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The vacuum UV photoabsorption spectrum of the geminal dichloroethylene (1,1-C\textsubscript{2}H\textsubscript{2}Cl\textsubscript{2}) in the 5–20 eV range. A vibrational analysis of the valence and Rydberg states

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Abstract

The vacuum UV photoabsorption spectrum of 1,1-C\textsubscript{2}H\textsubscript{2}Cl\textsubscript{2} is presented and discussed in detail in the 6–20 eV photon energy range. The broad band observed at 6.488 eV includes the 2b\textsubscript{1}(\pi) → \sigma^*, 2b\textsubscript{1}(\pi) → \pi^* valence transitions and the 2b\textsubscript{1}(\pi) → 3s Rydberg transitions. A quantum chemical calculation analysis is proposed and applied to the intertwined vibrational structure belonging to these transitions. For the \pi → \sigma^* and \pi → \pi^* transitions short vibrational progresses are observed, analyzed and tentatively assigned. The \pi → 3s Rydberg transition is characterized by a single progression starting at 6.746 eV. The fine structure observed between 7.5 and 10.1 eV has been analyzed in terms of vibronic transitions to ns- (\delta = 0.89), np- (\delta = 0.59 and 0.37) and nd-type (\delta = 0.16) Rydberg states all converging to the 1,1-C\textsubscript{2}H\textsubscript{2}Cl\textsubscript{2} (X^2B\textsubscript{1}) ionic ground state. The vibrational structure analysis excitation leads to the following wavenumbers: \omega_2 ≈ 1310 cm\textsuperscript{-1} (162 meV), \omega_4 ≈ 650 cm\textsuperscript{-1} (81 meV) and \omega_5 ≈ 290 cm\textsuperscript{-1} (37 meV). These modes can be assigned to the C=C stretching, to the symmetric C–Cl stretching and to the symmetric Cl–C–Cl bending vibrations respectively. By the same way, eight other Rydberg states were analyzed. For the first time the vacuum UV spectrum of 1,1-C\textsubscript{2}H\textsubscript{2}Cl\textsubscript{2} has been recorded in the 10–20 eV range, revealing intense broad bands which are assigned to transitions to Rydberg states converging to excited states of 1,1-C\textsubscript{2}H\textsubscript{2}Cl\textsubscript{2}. Assignments are also proposed for the vibrational excitations observed in this range.

1. Introduction

Further to their wide interest in many fields of both pure and applied chemistry, we initiated a few years ago the systematic investigation of ethylene and its halogenated derivatives. Several experimental methods are coupled to quantum chemical calculations. The results about the monosubstituted C\textsubscript{2}H\textsubscript{3}X (X = F, Cl and Br) have been reported [1]. The influence of the nature of the substituent on the properties of the neutral (valence and Rydberg) states and the cationic states were discussed in detail.

Following an early study of the three C\textsubscript{2}H\textsubscript{3}FCl isomers [2] by vacuum UV photoabsorption and photoelectron spectroscopy we reported a detailed investigation of the 1,1-C\textsubscript{2}H\textsubscript{2}F\textsubscript{2} molecular system by the same techniques [3]. With respect to C\textsubscript{2}H\textsubscript{3}F [1] and 1,1-C\textsubscript{2}H\textsubscript{2}FCl [2, 4] substitutional effects were observed on, e.g., the \pi → \pi^* transition whereas the 3s-Rydberg transition energy remains almost unaffected.

Unlike the situation for its two 1,2-isomers, the 1,1-C\textsubscript{2}H\textsubscript{2}Cl\textsubscript{2} vacuum UV photoabsorption spectroscopic data are very scarce in the literature. To our knowledge the earliest vacuum UV photoabsorption spectrum of the 1,1-C\textsubscript{2}H\textsubscript{2}Cl\textsubscript{2} molecule has been observed by Teegan and Walsh [5] in the 2100–1100 Å (5.9–11.3 eV) spectral region using a normal incidence vacuum spectograph. A classification of the Rydberg transitions and ionization energies of the [C = Cl]-\pi and the Cl-lone pair orbitals were proposed.
One of the latest vacuum UV photoabsorption spectra of the same molecule, in the same spectral region, has been reported by Walsh et al [6]. Besides a revision of the Rydberg series classification, a vibrational analysis and a corrected value of the lowest ionization energy have been presented. In a work on the photochemistry of chloroethylenes, Berry [7] measured the vacuum UV absorption spectrum of 1,1-C₂H₂Cl₂ between 260 and 140 nm (4.77–8.86 eV) but limited his analysis to the broad band between 240 and 180 nm (5.17–6.89 eV).

The present paper focuses on the vacuum UV photoabsorption spectrum of 1,1-C₂H₂Cl₂ (i) in the still unexplored range between 11.3 and 20 eV with medium resolution and (ii) in the 5.0–13.0 eV spectral region at higher resolution. The vibrational structure observed in the latter region will be analyzed.

2. Experimental

The experimental setup used in this work is the same as in previous works, using two VUV normal incidence monochromators from both BESSY synchrotron radiation facilities (Berlin, Germany) [1]. The first one, with a focal length of 1.5 m, allowed us to reach a resolving power of 1200 at 10 eV photon energy. It has been used in the 5–25 eV photon energy range. The accuracy of the energy scale calibration is estimated to be of the order of 2 meV and the peak position uncertainties are estimated to be ±4 meV. The second monochromator, used for high resolution measurements has a focal length of 3 m and leads to a resolving power of at least 13 000 at 10 eV. The peak position precision is ±2 meV. 1,1-C₂H₂Cl₂ from Aldrich (99% purity) was used without further purification.

To facilitate the characterization of weak signals superimposed on a continuum, we applied a FFT-based continuum subtraction procedure described previously [1, 3] and thoroughly investigated and validated by Marmet [8] and Carbonneau [9]. Recently, Palmer et al [10] applied a similar procedure to investigate the vacuum UV photoabsorption spectrum of the monohalobenzenes. The resulting continuum-free spectra are designated as Δ-plots.

3. Experimental results

The vacuum UV photoabsorption spectrum (PAS) of 1,1-C₂H₂Cl₂ between 5 and 15 eV photon energy is represented in figure 1 in terms of the absorbance log₁₀[I₀/I] as a function of the photon energy hν(eV).

The PAS is made of three regions with very different characteristics: (i) in the 5.0–7.5 eV range a number of weak broad bands are superimposed on a weak continuum; (ii) the 7.5–13 eV region contains a large number of weak to very strong sharp structures and bands superimposed on a very weak continuum with increasing intensity from 9 eV upwards; (iii) above 13 eV and up to 20 eV several weak broad bands are superimposed on a
strong continuum as shown in figure 2(a). Therefore, the latter region is also displayed by a $\Delta$-plot (figure 2(b)) in which the structures to be considered are enhanced.

In both figures vertical bars locate the structures and Rydberg series which will be considered in the following discussion. Shaded areas indicate the different convergence limits. The position in energy of the transitions to the vibrationless Rydberg states converging to the $\tilde{X}^2B_1$ ionic ground state and the successive ionic excited states are listed in tables 1 and 2 together with previously reported data [6].

### 4. Ab initio calculations

#### 4.1. Methods

The Gaussian 09 set of programs [12] was used for all calculations with the aug-cc-pVDZ basis set, which includes polarization and diffuse basis functions [13]. For comparison purposes, additional calculations were performed without diffuse functions (cc-pVDZ).
Table 1. Rydberg series observed in the vacuum UV photoabsorption spectrum of 1,1-C2H2Cl2 converging to the \( \hat{X}^2B_1 (1,1-C_2H_2Cl_2^-) \) ionic ground state at \( IE_{\text{ad}} = 9.826 \text{ eV} \). The energy positions (eV), wavenumbers (cm\(^{-1}\)), effective quantum numbers (\( n^* \)), average quantum defects (\( \ell \)) and assignments proposed in this work are provided. Comparison is made with the literature data [6]. Conversion factor: 1 eV = 8.065.545 eV [11].

| This work | [6] |
| --- | --- |
| --- | --- |
| eV | cm\(^{-1}\) | \( n^* \) (cm\(^{-1}\)) |
| 2b1 \( \rightarrow \) ns (\( \ell = 0.89 \pm 0.03 \)) | 6.746 | 54 410 | 2.102 |
| | 8.406 | 67 799 | 3.095 |
| | 9.016 | 72 719 | 4.098 |
| | 9.300 | 75 009 | 5.086 |
| | 9.464 | 76 332 | 6.130 |
| | 9.560 | 77 107 | 7.152 |
| 2b1 \( \rightarrow \) np\( \sigma \) (\( \ell = 0.59 \pm 0.05 \)) | 7.508 | 60 556 | 2.533 |
| | 8.716 | 70 299 | 3.536 |
| | 9.128 | 73 622 | 4.480 |
| | 9.358 | 75 477 | 5.480 |
| | 9.488 | 76 526 | 6.460 |
| | 9.582 | 77 284 | 7.467 |
| | 9.638 | 77 735 | 8.646 |
| | 9.678 | 78 058 | 9.588 |
| | 9.704 | 78 268 | 10.560 |
| | 9.720 | 78 397 | 11.329 |
| | 9.742 | 78 574 | (12.272) |
| | 9.786 | 78 929 | 18.443 |
| 2b1 \( \rightarrow \) np\( \pi \) (\( \ell = 0.37 \pm 0.05 \)) | 7.864 | 63 427 | 2.633 |
| | 8.796 | 70 944 | 3.634 |
| | 9.198 | 74 187 | 4.654 |
| | 9.519 | 76 776 | 5.657 |
| | — | — | 76 850 |
| | 9.648 | 77 816 | 8.743 |
| | 9.678 | 78 058 | 9.588 |
| | 9.704 | 78 268 | 10.560 |
| | 9.720 | 78 397 | 11.329 |
| | 9.742 | 78 574 | 12.727 |
| | 9.764 | 78 752 | 14.814 |
| | 9.782 | 78 897 | 17.585 |
| | 9.786 | 78 929 | 18.443 |
| 2b1 \( \rightarrow \) nd (\( \ell = 0.16 \pm 0.07 \)) | 8.130 | 65 734 | 2.849 |
| | 8.936 | 72 074 | 3.910 |
| | 9.244 | 74 558 | 4.835 |
| | 9.426 | 76 026 | 5.832 |
| | 9.544 | 76 978 | 6.946 |
| | 9.602 | 77 445 | (7.793) |
| | 9.648 | 77 816 | 8.743 |
| | 9.742 | 78 574 | 12.727 |
| | 9.764 | 78 752 | 14.814 |

The vertical excitation energies for the low-lying excited states have been calculated at the ground state geometry optimized at the DFT-M06-2X level [14]. The geometries of the first three excited states have been optimized at the TDDFT [15] level.
Table 2. Rydberg series converging to the excited states of 1,1-C\textsubscript{2}H\textsubscript{2}Cl\textsubscript{2} observed in the vacuum UV photoabsorption spectrum. The energy positions (eV), wavenumbers (cm\textsuperscript{-1}), effective quantum numbers (\(n^*\)) and assignments proposed in this work are provided. Conversion factor: 1 eV = 8 065.545 eV\textsuperscript{[11]}. 

| \(n^*\) | Assign. |
|---|---|
| 3a\textsubscript{1} \rightarrow ns/np/nd\textsuperscript{a} |
| 3a\textsubscript{1} \rightarrow np/nd\textsuperscript{b} |
| 3b\textsubscript{2} \rightarrow np/nd\textsuperscript{c} |
| 4a\textsubscript{1} \rightarrow ns/np/nd\textsuperscript{d} |

\(\text{cm}^{-1}\) cm\textsuperscript{-1} 

| eV | cm\textsuperscript{-1} | n* | Assign. |
|---|---|---|---|
| 9.016 | 72 719 | 2.347 | 3\(\sigma\) |
| 10.482 | 84 543 | 3.417 | 4\(\sigma\) |
| 9.602 | 77 445 | 2.646 | 3\(\pi\) |
| 10.694 | 86 253 | 3.688 | 4\(\pi\) |
| 9.904 | 79 881 | 2.46 | 3\(\pi\) |
| 10.994 | 88 672 | 3.42 | 4\(\pi\) |
| 10.552 | 85 108 | 2.91 | 3d |
| 11.590 | 93 480 | 4.92 | 5d |
| 11.732 | 94 625 | 5.97 | 6d |
| 11.878 | 95 802 | 7.04 | 7d |
| 11.948 | 96 367 | 8.99 | 9d |
| 12.056 | 97 238 | 5.612 | 6\(\pi\) |
| 12.224 | 98 755 | 7.467 | 8\(\sigma\) |
| 10.812 | 87 205 | 2.89 | 3d |
| 11.932 | 96 238 | 4.94 | 5d |
| 11.182 | 90 189 | 2.411 | 3\(\sigma\) |
| 11.996 | 96 754 | 2.986 | 3d |
| 12.63 | 101 868 | 2.06 | 3s |
| 13.54 | 109 207 | 2.44 | 3p |
| 14.15 | 114 127 | 2.85 | 4s/3d |
| 14.27 | 115 095 | 2.96 | 3d |
| 14.52 | 117 112 | 3.23 | 4s |
| 15.00 | 120 983 | 4.07 | 5s/4d |
| 15.20 | 122 596 | 4.68 | 5p |
| 15.36 | 123 887 | 5.44 | 6p |
| 15.94 | 128 565 | 2.31 | 3p |
| 16.15 | 130 178 | 2.40 | 4s/3d |
| 16.91 | 136 388 | 2.92 | 4s/3d |
| 17.08 | 137 760 | 3.09 | 3d |
| 17.30 | 139 534 | 3.37 | 4p |
| 17.70 | 142 760 | 4.12 | 5s/4d |

\(\text{a For practical reasons (see text) the convergence limit considered in these transitions is the vertical ionization energy }\text{IE}_{\text{vert}} = 11.647 \text{ eV.}\)

\(\text{b The convergence limits considered in these transitions are the adiabatic ionization energy values }\text{IE}_{\text{ad.}}\)

\(\text{c Nearly resonant with the ArII-resonance line at 13.48 eV [17].}\)

\(\text{d Absorption band with an asymmetric profile.}\)

\(\text{e Nearly resonant with the NeI-resonance line at 16.85 eV [17].}\)
4.2. Presentation of the results

The optimized geometry parameters are presented in Table 3.

The vertical excitation energies of several states are presented in Table 4, as well as the adiabatic excitation energies for the first three states.

The cc-pVDZ basis set was used for comparison purposes to emphasize the valence character of the excitations, since it does not include diffuse functions. Our results show that four states are superimposed around 6–7 eV. It also appears from these calculations that the first state shows a mixed $\pi \rightarrow \sigma^*$ and $\pi \rightarrow 3s$ character, and in a much less pronounced way, the third state also presents a major $\pi \rightarrow 3s$ and a minor $\pi \rightarrow \sigma^*$ mixed character. Such Rydberg–valence interactions involving $\sigma^*$ antibonding orbitals and the associated ‘Rydbergisation’ phenomenon have been reviewed by Ashfold et al [16].

The optimized geometry of the first excited valence state is characterized by a very large C–Cl bond length, related to the antibonding character of the $\sigma^*$ MO populated by the excitation. Due to the large equilibrium internuclear distance, this state is most probably nearly repulsive (low dissociation energy), so that its excitation is expected to produce a broad continuous band.

5. Discussion

The molecular orbital configuration of 1,1-C$_2$H$_2$Cl$_2$ in the C$_{2v}$ symmetry group is described by

$$1s^2(C1)\ 1s^2(C2)\ 1s^2(Cl1)\ 1s^2(Cl2)\ 2s^2(Cl1)\ 2s^2(Cl2)\ 2p^6(Cl1)\ 2p^6(Cl2)\ 1a_1^21b_2^22a_2^23a_2^22b_2^24a_2^21b_1^23b_2^25a_2^21a_2^44b_2^22b_2^2; \tilde{X}^1A_1,$$

where 1a$_1$ is the first outer-valence shell orbital.
We recently measured the HeI-photoelectron spectrum (PES) and the threshold photoelectron spectrum (TPES) of 1,1-C₂H₂Cl₂ and the results will be reported in a forthcoming paper [17]. The first adiabatic ionization energy is located at IE_{ad}(1,1-C₂H₂Cl₂, ß) = 9.826 ± 0.002 eV and the corresponding vertical value is IE_{vert}(1,1-C₂H₂Cl₂, ß) = 9.993 ± 0.004 eV, in very good agreement with available data [18–21].

At higher energies eight bands were observed by HeI-PES. For most of them the adiabatic ionization energy (IE_{ad}) could be measured at 11.520, 12.157, 12.497, 15.531, 15.539 and 18.496 eV [17]. The PES-band shape corresponding to the first excited state has a symmetric bell-shaped envelope and its maximum is measured at IE_{vert} = 11.647 eV. The fifth and sixth PES-bands at 13.521 and 15.539 eV involve two overlapping electronic states [17]. For the two components vertical ionization energies (IE_{vert}) were measured at 13.633 and 14.195 eV for the former and at about 15.82 and 16.16 eV for the latter [17].

5.1. The valence transitions (see figures 1, 3(a) and 4).

The characteristic broad band observed at low energy in the vacuum UV PAS of the ethylenic compounds has its maximum at 6.488 eV in 1,1-C₂H₂Cl₂ (figure 1). Compared to our observations in ethylene and its halogenated derivatives investigated up to now [1–4], it is fairly weak and extends between 5.0 and 7.4 eV. To enhance the very weak structures superimposed on the continuum the subtraction method has been applied. Figure 3(a) shows the result on an expanded photon energy scale where the red curve in the upper part of the figure represents the continuum to be subtracted from the original signal. The result of this operation (Δ-plot) is displayed in the lower part of figure 3(a) which clearly shows three different parts: (a) a noisy weak series of three broad doublet structures, (b) a series of four narrower simple peaks and (c) the beginning of a series of very narrow peaks extending above 7.0 eV photon energy.

The very weak signal between 5.0 and 6.0 eV might be considered as the possible end of a longer vibrational progression belonging to a valence excited singlet state. Possibly the σ'’/3s state could be involved. Robin [22] mentioned a π → σ transition at 6.01 eV in the trans-1,2-C₂H₂Cl₂ isomer. By quantum mechanical calculations, Arulmozhiraja et al [23] calculated this transition energy at 6.25 eV. The broadness of the observed features, compared to higher-energy peaks may be linked to the short lifetime of these vibronic states which likely predissociate. Our quantum chemical calculations reveal important C–Cl bond lengthening at the optimized geometry of this state which could be nearly repulsive (see table 3). Several photodissociation studies have been reported in the wavelength region of 155–250 nm (8.00–4.96 eV) [7] or 222–304 nm (5.58–4.08 eV) [24] or at 214.5 nm (5.78 eV) and at 235 nm (5.28 eV) [25]. The loss of HCl [7] and Cl(3p) [24, 25] were investigated. Curve crossings between (π, π'), (π, σ') and/or (n, σ') states were suggested. The observed structures in the 5.0–5.6 eV range may be associated with vibronic states which cannot be described by a first-order description separating the electronic and vibrational contributions.

Recent theoretical DFT calculations at B3LYP/6-311-G(d, p) level, devoted to the chloroethylene, are reported by Khvostenko [26]. They are focused on the prediction of the transition energies to valence singlet and triplet states. They do not, however, provide details shedding new light on the physical situation in this energy range.

The four following features between 6.2 and 6.6 eV have a more regular spacing of on average 134 ± 5 meV (1080 ± 40 cm⁻¹) with a regular intensity distribution, and are narrower than the lower lying structures but broader than the higher-energy ones. For these reasons it is believed that they correspond to another valence excited state, e.g. the (π, π') state. The feature at 6.488 eV corresponds to the maximum of the broad band. Walsh et al [6] observed the intensity maximum of a continuum at about 51 814 cm⁻¹ (or 6.42 eV) (see table 5).

The (π, π') state likely overlaps the (π, σ'/3s) state below 6.2 eV and the Rydberg (π, 3s/σ') state above 6.7 eV. As shown in table 5, over the narrow energy window of 6.22–6.62 eV the vibrational spacing regularly decreases from 139 to 128 meV likely suggesting a strong anharmonicity. This vibrational spacing could correspond to a strongly weakened C=C bond owing to the antibonding character of the π'’ MO. The C=C stretching vibration is characterized by a wavenumber of 1627 cm⁻¹ (202 meV) in the neutral ground state [27].

The main interest of a systematic study of the PAS of a series of halogenated ethylenes is to emphasize the effect of the substitution on the energy of the different valence and lowest Rydberg states. A comparison of the PAS between 5.5 and 8.2 eV is displayed in figure 4(a) for Cl-substituted only [1] and in figure 4(b) for mixed F- and Cl-substituted [1–4] ethylenes investigated in our laboratory.

Comparing the PAS of the three chlorinated compounds in the 5–8 eV photon energy range, the position of the maximum of the underlying continuum (denoted as π'’ in figure 4(a)) could be a measure of the shift to lower energy of the π → π’ vertical excitation energy induced by chlorination, as already pointed out by Robin [22]. In the PAS of the F- and Cl-substituted ethylenes a similar shift is observed for the π → σ’’ transition (see figure 4(b)). The effect on the π → 3s Rydberg transition is less obvious. The vertical and the adiabatic excitation energy being likely fairly close [1–3, 6], the adiabatic values will be compared. As shown in figure 4(a), with respect to C₂H₄, the shift to lower energies is important upon Cl substitution but is quite insensitive to the number of Cl atoms. This trend is confirmed for the tri- and the tetrachloroethylene [22].
The substitution of an H atom in C2H4 by one or two F atoms induces a rather limited shift to higher energies on the $\pi \rightarrow \pi^*$ vertical transition energy, i.e., at 7.4 and 7.5 eV in C2H4 and 1,1-C2H2F2 [1, 3] (see figures 4(b)) and 7.6 eV in C2H3F [1]. Contrarily, the substitution of an H/F atom by a Cl atom provides a large shift to lower energies on the same transition: 7.4 eV in C2H4 to 6.9 eV in C2H3Cl [1], to 7.0 eV in 1,1-C2H2FCl [2, 4] and to 6.4 eV in 1,1-C2H2Cl2.

5.2. The Rydberg transitions

As shown in figure 1, the PAS measured in the photon energy range of 7.4 eV to about 13.0 eV displays numerous structures of very variable intensities. Particularly from 7.4 eV up to about 10.0 eV the PAS exhibits long series of weak features besides two strong transitions. The wavy underlying continuum is fairly weak. This region is shown on an expanded energy scale between 7 and 13 eV in figures 3(b)–(d), the upper and lower part showing the original spectrum and the corresponding $\Delta$-plot respectively.

Figure 3. Expanded VUV photoabsorption spectrum of 1,1-C2H2Cl2 between 5.0 and 13.0 eV. The upper and lower parts show the absorbance and the corresponding $\Delta$-plot respectively for (a) 5.0–7.0 eV, (b) 7.0–9.0 eV, (c) 9.0–11.0 eV and (d) 11.0–13.0 eV. Long vertical bars indicate the vibrationless (0, 0) transitions to the indicated Rydberg transitions. For each transition, the progression(s) are identified by short vertical bars.
Figure 4. VUV photoabsorption spectra of (a) C2H4, C2H3Cl and 1,1-C2H2Cl2 and (b) of C2H4, 1,1-C2H2F2, 1,1-C2H2Cl2 and 1,1-C2H2FCl on an expanded photon energy scale between 5.5 and 8.2 eV. The vertical excitation energies (index v) to the valence states (σ* and π*) and the adiabatic excitation energies to the Rydberg (3s) states are indicated for each molecule.

Table 5. Energy positions (eV), wavenumbers (cm\(^{-1}\)) and assignments proposed for the vibrational structures observed in the vacuum UV photoabsorption spectrum of 1,1-C2H2Cl2 between 5.0 and 7.0 eV. Comparison is made with the literature data [6]. Conversion factor 1 eV = 8 065.545 cm\(^{-1}\) [11].

| Energy (eV) | Wavenbr. (cm\(^{-1}\)) | Assignments | Energy (cm\(^{-1}\)) | Assignments |
|------------|------------------------|-------------|----------------------|-------------|
| 5.112      | 41 231                 | (σ*)ν\(_1\) | 51 814 (~193 nm)     | Maximum intensity of the continuum |
| 5.252      | 42 360                 | (v\(_2\) = 1) |                      |             |
| 5.460      | 44 038                 | (v\(_1\) + 1) |                      |             |
| 5.625      | 45 369                 | (v\(_2\) = 1) |                      |             |
| 5.815      | 46 901                 | (v\(_1\) + 2) |                      |             |
| 5.987      | 48 288                 | (v\(_2\) = 1) |                      |             |
| 6.215      | 50 127                 | (π*)ν\(_v\)  |                      |             |
| 6.354      | 51 248                 | (v + 1)      |                      |             |
| 6.488      | 52 329                 | (v + 2)      |                      |             |
| 6.616      | 53 362                 | (v + 3)      |                      |             |
| 6.746      | 54 410                 | R3s(0,0)     |                      |             |
| 6.781      | 54 692                 | ν\(_v\)      |                      |             |
| 6.827      | 55 063                 | ν\(_4\)      |                      |             |
| 6.892      | 55 388                 | 2ν\(_4\)     |                      |             |
| 6.913      | 55 757                 | ν\(_2\)      |                      |             |
| 6.943      | 55 999                 | ν\(_2\) + ν\(_5\) |                |             |
| 6.989      | 56 370                 | na           |                      |             |
| 7.001      | 56 467                 | ν\(_2\) + ν\(_4\) |                |             |
| 7.085      | 56 644                 | 2ν\(_2\)     |                      |             |
| 7.113      | 57 370                 | 2ν\(_2\) + ν\(_5\) |                |             |
| 7.159      | 57 741                 | 2ν\(_2\) + ν\(_4\) |                |             |
| 7.189      | 57 983                 | 2ν\(_2\) + 2ν\(_5\) |              |             |
| 7.233      | 58 338                 | 2ν\(_2\) + 2ν\(_4\) |              |             |
| 7.245      | 58 435                 | 3ν\(_2\)     |                      |             |
| 7.275      | 58 677                 | 3ν\(_2\) + ν\(_5\) |                |             |
| 7.307      | 58 935                 | 3ν\(_2\) + 2ν\(_5\) |               |             |
| 7.319      | 59 032                 | 3ν\(_2\) + ν\(_4\) |                |             |
| 7.408      | 59 749                 | 4ν\(_2\)     |                      |             |
Due to the large number of Rydberg transitions accompanied by vibrational excitation, the assignment is attempted based on the Rydberg formula, even though this neglects the perturbations between Rydberg series. The previously mentioned relevant ionization thresholds are inserted in figure 1. The fine structure will be assigned mostly to the vibrational excitation involved in successive Rydberg transitions, rather than to Rydberg states with high principal quantum number n. The intensity distribution follows the Franck–Condon distribution in the former case, whereas in the latter case the intensity scales as \((n')^{-3} = (n - \delta)^{-3}\) where \(n'\) is the effective quantum number and \(\delta\) is the quantum defect, which is characteristic of a given Rydberg series. Robin [22] made a critical review of the analyses of Rydberg transitions and proposed rules and guidelines for assignments.

5.2.1. Rydberg transitions between 6.6 and 9.9 eV (see figure 1).
The vibrationless Rydberg transitions observed for 1,1-C2H2Cl2 between 6.7 and 9.9 eV are shown in figure 1. All detected Rydberg transitions are reported in table 1 with their effective quantum numbers. In the same table the previous data set of Walsh et al [6] is included for comparison. As mentioned earlier (see section 2) the estimated uncertainty on the measurements in the present spectrum is about 2 meV or 16 cm\(^{-1}\). No uncertainty estimation is provided by Walsh et al [6]. For the assignments reported in the present work the adiabatic ionization energy value IE\(_{\text{ad}}\)(1,1-C2H2Cl2, \(X^2B_1\)) = 9.826 ± 0.002 eV [17] has been used whereas the value determined by Walsh et al [6] was 9.85 eV.

Table 1 displays the excitation energies corresponding to the \(\pi \rightarrow \sigma^*\) Rydberg series converging to the first ionization energy limit. It is observed up to \(n = 8\) with an average quantum defect \(\delta = 0.89 \pm 0.03\). This series is not listed in the work of Walsh et al [6]. Only one Rydberg state vibrational progression starting at 67 730 cm\(^{-1}\) is mentioned [6], corresponding fairly well to 67 799 cm\(^{-1}\) (8.406 eV) in the present work and assigned to the vibrationless \(\pi \rightarrow \sigma^*\) Rydberg transition.

Two distinct \(\pi \rightarrow \nu\) Rydberg series are observed (see table 1), like in C\(_2\)H\(_2\), Br [1], 1,1-C\(_2\)H\(_2\), F\(_2\) [2], 1,1-C\(_2\)H\(_2\), F\(_2\) [3] and in the methyl monohalides CH3X (X = Cl, Br and I) [28]. These series are assigned taking into account the quantum defect value. As the core contains less orbitals of \(\pi\) symmetry than of \(\sigma\) symmetry, the \(\pi\)-type Rydberg orbitals are expected to interact more strongly with the ionic core and would therefore be characterized by a larger quantum defect.

The \(\pi \rightarrow \nu\) Rydberg series is starting at 7.508 eV whereas its \(\pi \rightarrow \nu\) counterpart starts at 7.864 eV. The splitting of 0.356 eV between the two \(\pi\)-type series is about twice as large as in 1,1-C\(_2\)H\(_2\), F\(_2\) [3] where an energy difference of 0.183 eV is measured. In 1,1-C\(_2\)H\(_2\), F\(_2\) the corresponding splitting is 0.405 eV [2, 4]. The two series are observed up to high values of the principal quantum number. The average quantum defects \(\delta = 0.59 \pm 0.05\) and 0.37 \pm 0.05 are determined for the \(\pi\)- and the \(\pi\)\(\pi\)-type Rydberg series respectively.

A \(\pi \rightarrow \nu\) series starts at 8.150 and most of its members are characterized by an average quantum defect \(\delta = 0.16 \pm 0.07\). Only two members would be characterized by \(\delta < 0.1\) likely suggesting the existence of a \(n\)\(\delta\) series. In the vacuum UV spectrum of 1,1-C\(_2\)H\(_2\), F\(_2\) [1] and of 1,1-C\(_2\)H\(_2\), Cl\(_2\) [2, 4] an \(\nu\)\(\nu\) series is observed with \(\delta = 0.14 \pm 0.02\) and \(\delta = 0.13 \pm 0.03\) respectively. For the corresponding \(\nu\)\(\nu\) series we inferred \(\delta = 0.04 \pm 0.03\) [3] and \(\delta = -0.11 \pm 0.02\) [2] respectively.

5.2.2. Vibrational analysis (see figures 3(a)–(c))
Let us consider the intense transitions between 6.6 and 13.0 eV. The intensity of the transitions to high n Rydberg states decreases rapidly, according to the \((n')^{-3}\) intensity scaling law. On the contrary, the intensity distribution of the vibrational transitions does not follow this law and can, therefore, become dominant.

To disentangle this spectrum, we assumed [22] that the vibrational wavenumbers of the Rydberg states within a series are similar to those of the ionic state to which this series converges. This approach has been shown efficient to interpret the vacuum UV spectra of the methyl halides [28], of C\(_2\)H\(_2\)F [1], and 1,1-C\(_2\)H\(_2\), F\(_2\) [3]. The convergence limit of most of the Rydberg states involved between 6.7 and 9.9 eV is IE\(_{\text{ad}}\)(1,1-C\(_2\)H\(_2\), Cl\(_2\), \(X^2B_1\)) = 9.826 ± 0.002 eV [17]. The cationic \(X^2B_1\) vibrational structure is dominated by the excitation of two vibrational normal modes characterized by the wavenumbers \(\omega_{\nu_1} = 1322 \pm 48\) cm\(^{-1}\) (0.163 ± 0.006 eV) and \(\omega_{\nu_2} = 653 \pm 24\) cm\(^{-1}\) (0.081 ± 0.003 eV) [17] (notation \(\omega\) for the neutrals and \(\omega\) for the ions). Two other very weak vibrations were also observed [17]. However, more than 95% of the available intensity is distributed over the C=C stretching \(\nu_1\) and the C–Cl symmetric stretching \(\nu_4\). For the purpose of the decomposition of the PAS we used the corresponding HeI-PES as a reference which was shifted to make its vibrationless transition to coincide with that of the successive transitions to the Rydberg states (see figure 3(a), red curve, for an example).

The result of this procedure is represented in figures 3(a)–(c) and the energy positions and assignments are summarized in table 5 for the 3s Rydberg state and in table 6 for the remaining Rydberg state.

In the \(\pi \rightarrow 3s\) transition region no comparison could be made with the results reported by Walsh et al [6]: only a continuum with an intensity maximum at 51 814 cm\(^{-1}\) (6.424 eV) has been mentioned.
Table 6. Energies (eV), wavenumbers (cm$^{-1}$) and assignments for the peaks in the photoabsorption spectrum of 1,1-C$_2$H$_2$Cl$_2$ between 7 and 10 eV (Rydberg series converging to the $\tilde{X}^2$B$_1$ ionic ground state). Comparison is made with the literature [6]. Conversion factor 1 eV = 8.065.545 eV [11].

| Energy (eV) | Wavenbr. (cm$^{-1}$) | Assignments | Wavenbr. (cm$^{-1}$) | Assignments |
|-------------|----------------------|--------------|----------------------|--------------|
| This work   |                      |              | [6]                  |              |

2b$_1$ $\rightarrow$ 3p$_{\sigma}$, n$^*$ $=$ 2.423

| 7.508       | 60 556               | (0, 0)       |                      |              |
| 7.538       | 60 798               | $\nu_5$      |                      |              |
| 7.596       | 61 266               | $\nu_4$      |                      |              |
| 7.648       | 61 685               | ($4\nu_5$)   |                      |              |
| 7.668       | 61 846               | $\nu_5$      |                      |              |
| 7.756       | 62 556               | $\nu_5 + \nu_4$ |                      |              |
| 7.786       | 62 798               | ($\nu_3 + 3\nu_5$) |                      |              |
| 7.808       | 62 976               | $\nu_3 + 4\nu_5$ |                      |              |
| 7.832       | 63 149               | 2$\nu_3$     |                      |              |
| 7.918       | 63 863               | 2$\nu_3 + \nu_4$ |                      |              |
| 7.996       | 64 492               | 3$\nu_3$     |                      |              |
| 8.078       | 65 133               | 3$\nu_3 + \nu_4$ |                      |              |

$2b_1$ $\rightarrow$ 3p$_{\pi}$, n$^*$ $=$ 2.633

| 7.864       | 63 427               | (0, 0)       |                      |              |
| 7.940       | 64 040               | $\nu_4$      |                      |              |
| 7.984       | 64 395               | (3$\nu_5$)   |                      |              |
| 8.026       | 64 734               | $\nu_5$      |                      |              |
| 8.108       | 65 395               | $\nu_5 + \nu_4$ |                      |              |
| 8.128       | 65 537               | $\nu_5 + 3\nu_5$ |                      |              |
| 8.188       | 66 041               | 2$\nu_3$     |                      |              |
| 8.266       | 66 670               | 2$\nu_3 + \nu_4$ |                      |              |
| 8.346       | 67 315               | 3$\nu_4$     |                      |              |
| 8.446       | 68 121               | 3$\nu_3 + \nu_4$ |                      |              |
| 8.516       | 68 686               | 4$\nu_3$     |                      |              |
| 8.586       | 69 251               | 4$\nu_3 + \nu_4$ |                      |              |
| 8.614       | 69 477               | ($4\nu_3 + 3\nu_5$) |                      |              |
Table 6. (Continued.)

| Energy (eV) | Wavenbr. (cm\(^{-1}\)) | Assignments | Wavenbr. (cm\(^{-1}\)) | Assignments |
|------------|-------------------------|--------------|-------------------------|--------------|
| 8.150      | 65 734                  | (0, 0)       |                         |              |
| 8.228      | 66 363                  | \(\nu_4\)    |                         | 66 302       |
| 8.312      | 67 040                  | \(\nu_3\)    |                         | 67 109       |
| 8.390      | 67 670                  | \(\nu_3 + \nu_4\) |                     | 67 610       |
| 8.474      | 68 347                  | 2\(\nu_4\)   |                         | 68 292       |
| 8.554      | 68 993                  | 2\(\nu_3 + \nu_4\) |                    | 68 925       |
| 8.636      | 69 654                  | 3\(\nu_5\)   |                         | 69 575       |
| [8.716]    | 70 299                  | 3\(\nu_3 + \nu_4\) |                | [70 310]     |
| 8.788      | 70 880                  | 4\(\nu_3\)   |                         | 70 888       |
| 8.862      | 71 477                  | 4\(\nu_3 + \nu_4\) |                 | [71 551]     |

2b\(_1\) \rightarrow 3d, n' = 2.849

| Energy (eV) | Wavenbr. (cm\(^{-1}\)) | Assignments | Wavenbr. (cm\(^{-1}\)) | Assignments |
|------------|-------------------------|--------------|-------------------------|--------------|
| 8.406      | 67 799                  | (0, 0)       |                         | 67 730       |
| 8.486      | 68 444                  | \(\nu_4\)    |                         | 68 365       |
| 8.567      | 69 098                  | \(\nu_3\)    |                         | 69 039       |
| 8.646      | 69 735                  | \(\nu_3 + \nu_4\) |                    | 69 668       |
| 8.726      | 70 380                  | 2\(\nu_3\)   |                         | [70 310]     |
| 8.760      | 70 654                  | 2\(\nu_3 + \nu_5\) |                | [70 940]     |
| 8.808      | 71 046                  | 2\(\nu_3 + \nu_4\) |               | [71 940]     |
| 8.890      | 71 707                  | 3\(\nu_5\)   |                         |              |
| 8.981      | 72 441                  | 3\(\nu_3 + \nu_4\) |               |              |
| 9.056      | 73 041                  | 4\(\nu_5\)   |                         |              |

2b\(_1\) \rightarrow 4 s, n' = 3.093

| Energy (eV) | Wavenbr. (cm\(^{-1}\)) | Assignments | Wavenbr. (cm\(^{-1}\)) | Assignments |
|------------|-------------------------|--------------|-------------------------|--------------|
| [8.716]    | 70 299                  | (0, 0)       |                         | 70 221       |
| 8.796      | 70 944                  | \(\nu_4\)    |                         | 70 888       |
| 8.880      | 71 622                  | \(\nu_5\)    |                         | [71 551]     |
| 8.965      | 72 308                  | \(\nu_3 + \nu_4\) |                     | 72 234       |
| 9.044      | 72 945                  | 2\(\nu_4\)   |                         | 72 879       |

2b\(_1\) \rightarrow 4p\(\sigma\), n' = 3.499

| Energy (eV) | Wavenbr. (cm\(^{-1}\)) | Assignments | Wavenbr. (cm\(^{-1}\)) | Assignments |
|------------|-------------------------|--------------|-------------------------|--------------|
| [8.716]    | 70 299                  | (0, 0)       |                         | 70 221       |
| 8.796      | 70 944                  | \(\nu_4\)    |                         | 70 888       |
| 8.880      | 71 622                  | \(\nu_5\)    |                         | [71 551]     |
| 8.965      | 72 308                  | \(\nu_3 + \nu_4\) |                     | 72 234       |
| 9.044      | 72 945                  | 2\(\nu_4\)   |                         | 72 879       |
Table 6. (Continued.)

| Energy (eV) | Wavenbr. (cm⁻¹) | Assignments | Wavenbr. (cm⁻¹) | Assignments |
|------------|----------------|-------------|----------------|-------------|
| [9.128]    | 73 622         | 2ν₃ + ν₄    | 73 536         |             |
| [9.198]    | 74 187         | 3ν₃         |                |             |
| 9.278      | 74 832         | 3ν₃ + ν₄    |                |             |
| 9.358      | 75 477         | 4ν₃         |                |             |
| 9.128      | 73 622         |             |                |             |
| 9.198      | 74 187         |             |                |             |
| 9.278      | 74 832         |             |                |             |
| 9.358      | 75 477         |             |                |             |

2b₁ → 4d, n° = 3.910

| Energy     | Wavenbr. (cm⁻¹) | Assignments | Wavenbr. (cm⁻¹) | Assignments |
|------------|----------------|-------------|----------------|-------------|
| 8.936      | 72 074         | (0, 0)      | 72 001         | 4d          |
| 9.016      | 72 719         | ν₄          | 72 648         |             |
| 9.098      | 73 380         | ν₃          | 73 300         |             |
| 9.178      | 74 026         | ν₃ + ν₄     | 73 952         |             |
| 9.258      | 74 671         | 2ν₃         | 74 620         |             |
| 9.340      | 75 332         | 2ν₃ + ν₄    | 75 234         |             |
| 9.426      | 76 026         | 3ν₃         |                |             |
| 9.506      | 76 671         | 3ν₃ + ν₄    |                |             |
| 9.582      | 77 284         | 4ν₃         |                |             |

2b₁ → 5pσ, n° = 4.415

| Energy     | Wavenbr. (cm⁻¹) | Assignments | Wavenbr. (cm⁻¹) | Assignments |
|------------|----------------|-------------|----------------|-------------|
| [9.128]    | 73 622         | (0, 0)      |                |             |
| [9.198]    | 74 187         | ν₄          |                |             |
| 9.300      | 75 009         | ν₃          |                |             |
| 9.368      | 75 558         | ν₃ + ν₄     |                |             |
| 9.464      | 76 332         | 2ν₃         |                |             |
| [9.544]    | 76 978         | 2ν₃ + ν₄    |                |             |

2b₁ → 5d, n° = 4.835

| Energy     | Wavenbr. (cm⁻¹) | Assignments | Wavenbr. (cm⁻¹) | Assignments |
|------------|----------------|-------------|----------------|-------------|
| 9.244      | 74 558         | (0, 0)      |                |             |
| 9.316      | 75 139         | ν₄          |                |             |
| 9.406      | 75 864         | ν₃          |                |             |
| [9.488]    | 76 526         | ν₃ + ν₄     |                |             |
| 9.560      | 77 107         | 2ν₃         |                |             |
| Energy (eV) | Wavenbr. (cm$^{-1}$) | Assignments | Wavenbr. (cm$^{-1}$) | Assignments |
|------------|---------------------|--------------|---------------------|--------------|
| 9.638      | 77 735              | 2ν$_3$ + ν$_4$|                     |              |
| 9.720      | 78 397              | 3ν$_3$       |                     |              |
| 9.800      | 79 042              | 3ν$_3$ + ν$_4$|                     |              |
| 9.884      | 79 720              | 4ν$_3$       |                     |              |
| 9.358      | 75 477              | (0, 0)       |                     |              |
| 9.440      | 76 139              | ν$_3$        |                     |              |
| 9.519      | 76 776              | ν$_3$        |                     |              |
| 9.602      | 77 445              | ν$_3$ + ν$_4$|                     |              |
| 9.678      | 78 897              | 2ν$_3$       |                     |              |
| 9.764      | 78 752              | 2ν$_3$ + ν$_4$|                   |              |
| 9.838      | 79 349              | 3ν$_3$       |                     |              |
| 9.920      | 80 010              | 3ν$_3$ + ν$_4$|                   |              |
| 10.002     | 80 671              | 4ν$_3$       |                     |              |

2b$_1$ $\rightarrow$ 6pσ$^*$, $n^*$ = 5.391

| Energy (eV) | Wavenbr. (cm$^{-1}$) | Assignments | Wavenbr. (cm$^{-1}$) | Assignments |
|------------|---------------------|--------------|---------------------|--------------|
| [9.544]    | 76 978              | (0, 0)       |                     |              |
| 9.624      | 77 623              | ν$_4$        |                     |              |
| 9.704      | 78 268              | ν$_3$        |                     |              |
| 9.782      | 78 058              | ν$_3$ + ν$_4$|                     |              |
| 9.864      | 79 558              | 2ν$_3$       |                     |              |
| 9.938      | 80 155              | 2ν$_3$ + ν$_4$|                   |              |
| 10.036     | 80 946              | 3ν$_3$       |                     |              |
| 10.120     | 81 623              | 3ν$_3$ + ν$_4$|                   |              |

* Energy positions corresponding to two or more assignments are given in square brackets.
Table 7. Analysis of the Rydberg series converging to the 1,1-C₂H₂Cl₂ ionic excited states ˚A₂B₂, ˚B₂A₂, ˚C₂A₁ and ˚D₂B₂. Energy positions (eV), wavenumbers (cm⁻¹), effective quantum numbers (n*) and assignments proposed in this work are provided. Conversion factor: 1 eV = 8 065.545 cm⁻¹ [11].

| Energy position (eV) | Assignment |
|---------------------|------------|
| Converging to IE_{vert} (˚A₂B₂) = 11.647 eV [17] |
| 4b₂ → 3pσ, n* = 2.347 |
| [9.016]  | 72 719  |
| [9.056]  | 73 041  |
| [9.098]  | 73 380  |
| [9.128]  | 73 622  |
| 9.164   | 73 913  |
| [9.198]  | 74 187  |
| 9.252   | 74 622  |
| 9.278   | 74 832  |
| 9.290   | 74 929  |

\[ \hbar \omega_{av} = 34 \pm 6 \text{ meV} \]
\[ \text{or } 274 \pm 50 \text{ cm}^{-1} \]

| 4b₂ → 3pπ, n* = 2.646 |
|---------------------|------------|
| [9.602]  | 77 445  |
| [9.624]  | 77 623  |
| 9.668   | 77 978  |
| [9.704]  | 78 264  |
| [9.720]  | 78 397  |
| 9.742   | 78 742  |
| [9.764]  | 78 852  |
| [9.800]  | 79 042  |

\[ \hbar \omega_{av} = 25 \pm 7 \text{ meV} \]
\[ \text{or } 200 \pm 60 \text{ cm}^{-1} \]

| 4b₂ → 4pσ, n* = 3.417 |
|---------------------|------------|
| 10.482  | 84 543  |

| 4b₂ → 4pπ, n* = 3.688 |
|---------------------|------------|
| 10.694  | 86 253  |
| 10.734  | 86 576  |
| 10.760  | 86 785  |

\[ \hbar \omega_{av} \approx 33 \text{ meV} \]
\[ \approx 266 \text{ cm}^{-1} \]

| Converging to IE_{ad} (˚B₂A₂) = 12.157 eV [17] |
|-------------------------------------------------|
| 1a₂ → 3pπ, n* = 2.46 |
| 9.904   | 79 881  |
| 9.938   | 80 155  |
| 9.970   | 80 413  |
| [10.002] | 80 672  |
| 10.036  | 80 946  |
| 10.064  | 81 171  |
| 10.098  | 81 446  |

\[ \hbar \omega_{av} = 32 \pm 2 \text{ meV} \]
\[ \text{or } 260 \pm 8 \text{ cm}^{-1} \]

| 1a₂ → 3d, n* = 2.91 |
|---------------------|------------|
| 10.552  | 85 108  |
| 10.592  | 85 430  |
| 10.622  | 85 672  |
| 10.660  | 85 979  |
| 10.694  | 86 253  |

\[ \hbar \omega_{av} = 36 \pm 4 \text{ meV} \]
\[ \text{or } 290 \pm 30 \text{ cm}^{-1} \]

| 1a₂ → 4pπ, n* = 3.42 |
|---------------------|------------|
| 10.994  | 88 672  |
| 11.018  | 88 866  |
| 11.048  | 89 108  |
| 11.076  | 89 334  |
| 11.104  | 89 560  |

\[ \hbar \omega_{av} = 27 \pm 3 \text{ meV} \]
\[ \text{or } 218 \pm 24 \text{ cm}^{-1} \]

| 1a₂ → 5d, n* = 4.92 |
|---------------------|------------|

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Table 7. (Continued.)

| Energy position | (eV) | (cm$^{-1}$) | Assignment |
|-----------------|------|-------------|------------|
| $1a_2 \rightarrow 6d, n' = 5.97$ |      |             | EE$_{ab}$  |
| $1a_2 \rightarrow 7d, n' = 7.04$ |      |             | EE$_{ab}$  |
| $1a_2 \rightarrow 9d, n' = 8.99$ |      |             | EE$_{ab}$  |
| $5a_1 \rightarrow 3d, n' = 2.89$ |      |             | EE$_{ab}$  |
| $5a_1 \rightarrow 5d, n' = 4.94$ |      |             | EE$_{ab}$  |
| $5a_1 \rightarrow 6p(\sigma), n' = 5.612$ |      |             | EE$_{ab}$  |
| $5a_1 \rightarrow 8p\sigma, n' = 7.467$ |      |             | EE$_{ab}$  |
| Converging to $IE_{ad}(C^2A_1) = 12.497$ eV$^{[17]}$ |      |             | EE$_{ab}$  |
| $3b_2 \rightarrow 3p\sigma, n' = 2.411$ |      |             | EE$_{ab}$  |
Above 60 000 cm$^{-1}$ the same authors [6] classified six sets of overlapping bands showing similar patterns and a spacing of $\omega = 1315 \pm 15$ cm$^{-1}$. With each member of these progressions weaker bands are observed, shifted to higher energies by about 630 cm$^{-1}$ [6]. This classification and their corresponding wavenumber as reported by Walsh et al [6] are inserted in table 6. The assignment of the 61 209 cm$^{-1}$ and the 60 500 cm$^{-1}$ band is uncertain [6].

Fairly good agreement is found with the results and assignments obtained in the present work. This allows us to assign each feature in the spectrum and to remove the uncertainty concerning the 61 209 cm$^{-1}$ and the 60 500 cm$^{-1}$ band. A value of the wavenumbers as averaged over the six Rydberg transitions provides $\omega_3 = 1307 \pm 32$ cm$^{-1}$ (0.162 \pm 0.004 eV) and $\omega_4 = 661 \pm 40$ cm$^{-1}$ (0.082 \pm 0.005 eV). These values are very close (within the uncertainty limits) to those reported earlier [6]. Additionally, the present analysis of the 3p\sigma and 3p\pi Rydberg transitions provides a third wavenumber $\omega_5 = 290 \pm 24$ cm$^{-1}$ (0.037 \pm 0.003 eV) assigned to the $\nu_5$ symmetric Cl–Cl–Cl bending vibration [17].

Compared to [6], four additional Rydberg states converging to IE$_{ad}$ = 9.826 eV are observed at higher energies, i.e., up to 10.120 eV. They also show a vibrational structure dominated by the $\nu_3$ and $\nu_4$ vibrational modes with an average wavenumber $\omega_3 = 1315 \pm 40$ cm$^{-1}$ (0.163 \pm 0.005 eV) and $\omega_4 = 637 \pm 40$ cm$^{-1}$ (0.079 \pm 0.005 eV). The intensity corresponding to the $\nu_3$ vibrational mode becomes probably too weak to be observed in these members of Rydberg series characterized by higher values of the principal quantum number.

The previous discussion showed that the application of the Rydberg formula together with constant vibrational parameters throughout the series converging to a given ionic state leads to satisfactory results. This suggests that Rydberg–Rydberg and Rydberg-continuum perturbations do not affect the spectra at the spectral resolution of this study.

5.2.3. Rydberg transitions between 9.0 and 20.0 eV (see figures 1 and 2)

In this photon energy range (figures 1 and 2) several Rydberg series converge to higher lying ionization energies corresponding to the removal of an electron respectively from the 4b$_2$ molecular orbital (MO) (IE$_{ad}$ = 11.46 eV [19] or 11.520 eV [17]), the 1a$_2$ MO (IE$_{ad}$ = 12.06 eV [19] or 12.157 eV [17]), the 5a$_1$ MO (IE$_{ad}$ = 12.497 eV [17]), and the 3b$_2$ MO (IE$_{ad}$ = 13.521 eV [17]) as determined by He-I PES. In this range, the ionization of the 4a$_1$ MO and 3a$_1$ MO is detected at IE$_{ad}$ = 15.539 eV and IE$_{ad}$ = 18.496 eV respectively [17]. Several members of these Rydberg series show very strong absorption, e.g., at 9.198, 9.720 and at 10.002 eV. Above 10.4 eV the underlying photoabsorption continuum shows a continuous and steady increase. Furthermore, the PAS shows an abundant structure between 9.1 and 13.0 eV (see figure 1) whereas only broad and weak structureless bands are detected between 13 and 20 eV (figure 2).

To the best of our knowledge, no data are available in the literature on this energy range. Walsh et al [6] reported an ‘intense, diffuse doublet’ at 1350 Å (74 120 cm$^{-1}$ or 9.190 eV) which corresponds to the absorption...
maximum at 9.198 eV observed in the present work. A second band at shorter wavelength, but ‘hindered by the presence of water and oxygen’ is observed by Walsh et al [6] mentioning a maximum of absorption at 78 135 cm$^{-1}$ (9.687 eV) which is a doublet. Also this observation should unambiguously correspond to the absorption observed at 9.720 eV in the present work. A third band is measured at 80 727 cm$^{-1}$ (10.009 eV) in very good agreement with the energy of 10.002 eV observed in the present work. Walsh et al [6] interpreted these bands as members of Rydberg series converging to an ionization energy of 10.4 eV with a quantum defect $\delta = 0.66$.

Owing to the steeply increasing (and even overwhelming) intensity of the underlying continuum, the interpretation of this part of the PAS is greatly facilitated by the subtraction method (see section 2). The resulting $\Delta$-plot in the 12–18 eV energy range is shown in figure 2. To avoid overcrowding, the result of the analysis is only partially shown by vertical bars in figure 1 between 9.0 and 13.0 eV and in figure 2 between 13 and 18 eV for the major Rydberg series. Their respective ionization limits are represented in these figures by shaded areas. The positions of the adiabatic excitation energies for the Rydberg series converging to the successive ionization limits are listed in table 2. The assignments proposed for most of these features are based on the value of their effective quantum numbers listed in the same table.

Noteworthy is that the Rydberg series observed in the 9.0–18.0 eV photon energy range are predominantly of np- or nd-character. The most intense features of the PAS involve 4b$_2 \rightarrow 3\sigma$ and 3p$\pi$ and 1a$_2 \rightarrow 3\pi$ transitions (see figures 1 and 3(c)). The 1a$_2 \rightarrow$ ns and 1a$_2 \rightarrow$ np$\sigma$ are symmetry-forbidden in the C$_{2v}$ point group. The photoelectron band corresponding to the 4b$_2$ MO ionization exhibits an extended vibrational progression, involving a single vibrational mode [17]. This bell-shaped band is characterized by IE$_{ad}$ = 11.520 eV and its IE$_{vert}$ = 11.647 eV [17]; this latter value is used as the convergence limit for the 4b$_2 \rightarrow$ np$\sigma$ and np$\pi$ Rydberg series. The third photoelectron band (corresponding to the $B^2A_2$ ionic state) has IE$_{ad}$ = IE$_{vert}$ = 12.157 eV exhibiting a long vibrational progression involving Cl–C–Cl bending vibrational motion [17].

Above 13.0 eV the PAS of 1,1-C$_2$H$_4$Cl$_2$ shows a further increase of about 20% of absorption and a succession of weak broad bands (see figure 2(a)). The corresponding $\Delta$-plot of this energy range is shown in figure 2(b). To increase the unfavorable signal/noise ratio the result is smoothed by fast Fourier transform (red curve FFTsm in figure 2(b)). Several well defined bands are clearly observed. Their respective maxima are listed in table 2. Noteworthy is the profile of the bands with maxima at 16.15 and 17.30 eV which both show a strong asymmetry on the high energy side. However, due to the low intensity and the probable superposition of vibrational transitions, we could not fit Fano profiles to these bands.

As long as the Rydberg–Rydberg and Rydberg-continua interactions might be considered as negligible, the results and assignments listed in table 2 are obtained. Two series are highlighted converging respectively to IE$_{vert}$ = 15.82 eV and to IE$_{ad}$ = 18.496 eV corresponding to the excited $F^2A_1$ and $F^2A_2$ states of the cation [17]. The members of both series are essentially ns/nd- and np-type Rydberg states. It will be shown that the resonant absorption of the 4a$_1 \rightarrow$ 3p transition induced by the ArII resonance line at 13.48 eV provides an extended population of the $\tilde{X}^2B_2$, $\tilde{A}^2B_2$, $B^2A_2$ and $C^2A_2$ ionic states through autoionization [17]. Similarly, but to a lesser extent, the 3a$_1 \rightarrow$ 4p transition induced by the NeI resonance line at 16.85 eV leads to autoionization to the same final ionic states [17].

### 5.2.4. Vibrational analysis (see figures 3(c) and (d))

The closeness of the first three convergence limits (IE$_{ad}$), i.e., 11.520, 12.157 and 12.497 eV [17], makes the vibrational analysis fairly difficult. To disentangle this part of the spectrum, the HeI-PES bands corresponding to these ionization limits have been used as a reference to perform the vibrational analysis. The sum of these overlapping contributions simulates qualitatively the $\Delta$-plot. The resulting analysis is shown in figures 3(c), (d) and summarized in table 7.

Owing to the difficulty to determine the adiabatic excitation energy, a number of members of np$\lambda$-Rydberg series are considered to converge to 11.647 eV, i.e., the IE$_{vert}$ of the $\tilde{A}^2B_2$ state of 1,1-C$_2$H$_4$Cl$_2$ [17]. The vertical excitation energies (IE$_{vert}$) of these members are listed in table 7. A number of the listed energy positions are in square brackets as corresponding to several possible assignments. Overlaps between close-lying transitions make the analysis difficult as shown in figure 3(c). For three Rydberg states we observe a vibrational wavenumber in the 200–270 cm$^{-1}$ range. This value is close, though smaller, than the value measured for the $\tilde{A}^2B_2$ cation state where $\omega^s_C = 282 \pm 40$ cm$^{-1}$ [17] which corresponds to the Cl–C–Cl bending vibration.

From 9.9 to 10.8 eV the 1a$_2 \rightarrow$ 3p$\pi$/3d Rydberg series show up clearly in the $\Delta$-plot with a regular vibrational spacing (see figure 3(c)).

The Rydberg series converging to the 1a$_2^{-1}$ ionization limit (the $B^2A_2$ ionic state) at 12.157 eV [17] all show a vibrational spacing of about 0.035 $\pm$ 0.004 meV (268 $\pm$ 32 cm$^{-1}$) as averaged over all observed transitions (see table 7). This energy should also correspond to the Cl–C–Cl bending vibration. This value is very close to the value measured for the $B^2A_2$ ionic state of 1,1-C$_2$H$_4$Cl$_2$, i.e., $\omega^s_C = 266 \pm 32$ cm$^{-1}$ [17].
To avoid overcrowding figure 3(c) and even more figure 3(d), the 5a_1^{-1}-Rydberg vibrational transitions are not all represented but are listed in table 7. Only the vibrational progression associated with the 5a_1 \rightarrow 8\sigma transition is drawn in figure 3(d). These Rydberg series are characterized by a more or less long vibrational progression with an average spacing spreading between 33 ± 2 meV (266 ± 16 cm\(^{-1}\)) and 40 ± 7 meV (320 ± 60 cm\(^{-1}\)). The most reasonable assignment corresponds to \nu_5 (Cl–Cl symmetric bending). In the \tilde{C} \tilde{2}A_1 cationic state the corresponding energy was determined at 42 ± 4 meV (339 ± 32 cm\(^{-1}\)) by HeI-PES and 39 ± 3 meV (314 ± 24 cm\(^{-1}\)) by TPES [17].

Finally Rydberg series have been observed between 11.2 and 12.17 eV with an abundant vibrational structure (see figure 3(d)). They converge to the \tilde{D}^3B_2 cationic state of 1,1-C_2H_2Cl_2 at IE_{ad} = 13.521 eV [17]. The 3b_2 \rightarrow 3\pi\sigma and 3b_2 \rightarrow 3d transitions have clearly been identified (see table 7). The associated vibrational structure with proposed assignments is listed in table 7.

For both transitions two wavenumbers are observed, i.e. \omega_{\lambda_a} = 750 ± 20 cm\(^{-1}\) and \omega_{\lambda_b} = 258 ± 40 cm\(^{-1}\) for the 3b_2 \rightarrow 3\pi\sigma transition and \omega_{\lambda_a} = 840 ± 16 cm\(^{-1}\) and \omega_{\lambda_b} = 274 ± 16 cm\(^{-1}\) for the 3b_2 \rightarrow 3d transition. It is noteworthy that in both cases \omega_{\lambda_a} \approx 3\omega_{\lambda_b} within the error limits. The lowest wavenumber of 258 cm\(^{-1}\) (or 274 cm\(^{-1}\)) may likely be assigned again to the \nu_5 Cl–Cl–Cl bending motion.

6. Conclusions

The VUV photoabsorption spectrum of 1,1-C_2H_2Cl_2 has been recorded at higher resolution with synchrotron radiation and thoroughly analyzed in the unexplored region above the 10.5 eV photon energy limit, up to 20 eV. Contrarily to the broad and strong bands usually observed in the high energy range, structures linked to vibrational excitation could be identified and tentatively assigned.

Quantum chemical calculations show that valence–valence (2b_1(\pi) \rightarrow \sigma^*/3s and \pi^*) and valence-Rydberg (2b_1(\pi) \rightarrow 3s/\sigma^*) transitions are involved between 5 and 7.2 eV. From these calculations the \sigma and \pi states appear strongly mixed, the former being antibonding. The vibrational structure of these states has been assigned. The present data are also considered in a broader framework, by comparing them with the situation taking place in previously investigated analog molecules, that is, C_2H_4, C_2H_3Cl [1], 1,1-C_2H_2F_2 [3] and 1,1-C_2H_2FCl [2, 4].

Between 6.7 and 9.7 eV, many vibronic Rydberg transitions have been identified: 2b_1 \rightarrow ns (n = 3–7), two types of np (n = 3–13 and 3–18) and one nd (n = 3–14). These transitions involve Rydberg states converging to the 1,1-C_2H_2Cl_2(X\tilde{X}B_2) ground ionic state. The vibrational structure associated with these transitions has been analyzed based on the data for the first band of the 1,1-C_2H_2Cl_2 HeI-PES [17]. The harmonics and combination transitions involving three vibrational modes, that is, \nu_3 = 1307 cm\(^{-1}\) (\nu_3 C–Cl stretching), \nu_4 = 661 cm\(^{-1}\) (\nu_4 C–Cl symmetric stretching) and \nu_5 = 290 cm\(^{-1}\) (Cl–Cl–Cl bending), have been identified.

Above 9.0 eV and up to 12.6 eV numerous transitions to Rydberg states converging to the successive excited states of 1,1-C_2H_2Cl_2 are observed. For most of them vibrational progressions are observed. Assignments are proposed and nearly all vibrational structures may be accounted for by the excitation of the Cl–Cl–Cl bending vibration with a wavenumber in the 210–290 cm\(^{-1}\) range.

Between 12.6 and 18.5 eV weak broad bands are superimposed on a strong continuum. Several Rydberg transitions are observed converging to the 4a_1^{-1} and 3a_1^{-1} ionization limits.

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