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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 Miller$^3$ 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 Mann$^7$ analyzed the microwave spectra of propene and CH$_3$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 ($\nu_4$) was derived by Lide and Christensen$^8$ from the microwave spectra of seven singly-substituted isotopomers and was further refined by Hirota and Morino$^9$ who analyzed the spectra of several doubly-deuterated species. A very detailed investigation of the internal rotation of propene has been reported by Hirota$^{10}$ 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 Johnson$^{14}$ 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
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 ~621 cm\(^{-1}\) above the ground state of CH\(_3\)CHCH\(_2\)\(^+\) to the second overtone of the methyl-torsional mode (~213) indicates a surprisingly large anharmonicity (in Ref. 14, the fundamental (~211) and the first overtone (~212) were reported to be at ~94 cm\(^{-1}\) and ~213 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 CH\(_3\)-internal rotation coordinate, has been used as a reference system in the discussion of conformational preferences in molecules having CH\(_3\)-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, CH\(_2\)).

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 CH\(_3\)-CH=X molecules, the destabilization of the staggered conformation by the interaction between the fully occupied \(\pi\) and \(\pi^*\) orbitals, the stabilization of the eclipsed conformation by the interaction between the \(\pi\) and \(\pi^*\) orbitals, the opposite effects from \(\pi\)-CH= and \(\pi^*-\pi^*\) 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 \textit{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 spectroscopy\(^{19}\) and the continual improvement of the resolution that can be achieved with this technique\(^{20\text{-}22}\) 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 \(\pi\) orbitals.\(^{25\text{-}27}\) The questions concerning the relative stability of the eclipsed and staggered conformations of cations containing CH\(_3\)-CH=X functionalities can now be answered experimentally. For instance, Kim and his co-workers\(^{26,29}\) have exploited mass-analyzed threshold-ionization spectroscopy to study the methyl-torsional motion in CH\(_3\)-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 \(\sim50\text{-}100\) cm\(^{-1}\)) in the cations compared to the neutrals (\(\sim1000\) cm\(^{-1}\)).

The electronic ground state of the propene radical cation has an unpaired electron in the 2\(\alpha\) molecular orbital, which is a bonding \(\pi\) orbital. Compared to the ground state of the neutral, one therefore expects more torsional flexibility along the bond connecting the HC and CH\(_2\) 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 CH\(_3\) 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\(_2\)H\(_4\)\(^+\).\(^{25,26,31,32}\)

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 (\(\nu_{\text{VUV}} = 2\nu_1 - \nu_2\)) in krypton using two tunable dye lasers. The wave number \(\nu_1\) of the tripled output of the first dye laser was held fixed at the position...
Propene-$\delta_6$ (>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 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 UV 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, delayed by 2.0 µs 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 µs 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 accuracy of about 0.5 cm$^{-1}$ by calculating the difference (2$\tilde{v}_1$ − $\tilde{v}_2$).

The overview PFI-ZEKE photoelectron spectra of the (X$^+$) and its assignment represents a challenge. In the photoelectron spectra of the 2$\tilde{a}''$ transition of propene$^{14}$ 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. To nevertheless assign the rotational structure, the photoelectron spectra of several deuterated isotopomers of propene, CH$_2$CDCH$_2$, CH$_3$CHCD$_2$, CD$_3$CHCH$_2$, and CD$_3$CDDC, 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 2$\tilde{a}''$ levels of all CH$_3$-containing isotopomers should be located at approximately the same energy but above the energy of the 2$\tilde{a}''$ 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 X$^+$ shows transitions of (a) CH$_3$CHCH$_2$, (b) CH$_3$CDCH$_2$, (c) CH$_3$CHCD$_2$, (d) CD$_3$CHCH$_2$, and (e) CD$_3$CDDC$_2$ in the wave number range from 78 500 cm$^{-1}$ to 124 310 cm$^{-1}$ (2011)
FIG. 2. Survey PFI-ZEKE photoelectron spectra of the $\tilde{X}^+ \rightarrow \tilde{X}$ transition in (a) CH$_3$CHCH$_2$, (b) CH$_3$CDCH$_2$, (c) CH$_3$CHCD$_2$, (d) CD$_3$CHCH$_2$, and (e) CD$_3$CDCD$_2$. The gray traces correspond to the photoionization spectra. The assignments of the vibrational bands in CH$_3$CHCH$_2$ of Ref. 14 that differ from ours are indicated by dotted vertical lines in panel (a). The assignments of the bands at high energy are tentative and are indicated by dashed diagonal lines.

80 500 cm$^{-1}$ are presented in Fig. 2. In each panel, the bottom horizontal axis corresponds to the VUV wave number, and the top horizontal axis to the internal wave number of the cations. The gray traces correspond to the photoionization spectra, obtained by monitoring the ion yield as a function of the VUV wave number. The sharp and strong rise of the photoionization signal from the zero level at the positions where the first bands in the PFI-ZEKE photoelectron spectra are observed confirms that these are the origin bands ($0_0^0$) of the corresponding isotopomers.
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 \( \nu_{20} \) and \( \nu_{21} \), 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–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 CH\(_3\)CHCH\(_2\) and CD\(_3\)CCHCD\(_2\), 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 CH\(_3\)CDCH\(_2\), CH\(_3\)CHCD\(_2\) and CD\(_3\)CCHCH\(_2\), 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 CH\(_3\)CDCH\(_2\), CH\(_3\)CHCD\(_2\) and CD\(_3\)CCHCH\(_2\) 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).

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

<table>
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<th>Deuteration</th>
<th>CH(_3) torsion</th>
<th>CH(_2) torsion</th>
<th>CCC bend</th>
<th>C=C stretch</th>
<th>CH(_2) deform.</th>
<th>CH bend</th>
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<td>Vanishing</td>
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<td>Weak</td>
<td>Weak</td>
<td>Strong</td>
<td>Vanishing</td>
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The assignments of all bands in Fig. 2 was carried out by exploiting the facts that (1) deuteration of the methyl (methylenne) 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 (20\(^1\)) of the methylene torsion and the first overtone (21\(^2\)) of the methyl torsion in CH\(_3\)CHCH\(_2\) (trace (a)), CH\(_3\)CDCH\(_2\) (trace (b)) and CD\(_3\)CCHCD\(_2\) (trace (e)). Indeed, without the spectra of CH\(_3\)CHCD\(_2\) (trace (c)) and CD\(_3\)CHCH\(_2\) (trace (d)), it would have been much more difficult to recognize, and prove, that the 20\(_0\) and 21\(_0\) bands, which are nominally forbidden by symmetry in the \( \tilde{X}^{1}\AA' ← \tilde{X}^{1}\AA'' \) 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 (\( \nu_{21} \))

According to the ab initio calculations of Burrill and Johnson\(^{14}\) 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 CH\(_3\)- and CD\(_3\)-containing isotopes, respectively. In their investigation of the photoelectron spectrum of CH\(_3\)CHCH\(_2\), Burrill et al. assigned bands located 94 cm\(^{-1}\), 213 cm\(^{-1}\) and 621 cm\(^{-1}\) above the origin to the 21\(_1\), 21\(_2\), and 21\(_3\) levels of CH\(_3\)CHCH\(_2\), however, without discussion of the fact that the 21\(_0\) and 21\(_0\) bands are forbidden by symmetry.

The analysis of our spectra confirms the former two assignments, but suggests a different assignment for the 21\(_3\) level. The 21\(_1\) levels of all CH\(_3\)-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 CD\(_3\)-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 (21\(_2\)) of the methyl torsion because of the forbidden nature of the 21\(_0\) band; however, our attempts to model the torsional motions on the basis of this assignment (see Sec. III D) were unsuccessful and consistently indicated 21\(_0\) as the only possible assignment.

The 21\(_2\) levels of the CH\(_3\)- and CD\(_3\)-containing isotopomers of the propene cations 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 21\(_2\) and 20\(_1\) levels in CH\(_3\)CHCH\(_2\), CH\(_3\)CDCH\(_2\) and CD\(_3\)CCHCD\(_2\) complicates the assignments. The spectra of CH\(_3\)CHCD\(_2\) and
TABLE II. Band centers (in cm$^{-1}$)\textsuperscript{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.

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<td>78994(4)</td>
<td>234(4)</td>
<td>...</td>
</tr>
<tr>
<td>$14^1$</td>
<td>...</td>
<td>[347]</td>
<td>...</td>
</tr>
<tr>
<td>$21^3$</td>
<td>...</td>
<td>...</td>
<td>241.8</td>
</tr>
<tr>
<td>$20^2$</td>
<td>78089(3)</td>
<td>329(3)</td>
<td>332.8</td>
</tr>
</tbody>
</table>

\textsuperscript{a}Only 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.

\textsuperscript{b}Corrected for the field-induced shift of the ionization energy.

\textsuperscript{c}The harmonic vibrational wave numbers calculated \textit{ab initio} at the level of UMP2/6-311(2p,d) are given in square brackets.

\textsuperscript{d}Vibrational wave numbers of the torsional levels calculated using a simple one-dimensional model (see text for more details).

\textsuperscript{e}Assignments proposed in Ref. 14.
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 (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 2₁₀ photoelectron band. The spectrum shows the 2₁₀ band to be about 2.5 times more intense than the 2₁¹ band, which highlights the Franck-Condon forbidden, but vibronically allowed, nature of the 2₁₀ bands with odd ν values. Intensity perturbations by torsion-rotation coupling, as observed, for instance, in toluene, 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 2₀² and 2₁² 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 Johnson 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 (ν₂₀) and the CCC bend (ν₁₄)

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
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(CH2)3 and CD3CHCH2, which enable the observation of the 201 and 202 levels of the cations as isolated spectral features, indicate that the 201 and 202 levels of the propene cation and a higher lying a higher lying 2A′ electronic state mediated by the methylene torsion (see Sec. III E for a more detailed discussion).

Our assignment of the 200 band at 482 cm−1 in the photoelectron spectrum of CH3CH2CH2 differs from that proposed by Burrill and Johnson who have assigned it to the 141 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 141 band of CH3CH2CH2 corresponds to the band observed at 414 cm−1, which Burrill and Johnson have assigned to the 201210 combination band.

Our spectra only enable the observation of a single combination band, 2010211, which is observed at 78933 cm−1 in the spectrum of CH3CH2CH2 [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 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=O stretching mode

In all spectra presented in Fig. 2, except that of CH3CH2CH2 (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=O stretching mode, 6′, on the basis of the very weak isotopic shifts observed upon deuteration (see Table I). The spectrum of CH3CH2CD2 reveals two lines in this region, so that the 6′ level of this isotopomer appears to be perturbed by a closely lying a′ vibrational level with which it shares its intensity.

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) CH3CH2, (b) CH3CD2, (c) CH3CH2CD2, (d) CD3CH2, and (e) CD3CD2D2 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.
Weak bands observed at around 1720 cm$^{-1}$ (80 321 cm$^{-1}$) and 1600 cm$^{-1}$ (80 347 cm$^{-1}$) in the spectra of CH$_3$CHCH$_2^+$ (panel (a)) and CD$_3$CDCH$_2^+$ (panel (e)), respectively, are assigned to the combination bands $6^1_{121}^0$ and $6^1_{201}^0$ because their positions relative to the $6^1_0$ band correspond closely to the positions of the $21^2$ and $20^1$ levels relative to the respective ground states of the cations. These assignments are summarized in Table IV.

2. The CH$_2$-deformation and CH-bending mode

The spectra of CH$_3$CHCH$_2^+$ and CD$_3$CHCH$_2^+$ 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–CH$_2$ 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 CH$_2$-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 CH$_3$CHCD$_2^+$ and CH$_3$CHCD$_2^+$ of the CD$_2$ deformation mode in CH$_3$CHCD$_2^+$ 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 ($v_{21}$) and methylene ($v_{20}$) torsional modes, which both reveal a positive anharmonicity. The positive anharmonic shifts of the $20^1_{21}$ levels further indicate a significant anharmonic coupling between these modes. Our data, however, do not contain sufficient information on combination levels $20^1_{21}$ 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 CH$_3$CHCD$_2^+$ the tentative assignment of the second overtone $21^3$ 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

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

where $\alpha$ 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

$$F = \hbar^2/2r I_a.$$

The quantity $r I_a$ is interpreted as the reduced moment of inertia of the internal rotation of the CH$_3$ group relative to the rigid molecular frame, $r$ being a reduction factor defined as

$$r = 1 - \sum s \lambda_s^2 I_a/I_s,$$

$I_a$ is the moment of inertia of the methyl top about its symmetry axis, $I_s$ ($g = a, b, c$) are the principal moments of inertia fixed in the frame part of the molecule, and $\lambda_s$ 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>
<thead>
<tr>
<th>CH$_3$H$_6$</th>
<th>CH$_3$CDCH$_2$</th>
<th>CH$_3$CHCD$_2$</th>
<th>CD$_3$CHCH$_2$</th>
<th>C$_3$D$_6$</th>
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</thead>
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<td>CH$_2$ rock</td>
<td>79851</td>
<td>79795</td>
<td>79405</td>
<td>79940</td>
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<td>79965</td>
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<td>6$^1_{21}$</td>
<td>80131</td>
<td>80108</td>
<td>80178</td>
<td>80209</td>
</tr>
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</table>
| 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.

$^a$The numbers in square brackets are the harmonic wave numbers calculated $ab$ initio at the UMP2/6-311G(2d,p) level.
Fourier-series expansion

\[ V(\alpha) = \frac{V_N}{2} (1 - \cos N\alpha) + \frac{V_{2N}}{2} (1 - \cos 2N\alpha) + \ldots \, , \tag{4} \]

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 \( \theta \) 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 representation⁷¹,⁴² on an equidistant grid of 51 points over a range of \( 2\pi \) and a calculation of \( I_a \) and \( I_x \) 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 \( v_{21} \) and \( v_{20} \) are observed in most spectra, the experimental data are insufficient to reliably determine the potential parameters \( V_{N} \). 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

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

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 ±60° and ±180° in the case of the methyl torsion and ±90° and ±270° 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 \( c \), and \( A \) 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 200 and 210 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 \( v_{21} \) 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 212 level of CH₃CHCD₂⁺, 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 211 level (1.6 cm⁻¹) are too small to be observed at our spectral resolution; the predicted splitting of the 212 level (9.5 cm⁻¹) may be responsible for the broader and asymmetric lineshapes of the 21₁₀ bands (Figs. 4(c) and 4(d), see also Fig. 7 in Sec. III E). The calculations also support our tentative assignment of the 21₁₀ band in the spectrum of CH₃CHCD₂⁺ (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 CH₃ torsional motion and CH₃ 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 CH₃CHCH₂ to the ground electronic state of CH₃CHCH⁺ 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 CH₃CHCD₂ (at a different position). For comparison, the fully relaxed \textit{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 \( \pm 10 \) degrees around the equilibrium position. On the left-hand side of the upper panel of Fig. 5, the potential energy function calculated \textit{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 \textit{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 CH₂-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 CD₂-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
radical cation are depicted in Fig. 6 as full (dashed) lines for the CH$_3$- (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$^0_0$ and 21$^0_0$ $\nu$' $\nu$' torsional bands with odd values of $\nu$ and $\nu'$ 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 $\tilde{X}^+$ $\rightarrow$ $\tilde{X}$ photoionizing transitions of CH$_3$CHCH$_2$ and CD$_3$CDCH$_2$, which correspond to the ejection of an electron from the outermost molecular orbital of $\alpha''$ 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, 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 $\alpha'$ 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$^0_0$ and 21$^0_0$ bands, contain additional information on the vibronic interaction. The relevant regions of the spectra of CH$_3$CHCH$_2$ and CD$_3$CHCH$_2$, in which the 20$^0_0$ band is observed as isolated band, are displayed on an enlarged scale in Fig. 7. The figure reveals that the 20$^0_0$ and 21$^0_0$ 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$^0_0$ 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$^0_0$ and 21$^0_0$ bands could be modelled by assuming that the vibronic coupling is primarily to the $\tilde{X}^+$ state which is formed by removing an electron from the 10$\alpha'$ 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 $\ell''$ and $\lambda''$, which result in the sharp central feature and several $\Delta K_a$ 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 band$^{40}$ 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$^0_0$ and 21$^0_0$ 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 values$^9$ 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$^0_0$ and 20$^0_0$ bands of CH$_3$CHCD$_2$ and of the 20$^0_0$ band of CD$_3$CHCH$_2$ (orange traces in Fig. 7) reproduce the experimentally observed contours well and show the characteristic features of transitions to cationic vibronic levels of $\alpha'$ symmetry discussed above. The calculated contours of the 20$^0_0$ bands of CD$_3$CHCH$_2$ and CH$_3$CHCD$_2$ (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$_3$CHCD$_2$ appears narrower than the experimental
FIG. 7. Enlarged view of the PFI-ZEKE photoelectron spectra of (a) CH$_3$CHCD$_2^+$ and (b) CD$_3$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 10 $a'$ 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 CH$_3$CHCD$_2^+$, which is significantly higher ($\sim 8.4$ cm$^{-1}$) than in CD$_3$CHCH$_2^+$ ($\sim 1.5$ 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 $\tilde{\tilde{X}}^+ 2A''$ and $\tilde{\tilde{A}}^+ 2A'$ 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 $\tilde{\tilde{X}}^+ \leftarrow \tilde{\tilde{X}}$ 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 ($v_{21}$) and methylene ($v_{20}$) 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 $\pi_{CC}$ 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 $\sim 400$ cm$^{-1}$ ($\sim 700$ cm$^{-1}$ in neutral propene) in the case of the methyl torsion and $\sim 8000$ cm$^{-1}$ ($\gg 10000$ 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.\textsuperscript{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.\textsuperscript{13} In the propene radical cation, the vibronic coupling to the $\tilde{\tilde{A}}^+ 2A'$ 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 $\tilde{X}^2\tilde{A}^+\tilde{A}^0$ 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$_3$CHCH$_2$ and CD$_3$CDCH$_2$ which could only be explained by invoking vibronic interactions.$^{30}$ The analysis of the rotational contours of the "forbidden" $20_0^0$ and $21_0^0$ bands indicates that the vibronic coupling to the $\tilde{A}^+\tilde{A}^0$ state of the cation, which is formed by removing an electron from the $10\alpha'$ 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 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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