Molecular Physics

An International Journal at the Interface Between Chemistry and Physics

ISSN: 0026-8976 (Print) 1362-3028 (Online) Journal homepage: <https://www.tandfonline.com/loi/tmph20>

One-colour (~ 220 nm) resonance-enhanced ($S_1 - S_0$) multi-photon dissociation of acetylene: probe of the $C_2 A^1 \Pi_u - X^1 \Sigma_g^+$ band by frequency-modulation spectroscopy

Jun Jiang, Zhenhui Du, Jacques Liévin & Robert W. Field

To cite this article: Jun Jiang, Zhenhui Du, Jacques Liévin & Robert W. Field (2020): One-colour (~ 220 nm) resonance-enhanced ($S_1 - S_0$) multi-photon dissociation of acetylene: probe of the $C_2 A^1 \Pi_u - X^1 \Sigma_g^+$ band by frequency-modulation spectroscopy, Molecular Physics, DOI: [10.1080/00268976.2020.1724340](https://doi.org/10.1080/00268976.2020.1724340)

To link to this article: <https://doi.org/10.1080/00268976.2020.1724340>

Published online: 06 Feb 2020.

Submit your article to this journal [↗](#)

View related articles [↗](#)

View Crossmark data [↗](#)

RESEARCH ARTICLE

One-colour (~ 220 nm) resonance-enhanced (S_1-S_0) multi-photon dissociation of acetylene: probe of the $C_2 A^1\Pi_u - X^1\Sigma_g^+$ band by frequency-modulation spectroscopy

Jun Jiang^a, Zhenhui Du^b, Jacques Liévin^c and Robert W. Field^d

^aCenter for Accelerator Mass Spectrometry, Lawrence Livermore National Laboratory, Livermore, CA, USA; ^bState Key Laboratory of Precision Measuring Technology and Instruments, Tianjin University, Tianjin, People's Republic of China; ^cService de Chimie Quantique et Photophysique, Université Libre de Bruxelles, Bruxelles, Belgium; ^dDepartment of Chemistry, Massachusetts Institute of Technology, Cambridge, MA, USA

ABSTRACT

In a recent paper, we demonstrated that one-colour (~ 220 nm), resonance-enhanced (S_1-S_0), photodissociation of acetylene generates strong C_2 Swan band ($d^3\Pi_g - a^3\Pi_u$) and C_2 Deslandres-d'Azambuja band ($C^1\Pi_g - A^1\Pi_u$) fluorescence, and long-lived ($> 3 \mu s$) fluorescence from an electronically-excited C_2H^* species. It was not known whether the $C_2 A^1\Pi_u$ and $X^1\Sigma_g^+$ states are also directly populated in this process. In this work, multiple vibration-rotation transitions between the $C_2 A$ -state $v = 2$ and the X -state $v = 0$ level are examined by time-resolved frequency-modulation (FM) spectroscopy. The photolysis laser wavelength is tuned into resonance at the one-photon level with S_1-S_0 transitions that populate individual rotational levels of the S_1 *trans*-conformer 3^2 , 3^3 , and 3^4 vibrational states. By comparing the *phase* of the FM signals from the $C_2 A-X$ transitions with that from the Rb D₁-line absorption transition, we determine that, for all of the probed $A-X$ transitions, the X -state level is more populated than the A -state level. We propose that the acetylene S_1 level is excited by the second photon to an acetylene dissociation precursor state, which undergoes sequential C-H bond-breaking to produce the $C_2 X$ state. The dissociation precursor is assigned as the 1^1B_g (*trans*-bent)/ 1^1B_1 (*cis*-bent) valence state, which correlates to a doubly-excited configuration, $(1\pi_u)^2(1\pi_g)^2$, at linear geometry. Based on the rotational distributions of the $C_2 X$ -state fragments, we believe that at least one of the transition states involved in the photolysis via $S_1 3^4$ has a larger CC-H bend-angle for the departing H-atom than that involved in the $S_1 3^2$ and 3^3 photolysis.

ARTICLE HISTORY

Received 13 November 2019
Accepted 19 January 2020

KEYWORDS

Frequency-modulation (FM) spectroscopy; photodissociation; transition state geometry; photolysis mechanism; nascent product distribution

1. Introduction

In a recent paper [1], we introduced a new photofragment fluorescence detection scheme to obtain rotationally-resolved action spectra of predissociated rotation-vibration levels of the S_1 state of acetylene in the $47,200 \text{ cm}^{-1}$

energy region, which lies $\sim 1100 \text{ cm}^{-1}$ above the acetylene predissociation threshold ($46,074 \pm 8 \text{ cm}^{-1}$ [2]). The fluorescing photofragments result from one-colour, multi-photon dissociation of acetylene, which is resonance-enhanced at the one-photon level by the acetylene

S_1-S_0 transition. The signal-to-noise ratio (S/N) of this photofragment fluorescence detection scheme, referred to as photofragment fluorescence action spectroscopy (PFAS), is superior to all of the other techniques that have been implemented in our laboratory to study predissociated S_1 acetylene levels. For example, the S/N of PFAS is $>10\times$ larger than that of direct S_1 laser-induced-fluorescence (LIF) detection and $\sim 5\times$ larger than that of H-atom fluorescence detection (which is an additional new detection scheme introduced in Ref. [1]). Most importantly, PFAS is exceptionally easy to implement, because a single ultraviolet (UV) laser serves *both* ‘excitation’ and ‘probe’ roles. The PFAS detection scheme has been essential to extension of the ongoing study of the S_1 *cis-trans* isomerisation process [3–13], which is hindered by the reduction in S_1 LIF signals due to predissociation.

In Ref. [14], we identified the molecular transitions which give rise to the strong photofragment fluorescence signals. The C_2 Swan ($d^3\Pi_g - a^3\Pi_u$) and C_2 Deslandres-d’Azambuja ($C^1\Pi_g - A^1\Pi_u$) emission bands were observed in the dispersed fluorescence spectra excited via individual rotational levels of the acetylene S_1 *trans*-conformer 3^4 , 3^5 , and *cis*-conformer 3^16^1 vibrational states. In a collision-free environment, long-lived ($>3\mu s$) visible fluorescence from an electronically excited C_2H^* species was also observed. However, we have been unable to assign the electronic transitions associated with this long-lived fluorescence signal. The relative quantum yields among the three fluorescing species were estimated to be $C_2H^* : C_2(d) : C_2(C) = >40 : 4 : 1$.

All three photofragment emission bands used for our acetylene PFAS detection scheme have been previously observed in 193 nm ArF photolysis studies of acetylene [15–19]. In those studies, the C_2 $A^1\Pi_u$ state was found to be the most abundant species. For example, the ratio of total quantum yields (i.e. summed over all rotation-vibration levels) for the C_2 $A^1\Pi_u$ and $X^1\Sigma_g^+$ state were estimated to be 19(3) : 1 [18, 19]. Results from *ab initio* calculations by Cui et al. [20] confirm the results of those studies. However, the C_2 $A^1\Pi_u - X^1\Sigma_g^+$ Phillips band emission, which accounted for $\sim 90\%$ of the total integrated emission intensity following 193 nm photolysis of acetylene [15], was not observed in our study of the one-colour, resonance-enhanced (S_1-S_0), multi-photon dissociation of acetylene at ~ 220 nm [14]. While transitions involving low-lying *A*-state vibrational levels ($v < 3$) were outside the long-wavelength limit of the operating range of the monochromator and photomultiplier tube (PMT) used in our study, a search for the (4, 0) band of the C_2 $A - X$ transition in the 691 nm region revealed no sign of the transitions. This, however, does not rule

out the possibility that lower-lying vibrational levels of the *A* state ($v \leq 3$) are directly populated via ~ 220 nm photolysis of acetylene.

The goal of this work is to study the production of the C_2 *A* and *X* states following one-colour (~ 220 nm), multi-photon dissociation of acetylene, which is resonance-enhanced at the one-photon level by the S_1-S_0 transition. Specifically, C_2 *A/X*-state fragments generated via laser-selected rotational levels of the intermediate S_1 *trans* 3^2 (226 nm), 3^3 (222 nm), and 3^4 (218 nm) vibrational states are probed, based on a modified form of frequency-modulation (FM) spectroscopy. As demonstrated in Ref. [21], this application of the FM technique allows one to determine, from the *phase* of an FM signal, the *sign* of the population difference in a two-level system probed by the frequency-modulated (FMed) beam – specifically, whether the two-level system is inverted. FM signals from an inverted two-level system are expected to have opposite phase with respect to signals from a reference absorption transition, e.g. the Rb D_1 -line absorption transition at 795 nm. In contrast, FM signals from a non-inverted system should have the same phase as the Rb absorption signal. This FM scheme, which combines both the signal and phase sensitivity of FM detection, is particularly suitable for observing the time-evolution of the quantum state distribution of transient molecular species generated by photochemical process. In addition, from the temporal profile of the FM signal, it is possible to distinguish between signals that arise from direct photodissociation products vs. secondary products (e.g. collisionally-induced or fluorescence-populated).

2. Experimental details

2.1. The FM setup

The FM setup used in this work differs from a conventional FM setup in the generation of the FMed beam and the method of the data collection, which is described in detail in Ref. [21] and briefly described here. The output of a Ti-sapphire laser (M Squared, Solstis), pumped by the 532 nm output of a diode pumped solid-state laser (Lighthouse Photonics, Sprout G18), is frequency-modulated by an electro-optic phase modulator (EOM) (New Focus, 4421), driven at ~ 940 MHz. However, instead of using continuous modulation, by pulsing the 940-MHz radio-frequency (*rf*) modulation input into the EOM, the Ti-sapphire output is frequency-modulated with a duration of ~ 350 ns at a repetition rate of 20 Hz. The time-domain FM signals are detected with an amplified high speed photodiode (Newport, 818-BB-21A), and collected on a fast oscilloscope (Tektronix,

Figure 1. An illustration for the use of the phase of the FM signal to determine the sign of the population difference in a two-level system (adapted from Ref. [21]). Relative amplitudes of the two FM sidebands at three characteristic carrier frequencies are shown in panels (a) and (c), respectively, for a non-inverted (absorption) and an inverted (stimulated emission) two-level system. The colour green is used when the FM carrier frequency is on-resonance with the transition centre frequency. The colours, red and blue, are used, respectively, for cases in which the FM carrier frequency is red and blue-detuned by equal amounts. The time-domain signals at the three carrier frequencies are shown in panels (b) and (d) for the two types of systems.

TDS6124C). In order to average the 940-MHz signal in a phase-coherent manner, part of the *rf* modulation reference, split by a directional coupler (Mini Circuits, ZEDC-15-2B), is used to trigger the fast oscilloscope (i.e. triggered by the steep turn-on of the *rf* reference). The *rf* trigger is also recorded at each laser carrier frequency, and used as a direct input in the demodulation of the collected time-domain signal.

The principle for the use of FM spectroscopy to determine the sign of the population difference in a two-level system is illustrated in Figure 1, which shows the FM beat note signals at three characteristic frequencies around the transition centre. The FM signals in Figure 1(b,d) result from, respectively, differential attenuation ($\Delta\delta_{\text{att}}$, see Figure 1(a)) and amplification ($\Delta\delta_{\text{amp}}$, see Figure 1(c)) of the two first-order sidebands, and oscillate at the modulation frequency. For a given two-level system (inverted or non-inverted), since $\Delta\delta$ has opposite sign when the carrier frequency is red- vs. blue-detuned, the phase of the beat signal is exactly reversed between the red- and blue-detuned cases. For a similar reason, given that $\Delta\delta_{\text{att}}$ (for a non-inverted two-level system) and $\Delta\delta_{\text{amp}}$ (for an inverted two-level system) have opposite sign at the same side of the transition centre

frequency, the FM signal from an absorption transition must be 180° out of phase with respect to that from a stimulated emission transition, as can be seen by comparing the same-colour traces in panels b and d of Figure 1. We must point out that, for simplicity, the frequency-dependent phase-shift (i.e. dispersion) experienced by the FMed beam is neglected in Figure 1. As discussed in Ref. [21], at the same side of the transition centre frequency, the FM dispersion signal from a non-inverted two-level system is also 180° out of phase with respect to that from an inverted two-level system. This means that the total FM signal, which is a linear combination of signals due to beam attenuation/amplification and beam dispersion, is of opposite phase for the absorption vs. stimulated emission transitions.

2.2. Probing the $C_2 A - X$ transitions

The C_2 fragments are generated by one-colour (~ 220 nm), resonance-enhanced ($S_1 \leftarrow S_0$), multi-photon dissociation of acetylene (BOC, atomic absorption grade 2.6 99.6% purity). The frequency-doubled output (218–227 nm) of a pulsed dye laser (Sirah Cobra-Stretch, dual-grating with 3000 lines/mm), pumped by the third harmonic of a Q-switched, injection-seeded Nd:YAG laser (Spectra-Physics Pro-270), is focused by an $f = 80$ cm lens to a beam waist at the centre of a single-pass flow cell (40 cm in length). The use of a focusing lens with a long focal-length is intended to maximise the spatial overlap between the UV photolysis beam and the FMed probe beam. The flow-rate inside the cell is controlled by a needle valve, and the cell pressure is maintained at 2 torr. The UV energy is ~ 300 $\mu\text{J}/\text{pulse}$ at the entrance port of the flow cell for all experiments described here.

The wavelength of the UV beam is tuned to each of the three individual $S_1 - S_0$ transitions which populate, respectively, the $K = 1, J = 8, e$ -symmetry levels of the $S_1 3^2$ and 3^3 vibrational states [22], and the $K = 1, J = 7, f$ -symmetry level of the $S_1 3^4$ vibrational state [23, 24]. From each intermediate S_1 rotation-vibration level, a second same-colour UV photon photodissociates the molecule into C_2 fragments. The C_2 fragments from the one-colour photolysis are probed by a counter-propagating FMed beam (~ 1 mm in diameter). For detection of C_2 produced via resonance with the acetylene $S_1 3^3$ and 3^4 vibrational levels, a high-reflectance mirror for the Nd:YAG 5^{th} harmonic (CVI Laser Optics, Y5-1025-45) is used as the beam combiner. For detection of C_2 produced via resonance with the $S_1 3^2$ vibrational level, a high-reflectance mirror at 225 nm is used. For experiments via all three intermediate S_1 levels, Q(2), Q(8), Q(14), Q(20), and Q(26) transitions of the

Figure 2. Level diagrams of (a) $C_2 A^1\Pi_u - X^1\Sigma_g^+$ transition, with the sign of the population difference to be determined by the phase of the FM signal, and (b) $^{85}\text{Rb } 5^2P_{1/2} \leftarrow 5^2S_{1/2}$ absorption transition.

(2 – 0) band of the $C_2 A - X$ transition [25, 26] are probed by the FMed beam (see Figure 2(a)). For experiments involving the $S_1 3^4$ vibrational state, an additional Q(32) transition is probed. The FMed beam power (measured in the *cw* modulation mode) is ~ 3.5 mW, ~ 5.5 mW and ~ 15 mW, respectively, for experiments involving $S_1 3^4, 3^3$, and 3^2 intermediate vibrational states. The resulting FM signals are normalised to the same power level for intensity comparison. During the course of the experiments, the UV photolysis laser power is maintained at an approximately constant level (i.e. the average laser power decreases by $< 5\%$ during experiments involving a single S_1 level).

To determine the sign of the population difference between the $C_2 A$ and X -state levels probed by the FMed beam, the phase of the FM signal from each $C_2 A - X$ transition must be compared with that of the $^{85}\text{Rb } 5^2P_{1/2} \leftarrow 5^2S_{1/2}$ transition (the D_1 -line absorption) near 795 nm [21]. A commercially available Rb cell (Thorlabs, GC19075-RB) is used for that purpose, and the FMed beam power is ~ 2.2 mW during the experiment. As discussed in Ref. [21], two ^{85}Rb absorption lines are expected to be resolved due to the hyperfine splitting (3 GHz) of the lower $5^2S_{1/2}$ level [27] (see Figure 2(b)). The hyperfine splitting (0.36 GHz) of the upper $5^2P_{1/2}$ is too small to be clearly resolved in the current experimental setup. Transitions from the less abundant ^{87}Rb species (27.8%) do not interfere significantly with the ^{85}Rb transitions, due to the larger hyperfine splitting (7 GHz) of the $^{87}\text{Rb } 5^2P_{1/2}$ level and its smaller natural abundance [28].

3. The $C_2 A - X$ transitions

3.1. Population in the $C_2 A$ and X -state vibrational levels

A typical FM signal from the observed $C_2 A - X$ transitions, recorded directly on a fast oscilloscope, is displayed

Figure 3. A typical time-trace of the observed $C_2 A(v=2) - X(v=0)$ transition. The FM signal oscillates at the *rf* modulation frequency (~ 940 MHz). The blue arrow indicates the approximate time at which the UV excitation occurs. The first 30 ns of the FM time-trace immediately after the UV excitation (colour-coded red) is sampled in the demodulated spectrum. A portion of the FM time-trace (colour-coded green) is used for background RAM correction.

in Figure 3. The time-domain signal has a rise-time of ~ 10 ns, followed by a decay with a time-constant of ~ 100 ns. While collisions inside the cell (2 torr) most likely contribute to the finite signal decay time, the short signal build-up time indicates that the observed $C_2 A - X$ transitions are likely not collisionally-induced. In addition, given the fast rise-time and short overall duration of the signal, our measurement cannot be affected by the much slower $C_2 A \rightarrow X$ radiative decay process, with A -state fluorescence lifetime on the order of $10 \mu\text{s}$ [29]. While we cannot completely rule out the $C_2 C \rightarrow A$ ($\tau = 31 - 36$ ns) [30] and $D \rightarrow X$ ($\tau = 15 - 18$ ns) [30, 31] radiative decay processes as sources for the A - and X -state populations measured in our FM experiment, the sharp rising edge in the observed FM time-trace, which is most likely laser-pulse (7 ns) limited, indicates that the contributions to the observed FM signal from those two fluorescence processes are significantly smaller than that from the direct photodissociation products.

In Figure 4(a,b), time-domain FM signals from the $^{85}\text{Rb } 5^2P_{1/2} \leftarrow 5^2S_{1/2}$ transition and the $C_2 A(v=2) - X(v=0)$ Q(14) transition (measured following photolysis via the $S_1 3^4$ vibrational state) are compared. The red and blue traces correspond, respectively, to the time-domain signals recorded at wavenumbers of the FM carrier that are red- and blue-detuned by the same amount, 0.016 cm^{-1} , from the transition centre wavenumber. As discussed in Section 2.1, for a given transition, a 180° phase change is expected for FM signals obtained with a red- vs. blue-detuned carrier. As can be seen by comparing the same-colour time-traces in Figure 4(a,b),

Figure 4. Time-domain FM signals from (a) the $^{85}\text{Rb } 5^2\text{P}_{1/2} \leftarrow 5^2\text{S}_{1/2}$ transition, excited from the $F'' = 2$ hyperfine component of the $5^2\text{S}_{1/2}$ state, and (b) the $\text{C}_2 \text{ A}(\nu = 2) - \text{X}(\nu = 0)$, Q(14) transition, generated via resonance of the photolysis beam with a single rovibronic transition into the S_1 acetylene 3^4 vibrational level. In each plot, the red and blue traces, correspond, respectively, to the FM signals collected at laser carrier wavenumbers that are red and blue-detuned by an equal amount, 0.016 cm^{-1} , from the transition centre wavenumber. In panel (b), the blue trace is scaled to match the amplitude of the red trace, due to the observed asymmetric lineshape (see discussion in Section 3).

with the same amount of detuning from the transition centre, FM signals from the $\text{C}_2 \text{ A} - \text{X}$ transition are observed to have the same phase as signals from the $^{85}\text{Rb } 5^2\text{P}_{1/2} \leftarrow 5^2\text{S}_{1/2}$ absorption transition. This implies that the population in the $J = 14, \nu = 0, \text{X}$ -state level is larger than that in the $J = 14, \nu = 2, \text{A}$ -state level. The same conclusion can be drawn for all of the $\text{A}(\nu = 2) - \text{X}(\nu = 0)$ two-level systems probed in this work.

In addition to direct time-domain inspection of the phase of the FM signals, the sign of the population difference between $\text{A}(\nu = 2)$ and $\text{X}(\nu = 0)$ levels can be determined by comparing the phase of the demodulated spectra of the observed $\text{C}_2 \text{ A} - \text{X}$ transitions with that of the Rb D_1 -line absorption transition (see Figure 5) [21]. As discussed in detail in Ref. [21] and references therein (e.g. Refs. [1–3, 13]), the demodulated signals have both in-phase and quadrature components (with respect to the phase of the rf modulation). The quadrature signal is proportional to the difference in attenuation (for a non-inverted two-level system) or amplification (for an inverted two-level system) experienced by the two first-order sidebands of the FMed beam; the in-phase

signal originates from the difference in phase shift experienced by the two side-bands and the carrier (see, for example, Eqs. 3–5 in Ref. [21]). The quadrature and in-phase signals are expected to have one and three zero-crossings, respectively, around each molecular transition. The frequency at the zero-crossing of the quadrature signal (and the second zero-crossing of the in-phase signal) corresponds to the transition frequency.

As can be seen in Figure 5, at the same side of the transition centre frequency, both the quadrature (panel c) and in-phase (panel d) signals from the observed $\text{C}_2 \text{ A} - \text{X}$ transition have the same phase/sign as the corresponding signals (in panels a and b, respectively) from the reference Rb transition. Again, this indicates that the probed $\text{C}_2 \text{ A}(\nu = 2) - \text{X}(\nu = 0)$ two-level system is not inverted. In Figure 6, demodulated spectra of multiple additional $\text{C}_2 \text{ A} - \text{X}$ vibration-rotation transitions are shown, measured following photolysis via the $\text{S}_1 3^4$ vibrational state. To generate those spectra, at each frequency step of the FMed laser, the first 30 ns of the FM time trace immediately after the UV excitation (i.e. colour-coded red in Figure 3) is used, in order to minimise the effect of collisions on the nascent C_2 population distribution. The transient nature of the sample (i.e. generated by 7 ns pulsed-laser photolysis) enables use of a portion of the FM time-trace (colour-coded green in Figure 3) before the UV excitation for subtraction of background residual amplitude modulation (RAM).

Notice that the FM lineshapes for all observed $\text{C}_2 \text{ A} - \text{X}$ transitions in Figure 6 are slightly asymmetric, with the magnitude of the lower-frequency lobe systematically larger by $\sim 20\%$ than that of the higher-frequency lobe. We currently do not have an explanation for this observed asymmetry. The asymmetry is not a result of background RAM, because the magnitude of RAM is small ($< 5\%$) compared to that of the strong C_2 signals observed following photodissociation via the $\text{S}_1 3^4$ vibrational state, for which this asymmetry is also observed. The asymmetry is not reduced even after subtraction of the background RAM. This asymmetry does not seem to result from systematic defects of the detection system, because the lineshapes for the observed I_2 transitions [21] and the Rb transition (from this work and Ref. [21]) appear to be nearly symmetric. The presence of asymmetry cannot affect the conclusions regarding the *sign* of the population differences (i.e. whether there is population inversion) between the $\text{C}_2 \text{ A}$ - and X -state levels, because the *sign* of the population differences is reflected in the *phase*, rather than in the magnitude, of the FM signal.

To summarise, from both the FM time-domain signals and the demodulated spectra, we reach the same conclusion that, for all of the $\text{C}_2 \text{ A}(\nu = 2) - \text{X}(\nu = 0)$ two-level systems probed in this work, there is more

Figure 5. Demodulated spectra of the observed $^{85}\text{Rb } 5^2\text{P}_{1/2} \leftarrow 5^2\text{S}_{1/2}$ transition (panels a and b), and the $\text{C}_2 \text{ A}(v' = 2, J' = 8) \leftarrow \text{X}(v'' = 0, J'' = 8)$ transition (panels c and d), measured following photodissociation via the $\text{S}_1 3^4$ vibrational state. The approximate locations for each transition centre are indicated by crosses. For the Rb transition, two absorption lines are resolved, due to the large hyperfine splitting of the lower $5^2\text{S}_{1/2}$ state. [27] In panels a and b, the $F' = 2,3 \leftarrow F'' = 3$ transition is shown in blue, and the $F' = 2,3 \leftarrow F'' = 2$ transition is shown in magenta.

population in the lower-energy X state. It is likely that this population relation applies to all other pairs of $\text{A}(v = 2) - \text{X}(v = 0)$ rotation-vibration levels that we have not probed in the experiment. Based on the time-evolution of the FM signal, the observed X-state population is most likely the nascent population. Contributions from secondary processes, e.g. collisions and fluorescence decays, are likely negligible compared to that from the primary photolysis process. We emphasise that since only the population differences are probed in the FM experiments, we cannot rule out the possibility that the $v = 2$ level of the $\text{C}_2 \text{ A}$ state is also photolytically populated, but with smaller *absolute* population than that of the X state. In the discussion in Sections 3.2 and 3.3, we assume that population in the A-state $v = 2$ level is minimal compared to that in the X-state $v = 0$, i.e. the signal intensity directly reflects the absolute population in the X-state level. In addition, to gain a more complete picture of the relative yield of the $\text{C}_2 \text{ A}$ - and X-state fragments, it would be necessary to carry out additional measurements for the (1,0) and (0,0) bands of the $\text{C}_2 \text{ A} - \text{X}$ transitions. Unfortunately, the transition wavelengths of these two

bands [25, 26] fall outside the operation range of the EOM used in our setup.

3.2. The $\text{C}_2 \text{ X}$ -state population distribution

Signal intensities from the first 30 ns of the FM time-trace of the probed transitions contain information about the nascent C_2 population in the $v = 0$ level of the X state. In Figure 7(a), the intensities of the observed $\text{C}_2 \text{ A} - \text{X}$ transitions are shown that result from resonance-enhanced photodissociation via the $\text{S}_1 3^4$, 3^3 , and 3^2 vibrational levels. The ratios of the maximum $\text{C}_2 \text{ A} - \text{X}$ FM signals are $\text{C}_2(3^4 : 3^3 : 3^2) = 15 : 3 : 1$. These relative intensities are similar to the observed relative transition intensities for excitation into the three intermediate S_1 vibrational levels [32–34], $\text{S}_1(3^4 : 3^3 : 3^2) \leftarrow \text{S}_0 = 14 : 4 : 1$. This suggests that the $\text{C}_2 \text{ X}$ -state photodissociation quantum yields are similar from all three selected S_1 acetylene vibrational levels.

It is also evident in Figure 7(b) that there are differences in the rotational distributions for the $\text{C}_2 \text{ X}$ -state fragments generated from the three S_1

Figure 6. The demodulated spectra of the $C_2 A(v=2) - X(v=0)$ transitions, generated via the S_1 acetylene 3^4 vibrational state. In each plot, the blue and red spectra, correspond, respectively, to the in-phase (blue, with three zero-crossings) and quadrature (red, with one zero-crossing) component of the FM signal. The vertical scales are identical in each plot.

Figure 7. Observed intensities of various Q-branch transitions of the $C_2 A - X (2, 0)$ band. (a) The signal intensities are normalised to the same FMed probe power. (b) The relative intensities are normalised to the maximum intensity from each acetylene intermediate level. (c) Comparison of the intensities of C_2 , generated via the 3^3 level, with a Boltzmann rotational distribution of 750 K.

acetylene vibrational levels. The maximum J -population is centred around $J = 8$ following photodissociation via the $S_1 3^4$ vibrational state, but the maximum rotational population shifts toward higher J -levels ($J = 14$) for 3^3 and 3^2 . In addition, the observed rotational population distributions cannot be fitted to Boltzmann distributions, as shown specifically in Figure 7(c) for the $C_2 X$ -state molecules generated via the $S_1 3^3$ vibrational level. We believe that the *non-statistical* nature of the observed rotational distributions implies the presence of dynamical constraints, such as the transition state geometry,

in the photodissociation process. Information about the dissociation transition states inferred from Figure 7 is discussed in Section 3.5.

3.3. Photodissociation mechanisms

Assuming that the photodissociation proceeds exclusively via a sequential C-H bond-breaking process, for all three acetylene S_1-S_0 excitation energies used in this work, the $C_2 v = 0 X$ -state fragments are energetically accessible via two same-colour photons, based on

the C-H bond dissociation energies of C_2H_2 [2] and C_2H [35]. Population of the C_2 A state requires at least three photons. The larger quantum yield in the C_2 X state than the A state is likely a direct consequence of the energetic advantage of the two-photon X-state dissociation channel over the three-photon A-state channel. The photodissociation pathway, proposed in this section, is summarised below

In this process, the S_1 acetylene is excited by a second photon to an electronically highly-excited acetylene state, $C_2H_2^*$, the ‘dissociation precursor state’. The proposed electronic assignment for this dissociation precursor state ($1^1B_g/1^1B_1$) is discussed in Section 3.4. Dissociation of $C_2H_2^*$ produces C_2H^{**} , which further dissociates to produce the C_2 X state. The excess energy is approximately 0.37 eV, 0.62 eV, and 0.87 eV, respectively, following photolysis via the S_1 3^2 , 3^3 , and 3^4 vibrational levels.

In our previous study of the one-colour (~ 220 nm), resonance-enhanced (S_1-S_0), photodissociation of acetylene [14], we showed that two-photon photodissociation leads to the production of a long-lived ($> 3 \mu s$), electronically-excited C_2H^* species, which fluoresces in the visible region. This long-lived C_2H^* species cannot be the precursor (i.e. C_2H^{**} in Equation (1)) to the production of the C_2 X state, given the fast rise-time of the signals from the observed C_2 A – X transitions. Therefore, for the PFAS-relevant, one-colour, resonance-enhanced photodissociation process of acetylene, we have now proposed two open dissociation channels in the 11 eV region: one that produces C_2 in the X state and the other that produces the long-lived C_2H^* species, which is the most abundant species among the three observed fluorescing photofragments [14]. This long-lived C_2H^* species can be further photolyzed to produce the C_2 C and d states (which are the other two fluorescing species detected in PFAS). The photodissociation pathways for the generation of C_2H^* and various C_2 electronic states are summarised in Figure 8(a). In our proposed ~ 220 nm photolysis mechanisms, we assume that the two open channels at the two-photon energy region originate from the same acetylene dissociation precursor.

Figure 8. A summary of the acetylene photodissociation pathways, following (a) the one-colour (~ 220 nm), resonance-enhanced (S_1-S_0) process and (b) the 193 nm ArF photolysis process (Ref. [20]). The dotted lines indicate the thermodynamic thresholds for the generation of various photodissociation products, with the exception of the long-lived C_2H^* species in panel (a), the assignment of which is currently unknown. The predissociation and first ionisation limits of acetylene are indicated by dashed lines. The mechanisms for the generation of the C_2 C and d states following 193 nm photolysis were not discussed in Ref. [20], and, as far as we know, are currently unknown.

The C_2 X state has been observed previously following 193 nm ArF photolysis studies of acetylene [17–19]. However, as mentioned in the Introduction, following 193 nm photolysis, the quantum yield for the C_2 A state was found to be $\sim 20\times$ larger than that for the X state [18, 19]. In contrast to the 220 nm photolysis process studied in this work, both the A and X states are energetically assessable with the same number of 193 nm photons (two). According to Cui et al. [20], the C_2 A and X states could both be generated via dissociation of the C_2H $4^2A'$ state, which is populated from the C_2H $\tilde{X}^2\Sigma^+$ state ($1^2A'$ in the C_s point-group) by the second 193 nm photon (see Figure 8(b)). A direct barrierless dissociation of C_2H on the $4^2A'$ potential energy surface (PES) could lead to production of the C_2 A state (which correlates to the C_2H $4^2A'$ state at large C-H bond length). In

Figure 9. Potential energy curves calculated at the 7-state-averaged CASSCF/D95(d,p) level (adapted from Ref. [20]) for seven electronic states of C_2H in C_s symmetry, with C-C bond length and CCH bend angle fixed at two sets of values. Solid lines denote A' states, and dashed lines denote A'' states. The adiabatic curves, which correlate to the $C_2(a^3\Pi_u) + H$ dissociation limit, are colour-coded blue, and the adiabatic curve, which correlates to the $C_2(X^1\Sigma_g^+) + H$ dissociation limit, is colour-coded red.

contrast, since the $C_2 X$ state correlates to the C_2H $2^2A'$ state (at $R_{CC} \sim 1.4$ Å, the equilibrium R_{CC} of the precursor $4^2A'$ state), C_2H most likely undergoes a sequence of internal conversions, $4^2A' \rightarrow 3^2A' \rightarrow 2^2A'$, preceding dissociation into the $C_2 X$ state on the $2^2A'$ surface. According to Ref. [20], the direct barrierless dissociation process (to produce the $C_2 A$ state) is more efficient than the sequential internal-conversion-assisted dissociation process (to produce the $C_2 X$ state).

Even though the $C_2 X$ state is most likely generated by the same number of photons (two) in the PFAS-relevant, 220 nm photolysis process as in the 193 nm photolysis, due to the difference in the photon energies, the mechanism by which the $C_2 X$ -state fragments are generated is qualitatively different for 220 nm vs. 193 nm photolysis processes (see Figure 8). Based on the linewidth (~ 100 cm $^{-1}$) of the observed absorption features in the 193 nm excitation region [36], the acetylene S_1 levels initially populated by the 193 nm photon (~ 50 fs lifetime) dissociate rapidly into C_2H ($\tilde{X}^2\Sigma^+$ and $\tilde{A}^2\Pi$) + H. As a consequence of this fast dissociation, the S_1 level is not directly involved in the subsequent steps of the photodissociation process and the observed $C_2 X$ -state populations are generated from the C_2H $\tilde{X}^2\Sigma^+$ molecules [18, 20, 37, 38] (see Figure 8(b)). In contrast, the S_1 intermediate levels involved in the 220 nm photolysis process studied in this work either lie below the acetylene predissociation threshold (the 3^2 and 3^3 $K = 1$ levels), or are only weakly predissociated (the 3^4 $K = 1$ level has a > 200 ns fluorescence lifetime [14]). Given that either zero or a negligible amount of the C_2H $\tilde{X}$ -state

species is present during the 220 nm photolysis pulse (7 ns), the production of the $C_2 X$ state must result from direct 220 nm photodissociation of the S_1 acetylene level (Equation (1b)) (see Figure 8(a)).

Based on the symmetry and vibrational characters of the intermediate S_1 *trans*-conformer levels (3^2 , 3^3 , and 3^4), some important characteristics of the dissociation precursor, $C_2H_2^*$, can be identified. First, since the S_1 *trans*-conformer, with *ungerade* electronic symmetry, is an intermediate in the photodissociation process, the transition into the $C_2H_2^*$ precursor state (in the 11 eV energy region) must be one-photon allowed from the S_1 level. This excludes all of the centro-symmetric *ungerade* acetylene valence states as candidates for the precursor. In addition, given the similar photodissociation cross-sections to produce the $C_2 X$ state from the three S_1 vibrational levels (3^2 , 3^3 , and 3^4), which have different numbers of quanta in the mode-3 *trans*-bending vibrational excitation, the CCH bend angle of the $C_2H_2^*$ precursor state, must not be too different from that of the S_1 *trans*-bent conformer. As a result, the $C_2H_2^*$ precursor is likely not an acetylene Rydberg state, all of which are known to have the linear equilibrium geometry of the cation core [39, 40]. The electronic assignment of the $C_2H_2^*$ dissociation precursor state is discussed in Section 3.4.

Energetically, the C_2H^{**} species (i.e. the dissociation product of $C_2H_2^*$ in Equation (1c)) can only be one of the low-lying electronic states [20, 41, 42], $\tilde{X}^2\Sigma^+$ ($1^2A'$), $\tilde{A}^2\Pi$ ($1^2A''$ and $2^2A'$), $2^2\Sigma^+$ ($3^2A'$), and $2^2\Pi$ (the $2^2A''$ component only), for which the

electronic symmetries shown in parentheses are the symmetry-labels in the C_s point-group. As shown in Figure 9, direct adiabatic dissociation (to produce the $C_2 X$ state) could take place on both $1^2A'$ and $2^2A'$ PES's of C_2H , because the $C_2 X$ state correlates to $1^2A'$ and $2^2A'$ states at different C-C bond lengths [20], i.e. $1^2A' \rightarrow C_2(X)+H$ at short C-C bond length (e.g. $R_{CC}=1.25 \text{ \AA}$) and $2^2A' \rightarrow C_2(X)+H$ at long C-C bond length (e.g. $R_{CC}=1.4 \text{ \AA}$). This change in the adiabatic correlation (as a function of C-C bond length) occurs because, while the $X^1\Sigma_g^+$ state is the lowest-energy C_2 state near the X -state equilibrium bond-length ($1.243 \text{ \AA}$) [43], the $C_2 a^3\Pi_u$ state becomes lower in energy than the X state at longer C-C bond-length ($> 1.35 \text{ \AA}$). There is, however, a large dissociation barrier on the $2^2A'$ PES (see the red curve in Figure 9(b)). This barrier might reduce the efficiency of direct adiabatic dissociation on that surface. However, if the dissociation precursor belongs to the $3^2A'$ electronic state, internal conversion to either $1^2A'$ or $2^2A'$ would be required. Symmetry constraints preclude the $C_2H 1^2A''$ and $2^2A''$ states from being the precursors for the $C_2 X$ state, unless there is an unusually strong electronic-rotational interaction between $2A''$ and $2A'$ electronic states [20]. Without such an interaction, only the $C_2 a^3\Pi_u$ state could be generated after dissociation of the $1^2A''$ and $2^2A''$ states of C_2H .

3.4. Assignment for the $C_2H_2^*$ dissociation precursor state

Based on the available experimental information on the $C_2H_2^*$ dissociation precursor state (from both this work and Ref. [14]) and results from a new *ab initio* calculation (MRCI) on the acetylene excited valence states [44], we propose that the $C_2H_2^*$ state is most likely the $1^1B_g(\text{trans-bent})/1^1B_1(\text{cis-bent})$ valence state. Before discussing the electronic assignment, we briefly summarise the known spectroscopic properties of the $C_2H_2^*$ dissociation precursor state. In Ref. [14], we reported observation of the $C_2 C$ and d states, and an unassigned long-lived C_2H^* species, all of which are formed subsequent to photodissociation via the S_1 *cis*-conformer $3^1\delta^1$ and *trans*-conformer 3^4 vibrational levels. Given that the photodissociation quantum yields for all three photolysis products (C_2H^* , and $C_2 C$ and d states) are similar from both of the two close-lying S_1 *trans*- and *cis*-conformer vibrational levels, we concluded that the one-photon transition probabilities into the super-excited $C_2H_2^*$ state are similar from these two *trans*- and *cis*-conformer S_1 vibrational levels. As discussed in Section 3.3, the $C_2H_2^*$ dissociation precursor state is most likely an excited valence state with non-linear equilibrium geometry. In

addition, if a *trans*-bent conformer exists for that excited valence state, the *trans*-conformer must have *gerade* electronic symmetry.

As summarised in Table 2 of Ref. [40], five singlet excited valence states have been experimentally characterised for the acetylene molecule. All five states support *trans*-bent conformers, but not the linear conformer. Four of these singlet valence states, which include the S_1 state, derive from the singly-excited electron configuration at linear geometry. Note that, the description, 'singly-excited', refers to excitation, at linear geometry, of one electron from the bonding $1\pi_u$ orbital into the anti-bonding $1\pi_g$ orbital, i.e. $(1\pi_u)^3(1\pi_g)^1 \leftarrow (1\pi_u)^4$. Given that all the singly-excited valence states are known to have *ungerade* electronic symmetry at the *trans*-bent geometry, they cannot be the $C_2H_2^*$ dissociation precursor state involved in the $\sim 220 \text{ nm}$ photolysis process. As a result, it is necessary to look beyond the singly-excited valence states for an identification of the $C_2H_2^*$ dissociation precursor state.

In Table 2 of Ref. [40], the doubly-excited, $(1\pi_u)^2(1\pi_g)^2$, $\tilde{C}'$ state is the only listed acetylene valence state in the two-photon energy region that has *gerade* symmetry at the *trans*-bent geometry (1^1A_g). However, as discussed below, based on the expected Franck-Condon weakness of the $\tilde{C}' \leftarrow S_1$ (*cis*) transition, we do not believe that the $\tilde{C}'$ state is a plausible candidate for the $C_2H_2^*$ state.

Experimentally [45], only the *trans*-conformer of the $\tilde{C}'$ state has been characterised via a two-colour, double-resonance excitation scheme, $1^1A_g(\tilde{C}') \leftarrow 1^1A_u(S_1) \leftarrow 1^1\Sigma_g^+(S_0)$, through various S_1 *trans*-conformer vibrational levels. Transitions into the $\tilde{C}'$ -state *trans*-conformer well are likely significantly weaker from the S_1 *cis*-conformer (1^1A_2) than from the S_1 *trans*-conformer, due to the large geometry change involved in a *trans* $\leftarrow$ *cis* electronic transition (because of small Franck-Condon factors). According to a new *ab initio* calculation on the acetylene valence states [44], the $\tilde{C}'$ -state PES supports a *cis*-bent equilibrium structure (with A_1 electronic symmetry) in addition to a *trans*-bent equilibrium structure. However, the $1^1A_1(\tilde{C}') \leftarrow 1^1A_2(S_1)$ transition is electric-dipole symmetry-forbidden. The $\tilde{C}' \leftarrow S_1$ (*cis*) transition is thus expected to be significantly weaker than the $\tilde{C}' \leftarrow S_1$ (*trans*) transition, which is inconsistent with the experimental observation that the transition probabilities into the $C_2H_2^*$ dissociation precursor state are similar from the S_1 *trans*- and S_1 *cis*-conformer vibrational levels.

As shown in Figure 4 of Ref. [40], the PES for the second-lowest energy, doubly-excited valence state supports a *trans*-bent equilibrium structure. The minimum of this *trans*-conformer well (1^1B_g) lies at $\sim 9.5 \text{ eV}$, which is well below the two-photon energy for the

~ 220 nm photolysis process (~ 11 eV). The (*trans* $\leftarrow$ *cis*) $1^1B_g \leftarrow 1^1A_2$ (S_1) electronic transition is expected to be significantly weaker than the (*trans* $\leftarrow$ *trans*) $1^1B_g \leftarrow 1^1A_u$ (S_1) transition. However, if the PES for this second doubly-excited state also supports a *cis*-conformer well (with B_1 symmetry), the transition probability for the *cis* $\leftarrow$ *cis* electronic transition, $1^1B_1 \leftarrow 1^1A_2$ (S_1) (which is a dipole-allowed *a*-axis transition), can be expected to be similar to that of the dipole-allowed, *trans* $\leftarrow$ *trans* transition, $1^1B_g \leftarrow 1^1A_u$ (S_1).

Given our current experimental knowledge of the $C_2H_2^*$ state, we believe that this second-lowest energy, doubly-excited state is the only reasonable candidate for the super-excited acetylene dissociation precursor state in the two-photon region. We further hypothesise that its PES supports both *trans*- and *cis*-bent equilibrium structures. While the existence of a *cis*-bent equilibrium geometry was not reported in Ref. [40], the new *ab initio* calculation on the acetylene valence states indicates that the second doubly-excited PES supports a *cis*-bent conformer ($T_e = 7.88$ eV, $\angle_{CCH} = 108.2^\circ$, $R_{CC} = 1.587$ Å, $R_{CH} = 1.117$ Å), in addition to the *trans*-bent conformer ($T_e = 9.29$ eV, $\angle_{CCH} = 115.2^\circ$, $R_{CC} = 1.564$ Å, $R_{CH} = 1.101$ Å). According to the Walsh diagram for the CC-H bending coordinate of the H-CC-H molecule, the doubly-occupied, anti-bonding $1\pi_g$ orbital correlates to the $4a_g$ and $3b_2$ orbitals for the 1^1B_g and 1^1B_1 states, respectively. Similar to the $\tilde{C}'$ state, the bent geometries for this $1^1B_g/1^1B_1$ state are due to stabilisation of the $4a_g$ (*trans*-bent) and $3b_2$ (*cis*-bent) orbitals with respect to the $1\pi_g$ orbital along the bending coordinate, because bending reduces the anti-bonding interaction in the $1\pi_g$ orbital. The larger R_{CC} values for the $(1\pi_u)^2(1\pi_g)^2$ 1^1B_1 *cis*- and 1^1B_g *trans*-conformers than their $(1\pi_u)^3(1\pi_g)^1$ S_1 counterparts (1.347 Å and 1.379 Å, respectively) [8, 12] can be explained by the presence of an additional electron in an anti-bonding $1\pi_g$ orbital. Detailed results from the new *ab initio* calculation will be reported in a future paper [44].

3.5. Transition state geometry

For the proposed sequential bond breaking process described by Equation (1), the rotational distribution of the C_2 X-state fragments is affected by both the rotation of the parent $C_2H_2^*$ precursor state, and the fragment (C_2H^{**} and C_2) recoil angular momenta induced by the two C-H bond breaking processes (Equations (1c) and (1d)). Given that the three sampled S_1 intermediate levels have similar rotational quantum number ($J = 8$ for the 3^2 and 3^3 states, and $J = 7$ for the 3^4 state), it is reasonable to assume that the $C_2H_2^*$ precursor state is populated in similar J values for excitation via the three S_1

rovibrational levels. This means that the difference in the observed X-state rotational population distributions (see Figure 7(b)) is most likely due to a difference in the C-H bond dissociation process among the three S_1 photolysis pathways.

We believe that the observed C_2 X-state rotational distributions contain important information about the geometry of the dissociation transition states, H-CCH and CC-H, involved in the production of the C_2 X state. As we propose below, the difference in the observed rotational population distributions might be a consequence of different transition state geometries along the three S_1 photolysis pathways. We further propose that at least one of the two transition states involved in the S_1 3^4 photolysis has a larger $\angle_{CC-H}$ (i.e. the H-atom departs nearly along the CC-bond direction) than that for the other two S_1 pathways. This interpretation is consistent with the vibrational character of the three intermediate S_1 vibrational levels.

To demonstrate the relationship between the C_2 rotational distribution and the transition state geometry, we use the CC-H bond dissociation process (Equation (1d)) as an example. Considering conservation of angular momentum, the recoil angular momentum, L , for the C_2 fragment induced by the process given by Equation (1d), is related to the H-atom recoil velocity, v , and the impact parameter, b (see Figure 10), by [46]

$$L\hbar = \mu vb, \quad (2)$$

where μ is the reduced mass for the CC+H system. As can be seen from Figure 10 and Equation (2), for the same H-atom recoil velocity, dissociation through a transition state with $\angle_{CC-H} = 90^\circ$ (with the largest possible b value, $b = R_{CC}/2$) leads to maximum rotational excitation in the C_2 fragment (constrained by Equation (2)) while dissociation through a transition state with $\angle_{CC-H} = 0^\circ$ (a linear geometry with $b = 0$) results in no additional rotational excitation. Similar arguments can be made about the rotational excitation in C_2H^{**} following dissociation of $C_2H_2^*$ (Equation (1c)). We emphasise that, without a definitive electronic assignment for the CCH^{**} state and information about its rovibrational distribution, it is not possible to disentangle the recoil angular momenta generated in the two dissociation steps, Equations (1c) and (1d), from the observed C_2 X-state rotational distributions. Nevertheless, some qualitative features about the transition states involved in the C_2 X-state generation can be inferred from those distributions.

As mentioned earlier in this section, among the S_1 3^2 , 3^3 , and 3^4 photolysis processes studied in this work, the

Figure 10. A cartoon for the transition state geometry in the CC–H dissociation channel. Due to the light mass of the hydrogen atom relative to that of the CC fragment, the centre of mass (c.m.) of the transition state is located close to the midpoint of the CC bond.

excess energy in generating the C_2 X state is largest following photolysis via the S_1 3^4 vibrational state. Assuming that the C_2H^{**} state is generated with similar rovibrational distributions via the three S_1 photolysis processes, the H-atom recoil velocity (for both steps described by Equations (1c) and (1d)) should be largest following excitation via the S_1 3^4 state. According to Equation (2), a departing H-atom with a larger recoil velocity imparts more torque to the remaining molecular fragment. With the same transition state geometry (and hence the same value of b), C_2 fragments generated via S_1 3^4 photolysis are thus expected to have the highest degree of rotational excitation. However, as can be seen in Figure 7(b), while there is a small hump at $J \sim 26$ for C_2 generated via the S_1 3^4 state, its maximum C_2 J -population appears to occur at a smaller J value than that generated via the S_1 3^2 and 3^3 states.

We propose that the lower C_2 rotational excitation following the S_1 3^4 photolysis could be explained by a smaller impact parameter, b , for at least one of the transition states involved in the S_1 3^4 photolysis than that in the S_1 3^2 and 3^3 pathways. While a shorter CC-bond at that transition state could lead to a smaller value of b , it is more likely that the transition state has a larger value of $\angle_{CC-H}$ along the S_1 3^4 pathway, i.e. the H-atom departs nearly along the CC-bond direction. For members of the S_1 3^n *trans*-bent vibrational progression, the A rotational constants increase much more rapidly as a function of n ($\sim 10\%$ increase per quantum of mode 3) compared to the B and C rotational constants ($\ll 1\%$ increase per quantum) [22, 24]. Therefore, while the effective CC bond lengths (~ 1.375 Å) are similar for the three intermediate S_1 levels, the effective $\angle_{CCH}$ is larger for the S_1 3^4 vibrational state (134.2°) than that for the S_1 3^2 and 3^3 states (127.8° and 130.4° , respectively). A larger effective

$\angle_{CCH}$ for the S_1 3^4 state could lead to a larger Franck-Condon overlap between the S_1 level and a near-linear dissociation pathway. In other words, photodissociation via the three S_1 vibrational levels retains some ‘memory’ of the S_1 vibrational character.

We emphasise that, based on the available information on the acetylene ~ 220 nm photolysis process, we cannot rule out the direct H_2 elimination pathway,

as a mechanism for the generation of the C_2 X state. The H_2 elimination path is two-photon allowed, and has a lower thermodynamic threshold (by ~ 4.5 eV) than the sequential bond-breaking path (Equation (1)). As discussed in Ref. [14], the transition state associated with this H_2 elimination path should have a near-*cis* geometry, i.e. the two hydrogen atoms on the same side of the CC bond. The H_2 elimination process would likely be more efficient for photodissociation from an S_1 *cis*-conformer level than from an S_1 *trans*-conformer level, because the *cis* level must have a significantly larger Franck-Condon overlap with the elimination reaction path than the *trans* level. For the generation of the C_2 C state following acetylene 220 nm photolysis studied in Ref. [14], the H_2 elimination pathway was ruled out based on the similar photodissociation quantum yields from the close-lying S_1 *cis* 3^16^1 and S_1 *trans* 3^4 $K = 1$ levels. To study the role of the direct H_2 elimination pathway in the generation of the C_2 X state, it would be informative to carry out a similar study to compare the photodissociation quantum yields from those two S_1 conformer levels. The photodissociation quantum yield should be higher from the S_1 *cis* level than the S_1 *trans* level if the H_2 elimination path contributes to the generation of the C_2 X state.

4. Conclusion

Using FM spectroscopy, we observe multiple vibration-rotation transitions of the C_2 $A^1\Pi_u(v=2) - X^1\Sigma_g^+(v=0)$ bands, following one-colour (~ 220 nm), resonance-enhanced (via the S_1 *trans*-conformer 3^2 , 3^3 , and 3^4 vibrational levels), photodissociation of acetylene. By comparing the phase of the FM signals from the C_2 $A - X$ transitions with that from the Rb D_1 -line absorption transition, we determine that, for all of the probed C_2 $A - X$ vibration-rotation transitions, the population in the X-state vibrational level is larger than that in the A-state vibrational level. The production of the C_2 X state is likely the result of a two-photon process via all three sampled S_1 acetylene intermediate vibrational

levels. The energetic advantage of the X -state dissociation channel (two photons) over the A -state channel (three photons) likely explains the difference in the quantum yields for the two channels. The photodissociation quantum yields for the $C_2 X$ state are similar from the three S_1 vibrational levels.

Given the long lifetime (> 200 ns) of the intermediate S_1 levels involved in the 220 nm photolysis process studied in this work, the production of the $C_2 X$ state must result from *direct* photo-excitation of the S_1 levels. We proposed that the super-excited acetylene molecule at the two-photon level ($C_2H_2^*$) undergoes a sequential C-H bond-breaking process to produce the $C_2 X$ state. The mechanism for the 220 nm acetylene photolysis process is qualitatively different from that of the widely studied 193 nm photolysis process. In 193 nm photolysis, the $C_2 X$ -state fragments are generated as a result of photo-excitation of the $C_2H \tilde{X}^2\Sigma_g^+$ molecule, which is the predissociation product of the S_1 acetylene level excited by the first 193 nm photon.

Based on the known spectroscopic characters of the $C_2H_2^*$ dissociation precursor state (from both this work and Refs. [1, 14]), we propose that the $C_2H_2^*$ state is most likely the second doubly-excited valence state, which has an $(1\pi_u)^2(1\pi_g)^2$ configuration at linear geometry. We base our suggestion on the fact that its potential energy surface supports both *trans*-bent (1^1B_g) (which was reported in Ref. [40]) and *cis*-bent (1^1B_1) conformers. The existence of the *cis*-bent conformer is confirmed by results of a new *ab initio* calculation [44].

From the observed $C_2 X$ -state rotational distributions, we further propose that, for the 220 nm photolysis of acetylene, the geometries of the two dissociation transition states along the sequential C-H bond-breaking path might be different following photo-excitation of the three sampled S_1 acetylene levels. At least one of the transition states involved in the S_1 3^4 photolysis appears to act as less bent than that involved in the other two S_1 photolysis pathways.

Acknowledgments

The authors are grateful to the anonymous reviewer for suggesting the doubly-excited state as a possible assignment for the super-excited acetylene precursor state at the two-photon level. The authors also thank Dr. Gregory Hall from Brookhaven National Laboratory for the loan of multiple FM components, and provided useful advice on the FM setup. This material is based upon work supported by the U.S. Department of Energy, Office of Science, Chemical Sciences, Geosciences, and Biosciences Division of the Basic Energy Sciences Office, under Award Number DE-FG0287ER13671. The Ti-sapphire laser and the solid-state 532 nm pump laser are provided by the Air Force Office of Scientific Research, under grant number FA9550-16-1-0117. The manuscript preparation was carried

out at Lawrence Livermore National Laboratory under the auspices of the U.S. Department of Energy under Contract DE-AC52-07NA27344.

Disclosure statement

No potential conflict of interest was reported by the author(s).

Funding

This work was supported by Air Force Office of Scientific Research [grant number FA9550-16-1-0117] and Basic Energy Sciences [grant number DE-FG0287ER13671] and Lawrence Livermore National Laboratory [grant number DE-AC52-07NA27344].

ORCID

Jun Jiang <http://orcid.org/0000-0002-3526-3797>

Zhenhui Du <http://orcid.org/0000-0002-3102-8773>

Robert W. Field <http://orcid.org/0000-0002-7609-4205>

References

- [1] J. Jiang, C.A. Saladrigas, T.J. Erickson, C.L. Keenan and R.W. Field, *J. Chem. Phys.* **149**, 174309 (2018).
- [2] D.H. Mordaunt and M.N. Ashfold, *J. Chem. Phys.* **101**, 2630 (1994).
- [3] A.H. Steeves, H.A. Bechtel, A.J. Merer, N. Yamakita, S. Tsuchiya and R.W. Field, *J. Mol. Spectrosc.* **256**, 256 (2009).
- [4] A.J. Merer, A.H. Steeves, J.H. Baraban, H.A. Bechtel and R.W. Field, *J. Chem. Phys.* **134**, 244310 (2011).
- [5] J.H. Baraban, A.R. Beck, A.H. Steeves, J.F. Stanton and R.W. Field, *J. Chem. Phys.* **134**, 244311 (2011).
- [6] J.H. Baraban, P.B. Changala, A.J. Merer, A.H. Steeves, H.A. Bechtel and R.W. Field, *Mol. Phys.* **110**, 2707 (2012).
- [7] J.H. Baraban, J. Stanton, A. Merer and R.W. Field, *Mol. Phys.* **110**, 2725 (2012).
- [8] J. Jiang, J.H. Baraban, G.B. Park, M.L. Clark and R.W. Field, *J. Phys. Chem. A* **117**, 13696 (2013).
- [9] P.B. Changala, *J. Chem. Phys.* **140**, 024312 (2014).
- [10] P.B. Changala, J.H. Baraban, J.F. Stanton, A.J. Merer and R.W. Field, *J. Chem. Phys.* **140**, 024313 (2014).
- [11] J.H. Baraban, P.B. Changala, G.C. Mellau, J.F. Stanton, A.J. Merer and R.W. Field, *Science* **350**, 1338 (2015).
- [12] J.H. Baraban, D.A. Matthews and J.F. Stanton, *J. Chem. Phys.* **144**, 111102 (2016).
- [13] P.B. Changala, J.H. Baraban, A.J. Merer and R.W. Field, *J. Chem. Phys.* **143**, 084310 (2015).
- [14] J. Jiang, A.K. Muthike, T.J. Erickson and R.W. Field, *J. Mol. Spectrosc.* **361**, 24 (2019).
- [15] J. McDonald, A. Baronavski and V. Donnelly, *Chem. Phys.* **33**, 161 (1978).
- [16] H. Okabe, R. Cody and J. Allen, *Chem. Phys.* **92**, 67 (1985).
- [17] R. Urdahl, Y. Bao and W.M. Jackson, *Chem. Phys. Lett.* **152**, 485 (1988).
- [18] B. Balko, J. Zhang and Y.-T. Lee, *J. Chem. Phys.* **94**, 7958 (1991).
- [19] O. Sorkhabi, V.M. Blunt, H. Lin, D. Xu, J. Wrobel, R. Price and W.M. Jackson, *J. Chem. Phys.* **107**, 9842 (1997).

- [20] Q. Cui and K. Morokuma, *J. Chem. Phys.* **108**, 626 (1998).
- [21] J. Jiang, Z. Du and R.W. Field, *Mol. Phys.* **0**, 1 (2019).
- [22] J. Watson, M. Herman, J. Van Craen and R. Colin, *J. Mol. Spectrosc.* **95**, 101 (1982).
- [23] J. Van Craen, M. Herman, R. Colin and J. Watson, *J. Mol. Spectrosc.* **111**, 185 (1985).
- [24] A.J. Merer, Z. Duan, R.W. Field and J.K. Watson, *Can. J. Phys.* **87**, 437 (2009).
- [25] J.G. Phillips, *Astrophys. J.* **107**, 389 (1948).
- [26] J. Chauville, J. Maillard and A. Mantz, *J. Mol. Spectrosc.* **68**, 399 (1977).
- [27] D.A. Steck, *Rubidium 85 D Line Data* (2013). <http://steck.us/alkalidata/>.
- [28] D.A. Steck, *Rubidium 87 D Line Data* (2013). <http://steck.us/alkalidata/>.
- [29] W. Bauer, K. Becker, C. Hubrich, R. Meuser and J. Wildt, *Astrophys. J.* **296**, 758 (1985).
- [30] L. Curtis, B. Engman and P. Erman, *Phys. Scr.* **13**, 270 (1976).
- [31] W.H. Smith, *Astrophys. J.* **156**, 791 (1969).
- [32] C. Ingold and G. King, *J. Chem. Soc.* 2702 (1953).
- [33] J.K. Watson, *J. Mol. Spectrosc.* **207**, 276 (2001).
- [34] G.B. Park, *J. Chem. Phys.* **141**, 134304 (2014).
- [35] W.-Y. Chiang and Y.-C. Hsu, *J. Chem. Phys.* **112**, 7394 (2000).
- [36] P. Foo and K. Innes, *Chem. Phys. Lett.* **22**, 439 (1973).
- [37] A.M. Wodtke and Y. Lee, *J. Phys. Chem.* **89**, 4744 (1985).
- [38] Y.-C. Hsu, F.-T. Chen, L.-C. Chou and Y.-J. Shiu, *J. Chem. Phys.* **105**, 9153 (1996).
- [39] M. Takahashi, M. Fujii and M. Ito, *J. Chem. Phys.* **96**, 6486 (1992).
- [40] F. Laruelle, S. Boyé-Péronne, D. Gauyacq and J. Liévin, *The Journal of Physical Chemistry A* **113**, 13210 (2009).
- [41] S.-K. Shih, S.D. Peyerimhoff and R.J. Buenker, *J. Mol. Spectrosc.* **74**, 124 (1979).
- [42] D. Duflo, J.-M. Robbe and J.-P. Flament, *J. Chem. Phys.* **100**, 1236 (1994).
- [43] K.-P. Huber and G. Herzberg, *Molecular Spectra and Molecular Structure: IV. Constants of Diatomic Molecules* (Van Nostrand Reinhold Company, Princeton, NJ, 1979).
- [44] J. Liévin, J. Jiang and R.W. Field, Work under preparation.
- [45] J.K. Lundberg, Y. Chen, J.-P. Pique and R.W. Field, *J. Mol. Spectrosc.* **156**, 104 (1992).
- [46] D.H. Mordaunt, M.N. Ashfold, R.N. Dixon, P. Löffler, L. Schnieder and K.H. Welge, *J. Chem. Phys.* **108**, 519 (1998).