



High-lying Rydberg states and ionization energy of vinyl chloride studied by two-photon resonant ionization spectroscopy

Jia-lin Chang^a, Jau-Chin Shieh^b, Jen-Chieh Wu^b, Runhua Li^a, Yit-Tsong Chen^{a,b,*}

^a Institute of Atomic and Molecular Sciences, P.O. Box 23-166, Taipei 106, Taiwan

^b Department of Chemistry, National Taiwan University, Taipei 106, Taiwan

Received 14 April 2000; in final form 7 June 2000

Abstract

High-lying Rydberg states of jet-cooled vinyl chloride at 9.3–10 eV are investigated using 2 + 1 resonance-enhanced multiphoton ionization spectroscopy. Four Rydberg series are observed and tentatively assigned as due to the transitions of $\pi \rightarrow ns$, $np\sigma$, $np\pi$, and nf Rydberg orbitals associated with quantum defects of 0.94, 0.89, 0.48, and 0.02, respectively. All of the four series converge to the same ionization energy limit corresponding to the ground state of vinyl chloride cation. The adiabatic ionization energy of vinyl chloride is determined to be $80\,720 \pm 6 \text{ cm}^{-1}$, in excellent agreement with previously reported values. © 2000 Elsevier Science B.V. All rights reserved.

1. Introduction

The spectroscopy [1–9] and photodissociation dynamics [10–17] of vinyl chloride ($\text{C}_2\text{H}_3\text{Cl}$) have been intensively examined in the past decades. Vinyl chloride, being an atmospheric pollutant, is of interest because it has been widely used in the industry for poly(vinyl chloride) production. The understanding of its photochemical processes is therefore very important. While photodissociation experiments usually measure the internal state, velocity, and angular distributions of photofragments, which are closely related to the topological features of the potential

energy surface of photodissociative molecules, spectroscopic investigation is the most stringent examination for molecular excited states and their corresponding potential energy surfaces.

Walsh reported the vacuum-ultraviolet (VUV) absorption spectrum of vinyl chloride at 105–220 nm and identified two Rydberg series which converge to $\sim 10 \text{ eV}$ [18]. Sood and Watanabe measured the absorption and ionization coefficients of the same molecule in the region of 107.5–200 nm [19]. In addition to the two series observed by Walsh, Sood and Watanabe found two new Rydberg series. Berry recorded the VUV absorption spectra of chloroethylenes up to $70\,000 \text{ cm}^{-1}$ but without spectroscopic assignment [20]. The early studies on the excited electronic states of chloroethylenes before 1984 have been reviewed by Robin [21]. Recently, Loch et al. reported the absorption spectrum of vinyl chloride at 8–12 eV (103–155 nm) and determined the first

* Corresponding author. Academia Sinica, Institute of Atomic and Molecular Sciences, P.O. Box 23-166, Taipei 106, Taiwan. Fax: +886-2-2362-0200; e-mail: ytchen@pub.iam.sinica.edu.tw

ionization energy (IE) of vinyl chloride to be 10.013 ± 0.005 eV [2], in agreement with that obtained from photoelectron spectroscopy [3]. The two-photon resonance-enhanced multiphoton ionization (REMPI) spectroscopy of vinyl chloride was studied first by Williams and Cool in the spectral range of 7.1–9.3 eV ($57\,100$ – $75\,000$ cm^{-1}) [1]. Many vibronic structures were observed and assigned below $75\,000$ cm^{-1} .

In this Letter, we report the 2 + 1 REMPI spectrum of vinyl chloride at 9.3–10 eV ($75\,000$ – $80\,650$ cm^{-1}) which is complementary to that obtained by Williams and Cool [1]. We have identified and assigned four Rydberg series of vinyl chloride, all of which converge to the same first IE limit. The adiabatic IE of vinyl chloride determined from this study is $80\,720 \pm 6$ cm^{-1} , in excellent agreement with previously reported values. The 2 + 1 REMPI spectrum of vinyl chloride at 7.4–10 eV has been re-examined in our laboratory, and a complete assignment facilitated with calculated Franck–Condon factors by ab initio methods [22,23] will be discussed in a later publication.

2. Experiment

The experimental details for obtaining 2 + 1 REMPI molecular spectroscopy in our laboratory were described in an earlier publication [24]. Briefly, vinyl chloride was seeded in 2 atm He to form a 10% mixture and was expanded into a vacuum chamber through a pulsed valve. A focused laser beam crossed the collimated molecular beam and ionized vinyl chloride. The ions were repelled by electric field in a direction perpendicular to both laser and molecular beams. The ions then moved across a field-free time-of-flight (TOF) tube and were finally detected by a microsphere plate. Due to the weak $\text{C}_2\text{H}_3\text{Cl}^+$ signal (too weak to be seen in Fig. 1), a photon counter was utilized to obtain the REMPI spectrum of vinyl chloride when gated on this parent ion ($m/z = 62$). Alternatively, the signal of the $m/z = 27$ mass channel (C_2H_3^+), the strongest in the TOF observation (Fig. 1), was monitored as a function of laser wavelength for better signal-to-noise ratio. Care was taken to insure that the REMPI

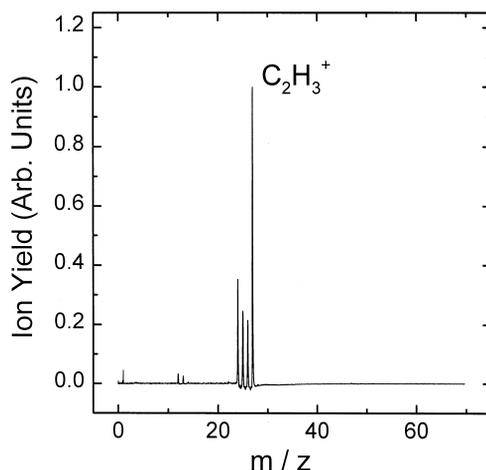


Fig. 1. Typical TOF mass spectrum of vinyl chloride excited at 250 nm via 2 + 1 REMPI.

spectra are identical by monitoring either the fragmentary C_2H_3^+ or the parent $\text{C}_2\text{H}_3\text{Cl}^+$. Optogalvanic spectroscopy of Ne was employed to calibrate the laser wavelength.

The polarization-ratio of vinyl chloride in a two-photon absorption process was also measured. The polarization-ratio, Ω , is defined as the band-intensity ratio for circularly to linearly polarized radiations. For the polarization experiments, a linear polarizer was used to form linearly polarized laser radiation. The linearly polarized laser then passes through a double Fresnel rhomb and a Fresnel rhomb, functioning respectively as half-wave and quarter-wave retarders. By rotating the double Fresnel rhomb, the polarization vector of the laser is set at $0^\circ/45^\circ$ with respect to the optical axis of the Fresnel rhomb to form linearly/circularly polarized radiation. Further details for the quantitative determination of polarization-ratios can be found in Ref. [24].

3. Results and discussion

Fig. 2 shows the REMPI spectrum of vinyl chloride at $76\,000$ – $80\,750$ cm^{-1} . The positions of sharp and well-resolved peaks are tabulated in Table 1, while the peaks with very weak intensity or congested with other bands are listed in parentheses. The dramatic rise on the right side of Fig. 2 at $\sim 80\,600$

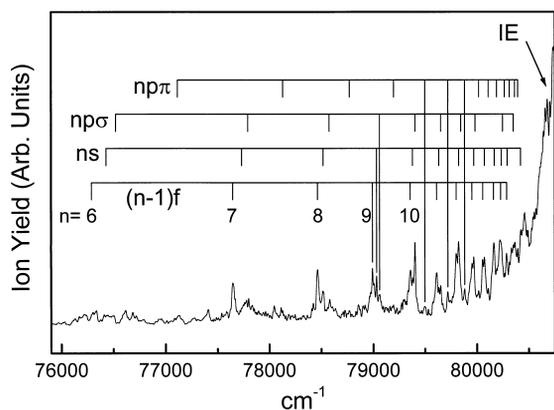


Fig. 2. Composite 2+1 REMPI spectrum of vinyl chloride at 9.4–10 eV.

cm^{-1} marks the onset of the ionization continuum of vinyl chloride. The observed transitions are analyzed using the Rydberg formula [25]

$$\nu = IE - R/(n - \delta)^2 \quad (1)$$

where ν is the transition frequency in cm^{-1} , $R = 109\,736.3588 \text{ cm}^{-1}$ is the Rydberg constant taking the mass of vinyl chloride into account, n is a

Table 1

Peak positions (cm^{-1}), ionization energies, and quantum defects for the four Rydberg series of vinyl chloride observed at 9.3–10 eV^a

n	(π, ns)	($\pi, np\sigma$)	($\pi, np\pi$)	(π, nf)
5				76288
6	(76428)	(76520)	77112	77646
7	(77732)	77790	78128	78464
8	78518	78575	(78770)	78992
9	79032	79060	(79195)	79356
10	79379	79403	79498	79611
11	79632	79650	79720	79800
12	79823	(79844)	79881	79951
13	79970	(79983)	80017	80056
14	80073		80109	80160
15	(80167)		80190	80229
16	(80235)	(80248)	(80265)	80288
17	(80293)		80313	
18		80351	80364	
19			80394	
20	80421			
IE	80720 ± 2	80729 ± 3	80714 ± 3	80716 ± 2
δ	0.94 ± 0.01	0.89 ± 0.01	0.48 ± 0.01	0.02 ± 0.01

^a The values in parentheses belong to weak or congested bands.

principal quantum number, and δ is the corresponding quantum defect. Four Rydberg series have been identified as due to the promotion of a π -electron to the ns , $np\sigma$, $np\pi$, and nf Rydberg orbitals, supported by their δ values.

3.1. (π, ns) Rydberg series

The promotion of a π -electron to the ns Rydberg orbital results in the (π, ns) Rydberg state. Fig. 3 shows the best fit of the $\pi \rightarrow ns$ transitions to the Rydberg formula rendering a converged limit at $80720 \pm 2 \text{ cm}^{-1}$ with $\delta = 0.94$ ($n = 6-17, 20$). The δ value of 0.94 is quite typical for an s Rydberg series of hydrocarbon molecules ($\delta \sim 1.0$) [25]. In order to compare our data with those obtained from one-photon absorption spectra [2,18,19], we have re-examined the transitions reported previously. The R_2 series of Walsh [18] ($IE = 80877 \pm 103 \text{ cm}^{-1}$, $\delta = 0.94$, $n = 3-9$) and of Sood and Watanabe [19] ($IE = 81008 \pm 177$, $\delta = 0.97$, $n = 3-7, 9$) should correspond to this (π, ns) series. The more accurate $IE = 80720 \pm 2 \text{ cm}^{-1}$ value, obtained from the present experiment, is resulted from the higher spectral resolution and the better fitting of the Rydberg states with higher n quantum numbers. It is well known that deviation from the Rydberg formula is amplified when orbitals of smaller n are included in the fitting. The reasoning for that is stemmed from the probable penetration of the low-lying s electrons into molecular core [24,25].

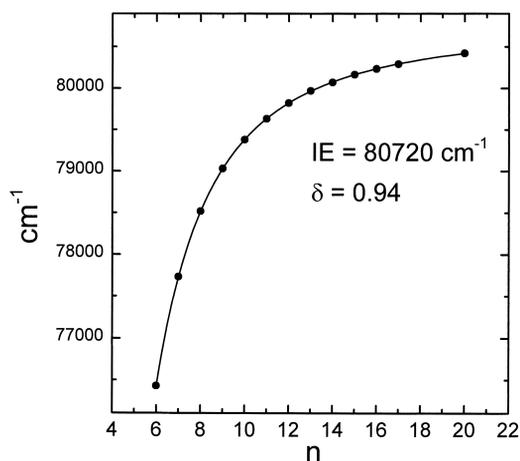


Fig. 3. Best fit of the (π, ns) series to the Rydberg formula.

In a previous study by Locht et al. [2], this *s* Rydberg series, however, was assigned as an *nd* ($n = 3-11, 16$) series with $IE = 80756 \pm 38 \text{ cm}^{-1}$ and $\delta = 0$. We believe that the *nd* ($\delta = 0$) and *ns* ($\delta = 1.0$) Rydberg series assigned by Locht et al. should be the $(n+1)s$ ($\delta = 1.0$) and $(n-1)d/f$ ($\delta = 0$) series, respectively. With this correction, these two series would then be consistent with our assignment of the *ns* ($\delta = 0.94$) and the *nf* ($\delta = 0.02$, see Section 3.4) Rydberg series. In the present study, higher resolution ($\sim 2 \text{ cm}^{-1}$) to discern the detailed spectral features and better fitting to the Rydberg formula should give more definitive conclusion. For example, taking a closer look at Fig. 2, we have resolved the peaks of $(n-1)f$, *ns* and *np σ* series (e.g., 8f, 9s, and 9p σ), even though they are clustered together. In sharp contrast, the previous low-resolution ($\sim 40 \text{ cm}^{-1}$) one-photon absorption spectra [2,18,19] were unable to observe the *np σ* Rydberg states at all.

3.2. (π , *np σ*) Rydberg series

Vinyl chloride is a planar molecule of C_s symmetry and therefore possessed of one *np π* (out-of-plane) and two *np σ* (in-plane) molecular orbitals. By definition, the molecular plane is designated as *yz*-plane. The *np $_x$* thus corresponds to the *np π* Rydberg orbital, and the *np $_y$* and *np $_z$* correlate with the *np σ* orbitals. In this study, we have observed two (π , *np*) series, and attributed them to (π , *np σ*) and (π , *np π*). The (π , *np σ*) series, converging to $80729 \pm 3 \text{ cm}^{-1}$ with $\delta = 0.89$ ($n = 6-13, 16, 18$), is observed for the first time (Table 1). The (π , *np π*) series will be discussed in Section 3.3.

The quantum defect (0.89) for the *np σ* series of vinyl chloride is slightly larger than those for the $3p_y$ (0.76) and $3p_z$ (0.72) Rydberg states of ethylene (C_2H_4) [26]. The *np $_y$* and *np $_z$* ($n > 3$) Rydberg states of ethylene and other chloroethylenes have unfortunately not been reported to date for comparison. Comparing with ethylene, the presence of the Cl atom in C_2H_3Cl is responsible for the larger δ value in the *np σ* Rydberg series. The Cl atom, a third-row element, is expected to cause larger quantum defect than the C (second-row) and H (first-row) atoms. It

is difficult, however, to distinguish the contribution of (π , *np $_y$*) from that of (π , *np $_z$*) at the present study. Consequently, this series is denoted as (π , *np σ*).

3.3. (π , *np π*) Rydberg series

The series converging to $80714 \pm 3 \text{ cm}^{-1}$ with $\delta = 0.48$ ($n = 6-19$) is due to the $\pi \rightarrow np\pi$ (*np $_x$*) transition (Table 1; e.g., 10, 11, and 12p π in Fig. 2). The observed quantum defect is close to a typical value ($\delta \sim 0.5$) for the *np* Rydberg states of hydrocarbons [25]. This series corresponds to the R_3 series reported by Sood and Watanabe [19] ($IE = 80735 \pm 31 \text{ cm}^{-1}$, $\delta = 0.61$, $n = 3-8$) and the *np* series of Locht et al. [2] ($IE = 80754 \pm 10 \text{ cm}^{-1}$, $\delta = 0.59$, $n = 4-14, 24$). Identifying this series as due to (π , *np π*), rather than (π , *np σ*), is based on a polarization-ratio measurement.

According to the two-photon theory for a C_s molecule, $\Omega = 3/2$ for the transitions from the A' ground state to A'' excited electronic states and $\Omega < 3/2$ for those to the A' states. Within a C_s group, the (π , *np π*) Rydberg states of C_2H_3Cl are of A' symmetry and the (π , *np σ*) states are A'' . Our polarization-ratio experiment on this series clearly indicates A' symmetry ($\Omega < 0.8$) for the upper states. The A' symmetry of (π , *np π*) is also consistent with that of $3p_x$ and $4p_x$ Rydberg states reported by Williams and Cool [1]. Accordingly, this series can be unambiguously assigned as the (π , *np π*) Rydberg states. It is worthwhile to note that the quantum defect (0.89) of the in-plane Rydberg orbitals (*np σ*) is more pronounced than that (0.48) of the out-of-plane (*np π*) orbital, because of the effective contribution of the Cl atom to the *np σ* orbitals in vinyl chloride.

3.4. (π , *nf*) Rydberg series

The series converging to $80716 \pm 2 \text{ cm}^{-1}$ with $\delta = 0.02$ ($n = 5-16$), obtained in this study, is (π , *nf*) Rydberg series, and is the same R_1 series as Walsh [18] ($IE = 80648 \pm 6$, $\delta = 0.04$, $n = 4-11$) and Sood and Watanabe [19] ($IE = 80656 \pm 16 \text{ cm}^{-1}$, $\delta = 0.04$, $n = 4-9$) reported. The *ns* Rydberg series assigned by Locht et al. [2] should be the *nf* series ($IE = 80754 \pm 10 \text{ cm}^{-1}$, $\delta = 0.09$, $n = 4-9$) as

mentioned earlier. This series is assigned as (π , nf), rather than (π , nd), based on the following examinations. First, no 3d signals with $\delta \sim 0.02$ were observed in the REMPI spectra obtained by us and by Williams and Cool [1]. Second, the observed series starts with $n = 4$ (a weak transition at $\sim 73\,700\text{ cm}^{-1}$, not listed in Table 1), and the very small δ value is also favorable to the (π , nf) assignment. Furthermore, the $n = 3$ Rydberg members observed by Walsh [18] ($67\,979\text{ cm}^{-1}$), Sood and Watanabe [19] ($68\,000\text{ cm}^{-1}$), and Loch et al. [2] (8.498 eV , $68\,543\text{ cm}^{-1}$) are probably due to the $n_{\text{Cl}} \rightarrow 3s$ transition reported by Williams and Cool [1] ($67\,904$ and $68\,608\text{ cm}^{-1}$). In Fig. 2, sharp spectral features for the (π , nf) Rydberg series of vinyl chloride are shown, similar to those observed in ethylene [26] and other chloroethylenes [1,27].

3.5. Adiabatic IE

The four identified Rydberg series fit the Rydberg formula very well with uncertainty of only a few cm^{-1} (Table 1). The four Rydberg series all converge to the same ionization limit, corresponding to the $^2A''$ ground state of $\text{C}_2\text{H}_3\text{Cl}^+$. We have taken the average IE value of the four Rydberg series, $80\,720 \pm 6\text{ cm}^{-1}$ ($10.0080 \pm 0.0007\text{ eV}$), as the adiabatic IE of vinyl chloride (Table 1). Our adiabatic IE is in excellent agreement with previous values obtained from different methods, such as VUV absorption [2] ($10.013 \pm 0.005\text{ eV}$), photoelectron [3] ($10.00 \pm 0.1\text{ eV}$), and photoionization spectroscopy [4] ($9.98 \pm 0.02\text{ eV}$).

4. Conclusion

We have observed and assigned four Rydberg series of vinyl chloride at 9.3–10 eV using 2 + 1 REMPI spectroscopy. Identification for the new (π , $np\sigma$) Rydberg series and reassignment for the others, (π , ns), (π , $np\pi$), and (π , nf), have been made. The adiabatic ionization energy of vinyl chloride is determined to be $80\,720 \pm 6\text{ cm}^{-1}$, in agreement with previously reported values, nevertheless with better accuracy. With the aid of calculated

Franck–Condon factors by ab initio methods, a comprehensive analysis for the vibronic spectrum of vinyl chloride at 6–10 eV is underway, and will be discussed in a later publication.

Acknowledgements

This work is supported by National Science Council of ROC (Grants No. 89-2113-M-001-032) and by China Petroleum. J.L.C. is grateful to Academic Sinica for his postdoctoral fellowship at IAMS.

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