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ARTICLES

Vibrational Structure of Vinyl Chloride Cation Studied by Using One-Photon Zero-Kinetic Energy Photoelectron Spectroscopy

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The vibrational structure of vinyl chloride cation, CH_2CHCl^+ ($\tilde{X}^2A''$), has been studied by vacuum ultraviolet (VUV) zero-kinetic energy (ZEKE) photoelectron spectroscopy. Among nine symmetric vibrational modes, the fundamental frequencies of six modes have been determined. The first overtone of the out-of-plane CH_2 twist vibrational mode has been also measured. In addition to these, the combination and overtone bands of the above vibrational modes about 4500 cm^{-1} above the ground state have been observed in the ZEKE spectrum. The vibrational band intensities of the ZEKE spectrum can be described approximately by the Franck−Condon factors with harmonic approximation. The ZEKE spectrum has been assigned based on the harmonic frequencies and Franck−Condon factors from theoretical calculations. The ionization energy (IE) of CH_2CHCl is determined as 80705.5 ± 2.5 (cm^{-1}) or 10.0062 ± 0.0003 (eV).

I. Introduction

The electronic and vibrational structure of vinyl chloride (CH_2CHCl) has attracted great attention due to its importance in the chemical industry and in the environment. For the cation, although with much less studied in comparison with the neutral, various experimental and theoretical methods have been employed to study its electronic and vibrational structure. For example, the photoelectron spectroscopic (PES) and threshold photoelectron spectroscopic (TPES) methods have been used to measure the vibrational structure of the cation.[1−4] In the TPES spectrum, four fundamental vibrational bands have been identified with uncertainties larger than 20 cm^{-1}, and highly overlapped overtone and combination bands have also been observed.[4] Recently, using the one-photon mass-analyzed threshold ionization (MATI) method, Lee and Kim[5] have measured the vibrational structure for the first excited state of the vinyl chloride cation. The MATI spectrum they obtained has much higher resolution than the PES spectrum. Unfortunately, due to the weak vacuum ultraviolet (VUV) intensities around the ionization energy (IE) of vinyl chloride, they have not obtained the vibrational spectrum for the ground electronic state of vinyl chloride cation.

For CH_2CHCl, the vibrational frequency difference between the modes of the HCC bending (υ_6) and H−CC−H rocking (υ_5) is about 100 cm^{-1}. The reported PES data with a resolution of 70 cm^{-1} in this region would have difficulties to resolve these two fundamentals.[1−4] In fact, as shown below, the previously observed band at 1320 (±70) cm^{-1} in the PES spectrum consists of two fundamentals in our ZEKE spectrum.

In another respect, the IE of CH_2CHCl is important for its thermal chemistry.[6] The photoionization efficiency spectroscopy (PI), PES, and TPES methods have been used to determine its IE.[1−9] Recently, the energy levels of the Rydberg series for CH_2CHCl have been measured by two-photon RMEPI and also VUV photon-absorption spectroscopic methods. The IE has been thus determined by extrapolation of the Rydberg series.[10,11] The

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reported IE values from PI, PES, and TPES measurements have uncertainties usually larger than 0.01 eV (80 cm^{-1}),[1−7] and the reported data from extrapolation of the Rydberg series has an uncertainty of 6 cm^{-1}.[10]

In this paper, we will report a zero-kinetic energy (ZEKE) photoelectron spectroscopic study of CH_2CHCl^+ ($\tilde{X}^2A''$) using VUV laser. The vibrational excitations measured in the ZEKE spectrum are about 4500 cm^{-1} above the ground state. The vibrational band intensities are found to be described approximately by the Franck−Condon factors calculated using the harmonic approximation. The vibrationally resolved spectrum is assigned based on the vibrational frequencies from ab initio quantum chemical calculations. Accurate IE for CH_2CHCl has also been determined.

II. Experimental Method

The XUV/VUV photoelectron and photoion spectrometer has been described previously.[12] Briefly, coherent VUV radiation was generated by using the resonance-enhanced four-wave difference mixing ($2\omega_1 - \omega_2$) in a pulsed Kr jet. A Nd:YAG pumped two dye laser system was used in the experiments. One laser beam from the tripling of one dye laser beam was fixed at frequency ω_1 so that the $2\omega_1$ matches the resonance line of Kr, $4p^5(^2P_{1/2})5p[1/2]_0 \leftarrow (4p^6)^1S_0$ (98855.1 cm^{-1}). The wavelength of the other dye laser beam (ω_2) was tuned from 535 to 750 nm.

The apparatus consists of four vacuum chambers: (A) a frequency mixing chamber, which houses the pulsed Kr jet (diameter = 1 mm); (B) a monochromator chamber, which houses a gold-coated toroidal grating; (C) an ionization chamber, which is equipped with time-of-flight tubes for electrons (26 cm); in this chamber, an MCP detector was installed to monitor the VUV intensities; (D) a molecular beam source chamber, which houses a pulse valve (diameter = 0.7 mm) to produce a pulse molecular beam. The beam enters into the ionization chamber through a skimmer (diameter = 1 mm).

The electron signals from the pulsed field ionization and the VUV radiation signals were fed into two identical boxcars (SR 245, Stanford Research Systems) and transferred to a personal computer. The electric pulses used to synchronize the two pulse valves and the Nd:YAG laser were provided by a digital delay generator (DG 535, Stanford Research Systems). The pulse voltages used to ionize the molecules were provided by another DG 535 with high-voltage option, and the ionization electric field ranged from 0.75 to 1.5 V/cm with a typical delay of 3 μs relative to the VUV laser pulse. The effects of the applied electric field in decreasing the threshold of ionization energies have been corrected for all reported spectra in the following discussions. The sample was a premixture of CH_2CHCl with Ar (5%/95%), and the stagnation pressure was about 1000 torr. In the experiments, the pressures for the molecular beam source chamber and ionization chamber were around 2×10^{-3} and 2×10^{-5} Pa, respectively. To avoid sampling of dimers and clusters, we find that it is necessary to time the VUV laser to hit the early part of the molecular beam pulse. The frequencies of the dye lasers were calibrated by He/Ne and He/Ar optgalvanic lamps.

III. Results and Discussion

III.a. ZEKE Spectrum and the Vibrational Band Assignments. The valence electronic configuration of the vinyl chloride ground state is[4] $(1a')^2(2a')^2(3a')^2(4a')^2(5a')^2(6a')^2(1a'')^2(7a')^2(2a'')^2$, $\tilde{X}^1A'$. The cation is formed by removing one electron from the outmost (2a″) orbital, which is related to the conjugative π orbital of C═C−Cl. It is therefore expected that the parameter of the geometrical structure related to this delocalized π bond will be changed upon ionization. The calculated geometrical structures of vinyl chloride and its cation have been reported.[10,13] Figure 1 shows the calculated results at the level of RMP2/6-311++g(3df,3dp) using the MOLPRO software package.[14] It is seen that the ionization does not greatly change the geometrical structure, and the 0° transition band in the ZEKE spectrum is expected to be the strongest one. The main changes upon ionization are the bond lengths of C═C (1.327 → 1.401 Å) and C−Cl (1.723 → 1.623 Å), the bond angles of Cl−C═C (122.9° → 121.3°), and also two of the H−C═C angles (123.6° → 121.7°, 122.0° → 120.8°). For the three C−H bonds, the lengths of two bonds which connect the same carbon atom change little (+0.003 Å) and the length of the other C−H bond that connects the same carbon atom with the chlorine atom increases also very little (+0.006 Å). In the PES and ZEKE spectrum, it is known that the excitation of a vibrational mode means the changes of the molecular structure related to the corresponding vibrational mode in the ionization. Therefore, we may expect to observe the vibrational excitations of the C−Cl stretching, C═C stretching, and also bending vibrations related to the angles of H−C═C and Cl−C═C. In another respect, the C−H stretching vibrational excitations should be weak.

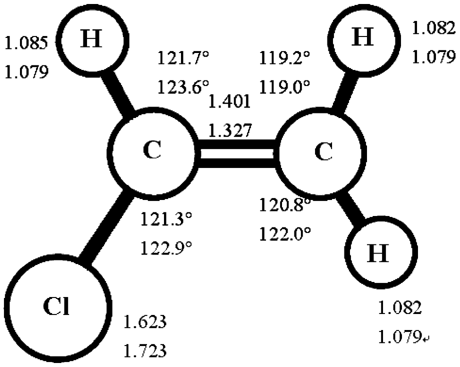

Figure 1. Calculated equilibrium geometrical structures of $CH_2CHCl(X^1A')$ and CH_2CHCl^+ ($\tilde{X}^2A''$) at the level of RMP2/6-311g++(3df,3pd). The bond lengths (in Å) and angles (in deg) are indicated. The numbers in the lower and upper rows are for neutral and cation, respectively.

Figure 2 shows the one-photon ZEKE spectrum of CH_2CHCl. The variations of VUV intensities with the photon energies are also shown in Figure 2. The structures of the VUV intensities are due to efficiencies of four-wave mixing. Except the 0° transition band, the spectrum has been normalized to the VUV intensities pulse by pulse. It is seen that the VUV intensities between the first and the second vibrational bands are very weak; we have not measured these two vibrational bands within the same laser scan, and hence reliable relative intensity of the 0° transition band to other vibrational bands has not been determined in our experiments. The relative intensity of the 0° transition band shown in Figure 2 (also in Figure 3) is scaled according to that reported from the PES spectrum.[3]

The assignments of vibrational bands are also depicted in Figure 2. For the assignment of ZEKE spectrum with strong vibrational excitations, theoretical band intensities and harmonic frequencies should be very helpful. If there is no coupling between the electronic and vibrational motion and also the interaction between the rotational and vibrational (Coriolis force) motion is weak for the cation, the vibrational intensities in the ZEKE spectrum should be approximately described by the Franck−Condon (FC) factors.[12,15−17] For vinyl chloride cation, the first excited state is about 1.6 eV above the ground electronic

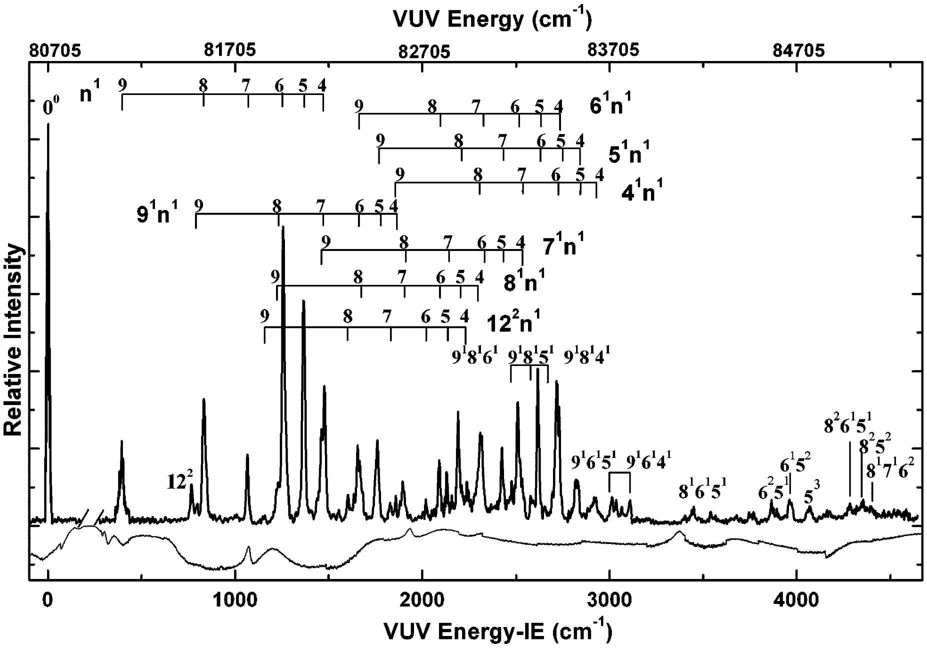

Figure 2. ZEKE spectrum of CH_2CHCl. The vibrational band assignments are shown in the figure, and the band positions are listed in Table 2. The intensities of VUV light from four-wave mixing are also shown in the figure. The higher VUV intensities have more negative values. The relative intensities of the ZEKE spectrum have been normalized to the VUV intensities pulse by pulse except the 0° transition band, which is scaled according to that reported in the PES spectrum (ref 3).

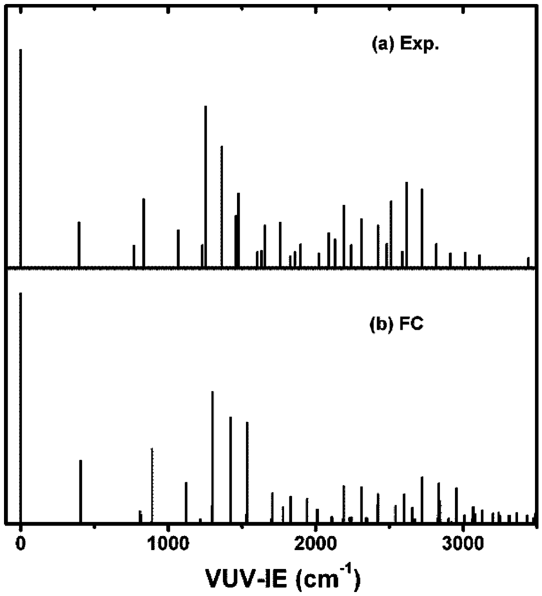

Figure 3. (a) Vibrational band intensities from the ZEKE spectrum. (b) The Franck−Condon (FC) factors calculated by assuming the harmonic approximation. The equilibrium geometrical structures, harmonic frequencies, and normal vibrational modes are calculated at the level of UMP2/6-311++g(3df) by Gaussian 2003.

state.[1−5] It is therefore expected that the FC factors should be good in describing the vibrational intensities of the ZEKE spectrum of CH_2CHCl for low-quantum vibrational excitations.

Panels a and b of Figure 3 show the vibrational band intensities from the ZEKE spectrum and FC factors, respectively. The FC factors were calculated by using MolFC program.[18] This program considers the difference in the equilibrium geometrical structures between the cation and neutral (Duschinsky effect); however, it assumes harmonic approximations for all vibrational excitations. The input parameters include the equilibrium geometrical structures, harmonic frequencies, and normal vibrational modes for neutral and cation. These parameters we used were from ab initio calculations at the level of UMP2/6-311++g(3df) by Gaussian 2003.[19] From Figure 3, it is seen that the FC factors agree well with the intensities of the most vibrational bands in the ZEKE spectrum.

TABLE 1: Fundamental Vibrational Frequencies from PES and ZEKE Experiments and Harmonic Vibrational Frequencies from ab Initio Calculations

symmetry	mode (υ_n)	approximated vibration[a]	calculation (cm^{-1})[b]	PES (cm^{-1})[c]	ZEKE (cm^{-1})[d]
a′	1	CH_2 a-stretch	3313		
a′	2	CH stretch	3210		
a′	3	CH_2 s-stretch	3175		
a′	4	C═C stretch, ip-CH_2 bend	1537		1477(2)
a′	5	ip-H−CC−H rock	1429	1320(70)[e]	1367(2)
a′	6	ip-HCC bend, C═C stretch	1301	1320(70)[e]	1257(2)
a′	7	ip-CH_2 rock, ip-CH rock	1122	1130(60)	1067(2)
a′	8	C−Cl stretch, ip−CH_2 rock	882	820(20)	834(2)
a′	9	ip-C═C−Cl bend	409	430(40)	394(3)
a″	10	CH_2 op-rock	1034		
a″	11	CH op-rock	881		
a″	12	CH_2 op-twist	396		384(2)[f]

[a] Approximated vibrational modes: a denotes asymmetry, s denotes symmetry, ip denotes in-plane, and op denotes out-of-plane. [b] Calculation results at the level of RMP2/6-311g++(3df,3dp) using MOLPRO package (ref 14). If the calculated harmonic frequencies are scaled down using a factor of 0.96, the scaled harmonic frequencies can be in agreement with the experimental data with relative accuracies of ∼1%. [c] From ref 4. [d] From this work. [e] The band was originally assigned as υ_4. The digits in the parentheses represent the uncertainties in the last digits quoted. [f] The fundamental was not observed, and this value is the half of the overtone frequency observed.

On the basis of the FC factors and harmonic frequencies from the ab initio calculations, the fundamental vibrational frequencies in the ZEKE spectrum are easily identified. The observed fundamentals and the calculated harmonic vibrational frequencies are listed in Table 1. We observed six planar symmetric vibrational modes of $CH_2CHCl(\tilde{X}^2A'')$, which include vibrations of C═C stretching and in-plane (ip) CH_2 bending (υ_4), ip-H−CC−H rocking (υ_5), ip-H−C═C bending and C═C stretching (υ_6), ip-CH_2 rocking and ip-CH rock (υ_7), C−Cl stretching and ip-CH_2 rocking (υ_8), and ip- C═C−Cl bending (υ_9). The

TABLE 2: Observed Vibrational Band Positions in the ZEKE Spectrum and Their Assignments

band position[a]	assignment[b]	band position[a]	assignment[b]
394(3)	9^1	2242(4)	$4^1 12^2$
768(2)	12^2	2312(4)	$4^1 8^1$
834(2)	8^1	2323(3)	$6^1 7^1$
1067(2)	7^1	2425(2)	$5^1 7^1$
1155(4)	$9^1 12^2$	2477(3)	$9^1 8^1 6^1$
1228(4)	$8^1 9^1$	2511(3)	6^2
1257(2)	6^1	2545(2)	$4^1 7^1$
1367(2)	5^1	2588(4)	$9^1 8^1 5^1$
1462(2)	$7^1 9^1$	2618(3)	$5^1 6^1$
1477(2)	4^1	2722(4)	$4^1 6^1$, 5^2
1603(3)	$8^1 12^2$	2826(4)	$4^1 5^1$
1634(2)	$8^1 9^2$	2916(4)	4^2
1660(5)	$6^1 9^1$, 8^2	3015(4)	$9^1 6^1 5^1$
1759(3)	$5^1 9^1$	3108(4)	$5^2 9^1$, $9^1 6^1 4^1$
1829(4)	$7^1 12^2$	3445(4)	$8^1 6^1 5^1$
1858(2)	$4^1 9^1$	3865(4)	$6^2 5^1$, $8^3 5^1$
1898(4)	$7^1 8^1$	3965(4)	$6^1 5^2$
2022(3)	$6^1 12^2$	4066(4)	5^3
2090(3)	$6^1 8^1$	4283(4)	$8^2 6^1 5^1$
2131(2)	$5^1 12^{12}$, 7^2	4351(4)	$8^2 5^2$
2192(2)	$5^1 8^1$	4395(4)	$8^1 7^1 6^2$

[a] Units are in cm^{-1}. The position is relative to the IE (80705.5 ± 2.5 cm^{-1}) determined in this work. The digits in the parentheses represent the uncertainties in the last digits quoted. [b] Approximated vibrational modes are listed in Table 1.

other three unobserved symmetric modes are C−H stretching vibrations (υ_1, υ_2, and υ_3). The overtone of the CH$_2$ out-of-plane twist vibration (υ_{12}) appears also in the ZEKE spectrum, and it is predicted by the calculated FC factor. From Table 1, it is seen that the harmonic frequencies from the ab initio calculations at the level of RMP2/6-311g++(3df,3dp) are about 4% larger than the measured fundamental frequencies. If the calculated harmonic frequencies are scaled down using a factor of 0.96, then the scaled harmonic frequencies can be in agreement with the experimental data with relative accuracies of ∼1%.

In addition to the fundamentals, the combination and overtone vibrational bands have been also observed, i.e., 4^1n^1, 5^1n^1, 6^1n^1, 7^1n^1, 8^1n^1, 9^1n^1, and 12^2n^1, where n represents observed fundamental vibrational modes ($n = 4, 5, 6, 7, 8$, and 9). Several other combination bands which involve three fundamentals have also been observed and assigned. These excited bands are assigned with the guidance of the FC factors and also the fundamentals which have been identified at the first step of analysis. Table 2 lists all the vibrational bands observed in the ZEKE spectrum and the associated assignments.

It is noted that in the PES spectrum the band at 1320 (±70 cm^{-1}) was assigned from the υ_4 vibrational band (C=C stretching and ip-CH$_2$ bending vibration).[4a] Due to the much higher resolution of the ZEKE spectrum relative to the PES spectrum, it is found that this band assigned as one band previously, in fact, consists of two vibrational bands υ_5 (ip-H−CC−H rocking) and υ_6 (ip-H−C=C bending and C=C stretching) at 1367 ± 2 and 1257 ± 2 cm^{-1}, respectively. The υ_4 band is at 1477 ± 2 cm^{-1} in our ZEKE spectrum.

The vibrational structures of polyatomic molecules are important to understand the potential energy surface in the molecule. Vinyl chloride is a typical organic molecule, and the ground electronic state of the cation has no appreciable coupling with the first excited electronic state. Accurate calculations about the vibrational structure of the cation may be possible. The vibrational energy levels reported in this paper for vinyl chloride cation may provide a good test example for future accurate theoretical calculations.

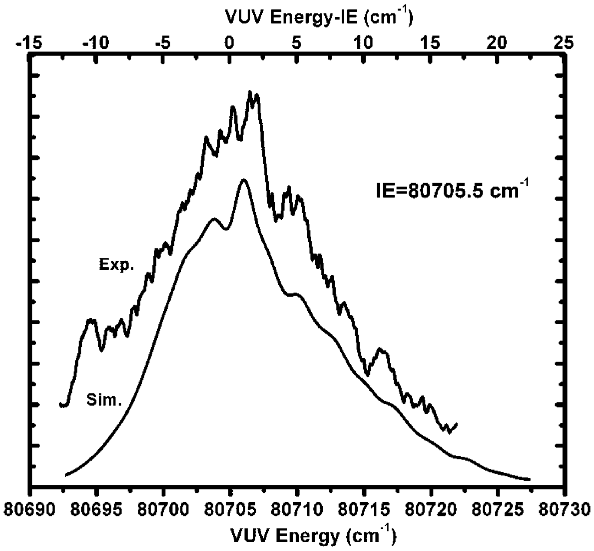

Figure 4. Upper curve is the 0° transition band of the ZEKE spectrum of CH$_2$CHCl. The pulsed electric field used to ionize Rydberg molecules was ∼0.75 V/cm. The lower curve is the semiempirical fitting aiming to obtain the IE.

TABLE 3: Ionization Energy (IE) for CH$_2$CHCl

IE (eV)[a]	method	ref
9.99(2)	PI[b]	8
9.98(2)	PI[b]	9
10.01	PE[c]	1
10.013(5)	RS[d]	4b
10.0080(7)	RS[d]	10
9.980	ab initio[e]	14
9.957	ab initio[e]	14
10.0062(3)	ZEKE[f]	this work

[a] Units are in eV. The digits in the parentheses represent uncertainties in the last significant digits quoted. [b] Photoionization efficiency curve. [c] Photoelectron spectroscopy. [d] Extrapolation from the Rydberg series. [e] Calculation results using MOLPRO software package at the level of RMP2/vtz (upper row) and RMP2/6-311++g(3df,3dp) (lower row), respectively. Zero-point vibration energies have been taken into account. [f] Zero-kinetic energy photoelectron spectroscopy.

III.b. Ionization Energy. The resolution of our ZEKE spectrum is around 1 cm^{-1}.[15] With this resolution, a rotationally resolved spectrum could not be obtained for vinyl chloride cation due to its small rotational constants. The upper curve in Figure 4 shows the 0° transition band of the ZEKE spectrum for vinyl chloride. Due to the weak VUV light intensity in this photon energy region, the curve shown was an accumulation of 125 min (20 Hz laser), and the pulsed field used to ionize the Rydberg molecules was ∼0.75 V/cm. It is seen that the vibrational band has a width around ∼15 cm^{-1}. To determine the band origin or the IE as accurately as possible, we have done a semiempirical fitting of the band profile using a method described previously.[12,20] The lower curve of Figure 4 is from the fitting. The rotational constants used from the ab initio calculations (UMP2/6-311++g) are $A = 1.851$, $B = 0.186$, $C = 0.169$ cm^{-1}, for neutral and $A^+ = 1.790$, $B^+ = 0.199$, $C^+ = 0.178$ cm^{-1} for the cation. The rotational temperature is assumed to be 10 K. The IE thus determined is 80705.5 ± 2.5 (cm^{-1}) or 10.0062 ± 0.0003 (eV). The uncertainties are mainly from the Stark shift and the calibration of the dye laser. Table 3 lists our measured IE and ab initio calculation results along with some of the reported measurements by PE, TPES, and PIE methods. A more complete list of previously measured IEs can be found in ref 21. Although our results are in agreement with most of the previous measurements,[21] our data has higher accuracy.

IV. Summary

The one-photon ZEKE spectrum of CH_2CHCl has been measured for vibrational energies about 4500 cm^{-1} above the vibrational ground state of the cation. Among 12 vibrational modes, the fundamentals for 6 modes have been determined. The overtone for out-of-plane CH_2 twist vibration is also observed. The vibrational band intensities of the ZEKE spectrum can be described approximately by the FC factors with harmonic approximation. The ZEKE spectrum has been assigned based on the FC and ab initio quantum chemical calculations. The IE of CH_2CHCl is determined to be 80705.5 ± 2.5 (cm^{-1}).

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