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Torsional vibrational structure of the propene radical cation studied by high-resolution photoelectron spectroscopy

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The pulsed-field-ionization zero-kinetic-energy photoelectron spectra of the $\tilde{X}^+{}^2A'' \leftarrow \tilde{X}^1A'$ transition of CH_3CHCH_2 (propene), CD_3CDCD_2 , and several partially deuterated isotopomers have been recorded in the region of their adiabatic ionization thresholds and up to 2000 cm^{-1} of internal energy of the cations. The vibrational structure has been assigned on the basis of the frequency shifts resulting from deuteration of selected sites of the propene molecule. Two highly anharmonic progressions have been identified and assigned to the two torsional modes of the propene cation, the methyl and methylene torsions. The positions of the torsional levels could be approximately reproduced using one-dimensional models, allowing a semi-quantitative description of the potential energy surface along each torsional coordinate. The observation of forbidden vibrational bands and the analysis of their partially resolved rotational contours reveal the importance of the vibronic coupling between the $\tilde{X}^+{}^2A''$ and the $\tilde{A}^+{}^2A'$ states mediated by the methylene (ν_{20}) and methyl (ν_{21}) torsional modes.

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I. INTRODUCTION

Propene is a small hydrocarbon of relevance to atmospheric chemistry and astrophysics^{1,2} and of multiple industrial uses. Propene is also the simplest molecule having a single methyl rotor adjacent to a carbon-carbon double bond and has therefore been the object of several theoretical and experimental studies aiming at a better understanding of the hindered internal rotation of the methyl group.^{3–12}

The far-infrared spectrum of propene was measured by Fateley and Miller³ in the context of a much broader and thorough investigation of the torsional spectra of molecules having a methyl rotor. From the analysis of the spectrum, the parameters V_3 and V_6 describing the potential energy along the methyl torsional coordinate as a Fourier series were determined for the $\tilde{X}^1A'$ ground state of propene. Möller *et al.*⁴ measured the spectrum at higher resolution and succeeded in partially resolving the K_a structure of the main torsional band. Persisting ambiguities in the analysis of the vibrational structure of propene at higher energies were clarified by Silvi *et al.*⁵ who measured the IR and Raman spectra of four isotopic species of propene between 200 cm^{-1} and 4000 cm^{-1} . Durig *et al.*⁶ recorded both the Raman and far-infrared spectra of propene, analyzed the K_a structure and used the results to characterize the torsional motion.

Propene has also been studied extensively by microwave spectroscopy. Lide and Mann⁷ analyzed the microwave spectra of propene and $\text{CH}_3^{13}\text{CHCH}_2$, determined the structure of the molecule, and estimated the torsional potential barrier from the tunneling splittings observed in the microwave spectrum of the ground state. The complete substitution structure of propene (r_s) was derived by Lide and Christensen⁸ from the microwave spectra of seven singly-substituted iso-

topomers and was further refined by Hirota and Morino⁹ who analyzed the spectra of several doubly-deuterated species. A very detailed investigation of the internal rotation of propene has been reported by Hirota¹⁰ who also observed and analyzed the tunneling splittings in the first two excited torsional levels. More recently, the measurements have been extended to the millimeter-wave and submillimeter-wave regions of the electromagnetic spectrum.^{11,12}

The data obtained from microwave and far-infrared studies are complementary. Resolving the line splittings arising from the methyl internal rotation in the ground vibrational state allows for an estimation of the barrier height V_3 . The parameter V_6 , which is the coefficient of the next member of the Fourier-series expansion of the torsional potential, can only be derived if excited torsional states are observed, either in the far-infrared or in the microwave spectra. To interpret a torsional spectrum in the far-infrared region, the reduced internal rotation constant F is needed, which can be derived from the geometrical structure of the molecule as determined from microwave studies. An important aspect of the methyl internal rotation is that it almost always represents a complex motion and not just a pure torsion, and *ab initio* calculations are essential to predict which nuclear motions are coupled to the methyl internal rotation.¹³

In contrast to the considerable efforts invested in the characterization of the neutral species, only little experimental information is available on the propene radical cation. The photoelectron spectrum of the ground cationic state of propene has been recorded at low energy by Burrill and Johnson¹⁴ at a resolution sufficient to observe the vibrational structure. The spectrum consists of many partially overlapping spectral features which renders the assignment of the vibrational structure challenging. Moreover, because of the pronounced anharmonicity of the torsional modes, harmonic frequencies calculated *ab initio* cannot be used to reliably predict the

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FIG. 1. Schematic representation of the eclipsed (a) and staggered (b) conformations of propene. (c) and (d) Definition of the torsional angles α and θ for the CH₃ and CH₂ torsions, respectively. The structures displayed in (c) and (d) correspond to the minimum energy geometries.

positions of the excited torsional states of the propene radical cation. Several assignments proposed in Ref. 14 are ambiguous. For example, the assignment of a vibrational level observed at $\sim 621\text{ cm}^{-1}$ above the ground state of $\text{CH}_3\text{CHCH}_2^+$ to the second overtone of the methyl-torsional mode (21^3) indicates a surprisingly large anharmonicity (in Ref. 14, the fundamental (21^1) and the first overtone (21^2) were reported to be at $\sim 94\text{ cm}^{-1}$ and $\sim 213\text{ cm}^{-1}$, respectively).

The almost complete lack of experimental data on the propene radical cation stands in contrast to the fact that this cation, in particular the height of the torsional barrier along the CH₃-internal rotation coordinate, has been used as a reference system in the discussion of conformational preferences in molecules having CH₃-CH=X functionalities (see Refs. 15 and 16 and in particular also Refs. 17 and 18 for reviews of the early literature). Questions that resulted in much debate are (i) whether the energetically most stable conformation is the eclipsed [Fig. 1(a)] or the staggered [Fig. 1(b)] one, and (ii) what the actual physical or chemical reasons are for the preference of specific conformations in specific electronic states of the neutral and singly-charged anions and cations and in the presence of specific X groups (e.g., X=O, NH, CH₂).

As often the case in physical-organic chemistry, many possible, and not necessarily mutually exclusive explanations can be invoked, such as, in the case of the conformational stability of the CH₃-CH=X molecules, the destabilization of the staggered conformation by the interaction between the fully occupied π_{CH_3} and $\pi_{\text{C=X}}$ orbitals, the stabilization of the eclipsed conformation by the interaction between the π_{CH_3} and $\pi_{\text{C=X}}^*$ orbitals, the opposite effects from $\pi_{\text{CH}_3}^*-\pi_{\text{C=X}}^*$ interactions, the destabilization resulting from the partial four-electron cycles with anti-aromatic character, and the destabilization resulting from the interaction between the central CH bond and the methyl CH bond that is “eclipsed” in the staggered conformation [see Fig. 1(b)]. The discussion of these effects, which can to some extent be rationalized by *ab initio* quantum chemical calculations, contributes to sharpen chemists’ intuition concerning molecular structure.

The development of pulsed-field-ionization zero-kinetic-energy (PFI-ZEKE) photoelectron spectroscopy¹⁹ and the continual improvement of the resolution that can be achieved with this technique^{20–22} makes it possible to obtain information on the methyl-torsional motion of molecular cations^{14,23,24} and to study in detail the effects of removing an electron from bonding π_{CC} orbitals.^{25–27} The questions concerning the relative stability of the eclipsed and staggered conformations of cations containing CH₃-CH=X functionalities can now be answered experimentally. For instance, Kim and his co-workers^{28,29} have exploited mass-analyzed threshold-ionization spectroscopy to study the methyl-torsional motion in $\text{CH}_3\text{-CX=CH}_2^+$ (X=Cl, Br) and found that the eclipsed form [Fig. 1(a)] is favored both in the neutral and the cation, but that the barrier is very strongly reduced (to $\sim 50\text{--}100\text{ cm}^{-1}$) in the cations compared to the neutrals ($\sim 1000\text{ cm}^{-1}$).

The electronic ground state of the propene radical cation has an unpaired electron in the $2a''$ molecular orbital, which is a bonding π_{CC} orbital. Compared to the ground state of the neutral, one therefore expects more torsional flexibility along the bond connecting the HC and CH₂ groups. The propene radical cation should possess two low-frequency, possibly coupled, torsional modes and thus represents an ideal molecular system to study the effects of torsional motions along two adjacent bonds. Photoelectron spectroscopy is well suited to characterize these motions because changes in the torsional potentials that result from ionization lead to the observation of vibrational progressions in the corresponding modes, an advantage that was well demonstrated by the previous investigation by Burrill and Johnson.¹⁴

The general aim of the present work was to characterize and model the vibrational energy level structure of the propene cation at low energies and so obtain a better understanding of the large-amplitude torsional motions. More specific goals were (i) to resolve ambiguities in previous assignments of the low-lying vibrational levels of the propene radical cation by recording photoelectron spectra of several deuterated isotopomers and systematically analyzing the isotopic shifts, (ii) to derive quantitative information on the potential energy surface along the torsional modes, primarily in the form of barrier heights and widths and verify theoretical predictions concerning the relative energies of the conformers and the torsional barrier along the CH₃ internal rotation coordinate, and (iii) to gain information on vibronic interactions in the cation that could complement that obtained in our previous study of the rotational structure of the vibrational ground state,³⁰ and in studies of vibronic interactions in the ground state of C_2H_4^+ .^{25,26,31,32}

II. EXPERIMENTAL

The photoelectron spectra of propene and its deuterated isotopomers were recorded using a vacuum ultraviolet (VUV) laser system with a bandwidth of about 0.2 cm^{-1} .³³ The VUV radiation was generated by resonance-enhanced difference-frequency mixing ($\tilde{\nu}_{\text{VUV}} = 2\tilde{\nu}_1 - \tilde{\nu}_2$) in krypton using two tunable dye lasers. The wave number $\tilde{\nu}_1$ of the tripled output of the first dye laser was held fixed at the position

$2\tilde{\nu}_1 = 94\,092.86\text{ cm}^{-1}$ of the $(4p)^5\ (^2P_{3/2})\ 5p\ [1/2]\ (J = 0) \leftarrow (4p)^6\ (^1S_0)$ two-photon resonance of krypton, and the VUV wave number was scanned by tuning the wave number $\tilde{\nu}_2$ of the second dye laser, which was calibrated using an optogalvanic cell. The VUV wave number was determined with an accuracy of about 0.5 cm^{-1} by calculating the difference $(2\tilde{\nu}_1 - \tilde{\nu}_2)$.

Propene- h_6 (>99% purity) and propene- d_6 (isotopic purity of 99%) were purchased from Aldrich and Isotec, respectively, and were used without further purification. The partially deuterated isotopomers were synthesized following instructions found in the literature^{34–36} and purified to a level of better than 99% as determined by high-pressure liquid chromatography. The identity of the isotopomers was verified by time-of-flight mass spectrometry and photoionization spectroscopy (see gray traces in Fig. 2 below).

Mixtures of about 10%–20% propene in Ar were introduced into the chamber through a pulsed nozzle operated at a stagnation pressure of ~ 3 bar and used to form a supersonic expansion. The supersonic beam was skimmed and subsequently intersected the VUV laser beam at right angles in the photoionization region where the rotational temperature was estimated to be ~ 10 K from the rotational contours of the observed bands of the photoelectron spectra.

To achieve high resolution in the photoelectron spectra, a multipulse electric-field sequence,²¹ delayed by $2.0\ \mu\text{s}$ relative to the time of photoexcitation was applied. The electric fields also accelerated the electrons toward a microchannel-plate detector located at the end of a magnetically shielded time-of-flight tube. The pulse sequence consisted typically of three electric field steps: a positive discrimination pulse of 90 mV/cm and $1\ \mu\text{s}$ duration, followed immediately by two successive 250-ns-long negative extraction pulses of -70 mV/cm and -107 mV/cm . Two time gates were set at the positions corresponding to the times of flight of the electrons produced by these two extraction pulses and the integrated electron signals were recorded as a function of the laser wave number and stored in a personal computer. A good compromise between high resolution and signal-to-noise ratio was reached in the spectra obtained with the -107 mV/cm field pulse. A correction of $(+1.25 \pm 0.3)\text{ cm}^{-1}$ was introduced to compensate for the field-induced shift of the ionization thresholds.²¹ The overview spectra were recorded as described above, but with a simpler two-pulse electric-field sequence consisting of a 90 mV/cm discrimination pulse followed by a -900 mV/cm extraction pulse necessitating a correction of $(+2.2 \pm 0.50)\text{ cm}^{-1}$.

III. RESULTS AND DISCUSSION

A. General considerations

The equilibrium geometry of propene in the $\tilde{X}^1A'$ ground electronic state has been found to be C_s .¹³ The ground-state electronic configuration is $\dots(1a'')^2(9a')^2(10a')^2(2a'')^2$. The HOMO orbital ($2a''$) has a nodal plane containing the three carbon atoms and is predominantly a π orbital with C=C bonding character. Ionization out of this orbital gives rise to the $\tilde{X}^{+2}A''$ ground electronic state of the cation. *Ab initio*

calculations¹⁴ indicate that the plane of symmetry is preserved upon ionization out of this orbital so that the equilibrium geometry of the cation is predicted to be of C_s symmetry, although more sophisticated *ab initio* calculations would be needed to verify this prediction. Propene has 21 nondegenerate normal modes, 14 of a' and 7 of a'' symmetry. The lowest frequency modes in the case of the propene radical cation are the $\nu_{21}(a'')$ and $\nu_{20}(a'')$ normal modes, corresponding predominantly to the methyl internal rotation and the CH_2 torsion, respectively, followed by the CCC bending mode $\nu_{14}(a')$. These modes are energetically well separated from the higher frequency modes so that their numbering does not change upon isotopic substitution. The other vibrational modes of the cation are labeled by indicating the main component of the motion to avoid confusion arising from changes in the numbering of the modes of the different isotopomers.

Upon removal of an electron from the $2a''$ molecular orbital, the C=C bond strength is expected to be weakened and the torsional flexibility enhanced. *Ab initio* calculations predict an increase of the C=C bond length from $1.336 \pm 0.004\text{ \AA}$ (Ref. 8) to about $1.4169\text{ \AA}$.¹⁴ Based on chemical intuition and the Franck-Condon principle, one expects vibrational progressions to be observed in all three low-frequency modes mentioned above, and also in the C=C stretching, the CH_2 deformation and the CH bending modes. Consequently, the photoelectron spectrum of the $\tilde{X}^+ \leftarrow \tilde{X}$ transition of propene has a high density of bands even at low energies and its assignment represents a challenge.

In the photoelectron spectra of the $\tilde{X}^+ \leftarrow \tilde{X}$ transition of propene¹⁴ and its deuterated isotopomers (see Fig. 2 below) the origin band is by far the most intense. The weakness of the low-frequency bands necessitated the use of a large field-ionization pulse (0.9 V/cm) which limited the experimental resolution to about 1 cm^{-1} . Consequently, no rotational structure could be observed for these bands that would have allowed the unambiguous determination of the vibronic symmetry of the cationic levels using rovibronic photoionization selection rules, as was possible for the origin band.³⁰ To nevertheless assign the vibrational structure, the photoelectron spectra of several deuterated isotopomers of propene, CH_3CDCH_2 , CH_3CHCD_2 , CD_3CHCH_2 , and CD_3CDCD_2 , were also recorded and the identity of each vibrational band was deduced from the magnitude of the isotope shifts. Indeed, the Franck-Condon active modes are expected to be unambiguously identifiable by the isotopic shifts caused by deuteration at specific carbon sites. The anticipated effects of such deuterations are summarized in Table I from which one can conclude, for instance, that the 21^1 levels of all CH_3 -containing isotopomers should be located at approximately the same energy but above the energy of the 21^1 levels of the CD_3 -containing isotopomers. In favorable cases, the analysis of the rotational contours of the vibrational bands enabled us to independently confirm the assignments made on the basis of isotopic shifts.

The overview PFI-ZEKE photoelectron spectra of the $\tilde{X}^{+2}A''(\nu_i^{\nu_i}) \leftarrow \tilde{X}^1A'(0^0)$ transitions of (a) CH_3CHCH_2 , (b) CH_3CDCH_2 , (c) CH_3CHCD_2 , (d) CD_3CHCH_2 , and (e) CD_3CDCD_2 in the wave number range from $78\,500\text{ cm}^{-1}$ to

TABLE I. Anticipated magnitude of the isotopic shifts resulting from deuteration at specific carbon sites of the propene radical cation.

Deuteration	CH ₃ torsion $\nu_{21}(a'')$	CH ₂ torsion $\nu_{20}(a'')$	CCC bend $\nu_{14}(a')$	C=C stretch a'	CH ₂ deform. a'	CH bend a'
CH ₃ $\leftrightarrow$ CD ₃	Strong	Vanishing	Weak	Vanishing	Vanishing	Vanishing
CH $\leftrightarrow$ CD	Vanishing	Vanishing	Vanishing	Vanishing	Vanishing	Strong
CH ₂ $\leftrightarrow$ CD ₂	Vanishing	Strong	Weak	Weak	Strong	Vanishing

The assignments of the vibrational bands indicated in Fig. 2 were obtained from the analysis of the isotopic shifts on the basis of the expectations summarized in Table I. The assignments and the spectral positions are presented in Table II. As will be discussed in more detail in Secs. III B–III D, they are in agreement with the results of *ab initio* quantum chemical calculations, and, in the case of the two torsional modes ν_{20} and ν_{21} , they are supported by predictions made in the realm of simple one-dimensional models for the torsional motions.

To facilitate the discussion of the vibrational level structure of the propene radical cation and its deuterated isotopomers presented in Secs. III B and III C, we chose to give the experimentally determined positions relative to the ground state of the ion rather than to the ground state of the neutral molecules as directly measured in the PFI-ZEKE photoelectron spectra. This choice necessitated the determination of the adiabatic ionization energies of each isotopomer at a higher accuracy than the full widths at half maximum of typically 10 – 15 cm⁻¹ of the rotational contours of the origin bands.

In our previous study of the rotational structure of CH₃CHCH₂ and CD₃CDCD₂, the adiabatic ionization energies of these two isotopomers were determined to be 78 602.0(4) cm⁻¹ and 78 759.9(5) cm⁻¹, respectively.³⁰ To determine the adiabatic ionization energies of CH₃CDCH₂, CH₃CHCD₂ and CD₃CHCH₂, the PFI-ZEKE photoelectron spectra of their origin bands were measured at higher resolution, as explained in Sec. II, and the partially resolved rotational structures were analyzed with the procedure described in Ref. 30. The high-resolution spectra of CH₃CDCH₂, CH₃CHCD₂ and CD₃CHCH₂ are displayed in Fig. 3, where the position of the adiabatic ionization energy is indicated by a vertical dotted line centered at the origin of the wave-number scale. The values of the adiabatic ionization energies derived from the analysis of the partially resolved rotational structures are summarized in Table III. The uncertainties of 1 cm⁻¹ or less make an insignificant contribution to the uncertainties of 3 cm⁻¹ or more in the positions of the vibrational levels of the cations determined from the photoelectron spectra displayed in Fig. 2 (see Table II).

B. The low-frequency modes ν_{21} (methyl torsion), ν_{20} (methylene torsion), and ν_{14} (CCC bend)

The assignments of all bands in Fig. 2 was carried out by exploiting the facts that (1) deuteration of the methyl (methylene) group does not strongly affect any vibrational progressions in this region except the methyl (methylene) torsion, and (2) deuteration of the methyl and methylene groups both induce a weak shift of the C–C–C bending levels towards lower

wave number (see Table I). The information contained in the photoelectron spectra of all five isotopomers of propene depicted in Fig. 4 turned out to be necessary for an unambiguous assignment because of an accidental overlap of the positions of the fundamental (20¹) of the methylene torsion and the first overtone (21²) of the methyl torsion in CH₃CHCH₂ (trace (a)), CH₃CDCH₂ (trace (b)) and CD₃CDCD₂ (trace (e)). Indeed, without the spectra of CH₃CHCD₂ (trace (c)) and CD₃CHCH₂ (trace (d)), it would have been much more difficult to recognize, and prove, that the 20₀¹ and 21₀¹ bands, which are nominally forbidden by symmetry in the $\tilde{X}^+{}^2A'' \leftarrow \tilde{X}^1A'$ photoionizing transition, make a significant contribution to the intensity distributions as a result of vibronic interactions. The assignments of all bands observed in Fig. 4 and summarized in Table II are now discussed separately for each progression.

1. The methyl torsion (ν_{21})

According to the *ab initio* calculations of Burrill and Johnson¹⁴ and also to those carried out at the UMP2/6-311G(2d,p) level in the realm of the present study, the methyl torsion is the lowest-frequency mode of the propene cation, with a fundamental wave number expected at a position of ~ 90 cm⁻¹ and ~ 70 cm⁻¹ above the ground state in CH₃- and CD₃-containing isotopes, respectively. In their investigation of the photoelectron spectrum of CH₃CHCH₂, Burrill *et al.* assigned bands located 94 cm⁻¹, 213 cm⁻¹ and 621 cm⁻¹ above the origin to the 21¹, 21², and 21³ levels of CH₃CHCH₂⁺, however, without discussion of the fact that the 21₀¹ and 21₀³ bands are forbidden by symmetry.

The analysis of our spectra confirms the former two assignments, but suggests a different assignment for the 21³ level. The 21¹ levels of all CH₃-containing isotopomers of the propene cations are observed at positions in the range 90 – 100 cm⁻¹ above the respective origins and those of the two CD₃-containing isotopomers in the range 70 – 80 cm⁻¹, leaving no doubt that they correspond to the methyl torsion. Initially, we were tempted to assign these bands to the first overtone (21₀²) of the methyl torsion because of the forbidden nature of the 21₀¹ band; however, our attempts to model the torsional motions on the basis of this assignment (see Sec. III D) were unsuccessful and consistently indicated 21₀¹ as the only possible assignment.

The 21² levels of the CH₃- and CD₃-containing isotopomers of the propene cation are observed in the ranges 200 – 220 cm⁻¹ and 150 – 160 cm⁻¹, respectively. However, as mentioned above, the accidental near degeneracy of the 21² and 20¹ levels in CH₃CHCH₂⁺, CH₃CDCH₂⁺ and CD₃CDCD₂⁺ complicates the assignments. The spectra of CH₃CHCD₂⁺ and

TABLE II. Band centers (in cm^{-1})^a, experimental and calculated vibrational wave numbers and assignment of the low-lying vibrational levels of the propene radical cation and several of its deuterated isotopomers.

Label	C_3H_6^+			$\text{CH}_3\text{CDCH}_2^+$		
	$E_{\text{obs}}^{\text{b}}$	$(E_{\text{obs}} - E_i)^{\text{c}}$	$E_{\text{calc}}^{\text{d}}$	$E_{\text{obs}}^{\text{b}}$	$(E_{\text{obs}} - E_i)^{\text{c}}$	$E_{\text{calc}}^{\text{d}}$
0^0	78602.0(4)	0.0 (0.0) ^e	0.0 0.14	78605.9(10)	0.0	0.0 0.11
21^1	78700(3)	98(3) (94) ^e , [92]	99.2 100.8	78705(3)	99(3) [92]	96.1 97.3
20^1	78822(3)	220(3) (213) ^e , [227]	216.6 216.6	78823(3)	217(3) [223]	213.2 213.2
21^2	78815(7)	213(7) (213) ^e	210.4 219.9	78818(7)	212(7)	204.9 212.8
$20^1 21^1$	78933(4)	331(4)	...	78934(4)	328(4)	...
14^1	79016(4)	414(4) (478) ^e , [421]		79015(4)	409(4) [417]	
21^3	...	... (621) ^e	319.4 359.9	...	...	311.5 346.5
20^2	79084(3)	482(3) ...	486.3 486.3	79083(3)	477(3) ...	478.6 478.6
Label	$\text{CH}_3\text{CHCD}_2^+$			$\text{CD}_3\text{CHCH}_2^+$		
	$E_{\text{obs}}^{\text{b}}$	$(E_{\text{obs}} - E_i)^{\text{c}}$	$E_{\text{calc}}^{\text{d}}$	$E_{\text{obs}}^{\text{b}}$	$(E_{\text{obs}} - E_i)^{\text{c}}$	$E_{\text{calc}}^{\text{d}}$
0^0	78658.7(10)	0.0	0.0 0.12	78695.1(10)	0.0	0.0 0.02
21^1	78751(3)	92(3) [89]	97.4 98.8	78772(3)	77(3) [72]	75.2 75.4
20^1	78825(3)	166(3) [174]	158.5 158.5	78904(3)	209(3) [223]	211.9 211.9
21^2	78857(7)	198(7)	207.2 215.8	78857(3)	162(3)	164.9 166.4
$20^1 21^1$	78932(4)	273(4)	...	...	...	...
14^1	79036(4)	377(4) [381]		79072(3)	377(3) [384]	
21^3	78974(4)	315(4) ...	314.9 352.2	...	...	256.9 265.6
20^2	79013(3)	354(3) ...	352.2 352.2	79158(3)	463(3) ...	475.6 475.6
Label	C_3D_6^+					
	$E_{\text{obs}}^{\text{b}}$	$(E_{\text{obs}} - E_i)^{\text{c}}$	$E_{\text{calc}}^{\text{d}}$			
0^0	78759.9(5)	0.0	0.0 0.01			
21^1	78830(3)	70(3) [68]	70.0 70.1			
20^1	78912(3)	152(3) [165]	149.9 149.9			
21^2	78912(3)	152(3)	154.1 155.0			
$20^1 21^1$	78994(4)	234(4)	...			
14^1	...	[347]	...			
21^3	...	...	241.8 247.0			
20^2	78089(3)	329(3)	332.8 332.8			

^aOnly the transition wave numbers observed in the spectral region from the ionization threshold and up to 500 cm^{-1} of internal energy are listed in this table.^bCorrected for the field-induced shift of the ionization energy.^cThe harmonic vibrational wave numbers calculated *ab initio* at the level of UMP2/6-311(2p,d) are given in square brackets.^dVibrational wave numbers of the torsional levels calculated using a simple one-dimensional model (see text for more details).^eAssignments proposed in Ref. 14.

TABLE III. Adiabatic ionization energies of propene and its deuterated isotopomers.

	C ₃ H ₆	CH ₃ CDCH ₂	CH ₃ CHCD ₂	CD ₃ CHCH ₂	C ₃ D ₆
E_i/cm^{-1} ^a	78602.0(4)	78605.9(10)	78658.7(10)	78695.1(10)	78759.9(5)
Ref.	30	This work	This work	This work	30

^aThe values of the adiabatic ionization energies have been corrected for the field-induced shift. The numbers in parentheses represent the estimated uncertainties.

CD₃CHCH₂⁺ represent the key to the assignment because the 20¹ level of the former isotopomer and the 21² level of the latter one are shifted to lower wave numbers. The shifts enable the observation of both levels as distinct bands in Fig. 4 [see traces (c) and (d)]. The spectrum of CD₃CHCH₂⁺ [trace

FIG. 3. High-resolution PFI-ZEKE photoelectron spectra of the origin bands of (a) CH₃CDCH₂⁺, (b) CH₃CHCD₂⁺, and (c) CD₃CHCH₂⁺. The bands have been aligned so that their centers coincide at the origin.

(d) in Fig. 4] is particularly instructive because it enables the observation of the 21² level in isolation from any other vibrational bands of *a'* symmetry that could perturb the intensity of the 21₀² photoelectron band. The spectrum shows the 21₀² band to be about 2.5 times more intense than the 21₀¹ band, which highlights the Franck-Condon forbidden, but vibronically allowed, nature of the 21₀^v bands with odd *v* values. Intensity perturbations by torsion-rotation coupling, as observed, for instance, in toluene,³⁷ and which can be very significant near the top of the barrier, are not expected to be dominant in the present case. The observation of different line-shapes for the 20₀¹ and 21₀² bands in Figs. 4(c) and 4(d) lends further support to our assignment and provides information on the vibronic coupling mechanism, as will be discussed in Sec. III E.

Higher members of the methyl torsional progressions are too weak to be observed in our spectra with the exception of the spectrum of CH₃CHCD₂⁺ which could be recorded with a particularly high signal-to-noise ratio. As will be explained in more detail in Subsection III D, we assign the very weak line observed at 315 cm⁻¹ in trace (c) of Fig. 4 to the lower tunneling component of the 21³ level that is located close to the maximum of the potential barrier along the methyl torsional coordinate. In their study of the photoelectron spectrum of undeuterated propene, Burrill and Johnson¹⁴ assigned a level observed at 621 cm⁻¹ to the 21³ level. The assignment of this level, which is also observed as a very weak band in our spectrum, is incompatible with our observations, which instead suggest the 20²21¹ combination band as a possible, more plausible assignment.

2. The methylene torsion (ν_{20}) and the CCC bend (ν_{14})

Upon removal of an electron from the outermost occupied orbital of *a''* symmetry, which has a dominant π_{CC} bonding character, the π_{CC} bond is weakened and the torsional flexibility around this bond enhanced, as mentioned above. One of the consequences is a very strong reduction of the fundamental wave number of the CH₂ torsional mode from 990 cm⁻¹ in the ground state of CH₃CHCH₂⁵ to only about 230 cm⁻¹ in the ground state of CH₃CHCH₂⁺ according to *ab initio* calculations (see Table II). This prediction is confirmed by our analysis which identifies the fundamental of the methylene torsion at ~ 220 cm⁻¹ in the CH₂-containing isotopomers and at ~ 160 cm⁻¹ in the CD₂-containing isotopomers (see Table II and Fig. 4).

The first overtone of the methylene torsion can also readily be assigned on the basis of isotopic shifts to the spectral features observed at ~ 470 cm⁻¹ and ~ 350 cm⁻¹ in the CH₂- and CD₂-containing isotopomers, respectively. Like the

FIG. 4. Enlarged view of the PFI-ZEKE photoelectron spectra of propene at low energies. The stick spectra indicate the calculated positions of the methyl and methylene torsional levels in (a) $\text{CH}_3\text{CHCH}_2^+$, (b) $\text{CH}_3\text{CDCH}_2^+$, (c) $\text{CH}_3\text{CHCD}_2^+$, (d) $\text{CD}_3\text{CHCH}_2^+$, and (e) $\text{CD}_3\text{CDCH}_2^+$ according to one-dimensional torsional models (see text for details). In trace (a), the assignments of Ref. 14 that differ from ours are given in parentheses. The dashed lines indicate the parts of the progressions that were not observed experimentally but are predicted by our one-dimensional model.

methyl torsional mode, the methylene torsional mode of the propene cation is thus also characterized by a positive anharmonicity, which indicates that the potential along these torsional modes is flat in the vicinity of the minima. The spectra of CH_3CHCD_2 and CD_3CHCH_2 , which enable the observation of the 20^1 and 20^2 levels of the cations as isolated spectral features, indicate that the 20_0^2 band is about twice as strong as the 20_0^1 band. As explained above, the 20_0^1 band is forbidden by symmetry. The observed intensity distribution thus betrays a vibronic interaction between the $\tilde{X}^+ 2A''$ ground state of the propene cation and a higher lying $2A'$ electronic state mediated by the methylene torsion (see Sec. III E for a more detailed discussion).

Our assignment of the 20_0^2 band at 482 cm^{-1} in the photoelectron spectrum of CH_3CHCH_2 differs from that proposed by Burrill and Johnson who have assigned it to the 14_0^1 band on the basis of a harmonic wave number of 420 cm^{-1} calculated *ab initio* for the CCC bending mode.¹⁴ Our spectra (see Fig. 4) indicate that the 14_0^1 band of CH_3CHCH_2 corresponds to the band observed at 414 cm^{-1} , which Burrill and Johnson have assigned to the $20_0^121_0^1$ combination band.

Our spectra only enable the observation of a single combination band, $20_0^121_0^1$, which is observed at $78\,933\text{ cm}^{-1}$ in the spectrum of CH_3CHCH_2 [Fig. 2(a), 331 cm^{-1} of internal energy in the cation] and is subject to the isotopic shifts anticipated on the basis of the spectra of the other isotopomers (see Figs. 2 and 4 and Table I). This assignment indicates a

positive anharmonic shift in the range $12 - 14\text{ cm}^{-1}$ which indicates that the two torsional modes are coupled.

C. Assignments of other modes

Because of the existence of several low-frequency vibrational modes in the propene cation, the density of the vibrational levels increases rapidly with increasing wave number. Numerous perturbations result which render a detailed analysis of the spectrum at the resolution achieved in our investigation impossible. Consequently, we only present here a tentative interpretation and qualitative analysis of the main spectral features observed at internal energies of the cations beyond the first members of the torsional progressions discussed in Secs. III A and III B.

1. The C=C stretching mode

In all spectra presented in Fig. 2, except that of CH_3CHCD_2 (panel (c)), an intense line is observed in the wave-number range between 1450 cm^{-1} and 1550 cm^{-1} . This line can be assigned to the fundamental of the C=C stretching mode, 6^1 , on the basis of the very weak isotopic shifts observed upon deuteration (see Table I). The spectrum of $\text{CH}_3\text{CHCD}_2^+$ reveals two lines in this region, so that the 6^1 level of this isotopomer appears to be perturbed by a close-lying a' vibrational level with which it shares its intensity.

TABLE IV. Band centers, experimental and calculated^a vibrational wave numbers and their assignment for the propene radical cation and several of its deuterated isotopomers at high energies.

	C ₃ H ₆	CH ₃ CDCH ₂	CH ₃ CHCD ₂	CD ₃ CHCH ₂	C ₃ D ₆
CH ₂ rock	79851	79795	79405	79940	79671
	1249 [1240]	1189 [1228]	746 [801]	1245 [1221]	911 [954]
CH bend	79875	79433	79919	79965	79702
	1273 [1287]	827 [834]	1260 [1302]	1270 [1297]	942 [970]
6 ¹	80131	80108	80178	80209	80205
	1529 [1599]	1502 [1577]	1519 [1572]	1514 [1586]	1445 [1498]
6 ¹ 2 ¹²	80321	...	...	...	80347
	1719				1587
6 ¹ 20 ¹	80334	...	...	...	80347
	1732				1587

^aThe numbers in square brackets are the harmonic wave numbers calculated *ab initio* at the UMP2/6-311G(2d,p) level.

Weak bands observed at around 1720 cm⁻¹ (80 321 cm⁻¹) and 1600 cm⁻¹ (80 347 cm⁻¹) in the spectra of CH₃CHCH₂⁺ (panel (a)) and CD₃CDCH₂⁺ (panel (e)), respectively, are assigned to the combination bands 6₀¹21₀² and 6₀¹20₀¹ because their positions relative to the 6₀¹ band correspond closely to the positions of the 21² and 20¹ levels relative to the respective ground states of the cations. These assignments are summarized in Table IV.

2. The CH₂-deformation and CH-bending mode

The spectra of CH₃CHCH₂⁺ and CD₃CHCH₂⁺ in panels (a) and (d) of Fig. 2 display a doublet between 1200 cm⁻¹ and 1300 cm⁻¹, which shifts to the region between 900 cm⁻¹ and 950 cm⁻¹ upon full deuteration (panel (e)). Deuteration at the central (panel (b)) or methylenic (panel (c)) positions results in a shift to lower wave number of only one of the two lines. From Table I, one can conclude that the corresponding vibrational motions involve primarily the CH-CH₂ part of the molecule. The general considerations presented in Subsection III A further enable us to assign these two bands to the fundamentals of the CH₂-deformation and CH-bending modes. Harmonic wave numbers obtained in *ab initio* calculations performed at the UMP2/6-311G(2d,p) level (see Table IV) support these assignments.

The fundamental of the CH(CD) bending mode in CH₃CDCH₂⁺ and CH₃CHCD₂⁺ and of the CD₂ deformation mode in CH₃CHCD₂⁺ are observed within clusters of transitions, which results in ambiguities and additional uncertainties in their positions. The wave numbers listed in Table IV correspond, in each case, to the intensity maxima of the line clusters indicated by the dashed lines in Fig. 2.

D. One-dimensional models for the methyl and methylene torsional motions in the propene cation

The photoelectron spectra of propene and several deuterated isotopomers presented in Secs. III A–III C are dominated, at low energies, by two vibrational progressions in the methyl (ν₂₁) and methylene (ν₂₀) torsional modes, which both reveal a positive anharmonicity. The positive anharmonic shifts of the 20¹21¹ levels further indicate a significant an-

harmonic coupling between these modes. Our data, however, do not contain sufficient information on combination levels 20^v21^{v'} to justify a two-dimensional modeling of the coupled methyl and methylene motions. However, the observation of the fundamental and the first overtone of both modes, and in the case of CH₃CHCD₂⁺ the tentative assignment of the second overtone 21³ of the methyl torsion, make it possible to obtain a semi-quantitative estimate of the potential barriers separating the equivalent equilibrium structures along these torsional motions in the realm of simple one-dimensional models. Clearly, the significance of one-dimensional models of the coupled torsional motions in a molecular ion such as propene must not be overestimated; their main merits are (1) to offer qualitative insights on the effect of photoionization on the torsional flexibility in a simple alkene and (2) to provide supporting evidence for the spectral assignments differing from earlier assignments.

In the case of the methyl internal rotation, the Hamiltonian for the one-dimensional motion is given by the expression

$$\hat{H} = -F \frac{\partial^2}{\partial \alpha^2} + V(\alpha), \quad (1)$$

where α is the internal-rotation angle defined in Fig. 1(c) and F is the reduced rotational constant accounting for the motion of the methyl rotor around the axis of the methyl group

$$F = \hbar^2 / 2r I_\alpha. \quad (2)$$

The quantity $r I_\alpha$ is interpreted as the reduced moment of inertia of the internal rotation of the CH₃ group relative to the rigid molecular frame,^{38–40} r being a reduction factor defined as

$$r = 1 - \sum_g \frac{\lambda_g^2 \cdot I_\alpha}{I_g}. \quad (3)$$

I_α is the moment of inertia of the methyl top about its symmetry axis, I_g ($g = a, b, c$) are the principal moments of inertia fixed in the frame part of the molecule, and λ_g are the direction cosines between the top axis and the principal axes. $V(\alpha)$ is the one-dimensional torsional potential function, which has a period of $2\pi/N$ and can therefore be represented by a

TABLE V. Experimentally determined and *ab initio* calculated[§] potential energy parameters for the methyl internal rotation and the CH₂ torsion in propene and the propene radical cation.

Neutral ($\tilde{X}^1A'$)			Cation ($\tilde{X}^+{}^2A''$)		
CH ₃ torsion					
V_3/cm^{-1}	V_6/cm^{-1}	Ref.	V_3/cm^{-1}	V_6/cm^{-1}	Ref.
708.5	−21.2	6	429		14 [§]
693.7	−14.0	6	395.3		29 [§]
692.4 ± 6		7			
698.4 ± 0.5	−13 ± 2	10	A^a/cm^{-1}	$c^a/\text{degrees}$	Ref.
682.9	−4.78	45	400	17	This work
689.1	−13.5 ^b	13 [§]			
684.7		29 [§]			
CH ₂ torsion					
			A^a/cm^{-1}	$c^a/\text{degrees}$	Ref.
			8000(−CH ₂)	23	This work
			8900(−CD ₂)	23	This work

^aIn the case of the cation, the potential energy barrier along the torsional coordinate was described by a gaussian function the height and width of which are determined by the parameters A and c , respectively (see text for more details).

^b $V_9 = 0.2 \text{ cm}^{-1}$.

Fourier-series expansion

$$V(\alpha) = \frac{V_N}{2}(1 - \cos N\alpha) + \frac{V_{2N}}{2}(1 - \cos 2N\alpha) + \dots, \quad (4)$$

with $N = 3$. In the case of the CH₂ torsion, we use similar expressions, the only differences being the definition of the torsional angle, which we label θ as defined in Fig. 1(d), and the period of the potential function, which is given by $2\pi/N$ with $N = 2$.

The one-dimensional Schrödinger equation corresponding to Eq. (1) was solved numerically using a discrete variable representation^{41,42} on a equidistant grid of 51 points over a range of 2π and a calculation of I_α and I_g in the way implemented by Makarewicz in Ref. 43. Initial calculations relied on the equilibrium geometry of the cation optimized *ab initio* at the level of UMP2/3-611G(2d,p).

Attempts at fitting the potential parameters to the vibrational term energies observed experimentally retaining only the first two terms of the expansion in Eq. (4) revealed that a reasonable agreement with the experimental observations can only be reached if the ratio $|V_{2N}/V_N|$ exceeds the value of 20%, the parameter V_{2N} being negative. The large negative value of V_{2N} signifies that the potential energy surface along each torsional coordinate has a flat bottom and implies that higher-order terms should be retained in the Fourier-series expansion. Because only the fundamental and the first overtone of ν_{21} and ν_{20} are observed in most spectra, the experimental data are insufficient to reliably determine the potential parameters V_{iN} . Instead of using Eq. (4), the potential barriers along the torsional motion of the CH₃ or CH₂ group were described as sums of Gaussian functions

$$f(x) = A \sum_b \exp\left(\frac{-(x-b)^2}{2c^2}\right), \quad (5)$$

where A represents the height of the barriers, b their central positions and c their width. To obtain a periodic potential, the parameter b was given the values $\pm 60^\circ$ and $\pm 180^\circ$ in the case of the methyl torsion and $\pm 90^\circ$ and $\pm 270^\circ$ in the case of

the methylene torsion, and the calculations were performed in the intervals $-180^\circ \leq \alpha \leq +180^\circ$ and $-90^\circ \leq \theta \leq +270^\circ$, respectively.

The advantage of Eq. (5) is that each potential is only described by two potential parameters A and c . A and c were adjusted until a good agreement with the experimental vibrational wave numbers was obtained. The optimized values of the potential parameters are presented in Table V and the corresponding calculated vibrational wave numbers of the torsional sublevels are compared with the experimental values in Table II. The calculated positions are also indicated by vertical bold lines in Fig. 4 to facilitate the comparison with the experimental observations. The transition intensities were not calculated because the bands 20_0^v and 21_0^v with odd v values derive their intensities from vibronic interactions, as explained in Subsection III E. The height of the vertical bold lines in Fig. 4 was thus chosen so as to match the experimentally observed intensities.

With one set of parameters, $A = 400 \text{ cm}^{-1}$ and $c = 17^\circ$, it was possible to reproduce satisfactorily the progressions associated with ν_{21} for all isotopomers, i.e. more than 10 line positions, as shown in Fig. 4. The agreement between the results of our one-dimensional calculations and the experimental results is overall very satisfactory, the only exception being the 21^2 level of $\text{CH}_3\text{CHCD}_2^+$, the position of which appears to be overestimated by the calculations. We thus conclude that our one-dimensional model is likely to predict reliable order-of-magnitude estimates of the tunneling splittings. The predicted tunneling splitting of the origin (0.14 cm^{-1}) and the 21^1 level (1.6 cm^{-1}) are too small to be observed at our spectral resolution; the predicted splitting of the 21^2 level (9.5 cm^{-1}) may be responsible for the broader and asymmetric lineshapes of the 21_0^2 bands (Figs. 4(c) and 4(d), see also Fig. 7 in Sec. III E). The calculations also support our tentative assignment of the 21_0^3 band in the spectrum of CH_3CHCD_2 (see Fig. 4(c)), and suggests that it corresponds to a transition to the tunneling component of e symmetry.

FIG. 5. Potential energy function along the CH_3 torsional motion and CH_3 torsional levels of propene in its ground neutral (Refs. 6 and 13) and ground cationic state (see Tables II and V). The arrows depict the transitions from the ground electronic state of CH_3CHCH_2 to the ground electronic state of $\text{CH}_3\text{CHCH}_2^+$ that were observed experimentally. The dashed arrow depicts the transition from $v'' = 0$ to the lower component of the $v' = 3$ vibrational level which was only observed in the photoelectron spectrum of CH_3CHCD_2 (at a different position). For comparison, the fully relaxed *ab initio* potential energy along the methyl coordinate calculated at the UMP2/6-311G(2d,p) level without zero-point-energy corrections is shown by a dashed line.

The potential energy functions along the methyl-torsion coordinate of the neutral species and the cation are displayed in the lower and upper panels of Fig. 5, respectively. Ionization out of the double bond leads to a significant reduction of the barrier to $\sim 400 \text{ cm}^{-1}$ and to a more pronounced flat-bottom nature of the potential energy function near the minima, which suggests that the torsion of the methyl group around the top axis is almost free in a region of more than ± 10 degrees around the equilibrium position. On the left-hand side of the upper panel of Fig. 5, the potential energy function calculated *ab initio* at the UMP2/6-311G(2d,p) level without including zero-point-energy corrections is displayed with a dashed line. The barrier height is estimated to be 429 cm^{-1} which is in good agreement with the barrier height of 400 cm^{-1} resulting from our one-dimensional analysis. However, the *ab initio* calculations do not reproduce the large widths of the potential wells predicted by our one-dimensional model.

The coefficients of the Fourier-series expansion [Eq. (4)] were determined by a fit to a set of 69 points calculated according to Eq. (5) with $A = 400 \text{ cm}^{-1}$ and $c = 17^\circ$ in

the interval $-60^\circ \leq \alpha \leq 60^\circ$. The results of the fit are $V_3 = 381.9 \pm 0.1 \text{ cm}^{-1}$, $V_6 = -117.9 \pm 0.1 \text{ cm}^{-1}$, $V_9 = 16.66 \pm 0.02 \text{ cm}^{-1}$, and $V_{12} = -1.088 \pm 0.020 \text{ cm}^{-1}$. These results explain why our attempts at determining the potential parameters of Eq. (4) remained unsuccessful. The same procedure was followed to estimate the potential energy function along the methylene torsion. However, it was not possible to reproduce the experimentally observed positions of all different propene isotopomers with the same set of potential parameters. For the three CH_2 -containing isotopomers, the optimal values of the potential parameters were found to be $A = 8000 \text{ cm}^{-1}$ and $c = 23^\circ$, whereas for the two CD_2 -containing isotopomers a reasonable agreement with the experimental results could only be obtained by increasing the barrier height to 8900 cm^{-1} keeping the value of c unchanged. The potential parameters are summarized in Table V and the calculated positions of the methylene torsional levels are compared to the experimental results in Table II and are also indicated with vertical lines in Fig. 4 to facilitate the comparison.

The potential energy functions resulting from our one-dimensional analysis of the methylene torsion of the propene

FIG. 6. Potential energy functions along the CH_2 torsional coordinate of the propene radical cation depicted as full (dashed) lines for the CH_2 - (CD_2 -) containing isotopomers. The lowest CH_2 -torsional levels calculated for the undeuterated species are indicated by horizontal lines.

radical cation are depicted in Fig. 6 as full (dashed) lines for the CH_2 - (CD_2 -) containing isotopomers. The calculations indicate that the tunneling splittings resulting from the methylene torsion are negligible at our spectral resolution in the energy range studied experimentally.

E. Vibronic coupling

The observation of the 20_0^v and $21_0^{v'}$ torsional bands with odd values of v and v' in the photoelectron spectrum of propene indicates the presence of vibronic interactions. Indeed, these bands have zero Franck-Condon factors. Vibronic interactions had also to be invoked to explain the prominent central rotational branch with $\Delta K_a = K_a^+ - K_a'' = 0$ and $\Delta N = N^+ - N'' = 0$ in the spectrum of the 0_0^0 origin bands of the $\tilde{X}^+ \leftarrow \tilde{X}$ photoionizing transitions of CH_3CHCH_2 and CD_3CHCH_2 , which correspond to the ejection of an electron from the outermost molecular orbital of a'' symmetry. This orbital has a nodal plane containing the three carbon atoms, and its single-center expansion consists primarily of $(\ell'' = 1, \lambda'' = \pm 1)$, $(\ell'' = 2, \lambda'' = \pm 1)$ and $(\ell'' = 2, \lambda'' = \pm 2)$ contributions, $\lambda'' = \pm 0$ being forbidden by symmetry (see Ref. 30 for a complete discussion). In the orbital ionization approximation,⁴⁴ the rotational selection rules can be expressed as $(\Delta N, \Delta K_a) = (\ell'', \lambda'')$. The observation of a $\Delta K_a = 0$ branch thus indicates an admixture of an a' molecular orbital contribution at geometries deviating from C_s symmetry.

The rotational contours of the bands observed in Figs. 2 and 4, in particular those of the forbidden 20_0^1 and 21_0^1 bands, contain additional information on the vibronic interaction. The relevant regions of the spectra of CH_3CHCH_2 and CD_3CHCH_2 , in which the 20_0^1 band is observed as isolated band, are displayed on an enlarged scale in Fig. 7. The figure reveals that the 20_0^1 and 21_0^1 bands have a similar asymmetric lineshape with a narrow spike on its low-frequency side that differs from the more symmetric lineshapes of the allowed 21_0^2 and other Franck-Condon allowed bands.

As explained in Refs. 25 and 44, the rotational structure of Franck-Condon forbidden transitions directly reflects the symmetry and molecular-orbital structure of the electronic state that is coupled by vibronic interactions. The rotational contours of the 20_0^1 and 21_0^1 bands could be modelled by assuming that the vibronic coupling is primarily to the $\tilde{A}^+$ state which is formed by removing an electron from the $10a'$ orbital depicted in the inset of Fig. 7. Characteristic features of this orbital are the significant $\lambda'' = 0$ contributions and the slow convergence of the single-center expansion with ℓ'' and λ'' , which result in the sharp central feature and several ΔK_a branches on both sides of this spectral feature (see Fig. 7).

Compared to the relative branch intensities $(\Delta N, |\Delta K_a|) = (\ell'', |\lambda''|)$ of $(0, 0) = 0.4$, $(1, 1) = 0.3$, $(2, 1) = 1.3$ and $(2, 2) = 0.6$ used to reproduce the rotational structure of the 0_0^0 origin band³⁰ and of other Franck-Condon allowed bands, relative branch intensities of $(0, 0) = 0.3$, $(1, 0) = 0.3$, $(1, 1) = 0.5$, $(2, 0) = 0.3$, $(2, 1) = 0.4$ and $(2, 2) = 0.8$ were used to reproduce the contours of the Franck-Condon forbidden 20_0^1 and 21_0^1 bands. The $|\lambda''| = 1$ components correspond to orbital contributions with a yz nodal plane, because there cannot be an xz nodal plane by symmetry (see inset of Fig. 7). In the calculations presented in Fig. 7, the rotational constants of the neutral and cationic species were held fixed to either the experimentally determined values⁹ when available or to the values predicted by *ab initio* calculations at the MP2/6-311G(2d,p) level. The calculated rotational contours of the 21_0^1 and 20_0^1 bands of CH_3CHCH_2 and of the 20_0^1 band of CD_3CHCH_2 (orange traces in Fig. 7) reproduce the experimentally observed contours well and show the characteristic features of transitions to cationic vibronic levels of a' symmetry discussed above. The calculated contours of the 20_0^2 bands of CD_3CHCH_2 and CH_3CHCH_2 (dashed magenta traces) are overall broader. Whereas in the former case the calculated and experimental spectra resemble each other closely, the calculated spectrum of CH_3CHCH_2 appears narrower than the experimental

FIG. 7. Enlarged view of the PFI-ZEKE photoelectron spectra of (a) $\text{CH}_3\text{CHCD}_2^+$ and (b) $\text{CD}_3\text{CHCH}_2^+$ at low energies. The calculated rotational contours of the bands having a'' (a') vibrational symmetry are shown with a solid orange line (dashed magenta line). The inset in a) shows a schematic diagram of the $10a'$ orbital of neutral propene based on a Hartree-Fock calculation.

spectrum. We attribute this difference to the tunneling splitting of the 21^2 torsional level of $\text{CH}_3\text{CHCD}_2^+$, which is significantly higher ($\sim 8.6\text{ cm}^{-1}$) than in $\text{CD}_3\text{CHCH}_2^+$ ($\sim 1.5\text{ cm}^{-1}$) according to our one-dimensional calculations (see Table II).

The comparison of calculated and experimental contours does not only confirm the vibrational assignments made on the basis of isotopic substitution, it also indicates that the two torsional modes mediate the vibronic interactions between the $\tilde{X}^+{}^2A''$ and $\tilde{A}^+{}^2A'$ electronic states. This vibronic interaction is probably one of the reasons for the flat-bottom nature of the effective one-dimensional torsional potentials derived in Subsection III D.

IV. SUMMARY AND CONCLUSIONS

The PFI-ZEKE photoelectron spectra of the $\tilde{X}^+ \leftarrow \tilde{X}$ photoionizing transition of propene and several deuterated isotopomers have enabled us to obtain new information on the low-frequency modes of the propene cation, in particular on the methyl (ν_{21}) and methylene (ν_{20}) torsions, which are observed as vibrational progressions with a characteristic, strong positive anharmonicity. The systematic analysis of isotopic shifts resulting from deuteration at specific carbon sites was essential in deriving unambiguous assignments.

Upon removal of an electron from the π_{CC} bonding orbital, the flexibility of propene along both the methyl and methylene torsional modes is considerably enhanced. The

following conclusions can be drawn from an analysis of the observed positions of the torsional levels with simple one-dimensional models:

(1) The potential barriers separating equivalent equilibrium structures along the methyl and methylene torsion in the cation are much reduced compared to the neutral molecule to $\sim 400\text{ cm}^{-1}$ ($\sim 700\text{ cm}^{-1}$ in neutral propene) in the case of the methyl torsion and $\sim 8000\text{ cm}^{-1}$ ($\gg 10000\text{ cm}^{-1}$ in neutral propene) in the case of the methylene torsion, and so are the corresponding vibrational frequencies. The eclipsed conformation is the most stable both in the neutral and the cation. The magnitude of the reduction of the barrier along the methyl torsion corresponds closely to that predicted theoretically by Dorigo *et al.*¹⁸ As pointed out by these authors, the dominant effect favoring the eclipsed conformation is the repulsion of the methyl C–H and the central C–H bonds, which destabilizes the staggered conformation.

(2) The one-dimensional potential energy functions that best describe the experimental observations are unusually flat near the equilibrium geometries and give rise to pronounced positive anharmonicities. A similar, though less pronounced effect observed in the methyl torsion of neutral propene has been attributed to the fact that this torsional mode is not localized but involves motions of the CH_2 group and the central CH bond resulting in a flat-bottom effective one-dimensional minimum-energy path and a negative V_6 coefficient.¹³ In the propene radical cation, the vibronic coupling to the $\tilde{A}^+{}^2A'$ state probably contributes to accentuate the flat-bottom nature of the effective one-dimensional torsional potentials.

(3) The observation of the 20_0^1 and 21_0^1 bands, which are forbidden in first approximation, indicates that vibronic interaction of the $\tilde{X}^+ 2A''$ ground state of the cation with higher-lying electronic states of A' symmetry mediated by the methyl and methylene torsions are important. This observation corroborates the observation made in our previous study of the rotational structure of the origin band of the photoelectron spectrum of CH_3CHCH_2 and CD_3CDCD_2 which could only be explained by invoking vibronic interactions.³⁰ The analysis of the rotational contours of the "forbidden" 20_0^1 and 21_0^1 bands indicates that the vibronic coupling to the $\tilde{A}^+ 2A'$ state of the cation, which is formed by removing an electron from the $10a'$ molecular orbital of the neutral molecule, plays an important role and is mediated by the torsional vibrational motions. More generally, our results imply that the treatment of large-amplitude torsional motions and conformational changes in radical cations with unsaturated backbones should include excited electronic configurations and vibronic-coupling effects.

The one-dimensional analysis of the methyl and methylene torsions in the propene radical cation represents a first step towards a full characterization of the vibronic interactions and large-amplitude motions in the $\tilde{X}^+ 2A''$ ground state. High-level *ab initio* calculations including vibronic interactions and experiments at still higher resolution would be particularly useful to reach this goal and also to assess the limits of the simple models employed in our analysis.

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