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The photoabsorption spectrum of vinylchloride (C_2H_3C1) in the 8-12 eV range

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Abstract

The photoabsorption spectrum of vinylchloride (C_2H_3C1) has been measured using synchrotron radiation and has been analyzed in detail between 8.0 eV and 12.0 eV photon energy. Valence to virtual valence and Rydberg transitions have been identified and classified. Tentative assignments were based on ionization energies as measured by He(I) and threshold photoelectron spectroscopy, as reported in the joined paper [1]. Many features have been identified as being members of vibrational progressions belonging to the observed Rydberg series.

1. Introduction

The energy and structure of the neutral as well as the ionic ground and excited states of ethylene and its halogenated derivatives are of considerable interest for understanding the gas phase photochemistry and ion chemistry of this class of compounds which play an important role in many fields of chemistry.

On the other hand, though having been the subject of extended investigations by several mass spectrometric and spectroscopic techniques, these compounds remain ideal molecular systems for the study of the influence of the position and nature of the substituent on the dynamics of isolated molecular ions and clusters [2, 3]. This requires the detailed examination of well-chosen members of these chemical compounds.

For these reasons, we were interested firstly in extending the spectroscopic data related to these molecular systems by investigating e.g. their photoabsorption spectrum. We started with vinylchloride (C_2H_3C1) for which the only known vacuum UV photoabsorption spectrum was published by Sood and Watanabe in 1966 [4]. We will report here on the photoabsorption spectrum of this molecular species between 8 and 12 eV photon energy. Photoionization experiments related to this molecule will be described in a companion paper [1].

2. Experimental

In the experiment reported here, we used the vacuum UV light from the synchrotron radiation provided by the electron storage ring BESSY (Berlin). This light is dispersed by a 3 m normal incidence monochromator (3m-NIM-l line) equipped with a 2400 lines/mm Pt-grating. The entrance and exit slit widths were set at 50 µm to 200 µm depending on the signal intensity. The experimental resolution obtained in these conditions was estimated to be about 0.03 nm to 0.09 nm respectively. Owing to the second order contribution at low photon energy, LiF or MgF_2 windows were used in the 8.0-11.8 eV and 8.0-10.8 eV ranges respectively. The photon energy scale of the monochromator is calibrated with rare gas photoabsorption and/or threshold photoelectron spectra to reach an accuracy better than 2-3 meV. For this purpose, usually Ar and sometimes Xe are used.

The light beam is focussed into an ion chamber, in the focussing plane of a tandem electron spectrometer consisting of two 180° electrostatic deflectors, shown in Fig. 1 and used for photoelectron spectroscopic experiments. The photoelectron signal of a gold diode, inserted in the ion chamber, in front of the 3m-NIM monochromator exit slit is used to measure relative photoabsorption cross sections of a target gas filling the ion chamber at a known pressure. The collected photoelectron signal from the gold diode is recorded as a function of the photon energy. This signal is normalized to the blank spectrum obtained by measuring the photoelectron signal from the gold diode without sample gas in the ion chamber. During these measurements the power supplies of the electron spectrometer and the channeltron are switched off.

The C_2H_3C1 sample used in these experiments, purchased from Linde AG (99% purity), is introduced without further purification. The ultimate vacuum in the ionization chamber is about 10^{-8} mbar. Unless otherwise stated, the 3m-NIM monochromator entrance and exit slit widths are 200 µm for the present experiment.

[1] Chercheur qualifié du FNRS

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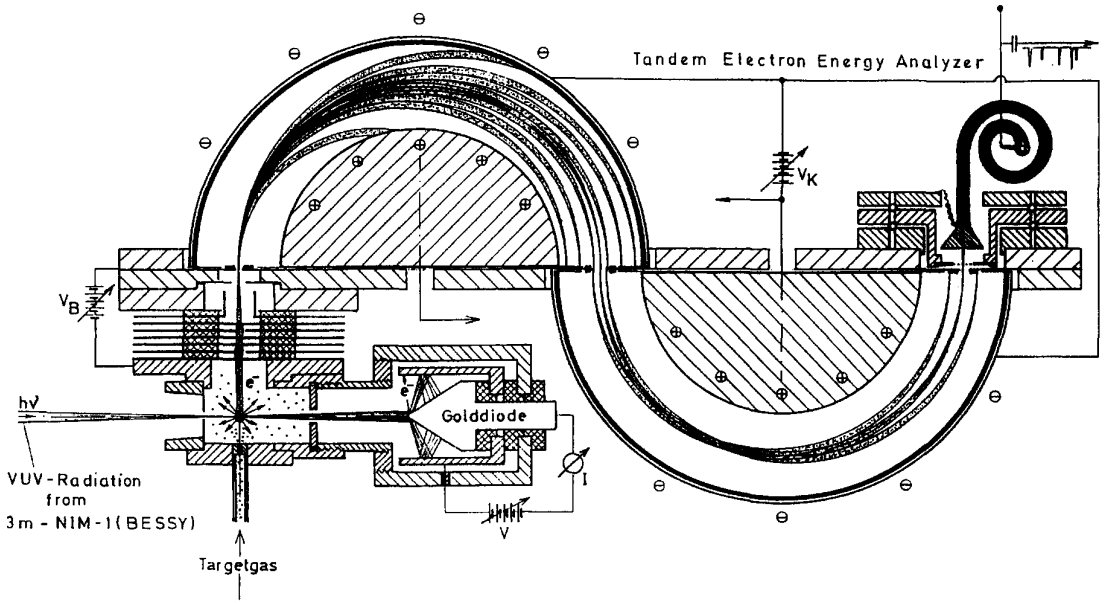
3. Experimental results

The vacuum UV absorption spectrum, recorded between 8.0 eV and 11.8 eV with MgF_2 and LiF windows, is shown in Fig. 2a-c in an expanded photon energy scale. The comparison of the spectrum obtained by Sood and Watanabe [4] with the present results reveals additional previously unresolved structures, e.g. in the energy regions around 8.5 eV or in the 9.1-9.5 eV photon energy range. Between the first and the second ionization limits (at 10.013 and 11.672 eV, respectively [1]) numerous well-resolved features are observed. It must be mentioned that the former authors used a 1 m NIM monochromator equipped with a 1200 lines/mm grating and an LiF window. A H_2 discharge lamp was used as excitation source.

Fig. 1. *Experimental setup used in this work showing the ionization chamber and the gold-diode.*



4. Discussion

4.1. The valence transitions

The photoabsorption spectrum of C_2H_3Cl shows abundant sharp structures superimposed on broad bands. This is clearly illustrated in Fig. 3 displaying the overall spectrum observed from 8.0 eV to 12.0 eV using LiF and MgF_2 windows. This general shape leads us to assume that both valence excitations and Rydberg transitions contribute to the spectrum. This has already been observed in photoabsorption spectra of similar compounds, i.e. in the fluorochloroethenes [5]. This result is not easy to compare with the spectrum published on an extended wavelength scale by Sood and Watanabe [4]. However, more recently Sze et al. [6] investigated the electron energy loss spectrum of C_2H_3Cl. These authors mentioned also the presence of underlying valence to virtual valence transitions which would be consistent with the apparently rising background and overall intensity distribution in this photon energy range. Some of these bands were tentatively identified in the photoabsorption spectrum and characterized by 'maxima' labeled A to E in Fig. 3. Several bands could be located successively at about 8.54 eV, 9.40 eV, 9.85 eV, around 10.3 eV, at 10.68 eV and at 11.56 eV. With the help of a term scheme shown in Fig. 4, based on data published by Sze et al. [6] and on the photoelectron spectroscopic results obtained in this work (see Table 1 in the companion paper [1]), an assignment could be attempted and the result is shown in Table 1. In the energy range investigated in this work, nearly all transitions predicted in this scheme seem to be observed.

4.2. The Rydberg transitions

In the energy range covered in the present study most of the Rydberg transitions can be classified and identified by using the series formula

$$E_{\mathrm{Rydb}} = \mathrm{IE} - \Re/(n-\delta)^2$$

where E_{Rydb} is the observed Rydberg energy, IE is the ionization energy, $\Re$ is the Rydberg constant (taken to be 13.605 eV), n is the principal quantum number and δ is the quantum defect associated with the Rydberg state. Its

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Fig. 2. *The photoabsorption spectrum of C_2H_3Cl recorded between 8.0 eV and 12.0 eV and shown on an extended photon energy scale. Interpretation and assignments in terms of Rydberg series are included.*

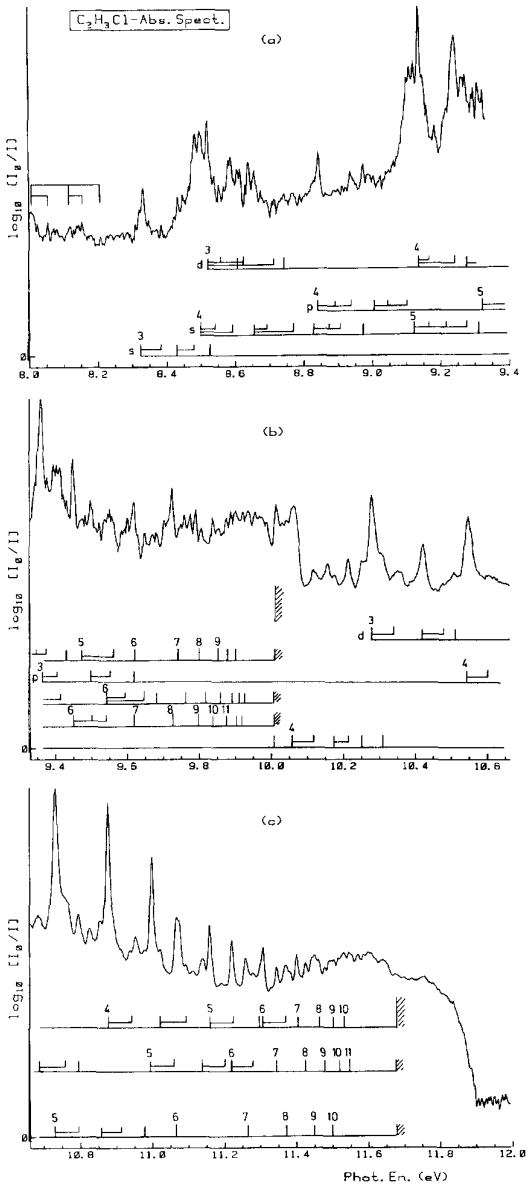

Table 1 *Correlation between predicted and observed valence → virtual valence transitions in the photoabsorption spectrum of C_2H_3Cl and tentative assignments. Energies are expressed in eV*

Energies		Assignment
observed	predicted	
-	7.96	$p_{\parallel}(Cl) \rightarrow \sigma^*(C\text{-}Cl)$
8.54	8.35	$p_{\parallel}(Cl) \rightarrow \pi^*(C{=}C)$
9.38	9.47	$p_{\perp}(Cl) \rightarrow \sigma^*(C\text{-}Cl)$
	9.80	$\sigma(C\text{-}Cl) \rightarrow \sigma^*(C\text{-}Cl)$
9.83		
-	9.85	$p_{\perp}(Cl) \rightarrow \pi^*(C{=}C)$
10.3-10.7	10.18	$\sigma(C\text{-}Cl) \rightarrow \pi^*(C{=}C)$
11.56	11.63	$5a' \rightarrow \sigma^*(C\text{-}Cl)$
-	12.01	$5a' \rightarrow \pi^*(C{=}C)$

value is essentially related to the nature of the Rydberg orbital. The ionization energies used in this formula are those determined in the present work, i.e. 10.013 ± 0.005 eV and 11.672 ± 0.005 eV respectively, corresponding to the ground state and first excited state of the molecular ion (see Table 1 in Ref. [1]). As shown in Fig. 2a-c the fine structure has essentially been assigned to $\pi \rightarrow n$s, np and nd and to $p_{\parallel}$(Cl) $\rightarrow n$s, np and nd transitions, respectively.

Fig. 3. *Photoabsorption spectrum of C_2H_3Cl, recorded with a LiF window, between 8.0 eV and 12.0 eV photon energy, showing clearly the underlying contribution from valence to virtual valence transitions indicated by letters A to E.*

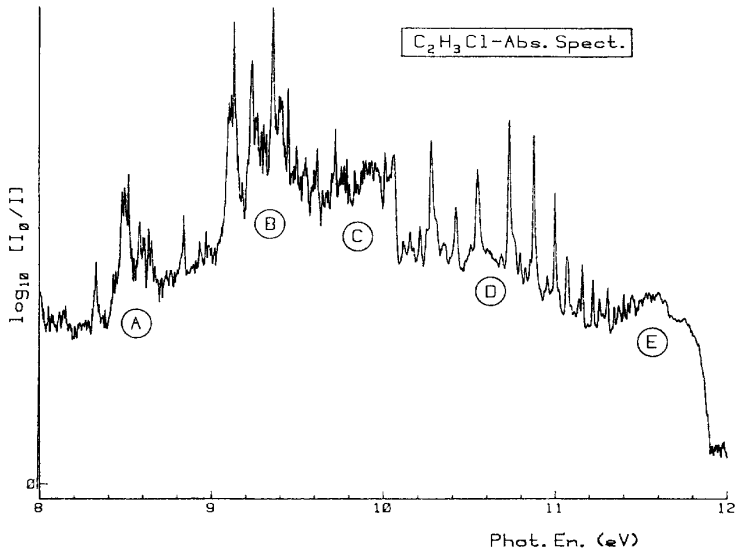

Table 2 *Energies (eV) and effective quantum numbers (n*) of three Rydberg series converging to the vibrationless $\tilde{X}^2A''$ vibronic state of $C_2H_3Cl^+$ with the limit at 10.013 eV*

$\pi \rightarrow n$s	n*	n	$\pi \rightarrow n$p	n*	n	$\pi \rightarrow n$d	n*	n
8.498	2.996	4	8.842	3.408	4	8.522	3.020	3
9.121	3.906	5	9.322	4.438	5	9.136	3.940	4
9.451	4.920	6	9.546	5.400	6	9.472	5.016	5
9.622	5.900	7	9.681	6.412	7	9.631	5.969	6
9.727	6.900	8	9.760	7.335	8	9.745	7.126	7
9.793	7.848	9	9.820	8.400	9	9.803	8.148	8
9.839	8.794	10	9.856	9.311	10	9.850	9.138	9
-	-		9.889	10.477	11	9.877	10.001	10
-	-		-	-		9.901	11.024	11
-	-		9.923	12.436	13	-	-	
-	-		9.937	13.390	14	-	-	
-	-		9.988	23.320	24	9.961	16.175	16

Table 3 *Energies (eV) and effective quantum numbers (n*) of three Rydberg series converging to the vibrationless $\tilde{A}^2A'$ vibronic state of $C_2H_3Cl^+$ with the limit at 11.672 eV*

$p_{\parallel} \rightarrow n$s	n*	n	$p_{\parallel} \rightarrow 6n$p	n*	n	$p_{\parallel} \rightarrow n$d	n*	n
8.333	2.018	3	9.361	2.426	3	10.278	3.124	3
10.065	2.908	4	10.549	3.480	4	10.878	4.140	4
10.731	3.798	5	11.001	4.504	5	11.160	5.155	5
11.076	4.771	6	11.223	5.507	6	11.310	6.122	6
11.259	5.726	7	11.346	6.460	7	11.403	7.085	7
11.370	6.693	8	11.427	7.456	8	11.463	8.030	8
11.445	7.691	9	11.481	8.445	9	11.506	8.999	9
11.496	8.823	10	11.517	9.376	10	11.532	9.831	10
-	-		11.547	10.440	11	-	-	

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Table 4 *Comparison of energies (eV) and assignments of the photoabsorption spectrum (a) and the electron energy loss spectrum (b) as proposed by Ref. [4], Ref. [6] and in the present work (1 eV = 8 065.73 cm^{-1})*

(a)

Ref. [4]		This work		Ref. [4]		This work	
Design.	Energy	Assign.	Energy	Design.	Energy	Assign.	Energy
$R_3(3)$	8.838	4p	8.842	$R_2(3)$	8.635	3d	8.522
$R_3(4)$	9.309	5p	9.322	$R_2(4)$	9.217	4d	9.136
$R_3(5)$	9.544	6p	9.546	$R_2(5)$	9.496	5d	9.472
$R_3(6)$	9.671	7p	9.681	$R_2(6)$	9.649	6d	9.631
$R_3(7)$	9.756	8p	9.760	-	-	7d	9.745
				$R_2(8)$	9.802	8d	9.803

Ref. [4]		This work	
Design.	Energy	Assign.	Energy
$R_1(2)$	8.431	4s	8.498
$R_1(3)$	9.134	5s	9.121
$R_1(4)$	9.447	6s	9.451
$R_1(5)$	9.615	7s	9.622
$R_1(6)$	9.716	8s	9.727
$R_1(7)$	9.790	9s	9.793
$R_1(8)$	9.832	10s	9.839

(b)

Ref. [6]		This work		Ref. [6]		This work	
Conv.limit: 10.01 eV				Conv.limit: 11.67 eV			
Assign.	Energy	Assign.	Energy	Assign.	Energy	Assign.	Energy
3d	8.449	4s	8.498	4p	9.322	3p	9.361
	8.549	3d	8.522	5s	10.235	3d	10.278
4d	9.203	4d	9.136	5p	10.513	4p	10.549
6s	9.322	5p	9.322	4d	10.700	5s	10.731
				6s	10.831	4d	10.878
				6p	10.950	5p	11.001

Table 5 *Energies (eV), effective quantum numbers (n*), assignments (0 means vibrationless level) and wavenumbers (ω_i^{Rydb} in cm^{-1}) of vibrational progressions observed in Rydberg series converging to the $\tilde{X}\,^2A''$ vibronic state of $C_2H_3Cl^+$*

Transit.	Energy	n^*	Limit [a]	Assign.	ω_i^{Rydb}
$\pi \rightarrow 4s$	8.498	2.996	10.013	0	$\omega_4^{Rydb} = 1300 \pm 20$
	8.540	2.995	10.056	ν_9	$\omega_8^{Rydb} = 800 \pm 70$
	8.587	2.984	10.113	$2\nu_9$	$\omega_9^{Rydb} = 310 \pm 40$
		2.992	10.107		
	8.657	2.995	10.173	ν_4	
	8.691	2.988	10.215	$\nu_4 + \nu_9$	
	8.765	2.998	10.278	$\nu_4 + \nu_8$	
	8.821	2.983	10.350	$2\nu_4$	
	8.869	2.988	10.392	$2\,\nu_4 + \nu_9$	
	8.899	2.963	10.449	$2\,\nu_4 + 2\nu_9$	
	8.975	2.987	10.500	$3\nu_4$	
$\pi \rightarrow 5s$	9.121	3.906	10.013	0	$\omega_4^{Rydb} = 1500$
	9.160	3.996	10.056	ν_9	$\omega_8^{Rydb} = 774$
	9.217	3.892	10.113	ν_8	$\omega_9^{Rydb} = 370 \pm 60$
		3.910	10.107	$2\nu_9$	
	9.280	3.923	10.164	$3\nu_9$	
	9.307	3.964	10.173	ν_4	
$\pi \rightarrow 6s$	9.451	4.920	10.013	0	$\omega_8^{Rydb} = 701$

	9.505	4.970	10.056	ν_9	$\omega_9^{Rydb} = 435$
	9.538	4.864	10.113	ν_8	
		4.890	10.107	$2\nu_9$	
$\pi \rightarrow 4p$	8.842	3.408	10.013	0	$\omega_4^{Rydb} = 1306$
	8.887	3.412	10.056	ν_9	$\omega_8^{Rydb} = 758$
	8.936	3.400	10.113	ν_8	$\omega_9^{Rydb} = 330 \pm 40$
		3.408	10.107	$2\nu_9$	
	9.004	3.411	10.173	ν_4	
	9.040	3.402	10.215	$\nu_4 + \nu_9$	
	9.100	3.398	10.278	$\nu_4 + \nu_8$	
	9.109	3.411			
$\pi \rightarrow 5p$	9.322	4.438	10.013	0	$\omega_8^{Rydb} = 750$
	9.415	4.416	10.113	ν_8	
$\pi \rightarrow 6p$	9.546	5.400	10.013	0	$\omega_8^{Rydb} = 830$
	9.601	5.469	10.056	ν_9	$\omega_9^{Rydb} = 440$
	9.649	5.416	10.113	ν_8	
		5.450	10.107	$2\nu_9$	
$\pi \rightarrow 3d$	8.522	3.020	10.013	0	$\omega_4^{Rydb} = 1310$
	8.552	3.007	10.056	ν_9	$\omega_8^{Rydb} = 742$
	(8.587)	(3.044)			$\omega_9^{Rydb} = 240$
	8.614	3.011	10.113	ν_8	
	(8.638)	(3.037)			
		3.019	10.107	$2\nu_9$	
	8.606	2.946	10.173	ν_4	
	8.714	3.010	10.215	$\nu_4 + \nu_9$	
	8.743	2.977	10.278	$2\nu_4$	
$\pi \rightarrow 4d$	9.136	3.940	10.013	0	$\omega_4^{Rydb} = 1282$
	9.160	3.994	10.056	ν_9	$\omega_8^{Rydb} = 980 \pm 14$
	9.241	4.078	10.113	ν_8	$\omega_9^{Rydb} = 302 \pm 100$
		3.963	10.107	$2\nu_9$	
	9.295	3.936	10.173	ν_4	
	9.346	4.050	10.215	$\nu_4 + \nu_9$	
	(9.379)	(4.060)			
	9.433	4.012	10.278	$\nu_4 + \nu_8$	
$\pi \rightarrow 5d$	9.472	5.016	10.013	0	$\omega_8^{Rydb} = 730$
	9.562	4.970	10.113	ν_8	or $\omega_9^{Rydb} = 365$
		4.996	10.107	$2\nu_9$	

[a] Ionization energies obtained in this work [1].

Nearly all features observed in the photoabsorption spectrum have been classified and assigned to vibronic Rydberg transitions. The energies and assignments of part of these features have been tabulated in Tables 2 and 3 for both the Rydberg series converging to the π^{-1} and $p_{\|}^{-1}$ ionization continua. Most of these transitions are observed up to fairly high *n* values.

The comparison with previous photoabsorption spectroscopic work could only be made in the energy range of Rydberg transitions converging to the lowest ionization energy as shown in Table 4(a). Except for the 3d state, there is fairly good agreement between the results published by Sood and Watanabe [4] and those obtained from the present spectrum, regarding both the energy levels and the assignment. In the former work R_1 R_2 and R_3 correspond to *n*s, *n*d and *n*p Rydberg states respectively. The series convergence was determined to be 10.00 ± 0.01 eV, in very good agreement with the present He(I) and TPES photoelectron spectroscopic data (see the companion paper [1]).

At the lower end of the photon energy range covered in this work, the first structures in the photoabsorption spectrum are observed between 8.006-8.207 eV and 8.333-8.531 eV. In both energy ranges they seem to correspond to vibrational progressions. However, the latter group shows fairly sharp features whereas the former exhibits more diffuse peaks. The effective quantum number characterizing the 8.006 eV and the 8.333 eV transitions is 1.926 and 2.018 respectively. Sood and Watanabe [4] mentioned (i) an $R_3(n = 2)$ series starting at 7.672 eV (61874 cm^{-1}) with a vibrational progression extending up to about 8.156 eV (65785 cm^{-1}) and (ii) a W state starting at 7.817 eV (63050 cm^{-1}) with a complex vibrational structure extending up to 8.228 eV (66360 cm^{-1}). These authors suggest that this latter progression involves non-Rydberg transitions. However,

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using five features observed between 8.006 eV and 8.207 eV effective quantum numbers ranging from 1.926 to 1.905 are calculated. This could suggest that these transitions already have Rydberg character. The effective quantum number of the sharply-shaped features starting at 8.333 eV oscillates between 2.018 and 1.993 (see Tables 3 and 6).

Fig. 4. *Term scheme and predicted term values of valence to virtual valence transitions in C_2H_3Cl between 6.3 eV and 12.0 eV photon energy.*

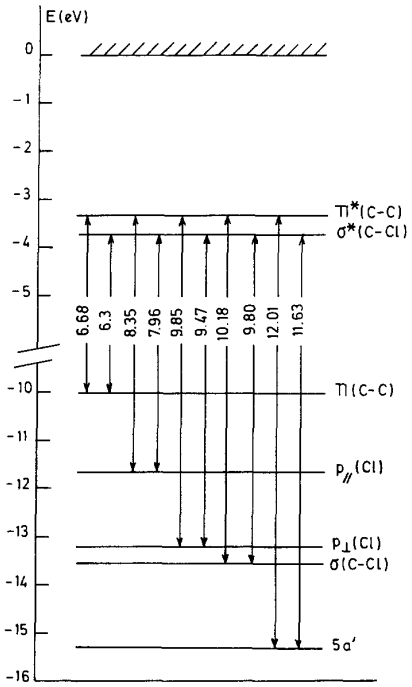

Table 6 *Energies (eV), effective quantum numbers (n*), assignments (0 means vibrationless level) and wavenumbers (ω_i^{Rydb} in cm^{-1}) of vibrational progressions observed in Rydberg series converging to the $\tilde{A}^2A'$ vibronic state of $C_2H_3Cl^+$*

Transit.	Energy	n^*	Limit [a]	Assign.	ω_i^{Rydb}
$p_{\|\|} \rightarrow 3s$	8.333	2.018	11.672	0	$\omega_6^{Rydb} = 800 \pm 10$
	8.369	2.011	11.733	ν_8	$\omega_8^{Rydb} = 363 \pm 70$
	8.432	2.005	11.814	ν_6	
	8.486	2.003	11.877	$\nu_6 + \nu_8$	
	8.531	1.993	11.955	$2\nu_6$	
$p_{\|\|} \rightarrow 4s$	10.065	2.908	11.672	0	$\omega_6^{Rydb} = 967 \pm 40$
	10.117	2.901	11.733	ν_8	$\omega_8^{Rydb} = 315 \pm 25$
	10.180	2.886	11.814	ν_6	
	10.216	2.862	11.877	$\nu_6 + \nu_8$	
	10.305	2.871	11.955	$2\nu_6$	
$p_{\|\|} \rightarrow 5s$	10.731	3.798	11.672	0	$\omega_6^{Rydb} = 1000 \pm 10$
	10.798	3.815	11.733	ν_8	$\omega_8^{Rydb} = 480 \pm 50$
	10.857	3.770	11.814	ν_6	
	10.911	3.753	11.877	$\nu_6 + \nu_8$	
	10.980	3.735	11.955	$2\nu_6$	
$p_{\|\|} \rightarrow 6s$	11.076	4.771	11.672	0	$\omega_6^{Rydb} = 940$
	11.115	4.692	11.733	ν_8	$\omega_8^{Rydb} = 310$
	11.193	4.681	11.814	ν_6	
$p_{\|\|} \rightarrow 3p$	9.361	2.426	11.672	0	$\omega_6^{Rydb} = 1020 \pm 100$
	9.406	2.418	11.733	ν_8	$\omega_8^{Rydb} = 400 \pm 40$
	9.499	2.424	11.814	ν_6	
	9.553	2.409	11.877	$\nu_6 + \nu_8$	

	9.613	2.410	11.955	$2v_6$	
$p_{\|\|} \rightarrow 4p$	10.549	3.480	11.672	0	$\omega_6^{Rydb} = 1000 \pm 100$
	10.602	3.469	11.733	v_8	$\omega_8^{Rydb} = 520 \pm 90$
	10.686	3.473	11.814	v_6	
	10.761	3.492	11.877	$v_6 + v_8$	
	10.798	3.429	11.955	$2v_6$	
$p_{\|\|} \rightarrow 5p$	11.001	4.504	11.672	0	$\omega_6^{Rydb} = 1113$
	11.070	4.530	11.733	v_8	$\omega_8^{Rydb} = 540 \pm 20$
	11.139	4.489	11.814	v_6	
	11.205	4.500	11.877	$v_6 + v_8$	
$p_{\|\|} \rightarrow 6p$	11.223	5.507	11.672	0	$\omega_8^{Rydb} = 450$
	11.280	5.480	11.733	v_8	
$p_{\|\|} \rightarrow 3d$	10.278	3.124	11.672	0	$\omega_6^{Rydb} = 950 \pm 100$
	10.339	3.124	11.733	v_8	$\omega_8^{Rydb} = 480 \pm 20$
	10.423	3.127	11.814	v_6	
	10.480	3.120	11.877	$v_6 + v_8$	
	10.510	3.068	11.955	$2v_6$	
$p_{\|\|} \rightarrow 4d$	10.878	4.140	11.672	0	$\omega_6^{Rydb} = 1137 \pm 50$
	10.941	4.146	11.733	v_8	$\omega_8^{Rydb} = 530 \pm 20$
	11.025	4.152	11.814	v_6	
	11.094	4.168	11.877	$v_6 + v_8$	
	(11.160)	(4.137)	(11.955)	$2v_6$	
$p_{\|\|} \rightarrow 5d$	11.160	5.155	11.672	0	$\omega_6^{Rydb} = 1090$
	11.223	5.165	11.733	v_8	$\omega_8^{Rydb} = 510$
	11.295	5.120	11.814	v_6	
$p_{\|\|} \rightarrow 6d$	11.310	6.122	11.672	0	$\omega_8^{Rydb} = 480$
	11.370	6.122	11.733	v_8	

[a] Ionization energies obtained in this work [1].

As mentioned earlier in this section, the present data can be compared with electron energy loss spectroscopic results published by Sze et al. [6]. Table 4(b) displays energy levels and assignments obtained by electron spectroscopy and the comparison with the present results. Despite a few differences of assignment, the energy levels in the two investigations correlate fairly well. On the other hand, Sze et al. [6] determined ionization energies by He(I) photoelectron spectroscopy. For the first two ionic states, energies of 10.16 eV and 11.64 eV were determined. They have to be compared with 10.01(3) eV and 11.67(2) eV obtained in this work. This discrepancy, particularly on the first ionization energy, can induce differences in assignments.

Tables 5 and 6 show detailed information on several Rydberg transitions exhibiting vibrational progressions and converging to the first and second ionization continuum respectively. The vibrational fine structure in the ionic state is determined by He(I) and threshold photoelectron spectroscopy (see the companion paper [1]). From both tables the assignment is made by gathering the features characterized by the same effective quantum number. This parameter is fairly constant for all observed vibrational progressions in the same Rydberg state.

Most of the Rydberg states listed in Table 5 show the excitation of three normal vibrational modes characterized by wavenumbers of 1 340 ± 90 cm^{-1}, 780 ± 80 cm^{-1} and 350 ± 70 cm^{-1} respectively as averaged over all the observed wavenumbers listed in the same table. These wavenumbers should be close to those of the $C_2H_3Cl^+(\tilde{X}\ ^2A")$ ionic state. A normal mode analysis performed on this ionic state at the MNDO level [7] allows us to suggest the following assignment for the observed wavenumbers. The highest wavenumber of 1 340 ± 90 cm^{-1} corresponds to the ν_4 normal mode consisting in a C=C stretching with a CH_2 scissoring contribution. The ν_8 mode (CH_2 rocking, C-Cl stretching) corresponds to the 780 ± 80 cm^{-1} wavenumber, whereas the 350 ± 70 cm^{-1} can be assigned to the ν_9 mode consisting in an in plane rocking of the CH_2 group. At the MNDO level, the excitation of these normal modes can be rationalized by analysing the geometry variations resulting from ionization to the $\tilde{X}\ ^2A"$ state: a lengthening of the C=C bond (from 1.33 Å to 1.43 Å)) and a shortening of the C-Cl bond (from 1.75 Å to 1.69 Å). Based on the Franck-Condon principle, the normal modes involving both C=C and C-Cl stretching have to be excited. The observation of a lowering of the C=C stretching wavenumber with respect to the neutral molecule has to be related to the lengthening (or weakening) of this bond, whereas to the increase of the C-Cl stretching vibration wavenumber corresponds to a strengthening (or shortening) of this bond. Indeed, in the neutral molecule these quantities, corresponding to the same normal vibrational modes, are 1608 cm^{-1}, 720 cm^{-1} and 395 cm^{-1} [8]. Sood and Watanabe [4] reported wavenumbers of about 1300 cm^{-1} and 410

cm^{-1} in very good agreement with the present observations. The $\omega_8 = 780 \pm 80$ cm^{-1} was not mentioned by these authors.

Similarly, in Table 6, Rydberg series were classified showing the excitation of two vibrational normal modes tentatively assigned to ν_6 (H-C-Cl scissoring) and ν_8 (CH_2 rocking, C-Cl stretching). As averaged over all the observed Rydberg series, except the 3s, the corresponding wavenumbers are $\omega_6 = 1020 \pm 70$ cm^{-1} and $\omega_8 = 450 \pm 80$ cm^{-1}. In the neutral molecule the wavenumbers corresponding to these normal vibrational modes are 1279 cm^{-1} and 720 cm^{-1} respectively [8]. No comparison could be made with previous results, Sood and Watanabe [4] mentioning "to be unable to make a satisfactory interpretation".

***Table** 7 Energy levels (eV) of Rydberg series converging to the $C_2H_3Cl^+$ ($A^2\tilde{A}''$) state. Comparison between photoionization mass spectrometric results [9] and the present photoabsorption spectroscopic work.*

Photoionization			Photoabsorption		
$p_{\|\|} \rightarrow ns$	$p_{\|\|} \rightarrow np$	$p_{\|\|} \rightarrow nd$	$p_{\|\|} \rightarrow ns$	$p_{\|\|} \rightarrow np$	$p_{\|\|} \rightarrow nd$
-			8.333		
10.28	-	-	10.065	9.361	10.278
10.86	10.54	10.72	10.731	10.549	10.878
11.15	10.98	11.05	11.076	11.001	11.160
11.29	11.20	11.25	11.259	11.223	11.310
	11.35	11.36	11.370	11.346	
		11.43	11.445		

Reinke et al. [9] measured the photoionization efficiency curve of $C_2H_3Cl^+$ and mentioned the presence of autoionization fine structure in the 10.3-11.6 eV photon energy range. They were able to classify and assign these features to *n*s-, *n*p- and *n*d-type Rydberg series. These are shown in Table 7 and compared to the present results. The energy levels are in very good agreement with the present observations. Concerning the *n*s and *n*d assignment these authors suggest the reversed interpretation compared to ours. It must be emphasized at this point that this assignment is not unambiguous as the (n + 1)s and *n*d Rydberg states are close in energy and can therefore interact. This will lead to a mixing of (n + 1)s and nd characters. However, the extent of this mixing is impossible to estimate based only on experimental information at moderate resolution.

5. Conclusion

The investigation of the photoabsorption spectrum of C_2H_3Cl with the help of synchrotron radiation allowed us to extend the analysis and assignments to higher energies, i.e. to the second ionization limit. Rydberg series up to high principal quantum numbers are identified. For the first members, the vibrational structure is disentangled. This data analysis appears to be most important to examine the TPES-and CIS spectra.

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References

[1] R. Locht, B. Leyh, K. Hottmann, H. Baumgartel, Chem. Phys. 220 (1997) 217.

[2] T. Baer, P.M. Guyon, High Resolution Laser Photoionization and Photoelectron Studies, I. Powis, T. Baer, C.Y. Ng (Eds.), Wiley, 1995, p. 1.

[3] C.Y. Ng, Vacuum Ultraviolet Photoionization and Photodisso-ciation of Molecules and Clusters. C.Y. Ng (Ed.), World Scientific, Singapore, 1991, p. 169.

[4] S.P. Sood, K. Watanabe, J. Chem. Phys. 45 (1966) 2913.

[5] G. Tornow, R. Locht, R. Kaufel, H. Baumgärtel, H.W. Jochims, Chem. Phys. 146 (1990) 115.

[6] K.H. Sze, C.E. Brion, A. Katrib, B. El-Issa, Chem. Phys. 137 (1989) 369.

[7] Dewar Research Group: the AMPAC package (containing the MNDO/3, MNDO and AM1 methods), Chemistry Department, University of Texas, Austin, TX 78712. The package was converted for an IBM3090 computer by R. Farren and E.R. Davidson, Department of Chemistry, Indiana University, Bloomington, IN 47405, and is distributed by the Quantum Chemistry Program Exchange under reference number 539.

[8] G. Herzberg, Molecular Spectra and Molecular Structure. ΠΙ. Electronic Spectra and Electronic Structure of Polyatomic Molecules, Van Nostrand, Princeton, NJ, 1967.

[9] D. Reinke, R. Krässig, H. Baumgärtel, Z. Naturforsch. 28a (1973) 1021.