-1} (as determined for the allene cation in Ref. [22]), and the rotational constant A at 5.0 cm^{-1} . The correlation diagram was calculated expressing the Hamiltonian in Eq. (16) in matrix form using the basis functions in Eq. (18) with $-40 \leq k_\gamma \leq 40$ and $v_6 \leq 20$ which resulted in matrices of dimension 3402 x 3402. Convergence tests showed that the eigenvalues of the levels up to 2500 cm^{-1} of internal energy have converged to better than 0.1 cm^{-1} for values of $|V_1| = 11000 \text{ cm}^{-1}$, $|V_2| = 5000 \text{ cm}^{-1}$, $|k_6| = 2000 \text{ cm}^{-1}$. In panels (a), (b) and (c), the value of the parameter changed is indicated along the bottom horizontal axis in units of cm^{-1} and the values of the parameters kept fixed are indicated below in parentheses. The vertical axis indicates the vibronic term values (in units of cm^{-1}) above the vibronic ground state $\tilde{X}^+(0^0)$ of the cation.

On the left of Fig. 5 (a), the structure of a free internal rotor, given by $A k_\gamma^2$, is obtained by setting $V_1 = V_2 = 0$, $k_6 = 0$ ($N = k_a = 0$ in the present case) and is superimposed on the harmonic energy level structure associated with ν_6 . As V_2 increases, the height of the D_{2h} saddle point above the minimum in the potential energy surface ($E_{D_{2h}} - E_{\text{min}}$) rises as $2V_2$ which is indicated by the thick gray line and on the energy scale on the top of the diagram (keeping $V_1 = k_6 = 0$ and $\tilde{\nu}_6 = 1911 \text{ cm}^{-1}$ fixed). The vibronic structure evolves into one that resembles that of a torsional harmonic oscillator at the border between panels (a) and (b). On the left of Fig. 5 (b), the states are labeled as harmonic oscillators in the notation $\nu_i^{v_i}$. Each torsion-vibronic energy level consists of

two doubly-degenerate levels of vibronic symmetry $\Gamma_{\text{ve}} = E^+$ and E^- (in $G_{16}^{(2)}$) because of the 'accidental' degeneracy arising when the D_{2h} potential barrier is high. In Fig. 5 (b), V_2 is kept fixed at $V_2 = 5000 \text{ cm}^{-1}$ and V_1 is increased. The thick gray line indicates the height of the D_{2h} saddle point above the minimum, as in panel (a), whereas the thick black line shows how the JT stabilization energy ($V_1^2/(8V_2)$) increases. The upper horizontal axis represents the value of $E_{D_{2d}} - E_{\text{min}}$. As V_1 increases, the D_{2h} barrier is lowered and the degeneracy between the torsion-vibronic energy levels of E^+ and E^- symmetry is lifted. A splitting of the energy levels becomes noticeable on the right-hand side of panel (b), resulting from tunneling through the D_{2h} barrier. Tunneling splittings arising from a motion through the D_{2h} potential barrier cannot be described by Eq. (2) and their prediction with the present model represents one of the main results of this article.

In Fig. 5 (c), the first-order JT coupling constant k_6 of the asymmetric C=C=C stretching mode is increased from 0 to 11000 cm^{-1} . The positions of the D_{2h} saddle point and of the conical intersection remain constant as indicated by gray and black lines, respectively. The absolute energy difference between the saddle points of C_{2v} geometry (see Fig. 4) and the D_2 minimum energy point is indicated by the dash-dotted line in Fig. 5 (c). The energy level structure changes significantly in the proximity of $k_6 = 3091 \text{ cm}^{-1}$, where the minimum energy path around the conical intersection becomes equipotential. This situation has been described by Markiewicz in the context of a chaotic motion [43]. The sudden change of the energy level structure arising in the vicinity of the k_6 value corresponding to an equipotential path around the conical intersection is also predicted by calculations (not shown) using the standard $E \otimes (b_1 \oplus b_2)$ JT Hamiltonian in Eq. (2). For values of $k_6 > 3091 \text{ cm}^{-1}$, the stationary point at the C_{2v} geometry becomes the minimum and the D_2 geometry point the saddle point. In the limit where the C_{2v} minima become very deep, the wave functions are confined to these minima and a harmonic oscillator energy levels structure is obtained with a harmonic wave number of $\approx 840 \text{ cm}^{-1}$ (right-hand side of Fig. 5 (c)).

From the diagonalization of the Hamiltonian $\mathbf{H}$ in Eq. (16), the adiabatic electronic wave functions can be obtained. Considering only the JT-active modes and setting $N =$

$k_a = 0$, the basis functions defined in Eq. (18) reduce to

$$\begin{aligned}\psi_{\text{rtve}} &= \frac{1}{2\pi} S_{00}(\theta, \phi) \exp(i0\chi) \exp(ik_\gamma\gamma) \Phi_{\text{vib}}(q_6) \Phi_{\text{elec}}(\Lambda) \\ &= \frac{1}{2\pi} \exp(ik_\gamma\gamma) \Phi_{\text{vib}}(q_6) \underbrace{\exp(i\Lambda\gamma) \phi_{\text{elec}}(\Lambda)}_{\Phi_{\text{elec}}(\Lambda)}.\end{aligned}\quad (20)$$

The electronic wave function $\Phi_{\text{elec}}(\Lambda)$ explicitly depends on the torsional coordinate γ as illustrated by Fig. 6. Upon increasing the half-dihedral angle γ by π the electronic wave function changes sign. This sign change exemplifies the coupling of the torsional motion and the electronic motion which results in the phase factor $\exp(i\Lambda\gamma)$. A vibronic angular momentum quantum number $\Omega = k_\gamma + \Lambda$ can now be defined, which must be odd because $|\Lambda| = 1$ (see Eq. (11)).

Generalized Franck-Condon factors I_i for the $\tilde{X}^+ \leftarrow \tilde{X}$ transition observed in the photoelectron spectra can be calculated as the square of the overlap integral of the adiabatic torsion-vibronic wave function Ψ_i of the i -th torsion-vibronic energy level of the cation (N_i^+ is a normalization constant; the coefficients c_Ω^i and $c_{v_6}^i$ describing the eigenvectors of the Hamiltonian in Eq. (16) in the basis of Eq. (18) can be chosen such that the wave function is real)

$$\Psi_i = N_i^+ \sum_{\Omega} \sum_{v_6} c_\Omega^i c_{v_6}^i \exp(i\Omega\gamma) \Phi_{\text{vib}}(q_6) \quad (21)$$

with the wave function ψ_0 of the neutral ground state:

$$I_i(\tilde{X}^+ \leftarrow \tilde{X}) = \left| \int_{-\pi}^{\pi} (\Psi_i)^* \psi_0 d\gamma \right|^2. \quad (22)$$

In the calculations of the vibronic intensity distributions in the photoelectron spectra of C_2H_4 and C_3H_4 presented in the next section, we only considered transitions from the $\tilde{X}(0^0)$ ground vibronic state because of the low temperature in the supersonic expansion [29, 30]. As explained previously [22, 30], the intensities $I_i(\tilde{X}^+ \leftarrow \tilde{X})$ of the transitions to the final states v_i from the $\tilde{X}(0^0)$ initial vibronic state ($\tilde{X}^+(\nu_j^{v_i}) \leftarrow \tilde{X}(0^0)$) can be approximately described as being proportional to the squares of the coefficients $c_{v_6=0}^i$ of

the wave functions

$$I_i(\tilde{X}^+ \leftarrow \tilde{X}) = \left| c_{v_6=0}^i N_i^+ N_0 \sum_{\Omega} (c_{\Omega}^i)^* \int_{-\pi}^{\pi} \exp(-i\Omega\gamma) \cdot \exp(-(\gamma - \gamma_{\text{neutral}})^2/a) d\gamma \right|^2, \quad (23)$$

where a is a constant proportional to the harmonic torsional wave number of the neutral ground state (see Ref. [40] for details) and γ_{neutral} is the half-torsional angle of the equilibrium reference geometry of the neutral ground state ($\gamma_{\text{neutral}} = \pi/2$ for allene, $\gamma_{\text{neutral}} = 0$ for ethene).

4 Comparison with experimental data

Allene and ethene are very similar in structure. Both have two CH_2 entities connected by a linear carbon chain. However, in its ground electronic state C_2H_4 is planar and of a minimum energy geometry of D_{2h} symmetry. Because allene has an extra carbon atom on axis, the terminal CH_2 entities are twisted with a half dihedral angle of $\gamma = 45^\circ$, and the neutral ground state geometry is of D_{2d} symmetry. If internal rotation is permitted, C_2H_4^+ and C_3H_4^+ have to be classified in $G_{16}^{(2)}$, as discussed above, leading to a doubly-degenerate electronic ground state at the point $\gamma = 45^\circ$ that is prone to a JT distortion along the torsional mode.

Even though the qualitative structure of the potential energy hypersurfaces of the $\tilde{X}^+$ states of the ethene and allene cations are similar, they are quantitatively different, as illustrated in Figs. 7(a) and (b), respectively. The bottom two panels of Figs. 7 (a) and (b) schematically depict cuts along γ through the potential energy surfaces of the neutral ground state and cationic ground state of ethene and allene, respectively. The potential energy cuts (thick black lines in the lower panels of Figs. 7 (a) and (b)) indicate the relative energetic positions of the stationary points in ethene and allene. In the top panels of Figs. 7 (a) and (b), the wave functions of the four lowest-lying vibronic levels (the two tunnel components of E^+ and E^- symmetry, as indicated on the right-hand side) are shown as full lines, and have been shifted vertically for clarity. The bottom panels of Figs. 7 (a) and (b) show the vibrational wave functions of the neutral ground states of

ethene and allene, respectively. Because of the different neutral ground state equilibrium structures, the minima lie at $\gamma_{\text{neutral}} = 0, \pm\pi/2, \pm\pi$ for C_2H_4 and at $\gamma_{\text{neutral}} = \pm\pi/4, \pm3\pi/4$ for C_3H_4 . The Franck-Condon active regions of the $\tilde{\text{X}}^+(\nu_i^{v_i}) \leftarrow \tilde{\text{X}}(0^0)$ transitions observed in the PFI-ZEKE photoelectron spectra presented in Refs. [29] and [30] correspond to the shaded areas.

The vibrational overlap integrals of the neutral ground state vibrational wavefunction and the ionic wavefunctions $\Psi_2(E^+)$ and $\Psi_4(E^-)$ vanish in ethene because these wavefunctions have a node at $\gamma = 0$. Whereas the overlap with $\Psi_1(E^+)$ is large, that with $\Psi_3(E^-)$ is extremely small, because, at low energies, the wings of this wavefunction, which has maximal amplitude at $\gamma = \pm\pi/2$, do not extend to the region near $\gamma = 0$. An alternation of intensity in the photoelectron spectrum results, the lower tunneling component (4^0 in ethene) being strong and the upper (4^1) being extremely weak. In allene, the vibronic intensity distribution is expected to be markedly different. Transitions to all tunneling components should carry intensity because neither the E^+ nor the E^- vibronic levels have nodes in the vertical excitation region at $\gamma = \gamma_0 = \pi/4$.

Considering a full period of the torsional motion ($-\pi/2 \leq \gamma \leq \pi/2$, see Fig. 4) with its four minima leads to the conclusion that, in the high- D_{2h} -barrier limit, the ground vibrational level should consist of four degenerate levels, two of E^+ and two of E^- symmetry. At finite values of the D_{2h} barrier height, these four levels split into two doubly-degenerate sets, the two E^+ (E^-) levels forming the lower (upper) tunneling level. The barrier at D_{2h} geometry on the potential energy surface of C_2H_4^+ is low so that the tunneling splitting of the lowest vibrational levels are easily resolvable in the photoelectron spectrum [29]. This barrier is higher in C_3H_4^+ , and the tunneling splittings of the low vibrational levels are much more difficult to resolve [30]. As a result, different nomenclatures are used to label the torsional levels of these two ions: Whereas the two E^+ and the two E^- levels correspond to the 0^0 and 4^1 levels of C_2H_4^+ , respectively, they form the four near-degenerate components of the 0^0 level of C_3H_4^+ .

4.1 The PFI-ZEKE photoelectron spectrum of C₂H₄

The PFI-ZEKE photoelectron spectra of the $\tilde{X}^+ \leftarrow \tilde{X}$ transition of C₂H₄ and C₂D₄ have been reported in Ref. [29]. The ethene cation was found to be distorted along the torsional mode to a dihedral angle $\tau = 29.2(5)^\circ$ ($\gamma = 14.60(25)^\circ$), and the vibronic structure was calculated using the model potential

$$V(\gamma) = 2k\gamma^2 + \epsilon (\exp(-4\alpha\gamma^2) - 1), \quad (24)$$

with a discrete variable-representation (DVR) method [44, 45] without consideration of the JT effect. The parameters k , ϵ and α were fitted to reproduce the vibronic structure observed experimentally, and a barrier height at the D_{2h} geometry relative to the minimum energy of $357(26) \text{ cm}^{-1}$ for C₂H₄⁺ was determined [29]. For C₂D₄⁺ the tunnel barrier was found to be $292(24) \text{ cm}^{-1}$ above the minimum with a dihedral angle of $27.8(5)^\circ$ ($\gamma = 13.90(25)^\circ$). Because of the low tunneling barrier at the D_{2h} geometry, C₂H₄⁺ exhibits a large tunneling splitting already for the lowest-lying torsional levels. An intensity alternation between $\tilde{X}^+(4^{v_4}) \leftarrow \tilde{X}(0^0)$ transitions with odd and even values for v_4 was observed. The observation of Franck-Condon-forbidden transitions to vibrational levels with odd values of v_4 was attributed to a Herzberg-Teller intensity-borrowing mechanism arising from the coupling to the $\tilde{A}^+$ state [29].

In the present analysis, we found that the b₂ vibrational modes can be ignored in the description of the photoelectron spectrum at low energies, in accord with the calculations of Ref. [35]. A potential model based on the Hamiltonian in Eq. (16) with $k_6 = 0$ was adequate to reproduce the vibronic structure observed in the PFI-ZEKE photoelectron spectra of both C₂H₄⁺ and C₂D₄⁺ in a least-squares fit. Terms in the Fourier series up to $V_4 \cos(8\gamma)$ needed to be included to achieve a good agreement between experimental and calculated vibrational term values. The results of the least-squares fit are summarized in Table 2 and compared to the experimental data of Ref. [29]. The tunneling barriers obtained from the potential parameters listed in Table 2 for C₂H₄⁺ and C₂D₄⁺ amount to 356.9 cm^{-1} and 292.8 cm^{-1} , respectively, and the dihedral angles could be determined to be 29.7° and 27.8° , respectively, in good agreement with the results of Ref. [29]. The

maximum deviation between calculated and observed vibronic term values is only 0.6 cm^{-1} (for the 4^2 level of C_2H_4^+).

Fig. 8 compares the relative vibrational intensities calculated using Eq. (23) with the experimental photoelectron spectrum of C_2H_4 from Ref. [29]. Our calculations, like those presented in Ref. [29], predict the transition to the 4^2 level of C_2H_4^+ to be the strongest, whereas the most intense transition of the experimental spectrum is to the 4^0 level. The last two columns of Table 2 also summarize the results obtained for C_2D_4 . Because we have not taken the Herzberg-Teller coupling to the $\tilde{\text{A}}^+$ state into account, the relative intensities of transitions to $v_4 = \text{odd}$ torsional levels are not reproduced. Compared to the analysis presented in Ref. [29], the present treatment offers the advantage that it includes the Jahn-Teller effect with a potential including (in principle) the conical intersection, though the b_2 modes turned out to be of negligible importance in the region of interest. The observed rotational levels lie well below the conical intersection so that the vibrational energy level structure is not significantly perturbed by the Jahn-Teller effect. The torsional mode is the only strongly JT-active mode in C_2H_4^+ and C_2D_4^+ so that the complexity of the energy structure arising from the second JT active mode (see Fig. 5 (c)) is not observable. Nevertheless, our results demonstrate that a quantitatively accurate description of the tunneling structure can be achieved with our Jahn-Teller formalism (Eq. 16), which would not have been possible with Eq. (2).

4.2 The photoelectron spectrum of C_3H_4

The PFI-ZEKE photoelectron spectra of the $\tilde{\text{X}}^+ \leftarrow \tilde{\text{X}}$ transition of allene (C_3H_4 and C_3D_4) have been reported in Ref. [30]. The rotational fine structure of the 4^2 and 4^3 vibrational bands in the PFI-ZEKE photoelectron spectra of C_3H_4 and C_3D_4 was found to be highly perturbed, and the presence of overlapping vibronic bands and of weak satellite bands suggested the importance of tunneling splittings and vibronic perturbations. Moreover, the broadening of the rotational lines of the 4^1 band compared to those of the 0^0 band also potentially indicated a small tunneling splitting of at most 0.1 cm^{-1} . The information available in the literature on the potential energy hypersurfaces of the allene cation is

limited, and we used the data presented in Ref. [22] to guide our calculations and restrict the range of possible values of our potential parameters.

As for the ethene cation, terms up to $V_4 \cos(8\gamma)$ were retained to describe the potential function along the torsional coordinate. In a first set of calculations, the JT effect was neglected and only one of the double-minimum potential functions depicted in Fig. 7 (b) was used to determine the vibrational structure of C_3H_4^+ in a one-dimensional DVR calculation. A least-squares fit of the potential parameters led to the results presented in panel (b) of Figure 9 and in the third column of Table 3. These calculations gave a good description of the vibrational intervals and tunneling splitting of the same order of magnitude as those inferred from the experiment, i.e., only significant for vibrational levels with $v_4 \geq 3$. Note that the strongly perturbed rotational structure of the photoelectron spectra prevented the determination of accurate tunneling splittings [30]. The calculations also enabled a satisfactory description of the intensity distribution observed experimentally, which is presented for comparison in Fig. 9 (a).

In a second set of calculations, the results of which are presented in panel (d) of Fig. 9 and in the last column of Table 3, the Jahn-Teller effect was treated as for the ethene cation above, i.e., with Eq. (16) but setting $k_6 = 0$, i.e. neglecting the effect of the C=C=C asymmetric stretching mode. These calculations led to an equally satisfactory description of the experimental data, and to a slight increase of the tunneling splitting of the 4^3 level (1.3 cm^{-1} instead of 1 cm^{-1}).

In a final set of calculations the C=C=C asymmetric stretching mode was also included; however, given that only three main vibrational intervals are known accurately from the experiment, a reliable determination of all four parameters (V_1 , V_2 , V_4 and k_6) was not possible and our parameters were restricted to a range compatible with those reported in Ref. [22]. The overall effect of the inclusion of ν_6 was a reduction of the tunneling splittings and the appearance of additional bands in the vicinity of the 4_0^1 and 4_0^3 bands (see Fig. 9 (c)). In particular, we found that restricting k_6 to $\approx 2000 \text{ cm}^{-1}$ led to a systematic overestimation of the interval between the 4^0 and 4^1 levels of C_3H_4^+ and of the intensity of the 4_0^2 band. Nevertheless, the calculations have the merit to provide a possible explanation for the satellite band observed in the vicinity of the 4^3 level of C_3H_4^+ .

Unfortunately, the number of vibrational intervals known accurately from the experiment is insufficient to provide a stringent test of our model. An accurate determination of the potential energy hypersurfaces and the identification of all Jahn-Teller active modes by quantum chemical methods, in combination with high-resolution photoelectron spectroscopic studies at higher energies would be extremely useful. Our vacuum-ultraviolet laser sources are based on resonance-enhanced four-wave mixing in Kr and Xe and are not suited to access the wave number range between 81 000 and 85 000 cm^{-1} . We are currently seeking alternative methods to generate such radiation to extend our high-resolution measurements to higher energies.

5 Conclusions

In common treatments of the Jahn-Teller effect, the potential energy surfaces are expanded in Taylor series of displacement coordinates from a reference geometry which corresponds to a conical intersection, or a (many-dimensional) seam of conical intersections. This treatment is adequate whenever the distortion caused by the Jahn-Teller effect is small. Limitations can occur when the Jahn-Teller distortions are large, as is the case whenever one of the Jahn-Teller active mode is a torsional coordinate.

The present article shows that the linear Jahn-Teller coupling in this particular case can be more conveniently described by Fourier series. Numerical calculations further demonstrate that tunneling splittings arising from potential barriers far removed from the conical intersection can be adequately described. To illustrate this point, comparison is made between the results of model calculations and high-resolution PFI-ZEKE photoelectron spectra of ethene and allene. In the case of the $E \otimes (b_1 \oplus b_2)$ Jahn-Teller effect, our calculations predict very large perturbations of the energy level structure whenever the Jahn-Teller coupling parameters are such that an almost equipotential minimum energy path results on the potential energy surface around the conical intersection.

The model presented here has the potential of treating the Jahn-Teller effect and internal rotations jointly. The formalism could be extended to a treatment of the rotational structure, and relevant matrix elements for such an extension are presented in the

Appendix.

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Appendix: Matrix elements of the rotation-torsion-vibronic JT Hamiltonian

The treatment presented in Section 3 can be extended to include the overall rotation of the molecule following the procedure introduced in Ref. [34] for ethene. The rotational Hamiltonian $\hat{H}_{\text{rot}}$ is

$$\begin{aligned}\hat{H}_{\text{rot}} &= \frac{1}{2}(B_x(\gamma) + B_y(\gamma))(\hat{J}_x^2 + \hat{J}_y^2) + \frac{1}{2}(B_x(\gamma) - B_y(\gamma))(\hat{J}_x^2 - \hat{J}_y^2) + A\hat{J}_z^2 \\ &= \frac{1}{2}(B_x(\gamma) + B_y(\gamma))(\hat{J}^2 - \hat{J}_z^2) + \frac{1}{4}(B_x(\gamma) - B_y(\gamma))(\hat{J}_+^2 + \hat{J}_-^2) + A\hat{J}_z^2,\end{aligned}\quad (25)$$

where the rotational constants $B_x(\gamma)$ and $B_y(\gamma)$ are functions of the torsion angle γ . From the inertial tensor they are determined as [34]:

$$\begin{aligned}\frac{1}{2}(B_x(\gamma) + B_y(\gamma)) &= B \left(1 - \frac{B^2}{4A^2} \cos^2(2\gamma)\right)^{-1} \\ \frac{1}{4}(B_x(\gamma) - B_y(\gamma)) &= \frac{B^2}{4A} \cos(2\gamma) \left(1 - \frac{B^2}{4A^2} \cos^2(2\gamma)\right)^{-1},\end{aligned}\quad (26)$$

where B is the rotational constant along x_m and y_m of the molecule in its D_{2d} geometry.

The matrix elements associated with the perpendicular rotational constants in allene

can be obtained as

$$\langle N, k_a, m; k_\gamma; v_6; \pm 1 | A \partial^2 / \partial \chi^2 | N, k_a, m; k_\gamma; v_6; \pm 1 \rangle = A k_a^2 \quad (27)$$

and from Eqs. (25) and (26) as

$$\begin{aligned} & B \langle N, k_a, m; k_\gamma; v_6; \pm 1 | \frac{(\hat{J}^2 - \hat{J}_z^2)}{(1 - \frac{B^2}{4A^2} \cos^2(2\gamma))} | N, k_a, m; k_\gamma \pm n; v_6; \pm 1 \rangle \\ &= \frac{1}{2\pi} B (J(J+1) - k_a^2) \cdot \int_{-\pi}^{\pi} \exp(-ik_\gamma \gamma) \frac{1}{(1 - \frac{B^2}{4A^2} \cos^2(2\gamma))} \exp(i(k_\gamma \pm n)\gamma) d\gamma \\ &= \frac{1}{2\pi} B (J(J+1) - k_a^2) \cdot \int_{-\pi}^{\pi} \frac{\exp(\pm in\gamma)}{(1 - \frac{B^2}{4A^2} \cos^2(2\gamma))} d\gamma, \end{aligned} \quad (28)$$

and

$$\begin{aligned} & \frac{B^2}{4A} \langle N, k_a \mp 2, m; k_\gamma; v_6; \pm 1 | \frac{\cos(2\gamma)(\hat{J}_+^2 + \hat{J}_-^2)}{(1 - \frac{B^2}{4A^2} \cos^2(2\gamma))} | N, k_a, m; k_\gamma \pm n; v_6; \pm 1 \rangle \\ &= \frac{1}{2\pi} \frac{B^2}{4A} \sqrt{[J(J+1) - (k_a \mp 1)(k_a \mp 2)][J(J+1) - (k_a \mp 1)k_a]} \cdot \\ & \quad \int_{-\pi}^{\pi} \exp(-ik_\gamma \gamma) \frac{\cos(2\gamma)}{(1 - \frac{B^2}{4A^2} \cos^2(2\gamma))} \exp(i(k_\gamma \pm n)\gamma) d\gamma \\ &= \frac{1}{2\pi} \frac{B^2}{4A} \sqrt{[J(J+1) - (k_a \mp 1)(k_a \mp 2)][J(J+1) - (k_a \mp 1)k_a]} \cdot \int_{-\pi}^{\pi} \frac{\cos(2\gamma) \exp(\pm in\gamma)}{(1 - \frac{B^2}{4A^2} \cos^2(2\gamma))} d\gamma. \end{aligned} \quad (29)$$

The restriction placed on the values of k_γ and k_a in Eq. (11) dictates that n has to be an even integer in Eqs. (28) and (29). The integrals in Eqs. (28) and (29) rapidly go to zero with increasing values of n and only nonzero matrix elements for $n \leq 10$ are given in Table 4. The matrix elements in Eqs. (28) and (29) can be interpreted as a -type and b/c -type Coriolis interactions [38], and may be important in understanding the perturbed rotational structures observed in the high-resolution PFI-ZEKE photoelectron spectra of the first (4^2) and second (4^3) overtones of the torsional mode in the allene cation discussed in Ref. [30].

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Captions

Fig. 1: Two-dimensional cuts along the JT-active modes q_a and q_b of the potential energy hypersurfaces characteristic of (a) the $E \otimes e$ and (b) the $E \otimes (b_1 \oplus b_2)$ JT effect. Equipotential lines are indicated in the contour map below the potential surfaces.

Fig. 2: Schematic representation of (a) the torsional mode ν_4 , (b) the asymmetric C=C=C stretching mode ν_6 of the allene cation and (c) the relationship between the torsional (τ) and half-torsional (γ) angles and the third Euler angle χ which gives the orientation of the molecule-fixed x_m axis. The motion of the atoms is indicated by the dashed arrows. In (a), τ and γ represent the torsional and half-torsional angles, respectively. x_m , y_m and z_m represent the molecule-fixed axis system. In (c), the molecule-fixed z_m axis lies along the C=C=C axis and comes out of the plane of the paper to form a right-handed axis system. χ_1 and χ_2 characterize the orientation of the planes of the H_1CH_2 and H_3CH_4 entities, respectively. X'' and Y'' represent the axes obtained after rotating the laboratory-fixed reference axis system by the first two Euler angles ϕ and θ (see Zare [39]).

Fig. 3: Cut through the potential energy hypersurface characteristic of the $E \otimes (b_1 \oplus b_2)$ JT effect along the torsional mode defined as (a) the half-torsional angle γ and (b) the torsional angle τ . These angles are indicated in the Newman projections corresponding

to conical intersections and saddle points.

Fig. 4: Potential energy surface along q_4 and q_6 characteristic of the $E \otimes (b_1 \oplus b_2)$ JT effect in the allene cation obtained by diagonalizing the potential energy operator contributions to Eq. (16). Along q_4 , the potential exhibits four minima of D_2 geometry and two conical intersections at the points of D_{2d} symmetry ($\gamma = -\pi/4, \pi/4$). Saddle points of C_{2v} symmetry are located at $\gamma = 0, \pm\pi$.

Fig. 5: Correlation diagram characterizing key aspects of the global treatment of the JT effect in the basis of a hindered internal rotor. (a) Correlation from a free internal rotation of the CH_2 entities ($V_2 = 0 \text{ cm}^{-1}$, on the left) to that to a completely hindered internal rotation equivalent to a close-to-harmonic torsional vibration for high barriers at the D_{2h} geometry ($V_2 = 5000 \text{ cm}^{-1}$, on the right). (b) Evolution of the energy level structure as a function of the parameter V_1 , which describes the JT coupling in the torsional mode, from $V_1 = 0 \text{ cm}^{-1}$ on the left to $V_1 = 11000 \text{ cm}^{-1}$ on the right. (c) Evolution of the energy level structure with increasing linear Jahn-Teller coupling constant k_6 . The vibrational energy relative to the vibrational ground state is shown on the vertical axis. The JT parameters are indicated below each panel. In panel (a) the top horizontal axis gives the energy difference between the minimum energy and the D_{2h} saddle point also indicated by the gray thick line throughout panels (a), (b) and (c). In panel (b) the energy difference between the minimum energy and the conical intersection at the D_{2d} geometry is indicated on the top horizontal axis and as a thick black line. The absolute energy difference between the C_{2v} and D_2 minima along the vibrational coordinates q_6 ($\gamma = \pi/4$) and γ ($q_6 = 0$) is indicated by the thick black dot-dashed line and given on the top horizontal axis in panel (c). In (a), (b) and (c) $\tilde{\nu}_6$ and A were held constant at

1911 cm^{-1} and 5.0 cm^{-1} , respectively.

Fig. 6: Schematic representation of the effect of increasing the half-torsional angle γ by π on the electronic wave functions. The terminal H atoms are labeled 1 to 4. The relative signs of wave functions Φ_{elec} corresponding to the two components with $\Lambda = +1$ and $\Lambda = -1$ of the electronically degenerate state are indicated in gray and white.

Fig. 7: Illustration of the different Franck-Condon regions accessed in single-photon photoelectron spectroscopic experiments of (a) ethene and (b) allene. On the bottom panels of (a) and (b), the potential energy path along γ corresponding to the neutral ground state $\tilde{X}^1A_{1g}^+$ (in $G_{16}^{(2)}$) of ethene and allene below that of the $\tilde{X}^+{}^2E^+$ of $C_2H_4^+$ and $C_3H_4^+$, respectively, is indicated. The vibrational energy level structure is overlaid and the wave function corresponding to the $\tilde{X}^1A_{1g}^+(0^0)$ is displayed. On the top panels of (a) and (b) the wave functions Ψ_i of the four lowest-lying vibrational energy levels of E^+ and E^- symmetry are shown. The gray-shaded area indicates the Franck-Condon region probed in the PFI-ZEKE photoelectron spectra of ethene [29] and allene [30].

Fig. 8: Comparison of the PFI-ZEKE photoelectron spectrum of the $X^+ \leftarrow X$ transition of ethene (from Ref. [29]) with vibronic calculations including the Jahn-Teller effect. The circles indicate the relative intensities, normalized to that of the transition to the 4^2 level, obtained by evaluating Eq. (23) using the potential parameters listed in Table 2. The dashed line corresponds to a convolution of the vibronic stick spectrum with a full width at half maximum of 50 cm^{-1} .

Fig. 9: Comparison of the PFI-ZEKE photoelectron spectrum of the $X^+ \leftarrow X$ transition of allene (from Ref. [30]) with vibronic calculations. In panel (a) the PFI-ZEKE photoelectron spectrum in the region up to 2500 cm^{-1} above the origin of the $\tilde{X}^+ \leftarrow \tilde{X}$ transition of allene is overlaid with the HeI photoelectron spectrum reproduced from Ref. [46]. The calculation depicted in panel (b) has been obtained in a one-dimensional DVR calculation neglecting the Jahn-Teller effect and based on the potential parameters listed in footnote *b* of Table 3. The calculations presented in panels (c) and (d) have been made using Eqs. (16) and (23) with the values for $V_{i=1,2,4}$ and k_6 given in footnotes *c* and *d* of Table 3, respectively.

Table 1: Character table of the extended molecular symmetry group $G_{16}^{(2)}$ reproduced from Ref. [34] (see text for details).

Table 2: Calculated and experimental wave numbers [29] for the torsional progression in ethene and ethene- d_4 . The vibrational wave numbers have been calculated using the model described in Eq. (16). Numbers in parentheses correspond to the uncertainties in the determination of the band centers in units of the last figure. Relative intensities calculated using Eq. (23) are also presented.

Table 3: Summary of the vibrational energy levels of $C_3H_4^+$ from experiment (first column) and the DVR calculations (second and third column) and using Eq. (16) (fourth column) neglecting the JT interaction along q_6 .

Table 4: Table of the integrals needed to evaluate the matrix elements of Eqs. (28) and (29).

Figure 1:

Figure 2:

Figure 3:

Figure 4:

Figure 5:

Figure 6:

Figure 7:

Figure 8:

Figure 9:

$G_{16}^{(2)}$	D_{2d}	E	E'	$(12)(34)$	$(12)(34)'$	E^* $E^{*'}_E$	$(12)(34)^*$ $(12)(34)^{*'}_E$	$(ab)(13)(24)$ $(ab)(14)(23)$	$(ab)(13)(24)'$ $(ab)(14)(23)'$	$(ab)(13)(24)^*$ $(ab)(14)(23)^{*'}_E$	$(ab)(14)(23)^*$ $(ab)(13)(24)^{*'}_E$	$(ab)(1423)^*$ $(ab)(1324)^*$ $(ab)(1423)^{*'}_E$ $(ab)(1324)^{*'}_E$	$(ab)(1423)^*$ $(ab)(1324)^*$ $(ab)(1423)^{*'}_E$ $(ab)(1324)^{*'}_E$	$(12)^*$ $(34)^*$ $(12)^{*'}_E$ $(34)^{*'}_E$	(12) (34) $(12)'$ $(34)'$
A_{16}^+	A_1	1	1	1	1	1	1	1	1	1	1	1	1	1	1
A_{2u}^+	A_2	1	1	1	1	1	1	-1	-1	-1	-1	1	1	-1	-1
A_{1u}^-	A_1	1	1	1	1	-1	-1	1	1	1	1	1	1	1	1
A_{2g}^-	A_2	1	1	1	1	-1	-1	-1	-1	1	1	1	1	-1	-1
B_{1g}^+	B_1	1	1	1	1	1	1	1	1	1	1	-1	-1	-1	-1
B_{2u}^+	B_2	1	1	1	1	1	1	-1	-1	-1	-1	-1	-1	1	1
B_{1u}^-	B_1	1	1	1	1	-1	-1	1	1	1	1	-1	-1	1	1
B_{2g}^-	B_2	1	1	1	1	-1	-1	-1	-1	1	1	1	1	-1	-1
E^+	E	2	2	-2	-2	2	-2	0	0	0	0	0	0	0	0
E^-	E	2	2	-2	-2	-2	2	0	0	0	0	0	0	0	0
E_1	A_1+B_1	2	-2	2	-2	0	0	2	-2	0	0	0	0	0	0
E_2	A_2+B_2	2	-2	2	-2	0	0	-2	2	0	0	0	0	0	0
E_g	E	2	-2	-2	2	0	0	0	0	2	-2	0	0	0	0
E_u	E	2	-2	-2	2	0	0	0	0	-2	2	0	0	0	0

Table 1:

ν^v	$\tilde{\nu}_{\text{obs}}[29]$	$\tilde{\nu}_{\text{calc}}$	$\tilde{\nu}_{\text{calc}}[29]$	$I_{\text{calc}}/I_{\text{max}}$	$I_{\text{obs}}/I_{\text{max}}$
<hr/> C ₂ H ₄ ⁺ <hr/>					
0 ⁰	0.0 (0)	0.0	0.0	0.94	1
4 ¹	83.7 (5)	83.4	83.8	0.00 ^b	0.35(5)
4 ²	438.2(4)	437.6	438.2	1.00	0.75(15)
4 ³	764.6(5)	764.7	764.5	0.00 ^b	0.25(5)
4 ⁴	1162.1(5)	1162.8	1162.1	0.19	0.15(5)
4 ⁵	1593.6(5)	1593.2	1592.4	0.00 ^b	-
<hr/>					
$V_1 = 12\,598.33\text{ cm}^{-1}$					
$V_2 = 2527.84\text{ cm}^{-1}$					
$V_4 = 520.22\text{ cm}^{-1}$					
$k_6 = 0$ (fixed)					
rms= 0.402					
<hr/> C ₂ D ₄ ⁺ <hr/>					
0 ⁰	0.0	0.0	0.0	0.78	0.80(15)
4 ¹	37.1(5)	36.9	37.1	0.00 ^b	0.20(5)
4 ²	275.5(4)	275.3	275.4	1.00	1
4 ³	469.0(4)	468.8	468.8	0.00 ^b	0.25(5)
4 ⁴	720.4(4)	720.8	720.7	0.12	0.20(5)
4 ⁵	982.2(10) ^a	995.2	995.1	0.00 ^b	-
4 ⁶	1291.5(4)	1291.4	1291.5	0.017	0.08(2)
<hr/>					
$V_1 = 13\,488.88\text{ cm}^{-1}$					
$V_2 = 2698.60\text{ cm}^{-1}$					
$V_4 = 496.26\text{ cm}^{-1}$					
$k_6 = 0$ (fixed)					
rms= 0.184					

^a was not used in the least-squares fit.

^b the Herzberg-Teller coupling to the $\tilde{\text{A}}^+$ state was neglected.

Table 2:

ν_i^v	$\tilde{\nu}_{\text{obs}}[30]$	$\tilde{\nu}_{\text{calc}}(\text{DVR})^b$	$\tilde{\nu}_{\text{calc}}(\text{Eq. (16)})^c$	$\tilde{\nu}_{\text{calc}}(\text{Eq. (16)})^d$
0_-^0	0.0	0.0	0.0	0.0
0_+^0	-	0.0	0.0	0.0
4_+^1	745.7	746.3	838.0	746.3
4_-^1	-	746.3	838.0	746.3
4_-^2	1463.5 ^a	1464.2	1515.7	1464.2
4_+^2	1464.7 ^a	1464.2	1515.8	1464.2
4_+^3	2144.7 ^a	2146.9	2074.4	2146.6
4_-^3	2149.8 ^a	2147.9	2074.9	2147.9

^a rough estimates from strongly perturbed rotational structure

^b $V_1 = 7369.6 \text{ cm}^{-1}$, $V_2 = 4647.1 \text{ cm}^{-1}$, $V_4 = 234.5 \text{ cm}^{-1}$, $k_6 = 0.0 \text{ cm}^{-1}$

^c $V_1 = 9444.9 \text{ cm}^{-1}$, $V_2 = 4554.6 \text{ cm}^{-1}$, $V_4 = 1021.3 \text{ cm}^{-1}$, $k_6 = 2258.0 \text{ cm}^{-1}$, $\tilde{\nu}_6 = 1911 \text{ cm}^{-1}$

^d $V_1 = 7530.0 \text{ cm}^{-1}$, $V_2 = 4690.9 \text{ cm}^{-1}$, $V_4 = 300.5 \text{ cm}^{-1}$, $k_6 = 0.0 \text{ cm}^{-1}$

Table 3:

n	$\frac{1}{2\pi} B \int_{-\pi}^{\pi} \frac{\exp(\pm i n \gamma)}{(1-C^2 \cos^2(2\gamma))} d\gamma$	$\frac{1}{2\pi} \frac{B^2}{4A} \int_{-\pi}^{\pi} \frac{\cos(2\gamma) \exp(\pm i n \gamma)}{(1-C^2 \cos^2(2\gamma))} d\gamma$
0	$\frac{B}{\sqrt{(1-C^2)}}$	0
± 2	0	$-A(1 - \frac{1}{\sqrt{1-C^2}})$
± 4	$\frac{B}{C^2} \cdot \frac{(2-C^2-2\sqrt{1-C^2})}{\sqrt{1-C^2}}$	0
± 6	0	$-\frac{A}{C^2}(4 - \frac{4}{\sqrt{1-C^2}} - C^2 + \frac{3C^2}{\sqrt{1-C^2}})$
± 8	$\frac{B}{C^4} \cdot \frac{(8+C^4-8\sqrt{1-C^2}+4C^2(-2+\sqrt{1-C^2}))}{\sqrt{1-C^2}}$	0
± 10	0	$-\frac{A}{C^4} \left[16 - \frac{16}{\sqrt{1-C^2}} + C^4(1 - \frac{5}{\sqrt{1-C^2}}) + 4C^2(-3 + \frac{5}{\sqrt{1-C^2}}) \right]$
$C = \frac{B}{2A}$		

Table 4: