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Photofragment emission yield spectroscopy of acetylene in the $\tilde{D}^1\Pi_u$, $\tilde{E}^1A$, and $\tilde{F}^1\Sigma_u^+$ states by vacuum ultraviolet and infrared vacuum ultraviolet double-resonance laser excitations

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The excitation spectra of the $\tilde{D}^1\Pi_u$, $\tilde{E}^1A$, and $\tilde{F}^1\Sigma_u^+$ states of C$_2$H$_2$ in the 135.3–130.8 nm range are measured under jet-cooled conditions by detecting fluorescence emitted from C$_2$H($\tilde{A}^2\Pi$) or C$_2$H($\tilde{B}^2A'$) photofragments. In the photofragment emission yield spectra, the origin bands of the $\tilde{D}→\tilde{X}$ and $\tilde{F}→\tilde{X}$ transitions are observed with Lorentzian profiles with bandwidth ($\Gamma$) of 58.9(4) and 66.7(2) cm$^{-1}$, respectively. By identifying the bending progressions of the $\tilde{E}→\tilde{X}$ transition appearing with narrower Lorentzian profiles with, $\Gamma$~40 cm$^{-1}$, the band previously considered to be the origin band of the $\tilde{E}→\tilde{X}$ transition is assigned to the transition to the second overtone ($v_3=3$) level in the near-cis bending ($v_3$) mode. The transitions to the C–H stretch excited levels in the $\tilde{D}$ and $\tilde{F}$ states are observed using the infrared-VUV double resonance excitation scheme. The $\tilde{D}$ $3\tilde{1}$, $\tilde{D}$ $1\tilde{3}$, $\tilde{F}$ $3\tilde{1}$, and $\tilde{F}$ $1\tilde{3}$ bands are identified at 74 334(3), 74 121(5), 74 522(3), and 74 388(3) cm$^{-1}$, respectively, with much broader bandwidth ($\Gamma$>100 cm$^{-1}$) than the $\tilde{D}→\tilde{X}$ and $\tilde{F}→\tilde{X}$ origin bands, indicating that the dissociation is accelerated significantly in both of the $\tilde{D}$ and $\tilde{F}$ states when the antisymmetric C–H stretch ($v_3$) mode in the $\tilde{D}$ and $\tilde{F}$ states is excited.


I. INTRODUCTION

Molecular Rydberg states undergo complex bond-breaking processes originating from their mixing with other Rydberg states as well as with nearby valence states. Among small polyatomic molecules, the Rydberg states of acetylene (C$_2$H$_2$) have been characterized relatively well by the recent laser spectroscopic studies. It has been known that the electronic transitions to the two Rydberg states, $\tilde{D}$ and $\tilde{F}$, and one valence $\tilde{E}$ state overlap with each other in the vacuum ultraviolet (VUV) wavelength region of 135–130 nm. The $\tilde{D}^1\Pi_u$ ($1\pi_u→3d\pi_u\Sigma$) and $\tilde{F}^1\Sigma_u^+$ ($1\pi_u→3d\pi_u\Sigma$) states are members of the Rydberg states which converge on the electronic ground state of C$_2$H$_2$(X$^2\Pi_u$) having a linear equilibrium geometry. Therefore, their equilibrium geometries are expected to be linear. 1–9 On the other hand, the $\tilde{E}^1A$ state is known to have near-cis equilibrium geometry with C$_2$ symmetry. 10

In spite of the previous spectroscopic efforts, 1–16 only fragmentary information has been obtained regarding the photodissociation mechanism through this Rydberg-valence complex composed of the $\tilde{D}$, $\tilde{E}$, and $\tilde{F}$ states. Suto and Lee 1 measured using a synchrotron radiation light source an absorption spectrum of C$_2$H$_2$ in this VUV wavelength region as well as an excitation spectrum monitoring the yields of the C$_2$H photofragments produced in the $\tilde{A}^2\Pi$ and $\tilde{B}^2\Sigma^+$ states, but the measurements were done at room temperature and the resolution of the spectrum was not sufficiently high to resolve the individual line shape of the overlapping vibronic bands in the $\tilde{D}→\tilde{X}$, $\tilde{F}→\tilde{X}$, and $\tilde{E}→\tilde{X}$ transitions. Later, Löffler et al. 11,12 measured the kinetic energy profiles of photofragment hydrogen atoms in the 133–121 nm range and identified two competing dissociation pathways which form, respectively, the C$_2$H fragments in the $X^2\Sigma^+$ and $\tilde{A}^2\Pi$ states. Considering the complex vibronic structure composed of the three overlapping band systems, it would be an important step to resolve these vibronic bands and derive their rate of dissociation from the respective vibrational levels for understanding the dissociation mechanisms.

In the investigation of the photodissociation through such electronically highly exited states, measurements of a high-resolution excitation spectrum using a tunable VUV laser light source is most promising especially when molecules are prepared at ultralow temperature under jet-cooled conditions. As has been demonstrated for the photodissociation process of OCS via the 2$^1\Sigma^+$ state, the high-resolving power of the method enables us to discuss absorption peak profiles characteristic of molecules which dissociate in an ultrashort time scale. 17

In the present study, photodissociation processes of C$_2$H$_2$ via the three electronic states, $\tilde{D}$, $\tilde{E}$, and $\tilde{F}$, i.e.,
The spectral bandwidth of the VUV light was estimated to be ~0.4 cm⁻¹ by the peak width of the rotational transitions in the LIF spectrum of the A–X (7, 0) band of CO.

The tunable IR laser output of an optical parametric oscillator and amplifier (OPO/OPA) laser (Continuum Mirage 3000) pumped by an injection-seeded Nd:YAG laser (Continuum Powerlite 8000) was used to prepare C₂H₂ in its specific rotational levels of the ν₁ (λ = 3.03 μm) and ν₅ + ν₆ (λ = 1.52 μm) vibrational states. The fundamental (λ = 1064 nm) and frequency-doubled (λ = 532 nm) outputs of the Nd:YAG laser were introduced into the IR laser which consists of one OPO crystal and two OPA crystal pairs. The output pulse energy of the signal radiation from the first OPA was typically 25 mJ/pulse at ~0.8 μm. This signal beam was frequency-doubled in a KDP crystal and led to a wavemeter (Burleigh WA-5500) to monitor the wavelength. On the other hand, the idler radiation from the first OPA is guided to the second OPA crystal pair and used as an oscillator. The output energies of the signal and idler radiation from the second OPA were typically 15 mJ/pulse at ~1.5 μm and 4 mJ/pulse at ~3 μm, respectively. These two mid-IR beams were separated from each other by a 45° anhydrous-quartz prism.

The wavelength of the signal or idler radiation of the second OPA signal was locked on a rotational line of the vibrational band of C₂H₂ by monitoring the photo-acoustic spectrum. The spectral linewidth of the IR radiation was estimated to be 0.07 cm⁻¹ from the IR-VUV double-resonance excitation spectra obtained by scanning the wavelength of the IR light.

The visible fluorescence from the C₂H (A, B) fragments produced by the photolysis of C₂H₂ in the VUV region was detected by a photomultiplier tube (Hamamatsu R928) through a light collection lens pair located in the direction perpendicular to both the laser beams and the free jet. The signal from the photomultiplier tube was preamplified and averaged by a boxcar integrator (Stanford SR250), and was sent to a personal computer through an analog/digital converter.

II. EXPERIMENT

A pure acetylene gas with the stagnation pressure of ~2 atm was expanded through a pulsed valve with 0.2 mm orifice diameter (General Valve 9-279-900) into the vacuum chamber to form a pulsed supersonic free jet. The background pressure in the vacuum chamber was kept <10⁻⁴ Torr. The vacuum pumping system of the chamber was the same as that described previously. The rotational temperature of C₂H₂ in the free jet was estimated to be ~5 K by measuring laser induced fluorescence (LIF) spectra of the A–X transition of C₂H₂ under the same jet-cooled conditions. The collimated VUV beam was introduced into the main vacuum chamber and crossed the free jet at right angles, 15 mm downstream from the orifice of the pulsed valve. In the IR-VUV double resonance experiment, the collimated IR beam was counterpropagated collinearly with the VUV beam. At the laser beam-jet interaction region, the diameters of IR and VUV beams were ~5 and 2 mm, respectively.

The visible fluorescence from the C₂H (A, B) fragments produced by the photolysis of C₂H₂ in the VUV region was monitored by a photomultiplier tube (Hamamatsu R1259). The laser beams were separated from the vacuum laser beam by a 30° lithium fluoride prism. Three light baffles were placed between the prism and the main chamber in order to eliminate the visible (ω₁) and UV (ω₂) scattered light in the chamber. The spectral bandwidth of the VUV light was estimated to be ~0.4 cm⁻¹ by the peak width of the rotational transitions in the LIF spectrum of the A–X (7, 0) band of CO.

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In the $\tilde{X}^{1}S_{\text{g}}^{+}$, $\tilde{D}^{1} \Pi_{\text{u}}$, and $\tilde{F}^{1} \Sigma_{\text{u}}^{+}$ states whose equilibrium structure is linear, the normal modes are: $v_{1}$ (C–H symmetric stretch), $v_{2}$ (C–C stretch), $v_{3}$ (C–H antisymmetric stretch), $v_{4}$ (trans-bend), and $v_{5}$ (cis-bend). In the nonplanar $\tilde{E}^{1} A$ state, the normal modes are the $v_{1}$ (C–H symmetric stretch), $v_{2}$ (C–C stretch), $v_{3}$ (near cis-bend), $v_{4}$ (torsion), $v_{5}$ (C–H antisymmetric stretch), $v_{6}$ (near-trans bend).\(^{10}\) It should be noted that the classification as well as the numbering of the normal modes for the $\tilde{E}$ state with $C_{2}$ symmetry is different from those in the $\tilde{X}$, $\tilde{D}$, and $\tilde{F}$ states with $D_{\infty h}$ symmetry.

Regarding the assignment of the origin of the $\tilde{E} \rightarrow \tilde{X}$ band, consensus has not been reached yet. Herman and Colin assigned the band observed at 74 629 cm\(^{-1}\) to the origin of the $\tilde{E} \rightarrow \tilde{X}$ band,\(^{6}\) which corresponds to the peak appearing in our PHOFREY spectrum at 74 615 cm\(^{-1}\). The same assignment was adopted later by Lundberg et al.\(^{10}\) On the other hand, Ashfold et al. assigned the transitions at 74 629 cm\(^{-1}\) to the $3 \nu'_{3}$ band ($\nu'_{3}$: C–H antisymmetric stretch).\(^{14}\) When 74 615 cm\(^{-1}\) is adopted as the origin of the $\tilde{E} \rightarrow \tilde{X}$ band, the bands observed at $\sim$74 029 and $\sim$75 011 cm\(^{-1}\) need to be assigned as hot-band transitions from the trans-bend excited level in the $\tilde{X}$ state. However, under jet-cooled conditions hot-bands are not expected to appear with such strong intensities. Therefore, it may not be appropriate to regard the band at 74 615 cm\(^{-1}\) as the $\tilde{E} \rightarrow \tilde{X}$ origin band.

When adopting the peak at 72 753 (Ref. 14), 72 746 (Ref. 15) or 72 744 (Ref. 16) cm\(^{-1}\) as the origin band transition, the peak at 74 615 cm\(^{-1}\) in the present study can be assigned to the $\tilde{E}$ (3 $\nu'_{3}$) band ($\nu'_{3}$: near cis-bend), and other unassigned peaks in Fig. 1 can be interpreted straightforwardly as members in the two progressions, $\tilde{E}$ ($n \nu'_{3}$) ($n = 2$–5) and $\tilde{E}$ ($\nu'_{2} + n \nu'_{3}$) ($n = 1$–3) with respect to the $\nu'_{3}$ mode. The vibrational assignments for the transitions to the $\tilde{D}$, $\tilde{E}$, and $\tilde{F}$ states are shown in Fig. 1, where the $\tilde{F}$ ($n' \nu'_{3}$)$\rightarrow\tilde{X}$ ($n'' \nu''_{3}$) transition is denoted as $\tilde{F}^{1} 3\tilde{u}^{n''}$, for example.

The peak positions of the $\tilde{E} \rightarrow \tilde{X}$ bands appearing in our PHOFREY spectrum are in good agreement with those in the two-photon resonance multiphoton ionization spectra recorded by Ashfold et al.\(^{14}\) and Takahashi et al.\(^{15}\) These two groups interpreted the vibrational progression as that of the $1\Delta_{g}$ Rydberg ($1 \Sigma_{g}^{+} \rightarrow 3 p \pi_{g} R$) state. However, the transition to the $1\Delta_{g}$ Rydberg state should be symmetrically forbidden in the one-photon absorption scheme as far as the equilibrium structure is linear. Therefore, the agreement between the one-photon and the two-photon transitions can be regarded as an evidence that the $\tilde{E}$ state has a nonlinear equilibrium structure. The $\tilde{E}^{1} A$ valence state with a near-cis $C_{2}$ symmetry is possibly formed by the interaction between the $1\Delta_{g}$ ($1 \Sigma_{g}^{+} \rightarrow 3 p \pi_{g} R$) Rydberg state and the $1\Sigma_{u}^{+}$ ($1 \pi_{u} \rightarrow 1 \pi_{g}$) valence state because both of these two electronic states are expected to be located around the wavelength region investigated in the present study.\(^{3,9}\)

![Figure 1. The PHOFREY spectrum of C\(_{2}\)H\(_{2}\) in the 73 950–76 800 cm\(^{-1}\) range recorded by monitoring the fluorescence emitted from the C\(_{2}\)H(A, B) fragments. The assignments of the vibronic bands are given above the corresponding peak profiles. The sharp dips with an asterisk in the lower figure are caused by the intensity drop of the VUV light source associated with the self-absorption of Kr.](image)

**B. Origin bands of the $\tilde{D}$ and $\tilde{F}$ states**

In the upper panel of Fig. 1, the six vibronic bands, $\tilde{E}^{2} 3\tilde{u}$, $\tilde{D}^{0} 0\tilde{u}$, $\tilde{E}^{2} 3\tilde{u}$, $\tilde{F}^{0} 0\tilde{u}$, $\tilde{E}^{2} 3\tilde{u}$, and $\tilde{E}^{2} 3\tilde{u}$, are identified in the increasing order of their band center wave numbers. Among them, the band origin transitions of the $\tilde{D} \rightarrow \tilde{X}$ and $\tilde{F} \rightarrow \tilde{X}$ bands appear with the largest intensities at $\sim$74 500 cm\(^{-1}\) and $\sim$74 750 cm\(^{-1}\), respectively. In order to derive the bandwidth and the band center wave numbers of these six vibronic bands, the least-squares fit was performed for the spectral shape of the entire region in the upper panel of Fig. 1. In the numerical synthesis of the spectrum, a Lorentzian-type line profile $f_{\nu}^{0}(\nu, \nu_{0}, I_{0})$ is adopted for the five transitions and an asymmetric line profile,\(^{16}\)

$$f_{\nu}^{0}(\nu, \nu_{0}, I_{0}) = \frac{I_{0}}{\nu_{0}} \left( q + \frac{(2(\nu - \nu_{0}))}{\nu_{0}^{2}} \right)^{2},$$

was adopted for the $\tilde{F}^{0} 0\tilde{u}$ band, where the parameters $I_{0}$, $\nu_{0}$, and $\Gamma_{0}$ represent an intensity factor, a band center wave number, and a bandwidth, respectively, and $q$ denotes an asymmetric parameter.\(^{32}\) The synthesized spectrum,

$$I(\nu) = \sum a_{\nu} f_{\nu}^{0}(\nu, \nu_{0}, I_{0}) + b f_{\nu}^{0}(\nu, \nu_{0}, I_{0}),$$

was fitted to the observed spectrum. The results of the least-squares fit are summarized in Fig. 2 and Table I. Though the degree of asymmetry for the $\tilde{F}^{0} 0\tilde{u}$ band is small, as represented by the relatively large value of $q$, $q$
= 21.3(6), the inclusion of the q parameter reduced largely the standard deviation of the fit. The FWHMs of the $\tilde{D} - \tilde{X}$ and $\tilde{F} - \tilde{X}$ origin band transitions, $\Gamma(\tilde{D}_0) = 58.9(4)$ and $\Gamma(\tilde{F}_0) = 66.7(2)$ cm$^{-1}$, which can be converted, respectively, to the lifetime $\tau$ of $\tau = 89$ and 79 fs, indicate that the ultrafast dissociation proceeds through these two vibrational levels with comparable rates.

As shown in Table I, the bandwidths of the four $\tilde{E} - \tilde{X}$ transitions are all $\sim 40$ cm$^{-1}$, and are much narrower than those of the $\tilde{D} - \tilde{X}$ and $\tilde{F} - \tilde{X}$ transitions (60–180 cm$^{-1}$), suggesting that the nature of the $\tilde{E}$ state is intrinsically different from the $\tilde{D}$ and $\tilde{F}$ Rydberg states.

### C. $\nu_2$ bands of the $\tilde{D}$ and $\tilde{F}$ states

In the lower panel of Fig. 1, the VUV light intensity fluctuates due to the self-absorption of a Kr gas$^{30}$ used as a nonlinear medium for the four-wave difference mixing. The effect of the intensity fluctuation can not be canceled out completely even after the intensity normalization procedure, and it causes sharp dips marked by an asterisk in the intensity normalized spectrum. Though the least-squares fit using multiple Lorentzian profiles was not performed for the spectrum in the lower panel, it can be read readily from the spectrum that the widths of the $\tilde{D} 2_{1}^1$ band ($\sim 80$ cm$^{-1}$) and the $\tilde{F} 2_{1}^2$ band ($\sim 50$ cm$^{-1}$), are comparable with those of the $\tilde{D} 0_{1}^0$ and $\tilde{F} 0_{1}^0$ origin bands in the upper panel. These bandwidths obtained here are consistent with the corresponding bandwidths of $\Gamma(\tilde{D}_0) = 87$ cm$^{-1}$ and $\Gamma(\tilde{F}_2) = 53$ cm$^{-1}$ reported previously by H-atom fragment action spectroscopy.$^{11,12}$

### D. $\nu_3$ and $\nu_1' + \nu_3'$ bands of the $\tilde{D}$ and $\tilde{F}$ states

In order to investigate an effect of the antisymmetric CH stretch excitation on the predissociation rate in the $\tilde{D}$ and $\tilde{F}$ states, the IR-VUV double resonance excitation scheme was adopted. Acetylene was excited first to the $\nu_3'$ and $\nu_1' + \nu_3'$ levels in the electronic ground state, and then, it was excited to the corresponding levels in the $\tilde{D}$ and $\tilde{F}$ states by the VUV light,

$$C_2H_2(\tilde{X}) + h\nu_{\text{IR}} \rightarrow C_2H_2(\tilde{X} \nu_3'),$$  \hspace{1cm} (4)

$$C_2H_2(\tilde{X} \nu_3') + h\nu_{\text{VUV}} \rightarrow C_2H_2(\tilde{D} \nu_1', \tilde{F} \nu_3'),$$  \hspace{1cm} (5)

and

$$C_2H_2(\tilde{X}) + h\nu_{\text{IR}} \rightarrow C_2H_2(\tilde{X} \nu_1'' + \nu_3'''),$$  \hspace{1cm} (6)

$$C_2H_2(\tilde{X} \nu_1'' + \nu_3''') + h\nu_{\text{VUV}} \rightarrow C_2H_2(\tilde{D} \nu_1' + \nu_3', \tilde{F} \nu_1' + \nu_3').$$  \hspace{1cm} (7)

The observed IR-VUV double resonance excitation spectrum is shown in Fig. 3(a). The broad shoulders identified at the positions indicated by an arrow in Figs. 3(b) and 3(c) appeared only when the IR laser light was introduced, and therefore, they were assigned to the double resonance transitions. It is expected that the fundamentals of the C–H antisymmetric stretch ($\nu_3'$) of the $\tilde{D}$ and $\tilde{F}$ states are also close to $\nu_3'' = 3294.8$ cm$^{-1}$ of the electronic ground state, and that the $3_{1}^1$ bands of the $\tilde{D} - \tilde{X}$ and $\tilde{F} - \tilde{X}$ transitions should appear near their electronic band origin transitions. Therefore, the broad bands located at $\sim 74 300$ and $\sim 74 500$ cm$^{-1}$ in Fig. 3(b) were assigned to the $\tilde{F} 3_{1}^1$ and $\tilde{D} 3_{1}^1$, respectively.

Since these $3_{1}^1$ bands of the $\tilde{D}$ and $\tilde{F}$ states are shifted by about 200 cm$^{-1}$ to the lower wave number side from the respective electronic origins, the $1_{1}^1 3_{1}^1$ bands are expected to be shifted further by 200 cm$^{-1}$. Consequently, the broad

### Table I. Determined term values and bandwidths of the vibronic bands of the $\tilde{D}$, $\tilde{E}$, and $\tilde{F}$ states of acetylene.

<table>
<thead>
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<th>State</th>
<th>Assignment</th>
<th>Term value / cm$^{-1}$</th>
<th>Vibrational term value / cm$^{-1}$</th>
<th>Width/cm$^{-1}$</th>
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<td>$\tilde{D}$</td>
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<td>74 490.2(1)</td>
<td>0</td>
<td>58.9(4)</td>
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<td></td>
<td>2$^1$</td>
<td>76 270$^b$</td>
<td>1780</td>
<td>87$^b$</td>
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<tr>
<td></td>
<td>3$^1$</td>
<td>77 629(3)$^c$</td>
<td>3139(3)</td>
<td>184(13)</td>
</tr>
<tr>
<td></td>
<td>1$^3_{1}^1$</td>
<td>80 677(5)$^d$</td>
<td>6187(5)</td>
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<tr>
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<td>1276</td>
<td>50(4)</td>
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<td>3$^3$</td>
<td>74 614.5(3)</td>
<td>1861.5</td>
<td>26(1)</td>
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<tr>
<td></td>
<td>2$^3_{1}^1$</td>
<td>75 011(1)</td>
<td>2258</td>
<td>40(4)</td>
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<tr>
<td></td>
<td>3$^3$</td>
<td>75 243(1)</td>
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<td>55(5)</td>
</tr>
<tr>
<td></td>
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<td>75 580$^e$</td>
<td>2827</td>
<td>37$^b$</td>
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<tr>
<td></td>
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<td>43$^b$</td>
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<td>76 100$^d$</td>
<td>3347</td>
<td>43$^b$</td>
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<tr>
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<td>0</td>
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<td></td>
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<td>76 480$^b$</td>
<td>1729</td>
<td>53$^b$</td>
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<td>77 817(3)$^f$</td>
<td>3066(3)</td>
<td>103(5)</td>
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<td></td>
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<td>80 944(3)$^d$</td>
<td>6193(3)</td>
<td>149(14)</td>
</tr>
</tbody>
</table>

$^a$The number in parentheses represents a standard deviation (1$\sigma$) obtained from the fit.

$^b$References 11 and 12.

$^c$Calculated from the hot-band transition from the $\nu_3'$ (= 3294.8323(4) cm$^{-1}$) level.

$^d$Calculated from the hot-band transition from the $\nu_3' + \nu_3''$ (= 6556.4561(5) cm$^{-1}$) level.

$^e$The Lorentzian fit was not performed because of the weak intensity.

$^f$The origin band wave number, 72 753(10) cm$^{-1}$, reported in Ref. 14 is adopted to obtain vibrational term values.

$^g$The asymmetric parameter was determined as $q = 21.3(6)$. 

[Note: The table content is not directly transcribed due to the nature of the question.]
bands located at \( \approx 74\,100 \) and \( \approx 74\,400 \,\text{cm}^{-1} \) in Fig. 3(c) were assigned to \( \tilde{D}\, 1_{1}^{1}\, 3_{1}^{1} \) and \( \tilde{F}\, 1_{1}^{1}\, 3_{1}^{1} \), respectively.

In order to confirm that these new bands are double resonance transitions, the IR laser wavelength was scanned in the narrow wavelength range around the centers of the \( \nu_{3}^{v} \) and \( \nu_{3}^{v} + \nu_{3}^{s} \) band, while fixing the UV wavelength at the double resonance (DR) peak. In addition, photoacoustic (PA) spectrum of acetylene was measured simultaneously to assign the rotational transitions appearing in the DR-IR excitation spectrum. The two kinds of IR excitation spectra obtained for the \( \nu_{3} \) transition are shown in Fig. 4. They are (i) the DR-IR excitation spectrum obtained by monitoring the total fluorescence emitted from the \( \tilde{A} \) and \( \tilde{B} \) states of the \( \text{C}_{2}\text{H} \) photofragments (upper trace) and (ii) the PA-IR excitation spectrum (lower trace).

In the IR wave number range in Fig. 4, two rotational band origins for the vibrational transition to the \( \nu_{3}^{v} \) level, 3294.8323(4) \,\text{cm}^{-1} \), and to that at \( \nu_{3}^{v} + \nu_{3}^{s} + \nu_{3}^{s} \) level, 3281.8934(3) \,\text{cm}^{-1} \), are located. These two levels interact with each other through the 3/245 Fermi resonance.\(^{33}\) The rotational assignments for the \( \nu_{3}^{v} \) and \( \nu_{3}^{v} + \nu_{3}^{s} + \nu_{3}^{s} \) bands are shown just above the DR-IR excitation spectrum. Though the PA-IR excitation spectrum exhibits a pressure broadening, the wave number positions of the sharp peaks \((J \leq 5)\) in the DR-IR excitation spectrum measured under jet-cooled conditions are in good agreement with the centers of the rovibrational peaks in the PA-IR excitation spectrum. On the basis of this frequency match of the rotational transitions, the fluorescence peaks in the upper trace of Fig. 4 and the shoulder appearing at 74,500 \,\text{cm}^{-1} \) in Fig. 3(b) were assigned unambiguously to the IR-VUV DR transition, i.e., the \( \tilde{F}\, 3_{1}^{1} \) band.

The least-squares fit was performed for the observed peak profiles in the IR-VUV DR PHOFREY spectra in Figs. 3(b) and 3(c). In Fig. 5, the observed and best-fit convoluted spectra are shown with the Lorentzian components for the \( \tilde{D}\, 1_{1}^{1}\, 3_{1}^{1} \) and \( \tilde{F}\, 1_{1}^{1}\, 3_{1}^{1} \) bands in the upper panel and those for the \( \tilde{D}\, 3_{1}^{1} \) and \( \tilde{F}\, 3_{1}^{1} \) bands in the lower panel. In the least-squares fit, the band-center wave numbers and bandwidths of the respective one-photon excitation bands, which overlap
with these double resonance bands, were fixed to the same values as those determined in Sec. III B.

From the least-squares fit, the FWHMs of the \( \tilde{D} 3^1, \tilde{F} 3^1, \tilde{D} 1^1 3^1, \) and \( \tilde{F} 1^1 3^1 \) bands were determined to be \( \Gamma(\tilde{D}_3) = 184(13), \Gamma(\tilde{F}_3) = 103(5), \Gamma(\tilde{D}_{13}) = 139(19), \) and \( \Gamma(\tilde{F}_{13}) = 149(14) \text{ cm}^{-1} \), respectively. This significant broadening identified for all the \( \nu'_3 \) excited levels suggests that the \( \nu'_3 \) mode accelerates the rate of dissociation through the \( \tilde{D} \) and \( \tilde{F} \) states to a large extent. In the \( \tilde{F} \) state, the additional excitation in the \( \nu'_1 \) mode increased further the dissociation rate, i.e., \( \Gamma(\tilde{F}_0) < \Gamma(\tilde{F}_1) < \Gamma(\tilde{F}_{13}) \), while in the \( \tilde{D} \) state, the additional \( \nu'_1 \) excitation effected in a different way, i.e., \( \Gamma(\tilde{D}_0) < \Gamma(\tilde{D}_1) < \Gamma(\tilde{D}_{13}) \).

### E. Mechanism of the \( \text{C}_2\text{H} (\tilde{A}, \tilde{B}) \) formation

Herman and Colin measured an absorption spectrum of the \( \tilde{D} - \tilde{X} \) and \( \tilde{F} - \tilde{X} \) transitions under bulk conditions. From their absorption spectrum, the ratio \( R = I(\tilde{D})/I(\tilde{F}) \) of the spectral intensities, \( I(\tilde{D}) \) and \( I(\tilde{F}) \), of the \( \tilde{D} - \tilde{X} \) and \( \tilde{F} - \tilde{X} \) origin-band transitions were estimated to be \( R \sim 0.17(2) \). In contrast, the intensity ratio is \( R = 0.4(1) \) in our PHOFREY spectrum shown in the upper panel of Fig. 1, indicating that the quantum yield of \( \text{C}_2\text{H}(\tilde{A}, \tilde{B}) \) from the vibrational ground state of the \( \tilde{D} \) state is larger than that from the vibrational ground state of the \( \tilde{F} \) state by a factor of 2.4.

Löffler et al.\(^ {11,12} \) measured one-photon VUV excitation spectra of jet-cooled acetylene in the 75 600–76 600 cm\(^{-1} \) region by the H-atom fragment action spectroscopy. The intensity of the \( \tilde{F} 2^1 \) band was 1.5 times as large as that of the \( \tilde{D} 2^1 \) band in their spectrum, while the \( \tilde{F} 2^1 \) band is slightly weaker than the \( \tilde{D} 2^1 \) band in our PHOFREY spectrum in the lower panel of Fig. 1. Because the dissociation rate in this energy region is much faster than a radiative relaxation rate, and only minor contribution is expected from the elimination of a molecular hydrogen,\(^ {7,34} \) the quantum yield of the H-atom production is considered to be unity. Therefore, the differences above indicate that the quantum yield of the \( \text{C}_2\text{H}(\tilde{A}, \tilde{B}) \) production is larger in the \( \nu'_2 \) excited state of the \( \tilde{D} \) state than in the \( \nu'_1 \) excited state of the \( \tilde{F} \) state.

The preference of the \( \text{C}_2\text{H}(\tilde{A}, \tilde{B}) \) formation in the \( \tilde{D} \) state compared with the \( \tilde{F} \) state identified both in the origin and \( 2^1 \) bands may be ascribed to the \( \Pi \) electronic character of the \( \tilde{D} \) state. Because the potential energy surfaces which lead to the fragmentation into \( \text{C}_2\text{H}(\tilde{A}, \tilde{B}) \) are known to have a \( \Pi \) character,\(^ {19} \) the dissociation through the \( \tilde{D} \) state having the same \( \Pi \) character would be preferred to that through the \( \tilde{F} \) state having a \( \Sigma \) electronic character.

In Fig. 6, the bandwidths of the observed peaks in the PHOFREY spectra listed in Table I are plotted as a function of their term values. Since the \( \nu'_1 \) coordinate corresponds with the dissociation coordinate in the linear geometry, the bandwidth broadening associated with the \( \nu'_1 \) excitation could be ascribed to a larger overlap between the vibrational wave functions of the \( \nu'_2 \) excited levels in the \( \tilde{D} \) and \( \tilde{F} \) Rydberg states and the continuum wavefunction of a repulsive state leading to the \( \text{C}_2\text{H} + \text{H} \) dissociation. The different behavior of the dissociation rate in the \( \tilde{D} \) and \( \tilde{F} \) states identified when \( \nu_1 \) is excited in addition to \( \nu_2 \). For \( \Gamma(\tilde{D}_3) > \Gamma(\tilde{D}_{13}) \), and \( \Gamma(\tilde{F}_0) < \Gamma(\tilde{F}_{13}) \), may indicate that the simultaneous excitation of the \( \nu_1 \) and \( \nu_3 \) modes enhances the wave function overlap with the continuum state in the \( \tilde{F} \) state, while it reduces the overlap in the \( \tilde{D} \) state.

The bandwidths for the transition to the \( \tilde{E} \) state levels \( (\Gamma \sim 40 \text{ cm}^{-1}) \) are much narrower than those for the \( \tilde{D} \) and \( \tilde{F} \) states \( (\Gamma = 60–180 \text{ cm}^{-1}). \) This means that the dissociation proceeds much slower in the \( \tilde{E} \) state. Since the equilibrium geometry of the \( \tilde{E} \) state is considered to be displaced from the planar configuration, the slow dissociation rate in the \( \tilde{E} \) state implies that dissociative wave functions on the continuum state have a probability distribution considerably displaced from the \( \tilde{E} \) state geometry, i.e., the dissociation may proceed from planar or linear geometry.

On the basis of the H-atom fragment action spectroscopy of acetylene, Löffler et al.\(^ {12} \) suggested the existence of the statistical pres dissociation pathways from the \( \tilde{D}, \tilde{E}, \) and \( \tilde{F} \) states, which produce \( \text{C}_2\text{H}(\tilde{A}) \) photofragments via mixing with the \( \tilde{A} \) or \( \tilde{B} \) state. When the dissociation from the \( \tilde{D}, \tilde{E}, \) and \( \tilde{F} \) manifolds proceeds through such a common intermediate state, the relative yields of \( \text{C}_2\text{H}(\tilde{A} \text{ or } \tilde{B}) \) for these electronic states are expected to be almost the same. Therefore, the clear dependences of the \( \text{C}_2\text{H} \) yields on the initially excited electronic state as well as on their vibrational states identified in the present study indicate that the memory of the electronic and vibrational characters of the initially prepared state is preserved persistently in the course of the photodissociation.

### IV. SUMMARY

The \( \tilde{D} 1^1 \Pi_u \) and \( \tilde{F} 1^1 \Sigma^+_u \) Rydberg states and the \( \tilde{E} 1^1 \Lambda \) valence state of jet-cooled \( \text{C}_2\text{H}_2 \) located in the 135.3–130.8 nm region were investigated by measuring excitation spectra
called VUV photofragment yield (PHOFREY) spectra and IR-VUV double resonance PHOFREY spectra, in which visible emission from the C$_2$H($\tilde{A}, \tilde{B}$) photofragments was monitored. The term values and homogeneous bandwidths of the vibrational levels in the three overlapping electronic states were determined with high-precision from least-squares fits to the observed peaks profiles broadened by a fast dissociation process.

Among the new spectroscopic findings, the observation of the transitions of $\tilde{D} 3_1^1$, $\tilde{D} 1_1^1 3_1^1$, $\tilde{F} 3_1^1$, and $\tilde{F} 1_1^1 3_1^1$ are noteworthy. Their vibrational assignments were confined by scanning the IR wavelength in the IR-VUV DR measurements. It should be mentioned also that the present measurements under jet-cooled conditions enabled us to assign securely the relatively weak $n\nu'_4$ ($n = 2$–5) and $\nu'_2 + n\nu'_3$ ($n = 1$–3) progressions of the $\tilde{E} - \tilde{X}$ transition.

Regarding the photodissociation rate, it was found that the $\tilde{D}$ and $\tilde{F}$ Rydberg states behaved in a similar manner, i.e., the lifetime broadening of the origin bands for the $\tilde{D}$ and $\tilde{F}$ states were 58.9 and 66.7 cm$^{-1}$, respectively, and the peak-width became approximately twice as large as that for the origin bands once the C–H asymmetric stretch was excited. However, the quantum yield for the production of C$_2$H($\tilde{A}, \tilde{B}$) fragment through the 0$^0$ and 2$^1$ levels of the $\tilde{D}$ Rydberg state was approximately twice as larger as that through the corresponding levels of the $\tilde{F}$ Rydberg state. On the other hand, the broadened widths for the $\tilde{E}$ state levels were in the range of 26–50 cm$^{-1}$, and no clear dependence on the vibrational mode was identified.

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