

# The strong field photoelectron spectroscopy of acetylene: Evidence for short-lived $4p$ *gerade* states via electric field-induced resonance-enhanced multiphoton ionization

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We report the intense field photoelectron spectra of acetylene, excited using 780 nm, 135 fs radiation for intensities ranging from 5.7 to  $8.6 \times 10^{13} \text{ W cm}^{-2}$ . Three features observed at 1.59, 1.95, and 2.13 eV are repeated at higher energies throughout the spectra as above threshold ionization features. A method for analysis of the spectra and assignment of peaks is presented, based on intensity dependent shifting of intermediate states and ponderomotive shifts of the ionization potential. We present evidence for the observation of previously unobserved *gerade* states in the region of 9.81–10.35 eV. © 2000 American Institute of Physics. [S0021-9606(00)00702-9]

The photoelectron spectroscopy of polyatomic molecules exposed to intense ( $> 10^{13} \text{ W/cm}^2$ ), near infrared radiation provides a basis for understanding the properties of molecules in regimes where the electric field of the laser is on the order of the field binding valence electrons to nuclei. This relatively unexplored area is expected to involve Stark shifting of excited states,<sup>1</sup> massive shifting of ionization potentials (IP),<sup>1</sup> above threshold ionization (ATI),<sup>2</sup> and tunnel ionization.<sup>3</sup> Similar investigations of atomic systems revealed evidence for ATI,<sup>2</sup> Freeman resonances,<sup>4</sup> and shifting of the ionization potential to the full ponderomotive potential of the laser.<sup>5</sup> In this report, we focus on the intense field photoelectron spectroscopy of a polyatomic molecule, acetylene,  $\text{C}_2\text{H}_2$ . This molecule is investigated because of the relative simplicity of the single photon photoelectron spectra,<sup>6</sup> displaying well-separated peaks with little vibrational structure due to significant Franck–Condon overlap between ground state neutral and ionic systems. Additionally, we sought a molecule for which the spectroscopy is reasonably well understood at high excitation energies.

Much work has been done with low intensity ( $< 10^7 \text{ W cm}^{-2}$ ) nanosecond lasers to elucidate the high lying electronic states of acetylene.<sup>7–16</sup> *Ungerade* states have been observed at 5.23,<sup>17</sup> 6.71,<sup>18</sup> 8.16,<sup>19</sup> and 9.24 (Ref. 19) to 10.59 eV,<sup>15</sup> as shown in Fig. 1. Previous work has characterized *gerade* states in the energy region 9.02 eV–9.62 eV (Refs. 11, 12) and in the region very close to the ionization limit of 11.4 eV.<sup>15</sup> It has been suggested that a fast nonradiative decay channel exists above about 9.4 eV, inhibiting the observation of higher lying *gerade* states.<sup>11,15</sup> All previous spectroscopic investigations have been performed in the perturbative limit, that is where the electric field of the laser causes a small perturbation to the field-free molecular Hamiltonian. Thus in the previous work, the laser frequency must be tuned to probe various excited states. In the intense-field limit, the electric field of the laser causes a significant per-

turbation to (with shifts of) the corresponding electronic states of the molecule. This allows a novel state-selective spectroscopic interrogation of the molecule via field-induced resonance-enhanced multiphoton ionization (FIREMPI), using only the fundamental frequency of the laser. Here, we study the intense field photoelectron spectra of  $\text{C}_2\text{H}_2$  using ultrafast, near infrared laser pulses. From the measured photoelectron spectra and their intensity dependence we present evidence for the observation of *gerade* states in the region 9.81–10.35 eV.

The experimental apparatus<sup>20</sup> consists of a 10 Hz, regeneratively-amplified 780 nm, Ti: sapphire femtosecond laser system capable of producing energies of 1.5 mJ/pulse, with a pulse duration of 135 fs. The laser was focused to a 90  $\mu\text{m}$  diam spot size using a 20 cm focal length lens. Photoelectron spectra were collected using a linear time of flight system with a  $\mu$ -metal shielded ionization and drift region.  $\text{C}_2\text{H}_2$  gas was leaked into the chamber at a pressure of  $2.5 \times 10^{-5}$  Torr. The background pressure of the chamber was  $3 \times 10^{-8}$  Torr.

The photoelectron spectrum for  $\text{C}_2\text{H}_2$  excited using  $5.7 \times 10^{13} \text{ W cm}^{-2}$ , 780 nm radiation is shown in Fig. 2(a). There is a triplet of peaks visible in the low energy region of the spectrum, whose constituent members have kinetic energies 1.59 eV, 1.95 eV, and 2.13 eV. The triplet is repeated at higher kinetic energies as a result of higher order ATI as denoted by the vertical dashed lines. The energy spacing between any constituent peak and the next ATI feature is the photon energy, which at 780 nm is 1.59 eV. Figures 2(b) and 2(c) shows the photoelectron spectra obtained at higher values of laser intensity corresponding to  $6.88 \times 10^{13} \text{ W cm}^{-2}$  and  $8.61 \times 10^{13} \text{ W cm}^{-2}$ , respectively. The relative intensity of a feature in the triplet is observed to vary as a function of laser intensity. At higher intensity, the lowest energy feature (1.59 eV) increases in cross section, while the feature at 2.13 eV diminishes.

To determine the origin and fluence dependence of the features observed in the intense laser photoelectron spectrum, we assume that an intermediate state shifts into reso-

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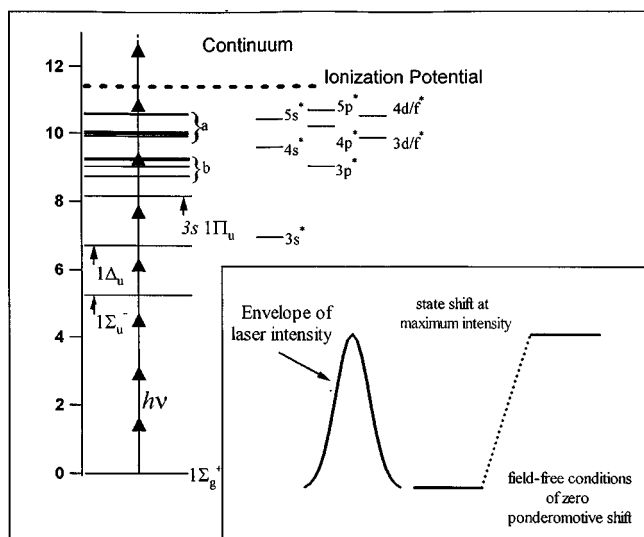


FIG. 1. Energy level diagram for acetylene. Rydberg states calculated from  $E_{\text{state}} = \text{IP} - R_M / (n - \delta)^2$ , where  $R_M = 13.6055$  eV,  $\text{IP} = 11.4$  eV, and  $\delta = 1.25$  for  $s$  levels, 0.6 for  $p$  levels, and 0 for  $d$  and  $f$  levels. (a) Includes  $3d\ ^1\Pi_u$ ,  $4s\ ^1\Pi_u$ ,  $3d\ ^1\Pi_u$ ,  $3d\ ^1\Delta_u$ ,  $3d\ ^1\Sigma_u^-$ ,  $4d\ ^1\Pi_u$ ,  $5s\ ^1\Pi_u$ ,  $4d\ ^1\Pi_u$ . (b) Includes  $3p\ ^1\Pi_g$ ,  $3p\ ^1\Delta_g$ ,  $3p\ ^1\Sigma_g^-$ ,  $3p\ ^1\Sigma_g^+$ ,  $3d\ ^1\Pi_u$ ,  $3d\ ^1\Sigma_u^+$ .

nance with some  $l$  photon excitation process.<sup>21</sup> Shifts of several electronvolts are possible at the laser intensities employed here. The resonantly excited molecule then absorbs  $m$  additional photons to exceed the ionization potential (IP) (which has also undergone a field-induced shift to higher energies). It is important to note that the energy of the  $l$  photon resonance can exceed the field free IP. This is because the IP can be shifted to some higher, intensity dependent value,  $\text{IP}'(I)$ , by any fraction of the maximum, intensity dependent ponderomotive potential [ $U_p(I)$ ] as given by

$$U_p(I) = \frac{e^2 E_0^2}{4m_e \omega^2}, \quad (1)$$

where  $e$  is the fundamental charge,  $E_0 = (2I/\epsilon_0 c)^{1/2}$  is the electric field of the laser,  $m_e$  is the electron mass and  $\omega$  is the angular frequency. Given the ionization potential of acetylene (11.4 eV) and the maximum ponderomotive shift obtainable from our laser (4.9 eV), we need only consider the 6, 7, 8, and 9 photon resonances as shown in Fig. 1. The intensity of a given feature as a function of laser intensity is also important. Bucksbaum *et al.*<sup>21</sup> have shown that states shift through a continuum of energies as the laser pulse oscillates in intensity as shown in the inset to Fig. 1. Furthermore states shifting into  $l$ -photon resonance by a value close to the maximum ponderomotive potential spend the most time in resonance leading to an enhancement of signal. To assign a feature we analyze all states lying within the maximum ponderomotive shift of the  $l$  photon resonance and calculate the expected electron kinetic energy for each. States that correspond to the observed features are then analyzed for an intensity dependence in light of the shift required for resonance.

The procedure for assigning the origin of the observed features begins with the Hamiltonian for a free-electron interacting with a radiation field,

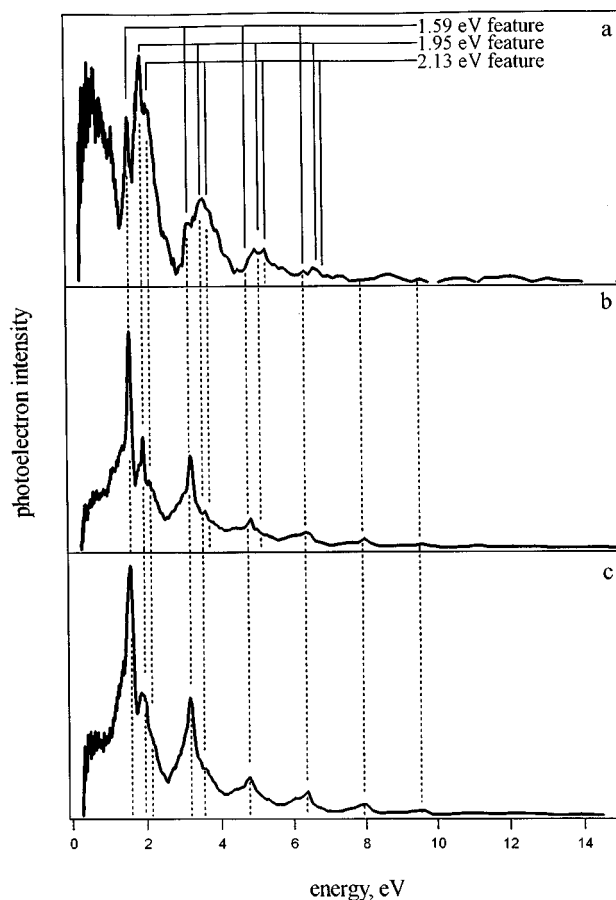


FIG. 2. The photoelectron spectra of acetylene obtained as a function of 780 nm laser intensity. The scaling factors are 0.25:1:1 for a, b, c, respectively. (a) Photoelectron spectrum of acetylene obtained using 780 nm,  $5.74 \times 10^{13}$  W/cm<sup>2</sup> (corresponding to a maximum ponderomotive potential of 3.3 eV). (b) Photoelectron spectrum of acetylene obtained using 780 nm,  $6.88 \times 10^{13}$  W/cm<sup>2</sup> (corresponding to a maximum ponderomotive potential of 3.9 eV). (c) Photoelectron spectrum of acetylene obtained using 780 nm,  $8.61 \times 10^{13}$  W/cm<sup>2</sup> (corresponding to a maximum ponderomotive potential of 4.9 eV).

$$H = \frac{[p - (e/c)\mathbf{A}]^2}{2m_e} = \frac{p^2}{2m_e} - \frac{e}{2m_e}(\mathbf{p} \cdot \mathbf{A} + \mathbf{A} \cdot \mathbf{p}) + \frac{e^2 \mathbf{A}^2}{2m_e c^2}, \quad (2)$$

where  $\mathbf{p}$  is the conjugate momentum and  $\mathbf{A}$  is the vector potential of the radiation field. It has been shown<sup>22-24</sup> that the  $\mathbf{A}^2$  term will affect all states of the atomic or molecular system equally, raising the ground state and continuum states by a similar amount. This alone will change neither the apparent IP nor create any field-induced resonances. The  $\mathbf{A} \cdot \mathbf{p}$  term however, shifts the ground state and states near the continuum by different amounts. Excited states near the ionization potential have negligible  $\mathbf{A} \cdot \mathbf{p}$  shift. The ground state (if separated from excited states by many eV and if  $\text{IP} \gg h\nu$ ) experiences a negative shift of magnitude slightly greater than the ponderomotive potential.<sup>22-25</sup> This causes the apparent increase in the IP and an apparent shift in the energy required to excite to intermediate states. For states near the 6, 7, 8, and 9 photon resonances in acetylene, we assume the

shift is equal to that for continuum states, although it is acknowledged that a calculation is required to estimate the actual shift.<sup>24,26</sup> The calculated photoelectron kinetic energies are compared with the measured values to elucidate the intermediate states giving rise to features. To determine the possible kinetic energies for electrons ejected during intense laser ionization, we first calculate  $U'_p(I)$ , the shift required for a given state to achieve  $l$ -photon resonance,

$$U'_p(I) = lh\nu - E_{\text{state}}, \quad (3)$$

where  $E_{\text{state}}$  is the field-free energy of a given state.  $U'_p(I)$  is defined because resonance may occur at any intensity up to that providing the full ponderomotive potential. The IP of the system is shifted simultaneously in the laser field by

$$\text{IP}'(I) = \text{IP} + U'_p(I). \quad (4)$$

Thus, the kinetic energy of the photoelectron generated by absorbing  $m$  additional photons above the  $l$  photon resonance is

$$E_{\text{feature}} = (l+m)h\nu - (\text{IP} + U'_p(I)). \quad (5)$$

We examine all possible  $l$ -photon resonances and consider whether a given resonance is possible. Often it is easy to eliminate some  $lh\nu$  resonances, as they would require a ponderomotive shift greater than the maximum available for the intensity of the laser employed or would require shifting of a state from a well-characterized region where none are known to exist. From here, we examine the selection rules to determine which candidate states have the proper symmetry to allow excitation. We note that acetylene is a centrosymmetric molecule belonging to the  $D_{\infty h}$  point group and has a  ${}^1\Sigma_g^+$  electronic ground state. The  $\Pi_u$  symmetry representation for the electric dipole operator allows all states to be excited in principle for resonances requiring four or more photons. The parity selection rule, however, provides an important restriction. The selection rule  $g \leftrightarrow g(u)$  applies to all processes involving an even (odd) number of photons.

It is proposed that the 1.59 eV feature is the first ATI peak of a lowest order MPI feature that should be observed at 0 eV. We do not expect to see a 0 eV kinetic energy peak, or any peaks with kinetic energies below about 0.5 eV, as these are precluded by the instrument response function. A (6+4) photon transition [ $U'_p(I) = 2.91$  eV] would require a *gerade* state at 6.63 eV by Eq. (3). In the well-characterized region below 9.4 eV, no such states have yet been observed. To allow a (7+3) photon transition [ $U'_p(I) = 2.91$  eV], an *ungerade* state at 8.22 eV is required. There is one possible *ungerade* state in this region, corresponding to the  $3s\ {}^1\Pi_u$  state at 8.16 eV.<sup>19</sup> For an (8+2) photon process ( $U'_p = 2.91$  eV) a *gerade* state in the region of 9.81 eV is required. All states previously observed in the region of 9.81 eV are *ungerade*.<sup>15,19</sup> However, *gerade* states above 9.4 eV have not yet been well characterized. The (9+2) photon transition [ $U'_p(I) = 4.5$  eV] requires an *ungerade* state at 9.81 eV. This region is well characterized for *ungerade* states and none have previously been observed around 9.81 eV.<sup>15,19</sup> The maximum available ponderomotive shifts in Figs. 2(a) and 2(b) are 3.3 eV and 3.9 eV, respectively. The nine photon resonant process requires a  $U'_p(I)$  of 4.5 eV yet the 1.59 eV

feature is present in all spectra. We conclude that the (9+2) photon process cannot be active in these spectra.

The peak observed at 1.95 eV is taken to be the first ATI feature of an expected MPI peak with 0.36 eV of kinetic energy. The (6+4) photon process [ $U'_p(I) = 2.55$  eV] would require the existence of a *gerade* state at 6.99 eV. No such states have yet been observed in this well-characterized region. The (7+3) photon process [ $U'_p(I) = 2.55$  eV] requires the existence of an *ungerade* state at 8.58 eV. Again, in this well characterized region, no such states have yet been observed. For an (8+2) photon case [ $U'_p(I) = 2.55$  eV] a *gerade* state in the region 10.17 eV is required. Thus far, the only observed states in this region are *ungerade*.<sup>15</sup> However, *gerade* states may also exist in this region, as detailed subsequently. The (9+2) photon transition [ $U'_p(I) = 4.14$  eV] would require an *ungerade* state in a well-characterized region at 10.17 eV, where none have been observed. The  $U'_p(I)$  required suggests that the (9+2) process would not be active at all intensities. Since the feature is observed with  $U'_p(I)$  as low as 3.3 eV, the (9+2) photon possibility is eliminated.

The peak observed at 2.13 eV is taken to be the first order ATI peak of the peak with 0.54 eV of kinetic energy. The (6+4) photon process [ $U'_p(I) = 2.37$  eV] would require the existence of a *gerade* state in a well-characterized region at 7.17 eV, where none have been observed. The (7+3) photon process [ $U'_p(I) = 2.37$  eV] requires the existence of an *ungerade* state at 8.76 eV. No such states have yet been observed in this well characterized region. For an (8+2) photon case [ $U'_p(I) = 2.37$  eV] a *gerade* state in the region of 10.35 is required. No *gerade* states have previously been observed in this region. However, *gerade* states may also exist in this region, as detailed subsequently. The (9+2) photon process [ $U'_p(I) = 3.96$ ] requires an *ungerade* state in the well-characterized region at 10.35 eV where none have been observed. The ponderomotive potential of the (9+2) process also eliminates this as a possibility.

The seven and eight photon resonances are the most likely candidates for the origin of these features. There are two possible states that might account for the 1.59 eV feature. The first is the  $3s\ {}^1\Pi_u$  state mentioned earlier that corresponds to a (7+3) photon resonant process. The second is a 9.81 eV *gerade* state that would correspond to an (8+2) photon resonant process. Ashfold *et al.*<sup>12</sup> have suggested that detection of short lived *gerade* states corresponding to  $np$  ( $n=4-7$ ) Rydberg series in the region above 9.42 eV may be precluded by rapid nonradiative decay channels when nanosecond excitation is employed. To determine possible Rydberg states in the relevant energy region, we have carried out a simple quantum defect calculation<sup>26</sup> using the equation,

$$E_{\text{state}} = \text{IP} - \frac{R_M}{(n-\delta)^2}, \quad (6)$$

where  $R_M$  is the mass-corrected Rydberg constant having a value of 13.6055 eV, IP = 11.4 eV and  $\delta$ , the quantum defect has a value of 1.25 for  $s$  levels, 0.6 for  $p$  levels, and 0 for  $d$  and  $f$  levels for  $\text{C}_2\text{H}_2$ .<sup>26</sup> The calculated Rydberg energy levels have been included in the energy level diagram presented in Fig. 1 and are also listed in Table I. The ordering of the  $p$

TABLE I. Calculated and measured state energies for acetylene.

Energy (eV)	State	Ref.	Calculated QD energy (eV)	Series
10.591	$4d\ ^1\Pi_u$	15	10.697	$5p$
10.567	$5s\ \Pi_u$	15	10.54	$4d/f$
10.556	$4d\ ^1\Phi_u$	15	10.432	$5s$
10.05	$3d\ ^1\Sigma_u^-$	16	10.223	$4p$
9.998	$3d\ ^1\Delta_u$	15		
9.976	$3d\ ^1\Pi_u$	15		
9.933	$4s\ ^1\Pi_u$	15		
9.911	$3d\ ^1\Phi_u$	15	9.888	$3d/f$
9.27	$3d\ ^1\Sigma_u^+$	19	9.601	$4s$
9.24	$3d\ ^1\Pi_u$	19		
9.24	$3p\ ^1\Sigma_g^-$	16		
9.21	$3p\ ^1\Sigma_g^+$	12		
9.02	$3p\ ^1\Delta_g$	12	9.038	$3p$
8.91	$3p\ ^1\Pi_g$	16		
8.16	$3s\ ^1\Pi_u$	8		
6.71	$^1\Delta_u$	18	6.957	$3s$
5.23	$^1\Sigma_u^-$	18		
0.0	$^1\Sigma_g^+$	...		

states within a given  $np$  level is  $^1\Pi_g, ^1\Delta_g, ^1\Sigma_g^-, ^1\Sigma_g^+$  in order of increasing energy as shown from *ab initio* studies.<sup>16</sup> The  $^1\Pi_g$  origin of the  $3p$  Rydberg series is 9.038 eV. While it is possible that higher  $3p$  states may account for the 1.59 eV feature, the  $^1\Sigma_g^+$  state is likely to be too low in energy. The  $^1\Pi_g$  origin of the  $4p$  Rydbergs series is 10.223 eV. It is possible that the 1.59 eV feature could correspond to the  $4p\ ^1\Pi_g$  state.

The 1.95 and 2.13 eV features cannot be attributed to any *ungerade* states in the well-characterized region extending nearly to the ionization limit. Therefore, we consider whether short-lived *gerade* Rydberg states may be responsible for these. The  $4p$  Rydberg series (10.223 eV), is likely to contain the appropriate *gerade* states for the 1.95 and 2.13 eV features. Although *gerade f* states have been observed,<sup>15</sup> we eliminate this possibility on the basis that the quantum defect energy for the lowest  $4f$  series is 10.54 eV. This is too high to account for all observed features. Given the combined calculation and experimental error, the states at 9.81, 10.17, and 10.35 eV may all belong to the  $4p$  Rydberg series. The 9.81 eV feature may arise from the  $^1\Pi_g$  state, the 10.17 eV feature from the  $^1\Delta_g$  state and the 10.35 eV feature from the  $^1\Sigma_g^-$  state.

Examination of Figs. 2(a)–2(c) reveals that the integrated signal of the 1.59, 1.95, and 2.13 eV features depend on laser intensity. As the maximum ponderomotive potential increases from 3.3 to 4.9 eV, the feature at 1.59 eV increases in intensity by approximately a factor of 11, while the feature at 2.13 eV remains constant or slightly declines. This intensity dependence suggests that the 1.59 eV state does not originate from the (7+3) photon process if the 1.95 and 2.13 eV features arise from an (8+2) photon transition. This is because the 8 photon resonant excitations should increase more rapidly than the 7 photon transition with increasing laser intensity. The 1.59 eV feature increases the most rapidly. This suggests that the 1.59 eV feature has equal or higher order than the 1.95 and 2.13 eV features. Assuming 8 photon transitions for all these features, we capture the observed intensity dependence by considering the ponderomo-

TABLE II. Calculated values for potential states.

Feature	Process	$Up'(I)$ eV	$E_{\text{state}}$	Required parity	Possibly active
1.59 eV	(6+4)	2.91	6.63	<i>gerade</i>	No
	(7+3)	2.91	8.22	<i>ungerade</i>	Yes
	(8+2)	2.91	9.81	<i>gerade</i>	Yes
1.95 eV	(9+2)	4.5	9.81	<i>ungerade</i>	No
	(6+4)	2.55	6.99	<i>gerade</i>	No
	(7+3)	2.55	8.58	<i>ungerade</i>	No
2.13 eV	(8+2)	2.55	10.17	<i>gerade</i>	Yes
	(9+2)	4.14	10.17	<i>ungerade</i>	No
	(6+4)	2.37	7.17	<i>gerade</i>	No
	(7+3)	2.37	8.76	<i>ungerade</i>	No
	(8+2)	2.37	10.35	<i>gerade</i>	Yes
	(9+2)	3.96	10.35	<i>ungerade</i>	No

tive shifts required for each transition as listed in Table II. States which shift into resonance at higher values of  $U_p'(I)$  are in resonance longer as the maximum  $U_p$  of the laser increases. The ponderomotive shifts required for the features at 1.59, 1.95, and 2.13 eV features are 2.91, 2.55, and 2.37 eV, respectively. As the maximum ponderomotive potential available increases from 3.3 to 4.9 eV, we expect the intensity of the 1.59 eV feature to increase relative to the other two. This is found to be the case. Conversely, at the maximum ponderomotive shift of 4.9 eV, the 2.13 eV feature is diminished. From this intensity trend we conclude that the 1.59, 1.95, and 2.13 eV features arise from an (8+2) photon transition. Since the intensities of the 1.59, 1.95, and 2.13 eV features vary independently with laser intensity, we eliminate the possibility of the triplet representing vibrational structure within a given Rydberg state.

We have studied the strong field photoelectron spectroscopy of  $C_2H_2$ . We have outlined a method for analysis and assignment of such spectra based on intensity dependent shifting of intermediate states into resonance. We observe ATI features originating at 1.59, 1.95, and 2.13 eV. We conclude that the intermediate states are previously unobserved *gerade* states in the region of 9.81–10.35 eV and are assigned to an (8+2) photon process.

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