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Citation: The Journal of Chemical Physics **140**, 181101 (2014); doi: 10.1063/1.4876017
View online: http://dx.doi.org/10.1063/1.4876017
View Table of Contents: http://scitation.aip.org/content/aip/journal/jcp/140/18?ver=pdfcov
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Communication: State-to-state photoionization and photoelectron study of vanadium methylidyne radical (VCH)

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(Received 6 April 2014; accepted 30 April 2014; published online 12 May 2014)

By employing the infrared (IR)-ultraviolet (UV) laser excitation scheme, we have obtained rotationally selected and resolved pulsed field ionization-photoelectron (PFI-PE) spectra for vanadium methylidyne cation (VCH^+). This study supports that the ground state electronic configuration for VCH^+ is $\ldots 7\sigma^2 8\sigma^2 3\pi^4 9\sigma^1$ ($\tilde{X}^2\Sigma^+$), and is different from that of $\ldots 7\sigma^2 8\sigma^2 3\pi^4 1\delta^1$ ($\tilde{X}^2\Delta$) for the isoelectronic TiO^+ and VN^+ ions. This observation suggests that the addition of an H atom to vanadium carbide (VC) to form VCH has the effect of stabilizing the 9σ orbital relative to the 1δ orbital. The analysis of the state-to-state IR-UV-PFI-PE spectra has provided precise values for the ionization energy of VCH, IE(VCH) = 54 641.9 ± 0.8 cm^{-1} (6.7747 ± 0.0001 eV), the rotational constant $B^+ = 0.462 \pm 0.002$ cm^{-1}, and the v_2^+ bending (626 ± 1 cm^{-1}) and v_3^+ V–CH stretching (852 ± 1 cm^{-1}) vibrational frequencies for $VCH^+(\tilde{X}^2\Sigma^+)$. The IE(VCH) determined here, along with the known IE(V) and IE(VC), allows a direct measure of the change in dissociation energy for the V–CH as well as the VC–H bond upon removal of the 1δ electron of $VCH(\tilde{X}^3\Delta_1)$. The formation of $VCH^+(\tilde{X}^2\Sigma^+)$ from $VCH(\tilde{X}^3\Delta_1)$ by photoionization is shown to strengthen the VC–H bond by 0.3559 eV, while the strength of the V–CH bond remains nearly unchanged. This measured change of bond dissociation energies reveals that the highest occupied 1δ orbital is nonbonding for the V–CH bond; but has anti-bonding or destabilizing character for the VC–H bond of $VCH(\tilde{X}^3\Delta_1)$.
 [http://dx.doi.org/10.1063/1.4876017]

Accurate structural and energetic measurements of transition metal carbides (MC) and methylidynes (MCH) and their cations (MC^+ and MCH^+) are essential for fundamental understanding of catalytic processes, such as the chemical activation of C–H and C–C bonds in hydrocarbon reactions, involving transition metal species as the catalyst.[1] Previous rotationally resolved spectroscopic studies have provided precise spectroscopic constants and thus structural parameters for many neutral MC and MCH species.[2–8] However, similar rotationally resolved spectroscopic studies on MC^+ and MCH^+ ions are lacking. We have recently succeeded in performing high-resolution pulsed field ionization-photoelectron (PFI-PE)[9,10] studies for diatomic MX^+ (X = C, O, and N) species based on two-color visible-ultraviolet (VIS-UV) excitation scheme, which has allowed fully rotationally selected and resolved spectroscopic measurement for MX^+ cations.[11–16] These studies have not only provided reliable rovibrational constants, but also accurate ionization energies (IEs) of MXs. To our knowledge, a fully rotationally resolved PFI-PE measurement for triatomic transition metal-containing cations has not been reported previously. This communication presents such a high-resolution photoelectron study for vanadium methylidyne cation (VCH^+) using the infrared (IR)-UV-PFI-PE method.

The previous high-resolution spectroscopic study[3,4] has established that the VCH ground state is linear with the electronic configuration of $\ldots 7\sigma^2 8\sigma^2 3\pi^4 9\sigma^1 1\delta^1$ ($\tilde{X}^3\Delta_1$). Highly precise values for the rotational constant B'' (0.49369 cm^{-1}) and the v_2 bending (564 cm^{-1}) and v_3 V–CH stretching (838 cm^{-1}) vibrational frequencies of $VCH(\tilde{X}^3\Delta_1)$ have also been determined.[3] The highly precise IE(VCH) determined here, together with the known IE(V)[17] and IE(VC),[16] is most valuable for benchmarking theoretical energetic predictions[10,18] for the VCH/VCH^+ system because the 0 K bond dissociation energies (D_0's) for the V^+–CH and V–CH bonds are related to the IE(V) and IE(VCH) by the relation, $D_0(V^+–CH) - D_0(V–CH) = IE(V) - IE(VCH)$ based on conservation of energy.[18] Similarly, the D_0 values for the VC^+–H and VC–H bonds are related to the IE(VC) and IE(VCH) as $D_0(VC^+–H) - D_0(VC–H) = IE(VC) - IE(VCH)$. We note that a value of 4.94 ± 0.09 eV for $D_0(V^+–CH)$ was obtained in a previous collision-induced ion dissociation study.[19]

The experimental apparatus and procedures used are similar to those reported previously.[12–15] Cold VCH molecules in the form of a pulsed supersonic beam (30 Hz) were prepared by using a laser ablation beam source.[20] The VCH molecules were produced in the ablation source by reactions between laser ablated V species and CH_4. The VCH supersonic beam passes through a conical skimmer before intersecting the laser beams at the photoionization/photoexcitation (PI/PEX) center for photoionization efficiency (PIE) and PFI-PE measurements. Two tunable dye lasers pumped by the same Nd:YAG laser (30 Hz) were used. One dye laser provided the IR ω_1 output and the other gave the UV ω_2 output as required by the experiment. A dc electric field was used to extract photoions from the PI/PEX region for PIE measurements. The PFI-PE

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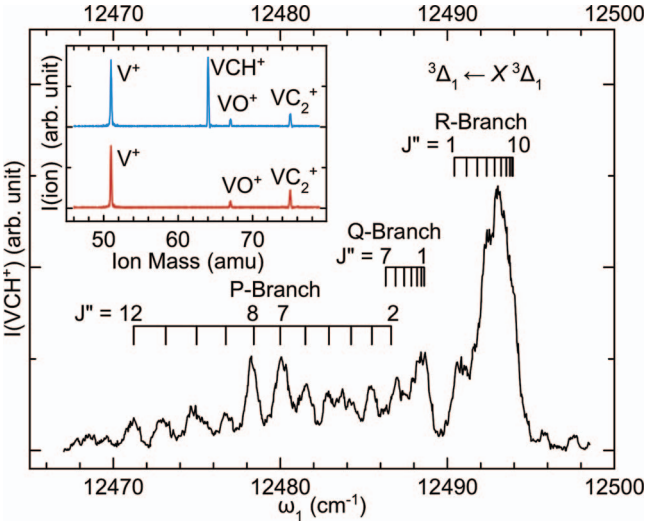

FIG. 1. The VCH*($^3\Delta_1$) ← ($\tilde{X}^3\Delta_1$; 000) excitation band recorded by setting $\omega_2 = 43\,022.76$ cm^{-1} and scanning ω_1 in the range of 12 467–12 499 cm^{-1}. Rotational transitions of the P, Q, R-branch identified by simulation are marked on top of the spectrum. The inset compares the TOF mass spectrum (upper curve) for the molecular beam observed by setting $\omega_1 = 12\,493$ and $\omega_2 = 42\,274$ cm^{-1} with that (lower curve) recorded under the same experimental conditions except with the ω_1 beam off. The comparison shows that VCH^+ ions are only formed by IR-UV photoionization.

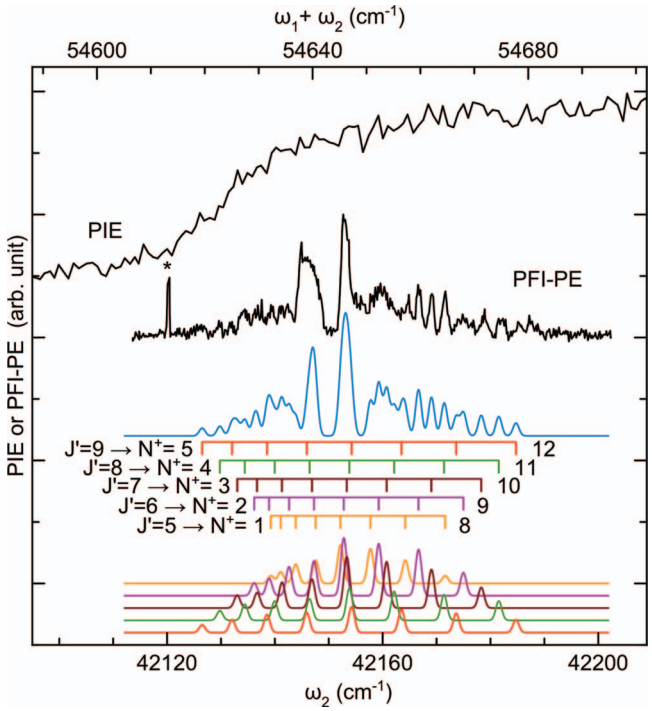

FIG. 2. Comparison of the IR-UV-PIE spectrum (top curve) and the IR-UV-PFI-PE spectrum (2nd curve from the top) for the $VCH^+(\tilde{X}^2\Sigma^+; 000)$ origin band recorded by setting $\omega_1 = 12\,493$ cm^{-1} and scanning the ω_2 in the range of 42 095–42 209 cm^{-1}. The best simulated spectrum (blue curve) for the IR-UV-PFI-PE origin band represents the sum of the simulated J' (= 5, 6, 7, 8, and 9) → N^+ state-to-state spectra (bottom curves) shown as the orange, purple, brown, green, and red spectra, respectively.

measurements were made by employing a pulsed PFI-PE detection scheme as described in detail previously.[12–15]

The well-characterized VCH*($^3\Delta_1$) band[3] at 800.5 nm is selected to prepare the intermediate state for IR-UV-PIE and IR-UV-PFI-PE studies. By fixing UV $\omega_2 = 43\,022.76$ cm^{-1} and scanning IR ω_1 in the range of 12 467–12 499 cm^{-1}, the detection of VCH^+ ions thus produced yields the excitation spectrum for the VCH*($^3\Delta_1$) band as shown in Fig. 1. Although the resolution of this spectrum was significantly lower than that achieved in the previous higher resolution study[3] of Barnes *et al.*, we are still able to identify several well-resolved rotational transitions. The assigned rotational transitions for the P, Q, and R branches as marked on top of the excitation spectrum were based on spectral simulation using the spectroscopic constants reported[3] previously. The relatively strong P(7) and P(8) rotational transitions were used for the respective single $J' = 6$ and $J' = 7$ selected IR-UV-PFI-PE measurements. The most intense peak of the excitation spectrum is the R-branch band head at 12 493 cm^{-1}. Selecting this peak by IR ω_1 gives the highest PIE and PFI-PE signals for IR-UV measurements. However, due to spectral congestion, the simulation shows that IR excitation at the R-branch band head would result in simultaneous excitations of the $J' = 5$, 6, 7, 8, and 9 levels of VCH*($^3\Delta_1$).

The inset of Fig. 1 compares the TOF mass spectrum (upper spectrum) of the molecular beam recorded by setting $\omega_1 = 12\,493$ cm^{-1} and $\omega_2 = 42\,274$ cm^{-1} and that (lower spectrum) obtained under the same experimental conditions except that the ω_1 beam was blocked. The VCH^+ peak is found to be discernible only as both ω_1 and ω_2 beams are turned on, confirming that VCH^+ ions are produced solely by IR-UV photoionization of VCH. The fact that the V^+, VO^+, and VC_2^+ ion intensities are nearly identical with or without the ω_1 beam indicates that these ions are produced by two-photon and/or multiphoton UV photoionization of impurity species in the molecular beam.

By parking ω_1 at 12 493 cm^{-1} and scanning ω_2 in the energy range of 42 095–42 209 cm^{-1}, which corresponds to the total energy ($\omega_1 + \omega_2$) range of 54 588–54 702 cm^{-1}, we obtained the IR-UV-PIE spectrum for VCH^+ shown as the top spectrum of Fig. 2. The PIE spectrum exhibits a step-like structure at the total energy range of 54 610–54 640 cm^{-1}. After taking into account the Stark shift induced by the dc electric field used for ion extraction, we obtained the IE(VCH) = 54 640 ± 14 cm^{-1}.

The location of the PIE step allows the PFI-PE measurement for the $VCH^+(\tilde{X}; v_1^+v_2^+v_3^+ = 000)$ origin band to be focused in a narrower energy range. Figures 3(a) and 3(b) depict the $J' = 6$ and $J' = 7$ selected IR-UV-PFI-PE spectra (black curves) for the origin band obtained by setting ω_1 to excite the P(7) and P(8) transitions at 12 480.05 cm^{-1} and 12 478.26 cm^{-1}, respectively, while scanning ω_2 in the range of 42 121–42 183 cm^{-1}. The sharp structures marked by asterisks in the figures are attributed to background resonances originated from photoionization of V atoms, which are produced in abundance by the laser ablation source. Excluding these background peaks reveals a series of well-resolved rotational transitions with intensity patterns similar to those observed in previous two-color state-to-state PFI-PE measurements of other molecular systems.[12–15,21,22] The blue spectra of Figs. 3(a) and 3(b) are the best simulated spectra constructed by assuming a Gaussian instrumental profile (FWHM = 1.3 cm^{-1}) for the PFI-PE detection. The

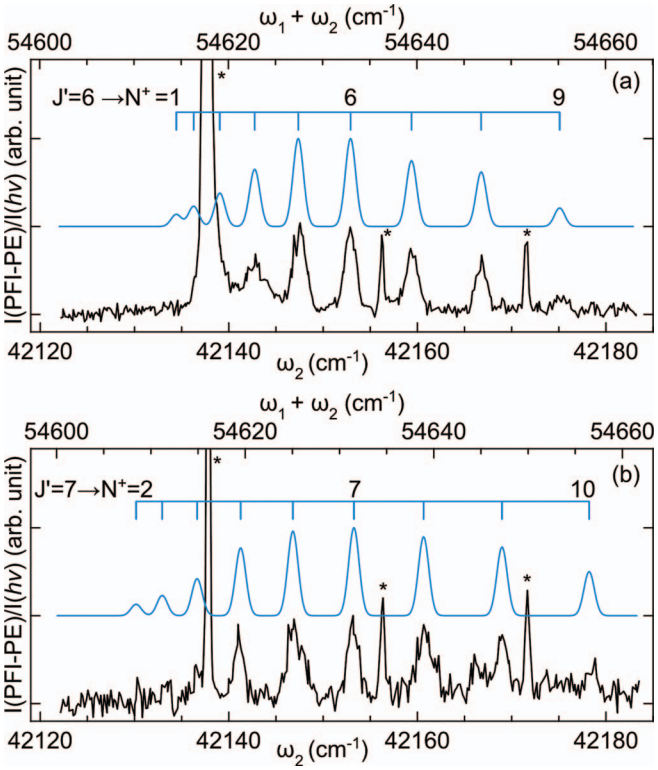

FIG. 3. (a) The $J' = 6$ and (b) $J' = 7$ selected IR-UV-PFI-PE spectra for the $VCH^+(\tilde{X}^2\Sigma^+; 000)$ origin band obtained by setting the $\omega_1 = 12\,480.05$ and $12\,478.26\ cm^{-1}$, respectively. The blue curves are the simulated state-to-state spectra constructed by using a Gaussian instrumental profile (FWHM $= 1.3\ cm^{-1}$) for the PFI-PE detection. The N^+-assignments are marked on top of the simulated spectra.

N^+-assignments marked in Figs. 3(a) and 3(b) are based on the least square fits to the standard equation, $v^+ = {v_{000}}^+ + B^+N^+(N^+{+}1) - B''J''(J''{+}1)$, where v^+ represents the photoionization transition frequency, ${v_{000}}^+$ is the transition frequency for the origin of the origin band, and B'' and B^+ are the respective rotational constants for the $VCH(\tilde{X};000)$ and $VCH^+(\tilde{X};000)$ ground states. Since the rotational constant B'' for $VCH(\tilde{X}^3\Delta_1)$ is known, the least square fits for the IR-UV-PFI-PE spectra provide the values, $B^+ = 0.462 \pm 0.002\ cm^{-1}$ and ${v_{000}}^+ = 54\,642.9 \pm 0.8\ cm^{-1}$ after correcting for the Stark shift[13] induced by the PFI electric field. The latter value gives the adiabatic IE(VCH) $= 54\,641.9 \pm 0.8\ cm^{-1}$ (6.7747 ± 0.0001 eV).

As shown in the rotational assignment of the IR-UV-PFI-PE spectrum of Fig. 3(a), the $J' = 6 \rightarrow N^+ = 4$–9 rotational peaks are clearly discernible. The formation of the $N^+ = 2$ and 3 rotational peaks was obscured by the strong background peak at $\omega_2 = 42\,137.8\ cm^{-1}$. A minute structure appears to coincide with the simulated positions of the $N^+ = 1$ rotational peaks. However, since this structure is close to the noise level, its identification must be considered as tentative. The simulation of the IR-UV-PFI-PE spectra of Fig. 3(b) clearly identifies the $N^+ = 2$–10 rotational peaks. The intensity patterns for the $J' \rightarrow N^+$ transitions observed in Figs. 3(a) and 3(b) are consistent with those found in previous two-color state-to-state photoionization studies,[12–15,21,22] showing that the $|\Delta N^+| = |N^+ - J'|$ changes are ≤5, and the photoionization cross section increases as $|\Delta N^+|$ decreases.

Vanadium methylidyne is isoelectronic with vanadium nitride (VN)[15] and titanium monoxide (TiO);[14] and these species are known to have the same ground state electronic configuration[6,7] of $\ldots 7\sigma^2 8\sigma^2 3\pi^4 1\delta^1 9\sigma^1\ (\tilde{X}^3\Delta_1)$. The recent VIS-UV-PFI-PE studies[14,15] show that photoionization of VN and TiO gives the $VN^+(\tilde{X}^2\Delta_{3/2})$ and $TiO^+(\tilde{X}^2\Delta_{3/2})$ ground states with the electronic configuration of $\ldots 7\sigma^2 8\sigma^2 3\pi^4 1\delta^1$. The determination of the $VN^+(\tilde{X}^2\Delta_{3/2})$ and $TiO^+(\tilde{X}^2\Delta_{3/2})$ ground states is further confirmed by the observation of the excited $VN^+(\tilde{X}^2\Delta_{5/2})$ and $TiO^+(\tilde{X}^2\Delta_{5/2})$ spin-orbit states at 307.3 and 211.3 cm^{-1} above the $VN^+(\tilde{X}^2\Delta_{3/2})$ and $TiO^+(\tilde{X}^2\Delta_{3/2})$ ground states, respectively.[14,15] Since the IR-UV-PFI-PE spectra of Figs. 3(a) and 3(b) cannot identify the lowest N^+ value, the term symmetry of the $VCH^+(\tilde{X})$ ground state cannot be directly determined. However, if the $VCH^+(\tilde{X})$ ion ground state were of $^2\Delta_{3/2}$ symmetry, we should have observed the excited $^2\Delta_{5/2}$ spin-orbit state for VCH^+ at ≈200–300 cm^{-1} above the $VCH^+(\tilde{X})$ ground state. Considering the fact that such an excited spin-orbit state was not found in a careful search, we conclude that the $VCH^+(\tilde{X})$ ground state is of $^2\Sigma^+$ symmetry with the electronic configuration of $\ldots 7\sigma^2 8\sigma^2 3\pi^4 9\sigma^1$. That is, photoionization of $VCH(\tilde{X}^3\Delta_1)$ to form $VCH^+(\tilde{X}^2\Sigma^+)$ involves the removal of the electron residing in the 1δ instead of the 9σ orbital as in the case of TiO and VN.[6,7,14,15] This observation suggests that the addition of an H atom to VC to form $VCH(\tilde{X}^3\Delta_1)$ has the effect of stabilizing the 9σ orbital, such that photoionization of VCH favors the ejection of an electron from the 1δ orbital. Titanium methylidyne (TiCH)[5] is isoelectronic with VCH^+. The fact that the $TiCH(\tilde{X})$ ground state is found to have the $^2\Sigma^+$ symmetry[5] can be taken as strong support for the symmetry assignment of $VCH^+(\tilde{X}^2\Sigma^+)$ in the present study.

Using the known IE(V) = 6.7463 ± 0.0001 eV[17] and the IE(VCH) = 6.7747 ± 0.0001 eV determined in the present study, the difference $D_0(V^+–CH) - D_0(V–CH)$ is determined to be −0.0284 eV. The IE(VC) has recently been determined to be 7.1306 ± 0.0001 eV.[16] By combining this value with the IE(VCH), we find that the $D_0(VC^+–H)$ is stronger than the $D_0(VC–H)$ by 0.3559 ± 0.0001 eV. This observed D_0 change reveals the highest occupied 1δ orbital is nonbonding in nature for the V–CH bond; but has anti-bonding or destabilizing character for the VC–H bond of $VCH(\tilde{X}^3\Delta_1)$.

The PFI-PE signal was too low for single J'-selected IR-UV-PFI-PE measurements of the excited VCH^+ ($\tilde{X}^2\Sigma^+$; ${v_1}^+{v_2}^+{v_3}^+ = 010$ and 001) vibrational bands. These bands are expected to appear at ≈600 and 850 cm^{-1} above the IE(VCH) based on the known v_2 bending and v_3 V–CH stretching vibrational frequencies of $VCH(\tilde{X}^3\Delta_1)$.[3] By parking the IR ω_1 at the R-branch band head of the $VCH^*(^3\Delta_1)$ band, we have obtained the IR-UV-PFI-PE spectra for the excited $VCH^+(\tilde{X}^2\Sigma^+; 010$ and 001) vibrational bands [top spectra of Figs. 4(a) and 4(b)]. We have also measured the IR-UV-PFI-PE spectrum (black spectrum of Fig. 2) for the $VCH^+(\tilde{X}^2\Sigma^+; 000)$ origin band under the same experimental conditions for comparison with the single J'-selected IR-UV-PFI-PE of Figs. 3(a) and 3(b). Such a comparison is useful for validating the simulation scheme employed in this study.

The best simulated spectra for the (000), (010), and (001) IR-UV-PFI-PE bands [shown as the blue spectra in

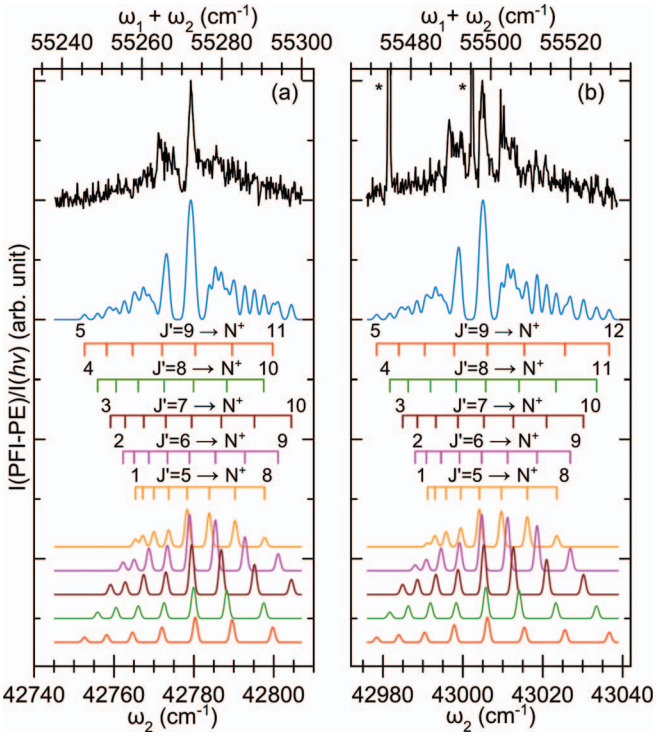

FIG. 4. Comparison of the IR-UV-PFI-PE spectra (top spectra) and the best simulated spectra (blue spectra) for the (a) $VCH^+(\tilde{X}^2\Sigma^+;\ 010)$ and (b) $VCH^+(\tilde{X}^2\Sigma^+;\ 001)$ vibrational bands. The IR-UV-PFI-PE spectra are obtained by setting the $\omega_1 = 12\,493\ cm^{-1}$ and scanning ω_2 in the 42 745–42 807 cm^{-1} for (a) and 42 975–43 038 cm^{-1} for (b). The best simulated spectra represent the sum of the simulated J' (= 5, 6, 7, 8, and 9) → N^+ state-to-state spectra (bottom spectra) shown as the orange, purple, brown, green, and red spectra, respectively.

Figs. 2, 4(a), and 4(b)] are obtained by summing the simulated J' (= 5, 6, 7, 8, and 9) → N^+ spectra (bottom spectra), which are shown as the orange, purple, brown, green, and red spectra, respectively. The simulation[12–15] assumes a Gaussian instrumental profile (FWHM = 1.3 cm^{-1}) for the PFI-PE detection and takes into account the bandwidth of ω_1, the Boltzmann populations of J''-rotational levels based on an estimated rotational temperature of 35 K for the VCH molecular beam, and the overlaps of the rotational transitions with the excitation profile of the ω_1 output. The ΔN^+-dependence of the photoionization cross sections follows the patterns observed in the present and previous single J'-selected PFI-PE measurements.[12–15,21,22] Since the B^+ values for the (010) and (001) vibrationally excited states are not known, the B^+ value for the $VCH^+(\tilde{X}^2\Sigma^+;\ 000)$ ground state is used for simulations of these excited vibrational bands. As shown in the simulated state-to-state spectra of Figs. 2, 4(a), and 4(b), the maximum photoionization cross sections occur at the $|\Delta N^+| = 0$ transitions. The best simulated spectra reproduce the experiment IR-UV-PFI-PE spectra satisfactorily.

The simulation for the IR-VUV-PFI-PE spectrum of Fig. 2 yields the $\nu_{000}{}^+ = 54\,643 \pm 1\ cm^{-1}$, which is in excellent agreement with the $\nu_{000}{}^+ = 54\,642.9 \pm 0.8\ cm^{-1}$ determined by the analysis of the J'-selected and N^+-resolved IR-UV-PFI-PE spectra of Figs. 3(a) and 3(b). The $\nu_{010}{}^+$ and $\nu_{001}{}^+$ values determined by the spectral simulation are 55 269 ± 1 and 55 495 ± 1 cm^{-1}. Since $J'' = 1$ is the lowest rotational state of $VCH(\tilde{X}^3\Delta_1;\ 000)$, the IEs for the formation of $VCH^+(\tilde{X}^2\Sigma^+;\ 010$ and $001)$ from $VCH(\tilde{X}^3\Delta_1;\ 000)$ are determined as 55 268 ± 1 and 55 494 ± 1 cm^{-1}, respectively. These values give the frequencies of 626 ± 1 and 852 ± 1 cm^{-1} for the respective $\nu_2{}^+$ and $\nu_3{}^+$ vibrational modes of $VCH^+(\tilde{X}^2\Sigma^+)$, which are similar to the known vibrational frequencies[5] of 578 and 855 cm^{-1} for the respective ν_2 and ν_3 vibrational modes of TiCH. The similar values observed for the $\nu_3{}^+$ frequency for $VCH^+(\tilde{X}^2\Sigma^+)$ and the ν_3 (= 838 cm^{-1}) frequency for $VCH(\tilde{X}^3\Delta_1)$ are consistent with the finding that $D_0(V^+–CH) \approx D_0(V–CH)$. The $\nu_2{}^+$ frequency of VCH^+ $(\tilde{X}^2\Sigma^+)$ is found to be significantly higher (by 62 cm^{-1}) than the ν_2 (564 cm^{-1}) frequency of VCH $(\tilde{X}^3\Delta_1)$. Since the excited $\nu_1{}^+$ (VC^+-H stretching) vibrational band of $VCH^+(\tilde{X}^2\Sigma^+)$ was expected to be out of the energy range of the present experiment and thus was not measured, a direct comparison between the ν_1 frequency for $VCH(\tilde{X}^3\Delta_1)$ and $\nu_1{}^+$ frequency for the ion cannot be made. On the basis of the higher $D_0(VC^+–H)$ value compared to the $D_0(VC–H)$ value observed here, we expect the $\nu_1{}^+$ stretching frequency for VCH^+ $(\tilde{X}^2\Sigma^+)$ to be higher than the ν_1 frequency for VCH $(\tilde{X}^3\Delta_1)$.

This work was supported by the NSF Grant No. CHE 0910488 and the U.S. Department of Energy (DOE), Basic Energy Sciences Contract No. DE-FG02-02ER15306.

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