The vacuum UV photoabsorption spectroscopy of the cis-1,2-dichloroethylene (1,2-ClHC=CHCl) in the 5-20 eV range. An experimental and theoretical investigation

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I. INTRODUCTION

The chlorinated derivatives of ethylene are important reactants in several industrial applications. They are also used to replace long-living ozone-depleting agents. As a consequence, these compounds became widely spread but were found to be abundant atmospheric air pollutants. Their toxicity and potential carcinogenicity have been investigated. Several groups studied the release of the highly ozone-depleting Cl atom and HCl molecule by UV photons or atmospheric OH attack in the three isomers of dichloroethylene. Gas-phase ion chemistry of these compounds has also been reported. These aspects were almost only investigated in the two 1,2-C₂H₂Cl₂ isomers. However,
the studies on the photoabsorption spectrum of both compounds remain scarce and mainly restricted to the 160-135 nm (or 7.75-9.18 eV) wavelength region.

The first vacuum UV photoabsorption spectrum (PAS) of the two 1,2-C_2H_2Cl_2 isomers has been reported by Mahncke and Noyes\(^{10}\) in 1935. They recorded the spectra between the visible region and 75 nm (16.53 eV). They roughly divided them into three parts: (i) a broad continuum starting at 240 nm (5.17 eV) with a maximum at 190 nm (6.52 eV), (ii) a discrete absorption spectrum extending from 157 nm (7.90 eV) to 135 nm (9.18 eV) and (iii) a continuous absorption below 128 nm (9.69 eV) in the cis-isomer and a series of diffuse bands in the trans-isomer. A Rydberg series classification and a vibrational analysis were attempted. Ionization energies were obtained by Rydberg series extrapolation. Analysis were attempted. Ionization energies were obtained by

Walsh\(^{11}\) recorded the vacuum UV PAS of all chloroethylenes, except the 1,1-C_2H_2Cl_2 species. Beside the broad continuum peaking at 185-195 nm (6.70-6.36 eV), vibrational progressions of different Rydberg series were observed and analyzed in all spectra.

Walsh and Warsop\(^{12}\) reported a detailed analysis of the vacuum UV PAS of the cis-1,2-C_2H_2Cl_2. They mention the continuum peaking at 190 nm (6.52 eV) but their attention was focused on the analysis and discussion of the discrete spectrum measured between 167 and 143 nm (7.42-8.67 eV).

In a paper on the photochemical HCl-loss from chloroethylenes, Berry\(^4\) measured the vacuum UV absorption spectrum of all chlorinated derivatives of ethylene in the 260-140 nm range (4.77-8.86 eV) and analyzed in more detail the broad band located between 240 and 180 nm (5.17-6.88 eV). The discrete part of the spectrum has not been analyzed.

Closely related to photoabsorption spectroscopy, the low electron energy-loss spectroscopy of all chloro-substituted ethylenes C_2H_2Cl_{4-x} has been reported by Koerting et al.\(^{13}\) This work was essentially focused on the singlet-triplet valence transitions. Excitations to singlet valence and Rydberg states below 7.0 eV were also observed.

On the quantum chemical level, Arulmoziraja et al.\(^{14}\) presented an extended high-level theoretical study on the electronic transitions in the cis- and trans-dichloroethylenes, and in tetrachloroethylene using the SAC–CI theory. The main purpose was to obtain the electronic spectra and to assign excitations to valence and Rydberg states of both singlet and triplet multiplicity. More recently, Khvostenko\(^{15}\) reported DFT calculations at the B3LYP/6-311-G(d,p) level of the transitions to excited valence singlet and triplet states of chloroethylene molecules.

We recently reported on the vacuum UV PAS study of 1,1-C_2H_2Cl_2\(^{16}\) observed and analyzed between 5 eV and 20 eV photon energy. In the frame of our work on this series of molecular systems, the aim of the present paper is to propose a detailed analysis of the vacuum UV photoabsorption spectrum of the cis-1,2-C_2H_2Cl_2 isomer (i) at medium resolution but for the first time in the 10-20 eV photon energy range and (ii) at higher resolution between 5.0 and 13.0 eV, with vibrational structure analysis. Quantum chemical calculations will be used to support the assignments. In a near future a similar work on the trans-1,2-C_2H_2Cl_2 isomer will be reported.\(^{17}\)

II. EXPERIMENTAL

The experimental setup used in this work at the BESSY I and II synchrotron radiation facilities (Berlin, Germany) has been described previously.\(^{18}\) Briefly, two monochromators have been used. For medium resolution spectra (resolving power of 1200 at h = 10 eV), a modified 1.5 m-NIM 225 McPherson monochromator equipped with a 1200 lines/mm gold-coated laminar Zeiss grating was used. High resolution measurements (resolving power of about 15000 at 10 eV) have been reached with a 3m-NIM monochromator equipped with an Al/MgF\(_2\) spherical grating of 600 lines/mm.

The synchrotron radiation intensity and the pressure inside the cell were monitored, ensuring reliable absorption data. The sample pressure was kept in the 30-40 bar to prevent saturation. The cis-1,2-C_2H_2Cl_2 sample purchased from Aldrich (99% stated purity) was used without further purification.

As described and discussed in detail in previous works, a continuum subtraction procedure has been applied to better identify and characterize weak and/or diffuse structures superimposed on an intense continuum.\(^{19,20}\) The resulting spectrum is denoted as Δ-plot. This data handling procedure has been validated by Marmet\(^{21}\) and Carbonneau.\(^{22}\)

The wavelength scales calibration is based on the Ar absorption spectrum between the \(^{2}\)P\(_{3/2}\) and the \(^{2}\)P\(_{1/2}\) ionic states, with an accuracy better than 2 meV. Between 6 eV and 20 eV photon energy, the photoabsorption spectrum has been recorded with energy increments of 15 meV, so that the energy

![FIG. 1. Vacuum UV photoabsorption spectrum of cis-1,2-C_2H_2Cl_2 between 5 eV and 13 eV photon energy. The continuous red curve corresponds to the strongly smoothed PAS curve by fast Fourier transform. Vertical bars locate valence and Rydberg transitions and shaded areas show their convergence limit. Dotted areas correspond to vertical ionization energies.](scitation.org/journal/adv)
positions have an uncertainty of about 8 meV. The 5-15 eV range has also been investigated with energy increments of 2 meV. Several parts of the spectrum, e.g., 7.0-10.0 eV and 11.6-12.2 eV, have also been recorded with 500 µeV energy steps. The energy positions are here known within ±2 meV. Reproducibility of energy positions has been checked with spectra recorded over several years.

III. EXPERIMENTAL RESULTS

Fig. 1 displays the vacuum UV PAS of cis-1,2-C_2H_2Cl_2 between 5 eV and 13 eV photon energy, with 2 meV energy increments. The whole 5-20 eV range may be split in four distinct regions: (i) the 5.0-7.2 eV region consists of a number of weak broad bands superimposed on a continuum; (ii) the 7.2-9.6 eV range contains a large number of weak to very weak sharp features and bands superimposed on a relatively weak continuum with steeply increasing intensity starting at 9.2 eV; (iii) the region above 9.2 eV and up to 13 eV consists of a series of weak, fairly narrow structures superimposed on a strong continuum; (iv) the spectral range above 13 eV is displayed in Fig. 2a and consists of several successive broad bands up to 20 eV; the corresponding Δ-plot is displayed in Fig. 2b. The positions of the Rydberg transitions and the convergence limits are identified.

Tables I and II list the energies of the vibrationless transitions to Rydberg states converging respectively to the ground

| TABLE I | Rydberg series observed in the vacuum UV photoabsorption spectrum of cis-1,2-C_2H_2Cl_2 converging to the \( \tilde{X}^{2}B_1 \) (cis-1,2-C_2H_2Cl_2^+) ionic ground state at 9.666 eV. Energy positions (eV), wavenumbers (cm\(^{-1}\)), effective quantum numbers (\( n^* \)), average quantum defects (\( \bar{\delta} \)) and assignments as proposed in this work (1 eV= 8065.545 cm\(^{-1}\)). Comparison is made with the literature data of Refs. 10–12.
<table>
<thead>
<tr>
<th>This Work</th>
<th>10</th>
<th>11</th>
<th>12</th>
</tr>
</thead>
<tbody>
<tr>
<td>eV</td>
<td>cm(^{-1})</td>
<td>( n^* )</td>
<td>( \bar{\delta} )</td>
</tr>
<tr>
<td>2b_1( \rightarrow )ns (( \bar{\delta}=0.96\pm0.01 ))</td>
<td></td>
<td>6.398 51603 2.040 - - -</td>
<td>8.192 66077 3.039 66020 65840 [65870]</td>
</tr>
<tr>
<td></td>
<td>9.390 75711 7.021 - - -</td>
<td>59734</td>
<td></td>
</tr>
<tr>
<td>2b_1( \rightarrow )np (( \bar{\delta}=0.53\pm0.01 ))</td>
<td></td>
<td>7.414 59798 2.458 - - -</td>
<td>8.547 68936 3.487 69060</td>
</tr>
<tr>
<td></td>
<td>8.985 72469 4.470 72408</td>
<td>9.214 74316 5.486 74240</td>
<td></td>
</tr>
<tr>
<td></td>
<td>9.340 75332 6.460 - - -</td>
<td>75648</td>
<td></td>
</tr>
<tr>
<td>2b_1( \rightarrow )nd (( \bar{\delta}=0.08\pm0.03 ))</td>
<td></td>
<td>8.089 65242 2.918 65260 65182</td>
<td>8.170 65895 3.015 [65870]</td>
</tr>
<tr>
<td></td>
<td>8.777 70791 3.912 70717 70725</td>
<td>9.097 73396 4.903 73328 73331</td>
<td></td>
</tr>
<tr>
<td></td>
<td>9.245 74566 5.865 74590</td>
<td>9.357 75469 6.636 75437</td>
<td></td>
</tr>
<tr>
<td></td>
<td>9.435 76048 7.674 - - -</td>
<td>75675</td>
<td></td>
</tr>
<tr>
<td>2b_1( \rightarrow )nd( \sigma ) (( \bar{\delta}=0.002\pm0.008 ))</td>
<td></td>
<td>8.170 65895 3.015 [65870]</td>
<td>8.806 71025 3.978 [70736]</td>
</tr>
</tbody>
</table>
TABLE II. Rydberg series converging to the ionic excited states observed in the vacuum UV photoabsorption spectrum of cis-1,2-C_{2}H_{2}Cl_{2}. Energy position (eV), wavenumber (cm^{-1}), effective quantum numbers (n∗) and assignments proposed in this work. The IE's used as convergence limit are IE_{ad} for 4b_{2}−1, 3a_{1}−1 and 2b_{2}−1 are 11.690 eV, 16.732 eV and 18.8 eV and IE_{ad} for 3a_{1}−1, 1b_{1}−1 and 1b_{2}−1 are 11.965 eV, 12.375 eV and 13.592 eV successively. Conversion factor: 1 eV = 8 065.545 cm^{-1}.24

<table>
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<tr>
<th>eV</th>
<th>cm^{-1}</th>
<th>n∗</th>
<th>Assign.</th>
</tr>
</thead>
<tbody>
<tr>
<td>8.446</td>
<td>67791</td>
<td>2.050</td>
<td>3s</td>
</tr>
<tr>
<td>10.252</td>
<td>82010</td>
<td>3.075</td>
<td>4p</td>
</tr>
<tr>
<td>10.584</td>
<td>84430</td>
<td>3.507</td>
<td>4p(π)</td>
</tr>
<tr>
<td>10.792</td>
<td>86527</td>
<td>3.892</td>
<td>4d</td>
</tr>
<tr>
<td>5a_{1}</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>10.880</td>
<td>87753</td>
<td>3.541</td>
<td>4p</td>
</tr>
<tr>
<td>11.120</td>
<td>89689</td>
<td>4.013</td>
<td>5s/4d</td>
</tr>
<tr>
<td>11.275</td>
<td>90939</td>
<td>4.441</td>
<td>5p(σ)</td>
</tr>
<tr>
<td>11.336</td>
<td>93044</td>
<td>5.631</td>
<td>6p(σ)</td>
</tr>
<tr>
<td>1a_{2}</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>11.342</td>
<td>91479</td>
<td>3.629</td>
<td>4p(π)</td>
</tr>
<tr>
<td>11.750</td>
<td>94770</td>
<td>4.666</td>
<td>5p(π)</td>
</tr>
<tr>
<td>1b_{1}</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>12.054</td>
<td>97222</td>
<td>3.041</td>
<td>4s/3d</td>
</tr>
<tr>
<td>3a_{1}</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>13.39</td>
<td>108000</td>
<td>2.02</td>
<td>3s</td>
</tr>
<tr>
<td>14.65</td>
<td>118160</td>
<td>2.56</td>
<td>3p</td>
</tr>
<tr>
<td>15.85</td>
<td>127840</td>
<td>3.93</td>
<td>4d/5s</td>
</tr>
<tr>
<td>16.15</td>
<td>130260</td>
<td>4.84</td>
<td>5d</td>
</tr>
<tr>
<td>2b_{2}</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>15.55</td>
<td>125420</td>
<td>2.03</td>
<td>3s</td>
</tr>
<tr>
<td>17.30</td>
<td>130534</td>
<td>2.97</td>
<td>4s/3d</td>
</tr>
</tbody>
</table>

*The vertical ionization energy is used as convergence limit for these series.
and to excited ionic states. Previous data from the literature are also mentioned.10–12

IV. AB INITIO CALCULATIONS: METHODS AND RESULTS

A. Computational tools

Quantum chemical calculations were performed with the Gaussian 09 program package.25 The aug-cc-pVDZ basis set containing polarization as well as diffuse functions26 was used throughout. In specific cases, calculations with the basic cc-pVDZ set, which does not include diffuse functions, were also performed.

Geometry optimizations have been performed at the CCSD(FC),27,28 DFT(M06-2X)25 and TDDFT26 levels.

The wavenumbers of the twelve vibrational normal modes were computed at the DFT(M06-2X) and TDDFT(M06-2X) levels.

B. Results of the calculations

The results of the geometry optimizations in the C_{2v}, C_{2} and C_{4v} symmetry point groups at different computational levels are presented in Table S1 (see supplementary material). These results are compared and discussed below.

The calculated vertical transition energies to several neutral excited states are listed in Table III with respect to the neutral ground state in the C_{2v} symmetry group. Only those neutral states excited with non-zero oscillator strength are mentioned.

The two lowest 1B_{1} excited states calculated at the TDDFT level show a mixed character involving similar configurations but with different weights. For the 1B_{1} at 5.98 eV, the main character is R′p′ (where R′ stands for “Rydberg state”) with an important [nCl+σ*CH] component whereas for the 2B_{1} at 6.35 eV the R′s character is dominant with a smaller [R′p′σ+nCl+σ*CH] component. These states are therefore expected to be strongly coupled but this coupling is probably overestimated at the TDDFT level, leading to a very low energy for the first state. The first 1B_{2} excited state, however, corresponds to a nearly pure π→π* configuration and has by far the largest oscillator strength.

The vibrational wavenumbers associated with the twelve normal modes represented in Fig. 3 have been calculated for the first four excited states of the neutral molecule at the
TDDFT level in the $C_{2v}$ symmetry group and are listed in Table IV. The presence of imaginary wave numbers indicates that these $C_{2v}$ geometries do not correspond to equilibrium situations. Table V reports the vibrational wavenumbers of the neutral ground state in the $C_{2v}$ group$^{31}$ and of the first $1^1B_2$ excited state ($\pi \rightarrow \pi^*$) in the $C_{2v}, C_2$ and $C_3$ groups, computed at the DFT (M06-2X) level.

These optimizations of the $3^1B_2$ excited state lead to an equilibrium geometry corresponding to a twisted situation of $C_2$ symmetry (all real wavenumbers, see Table V, column 5). In this geometry, the $\pi \rightarrow \pi^*$ state belongs to the $1^B$ representation. The C=C bond is moderately lengthened compared to the ground state but the bond angles are substantially modified (see Table S1). A saddle point is obtained in $C_3$ (one imaginary wavenumber, see Table V, column 6) and a third order critical point in $C_{2v}$ (stationary point with three imaginary wavenumbers, see Table IV, column 4 and Table V, column 4). Compared to the $C_2$ minimum, the stationary points in $C_4$ and $C_{2v}$ are destabilized by 1.13 eV and 1.24 eV, respectively. They are characterized by a very large C=C bond lengthening (nearly 0.2 Å) and large bond angle modifications.

Furthermore, at the optimized twisted $C_2$ geometry of the $3^1B_2$ state, the $\tilde{X}^1A$ state is higher in energy. Internal conversion from the $1^B$ state to the $\tilde{X}^1A$ state is expected to take place upon relaxation. Anticipating the publication of the calculation results on trans-1,2-C$_2$H$_2$Cl$_2$, it can be emphasized that the $3^1B_2$ optimized geometry is also that obtained from the optimization of the first excited state in the trans-isomer. It can therefore, be predicted that the isomerization is obviously photo-induced.
TABLE IV. Vibrational wavenumbers (cm\(^{-1}\)) calculated for the twelve normal modes (VNM) (see Fig. 3) of the first four excited states in the C\(_{2v}\) symmetry group at the TDDFT(M06-2X) level. For the neutral ground state comparison is made with experimental data.\(^{21}\) Imaginary wavenumbers are bold printed.

<table>
<thead>
<tr>
<th>State</th>
<th>VNM</th>
<th>1(^{1})B(_{1})</th>
<th>2(^{1})B(_{1})</th>
<th>3(^{1})B(_{2})</th>
<th>5(^{1})B(_{1})</th>
</tr>
</thead>
<tbody>
<tr>
<td>v(_{1})</td>
<td>3279</td>
<td>3048</td>
<td>3293</td>
<td>3320</td>
<td></td>
</tr>
<tr>
<td>v(_{2})</td>
<td>1529</td>
<td>1427</td>
<td>1269</td>
<td>1470</td>
<td></td>
</tr>
<tr>
<td>v(_{3})</td>
<td>933</td>
<td>1205</td>
<td>1112</td>
<td>1083</td>
<td></td>
</tr>
<tr>
<td>v(_{4})</td>
<td>481</td>
<td>778</td>
<td>760</td>
<td>765</td>
<td></td>
</tr>
<tr>
<td>v(_{5})</td>
<td>147</td>
<td>159</td>
<td>189</td>
<td>270</td>
<td></td>
</tr>
</tbody>
</table>

\(a_2/\alpha''\)

| v\(_{6}\) | 840  | 901  | \(^{i}\)439 | \(^{i}\)637 |
| v\(_{7}\) | \(^{i}\)297 | \(^{i}\)420 | \(^{i}\)964 | \(^{i}\)766 |

\(b_1/\alpha''\)

| v\(_{8}\) | 680  | 686  | \(^{i}\)738 | \(^{i}\)728 |

\(a_2/\alpha''\)

| v\(_{9}\) | 3251 | 3066 | 3281 | 3303 |
| v\(_{10}\) | 1029 | 1359 | 1266 | 1104 |
| v\(_{11}\) | 530  | 943  | 911  | 787  |
| v\(_{12}\) | \(^{i}\)312 | 533  | 484  | 485  |

V. DISCUSSION OF THE EXPERIMENTAL DATA

In the C\(_{2v}\) point group, the molecular orbital configuration of cis-1,2-C\(_2\)H\(_2\)Cl\(_2\) is given by

\[
\begin{align*}
1s^{2}(Cl) & \quad 1s^{2}(Cl) \quad 1s^{2}(Cl) \quad 1s^{2}(C2) \quad 2s^{2}(Cl2) \quad 2p_x^6 \quad 2p_y^6 \quad 2p_z^6 \quad (Cl) \quad 2p_x^6 \quad 2p_y^6 \quad 2p_z^6 \quad (Cl) \\
\times 2p_{x+y}^6(2Cl) & \quad 1a_1^2 \quad 1b_2^2 \quad 2a_1^2 \quad 2b_2^2 \quad 3a_1^2 \quad 3a_2^2 \quad 3b_2^2 \quad 4a_1^2 \quad 3b_2^2 \quad 1a_2^2 \\
\times 5a_1^2 \quad 4b_2^2 \quad 2b_1^2 \quad \chi^A_{2v} \quad A_1
\end{align*}
\]

where \(A_1\) is the deepest outer-valence shell orbital.

Geometry optimizations in other symmetry point groups (C\(_{1}\), C\(_{2}\) and C\(_{1}v\)) for the 1\(^{1}\)B\(_{1}\) and 2\(^{1}\)B\(_{1}\) states have been unsuccessful owing to the large variation of the electronic energies upon geometry change, leading to numerous crossings.

A. The valence transitions (Figs. 1, 4 and 5)

The characteristic low energy broad band observed in the vacuum UV PAS of the ethylene compounds displays a doublet maximum at 6.568 eV-6.620 eV in cis-1,2-C\(_2\)H\(_2\)Cl\(_2\) (Fig. 4). Compared to our observations in the chlorinated derivatives investigated up to now,\(^{16,37,38}\) this band has a similar intensity and extends between 5.3 eV and 7.3 eV. It results from the superposition of several contributions.

To enhance the weak structures superimposed on the continuum the subtraction method mentioned in Section II...
has been applied. The red curve in Fig. 5a represents the continuum which is subtracted from the original signal. The result of this subtraction operation is displayed in Fig. 5b which clearly shows two different parts: (i) between 5.0 eV and 6.0 eV a very weak series of peaks with spacing suggesting a vibrational progression and (ii) between 6.0 eV and 7.0 eV a more intense series of alternating broad and narrow peaks.

The very weak signal between 5.0 eV and 6.0 eV may be interpreted as part of the transitions to a longer vibrational progression belonging to a single valence excited state. A π→σ* state is a reasonable candidate. By quantum chemical calculations, Arulmozhiraja et al.14 calculated the π→σ*(1B1) transition energy at 6.45 eV in cis-1,2-C_2H_2Cl_2 whereas Khvostenko15 predicted this transition at 6.52 eV. The present calculations indicate a more complex situation where the final 1B_2 state has a strongly mixed Rydberg (R'p') character (see Table III). The predicted oscillator strength is very weak. At both DFT and TDDFT (M06-2X) levels the optimized geometry of the 1B_1 state in the C_2v point group corresponds, however, to a transition state whose vibrational wavenumbers have been calculated (see Table IV).

As discussed in Section IV B, optimization attempts in lower symmetry groups were unsuccessful. The identified peaks of the very weak signal are shown by dashed lines in Fig. 5b. An average separation of 0.12±0.01 eV (960±80 cm\(^{-1}\)) could be determined. This compares favorably with the values of 933 cm\(^{-1}\) (TDDFT) or 944 cm\(^{-1}\) (DFT) predicted for the in-plane C-H bending mode excitation \(v_3\) (see Fig. 3) and is compatible with the large change in the optimized H-CC angle (see Table SI).

The 6.0–7.0 eV energy range consists of a complex series of fairly narrow peaks entangled in a sequence of broader structures. As far as the diffuse features starting at 6.16 eV are concerned, a regularly distributed intensity is observed up to 7.0 eV at intervals of about 0.15±0.02 eV (2100±210 cm\(^{-1}\)). The maximum intensity for this progression is observed at 6.62 eV. The most probable transition at this energy is likely the π→σ*(3B_2) transition whose vertical energy is predicted at 6.55 eV at the TDDFT level (see Table III). As mentioned in Section IV B, this state has to cross the ground state, leading to an internal relaxation which may be responsible for the diffuseness of the detected structures. Arulmozhiraja et al.14 calculated this excitation at 6.93 eV. The vibrational structure with \(\omega=1200±160\) cm\(^{-1}\), superimposed on the strong continuum may likely be assigned to the \(v_3\)(C=C stretching) or \(v_4\)(C-H bending) vibrations (see Fig. 3) calculated at 1269 cm\(^{-1}\) and 1112 cm\(^{-1}\) respectively (see Table IV). The large change in the C=C bond length of the optimized geometry of the 3B_2 state (Table SI) is expected to induce an excitation of the C=C stretching vibration.

Fig. 4 compares the relative energy position of these two transitions in chlorinated compounds: C_2H_4 is used as a reference. Fig. 4a shows that the presence of a second Cl-atom induces a shift to lower energy of the \(\sigma^*\) and \(\pi^*\) states. For the latter a systematic energy lowering from 6.880 eV (C_2H_2Cl)37 to 6.620 eV (cis-1,2-C_2H_2Cl_2) and 6.482 eV (1,1-C_2H_2Cl_2)16 is observed. The substitution in cis-position induces a shift to higher energy with respect to the 1,1-isomer. Fig. 4b clearly shows the expected shift to lower energy produced by the substitution of F by a Cl-atom in the cis-isomers: from 7.11 eV58 to 6.62 eV.

The short sequence of narrower peaks observed between 6.4 eV and 7.0 eV and assigned to the \(\pi(2b_1)\rightarrow3s\) Rydberg transition will be discussed in the next section V B 1.

Above the photon energy of 7.0 eV, several valence transitions are predicted by quantum chemical calculations,
bands" at 60562 cm$^{-1}$ and leading to the 5$^{1}\text{B}_2$ interval of 0.146 ± 0.009 eV (1180 cm$^{-1}$) and n$^\pi \text{CCl}$ → $\pi^*$ at 9.15 eV (201 $\text{B}_2$) respectively (see Table III). For comparison, Arulmozhiraja et al.$^{14}$ calculated seven valence as well as Rydberg transitions taking place between 8.04 eV and 8.43 eV: the lowest n→$\pi^*$ excitation is at 8.04 eV whereas two n→$\sigma^*$ transitions were predicted at 8.24 eV and 8.38 eV. It is thus likely that both valence and Rydberg states are implied in this region of the absorption spectrum and the fine structure superimposed on the broad background might be interpreted as resulting from transitions to Rydberg states as discussed in the next section.

B. The Rydberg transitions

In Fig. 1 the PAS of cis-1,2-C$_2$H$_2$Cl$_2$ measured in the photon energy range of 7.0 eV to about 13.0 eV displays numerous structures of variable intensity. Particularly from 7.4 eV up to about 9.0 eV, it exhibits a series of weak to very weak sharp features besides one stronger and broad transition. The original spectrum and the corresponding $\Delta$-plot are displayed on an expanded energy scale in Fig. 6(a–d) for the 7.0-13.0 eV range. Between 7.0 and 10.0 eV, the spectrum has been recorded with 500 µeV energy increments.

As no prior information on the coupling among Rydberg states is available for this molecule, we used the Rydberg formula (1) as a zero-order assumption for the assignment of the spectral transitions:

$$E_{\text{Ryd}} = IE - R/(n - \delta)^2 = IE - R/\langle n' \rangle^2$$  \hspace{1cm} (1)

In (1), R=13.6057 eV$^{24}$ is the Rydberg constant, $\delta$ is the quantum defect, and IE represents the ionization energy corresponding to the ionic state to which the Rydberg series converges. Any significant Rydberg-Rydberg coupling is then expected to affect the quality of the fits of the Rydberg formula to the experimental data. Furthermore, in the absence of coupling between Rydberg series, the quantum defect $\delta$ has typical values which are characteristic of the angular momentum of the Rydberg orbital. When couplings are involved, these values may be perturbed. Such perturbations already allowed us to identify and quantitatively analyze transition between Hund’s coupling cases.$^{39}$ The quantum defect values are therefore important parameters to be determined.

The observed intensity distributions of the spectral features show Franck–Condon–like behaviors and do not follow the n$^{-3}$ law, so that vibrational excitation of the successive Rydberg states dominates the spectrum. If Rydberg-Rydberg couplings may be neglected, it is sensible to assume that the same potential energy surfaces characterize the Rydberg states and the ionic state to which they converge, so that similar vibrational structures are expected for a Rydberg state and the corresponding ionic state.$^{38}$ The quality of the fits indicates a posteriori whether this assumption holds. This procedure has already been successful to disentangle the vibrational structure in the vacuum UV spectra of C$_2$H$_3^+$.$^{40}$ 1,1-C$_2$H$_2$F$_2$.$^{41}$

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FIG. 5. (a) Vacuum UV photoabsorption spectrum of cis-1,2-C$_2$H$_2$Cl$_2$ on an expanded, photon energy scale between 5.0 eV and 7.5 eV. The continuous red curve labeled FFT-Sm corresponds to the strongly smoothed PAS curve by fast Fourier transform. (b) Δ-plot of the PAS. Vertical bars indicate the vibrational progressions. The red curve corresponds to the HeI-PES band of the 1$^1\text{B}_1$ cationic state of cis-1,2-C$_2$H$_2$Cl$_2$.
FIG. 6. Vacuum UV photoabsorption spectrum of cis-1,2-C\textsubscript{2}H\textsubscript{2}Cl\textsubscript{2} on an expanded photon energy scale between 7.0 eV and 13.0 eV. The upper and lower parts show the absorbance and the corresponding ∆-plot respectively for (a) 7.0-8.1 eV, (b) 8.0-9.1 eV, (c) 9.0-10.0 eV and (d) 10.0-13.0 eV. Vibrationless (0,0) transitions are indicated as long vertical bars, whereas the vibrational progressions are indicated as short bars. The $\tilde{X}^2B_1$-HeI-PES band is inserted by red, blue and magenta open dots. The 1$b_{1}^{-1}$ continuum lies at 13.592 eV.
and 1,1-C₂H₂FCl.²² In the present case, to make the comparison easier, the Δ-power of the appropriate PAS energy range will be compared to the Hel-PES of the cis-1,2-C₂H₂Cl₂ in its ground or excited states as measured in our laboratory.²³

1. Vibrationless Rydberg transitions between 6.4 eV and 10 eV (see Fig. 1)

The vibrationless Rydberg transitions observed for cis-1,2-C₂H₂Cl₂ and converging to the first ionization limit lie between 6.4 eV and 9.7 eV and are labeled in Fig. 1. Table I lists the energies and wavenumbers of these transitions with their associated effective quantum numbers and compares the results of the present work with previous investigations by Mahncke and Noyes,¹⁰ Walsh¹¹ and Walsh and Warsop.¹² The assignments are based on an adiabatic ionization energy for the ionic ground state equal to 9.666±0.006 eV,²³ in good agreement with the value provided by Walsh and Warsop (IE = 9.652 eV).¹² As mentioned in section II, the estimated uncertainty on the transition energies is 2 meV (16 cm⁻¹). No error estimation is available for the literature data.¹⁰⁻¹²

The observed π(2b₁)→ns Rydberg series converging to the first ionization energy limit are listed in Table I. The average quantum defect over the n=3 to 8 range is equal to $\delta = 0.96±0.01$. By quantum chemical calculation at the TDDFT level, the lowest $\pi$$\rightarrow$R(ns) vertical transition energy is equal to 6.35 eV (see Table III), in good agreement with the present experimental value at 6.398 eV.

Mahncke and Noyes¹⁰ identified a Rydberg series converging to 78103 cm⁻¹ (9.683 eV) with $\delta = 0.01$ but the first member of the series was missing, hidden in the 1850 Å (6.70 eV) Rydberg series starting at 65182 cm⁻¹ (16 cm⁻¹). Walsh and Warsop¹² reported a Rydberg series starting at 65182 cm⁻¹ (8.082 eV) converging to 77850 cm⁻¹ (9.652 eV) with $\delta = 0.93$.

Transitions from the π(2b₁) to np Rydberg orbitals lead to two well-defined ionization series (Table I), as was also observed in previous studies on 1,1-C₂H₂Cl₂,¹⁶ 1,1-C₂H₂F₂,¹¹ 1,1-C₂H₂FCl,¹² and CH₃X (X=Cl, Br and I).³⁹ The two series are observed up to n=8. We assign the series starting at 7.414 eV to the π(2b₁)→np transitions whereas the series starting at 7.740 eV is assigned to π(2b₁)→npα. These assignments are based on the good agreement with the theoretical predictions of the present work listed in Table III, π→Rnp (8¹B₁) and π→Rπ (1¹A₄) transitions were calculated at 7.44 eV and 7.90 eV successively. Both transitions have noticeable oscillator strength. The splitting of 0.326 eV between the two 3pβ-type states is very close to the value of 0.356 eV observed in 1,1-C₂H₂Cl₂.¹⁶ In 1,1-C₂H₂F₂, however, the splitting is substantially smaller (0.183 eV),⁶¹ while it is again of the same order of magnitude in 1,1-C₂H₂FCl (0.404 eV).⁵⁸,⁶²

Average quantum defects $\delta = 0.53±0.01$ and 0.34±0.02 are determined for the npσ- and the npπ-type Rydberg series respectively. The small dispersion of the quantum defects along the series is compatible with our assumed neglect of the Rydberg-Rydberg couplings. The difference between the quantum defects for the npσ- and the npπ series can be interpreted as follows. The presence of more σ orbitals than π orbitals in the ionic core leads to a stronger core-Rydberg interaction for σ-type Rydberg orbitals, so that a larger quantum defect should be observed for npσ compared to npπ Rydberg orbitals. In the C₂ point group, the npσ and npπ orbitals should rigorously be denoted by npα and npβ. However, assuming the molecular ion field to be nearly cylindrical (diatomic-like), the α, π, ... nomenclature is usually used.

A first π(2b₁)→nd0 series starts at 8.089 eV and its members are characterized by an average quantum defect $\delta = 0.08±0.03$. The second series starting at 8.170 eV is characterized by an average quantum defect $\delta = 0.002±0.008$. These $\delta$ values suggest nd0 and ndr Rydberg states respectively. In the vacuum UV spectrum of 1,1-C₂H₂F₂,¹¹ and of 1,1-C₂H₂FCl,³⁸,⁴² a nd0 series is observed with $\delta = 0.13±0.03$⁴¹ and 0.125±0.025⁴¹ respectively. For the corresponding ndr series $\delta = 0.04±0.03$⁴⁰ and $\delta = 0.11±0.02$⁴¹ were respectively determined. Surprisingly, the splitting between 3d0 and 3dπ is found to be equal to 0.081 eV in cis-1,2-C₂H₂Cl₂, although it is much greater, 0.214 eV, in 1,1-C₂H₂FCl²² and 0.109 eV in 1,1-C₂H₂F₂.⁴¹

Finally, a fairly strong broad and complex structured band is observed at about 8.5 eV, as already mentioned in Section V A, where the broad signal is interpreted as resulting from a valence-valence npCCl+πCCl→π transition. Superimposed fine structure is observed, however, whose energy positions are listed in Table VI. In the densitometer trace of the PAS published by Walsh and Warsop¹² a strong broad and roughly structured band is observed at 68 310 cm⁻¹ (8.469 eV) showing several shoulders between 67 294 cm⁻¹ (8.343 eV) and 68 697 cm⁻¹ (8.517 eV) but these structures were not discussed or assigned by the authors. The structures reported in Table VI, with an adiabatic excitation energy of 8.446 eV, do not fit into the possible Rydberg series converging to the ground ionic state and which have been detailed above. Based on our quantum chemical TDDFT computations (Table III), which predict the vertical (4b₂→3π̃) transition at 8.24 eV, we rather suggest to assign the structures starting at 8.446 eV to transitions to the vibrational levels of the lowest Rydberg state (3s) converging to the A²B₂ ionic state, whose vertical energy

<table>
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<tr>
<td>8.544</td>
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Table VI. Energy positions (eV), wavenumbers (cm⁻¹) and effective quantum numbers associated with the structures in the strong broad band observed at 8.5 eV in the vacuum UV-PAS of cis-1,2-C₂H₂Cl₂. Conversion factor: 1 eV=8065.545 cm⁻¹.²⁴

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ionization energy is equal to 11.690 eV. Based on the information from the photoelectron spectrum, we infer \( n^+ = 2.05 \pm 0.01 \) or \( \delta = 0.95 \pm 0.01 \), which is perfectly compatible with a 3s Rydberg state.

2. Vibrational analysis (Fig. 3, Fig. 5 and Fig. 6(a–c))

After having identified the vibrationless Rydberg transitions, the vibrational structure of the identified electronic states has to be disentangled. To this purpose we will rely on the assumption stated above, i.e. the vibrational structure of the Rydberg states should be close to that of the cationic states to which they converge. This information will be inferred from the Hel-PES. A comparison between the PAS and the Hel-PES of the ground state of the cation is illustrated in Fig. 5, Figs. 6a and 6b. Most of the Rydberg states observed between 6.4 eV and 9.9 eV converge to \( \text{IE}_{c}(\text{X}^2\text{B}_3) = (9.666 \pm 0.006) \text{eV of cis-1,2-Cl}_2\text{H}_2\text{Cl}_2 \). The electronic ground state of the cation mainly shows three vibrational modes \( \nu_{1}=1460 \pm 30 \text{ cm}^{-1} (181 \pm 4 \text{ meV} ), \nu_{2}=1160 \pm 20 \text{ cm}^{-1} (144 \pm 3 \text{ meV} ) \) and \( \nu_{4}=860 \pm 60 \text{ cm}^{-1} (107 \pm 8 \text{ meV} ) \). These values correspond to the C=C stretching, C-H in-plane bending and C-Cl stretching vibrations respectively.

The first Rydberg transition \( 2b_{1}(\pi \rightarrow \text{R3s}(2\text{B}_1)) \) with an adiabatic excitation energy of 6.398 eV (see Fig. 5) shows vibrational excitation at 6.568 eV \( (\nu=1) \), 6.752 eV \( (\nu=2) \) and 6.930 eV \( (\nu=3) \). The average wavenumber \( \bar{\omega }=1420 \pm 70 \text{ cm}^{-1} (176 \pm 9 \text{ meV} ) \) corresponds to \( \nu_{2} \) (C=C stretching) predicted at 1427 cm\(^{-1}\) (see Table IV). Excitations corresponding to smaller wavenumbers (short dashed vertical lines in Fig. 5) are likely hidden in the signal corresponding to the 3\( ^1\text{B}_2 \) valence excited state.

The application of the same procedure is displayed in Fig. 6(a–c). Table S2(a–c) reports the transition energies and the proposed corresponding assignments.

The 7.4-8.1 eV photon energy range shows weak broad bands alternating with stronger sharp peaks. The broad weak features have already been assigned earlier in this work (see section V A). The sharper features are assigned to the 2\( b_{1} \rightarrow 3\sigma \) and 2\( b_{1} \rightarrow 3\pi \) Rydberg transitions with adiabatic excitation energies at 7.414 eV and 7.752 eV respectively (see section V B 1 and Table I). Both states show an extended vibrational structure as analyzed in Table S1a and illustrated in Fig. 6a. Energy positions in square brackets indicate that at least two different assignments are possible and that these should be considered with caution. Intensity fluctuations may result from the overlap of several contributions. At least two vibrational modes are excited in both states, i.e. \( \omega =1420 \pm 20 \text{ cm}^{-1} (176 \pm 2 \text{ meV} ) \) and \( \omega ^{'}=795 \pm 15 \text{ cm}^{-1} (98 \pm 2 \text{ meV} ) \). In addition, two weaker modes are detected with wavenumbers of 1220 \pm 20 \text{ cm}^{-1} (151 \pm 3 \text{ meV} ) and of 190 \pm 30 \text{ cm}^{-1} (24 \pm 4 \text{ meV} ).

Their assignment relies on the comparison with the ground state cation. The first two wavenumbers should correspond to \( \nu_{1}(\text{C=C stretch})=1430 \pm 30 \text{ cm}^{-1} \) and to \( \nu_{4}(\text{C-Cl symmetric stretch})=860 \pm 60 \text{ cm}^{-1} \) respectively. The latter value is significantly higher in the cation than in the Rydberg state. However, this result agrees with the quantum chemical calculations performed on the two systems and in the present work: for the Rydberg excitation only the C=C stretching is significantly modified whereas the C-Cl stretching remains only slightly affected in most of the excited neutral states (e.g. see Table IV).

The wavenumber equal to 1220\pm 20 \text{ cm}^{-1} can be correlated with the value of 1160\pm 20 \text{ cm}^{-1} inferred from the Hel-PES for the ground state cation. This vibration corresponds to \( \nu_{3} \) (C–H bending) predicted at 1215 \text{ cm}^{-1} by ab initio calculations. The wavenumber of 190\pm 30 \text{ cm}^{-1} is not detected in the Hel-PES. An assignment to \( \nu_{5} \) (C–Cl bending) is proposed based on quantum chemical predictions (193 \text{ cm}^{-1} ). However, as mentioned in Table S2a, \( \nu_{5} \) is close to \( \omega _{4}+2\omega _{5} \) which introduce ambiguities in the assignments.

Table S2a also compares the present results to those reported by Walsh and Warsop (see Table S2a, col. 6). These authors proposed a classification of the bands and determined two wavenumbers, i.e. of about 1400 \text{ cm}^{-1} and 800 \text{ cm}^{-1}. The comparison of Table VIIa with Table I in Ref. 12 shows a very good agreement and the present work brings a strong argument supporting the assignments. These authors also mentioned a wave number of 1224 \text{ cm}^{-1} but rejected it because “...no frequency of this magnitude is observed in any other electronic transition of cis-dichloro ethylene or in the transitions of the other chloroethylenes”. As mentioned above, this wavenumber is very probably involved in both the two 3\( \sigma \) and 3\( \pi \) Rydberg states and very likely in combinations in the 3\( \pi \) Rydberg state.

Fig. 6b shows the PAS in the 8.0-9.1 eV range on an expanded energy scale. This part of the spectrum is much more crowded and the energy positions of the features are listed in Table S2b. The procedure described earlier in this section (Hel-PES inserted in Fig. 6b) leads to the assignments presented in the same table.

At least seven Rydberg transitions are observed. Six of them converge to the ground state of the cation and correspond to 2\( b_{1} \rightarrow 3\sigma_{3} \), 3\( d \), 4\( s \), 4\( d \), 4\( \sigma \) and 5\( s \) successively. The strong broad peak around 8.5 eV has already been interpreted as a superposition of a valence-valence \( (n_{\text{2C}},\text{Cl}^+ \rightarrow n_{\text{Cl}} \rightarrow \pi^*) \) and a valence-Rydberg \( (4\text{b}_{2} \rightarrow 3\text{b}_{2}) \) transition. (see section V B 1).

For the six Rydberg states, the vibrational analysis leads to four vibrational wavenumbers: \( \omega _{2}=1426 \pm 9 \text{ cm}^{-1} (177 \pm 1 \text{ meV} ) \), \( \omega _{3}=1180 \pm 20 \text{ cm}^{-1} (146 \pm 2 \text{ meV} ) \), \( \omega _{4}=806 \pm 7 \text{ cm}^{-1} (100 \pm 1 \text{ meV} ) \) and \( \omega _{5}=191 \pm 8 \text{ cm}^{-1} (24 \pm 1 \text{ meV} ) \). These values are close to those already mentioned for the 3\( \sigma \) and 3\( \pi \) states. We notice that \( \omega _{3} \) is slightly lower and closer to the value \( \omega _{4}^\prime =1160 \pm 20 \text{ cm}^{-1} \) of the cation ground state.

In Table S2b the assignments proposed in the present work are compared to the classifications attempted by Walsh and Warsop. These authors proposed two possible interpretations of the bands observed between 65000-69000 cm\(^{-1}\), assigned either to 2\( b_{1} \rightarrow 3\sigma_{3} \) or to 2\( b_{1} \rightarrow 3\sigma_{3} \) Rydberg
transitions. Three wavenumbers arose from their analysis at 1424 cm$^{-1}$, 813 cm$^{-1}$ and 197 cm$^{-1}$. These three values are in good agreement with the present results. However, they did not detect the wavenumber at 1177 cm$^{-1}$ observed in the present work.

Fig. 6c shows the 9.0–10.0 eV energy range on an expanded scale. A large number of weak to very weak structures as well as broad intense peaks at about 9.6 eV and 9.8 eV are observed. The $\Delta$-plot shown in the lower panel of Fig. 6c enhances these structures. Their energy positions and the proposed assignments in terms of transitions to vibrationally excited Rydberg states converging to the ionic ground state are listed in Table S2c. The majority of the observed transitions are interpreted as leading to nd ($n=5$–8) Rydberg states. As expected, the same vibrational normal modes are involved as for the previous series. The average wavenumbers are $\omega_{11}=1411\pm8$ cm$^{-1}$ (175±1 meV), $\omega_{12}=1170\pm20$ cm$^{-1}$ (145±3 meV), $\omega_{13}=807\pm20$ cm$^{-1}$ (100±2 meV) and $\omega_{14}=190\pm20$ cm$^{-1}$ (24±2 meV). The present energy range being almost outside the prospected region of previous photoabsorption works,$^{10-12}$ no comparison can be made. Only Mahncke and Noyes$^{10}$ mentioned a few discrete bands which have been introduced in Table S2c. Most of them fit the present data and possible assignments are proposed.

We could not observe any significant breakdown of the Rydberg formula or of the assumption of similar vibrational structures for the Rydberg states and the corresponding cationic state. This suggests that Rydberg-Rydberg or Rydberg-continuum interactions are too small to affect the energy positions at the resolution and accuracy reached in our spectra.

Beside the long sequence of weak structures, the present region also shows a strong complex structured doublet peak spread between 9.6 eV and 9.9 eV (see Fig. 1 and Fig. 6c, upper panel). The steep absorbance increase is likely linked to the opening of the $2b_{1}^{-1}$ ionization continuum at 9.666 eV. Rydberg states converging to higher lying ionization limits need to be considered. As shown in Fig. 1, three ionization continua are open between 11.5 eV and 12.2 eV, i.e. $4b_{2}^{-1}$ at 11.426 eV, $5a_{1}^{-1}$ at 11.965 eV and $6a_{2}^{-1}$ at 12.375 eV.$^{23,32-34}$

Based on the vibrational structure of the $\tilde{B}^{2}A_{1}$ photoelectron band,$^{23}$ the unassigned features observed in the 9.6–9.9 eV energy range could be interpreted (see Table VII and upper panel of Fig. 6c). The effective quantum number $n^*=2.426\pm0.005$, averaged over eight vibronic transitions, suggests an assignment to a $5a_{1}^{-1}$, $3p$ Rydberg transition.

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<th>Energy Position (eV)</th>
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| $9.648$ | $\Delta$=3.49 and 4.38 are obtained. The sub-structure at $n^*=3.44$, 3.87, 4.25 and 5.25, may be assigned to $5a_{1}^{-1}$, $4p$, 4d (or 5s), 5p and 6p transitions, respectively. The last two bands at 11.342 eV and 11.75 eV will be assigned to $6a_{2}^{-1}$, $4p$ and $5p$ transitions for which effective quantum numbers $n^*=3.49$ and 4.38 are obtained. The sub-structures detected in these bands could likely be assigned to vibrational excitations, e.g. of C-Cl bending for which a wave number of the order of 180 to 270 cm$^{-1}$ has been predicted for several Rydberg and valence states (see Table IV) and cationic states as well.$^{23}$

3. Rydberg transitions between 10 eV and 20.0 eV (see Figs. 1, 2, (6d))

The PAS of cis-1,2-C$_2$H$_4$Cl$_2$ between 10 eV and 13 eV has been recorded with 2 meV increments and is reproduced in Fig. 6d. The absorbance steadily increases over the whole energy range. It shows a sequence of weak broad bands. Several of these features are clearly consisting of very weak sub-structures. They become more apparent in the $\Delta$-plot (lower panel in Fig. 6d) and show intervals of the order of 30 meV (240 cm$^{-1}$). To try to disentangle this range of the PAS it would be reasonable to use the same hypotheses and assumptions applied earlier. Using the present data, term values and effective quantum numbers could be derived.

In this energy range three vertical ionization limits, lying close together, are involved, i.e. 11.690 eV (4b$_{1}^{-1}$), 12.028 eV (5a$_{1}^{-1}$), and 12.460 eV (6a$_{2}^{-1}$)$^{23,32-34}$ successively. They are inserted in Fig. 6d (upper panel). The sum of the associated continua contributes to the strong increase of the background observed in the PAS in this energy range. All three cationic states are characterized by an extended vibrational progression.$^{23}$

If we assume that the maxima at 10.252 eV, 10.584 eV and 10.792 eV (Table I) correspond to transitions to Rydberg states converging to the $4b_{2}^{-1}$ continuum at 11.69 eV, effective quantum numbers of 3.08, 3.51 and 3.89 are respectively obtained. This is compatible with $4b_{2}^{-1}$ at 4s, 4p and 4d assignments (Figure 6d).

The next four well identified bands lie at 10.880 eV, 11.120 eV, 11.275 eV and 11.536 eV (Table I). Based on their effective quantum numbers $n^*=3.44$, 3.87, 4.25 and 5.25, they may be assigned to $5a_{1}^{-1}$, $4p$, 4d (or 5s), 5p and 6p transitions, respectively. The last two bands at 11.342 eV and 11.75 eV will be assigned to $6a_{2}^{-1}$, $4p$ and $5p$ transitions for which effective quantum numbers $n^*=3.49$ and 4.38 are obtained. The sub-structures detected in these bands could likely be assigned to vibrational excitations, e.g. of C-Cl bending for which a wave number of the order of 180 to 270 cm$^{-1}$ has been predicted for several Rydberg and valence states (see Table IV) and cationic states as well.$^{23}$

**TABLE VII.** Analysis of the high energy bands observed in the vacuum UV photoabsorption spectrum of cis-1,2-C$_2$H$_4$Cl$_2$. Energy positions (eV), corresponding wavenumbers (cm$^{-1}$), effective quantum numbers ($n^*$) and assignments as proposed in this work. Conversion factor: 1 eV= 8065.545 eV.$^{24}$

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<th>Energy Position (eV)</th>
<th>Assignment</th>
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The width of all these bands has likely to be related to the short lifetimes of these Rydberg states. In a forthcoming paper\textsuperscript{25} it will be shown that these Rydberg states mainly undergo resonant autoionization to the ionic ground state of cis-1,2-C\textsubscript{2}H\textsubscript{2}Cl\textsubscript{2} (X\textsuperscript{2}B\textsubscript{1}) giving rise to threshold photoelectrons.

A broad band spreads from 12.054 eV to 12.412 eV and consists of five narrower well resolved regularly spaced features with a regular intensity distribution. Assuming the D\textsuperscript{2}B\textsubscript{1} state of the cation at 13.592 eV as convergence limit\textsuperscript{23} (see Table IV) an average effective quantum number \(n^*=3.00\pm0.02\) is obtained. Therefore, this band is tentatively ascribed to a 1B\textsubscript{1}→4s/3d Rydberg transition. The vibrational analysis leads to an averaged wavenumber \(\tilde{\omega}=722\pm30\) cm\textsuperscript{-1} which could likely be assigned to \(v_4\) (C-Cl stretch/C-H bending) as predicted for other lower lying neutral excited states (see Table IV).

The energy range between 13 eV and 20 eV has been recorded with the 1.5m-NIM monochromator and with 15 meV energy increments. This high energy range only shows a few very broad bands superimposed on a slower increasing continuum as shown in Fig. 2b. The band maxima are listed in Table II. In the same energy range five ionic excited states are observed in the HeI PES, i.e. at 13.592 (1B\textsubscript{1}→2), 14.083 eV (3B\textsubscript{2}→2), 15.531 eV (4a\textsubscript{1}→3), 16.638 eV (3a\textsubscript{1}→3) and at 18.84 eV (2B\textsubscript{2}→2) successively.\textsuperscript{23,32–34}

In Fig. 2b the \(\Delta\)-plot has been reproduced and slightly smoothed by FFT to increase the signal/noise ratio. At least six broad bands are characterized by a full width half-maximum (FWHM) ranging from 0.4 eV to 0.7 eV. A last very broad band extends from 16.8 eV to 19.5 eV. The energy position of the successive maxima is listed in Table II. A tentative classification based on the vertical ionization energies and the inferred effective quantum numbers is also provided in Table IV.

VI. CONCLUSIONS

The measurement of the VUV photoabsorption spectrum of cis-1,2-C\textsubscript{2}H\textsubscript{2}Cl\textsubscript{2} at higher resolution by using synchrotron radiation enabled us to extend the data above the 10.5 eV photon energy limit and, for the first time, up to 20 eV. In this energy range the absorbance drastically increases and numerous features measured between 7.41 eV and 9.94 eV (Table S2).

In the intermediate photon energy range, i.e. between 6.4 eV and 10.0 eV, a large number of narrow vibronic Rydberg transitions, i.e., 2B\textsubscript{2}→ns (n=3–8), two types of np (up to n=8) and two nd-type (up to n=9) series, have been identified and interpreted. The involved Rydberg states converge to the cis-1,2-C\textsubscript{2}H\textsubscript{2}Cl\textsubscript{2} (X\textsuperscript{2}B\textsubscript{1}) ground ionic state. By reference to the first band of the cis-1,2-C\textsubscript{2}H\textsubscript{2}Cl\textsubscript{2} Hel-PES,\textsuperscript{23} the vibrational structure has been assigned to four vibrational modes, including harmonics and combinations: \(\omega_2\approx1420\) cm\textsuperscript{-1} (C≡C stretching), \(\omega_3\approx1190\) cm\textsuperscript{-1} (C-H symmetric bending), \(\omega_4\approx800\) cm\textsuperscript{-1} (C-Cl symmetric stretching) and \(\omega_5\approx190\) cm\textsuperscript{-1} (C-Cl symmetric bending). These assignments are compared to those proposed on a more empirical basis in previous reports.\textsuperscript{11,12}

At 8.5 eV, 9.6 eV and above 10.0 eV numerous Rydberg transitions are observed, all assigned to members of series converging to the successive excited states of cis-1,2-C\textsubscript{2}H\textsubscript{2}Cl\textsubscript{2}+. For a few of them vibrational progressions are observed.

SUPPLEMENTARY MATERIAL

See supplementary material for the optimized geometry parameters of neutral ground and excited states of cis-1,2-C\textsubscript{2}H\textsubscript{2}Cl\textsubscript{2} (Table S1) and the list of the vacuum UV spectral features measured between 7.41 eV and 9.94 eV (Table S2).

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REFERENCES