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# Comprehensive vacuum ultraviolet photoionization study of the $\text{CF}_3^\bullet$ trifluoromethyl radical using synchrotron radiation

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The trifluoromethyl radical,  $\text{CF}_3^\bullet$ , is studied for the first time by means of threshold photoelectron spectroscopy (TPES). The radical is produced in the gas phase using the flash-pyrolysis technique from hexafluoroethane as a precursor.  $\text{CF}_3^+$  total ion yield and mass-selected TPES of the radical are recorded using a spectrometer based upon velocity map imaging and Wiley-McLaren time-of-flight coupled to the synchrotron radiation. The high resolution of the instrument and of the photons allows the observation of rich vibrational progressions in the TPES of  $\text{CF}_3^\bullet$ . By using Franck-Condon factors computed by Bowman and coworkers, we have been able to simulate the TPES. The initial vibrational temperature of the radical beam has been evaluated at  $350 \pm 70$  K. The structures have been identified as transitions between  $(n_1, n_2)$  and  $(n_1^+, n_2^+)$  vibrational levels of  $\text{CF}_3$  and  $\text{CF}_3^+$  with small excitation of the breathing mode,  $\nu_1^+$ , and large excitation ( $n_2^+ = 10$ –26) of the umbrella mode,  $\nu_2^+$ , in the cation. From the energy separation between the two resolved peaks of each band, a value of  $994 \pm 16 \text{ cm}^{-1}$  has been derived for the  $\nu_1^+$  breathing frequency of  $\text{CF}_3^+$ . For the high-lying  $n_2^+$  levels, the apparent  $\nu_2^+$  umbrella spacing,  $820 \pm 14 \text{ cm}^{-1}$ , is fairly constant. Taking into account the  $\nu_2^+$  anharmonicity calculated by Bowman and coworkers, we have deduced  $\nu_2^+ = 809 \pm 14 \text{ cm}^{-1}$ , and semi-empirical estimations of the adiabatic ionization energy  $\text{IE}_{\text{ad}}(\text{CF}_3^\bullet)$  are proposed in good agreement with most of previous works. A value of the vertical ionization potential,  $\text{IE}_{\text{vert}}(\text{CF}_3^\bullet) = 11.02 \text{ eV}$ , has been derived from the observation of a photoelectron spectrum recorded at a fixed photon energy of 12 eV. © 2012 American Institute of Physics. [<http://dx.doi.org/10.1063/1.4719529>]

## I. INTRODUCTION

Perfluorocarbons and derivatives are widely encountered in industrial processes such as semiconductor fabrication, primary aluminum production, plasma etching, etc. Once released in the atmosphere, they are known to act as very potent greenhouses gases.<sup>1</sup> One of their major fragmentation products is the  $\text{CF}_3^\bullet$  radical whose structural and ionization properties have already been extensively studied by means of gas-phase experiments<sup>2–14</sup> and quantum chemistry calculations.<sup>15–23</sup> Such an interest is in part explained by the geometrical features of the  $\text{CF}_3^\bullet/\text{CF}_3^+$  system: while the  $\text{CF}_3^\bullet$  radical has a  $\text{C}_{3v}$  geometry, its cation is characterized by a  $\text{D}_{3h}$  structure. Franck-Condon factors (FCFs) at the adiabatic ionization threshold of  $\text{CF}_3^\bullet$  are thus negligible and render the direct experimental determination of the adiabatic ionization energy ( $\text{IE}_{\text{ad}}$ ) of  $\text{CF}_3^\bullet$  extremely difficult. This large geometry difference is confirmed by the vertical ion-

ization of  $\text{CF}_3^\bullet$  which leads to the formation of vibrationally excited  $\text{CF}_3^+$  ( $n_2^+ = 20$ ) ( $n_2^+$  being the quantum number associated to the out-of-plane bending mode  $\nu_2^+$  of  $\text{CF}_3^+$ , see Table I for a description of the vibrational modes of  $\text{CF}_3^\bullet$  and  $\text{CF}_3^+$ ).<sup>21</sup> Currently, only one work is reported in the literature of a direct ionization study of  $\text{CF}_3^\bullet$ . In 1967, Lifshitz and Chupka<sup>2</sup> used a magnetic sector mass-spectrometer coupled to a hydrogen discharge lamp and a pyrolysis source to study the photoionization of  $\text{CF}_3^\bullet$  formed from the  $\text{CF}_3\text{CH}_2\text{ONO}$  precursor. They obtained a photoionization efficiency curve of  $\text{CF}_3^\bullet$  from threshold up to 12.5 eV and derived a value of  $\text{IE}_{\text{ad}} = 9.25 \pm 0.04 \text{ eV}$ . They also obtained an evaluation of the out-of-plane bending mode of  $\text{CF}_3^+$ ,  $\nu_2^+ = 830 \text{ cm}^{-1}$ , which is, to our knowledge, the only one existing in the gas phase (matrix experiments<sup>24</sup> give a value of  $\nu_2^+ = 798 \text{ cm}^{-1}$ ). To provide an estimation of  $\text{IE}_{\text{ad}}$ , indirect approaches have also been employed, mostly by measuring fragment appearance energies (AEs) of precursors such as  $\text{CF}_3\text{Br}$ <sup>7,11,13</sup> or  $\text{C}_2\text{F}_4$ .<sup>3,9</sup> A controversy has then appeared as two groups of values for  $\text{IE}_{\text{ad}}$  have emerged from the different studies: one stating  $\text{IE}_{\text{ad}} < 8.8 \text{ eV}$ ,<sup>7,10,13</sup> the other that  $\text{IE}_{\text{ad}}$  lies at  $\sim 9.0 \text{ eV}$ .<sup>3,9,11,12,16–19,21,25–27</sup> This controversy is currently not solved although some explanation involving the role of entropy has been proposed to explain this discrepancy.<sup>28</sup>

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TABLE I. Observed and calculated electronic ground state vibrational frequencies of  $\text{CF}_3^\bullet$  ( $\text{C}_{3v}$ ) and  $\text{CF}_3^+$  ( $\text{D}_{3h}$ ) in  $\text{cm}^{-1}$ . Symmetries of the vibrations are given in parenthesis.

|             |                   | $\text{CF}_3^\bullet$                                   |                    | $\text{CF}_3^+$       |                       |           |
|-------------|-------------------|---|--------------------|-----------------------|-----------------------|-----------|
|             |                   | Obs. <sup>a</sup>                                       | Calc. <sup>b</sup> | Obs.                  | Calc. <sup>b</sup>    | This work |
| Breathing   | $\nu_1$ ( $a_1$ ) | 695 <sup>c</sup> /701 <sup>d</sup>                      | 748                | $\nu_1^+$ ( $a_1'$ )  | 1041/997 <sup>e</sup> | 994       |
| Umbrella    | $\nu_2$ ( $a_2$ ) | 1103 <sup>c</sup> /1090 <sup>d</sup> /1089 <sup>f</sup> | 1139               | $\nu_2^+$ ( $a_1''$ ) | 804/830 <sup>e</sup>  | 809       |
| CF stretch  | $\nu_3$ ( $e$ )   | 1260 <sup>c,i</sup>                                     | 1285               | $\nu_3^+$ ( $e'$ )    | 1662 <sup>g</sup>     | 1642      |
| Deformation | $\nu_4$ ( $e$ )   | 508 <sup>g</sup>  | 558                | $\nu_4^+$ ( $e'$ )    | 632                   |           |

<sup>a</sup>We follow here the re-assignment of the experimental umbrella and breathing modes of  $\text{CF}_3^\bullet$  by Bowman *et al.*<sup>21</sup> For convenience, we call the breathing mode in the neutral  $\text{CF}_3^\bullet$ ,  $\nu_1$ , as in the cation  $\text{CF}_3^+$ .

<sup>b</sup>If not stated otherwise, from MULTIMODE calculations of Bowman *et al.*<sup>21</sup>

<sup>c</sup>From gas-phase study of Suto and Washida.<sup>46</sup>

<sup>d</sup>From gas-phase study of Carlson and Pimentel.<sup>48</sup>

<sup>e</sup>From CEPA-1 calculations of Horn *et al.*<sup>16</sup> The values given here correspond to the average of the 27 values provided in their work.

<sup>f</sup>From gas-phase study of Bozlee and Nibler.<sup>50</sup>

<sup>g</sup>From matrix-isolation study of Forney *et al.*<sup>24</sup>

<sup>h</sup>From gas-phase study of Lifshitz and Chupka.<sup>2</sup>

<sup>i</sup>From gas-phase study of Yamada and Hirota.<sup>49</sup>

It is in this context that we have begun to pay attention to the  $\text{CF}_3^\bullet/\text{CF}_3^+$  system with the aim of getting high resolution data on the  $\text{CF}_3^\bullet$  photoionization to obtain accurate vibrational constants and a high precision determination of IEs. Therefore the work presented in this paper shows the results of the direct photoionization study of  $\text{CF}_3^\bullet$ . This study has first consisted in the formation of the  $\text{CF}_3^\bullet$  radical by pyrolysis of hexafluoroethane. The radical was then ionized by synchrotron radiation in the 8.5–12.4 eV energy range. The corresponding cation has been detected applying a photoelectron-photoion coincidence technique and mass-selected threshold photoelectron spectroscopy (TPES). Due to the high energy resolution enabled by our experimental setup, we could observe, in the TPES of  $\text{CF}_3^\bullet$ , two rovibrational progressions from which vibrational constants can be extracted. In Secs. II and III, we will first give a short description of the experimental method followed by a presentation and discussion of the results obtained.

## II. EXPERIMENTAL METHOD

Experiments were carried out on the DESIRS beamline at the SOLEIL synchrotron facility in St. Aubin (France).<sup>29,30</sup> This undulator-based<sup>31</sup> vacuum ultraviolet (VUV)-beamline is equipped with a 6.65 m normal incidence monochromator<sup>32</sup> proposing several gratings depending on the required flux/resolution compromise. We have chosen a 200 gr/mm grating which offers a photon flux in the  $10^{12}$ – $10^{13}$  ph/s range with a moderate energy resolution. The slits were set to deliver a photon energy bandwidth between 5 and 20 meV at 9 eV, and the second order light was removed with an upstream gas filter filled with 0.25 mbars of Ar.<sup>33</sup> Absolute energy scale was provided by calibration via  $\text{N}_2$  and Ar-absorption bands. Absolute energies could thus be given in this work with a precision of 1.8 meV.

$\text{CF}_3^\bullet$  radicals were produced by a flash-pyrolysis technique<sup>34</sup> using hexafluoroethane as a precursor (Apollo Scientific, 99%).  $\sim 0.7$  bar of  $\text{C}_2\text{F}_6$  were injected into a continuous molecular beam in the SAPHIRS<sup>35</sup> vacuum chamber,

expanded through a 50  $\mu\text{m}$  nozzle and pyrolysed via a heated SiC tube. After traversing a  $\varnothing = 1$  mm skimmer, the radical beam is crossed at a right angle with the synchrotron radiation inside the interaction region of the versatile DELICIOUS II electron/ion imaging coincidence spectrometer.<sup>36</sup> Electrons and ions produced in the photoionization process are analyzed in coincidence by a velocity map imaging (VMI) and Wiley–McLaren time-of-flight (TOF) analyzer, respectively.

Different types of experiments may be performed with this instrument, mainly depending on the chosen extraction fields. In the present study, 3 settings have been applied. (i) The high extraction dc field (381.3 V/cm) allows collecting photoelectrons having kinetic energies up to 3.81 eV with an energy resolution of  $\Delta E/E = 5\%$ , and the multiplex recording of their energy and angular distributions. Ions accelerated with a second static field of 1250 V/cm are detected in coincidence with these electrons, leading to (angle-resolved) photoelectron-photoion ((AR)-PEPICO) spectra. When integrated over electron energies and angles, these AR-PEPICO data simply provide mass spectra via ion TOF. Measured as a function of  $h\nu$ , this provides total ion yield curves. (ii) Lowering the extraction field down to 8.5 V/cm enables the discrimination of fast photoelectrons. Only threshold electrons are thus taken into account with a kinetic energy resolution of 7 meV (total resolution of 8 meV when the photon resolution is also considered). These electrons are detected in coincidence with ions which are further accelerated with a second 8.5 V/cm field, leading to TPES. (iii) Finally, by inverting the polarities of the power supplies, the spectrometer can also record mass-selected ion images which are useful to obtain the kinetic energy release of the cations, in particular in the case of dissociative ionization.

Total ion yield curves and mass-selected TPES shown in this work have been obtained by scanning the photon energy in the 8.5–12.4 eV energy range with 10 and 2.5 meV steps, respectively, and by accumulating each point during 40 s. The pyrolysis power and photon flux (photodiode AXUV100 from IRD) were recorded at each scan point for normalization

purposes and hence, all spectra are corrected from false coincidences, pyrolysis power fluctuations, and photon flux variation.

Finally, we will be referring to vibronic transitions involving the  $\nu_1$  and  $\nu_2$  vibrational modes of  $\text{CF}_3^\bullet$  and  $\text{CF}_3^+$ . The nomenclature used to describe such transitions in the following: a transition from the  $(n_{\nu_1}, n_{\nu_2})$  vibrational state of the radical to the  $(n_{\nu_1}^+, n_{\nu_2}^+)$  state of the ion will be termed either  $(n_1, n_2) \rightarrow (n_1^+, n_2^+)$  or  $n_1 n_2 \rightarrow n_1^+ n_2^+$ . The nature of these modes is described in Table I.

### III. RESULTS AND DISCUSSION

#### A. Radical formation

Trifluoromethyl radicals have been produced by pyrolysis of hexafluoroethane,  $\text{C}_2\text{F}_6$ . One particular feature of the  $\text{C}_2\text{F}_6^+$  ion is that it is not stable even in its ionic ground state.<sup>37</sup>  $\text{C}_2\text{F}_6^+$  cannot therefore be observed experimentally which implies that optimization of the pyrolysis conditions has to be done by considering ionic fragments arising from dissociative ionization of  $\text{C}_2\text{F}_6$ , i.e.,  $\text{CF}_3^+$  below 14 eV and  $\text{CF}_2^+$  or  $\text{C}_2\text{F}_5^+$  above 14 eV,<sup>37</sup> and by comparing them with the  $\text{CF}_3^+$  signal coming from the direct ionization of the  $\text{CF}_3^\bullet$  radical. In Fig. 1, the mass spectra obtained at 11 and 17 eV with pyrolysis switched on and off are presented. The fragments produced from photoionization of  $\text{C}_2\text{F}_6$  are shown in Figs. 1(a) and 1(c). At 11 eV, no ions are observed (the energy is below the ionization threshold of  $\text{C}_2\text{F}_6$ ).<sup>38</sup> At 17 eV,  $\text{CF}_3^+$  and  $\text{C}_2\text{F}_5^+$  are produced with a 1:3 ratio (Fig. 1(c), considering signal areas). By switching on the pyrolysis, this ratio changes roughly to 1:1 (Fig. 1(d), signal areas), showing that another process leads to  $\text{CF}_3^+$ , assuming that the  $\text{C}_2\text{F}_5^+$  signal does not change significantly upon pyrolysis. This hypothesis is confirmed by the mass spectrum in Fig. 1(b) where no ion at  $m/z$  119 is observed at 11 eV. This energy is well above

the  $\text{C}_2\text{F}_5^\bullet$  ionization threshold,<sup>39</sup> showing that no  $\text{C}_2\text{F}_5^\bullet$  radicals are produced by pyrolysis, which validates the assumption that the  $\text{C}_2\text{F}_5^+$  signal remains constant upon the pyrolysis switching on. In Fig. 1(b), the apparition of a  $\text{CF}_3^+$  signal evidences that  $\text{CF}_3^\bullet$  radicals are produced by pyrolysis of  $\text{C}_2\text{F}_6$  and lead to  $\text{CF}_3^+$  ions.

The optimization of the  $\text{CF}_3^+$  signal has been achieved by varying the pyrolysis power and a good compromise between the ion signal vs the power is obtained with 50 W. Powers above this figure would decrease the lifetime of the SiC tube to unacceptable values. At 50 W, the destruction of the precursor is not complete and one has to confirm that the  $\text{CF}_3^+$  ion observed does not arise in part from dissociative photoionization of  $\text{C}_2\text{F}_6$ . Jarvis *et al.*<sup>37</sup> have shown in a mass-selected TPES study of  $\text{C}_2\text{F}_6$  that the AE of  $\text{CF}_3^+$  formed from ionization of  $\text{C}_2\text{F}_6$  is  $13.4 \pm 0.1$  eV. Hence, in our working energy range (8.5–12.4 eV), the  $\text{CF}_3^+$  signal observed should unambiguously be assigned to the nascent  $\text{CF}_3^\bullet$  radical. Nevertheless, it is well known that the pyrolysis source has the effect of depositing a large quantity of energy into the precursor producing thus vibrationally hot  $\text{C}_2\text{F}_6$ .<sup>40</sup> This causes a shift to lower energy in the appearance energies of fragments coming from dissociative photoionization of the hot precursor, including  $\text{CF}_3^+$ . Hence, the AE ( $\text{CF}_3^+$ ) needs to be measured under pyrolysis conditions to define the upper limit of our experimental energy window. Such a measurement was obtained by deconvoluting the signal from  $\text{CF}_3^+$  coming from direct and dissociative ionization, i.e., by recording mass-selected ion images. These images were thus recorded between 12.0 and 14.0 eV photon energy, with 0.2 eV steps. Figure 2 shows two of these images obtained at  $h\nu = 12.0$  and 14.0 eV. At low photon energies, the ion images are dominated by a thin, straight line of  $\text{CF}_3^+$  supersonic ions formed by direct ionization of the neutral radical. However, above the AE of the  $\text{CF}_3^+$  from  $\text{C}_2\text{F}_6$ , a ring appears around the center of the supersonic beam, belonging to the  $\text{CF}_3^+$  ions

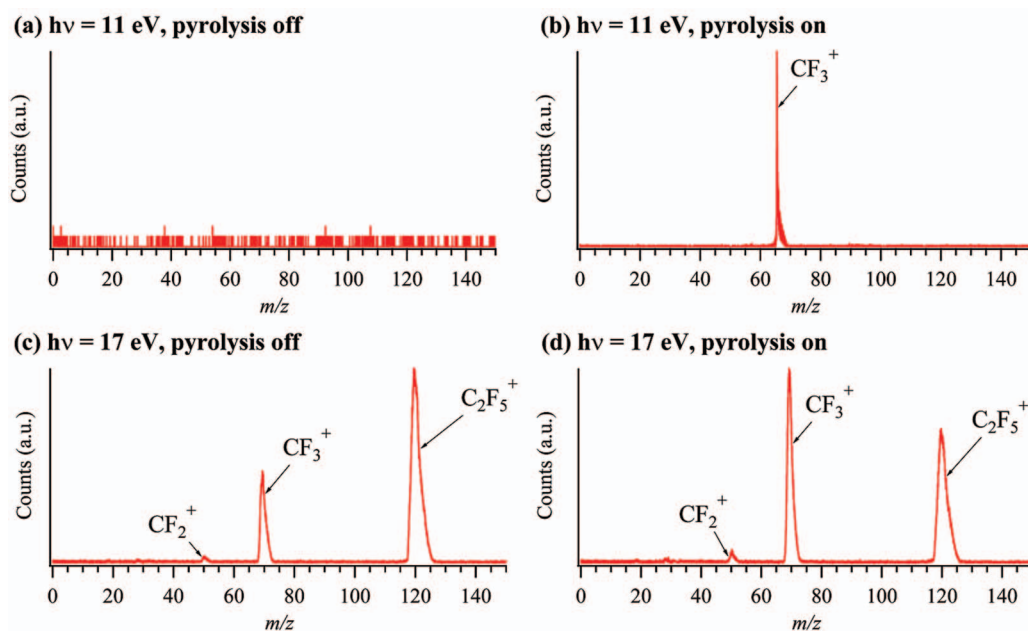


FIG. 1. TOF spectra of photoionized  $\text{C}_2\text{F}_6$  at (a) and (b) 11 eV and (c) and (d) 17 eV with pyrolysis (a)–(c) switched off and (b)–(d) switched on (50 W).



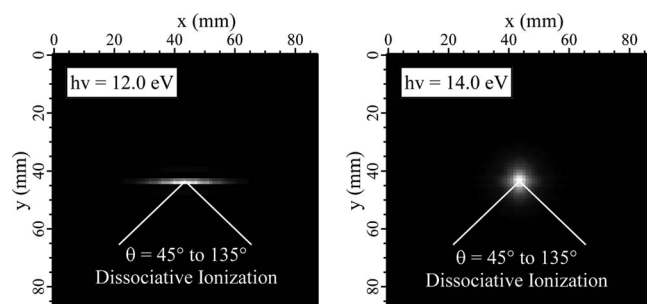


FIG. 2. Mass-filtered photoion velocity map images corresponding to the  $\text{CF}_3^+$  fragment, obtained at photon energies of 12.0 (left) and 14.0 eV (right). The relative amount of  $\text{CF}_3^+$  formed by dissociative ionization can be estimated by integrating an area of the image where the cold  $\text{CF}_3^+$  formed by direct ionization is assumed to be absent, such as the polar region delimited in the figure.

produced by dissociative ionization and hence, having a detectable amount of kinetic energy. To quantify the effect of dissociative ionization of the precursor, the kinetic energy distribution was integrated over a range of polar angles where the ions produced by direct ionization are not present (see Fig. 2 for details).

The result is plotted in Fig. 3 as percentage of dissociative ionization as a function of the photon energy. The AE estimated onset is located around 12.3 eV, 1.1 eV lower than the one measured by Jarvis *et al.*<sup>37</sup> This shows that the pyrolysis-surviving  $\text{C}_2\text{F}_6$  is storing thermal energy, most likely as vibrational excitation, which can then be released into fragmentation. In the present study, ion yield curve and mass-selected TPES spectra have been recorded up to 12.4 eV. Between 12.3 and 12.4 eV, the dissociative ionization represents at most  $\sim 2\%$  of the total  $\text{CF}_3^+$  signal. Although low, this contribution has to be taken into account in the present work, in particular in the case of the ion yield curve from which we can envisage to extract absolute photoionization cross sections<sup>41</sup> (see below).

## B. Ion yield

The ion yield associated with detection of mass-selected  $\text{CF}_3^+$  has been recorded in the 8.8–12.4 eV energy range

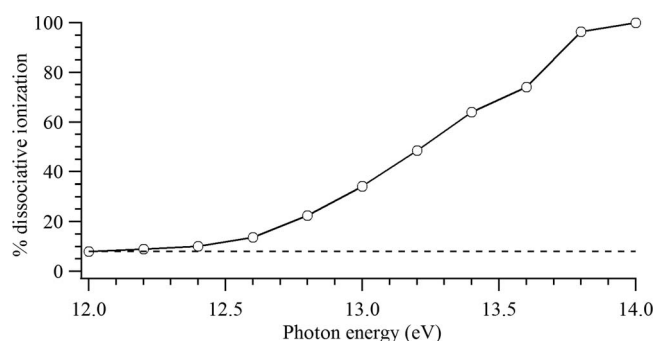


FIG. 3. Percentage of  $\text{CF}_3^+$  produced upon dissociative ionization events ( $\text{C}_2\text{F}_6 + h\nu \rightarrow \text{CF}_3^+ + \text{CF}_3 + e^-$ ) as a function of photon energy. The remaining percentage corresponds to direct photoionization of the nascent  $\text{CF}_3^\bullet$  radical. The baseline at 8%, represented by the dashed line, comes from imperfections of the VMI focusing and from the small transversal velocity component of the beam.

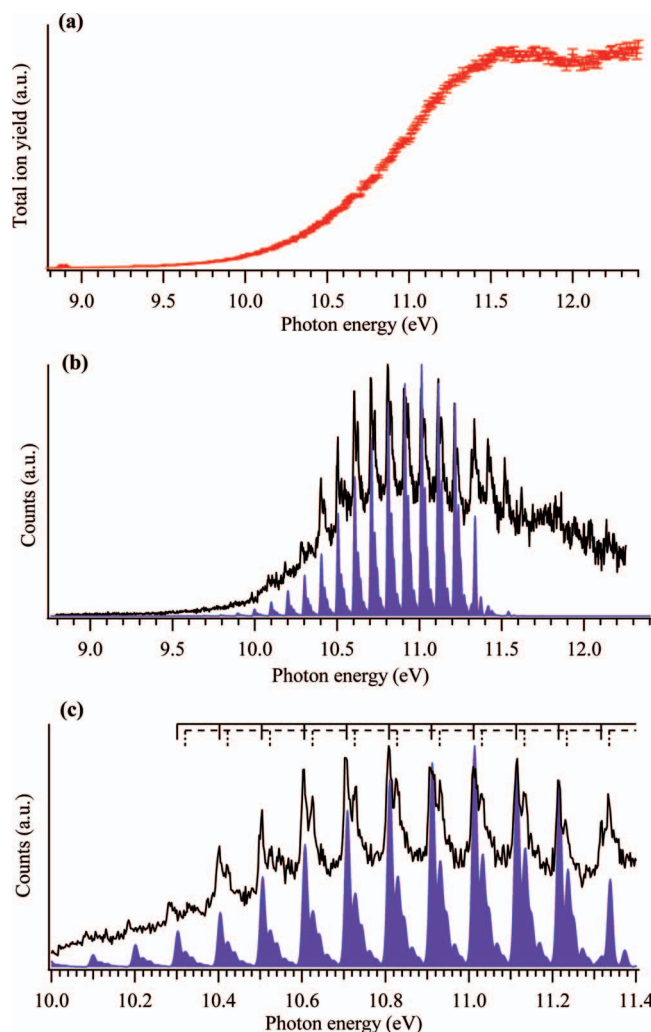


FIG. 4. (a)  $\text{CF}_3^+$  total ion yield curve recorded in the 8.8–12.4 eV energy range with a 20 meV photon resolution. (b) Mass-selected TPES of  $\text{CF}_3^\bullet$  recorded in the 8.5–12.4 eV energy range with an overall resolution of 8 meV (photons and electrons). (c) A zoom in the 10.0–11.7 eV region enables the observation of two vibrational progressions. The main one (solid line) is attributed to the  $(0,0) \rightarrow (0,n_2^+)$  excitation. The identification of the second progression (dashed line) is discussed in the text. The purple solid fill in panels (b) and (c) represents the simulated TPES based on calculated Franck-Condon factors,<sup>21</sup> and for a temperature of 350 K.

and is presented in Fig. 4(a). Since the extraction field is high enough to detect all the photoelectrons, the spectrum in Fig. 4(a) corresponds to the  $\text{CF}_3^+$  total ion yield vs the photon energy, providing a measurement of the relative photoionization cross sections of the radical over a broad energy range. In the spectrum, a slow onset can be appreciated, reaching a maximum around 11.5 eV. There is a slight decrease in ion signal for around 0.5 eV before climbing back up. A comparison is possible between this spectrum and the one that Lifshitz and Chupka<sup>2</sup> obtained in the 8.75–12.5 eV energy range. Their spectrum follows the same trends as our total ion yield spectrum, except in the 12.0–12.4 eV region where the signal increase is not as accentuated as in ours. This difference could be the sign of a contribution from the dissociative ionization of the hot precursor, which already starts from 12.3 eV in our spectrum as stated above. This feature shows us anyway that the upper part of our total ion yield curve has to be

considered with care, especially in the case of absolute cross section measurement.

### C. Mass-selected TPES

Mass-selected TPES of the  $\text{CF}_3^\bullet$  radical has been recorded in the 8.5–12.4 eV energy range and is displayed in Fig. 4(b). As already discussed, photoionization efficiency of  $\text{CF}_3^\bullet$  is expected to be very low in the threshold region ( $\sim 9.0$  eV) because of the large geometry difference between the radical and the ion. This feature is indeed observed in the spectrum where a very slow onset takes place between 9.0 and 9.7 eV. From 9.7 eV, the signal increases then in a more pronounced way until it reaches a maximum in the 11.0 eV region and decreases slowly up to 12.4 eV (in accordance with an evaluated value of 11.02 eV for  $\text{IE}_{\text{vert.}}(\text{CF}_3^\bullet)$  from a PES recorded at 12 eV).<sup>42</sup> One noticeable feature of this spectrum is the presence of sharp structures in the 10.3–11.6 eV regions (Fig. 4(c)) which mainly consist in two progressions having the same period of 0.102 eV and shifted from each other by  $\sim 0.020$  eV. In their experimental work, Lifshitz and Chupka<sup>2</sup> also observed a pattern composed of steps separated from each other by  $830\text{ cm}^{-1}$  (0.103 eV) in the photoionization efficiency curve of  $\text{CF}_3^\bullet$ . They attributed this pattern to the excitation of the  $\nu_2^+$  bending mode of  $\text{CF}_3^+$  and justified this attribution by the geometry difference between the  $\text{CF}_3^\bullet$  radical ( $\text{C}_{3v}$ ) and its ion ( $\text{D}_{3h}$ ) implying a predominant excitation of the out-of-plane bending mode of the ion (see Table I for description of the vibrational modes of  $\text{CF}_3^\bullet$  and  $\text{CF}_3^+$ ). Horn *et al.*<sup>16</sup> have also studied the photoionization of the  $\text{CF}_3^\bullet$  radical using coupled electron pair approximation (CEPA) calculations. In their work, they present two simulated spectra: a low-temperature (10 K) stick spectrum and a spectrum at 150 K with the sticks convoluted by a  $480\text{ cm}^{-1}$  full width at half maximum Gaussian. In the first spectrum, they observed three  $\nu_2^+$  progressions corresponding to  $(0, n_2^+)$ ,  $(1, n_2^+)$ , and  $(2, n_2^+)$  final states which reduce to only one progression in the second spectrum after convolution. This explains why only one progression is observed in the experimental work of Lifshitz and Chupka, done at a relatively low photon resolution (16 meV at 11 eV) and high temperature of the radical (500 K).<sup>2</sup>

In the present work, we observe two vibrational progressions in the TPES depicted in Figs. 4(b) and 4(c). In the following, we are going to show that the first one corresponds to excitation of the  $\nu_2^+$  mode of  $\text{CF}_3^+$  whereas the second one is a superposition of different progressions, mainly the  $(1, 0) \rightarrow (0, n_2^+)$  and  $(0, 0) \rightarrow (1, n_2^+)$  ones. To this end, we have undertaken a modeling of the photoionization process of  $\text{CF}_3^\bullet$ . This was possible due to the theoretical work of Bowman and coworkers who determined the Franck-Condon factors for the photoionization of  $\text{CF}_3^\bullet$ .<sup>21</sup> Briefly, they have applied the polyatomic variational code MULTIMODE<sup>43</sup> to obtain the rovibrational wavefunctions of  $\text{CF}_3^\bullet$  and  $\text{CF}_3^+$  in their ground electronic states for different vibrational levels involving the  $\nu_1/\nu_1^+$  and  $\nu_2/\nu_2^+$  modes and have thus deduced the FCFs corresponding to the photoionization process. These factors have been essential in this work to (i) obtain an estimation of

the temperature of our system, (ii) model our TPES, and (iii) extract experimental values for  $\nu_1^+$ ,  $\nu_2^+$ , and  $\text{IE}_{\text{ad.}}(\text{CF}_3^\bullet)$ . We have then proceeded as follows. First, each transition intensity has been modeled by the convolution of the FCF with a Gaussian curve to take into account our experimental resolution (8 meV). For combination bands,  $(n_1, n_2) \rightarrow (n_1^+, n_2^+)$ , we have assumed that the FCFs can be approximated by the products of the FCFs implying only one mode,  $\text{FCF}((n_1, 0) \rightarrow (n_1^+, 0)) \times \text{FCF}((0, n_2) \rightarrow (0, n_2^+))$ . Then, each transition intensity has been weighed by the Boltzmann factor  $\exp(-E_i/kT)$ , which accounts for the initial thermal vibrational population  $(n_1, n_2)$  of the neutral at temperature  $T$  ( $E_i$  is the initial vibrational energy of  $\text{CF}_3^\bullet$  and  $k$  is the Boltzmann constant), before summation. The transition energies are calculated assuming a simple harmonic model,  $\Delta E((n_1, n_2) \rightarrow (n_1^+, n_2^+)) = E_0 + n_1^+ \cdot \nu_1^+ + n_2^+ \cdot \nu_2^+ - n_1 \cdot \nu_1 - n_2 \cdot \nu_2$ , which is sufficient to describe the different transitions within several main peaks of the TPES, as it will be shown. However, a discussion of the vibrational anharmonicity will be given further in this work to derive a corrected value of the ionization potential. The model used is simple but has already been shown to provide a good and reliable overview of the relative vibrational populations according to the initial vibrational temperature.<sup>40,44</sup> Bowman *et al.*<sup>21</sup> have calculated the FCFs of  $\text{CF}_3^\bullet$  for several initial vibrational levels  $(n_1, n_2)$  of  $\text{CF}_3^\bullet$  with  $n_1 = 0-5$  and  $n_2 = 0-5$  (the two other vibrational modes of  $\text{CF}_3^\bullet/\text{CF}_3^+$ ,  $\nu_3/\nu_3^+$  and  $\nu_4/\nu_4^+$  have not been considered). Among the available calculated transitions, we have taken into account only the strongest ones according to their FCF and Boltzmann factor at the temperature range that we assume for  $\text{CF}_3^\bullet$  (see below).<sup>42</sup> It should be noted that the hot bands which have been taken into account for the simulation only concern transitions from excited  $n_1$  levels of the neutral radical as transitions from excited  $n_2$  levels have very small intensities. The TPES has been calculated for different initial temperatures of the radical leading, by comparison to the experimental TPES, to an estimated value of  $350 \pm 70$  K, in good agreement with previous pyrolysis experiments.<sup>40</sup> The simulated spectrum at 350 K is presented in the whole energy range (8.8–12.4 eV) in Fig. 4(b). Though the general behavior is well reproduced, there are several discrepancies between experiment and simulation: (i) the ratio between the intense structureless underlying background and the peaks is higher in the experimental spectrum than in the simulated one, (ii) the intensities of the peaks are not completely reproduced by the simulation, especially in the region below 10.9 eV, and (iii) the experimental spectrum extends above 11.5 eV up to 12.5 eV whereas the simulated spectrum is vanishing in this region.

Various hypotheses could account for these differences. Only pure vibronic transitions have been considered in the model. If the rotation is also considered, as it should be, the presence of wide P and R branches superimposed on sharp Q branches may contribute to a stronger background to peak ratio because of a congestion effect. Autoionization may also play a role in the photoionization process due to the high density of neutral states at threshold. In both absorption and emission studies of the  $\text{CF}_3$  radical,<sup>45-47</sup> high lying vibronic states of  $\text{CF}_3^\bullet$  have been identified. Autoionization has also

been proposed by Lifshitz and Chupka to account for several peaks below 10 eV in their photoionization efficiency curve of  $\text{CF}_3$ .<sup>2</sup> Finally, not all vibrational transitions have necessarily been taken into account. Only two of the four vibrational modes of  $\text{CF}_3^\bullet$  and  $\text{CF}_3^+$  have indeed been considered in the multi-dimensional calculations performed by Bowman *et al.*<sup>21</sup> The contribution of the  $\nu_3/\nu_3^+$  and  $\nu_4/\nu_4^+$  modes may thus be in part responsible for the difference observed between the experimental and simulated spectra. Moreover, the FCFs calculated by Bowman and coworkers<sup>21</sup> do indeed dramatically decrease in region above 11.5 eV to become null. The authors point out this feature, which differs from one-dimensional FCF calculation, by explaining that the inherent multi-dimensional nature of the  $\text{CF}_3^+$  vibrational states gives rise to a multitude of FCFs which have not all been calculated. We do not have any other explanation than the one offered by Bowman *et al.*

### D. The umbrella mode of $\text{CF}_3^+$

In Fig. 5 are represented over a short energy range the experimental and simulated TPES and the 14 transitions which have been used to obtain the simulated spectra. The largest feature of the band is accurately fitted with the  $00 \rightarrow 0n_2^+$  simulated transition (red curve). The good match between experimental and simulated steps is important because it means that  $\Delta G(n_2^+) = E(n_2^+ + 1) - E(n_2^+)$  can be derived from the energy differences between two consecutive peaks of the  $00 \rightarrow 0n$  progression. A comparison of our measured values of  $\Delta G(n_2^+)$  with those calculated by Bowman is shown in Fig. 6. Two possible attributions,  $n\nu_2^+ = 17$  or 18, for the peak around 10.81 eV are possible. Taking into account the uncertainties of the experimental and theoretical determinations, any other hypothesis than the two proposed regarding the attribution of the 10.81 eV band is much less probable. According to the choice for the  $n_2^+$  attribution, we present in Fig. 6 two sets of experimental measures for  $\Delta G(n_2^+)$  which correspond either to  $n_2^+ = 13-24$  or  $14-25$ . As seen in Fig. 6, our experimental values for  $\Delta G(n_2^+)$  are in good accordance

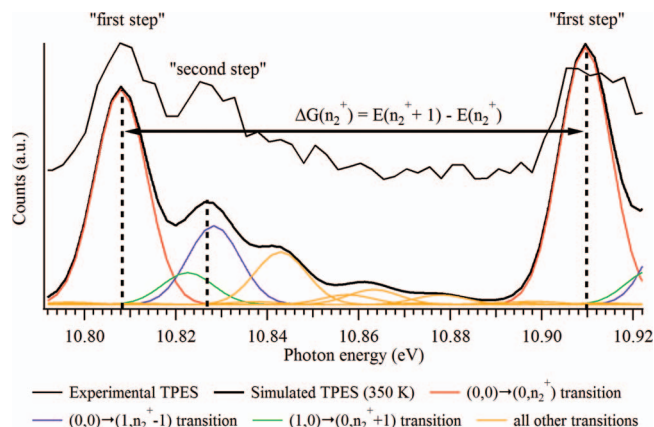


FIG. 5. Experimental (black) and simulated (bold black) TPES at 350 K of  $\text{CF}_3^\bullet$  in the 10.792–10.922 eV energy region. The simulation is obtained by summing 14 vibronic transitions (colored curves). Two attributions,  $n_2^+ = 17$  or 18, associated with two different origin in energy, are discussed in the text.

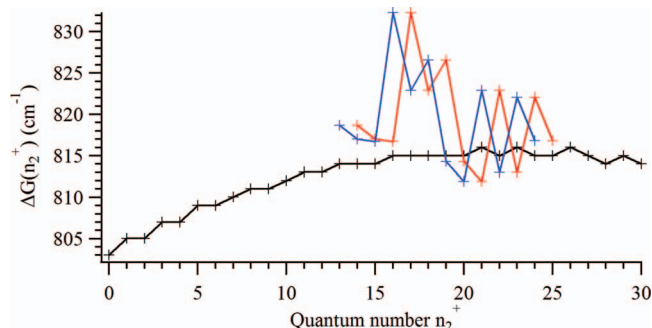


FIG. 6. Variation of  $\Delta G(n_2^+)$  with the quantum number  $n_2^+$  as calculated by Bowman *et al.*<sup>21</sup> (black line) and as measured experimentally in this work with two different attributions:  $n_2^+ = 13-24$  (blue line) or  $n_2^+ = 14-25$  (red line).

with those of Bowman. For  $n_2^+$  values between  $\sim 13$  and 25, we have an average value of  $\Delta G(n\nu_2^+) = 820 \pm 14 \text{ cm}^{-1}$  whereas Bowman proposed  $\Delta G(n_2^+) = 816 \text{ cm}^{-1}$ . These values are also close from the spacing between consecutive features observed by Lifshitz and Chupka, about  $830 \text{ cm}^{-1}$ , in their photoionization spectra<sup>2</sup> and by Basco and Hathorn,<sup>45</sup> about  $820 \text{ cm}^{-1}$ , in their VUV absorption spectra. In the latter study, their final state is not an ionic state but a highly excited Rydberg state of  $\text{CF}_3^\bullet$ . Nevertheless, it is known that high Rydberg states converging to the ground ionic states should be of similar nature, and hence, it is not surprising that they observe an absorption progression with a similar spacing around  $820 \text{ cm}^{-1}$ . However, these  $\Delta G(n_2^+)$  values measured for large quantum numbers should not be considered as a measurement of  $\nu_2^+$  because anharmonicity has to be taken into account. As visible in Fig. 6, the calculated values by Bowman shift by about  $11 \text{ cm}^{-1}$  over the  $n_2^+ = 0-30$  range due to a negative anharmonicity and the  $\nu_2^+$  value they obtained is thus  $804 \text{ cm}^{-1}$ . If one can put more confidence to the calculated difference ( $11 \text{ cm}^{-1}$ ) than to the absolute determination of a single frequency ( $804 \text{ cm}^{-1}$ ), then our experimental determination of  $\Delta G(n_2^+) = 820 \pm 14 \text{ cm}^{-1}$  for high  $n_2^+$  would lead to an estimation of  $\nu_2^+ = 809 \pm 14 \text{ cm}^{-1}$  (for both choice of  $n_2^+$  attribution). The precision given here corresponds to the standard deviation of our measurements and does not include the precision of calculations that we were not able to estimate.

### E. The breathing mode of $\text{CF}_3^+$

Back to Fig. 5, another property of  $\text{CF}_3^+$  can be extracted. The energy difference,  $E_{12}$ , between the two most intense transitions,  $(0,0) \rightarrow (0, n_2^+)$  (red curve) and  $(0,0) \rightarrow (1, n_2^+ - 1)$  (purple curve), is  $\nu_1^+ - \Delta G(n_2^+)$ , and hence can provide a direct measurement of the  $\nu_1^+$  frequency. For a low temperature of the radical, the  $(0,0) \rightarrow (1, n_2^+ - 1)$  transition is the only one contributing to the second most intense band (see the example of Horn *et al.*<sup>16</sup> at 10 K), and  $E_{12}$  can be easily extracted by measuring the energy difference between the maxima of the two peaks. However, the higher the temperature, the more the  $(1,0) \rightarrow (0, n_2^+ + 1)$  transition (green curve) will also contribute to the second peak and thus shift its maximum to lower energies by a quantity,  $\Delta E$  relative to the exact position of the



$(0,0) \rightarrow (1,n_2^+ - 1)$  transition. We can bracket this shift by simulating the spectrum over the  $\text{CF}_3$  temperature range, 300–400 K, that was found to be the best to fit the experimental TPES (see above). The shift increases from 0.4 meV for  $T = 300$  K to 1.3 meV for  $T = 350$  K and 1.8 meV for  $T = 400$  K. From 11 measurements, we obtained an average uncorrected  $\nu_1^+$  value of  $983 \text{ cm}^{-1}$  with a standard deviation of  $16 \text{ cm}^{-1}$ . By applying the correction of 1.3 meV (for  $T = 350$  K), we finally determine the value  $\nu_1^+ = 994 \pm 16 \text{ cm}^{-1}$  for the breathing mode frequency, which is, to our knowledge, the first measurement ever done in the gas phase.

## F. The adiabatic ionization potential of $\text{CF}_3$

The next point to be addressed in this work concerns the adiabatic ionization energy ( $\text{IE}_{\text{ad.}}$ ) of  $\text{CF}_3^\bullet$ . As mentioned in the Introduction, many experimental<sup>2,3,5,7,9–13,26,27</sup> and theoretical<sup>16–19,21,22,25</sup> works have already been undertaken to obtain an evaluation of this energy. Because of the low FCFs at threshold, a direct measurement of  $\text{IE}_{\text{ad.}}(\text{CF}_3^\bullet)$  is not possible from our TPES spectrum (Fig. 4(b)). We propose here an estimation of  $\text{IE}_{\text{ad.}}(\text{CF}_3^\bullet)$  by combining the experimental determination of the energies of the intense  $(0,0) \rightarrow (0,n_2^+)$  transitions observed for large values of  $n\nu_2^+$  and the vibrational energy calculations of the corresponding  $(0,n_2^+)$  levels of  $\text{CF}_3^+$  by Bowman and coworkers.<sup>21</sup> Namely, we will extract  $\text{IE}_{\text{ad.}}$  from the relation

$$E_{\text{EXP}}((0,0) \rightarrow (0,n_2^+)) = \text{IE}_{\text{ad.}} + E_{\text{THEO}}((0,n_2^+)). \quad (1)$$

The justification of the method relies on several facts. First of all, Bowman calculations have shown (see Fig. 6) that the anharmonicity cannot be neglected for the umbrella mode in  $\text{CF}_3^+$  when we consider the full  $n_2^+$  range, 0–30. It is interesting to note in Fig. 6 that, if we only consider the range of  $n_2^+$  values experimentally observed (10–26), the  $\nu_2^+$  spacing ( $\Delta G(n_2^+)$ ) is roughly constant and we could think that the anharmonicity is negligible, which is not the case. Hence, we cannot use a simple harmonic model to directly derive  $\text{IE}_{\text{ad.}}$  only from the experimental determination of the  $(0,0) \rightarrow (0,n_2^+)$  transition energies and the  $\nu_2^+$  spacing for large value of  $n_2^+$ . Second, we believe that the precision of Bowman calculations is certainly better for the determination of vibrational energies than for the absolute value of  $\text{IE}_{\text{ad.}}$ , which he has found to be  $73\,052 \text{ cm}^{-1}$  (9.057 eV). Hence, combining experimental transition energies and calculated vibrational energies, which include anharmonic corrections, appears to be for us the best method to derive  $\text{IE}_{\text{ad.}}$ .

However, as outlined above, there are two possibilities for identification of the bands: the band observed at  $h\nu = 10.40 \text{ eV}$  could be assigned to the  $(0,0) \rightarrow (0,n_2^+)$  transition with  $n_2^+ = 13$  or 14. Any other attribution would lead to unrealistic differences between the calculated and extrapolated  $\text{IE}_{\text{ad.}}(\text{CF}_3^\bullet)$ , within the experimental and theoretical precisions. In the first hypothesis, the experimental transition energies for large  $n_2^+$  are higher than the theoretical ones by  $0.045 \pm 0.003 \text{ eV}$  on average. In the second hypothesis, they are lower by  $0.056 \pm 0.003 \text{ eV}$ . We can simply report these energy differences to the adiabatic ion-

ization energy calculated by Bowman *et al.* to finally get two values for  $\text{IE}_{\text{ad.}}(\text{CF}_3^\bullet)$ : 9.102 eV or 9.001 eV for the 1st and 2nd hypothesis, respectively. Doing so is equivalent to using Bowman's calculated vibrational energies and experimental absolute transition energies to derive  $\text{IE}_{\text{ad.}}$  following Eq. (1). The two estimations obtained for  $\text{IE}_{\text{ad.}}(\text{CF}_3^\bullet)$  confirm previous works stating that  $\text{IE}_{\text{ad.}}(\text{CF}_3^\bullet)$  lies at  $\sim 9.0 \text{ eV}$ .<sup>9,11,12,16–19,21,22,26,27</sup> No particular argument is compelling us to decide between both values. As an example, our 9.102 eV value is in excellent agreement with the recent work of Harvey *et al.* who determined  $\text{IE}_{\text{ad.}}(\text{CF}_3^\bullet)$  to be  $9.090 \pm 0.015 \text{ eV}$ , based on an indirect method using the measured appearance energies of  $\text{CF}_3^+$  and  $\text{CF}^+$  from  $\text{C}_2\text{F}_4$ , and the  $\text{IE}_{\text{ad.}}$  of  $\text{CF}$ .<sup>27</sup> Another recent work by Bodi *et al.*<sup>26</sup> derived indirectly a value for  $\text{IE}_{\text{ad.}}(\text{CF}_3^\bullet)$  of 9.02 or 9.08 eV from the appearance energy of  $\text{CF}_3^+$  from  $\text{CF}_3\text{Br}$ , based on either the existing values of the  $\text{CF}_3\text{--Br}$  bond energy, or the enthalpies of formation of  $\text{CF}_3$ ,  $\text{CF}_3\text{Br}$ , and  $\text{Br}$ , respectively. Both values are in good agreement with our two estimations.

## IV. CONCLUSIONS

In this work, the  $\text{CF}_3^\bullet$  radical was successfully produced by pyrolysis of hexafluoroethane and studied by means of threshold photoelectron-photoion coincidence spectroscopy leading to mass-selected TPES. For the first time, a high resolution TPES spectrum of the  $\text{CF}_3^\bullet$  radical could be obtained in the 8.5–12.4 eV energy range. This TPES shows a long progression of peaks revealing a very large excitation of the umbrella vibrational mode ( $\nu_2^+$ ) and a very small excitation of the breathing vibrational mode ( $\nu_1^+$ ) in the  $\text{CF}_3^+$  cation. In each band, the resolution was sufficient to separate two peaks corresponding to the  $(0,0) \rightarrow (0,n_2^+)$  transition and to a combination of the  $(0,0) \rightarrow (1,n_2^+ - 1)$  and  $(1,0) \rightarrow (0,n_2^+ + 1)$  transitions.

Using vibrational energies and Franck-Condon factors calculated by Bowman and coworkers,<sup>21</sup> we could simulate a TPES which helped in assigning bands and in deriving spectrometric information on  $\text{CF}_3^+$ . We first deduce an initial vibrational temperature of the system of  $350 \pm 70 \text{ K}$ . Gas-phase values for the  $\nu_1^+$  frequency of the breathing vibrational mode of  $\text{CF}_3^+$  could also be obtained for the first time as  $\nu_1^+ = 994 \pm 16 \text{ cm}^{-1}$ . The  $n_2^+$  spacing ( $\Delta G(n_2^+)$ ) between bands observed only in a region of very excited  $n_2^+$  levels (10–26) is found to be almost constant,  $820 \pm 14 \text{ cm}^{-1}$ , but this should not be considered as a measure of  $\nu_2^+$  since the anharmonicity has been found to be non-negligible by Bowman. Inclusion of these anharmonicity corrections enable us to derive the  $\nu_2^+$  frequency of the umbrella vibrational mode  $\nu_2^+$  of  $\text{CF}_3^+$  as  $\nu_2^+ = 809 \pm 14 \text{ cm}^{-1}$  and two estimated values of the adiabatic ionization potential,  $\text{IE}_{\text{ad.}}(\text{CF}_3^\bullet) = 9.001$  or  $9.102 \text{ eV}$  confirming many previous experimental and theoretical works. The experimental TPES illustrates the difficulty in obtaining a precise value for the  $\text{IE}_{\text{ad.}}(\text{CF}_3^\bullet)$  by a direct method due to the long extrapolation involved from the first measurable vibrational transition ( $\sim 1.3 \text{ eV}$ ). A value of the vertical ionization potential could also be provided:  $\text{IE}_{\text{vert.}}(\text{CF}_3^\bullet) = 11.02 \text{ eV}$  by the observation of an

analyzed photoelectron spectra recorded at a fixed photon energy of 12 eV.

Furthermore, we have recorded the total ion yield in the 8.8–12 eV energy range, and we have shown in a previous study that the absolute photoionization cross sections of the  $\text{CH}_3^\bullet$  radical could be derived from a total ion yield curve by normalizing it with the absolute cross section measured with a laser at 118.2 nm.<sup>41</sup> In a same manner, further laser-based experiments may be envisaged for  $\text{CF}_3^\bullet$  in order to obtain the absolute photoionization cross sections of the radical in the reported energy range.

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