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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 $\tilde{X}^+ 2\text{A}'' \leftarrow \tilde{X} 1\text{A}'$ transition of CH$_2$CHCH$_2$ (propene), CD$_2$C$\text{D}$CD$_2$, 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 torkons. 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 $\tilde{X}^+ 2\text{A}''$ and the $\tilde{A}^+ 2\text{A}'$ states mediated by the methylene ($\nu_{20}$) and methyl ($\nu_{21}$) torsional modes.


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 $\tilde{X} 1\text{A}'$ 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 spectrum of propene and CH$_2$$^3$CHCH$_2$, determined the structure of the molecule, and estimated the torsional potential barrier from the tunneling splittings observed in the microwave spectrum of the ground state. The complete substitution structure of propene ($r_s$) was derived by Lide and Christensen$^5$ 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 CH₂CH₂⁺ to the second overtone of the methyl-torsional mode (2ν₁) indicates a surprisingly large anharmonicity (in Ref. 14, the fundamental (ν₁) and the first overtone (2ν₁) 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 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 πCH₂ and πC=–X orbitals, the stabilization of the eclipsed conformation by the interaction between the πCH₃ and πC=–X orbitals, the opposite effects from π*CH₃–πC=–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.

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

The development of pulsed-field-ionization zero-kinetic-energy (PFI-ZEKE) photoelectron spectroscopy and the continual improvement of the resolution that can be achieved with this technique makes it possible to obtain information on the methyl-torsional motion of molecular cations and to study in detail the effects of removing an electron from bonding πCC orbitals. 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 have exploited mass-analyzed threshold-ionization spectroscopy to study the methyl-torsional motion in CH₃–CX=–CH₂⁺ (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 ∼50–100 cm⁻¹) in the cations compared to the neutrals (∼1000 cm⁻¹).

The electronic ground state of the propene radical cation has an unpaired electron in the 2π* molecular orbital, which is a bonding πCC 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. 

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 vibrionic interactions in the cation that could complement that obtained in our previous study of the rotational structure of the vibrational ground state, and in studies of vibronic interactions in the ground state of C₂H₄.

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. The VUV radiation was generated by resonance-enhanced difference-frequency mixing (νVUV = 2ν₁ − ν₂) in krypton using two tunable dye lasers. The wave number ν₁ of the tripled output of the first dye laser was held fixed at the position
2\(\tilde{v}_1\) = 94 092.86 cm\(^{-1}\) of the (4p)\(^5\) (2P\(_{3/2}\)) 5p [1/2] (J = 0) \(\leftrightarrow\) (4p)\(^6\) (1S\(_0\)) two-photon resonance of krypton, and the VUV wave number was scanned by tuning the wave num-
ber \(\tilde{v}_2\) 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 differ-
cence (2\(\tilde{v}_1 - \tilde{v}_2\)).

Propene-\(d_6\) (>99% purity) and propene-\(d_6\) (isotopic purity of 99%) were purchased from Aldrich and Isotec, re-
spectively, 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 more than 99% as determined by high-pressure liquid chromatography. The identity of the isotopomers was veri-
cified 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 intro-
duced into the chamber through a pulsed nozzle operated at
a stagnation pressure of \(\sim 3\) bar and used to form a sup-
ersonic 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 \(\sim 10\) 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 \(\mu\)s rel-
ative 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 \(\mu\)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 inte-
grated 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 ra-
tio was reached in the spectra obtained with the \(-107\) mV/cm
d field pulse. A correction of (+1.25 ± 0.3) cm\(^{-1}\) was intro-
duced to compensate for the field-induced shift of the ion-
ization 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 fol-
lowed by a \(-900\) mV/cm extraction pulse necessitating a correc-
tion of (+2.2 ± 0.50) cm\(^{-1}\).

III. RESULTS AND DISCUSSION

A. General considerations

The equilibrium geometry of propene in the \(\tilde{X}^1A^\prime\) ground
electron state has been found to be \(C_3\).\(^{13}\) The ground-state
electronic configuration is \(\ldots(1a)^2(9a)^2(10a)^2(2a)^2\). The
HOMO orbital (2a\(^\prime\)) has a nodal plane containing the three
carbon atoms and is predominantly a \(\pi\) orbital with \(C=C\)
bonding character. Ionization out of this orbital gives rise to
the \(\tilde{X}^+2A^\prime\) ground electronic state of the cation. \(Ab initio\)
calculations\(^{14}\) indicate that the plane of symmetry is preserved
upon ionization out of this orbital so that the equilibrium ge-
ometry of the cation is predicted to be of \(C_3\) symmetry, al-
though more sophisticated \(ab initio\) calculations would be
needed to verify this prediction. Propene has 21 nondegen-
erate normal modes, 14 of \(a^\prime\) and 7 of \(a^\prime\) symmetry. The
lowest frequency modes in the case of the propene radical
cation are the \(v_{23}(a^\prime\prime)\) and \(v_{20}(a^\prime\prime)\) normal modes, corre-
sponding predominantly to the methyl internal rotation and
the \(CH_2\) torsion, respectively, followed by the CCC bending
mode \(v_{14}(a^\prime\)'). These modes are energetically well separated
from the higher frequency modes so that their number-
ing 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\(^\prime\) 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 ±
0.004 Å (Ref. 8) to about 1.4169 Å.\(^{14}\) Based on chemical
intuition and the Franck-Condon principle, one expects vibra-
tional 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. Conse-
quently, 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 propene\(^{14}\) and its deuterated isotopomers (see Fig. 2 be-
low) the origin band is by far the most intense. The weak-
ness of the low-frequency bands necessitated the use of a
large field-ionization pulse (0.9 V/cm) which limited the ex-
perimental resolution to about 1 cm\(^{-1}\). Consequently, no ro-
tational structure could be observed for these bands that
would have allowed the unambiguous determination of the vibric
symmetry of the cationic levels using rovibronic photoioniza-
tion selection rules, as was possible for the origin band.\(^{30}\) To
nevertheless assign the vibrational structure, the photoelec-
tron 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.\(^{30}\) In
favorable cases, the analysis of the rotational contours of the vibrational bands en-
abled us to independently confirm the assignments made on
the basis of isotopic shifts.

The overview PFI-ZEKE photoelectron spectra of the
\(\tilde{X}^+2A^\prime(\nu_1^+)\leftrightarrow\tilde{X}^1A^\prime(0^+)\) 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 cm\(^{-1}\) to
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 \textit{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 D, they are in agreement with the results of \textit{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.

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

<table>
<thead>
<tr>
<th>Deuteration</th>
<th>CH(<em>3) torsion ( \nu</em>{21}(a') )</th>
<th>CH(<em>2) torsion ( \nu</em>{20}(a') )</th>
<th>CCC bend ( \nu_{14}(a') )</th>
<th>C=C stretch ( a' )</th>
<th>CH(_2) deform. ( a' )</th>
<th>CH bend ( a' )</th>
</tr>
</thead>
<tbody>
<tr>
<td>CH(_3) ↔ CD(_3)</td>
<td>Strong</td>
<td>Vanishing</td>
<td>Weak</td>
<td>Vanishing</td>
<td>Vanishing</td>
<td>Vanishing</td>
</tr>
<tr>
<td>CH ↔ CD</td>
<td>Vanishing</td>
<td>Vanishing</td>
<td>Weak</td>
<td>Vanishing</td>
<td>Vanishing</td>
<td>Strong</td>
</tr>
<tr>
<td>CH(_2) ↔ CD(_2)</td>
<td>Vanishing</td>
<td>Strong</td>
<td>Weak</td>
<td>Weak</td>
<td>Strong</td>
<td>Vanishing</td>
</tr>
</tbody>
</table>

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\(_2\)-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 \( 21^1_0 \) band; however, our attempts to model the torsional motions on the basis of this assignment (see Sec. III D) were unsuccessful and consistently indicated \( 21^1_0 \) as the only possible assignment.

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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 (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 (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\(_2\)CDCD\(_2\) (trace (c)). 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\(_1\) bands, which are nominally forbidden by symmetry in the X\(^{1A'}\) A\(^{\prime}\) → X\(^{1A'}\) A\(^{\prime}\) 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 \textit{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 \( \sim 90 \) cm\(^{-1}\) and \( \sim 70 \) cm\(^{-1}\) above the ground state in CH\(_3\)- and CD\(_3\)-containing isotopomers, 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\(_1^0\), 21\(_2^0\), and 21\(_3^0\) levels of CH\(_3\)CHCH\(_2^+\), however, without discussion of the fact that the 21\(_1^0\) and 21\(_1^0\) bands are forbidden by symmetry.

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 (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\(_2\)CDCD\(_2\) (trace (c)). 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\(_1\) bands, which are nominally forbidden by symmetry in the X\(^{1A'}\) A\(^{\prime}\) → X\(^{1A'}\) A\(^{\prime}\) 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.

#### B. The low-frequency modes \( \nu_{21} \) (methyl torsion), \( \nu_{20} \) (methylenic torsion), and \( \nu_{14} \) (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).
TABLE II. Band centers (in cm$^{-1}$), 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.

<table>
<thead>
<tr>
<th>Label</th>
<th>$E_{\text{obs}}^b$</th>
<th>($E_{\text{obs}} - E_i$)$^c$</th>
<th>$E_{\text{calcd}}^d$</th>
<th>$E_{\text{obs}}^b$</th>
<th>($E_{\text{obs}} - E_i$)$^c$</th>
<th>$E_{\text{calcd}}^d$</th>
</tr>
</thead>
<tbody>
<tr>
<td>0$^0$</td>
<td>78602.0(4)</td>
<td>0.0</td>
<td>0.0</td>
<td>78605.9(10)</td>
<td>0.0</td>
<td>0.0</td>
</tr>
<tr>
<td></td>
<td></td>
<td>(0.0)$^e$</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>21$^1$</td>
<td>78700(3)</td>
<td>98(3)</td>
<td>99.2</td>
<td>78705(3)</td>
<td>99(3)</td>
<td>96.1</td>
</tr>
<tr>
<td></td>
<td></td>
<td>(94)$^f$,[92]</td>
<td>100.8</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>20$^1$</td>
<td>78822(3)</td>
<td>220(3)</td>
<td>216.6</td>
<td>78823(3)</td>
<td>217(3)</td>
<td>213.2</td>
</tr>
<tr>
<td></td>
<td></td>
<td>(213)$^g$,[227]</td>
<td>216.6</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>21$^2$</td>
<td>78815(7)</td>
<td>213(7)</td>
<td>210.4</td>
<td>78818(7)</td>
<td>212(7)</td>
<td>204.9</td>
</tr>
<tr>
<td></td>
<td></td>
<td>(213)$^g$</td>
<td>219.9</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>20$^2$</td>
<td>78933(4)</td>
<td>331(4)</td>
<td>...</td>
<td>78934(4)</td>
<td>328(4)</td>
<td>...</td>
</tr>
<tr>
<td>14$^1$</td>
<td>79016(4)</td>
<td>414(4)</td>
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<td>79015(4)</td>
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$^a$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.

$^b$Corrected for the field-induced shift of the ionization energy.

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

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

$^e$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 2′′ symmetry that could perturb the intensity of the 2120 photoelectron band. The spectrum shows the 2120 band to be about 2.5 times more intense than the 2110 band, which highlights the Franck-Condon forbidden, but vibronically allowed, nature of the 2120 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 2010 and 2120 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 (ν20) and the CCC bend (ν14)

Upon removal of an electron from the outermost occupied orbital of 2a′′ symmetry, which has a dominant πCC bonding character, the πCC 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$_3$CHCD$_2$ and CD$_3$CHCH$_2$, which enable the observation of the 201 and 202 levels of the cations as isolated spectral features, indicate that the 202 band is about twice as strong as the 201 band. As explained above, the 201 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 200 band at 482 cm$^{-1}$ in the photoelectron spectrum of CH$_3$CHCH$_2$ 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. Our spectra (see Fig. 4) indicate that the 141 band of CH$_3$CHCH$_2$ corresponds to the band observed at 414 cm$^{-1}$, which Burrill and Johnson have assigned to the 201 combination band.

Our spectra only enable the observation of a single combination band, 201, which is observed at 78933 cm$^{-1}$ in the spectrum of CH$_3$CHCH$_2$ [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 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$_3$CHCD$_2$ (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$^v$, on the basis of the very weak isotopic shifts observed upon deuteration (see Table I). The spectrum of CH$_3$CHCD$_2$ reveals two lines in this region, so that the 6$^v$ 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) CH$_3$CHH$_2$, (b) CH$_3$CDH$_2$, (c) CH$_2$CHCD$_2$, (d) CD$_2$CHCH$_2$, and (e) CD$_3$CDCD$_2$ 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.](image-url)
TABLE IV. Band centers, experimental and calculateda vibrational wave numbers and their assignment for the propene radical cation and several of its deuterated isotopomers at high energies.

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<th>CH$_3$CHCD$_2$</th>
<th>CD$_3$CHCH$_2$</th>
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</table>

$^a$The 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$^{-1}$ (80321 cm$^{-1}$) and 1600 cm$^{-1}$ (80347 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$^1$ 21$^2$ and 6$^1$ 20$^1$ because their positions relative to the 6$^1$ 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$_3$CHCH$_2^+$ and CH$_3$CHCD$_2^+$ and 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$^1$ levels further indicate a significant anharmonic coupling between these modes. Our data, however, do not contain sufficient information on combination levels 20$^1$ 21$^1$ 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

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

(1)

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

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

(2)

The quantity $r I_\alpha$ is interpreted as the reduced moment of inertia of the internal rotation of the CH$_3$ group relative to the rigid molecular frame, $^{38-40} r$ being a reduction factor defined as

$$r = 1 - \sum g \frac{\lambda_g}{I_g} I_\alpha.$$

(3)

$I_\alpha$ 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 $\lambda_g$ 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
Fourier-series expansion

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

with \( N = 3 \). In the case of the \( \text{CH}_2 \) 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 representation on an equidistant grid of 51 points over a range of \( 2\pi \) and a calculation of \( I_\theta \) and \( I_\theta \) in the way implemented by Makarewicz in Ref. 43. Initial calculations relied on the equilibrium geometry of the cation optimized \textit{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 \( V_{N}/V_N \). Instead of using Eq. (4), the potential barriers along the torsional motion of the \( \text{CH}_3 \) or \( \text{CH}_2 \) 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 ±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° ≤ \( \alpha \) ≤ +180° and −90° ≤ \( \theta \) ≤ +270°, 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 and 21 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 \( c = 17° \), 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 \( \text{CH}_3\text{CHCD}_2 \), 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 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 212 bands (Figs. 4(c) and 4(d), see also Fig. 7 in Sec. III E). The calculations also support our tentative assignment of the 210 band in the spectrum of \( \text{CH}_3\text{CHCD}_2 \) (see Fig. 4(c)), and suggests that it corresponds to a transition to the tunneling component of \( e \) symmetry.

### Table V. Experimentally determined and \textit{ab initio} calculated potential energy parameters for the methyl internal rotation and the \textit{CH}_3 torsion in propene and the propene radical cation.

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$^a$In 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).

$^b$\( V_0 = 0.2 \text{ cm}^{-1} \).
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 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...
radical cation are depicted in Fig. 6 as full (dashed) lines for the CH3- (CD2-) 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 201\textsuperscript{0} and 211\textsuperscript{0} 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 ∆K\textsubscript{a} = K\textsubscript{a} – K\textsubscript{a}' = 0 and ∆\textit{N} = N' – N" = 0 in the spectrum of the 00\textsuperscript{0} origin bands of the X\textsuperscript{1}→ X\textsuperscript{2} vibronic transitions of CH3CHCH2 and CD3CHCD2, 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, λ" = ±1), (\ell" = 2, λ" = ±1) and (\ell" = 2, λ" = ±2) contributions, λ" = ±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 (∆\textit{N}, ∆K\textsubscript{a}) = (\ell", λ"). The observation of a ∆K\textsubscript{a} = 0 branch thus indicates an admixture of an a' molecular orbital contribution at geometries deviating from C\textsubscript{3} symmetry.

The rotational contours of the bands observed in Figs. 2 and 4, in particular those of the forbidden 201\textsuperscript{0} and 211\textsuperscript{0} bands, contain additional information on the vibronic interaction. The relevant regions of the spectra of CH3CHCH2 and CD3CHCH2, in which the 201\textsuperscript{3} band is observed as isolated band, are displayed on an enlarged scale in Fig. 7. The figure reveals that the 201\textsuperscript{0} and 211\textsuperscript{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 211\textsuperscript{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 201\textsuperscript{0} and 211\textsuperscript{0} bands could be modelled by assuming that the vibronic coupling is primarily to the A\textsuperscript{1} 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 λ" = 0 contributions and the slow convergence of the single-center expansion with \ell" and λ", which result in the sharp central feature and several ∆K\textsubscript{a} branches on both sides of this spectral feature (see Fig. 7).

Compared to the relative branch intensities (\Delta\textit{N}, |∆K\textsubscript{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 00\textsuperscript{0} origin band\textsuperscript{30} 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 201\textsuperscript{0} and 211\textsuperscript{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\textsuperscript{9} when available or to the values predicted by \textit{ab initio} calculations at the MP2/6-311G(2d,p) level. The calculated rotational contours of the 211\textsuperscript{0} and 201\textsuperscript{0} bands of CH3CHCD2 and of the 201\textsuperscript{1} band of CD3CHCH2 (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 201\textsuperscript{2} bands of CD3CHCH2 and CH3CHCD2 (dashed magenta traces) are overall broader. Whereas in the former case the calculated and experimental spectra resemble each other closely, the calculated spectrum of CH3CHCD2 appears narrower than the experimental
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$8.6 cm$^{-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 $\tilde{X}^+ + 2A^+$ 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 ($v_{21}$) 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 $\pi_{1c}$ 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. 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. 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 $20^1_0$ and $21^1_0$ bands, which are forbidden in first approximation, indicates that vibronic interaction of the $\tilde{X}^+ \tilde{A}'$ 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$_3$C=CD$_2$ which could only be explained by invoking vibronic interactions. The analysis of the rotational contours of the "forbidden" $20^1_0$ and $21^1_0$ bands indicates that the vibronic coupling to the $\tilde{A}^+ \tilde{A}'$ state of the cation, which is formed by removing an electron from the 10$a'$ 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 $\tilde{X}^+ \tilde{A}'$ 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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