ARTICLE

High-resolution Absorption Spectra of Acetylene in 142.8-152.3 nm

Ya-hua Hu, Chen Zhen, Jing-hua Dai, Xiao-guo Zhou*, Shi-lin Liu

Hefei National Laboratory for Physical Sciences at Microscale, Department of Chemical Physics, University of Science and Technology of China, Hefei 230026, China

The absorption spectra of acetylene molecules was measured under jet-cooled conditions in the wavelength range of 142.8-152.3 nm, with a tunable and highly resolved vacuum ultraviolet (VUV) laser generated by two-photon resonant four wave difference frequency mixing processes. Due to the sufficient vibrational and rotational cooling effect of the molecular beam and the higher resolution VUV laser, the observed absorption spectra exhibit more distinct spectral features than the previous works measured at room temperature. The major three vibrational bands are assigned as a C–C symmetry stretching vibrational progress (v_2=0-2) of the $\widetilde{C}^1\Pi_u$ state of acetylene. The observed shoulder peak at 148.2 nm is assigned to the first overtone band of the *trans*-bending mode v_4 of the $\widetilde{C}^1\Pi_u$ state of acetylene. Additionally, the two components, $4_0^2(\mu^1\Pi_u)$ and $4_0^2(\kappa^1\Pi_u)$, are suggested to exhibit in the present absorption spectra, due to their Renner-Teller effect and transition selection rule. All band origins and bandwidths are obtained subsequently, and it is found that bandwidths are broadened and lifetimes decrease gradually with the excitation of vibration.

Key words: Acetylene, Vacuum ultraviolet, Absorption spectrum

I. INTRODUCTION

Acetylene molecules exist abundantly in the carbon stars [1], the planetary atmosphere [2-4], and the dense molecular cloud of the interstellar medium [5]. Acetylene's photodissociation and photoionization processes must greatly affect chemical reactions involving acetylene, and hence it is significant to understand the photochemical behavior of acetylene in these cases. Moreover, acetylene is a very common combustive gas widely used in industry. It plays an important role in combustion progresses. Therefore, many investigations of the photoexcitation, photoabsorption, and photodissociation of acetylene have been carried out, and a lot of photochemical data have been obtained over several decades.

The photoabsorption spectra of acetylene in the vacuum ultraviolet (VUV) wavelength region have been extensively investigated both experimentally [6-23] and theoretically [24-29], which has already been reviewed by Herzberg [30], Robin [31], and Wu *et al.* [19]. The absorption spectra of acetylene in the wavelength region of 105-152 nm were firstly measured by Price [7] with a 2-m grazing-incidence spectrograph. Most of the prominent vibrational bands were assigned as members of two Rydberg series, which were represented closely by

$$nR(^1\Pi_u \leftarrow {}^1\Sigma_g^+):$$
$$v_n = 92076 - \frac{R}{(n-0.50)^2} \quad (n = 3-10) \quad (1)$$

$$nR(^1\Sigma_u \leftarrow {}^1\Sigma_g^+):$$
$$v_n = 91950 - \frac{R}{(n-0.50)^2} \quad (n = 3-10) \quad (2)$$

The ionization potential energy was measured by a later photoionization experiment [32]. Subsequently, Wilkinson [10] and Nakayama *et al.* [12] re-examined the absorption spectra in the wavelength region of 128.0-152.0 nm and observed two non-Rydberg-type bands besides two Rydberg series mentioned above. Gerdanken and Schnepp have assigned the major absorption peaks in the 140-155 nm region as a C–C symmetry stretching (v_2) vibrational progress of the $\widetilde{C}^1\Pi_u$ state and a weak continuous absorption band of $\pi \rightarrow \pi^*$ transition [15]. Several groups have also measured the absorption spectra of acetylene in this region using synchrotron radiation as a light source [17,20,23]. More accurate absorption cross sections were measured, and the photodissociation dynamics were discussed by detecting the fluorescence of photofragments. In addition, Wu *et al.* [19] and Smith [21] performed measurements of the absorption cross sections of acetylene in the wavelength region of 140-150 nm by using a synchrotron radiation with a high spectral resolution of 7 pm at 295, 195, and 150 K, respectively, in order to study the contribution of the hot bands. No rotational structures, however, were distinguished.

As mentioned above, previous absorption spectra of acetylene in the VUV wavelength region were mostly obtained at room temperature. Although Wu [19] and Smith [21] have roughly investigated the influence from hot bands, those hot bands could not be eliminated entirely at 150 K. The contribution of the higher J rotational excitation in every vibrational band also probably exists in previous works, and thus the overlap of the various vibrational bands probably has a serious effect

_____

*Author to whom correspondence should be addressed. E-mail: xzhou@ustc.edu.cn

and makes distinct rotational structures blurry. In the present work, we combine the jet-cooled technique and a highly resolved tunable VUV laser source to make the absorption spectra simpler and deeply investigate the absorption spectra of acetylene in the wavelength region of 142.8-152.3 nm. A more reasonable spectral assignment is expected for the absorption spectra of acetylene, and the corresponding peak positions and bandwidths are determined subsequently.

II. EXPERIMENTS

The experimental setup includes a source of pulsed VUV laser generation, a pulsed supersonic molecular beam, and two VUV intensity monitors. The time delay between the VUV laser and the supersonic jet is controlled by a pulse generator (DG535, Stanford Research Systems). More details have been described elsewhere [33,34]. Only a brief description is given here.

The third harmonic output from a pulsed Nd:YAG laser (Spectra-Physics, Lab-190-10, pulse width 10 ns) is split into two beams to pump simultaneously two dye lasers (Sirah, PRLC-LG-18 and PRLC-LG-24). The VUV laser in the 142.8-152.3 nm region is generated by two-photon resonance four-wave difference frequency mixing technique in a xenon cell ($\omega_{VUV}=2\omega_1-\omega_2$), where ω_1 corresponds to the frequency of two-photon excitation of xenon atom, $(5p)^5(^2P_{1/2})6P[3/2]_2 \leftarrow (5p)^6(^1S_0)$, at $2\omega_1 = 89162.88$ cm^{-1}. Tunability of the VUV laser is achieved by scanning the wavelength of the other dye laser ω_2. The generated VUV laser from the Xe cell is separated from the two fundamentals by a LiF prism in a vacuum chamber, and only collinear VUV laser is let into the main chamber and crosses with the jet-cooled C$_2$H$_2$ (stagnation pressure 60.6-80.8 kPa.) molecular beam at 5 mm downstream from the nozzle orifice. The intensity of the VUV laser in the present experiment is estimated to be 0.1 µJ/pulse [33].

By directly recording intensities of VUV laser prior to and after the absorption by jet-cooled C$_2$H$_2$ molecules, a VUV absorption spectrum is obtained from transformation of the Beer-Lambert law, $I_l(\lambda)=I_0(\lambda)\exp[-N\sigma(\lambda)l]$, where $I_0(\lambda)$ and $I_l(\lambda)$ represent the measured VUV intensities before and after the absorption, respectively. N, $\sigma(\lambda)$, and l are molecular number density, absorption cross section at wavelength λ, and absorption path length, respectively. The absorption cross section $\sigma(\lambda)$ can be expressed as a natural logarithm of the ratio $I_l(\lambda)/I_0(\lambda)$, when N and l are kept constant during the experiment. In this way, the shot-to-shot fluctuation of VUV intensity and the variation of VUV intensity with wavelength could be normalized. Our recent measurement on the absorption spectrum of jet-cooled OCS molecule showed that less than 1% of the VUV intensity reduction by absorption could be obviously detected by this way, although the shot-to-shot intensity fluctuation of the VUV laser

generated by four-wave frequency mixing technique is more than 40% [34].

In order to increase the VUV absorption path length, a commercial slit nozzle (General Valve, 0.12 mm×12 mm) is used to produce a slit molecule beam along the propagation direction of the VUV laser. The wavelength and linewidth of the VUV laser are calibrated with the laser-induced fluorescence (LIF) spectrum of jet-cooled CO ($A^1\Pi \leftarrow X^1\Sigma^+$). The linewidth of the VUV laser is estimated to be ~0.3 cm^{-1} from the width of individual rotational lines in the CO LIF spectrum. Additionally, a rotational temperature of 60 K is derived from the spectral simulation. Under similar expansion conditions, the rotational temperature of C$_2$H$_2$ is expected to be 60 K too.

Gas samples of acetylene (C$_2$H$_2$) and carbon monoxide were purchased from Nanjing Spectral Gas Inc. (>99.9%, GC grade) without any further purified.

III. RESULTS AND DISCUSSION

A. Absorption spectra of acetylenein 142.8-152.3 nm

The absorption spectra of jet-cooled acetylene are shown in Fig.1. The solid line is for measurements under jet-cooled condition in the present work, while the dotted line is for data recorded by Campos *et al.* at room temperature by using synchrotron radiation as a light source [23]. Obviously, the present data agrees well with the previous result. The absorption spectra consists of three prominent vibrational absorption peaks, where the A and C peaks exhibit clear quasi-symmetric profiles, but the B peak shows typical asymmetric band contour. There is a weak shoulder peak near the major structure of the B peak at the lower energy. Since sufficient rotational cooling (~60 K) was obtained in the supersonic jet beam in the present experiment, the excitation of the rotational branches with the higher quan-
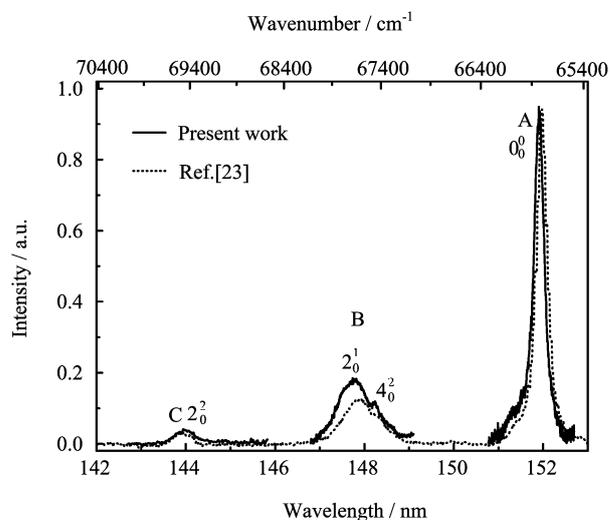
FIG. 1 Absorption spectrum of jet-cooled C$_2$H$_2$ molecule.

TABLE I Peak positions, FWHM (Γ), relative intensities (I) and assignments of major absorption bands of acetylene in the wavelength range of 142.8-152.3 nm, where an approximate doublet-peak fitting was applied to the second absorption peak.

Peak	Present work			Ref.[23]			v/cm^{-1}	Δv/cm^{-1}	Assignment
	λ/nm	Γ/cm^{-1}	I	λ/nm	Γ/cm^{-1}	I			
A	151.9	112	100	152.0	121	100	65830	0	0_0^0
	148.2	193	8.5				67461	1631	4_0^2
B	147.7	308	45	147.8	441	36.8	67693	1863	2_0^1
C	144.0	252	9.4	143.9	224	4.2	69453	3623	2_0^2
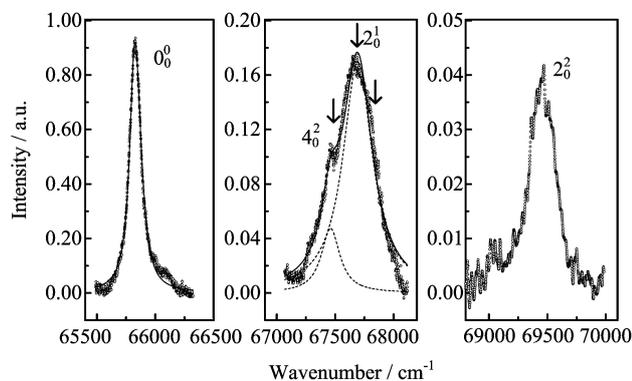
FIG. 2 Lorentzian profile fitting for all vibrational bands of acetylene in the wavelength range of 142.8-152.3 nm. The single peak profile is used for the v_2=0 and 2 bands, while the double-peak profile is applied for the v_2=1 band approximately. The cycles show the present experimental data, and the dotted lines present the simulated profiles.

FIG. 3 Normal vibrational modes and the corresponding symmetries of acetylene molecule and cation, while the vibrational frequencies (cm^{-1}) are from the NIST spectroscopic database [37]. [a] As the result of the Renner-Teller effect, the v_4 and v_5 bending mode would be split to three components, where the v_4 level corresponds to $\mu\Sigma_u^-$, $U\Delta_u$ and $\kappa\Sigma_u^+$ with the frequencies of 897, 666, and 487 cm^{-1}, respectively [35,36].

tum ($J>20$) could be eliminated entirely, and hence the high J rotational branches would have little contribution to the vibrational band (peak B). As a result, the shoulder peak can be distinguished easily in the present spectra.

By fitting the spectra with the least-square Lorentzian profile, the peak positions and FWHM widths are obtained and summarized in Table I. Since the B peak shows a characteristic of approximate double peaks, a double-peak fitting is applied to simulate the major and shoulder peak contour. Obviously, the present peak positions agree very well with the previous values, even though they are measured by various light sources under different experimental conditions. Unexpectedly, the present FWHM widths are moderately narrower than the previous data, especially for the absorption band at around 148 nm, which indicates that those absorption spectra measured at room temperature suffer seriously from the vibrational hot bands and/or the excitation of the rotational branches with the higher J quantum. Therefore, the present experimental absorption spectra of the $\widetilde{C}^1\Pi_u$ state of acetylene under jet-cooled condition are expected to directly show the vibrational spectral structure itself. The simulated and experimental spectra are compared and shown in Fig.2.

As mentioned above, previous experimental [10,12,17]

and theoretical studies [24,26,27] have gotten an agreement that the absorption of acetylene in a wavelength range of 140-155 nm corresponds to the $\widetilde{C}^1\Pi_u\leftarrow\widetilde{X}^1\Sigma_g^+$ transition, and molecular geometries of both electronic states are linear. As a typical Rydberg state, the vibrational frequencies of the $\widetilde{C}^1\Pi_u$ state should be close to those of the ion ground state. The normal vibrational modes and the corresponding symmetries of acetylene molecule and cation are shown in Fig.3. As shown in Table I, the interval energy among the three prominent peaks (A, B, and C) are 1863 and 1760 cm^{-1}, which is close to the vibrational frequency (1818 cm^{-1}) of symmetric C–C stretching mode v_2 of the $C_2H_2^+$ ground state [35,36], and hence the three prominent vibrational bands are definitely assigned as a v_2 vibrational progress of the 3s Rydberg state, namely, $\widetilde{C}^1\Pi_u(v_2$=0-2)$\leftarrow\widetilde{X}^1\Sigma_g^+$, which is in excellent agreement with the previous conclusion [12,15,17,22].

The transition symmetry of the v_2=1 vibrational band is the same as that of v_2=0 or 2 bands, as the v_2 vibrational symmetry is Σ_g^+. Therefore, the v_2=1 vibrational band, corresponding to the major component of

B peak, should exhibit the same quasi-symmetric profile as that of v_2=0 or 2 bands. However, the profile of the peak B shows distinct approximate double-peak shape in Fig.1, and a weak shoulder at the lower energy is visible. Thus this shoulder peak must come from the contribution of another vibrational transition of the $\widetilde{C}^1\Pi_u$ state. As shown in Table I, the resonant wavelength of the shoulder peak is around 148.2 nm (67461 cm^{-1}), which is 1631 cm^{-1} higher than the $\widetilde{C}^1\Pi_u$ state origin. Comparing with the vibrational frequencies of acetylene molecule and cation, this shoulder peak could not be explained as any vibrational hot band. In addition, the sufficient rotational cooling ($\sim$60 K) in the present work entirely eliminates the excitation of the rotational branches with the higher quantum (J>20), and hence the P rotational branch of the v_2=1 band could not extend to lower than 67500 cm^{-1}, which is too far from its peak position 67693 cm^{-1}. Therefore, the unique illumination for absorption of the shoulder peak observed at 67460 cm^{-1} is a contribution of the first overtone band of the *trans*-bending mode v_4 or v_5 modes. If we take the v_4 and the *cis*-bending mode v_5 frequencies to be those of the $C_2H_2^+$ ground state, the 4_0^2 and 5_0^2 vibronic levels of the $\widetilde{C}^1\Pi_u$ state should be around 1378 and 1438 cm^{-1} higher than the state origin (65830 cm^{-1}), and seem to be somewhat lower than that value we observed (1631 cm^{-1}).

According to Lievin's theoretical investigation [28], the predissociative C'^1A_g state of *trans*-bent geometry lies 7.7 eV above the ground state, which correlates adiabatically with a 3p Rydberg state ($^1\Pi_g$) of a linear molecule, and makes the molecule dissociate rapidly [38]. Moreover, the C'^1A_g state would cross with the $\widetilde{C}^1\Pi_u$ state and make the latter predissociative too. Therefore, we prefer to assign the observed shoulder peak as the first overtone band of v_4 rather than that of v_5, because the v_4 excitation is much more favorable for the coupling from the $\widetilde{C}^1\Pi_u$ state to the low-lying excited state, C'^1A_g.

In the present experiment, the measured errors coming from the fluctuation of the VUV laser radiation and the different sensitivities of VUV detectors have been already normalized. The intensity of each absorption band is proportionate to the Franck-Condon factor of its vibrational transition, once keeping the number density of the supersonic molecular beam. By integrating the absorption peak over bandwidth, the ratio of the Franck-Condon factor of three prominent peaks is obtained to be 1:0.45:0.094 in the present absorption spectra, which agrees well with the Campos *et al*'s result of 1:0.368:0.042 [23]. The uncertainty arising from the normalization and other measurement noises is estimated to be about 10%.

B. Spectral analysis of absorption spectrum of acetylene at 148 nm

In the wavelength region of present absorption spectra, the fast predissociation of acetylene leads to the serious broadening of rotational lines, and hence the vibrational band does not exhibit a distinct rotational structure. We tried to simulate the rotational contour of each vibrational band, and found the simulated rotational linewidth was close to the vibrational bandwidth, and thus the corresponding lifetime was in a magnitude of femtosecond timescale. In general, the period of rotational excitation is in a magnitude of picosecond timescale, and hence it is nonsense to discuss the rotational excitation and simulate the rotational branches in the present case. On the contrary, it is reasonable to obtain the lifetime of vibronic level from its bandwidth by fitting each vibrational band contour with Lorentzian profiles.

As mentioned above, the absorption spectrum of acetylene at 148 nm corresponds to excitations of the v_2 fundamental band and the first overtone band of v_4. Thus, an initial fitting with double peaks is applied to simulate this absorption band as shown in Fig.2. Although the A and C peak are fitted well with a single quasi-symmetric Lorentzian profile, the simulated spectrum of the absorption band at 148 nm could not agree with the experimental data, especially the characteristics marked with arrows in Fig.2. A simple assumption can be imagined that there is another contribution of other vibrational bands in this wavelength range. In fact, the excitation of *trans*-bending vibration v_4 mode would change the acetylene molecule from linear configuration to anti-bending geometry. A strong Renner-Teller splitting probably exists in this case. Recently, Yang *et al.* [35] and Tang *et al.* [36] have observed the vibronic level 4_0^2 of the $C_2H_2^+$ ground state was split into three new sub-vibronic levels, defined as $4_0^2(\mu^2\Pi_u)$, $4_0^2(U^2\Phi_u)$ and $4_0^2(\kappa^2\Pi_u)$ due to this kind of Renner-Teller effect. Since the present studied $\widetilde{C}^1\Pi_u$ state is a typical linear Rydberg state, a similar spectroscopic characteristic as the $C_2H_2^+$ ground state is expected that the 4_0^2 vibronic level of the $\widetilde{C}^1\Pi_u$ state would also be possibly split into three new sub-levels $4_0^2(\mu^1\Pi_u)$, $4_0^2(U^1\Phi_u)$, and $4_0^2(\kappa^1\Pi_u)$. However, the component $4_0^2(U^1\Phi_u)$ could not be observed in the present absorption spectrum, because its transition (ΔK=2) is forbidden by the transition selection rule (ΔK=0,±1). Therefore, only $4_0^2(\mu^1\Pi_u)$ and $4_0^2(\kappa^1\Pi_u)$ components and the 2_0^1 bands are expected to exist in the present absorption spectrum at 148 nm (corresponding energy is 67600 cm^{-1}), and three vibrational peaks (one vibrational peak 2_0^1 and two vibrational peaks 4_0^2) with Lorentzian profiles are used to simulate the absorption peak near 148 nm. The fit spectrum is shown in Fig.4 and the corresponding results are summarized in Table II. Obviously, the fit spectrum agrees well with the experimental result.

As shown in Table II, the band origin of vibronic band 2_0^1 is 67642 cm^{-1}, and hence the resonant frequency of vibrational mode v_2 of the $\widetilde{C}^1\Pi_u$ state of acetylene is determined to be 1811±1 cm^{-1}. On the other hand, only

TABLE II Band origins v_0, FWHMs (Γ), lifetimes (τ) and related intensities of various absorption bands of acetylene at 67600 cm^{-1}, which were obtained by the least-square Lorentzian profiles fitting. The first overtone excitation peak of v_4 mode was split into three sub-bands as $4_0^2(\mu^1\Pi_u)$, $4_0^2(U^1\Phi_u)$, and $4_0^2(\kappa^1\Pi_u)$ due to the Renner-Teller effect, whereas only $4_0^2(\mu^1\Pi_u)$ and $4_0^2(\kappa^1\Pi_u)$ components could be observed in the present absorption spectrum.

Assignment	v_0/cm^{-1}	Δv^a/cm^{-1}	Γ/cm^{-1}	τ/fs	I
$4_0^2(\mu^1\Pi_u)$	67446	1616	156	34	7.8
2_0^1	67642	1812	245	22	30
$4_0^2(\kappa^1\Pi_u)$	67782	1952	181	29	13

^{a}Energy related to the electronic state origin 65830 cm^{-1}.
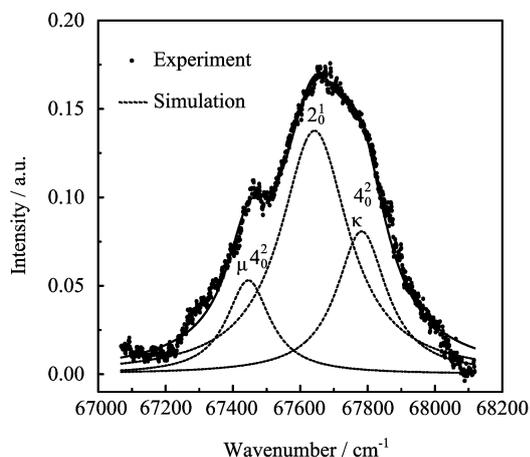
FIG. 4 Multi-peak fitting with Lorentzian profile on the absorption band of acetylene at 67600 cm^{-1}. The first overtone of v_4 vibrational band is split into three components according to the Renner-Teller effect, and only $4_0^2(\mu^1\Pi_u)$ and $4_0^2(\kappa^1\Pi_u)$ sub-vibrational bands are observed in the present absorption spectra.

two sub-vibronic components, $4_0^2(\mu^1\Pi_u)$ and $4_0^2(\kappa^1\Pi_u)$, are observed in the present absorption spectra, which are 1616 and 1952 cm^{-1} higher than the state origin respectively. The energy interval between these two sub-levels agrees with the Renner-Teller splitting of the $C_2H_2^+$ ground state [35,36]. It is interesting that the v_4 vibrational frequencies deduced from these two sub-levels are 808 and 976 cm^{-1}, respectively, which somewhat higher than those of the $C_2H_2^+$ ground state. A probable reason is that the strong coupling between the 4_0^2 vibronic level of the $\widetilde{C}^1\Pi_u$ state and the $2_0^4 3_0^1$ and 3_0^4 levels of the C'^1A_g state (v_3 is *trans*-bending mode with a frequency of 1303 cm^{-1}) raises the 4_0^2 vibronic level. Of course, an extensive theoretical study of the potential energy surfaces of these low-lying electronic states is expected to illuminate this abnormal phenomenon.

Although theoretical investigations indicated that the $\widetilde{C}^1\Pi_u$ state of acetylene is a typical bounding state, the coupling between it and the low-lying electronic states, however, would make molecule predissociate rapidly

[23,28]. As shown in Table II, the bandwidths of the vibrational peaks are about 200 cm^{-1}, and thus the corresponding lifetimes are in a magnitude of femtosecond. With the excitation of vibration, bandwidths are broadened and lifetimes decrease gradually.

IV. CONCLUSION

The absorption spectra of acetylene molecules were measured under jet-cooled conditions in the wavelength range of 142.8-152.3 nm, with a tunable and highly resolved VUV laser generated by two-photon resonant four wave difference frequency mixing processes. The sufficient rotational cooling temperature ($\sim$60 K) of the molecular beam is obtained under the jet-cooled condition and the resolution of VUV laser in our measurement is measured to be about 0.3 cm^{-1}. Thus the present observed absorption spectra exhibit moderately simpler spectral features than those previous works at room temperature. The major three vibrational bands lying at 151.9, 147.7, and 144.0 nm are assigned as a C–C symmetry stretching vibrational progress (v_2=0-2) of the $\widetilde{C}^1\Pi_u$ state of acetylene. The v_2 vibrational frequency of the $\widetilde{C}^1\Pi_u$ state is determined to be 1811$\pm$1 cm^{-1}, and the relative intensity ratio of three prominent bands (v_2=0-2) is measured to be 1:0.45:0.094, all of which agree very well with the previous conclusions.

Among three observed vibrational absorption peaks, the v_2=0 and v_2=2 peaks exhibit quasi-symmetric profiles, while the peak corresponding to v_2=1 excitation shows obviously shoulder peak shape. Although the highly resolved investigation still does not reveal any distinct rotational structure, we are still sure that the shoulder peak at around 148 nm comes from the contribution of other vibronic levels. Because the $\widetilde{C}^1\Pi_u$ state of acetylene is defined as a 3s linear Rydberg state, its vibrational frequencies should be close to those of $C_2H_2^+$. Thus the observed shoulder peak is assigned as the excitation of the first overtone of *trans*-bending vibration v_4, namely $\widetilde{C}^1\Pi_u(v_4=2) \leftarrow \widetilde{X}^1\Sigma_g^+$. Since the excitation of *trans*-bending vibration v_4 would change the acetylene molecule from linear configuration to bending geometry, a Renner-Teller splitting probably exists. Among three sub-vibrational levels as $4_0^2(\mu^1\Pi_u)$, $4_0^2(U^1\Phi_u)$ and $4_0^2(\kappa^1\Pi_u)$ after the Renner-Teller splitting, only two components, $4_0^2(\mu^1\Pi_u)$ and $4_0^2(\kappa^1\Pi_u)$, are observed in the present absorption spectra because of the restriction of the transition selection rule (ΔK=0,$\pm$1). Thus the multi-peak fitting with Lorentzian profile on the absorption spectrum at 148 nm subsequently shows the band origins and bandwidths of various sub-vibrational bands. Obviously, bandwidths are broadened and lifetimes decrease gradually with the excitation of vibration. In fact, in order to obtain more information of the dissociation dynam-

ics of the $\widetilde{C}^1\Pi_u$ state and internal energy distribution of photofragments, a photoionization mass spectrometer technique is being used to detect the hydrogen atom part.

V. ACKNOWLEDGMENTS

[1] S. T. Ridgeway, D. N. B. Hall, S. G. Kleinmann, D. A. Weinberger, and R. S. Wojslaw, Nature **264**, 345 (1976).
[2] G. F. Mitchell, S. S. Prasad, and W. T. Huntress, Astrophys. J. **244**, 1087 (1981).
[3] D. F. Strobel, Rev. Geophys. Space Phys. **13**, 372 (1975).
[4] H. Okabe, J. Chem. Phys. **75**, 2772 (1981).
[5] S. S. Prasad and W. T. Huntress Jr., Astrophys. J. Suppl. **43**, 1 (1980).
[6] G. Herzberg, Trans. Far. Soc. **27**, 378 (1931).
[7] W. C. Price, Phys. Rev. **47**, 444 (1935).
[8] W. C. Price and A. D. Walsh, Trans. Far. Soc. **41**, 381 (1945).
[9] G. Moe and A. B. F. Ducan, J. Am. Chem. Soc. **74**, 3136 (1952).
[10] P. G. Wilkison, J. Mol. Spectrosc. **2**, 387 (1958).
[11] E. W. Green Jr., J. Barnard, and A. B. F. Ducan, J. Chem. Phys. **54**, 71(1971)
[12] T. Nakayama and K. Watanabe, J. Chem. Phys. **40**, 558 (1964).
[13] M. Jungen, Chem. Phys. **2**, 367 (1973).
[14] P. D. Foo and K. K. Innes, Chem. Phys. Lett. **22**, 439 (1973).
[15] A. Gedanken and O. Schnepp, Chem. Phys. Lett. **37**, 373 (1976).
[16] M. Herman and R. Colin, J. Mol. Spectrosc. **85**, 449 (1981).
[17] M. Suto and L. C. Lee, J. Chem. Phys. **80**, 4824 (1984).
[18] C. Y. R. Wu, T. S. Chien, G. S. Liu, D. L. Judge, and J. J. Caldwell, J. Chem. Phys. **91**, 272 (1989).
[19] C. Y. R. Wu, F. Z. Chen, and D. L. Judge, J. Geophys. Res. **106**, 7629 (2001).
[20] F. Z. Chen, D. L. Judge, C. Y. R. Wu, J. Caldwell, H. P. White, and R. Wagener, J. Geophys. Res. **96**, 17518 (1991).
[21] P. Smith, K. Yoshino, W. H. Parkinson, and K. Ito, G. Stark, J. Geophys. Res. **96**, 17529 (1991).
[22] G. Cooper, G. R. Burton, and C. E. Brion, J. Electron Spectrosc. Related Phenomena **73**, 139 (1995).
[23] A. Campos, S. Boye, Ph. Brechignac, S. Douin, C. Fellows, N. Shafizadeh, and D. Gauyacq, Chem. Phys. Lett. **314**, 91 (1999).
[24] D. Demoulin and M. Jungen, Theoret. Chim. Acta. **34**, 1 (1974).
[25] S. Polezzo, M. Raimondi, and M. Simonetta, Theoret. Chim. Acta. **62**, 477 (1983).
[26] (a) M. Peric, Mol. Phys. **53**, 1177 (1984);
(b) M. Peric, Mol. Phys. **55**, 1129 (1985);
(c) M. Peric, Mol. Phys. **62**, 1339 (1987).
[27] J. O. Jensen, G. F. Adams, and C. F. Chabalowski, Chem. Phys. Lett. **172**, 379 (1990).
[28] J. Lievin, J. Mol. Spectrosc. **156**, 123 (1992).
[29] J. O. Jensen, G. F. Adams, and G. F. Chabalowski, J. Chem. Phys. **94**, 1332 (1991).
[30] G. Herzberg, *Electronic Spectra and Electronic Structure of Polyatomic Molecules*, New York: Van Nostrand Reinhold, (1966).
[31] M. B. Robin, *Higher Excited States of Polyatomic Molecules*, New York: Academic, 517 (1974).
[32] K. Watanabe and T. Namioka, J. Chem. Phys. **24**, 915 (1956).
[33] Q. F. Li, H. Wang, Y. Shi, J. H. Dai, S. L. Liu, S. Q. Yu, and X. X. Ma, Chin. J. Chem. Phys. **17**, 333 (2004).
[34] Q. F. Li, H. Wang, Y. Q. Yu, S. L. Liu, S. Q. Yu, and X. X. Ma, Chin. J. Chem. Phys. **18**, 474 (2005).
[35] J. Yang and Y. X. Mo, J. Phys. Chem. A **110**, 11001 (2006).
[36] S. J. Tang, Y. C. Chou, J. M. Lin, and Y. C. Hsu, J. Chem. Phys. **125**, 133201 (2006).
[37] J. E. Bartmess, *NIST Chemistry WebBook*, Eds.: P. J. Linstrom, and W. G. Mallard, NIST, Gaithersburg, (2005) (http://webbook.nist.gov).
[38] J. K. Lundberg, Y. Chen, J. Pique, and R. W. Field, J. Mol. Spectros. **156**, 104 (1992).