Photoelectron spectroscopy via the $1^1\Delta_u$ state of diacetylene

C. Ramos, P. R. Winter, and T. S. Zwier

Department of Chemistry, Purdue University, West Lafayette, Indiana 47907-1393

S. T. Pratt

Chemistry Division, Argonne National Laboratory, Argonne, Illinois 60439

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Photoelectron spectra are reported for one-photon resonant, two-photon ionization of jet-cooled diacetylene via a number of vibronic levels of the $1^1\Delta_u$ state. An improved value for the adiabatic ionization threshold is found to be $82.064 \pm 0.030$ cm$^{-1}$ (10.175$\pm$0.004 eV), in good agreement with the earlier result. The photoelectron spectra of different vibronic bands of the $1^1\Delta_u$ state nearly all show long progressions in what appear to be low frequency bending vibrations. At energies just above the ionization threshold, the observed progressions can be understood in terms of excitation of a single Renner-Teller active mode in the ion, with Renner-Teller parameters similar to those of the $\nu_4^+$ trans-bending mode in the ground state acetylene cation. © 2002 American Institute of Physics. [DOI: 10.1063/1.1448488]

I. INTRODUCTION

Diacetylene (1,3 butadiyne) is one of the most complex hydrocarbons that has been identified in the atmospheres of other planets, and reactions of metastable diacetylene may play a role in the formation of larger hydrocarbons in these atmospheres.\textsuperscript{1} Diacetylene is also thought to be involved in the reactions responsible for soot formation in hydrocarbon flames. In an ongoing series of experiments, the reactions of metastable diacetylene with itself and other unsaturated hydrocarbons are being investigated for their potential role in the reactions responsible for soot formation in hydrocarbon flames. In an ongoing series of experiments, the reactions of diacetylene with itself and other unsaturated hydrocarbons are being investigated for their potential role in these phenomena.\textsuperscript{1–6} In these experiments, metastable diacetylene is prepared by exciting selected vibronic bands of the $1^1\Delta_u \rightarrow X^1\Sigma_g^+$ transition in the expansion region of a pulsed supersonic jet. The molecules in the $1^1\Delta_u$ levels are thought to undergo rapid intersystem crossing into the triplet manifold, from which the reactions take place. To date, the assignment of the vibronic structure of the $1^1\Delta_u \rightarrow X^1\Sigma_g^+$ transition is incomplete, and the details of the intersystem crossing and the energetics within the triplet manifold are not well understood. As a step towards improving this situation, we have recorded photoelectron spectra for one-photon resonant, two-photon ionization of diacetylene via a number of vibronic levels of the $1^1\Delta_u$ state. A schematic energy level diagram of the relevant neutral and ionic states is shown in Fig. 1. These spectra provide insight into the assignment of the vibronic bands of the $1^1\Delta_u \rightarrow X^1\Sigma_g^+$ transition, as well as information on the vibrational frequencies of the $X^2\Pi_g$ ionic ground state. In addition, the envelopes of vibronic transitions observed in the photoelectron spectra provide information on the relative shapes of the potential surfaces in the $1^1\Delta_u$ and $X^2\Pi_g$ states.

The dominant configuration in the $X^1\Sigma_g^+$ neutral ground state is \ldots$(1\pi_u)^2(1\pi_g)^2(1\pi_{ux})^2(1\pi_{uy})^2$, where the lower lying $\sigma$ orbitals have been left out.\textsuperscript{7} Two configurations make the dominant contribution to the $1^1\Delta_u$ excited state, corresponding to \ldots$(1\pi_{ux})^2(1\pi_{uy})^2(1\pi_{gx})^2(1\pi_{gy})^2(2\pi_{ux})$, and \ldots$(1\pi_{ux})^2(1\pi_{uy})^2(1\pi_{gx})^2(1\pi_{gy})^2(2\pi_{uy})$. Similarly, the two dominant configurations for the $X^2\Pi_g$ ionic ground state of diacetylene are \ldots$(1\pi_u)^2(1\pi_g)^2(1\pi_{ux})^2(1\pi_{gy})^2$ and \ldots$(1\pi_{ux})^2(1\pi_{uy})^2(1\pi_{gx})^2(1\pi_{gy})$. High-level quantum chemical calculations have been carried out on the $1^1\Delta_u$ state by Karpfen and Lischka\textsuperscript{8} and, more recently, by Vila et al.\textsuperscript{9} The one-photon $1^1\Delta_u \rightarrow X^1\Sigma_g^+$ transition is nominally forbidden, but becomes allowed if the upper state is not linear.\textsuperscript{2,9–11} It can also become allowed through vibronic interactions with vibrations of $\pi_u$ and $\delta_g$ symmetry, which result in vibronic levels with the necessary $1^1\Pi_u$ and $1^1\Sigma_u^+$ symmetry for allowed single-photon transitions from the ground state.\textsuperscript{2} Only the $\nu_8$ and $\nu_9$ vibrations, which correspond to symmetric bending of the $\text{C}=$C–H and $\text{C}=$C–C angles, respectively, have $\pi_u$ symmetry, while vibrations with $\delta_g$ symmetry occur as overtones and combinations bands such as $\pi_u \times \pi_u$ and $\pi_u \times \pi_u$. The $\nu_8$ and $\nu_9$ vibrations, which correspond to asymmetric bending of the $\text{C}=$C–H and $\text{C}=$C–C angles, respectively, both have $\pi_u$ symmetry. Bandy et al.\textsuperscript{2} sought to distinguish between the possible mechanisms responsible for the $1^1\Delta_u \rightarrow X^1\Sigma_g^+$ transition by searching for the origin band and for bands that correspond to totally symmetric vibrations. Such bands cannot be vibronically induced and would only be observed if the $1^1\Delta_u$ state was nonlinear. In fact, such bands were observed in a study of matrix-isolated diacetylene, leading Chang and Graham\textsuperscript{12} to propose that the $1^1\Delta_u$ state was nonlinear. However, Bandy et al.\textsuperscript{2} found no evidence for the origin band or any other band with totally symmetric vibrational symmetry, leading them to conclude that the $1^1\Delta_u$ state was linear and that the $1^1\Delta_u \rightarrow X^1\Sigma_g^+$ transition was vibronically induced. Interestingly, this observation implies that the matrix effects in the work of Chang and Graham are not insignificant. Bandy et al.\textsuperscript{2} also concluded that both $1^1\Sigma_u^+$ and $1^1\Pi_u$ vibronic levels involving $\nu_8$ and $\nu_9$ vibrations in the $1^1\Delta_u$ state contribute to the observed spectrum and that the potential along the bending coordinates of the $1^1\Delta_u$ state is quite flat. Although resolved rotational structure would lend…
more insight into these assignments, the widths of the vibronic bands observed in the jet-cooled spectra are still considerably broader that the photon bandwidth, and no resolvable rotational structure is observed.

The HeI (hν = 21.2168 eV) photoelectron spectrum of diacetylene was recorded by Baker and Turner.\(^{13}\) This spectrum shows a strong origin band in the transition to the \(X^2\Pi_{g}\) ion ground state, as well as a progression of three additional bands of decreasing intensity that were assigned to the fundamental and overtones of the \(\nu_2\) \(\equiv\equiv C\) symmetric stretch. From this spectrum, Baker and Turner deduced an adiabatic ionization potential of 10.17 eV, in reasonable agreement with the value of 10.18 eV determined by Smith\(^{14}\) from the extrapolation of Rydberg series. The strong origin band in the photoelectron spectrum indicates the geometries of the ground state neutral and ion are similar, while the excitation of the \(\nu_2\) mode is a result of the weakening of the \(\equiv\equiv C\) bonds and the strengthening of the \(\equiv\equiv C\) bond upon ionization. This shift in bond lengths is consistent with the introduction of some cumulene character into the bonding in the \(X^2\Pi_{g}\) ionic ground state. The lack of excitation in any of the bending modes indicates that, like the neutral and \(1^1\Delta_u\) state, the ion is linear. Because the \(1^1\Delta_u\) state is vibronically induced by bending vibrations, it is expected that photoelectron spectra from this state will provide access to at least one of the bending modes of the ion, and long vibrational progressions are clearly observed in the spectra reported here.

The experimental details are discussed in the next section, followed by a review of background material on the vibrational frequencies of diacetylene, the Renner-Teller effect, and the selection rules for photoionization. The experimental data are then discussed, and the diacetylene results are compared with those for acetylene. Finally, the paper concludes with a discussion of potential areas for future study.

**II. EXPERIMENT**

The experiments were performed on jet-cooled samples of diacetylene using a magnetic bottle electron spectrometer\(^{15}\) equipped with a pulsed, differentially pumped molecular beam source.\(^{16}\) The diacetylene was synthesized as described previously,\(^{7}\) and was stored as a 5%–7% mixture in helium. Experiments were performed using this mixture with a backing pressure of approximately 1–2 bar. Experiment with other samples under these conditions indicate that the sample temperature is approximately 10 K in the interaction region. All of the photoelectron spectra were recorded using one-color, two-photon ionization by the frequency-doubled output of a Nd:YAG-pumped dye laser. The dye laser was used to generate light between 490 nm and 449 nm, which was then frequency doubled in a BBO crystal. The doubled light was then separated from the fundamental light by using a series of dichroic mirrors, reducing the initial intensity of the fundamental by a factor of \(~2000\). The doubled light was focused into the interaction region by using a 75 mm focal length lens. The vibronic structure of the \(1^1\Delta_u\) state was mapped out by scanning the laser through the region of interest and monitoring the total electron signal produced by one-photon resonant, two-photon ionization. The wavelength of the fundamental light was calibrated by using the optogalvanic effect in Ar. The resulting structure is similar to that observed previously, but the signal to noise ratio is somewhat poorer. By increasing the laser intensity somewhat, nonresonant two-photon ionization could also be observed, a result that was useful for calibrating the spectra as discussed below.

In the magnetic bottle electron spectrometer, photoionization occurs in a diverging 1 T magnetic field that parallelizes the trajectories of the electrons, resulting in a collection efficiency of approximately 50%. The electrons in the interaction region were accelerated in a field of about 0.5 V/cm, and were retarded by a similar field in the flight tube. This was accomplished by applying small positive or negative voltages to electrical grids located on the opposite side of the interaction region from the detector and at the entrance to the flight tube. The magnetic field within the interaction region can perturb the decay dynamics of highly excited molecules; however, it will not change the photoelectron energies. In general, the effects of the magnetic field on direct photoionization (i.e., not via autoionizing states) are not substantial, although it is possible that the intensities of some photoelectron peaks may be affected. In the present study, the intensities in the photoelectron spectra are discussed only in quali-
tative terms, and the effects of the magnetic field are not considered further.

The kinetic energies of the electrons were determined from their time-of-flight to the detector. Several methods were investigated to calibrate the energy scale of the photoelectron spectra. In the end, the most suitable method involved recording resonant or non-resonant two-photon ionization spectra at a number of different wavelengths, and monitoring the position of a given peak as a function of the two-photon energy. In particular, as in the single-photon photoelectron spectrum reported previously, the photoelectron band corresponding to the population of the vibrationless ground state of \( \text{C}_4\text{H}_2 \) is the strongest feature in the non-resonant two-photon ionization spectrum throughout the wavelength region of interest. By recording spectra at a number of different wavelengths, the differences in flight time can be correlated with differences in the two-photon energy. The positions of other photoelectron peaks can be referenced to this scale, and thus the relative energies of the observed photoelectron peaks can be determined. Knowledge of the adiabatic ionization energy of diacetylene then puts this relative scale on an absolute basis. This method has the advantage that the sample is its own calibration gas, removing questions about shifting contact potentials. A second advantage is that the uncertainty in the two-photon energies is extremely small compared to the energy resolution of the spectrometer. Finally, the method provides the energy differences between photoelectron peaks, so that uncertainty in the adiabatic ionization energy does not effect the determination of the relative peak energies. Based on the reproducibility of several calibrations based on this method, it is estimated that the band energies with respect to the origin are accurate to approximately \( \pm 50 \text{ cm}^{-1} \).

III. BACKGROUND CONSIDERATIONS

A. Vibrational frequencies in the \( \text{C}_4\text{H}_2 \, 1^1\Delta_u \) and \( \text{C}_4\text{H}_2^+ \, 2^3\Pi_g \) states

The vibrational modes and experimentally determined fundamental frequencies of diacetylene and its cation are summarized in Table I. As discussed by Bandy et al., there have been a number of previous studies of the \( 1^1\Delta_u \leftarrow \Sigma^+_g \), transition, and values have been extracted for a number of the fundamental vibrational frequencies in the \( 1^1\Delta_u \) state.\(^a,9,10,11,12\) Owing to the limited nature of the spectroscopic data, however, most of these values and assignments should be considered tentative at best. Table I also includes theoretical values for the vibrational frequencies of the \( 1^1\Delta_u \) and \( \text{C}_4\text{H}_2^+ \, 2^3\Pi_g \) states. Two significant calculations on the \( 1^1\Delta_u \) state have been reported. In the first, Karpfen and Lischka\(^a\) found this state to be bent, and calculated the potential for one of the Renner-Teller components of the state. In the second, Vila et al.\(^7\) recently reported the results of a higher level calculation in which the \( 1^1\Delta_u \) state was found to be linear, in agreement with the analysis of Bandy et al. Vila et al.\(^7\) also calculated the positions of the low-lying excited states in the triplet manifold. Vibrational frequencies for the \( 1^1\Delta_u \) state calculated by Vila et al. are provided in Table I. However, Vila et al. suggested that these values should be used only to discuss trends between different electronic states, and stated that calculations including a larger basis set and dynamical correlation effects will most likely be necessary to accurately predict the vibrational frequencies.

Experimental information on the vibrational frequencies of the ground state of the diacetylene cation was extracted from the \( A \, 2^3\Pi_u \leftarrow X \, 2^3\Pi_g \) emission spectrum by Calloman.\(^1,17,18\) This analysis yielded fundamental vibrational frequencies of \( 3136.9 \text{ cm}^{-1} \), \( 2176.6 \text{ cm}^{-1} \), and \( 860.6 \text{ cm}^{-1} \) for \( \nu_1 \), \( \nu_2 \), and \( \nu_3 \) of the \( X \, 2^3\Pi_g \) state, respectively. Calloman also reported a value for \( 2\nu_1 \) of \( 971.5 \text{ cm}^{-1} \). Based on an analysis of the Rydberg states of the neutral, Smith\(^14\) switched the assignments of Calloman for \( \nu_3 \) and \( 2\nu_1 \). The results of Smith also point to a calibration problem in the earlier absorption study of Price and Walsh.\(^19\) To our knowledge, no new information on the vibrational frequencies of the \( X \, 2^3\Pi_g \) state has appeared since that time. The spin–orbit constant in the \( X \, 2^3\Pi_g \) state is \( 33.3 \text{ cm}^{-1} \), and the doublet splitting is therefore too small to be resolved in the photoelectron spectra reported here. Table I also includes \( X \, 2^3\Pi_g \) vibrational frequencies obtained from B3LYP/6-31++G* calculations using the Gaussian program. This method is expected to produce reasonably accurate results for the vibrational frequencies, and the theoretical values are within a few percent of the experimental values for \( \nu_1 \), \( \nu_2 \), and \( \nu_3 \). Although the calculations were constrained to the linear geometry, the results show a small spitting of the doubly degenerate bending modes. This splitting is considerably smaller than that expected for the Renner-Teller interaction. Indeed, the theoretical calculations do not explicitly take the Renner-Teller interaction into consideration, and thus are probably of limited utility for the bending modes.

### Table I. Vibrational frequencies for the relevant electronic states of diacetylene and its cation.

<table>
<thead>
<tr>
<th>Vibrational mode</th>
<th>( X , 1^3\Sigma_g^+ )</th>
<th>( 1^1\Delta_u )</th>
<th>( X , 2^3\Pi_g )</th>
</tr>
</thead>
<tbody>
<tr>
<td>( \nu_1 )</td>
<td>3332</td>
<td>3633</td>
<td>3653</td>
</tr>
<tr>
<td>( \nu_2 )</td>
<td>2189</td>
<td>2343</td>
<td>2105</td>
</tr>
<tr>
<td>( \nu_3 )</td>
<td>872</td>
<td>918</td>
<td>964</td>
</tr>
<tr>
<td>( \nu_4 )</td>
<td>3333</td>
<td>3632</td>
<td>3661</td>
</tr>
<tr>
<td>( \nu_5 )</td>
<td>2019</td>
<td>2152</td>
<td>1971</td>
</tr>
<tr>
<td>( \nu_6 )</td>
<td>626</td>
<td>646</td>
<td>288</td>
</tr>
<tr>
<td>( \nu_7 )</td>
<td>483</td>
<td>529</td>
<td>269</td>
</tr>
<tr>
<td>( \nu_8 )</td>
<td>628</td>
<td>570</td>
<td>275</td>
</tr>
<tr>
<td>( \nu_9 )</td>
<td>220</td>
<td>221</td>
<td>258</td>
</tr>
</tbody>
</table>

\(^b\)Reference 2, Bandy et al.
\(^c\)Reference 7, Vila et al.
\(^d\)Reference 14, Smith and Ref. 17, Calloman. The values for \( \nu_1 \) and \( \nu_2 \) are those of Smith, who reversed the assignment of Calloman, whose values are given in parentheses.
\(^e\)This work. The doubly degenerate vibrations were split in the calculation, and both values are given.
B. The Renner-Teller effect in diacetylene

The degenerate bending vibrations of both the neutral $1^1\Delta_u$ state and the ionic $2\Pi_g$ state result in Renner-Teller interactions that split the electronic states into two components.\(^{20}\) Progressions and combination bands involving these vibrations in either state result in several vibronic components designated by their vibronic angular momentum, $K$, which is the sum of the vibrational angular momentum, $l$, and the projection of the electronic angular momentum on the linear axis, $\Lambda$. The bending modes responsible for Renner-Teller interactions in the $1^1\Delta_u$ state are the same as those that induce the vibronically allowed $1^1\Sigma_g^+ \rightarrow 1^1\Sigma_u^+$ transition. As indicated in the discussion above, Bandy et al.\(^2\) concluded that any barrier to linearity produced by the Renner-Teller interaction in the $1^1\Delta_u$ state is too small to trap the molecule in a bent configuration. Furthermore, the spectroscopic analysis of Calloman\(^17\) and the photoelectron spectrum of Baker and Turner\(^13\) indicate that the barrier to linearity in the $\text{C}_2\text{H}_4^+ \rightarrow 1^2\Pi_g^-$ state is also too small to trap the ion in a nonlinear geometry. The Renner-Teller active bending modes correspond to the lowest frequency vibrations of both the $1^1\Delta_u$ and $2\Pi_g$ states, and the splitting of the different vibronic components is expected to add considerable complexity to the $1^1\Delta_u \rightarrow 1^1\Sigma_g^+$ absorption spectrum and the $1^2\Pi_g \rightarrow 1^1\Delta_u$ photoelectron spectrum. Bandy et al.\(^2\) found that the observed level structure was qualitatively consistent with that expected for a Renner-Teller progression in one of the $\pi_b$ bending modes, but no quantitative analysis was possible given the limited nature of the experimental data. To our knowledge, there has been no analysis of the Renner-Teller interaction in the $\text{C}_4\text{H}_4^+ \rightarrow 1^2\Pi_g^-$ state.

The significantly lower bending frequencies in the $1^1\Delta_u$ state than in the $X^2\Pi_g$ state imply that the potential for the $1^1\Delta_u$ state is considerably flatter along the bending coordinate than the potential for the $X^2\Pi_g$ state. The difference between the two potential surfaces is at least in part due to the valence character of the orbital of the excited electron. This difference may also partially be a result of the difference in the form of the Renner-Teller interaction in the two states. In particular, for $\Pi$ states the splitting between the two Renner-Teller surfaces has the form $V^+ - V^- = ar^2 + br^4 + \cdots$, where $V^+$ and $V^-$ are the two electronic surfaces and $r$ is the displacement along the bending coordinate.\(^{20}\) For $\Delta$ states, the quantity $\alpha$ vanishes, and the splitting is only noticeable at larger displacements.

The photoelectron spectra presented below are obtained with the laser tuned to specific vibronic levels of the $1^1\Delta_u$ state, and the vibrational progressions observed in the spectra correspond to progressions in the ground electronic state of the ion. Thus, the Renner-Teller structure in a linear $2\Pi_g$ state is most relevant to the present work. As mentioned above, the spin–orbit splitting is small compared to the experimental resolution, and will be ignored in the present analysis. The details of the Renner-Teller effect in a molecule like diacetylene with four degenerate bending vibrations are quite involved. However, if it is assumed that the Franck–Condon factors to the ion involve only one $\pi_b$ mode, we can use the discussion presented previously for acetylene to reduce the energy expressions to those applicable to a single bending vibration in a triatomic molecule.\(^{21-23}\) It should be noted that the unexcited vibrations do produce a Renner-Teller shift of all the vibronic levels that is not included in the equations below; however, this shift is the same for all vibronic levels and can be ignored if the formulas are only used to determine the relative energies of the vibronic levels; that is, the splittings between levels.

With $V_b^+$ considered the active vibration, $V_b^+ = V_b^+ = V_b^+ = 0$, and $K^+ = K^+ = K^+ = 1$, $v_6^+ = 1, \ldots, 1$ or 0, the resulting formulas are:\(^{20}\)

$$E_{K^+v_b^+} = \alpha_0(v_b^+ + 1) - \frac{1}{2} \varepsilon v_b^+ \omega_0 K^+ (K^+ + 1)$$

for $K^+ = v_b^+ + 1$; \(1\)

$$E_{K^+v_b^+} = \alpha_0(v_b^+ + 1)(1 - \frac{1}{2} \varepsilon v_b^+ \omega_0 (v_b^+ + 1))$$

for $K^+ = 0$ (i.e., $\Sigma^\pm$ states); \(2\)

and

$$E_{K^+v_b^+} = \alpha_0(v_b^+ + 1)(1 - \frac{1}{2} \varepsilon v_b^+ \omega_0 \sqrt{(v_b^+ + 1)}^2 - K^+^2$$

for $0 < K^+ \leq v_b^+$. \(3\)

A schematic diagram of the resulting energy levels for the $a^2\Pi_g$ state is shown in Fig. 2.

C. Photoionization selection rules

The vibronic selection rules for photoionization of the $1^1\Delta_u$ state of diacetylene are similar to those for photoionization of the $\tilde{\Delta}^1\Delta_u$ state of acetylene, which have been discussed previously.\(^{21,22}\) The selection rules for the photoionizing transition are determined by considering the overall symmetry and quantum numbers of the complex of the photoion and the photoelectron. In $D_{\alpha \beta}$ symmetry, the dominant

\[ \begin{array}{c|c|c|c|c|c|c} \hline
K^+ & 0 & 1 & 2 & 3 & 4 & 5 \\
\hline
\Sigma & 1 & 2 & 3 & 4 & 5 & 6 \\
\Pi & 7 & 8 & 9 & 10 & 11 & 12 \\
\Delta & 13 & 14 & 15 & 16 & 17 & 18 \\
\Phi & 19 & 20 & 21 & 22 & 23 & 24 \\
\Gamma & 25 & 26 & 27 & 28 & 29 & 30 \\
\Phi & 31 & 32 & 33 & 34 & 35 & 36 \\
\hline
\end{array} \]
configurations of the $1^1\Delta_u$ and $X^2\Pi_g$ states suggest that photoionization occurs via the excitation of an electron in the $2\pi_u$ orbital into the ionization continuum. Thus, the $u\rightarrow g$ dipole selection rule suggests that the dominant photoelectron partial waves will have even $l$. In addition, the $2\pi_u$ orbital has nodal structure similar to that of a $4f\pi_u$ atomic orbital, which further suggests that the dominant partial waves will have $l=2$ and 4. The ejection of odd $l$ partial waves is only possible with a concurrent odd change in the orbital, which further suggests that the dominant partial waves are excited. In this case, the Franck-Condon principle for the ionizing transition would require excitation of a $\delta_g$ vibration in the ion, which is not possible at threshold. Thus, nonresonant two-photon ionization is expected to be the dominant process. By tuning the laser to longer wavelength, the threshold for the photoelectron peak is found to be $82\,064\pm30\,cm^{-1}$ (10.175±0.004 eV), in good agreement with the earlier value. This result has been corrected for the small repeller field applied in the ionization region, which decreases the observed ionization potential by $\sim4\,cm^{-1}$ from the field-free threshold.

In the absorption spectrum of Haink and Jungen,\(^{11}\) the lowest energy band in the $1^1\Delta_u\rightarrow X^2\Sigma_g^+$ spectrum, which is assigned as $6_0^+$, is quite intense, while the analogous band in the one-photon resonant, two-photon ionization spectrum is considerably weaker. As discussed by Bandy et al.,\(^2\) this difference results from the two-photon energy for this vibronic band being insufficient to populate the $v_6^+=1$ levels of the $X^2\Pi_g$ state. Because $v_6$ is a $\pi_g$ vibration, if the $v_6=1$ level is populated in the intermediate state, the $v_6^+=0$ level is forbidden within the Franck-Condon approximation, and can only be populated through vibronic interactions. Thus, the intensity of the $6_0^+$ band is expected to be quite small in the one-photon resonant, two-photon ionization spectrum.

Photoelectron spectra recorded at the position of the sharp peak labeled B in Fig. 5 of Ref. 2 show a single low energy peak due to the origin of the $C_4H_2^+$ cation, as expected, but also show an extremely intense photoelectron peak corresponding to very fast electrons. This fast peak almost certainly arises from two-photon resonant, three-photon ionization of atomic hydrogen via the $2s-1s$ two-photon resonance, which is resonant at $243.135\,nm$. Scans of the R2PI spectrum in the Purdue time-of-flight chamber so no signs of interference from this H-atom resonance in the R2PI spectrum under the focusing conditions used in Ref. 2. However, the interference observed in the photoelectron spectrum indicates that under tight focusing conditions, multiphoton processes can produce and photoionize hydrogen atoms.

Figure 4 shows the photoelectron spectrum obtained at $41\,270.7\,cm^{-1}$; that is, near the peak of the second vibronic

![Graph](https://via.placeholder.com/150)

**FIG. 3.** Photoelectron spectrum obtained at $41\,197.4\,cm^{-1}$, corresponding to a two-photon energy of $82\,394.7\,cm^{-1}$, which lies just above the adiabatic ionization energy of diacetylene. The photoelectron peak corresponds to the production of the $X^2\Pi_g$ ground state.

**IV. RESULTS AND DISCUSSION**

**A. The threshold region**

Figure 3 shows the photoelectron spectrum obtained at $242.734\,nm$, which is approximately halfway in between the two lowest energy bands in the $1^1\Delta_u\rightarrow X^2\Sigma_g^+$ spectrum reported by Bandy et al. Ionization at this energy is most likely due to a combination of both resonant and nonresonant two-photon processes. The two-photon energy corresponds to $82\,394.7\,cm^{-1}$; that is, just above the previously reported adiabatic ionization threshold of diacetylene\(^{13,14}\) (10.17 eV or $82026\,cm^{-1}$). As expected, the photoelectron spectrum shows a single peak at low kinetic energy, which must correspond to the population of the vibrationless level of the $X^2\Pi_g$ state of $C_4H_2^+$. Note that for the resonant ionization process via the $1^1\Delta_u$ state, the $\Delta K=\pm1$ selection rule can only be fulfilled if the vibrationless $C_4H_2^+ X^2\Pi_g$ state is accessed from a $\Sigma$ vibronic level of the $1^1\Delta_u$ state. This implies that for the resonant process, a $\delta_g$ vibration must be excited. In this case, the Franck-Condon principle for the ionizing transition would require excitation of a $\delta_g$ vibration.
band observed in the $1^1\Delta_u - X^1\Sigma_g^+$ spectrum of Bandy et al.\textsuperscript{2} The two-photon energy is 477 cm\(^{-1}\) above the adiabatic ionization threshold. The photoelectron spectrum shows a single intense peak corresponding to the population of a \(C_4H_3^+\) \(X^2\Pi_g\) state with 455\(\pm\)50 cm\(^{-1}\) of vibrational energy, and a very weak feature corresponding to the population of the vibrationless \(X^2\Pi_g\) state. The pump transition was tentatively assigned by Bandy et al. as a transition to a \(1^1\Sigma_u^+\) vibronic level resulting from two quanta in the \(v_6\) bending vibration, and has an energy 428 cm\(^{-1}\) above the expected position of the vibrationless \(1^1\Delta_u\) level based on the matrix data.\textsuperscript{12} If this is the case, the vibration in the \(1^1\Delta_u\) state will have \(\delta_g\) symmetry, and the Franck–Condon principle would favor excitation of vibrational levels in the ion with \(\delta_g\) symmetry. This would require two quanta in either \(\pi_u\) or \(\pi_g\) vibration of the ion. An alternative assignment for the pump transition would be to a \(1^1\Pi_u\) vibronic level in the \(1^1\Delta_u\) state with one quantum in a \(\pi_g\) vibration. In this case, the vibration in the ion could also have \(\pi_g\) symmetry, resulting in an ionic level with either \(\Sigma\) or \(\Delta\) vibronic symmetry.

Given the \(C_4H_3^+\) vibrational frequencies in Table I, it appears that the \(1^1\Delta_u\) vibrational band could correspond to either one quantum or two quanta in low-frequency bending vibrations. Because all of the bending vibrations have either \(\pi_u\) or \(\pi_g\) symmetry, one quantum would result in \(\Sigma\) or \(\Delta\) vibronic levels, and two quanta would result in \(\Pi\) or \(\Phi\) vibronic levels of the ion. If the \(\Delta K = \pm 1\) photoionization selection rule is assumed to apply, \(\Sigma\) or \(\Delta\) vibronic levels of the ion can be accessed via \(\Pi\) vibronic levels of the \(1^1\Delta_u\) state, while \(\Pi\) vibronic levels can only be accessed from \(\Sigma\) vibronic levels of the \(1^1\Delta_u\) state. The assignment of the intermediate level to a \(1^1\Pi_u\) vibronic level is preferred for two reasons. First, as discussed below, the 455 cm\(^{-1}\) band is thought to correspond to the lowest energy component of a \(v_6^+ = 1\) Renner-Teller triplet and, as such, will have \(\Sigma\) vibronic symmetry. (Given the uncertainty in the band position, the energy is consistent with the \(v_6^+\) frequency in Table I.) Second, the origin photoelectron band in Fig. 4 is quite weak. Although this might simply be the result of Franck–Condon factors, the vibrational frequencies in the \(1^1\Delta_u\) and \(X^2\Pi_g\) states are significantly different, which would likely produce a more extended vibrational envelope that includes significant intensity at the origin. (Higher members of the progression are not observed because the two-photon energy reaches 477 cm\(^{-1}\) above the ionization threshold.) On the other hand, the \(X^2\Pi_g\) state origin band is forbidden from a \(1^1\Pi_u\) intermediate level by the \(\Delta K = \pm 1\) selection rule, and is allowed from a \(1^1\Sigma_u^+\) level. Thus, the weakness of the origin photoelectron band observed in Fig. 4 is consistent with a \(1^1\Pi_u\) intermediate level. With this assignment, the weak origin band observed in Fig. 4 is produced either by nonresonant two-photon ionization, or by a small breakdown in the \(\Delta K = \pm 1\) selection rule.

B. The \(v_6^+ = 1\) and higher Renner-Teller multiplets

Figures 5(a), 5(b), and 5(c) show the photoelectron spectra obtained at 41 435 cm\(^{-1}\), 41 511 cm\(^{-1}\), and 41 670 cm\(^{-1}\), respectively. These photon energies correspond to two-photon energies lying 806 cm\(^{-1}\), 958 cm\(^{-1}\), and 1276 cm\(^{-1}\) above the adiabatic ionization threshold, respectively. Figure 5(a) corresponds to an energy between resonances in the \(1^1\Delta_u - X^1\Sigma_g^+\) transition, and the single peak corresponding to the production of the vibrationless \(X^2\Pi_g\) ground state is consistent with an essentially nonresonant two-photon ionization process. Figure 5(b) corresponds to ionization via the
resonance labeled D by Bandy et al.\textsuperscript{2} which they have tentatively assigned as a bending overtone or combination band. This spectrum shows four significant peaks. The first two peaks correspond to the population of the vibrationless ground state ion and the level observed in Fig. 4 that was assigned to the $v_6^+ \text{ or } v_7^+$ vibration. The two remaining peaks correspond to the population of $X^2\Pi_g$ vibronic levels with energies of 602±50 cm\textsuperscript{-1} and 885±50 cm\textsuperscript{-1}. It appears that the latter corresponds to the same vibronic band as that observed in Fig. 5(c). The different potentials of the 1 1 $\Delta_g$ and $X^2\Pi_g$ states along the bending coordinate, along with the selection rules for the 1 1 $\Delta_g \leftrightarrow X^1\Sigma_g^+$ and photoionizing transitions, make it likely that the three vibrationally excited peaks involve overtones or combination bands of $v_6^+$ or $v_7^+$, or Renner-Teller components of the same. While the former interpretation admits a number of different possible assignments, the latter has the potential for a more unified explanation, which is pursued here.

In principle, the three excited vibrational bands in Fig. 5(b) could correspond to the three Renner-Teller components of the $X^2\Pi_g$ state with $v_6^+$ or $v_7^+$ = 1. For the sake of simplicity in the following discussion, it is assumed that $v_6^+$ = 1 and $v_7^+$ = 0. As seen in Fig. 2, these three vibronic levels correspond to $2\Sigma_g^+ \text{, } 2\Sigma_g^-$, and $2\Delta_g$ components. If the intermediate state corresponds to a $\Pi_u$ vibronic level in the 1 1 $\Delta_u$ state, photoionization to all three vibronic levels is fully allowed and will result in the ejection of a photoelectron with even $l$. In contrast, the $X^2\Pi_g$ vibronic origin band would be nominally forbidden, which is consistent with the weak origin band in Fig. 5(b). With this assignment, the 602 cm\textsuperscript{-1} band corresponds to the $2\Delta_g$ component and the 455 and 885 cm\textsuperscript{-1} bands correspond to the $2\Sigma_g^+$ and $2\Sigma_g^-$ bands. Unfortunately, with the present resolution it is not possible to say which $\Sigma$ state lies at higher energy, and the ± label is left off in the discussion below.

The Renner-Teller parameters $\omega_6^+$ and $\epsilon_6^+$ can be calculated from the observed energies by using Eqs. (1) and (2). This was done by using the positions of the two $v_6^+$ = 1, $\Sigma$ components and Eq. (2) to determine $\epsilon_6^+$ and $\omega_6^+$, referencing the subband energies to the $v_6^+$ = 0, $X^2\Pi_g$ origin. The resulting values are $\omega_6^+ = 670$ cm\textsuperscript{-1} and $\epsilon_6^+ = 0.32$. With these parameters, the energy of the $2\Delta_g$ component is calculated to be 636 cm\textsuperscript{-1}, in reasonable agreement with experiment given the uncertainties in the band positions. Assuming $v_7^+$ = 0, these Renner-Teller parameters can also be used to predict the positions of the higher $v_6^+$ levels. These are given in Table II. Interestingly, the Renner-Teller parameters derived here for the trans-bending $v_6^+$ vibration of the ground state diacetylene cation are quite close to the values $\omega_6^+ = 694$ cm\textsuperscript{-1} and $\epsilon_6^+ = 0.30$ deduced for the trans-bending $v_6^+$ vibration in the ground state of the acetylene cation.\textsuperscript{22,23} While this observation appears to support the assignment of Fig. 5(b) as a Renner-Teller multiplet, it is interesting because the degenerate electronic state has $\Pi_u$ symmetry in acetylene and $\Pi_g$ symmetry in diacetylene. This implies that the trans bending of the terminal hydrogens has a similar effect on the two electronic states.

Figure 5(c) corresponds to ionization via a resonance that was not assigned by Bandy et al.\textsuperscript{2} but that lies at an energy ∼825 cm\textsuperscript{-1} above the 1 1 $\Delta_u$ origin. This spectrum shows a single intense peak corresponding to the population of an $X^2\Pi_g$ vibronic level with 870±50 cm\textsuperscript{-1} of internal energy. Thus, the dominant ionization process preserves the vibrational energy of the 1 1 $\Delta_u$ intermediate state. The Renner-Teller analysis for Fig. 5(b) implies that the single observed peak most likely corresponds to the higher energy $2\Sigma_g^+$ with $v_6^+$ = 1. While the weak origin band is consistent with a $\Pi_u$ vibronic level in the intermediate state, it remains to explain why only a single $v_6^+$ = 1 Renner-Teller component is observed, rather than all three as in Fig. 5(b). It is unlikely that the vibronic character of the 885 cm\textsuperscript{-1} band can provide the full explanation for this observation. If, as concluded above, it is a $2\Sigma_g^+$ band, the intermediate state will most likely have $\Pi_u$ symmetry. Thus, additional $2\Sigma_g^-$ and $2\Delta_g$ bands are expected. If this assignment is wrong and the photoelectron band corresponds to a $2\Pi_g$ vibronic level, transitions to other $\Pi_g$ vibronic levels, most notably the origin band, would be expected to be stronger. It is left to conclude that the observed transition is a part of the Franck–Condon factors between the intermediate vibronic level and the vibronic levels of the $X^2\Pi_g$ state of the ion. This conclusion is somewhat surprising because the bending vibrational frequencies in the 1 1 $\Delta_u$ state are significantly different from those in the $X^2\Pi_g$ state, and, as a result, the Franck–Condon factors would be expected to distribute intensity over a range of photoelectron bands.

It is worth mentioning that the observed vibrational energy in the final state for the peak in Fig. 5(c) is quite close to the value in Table I for the $X^2\Pi_g$, $v_5^+$ = 1 level. Unfortunately, although the vibrational frequency of $v_5$ in the 1 1 $\Delta_u$ and $X^2\Pi_g$ states are similar, this vibration corresponds to a nondegenerate symmetric stretch. As a result, the 1 1 $\Delta_u$, $v_5^+$ = 1 $\leftrightarrow X^1\Sigma_g^+$ transition is not vibronically allowed. Although such a transition would become allowed in the bent molecule, the work discussed above suggests that the 1 1 $\Delta_u$

<table>
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*Calculated by using Eqs. (1)–(3), and referencing the energies to that of the $\nu = 0$, $K = 1$ level.
the intermediate vibronic level has \( \Delta_2 \) symmetry, or that \( \Delta_2 \) vibronic levels are overlapped, or that both resonant and nonresonant two-photon processes contribute to the spectrum. The origin band is weak in Fig. 6(a), but fairly substantial in the remaining spectra. All four spectra show long progressions of bands, although the progression is weak in Fig. 6(d). Figure 6(a) corresponds to the fourth intense peak in the spectrum of Bandy et al., but this feature has not been assigned. The four excited vibrational bands in the photoelectron spectrum correspond to internal energies of \( 815 \pm 50 \text{ cm}^{-1}, 1043 \pm 50 \text{ cm}^{-1}, 1172 \pm 50 \text{ cm}^{-1}, \) and \( 1280 \pm 80 \text{ cm}^{-1} \). The 815 and 1043 cm\(^{-1}\) bands are also considerably broader than the other bands in Fig. 6(a), particularly when it is noted that the spread in flight time will increase with flight time. Thus, it is possible that these two bands result from more than one vibronic component. Interestingly, there is no sign of the 455 cm\(^{-1}\) band observed in Figs. 4 and 5. Figure 6(b) corresponds to a weak feature in the spectrum of Bandy et al., and is also not assigned. The six labeled photoelectron bands observed above the origin correspond to internal energies of \( 442 \pm 50 \text{ cm}^{-1}, 854 \pm 50 \text{ cm}^{-1}, 1040 \pm 50 \text{ cm}^{-1}, 1116 \pm 50 \text{ cm}^{-1}, 1288 \pm 50 \text{ cm}^{-1}, \) and \( 1504 \pm 80 \text{ cm}^{-1} \). Given the uncertainty of the peak energies, each of these peaks has a corresponding peak in Fig. 6(a) with the exception of the 442 cm\(^{-1}\) peak and the 1504 cm\(^{-1}\) peak. The excess energy in Fig. 6(a) is not sufficient to populate the 1504 cm\(^{-1}\) level.

In the simplest interpretation, the spectra of Figs. 6(a) and 6(b) result from transitions to a progression of Renner-Teller levels in the \( X^2\Pi_g \) state involving excitation of a single degenerate vibration. Spectra obtained via \( ^1\Sigma_u^+ \) vibronic bands in the \( \Delta_u \) state would be expected to show transitions to levels with \( v_j^\pm = \text{even} \), while those obtained via \( ^1\Pi_u \) vibronic levels would show transitions to levels with \( v_j^\pm = \text{odd} \). Assuming the progressions result from excitation of \( v_6^\pm \), the energies of the expected vibronic levels given in Table II may be used. Comparison with the peak energies in Fig. 6 show that although there are certainly a number of coincidences, it is unlikely that the observed progressions can be explained by a single Renner-Teller vibration. Most likely, the resonant intermediate levels involve combination bands of two or more vibrational modes, resulting in the complex character of the spectra.

Figure 6(c) corresponds to the fifth intense feature in the spectrum of Bandy et al., which is assigned as the \( 3_0^1 6_0^1 \) transition. This spectrum also shows a long progression of excited vibrational peaks, corresponding to internal energies of \( 822 \pm 50, 1256 \pm 50, 1512 \pm 50, 1792 \pm 50, \) and \( 1985 \pm 80 \text{ cm}^{-1} \), respectively. Figure 6(d) corresponds to a weaker feature to the high energy side of the \( 3_0^1 6_0^1 \) band, and has been assigned as a combination band of \( 3_0^1 \) and the bending overtone corresponding to the band whose spectrum is shown in Fig. 4. Figure 6(d) also shows series of excited vibrational peaks, but the intensities of these bands are quite weak and the corresponding internal energies are somewhat different from those in Figs. 6(a)–6(c). These energies are \( 943 \pm 50 \text{ cm}^{-1}, 1656 \pm 50 \text{ cm}^{-1}, 1960 \pm 50 \text{ cm}^{-1}, \) and \( 2177 \pm 80 \text{ cm}^{-1} \). With the assignments of Smith, the values of \( v_3^+ \) and \( v_2^\pm \) in the ground state ion are \( 971.5 \text{ cm}^{-1} \) and \( 860.5 \text{ cm}^{-1} \), respectively. These values are quite close to the energies of the first excited vibrational levels observed in Figs. 6(c) and 6(d), respectively. It is interesting that the difference between the resonance energies in the intermediate \( 1\Delta_u \) state corresponds to \( \approx 200 \text{ cm}^{-1} \). Thus, if the energies of \( v_3 \) and \( 2v_2 \) are somewhat higher in the \( 1\Delta_u \) state than in the \( X^2\Pi_g \) state, it is not inconceivable that the resonances used for Figs. 6(c) and 6(d) correspond to combination bands of a set of common vibrations plus \( v_3 \) and \( 2v_7 \), respectively. It is clear that a more complete assignment of the spectra of Fig. 6 will require a better understanding of the vibronic structure in the \( 1\Delta_u \) state.

Photoelectron spectra recorded on weaker features between 42300 cm\(^{-1}\) and 43000 cm\(^{-1}\) show progressions of
vibrational bands similar to those observed in Figs. 5 and 6, whereas spectra recorded off resonance tend to show a single strong photoelectron peak corresponding to the vibrationless \(X^2\Sigma_g^+\) ground state. At two-photon energies above \(\approx 84\) 200 cm\(^{-1}\), a second photoelectron peak is observed in the off-resonance spectra. This peak corresponds to an internal energy of \(\approx 2100\) cm\(^{-1}\), and, by analogy with the He\(\text{I}\) photoelectron spectrum,\(^{13}\) most likely corresponds to the population of the \(v_3^+ = 1\) level.

C. The \(2^6\Sigma_g^0\) and \(2^8\Sigma_g^0\) bands

The most intense bands in the \(1^1\Delta_u \rightarrow X^1\Sigma_g^+\) absorption spectrum and in the resonant two-photon ionization spectrum correspond to a progression in the \(v_2\) \(C\equiv C\) symmetric stretching vibration and is assigned as \(2^8\Sigma_g^0\). In monodeutero and perdeutero diacetylene, each member of this progression is split into two subbands, with the lower energy components assigned as the \(2^8\Sigma_g^0\) transitions and the higher energy components assigned as the \(2^6\Sigma_g^0\) transitions; thus, the \(2^6\Sigma_g^0\) progression may actually result from the same two overlapping sets of transitions. The excitation of \(v_6\) or \(v_7\) is necessary to make the \(1^1\Delta_u \rightarrow X^1\Sigma_g^+\) transition allowed because the \(v_2\) vibration is totally symmetric. Excitation of the \(v_2\) vibration occurs because the \(1^1\Delta_u\) state is closer to the cumulene structure than the ground state, resulting in a lengthening of the \(C\equiv C\) bond. The \(2^6\Sigma_g^0\) band is the strongest in the \(1^1\Delta_u \rightarrow X^1\Sigma_g^+\) absorption spectrum, but the \(2^6\Sigma_g^0\) and \(2^8\Sigma_g^0\) bands are almost as strong, while the \(2^6\Sigma_g^0\) band is considerably weaker.

Figures 7(a) and 7(b) show the photoelectron spectra obtained at 43 235.7 cm\(^{-1}\) and 45 315.2 cm\(^{-1}\), respectively; that is, near the peaks of the \(2^6\Sigma_g^0\) and \(2^8\Sigma_g^0\) \(1^1\Delta_u \rightarrow X^1\Sigma_g^+\) bands. These photon energies correspond to two-photon energies lying 4407 and 8566 cm\(^{-1}\) above the adiabatic ionization threshold, respectively. The \(2^6\Sigma_g^0\) band has been the principal one used for excitation in studies of the reactions of triplet diacetylene. The spectra are notable for both their complexity and the absence of the origin band. The absence of an origin band is consistent with the excitation of a \(1^1\Pi_u\) vibronic level in the \(1^1\Delta_u\) state, and thus consistent with the \(2^6\Sigma_g^0\) assignments of the pump transitions. The most striking aspect of Figs. 7(a) and 7(b) is that the lowest vibronic levels populated have 1230 cm\(^{-1}\) and 3033 cm\(^{-1}\) internal energy, respectively. This observation is discussed in more detail below.

If, as in the deuterated species,\(^2\) the \(2^6\Sigma_g^0\) band is a composite of two vibronic bands, the character of the photoelectron spectrum might be expected to change as the laser is tuned across the resonance. For this reason, a series of photoelectron spectra were recorded at \(\approx 18.6\) cm\(^{-1}\) intervals (\(\approx 37.2\) cm\(^{-1}\) in the two-photon energy) across this resonance. The biggest effect observed in these spectra is simply the weakening of the photoelectron signal, and there is no clear indication of the spectra changing character until the laser is tuned well into the wings of the resonance. Thus, if two vibronic bands are overlapped in the spectrum of the nondeuterated species, it is not possible to determine with the current photoelectron spectra.

Six strong bands are observed in Fig. 7(a), corresponding to the production of \(X^2\Pi_g\) vibrational levels with internal energies of 1230 \(\pm\) 50 cm\(^{-1}\), 1570 \(\pm\) 50 cm\(^{-1}\), 2420 \(\pm\) 50 cm\(^{-1}\), 3050 \(\pm\) 50 cm\(^{-1}\), 3390 \(\pm\) 60 cm\(^{-1}\), and 3745 \(\pm\) 60 cm\(^{-1}\). The first two of these correspond to energies less than the \(v_2^+\) fundamental frequency, and thus must have \(v_2^+ = 0\). The remaining bands could have \(v_2^+ = 0\) or 1. Interestingly, the 1230 cm\(^{-1}\) and 1570 cm\(^{-1}\) bands can be paired with the 3390 cm\(^{-1}\) and 3745 cm\(^{-1}\) bands, respectively, as their energies differ by approximately the \(v_2^+\) fundamental frequency. Thus, it appears that both the \(v_2^+ = 0\) and 1 levels have good Franck–Condon overlap with the \(1^1\Delta_u\) \(v_2^+ = 1\), \(v_6^0\) \(= 1\) level.

Five resolved bands are clearly observed in Fig. 7(b), corresponding to \(X^2\Pi_u\) internal energies of 3033 \(\pm\) 50 cm\(^{-1}\), 3335 \(\pm\) 50 cm\(^{-1}\), 3670 \(\pm\) 50 cm\(^{-1}\), 4508 \(\pm\) 60 cm\(^{-1}\), and 5148 \(\pm\) 60 cm\(^{-1}\). The first of these is relatively weak. Each of the remaining four bands can be paired with a band in the \(2^6\Sigma_g^0\) spectrum by subtracting the energy of the \(v_2^+\) vibration. Thus, the 1230 cm\(^{-1}\) and 1570 cm\(^{-1}\) \(v_2^+ = 0\) bands in Fig. 7(a) can be paired with the \(v_2^+ = 1\) bands at 3335 cm\(^{-1}\) and 3670 cm\(^{-1}\) in Fig. 7(b), respectively. Similarly, the 2420 cm\(^{-1}\) band in Fig. 7(a) can be paired with the 4508 cm\(^{-1}\) band in Fig. 7(b), and the 3050 cm\(^{-1}\), \(v_2^+ = 1\) band can be paired with the 5148 cm\(^{-1}\) band at 2 band. It appears likely that the 3033 cm\(^{-1}\) band in Fig. 7(b) also involves the combination of \(v_2^+ = 1\) and a low frequency vibration. The interesting aspect of this conclusion is that Fig. 7(b) appears to show no evidence for excitation of photoelectron bands with \(v_2^+ = 0\).

Because the \(v_2^+\) vibration is totally symmetric, there can be no selection rules restricting access to the \(v_2^+ = 0\) levels.

Although there appears to be a close connection between
the spectra in Figs. 7(a) and 7(b), the important remaining questions about the spectra are (1) what is the nature of the 1230 cm\(^{-1}\) and 1570 cm\(^{-1}\) vibrations in Fig. 7(a), and (2) why are no bands with lower internal energy observed? Examination of Table I shows that no fundamental frequencies of \(X^2\Pi_g\) fall in this energy region, and based on the \(\omega_6\) and \(\epsilon_6\) values determined above, the Renner-Teller components for \(v_6^+\) are not expected to fall in that range. The aim of understanding the photoelectron spectra out of the \(2g^6\) and \(2\Delta^6\) levels of the \(\Delta_u\) state, Franck-Condon profiles were modeled for transitions from various vibrational levels in the \(\Delta_u\) intermediate state to the \(X^2\Pi_g\) ground state of the cation. The calculation employed harmonic frequencies for all vibrations, and did not explicitly include the Renner-Teller effects on \(v_6\) and \(v_7\) in the \(X^2\Pi_g\) state of the cation. As a result, it is not expected that the calculation will reproduce the specific details of the transitions involving \(v_6\) and \(v_7\). However, the goal of the calculations was to discover qualitative effects with respect to the Franck-Condon progressions involving the totally symmetric vibrations \(v_2\) and \(v_3\), which should be treated reasonably well in this model. The Renner-Teller coupling may split the calculated transitions to modes involving one or more quanta in \(v_6\) and \(v_7\) into multiple features, but should not change the overlap integrals for the symmetric \(v_2\) and \(v_3\) vibrations. We were interested in seeing which modes are active in the Franck-Condon progressions from the \(\Delta_u\) states accessed in the R2PI process and how the intensity is distributed through the progressions, specifically with respect to the lack of intensity in the origin region, as observed in the photoelectron spectra.

The optimized geometry, along with the normal modes and frequencies, for the \(\Delta_u\) state was obtained from Vila et al.,\(^7\) and a calculation at the same level of theory (CAS/6-31G** 5d) was done to obtain the equilibrium geometry, frequencies, and normal modes of the ion. This information provided the input for calculating the Franck-Condon factors (FCFs) for the transitions from a specific vibrational level in the \(\Delta_u\) state to the ground state vibronic levels in the cation.\(^{25}\) The overlap integrals were calculated in the harmonic approximation, and no scaling was done on the Gaussian frequencies at any point during the calculations. Doktorov, Malkin, and Man’ko\(^{26}\) (DMM) derived recursion relations for the overlap integrals incorporating the Duschinsky transformation,\(^{26-28}\) expressing the overlap integral involving \(n\) quanta in mode \(j\) as a sum of integrals involving \((n-1)\) quanta in that mode using the Hermitian relationships. Lehmann\(^{25}\) recently derived a series of recursion relations similar to those of DMM, but capable of handling transitions from linear to bent states (but not vice versa). We have used Lehmann’s derivation\(^{25}\) as the basis for our code.

Sets of FCFs were calculated for transitions originating in the \(|v_2^+=1, v_6^+=1\rangle\) and \(|v_2^+=2, v_6^+=1\rangle\) levels in the \(\Delta_u\) state, and Fig. 8 shows the calculated Franck-Condon profiles for the transitions from these levels. As there is no clear correlation for \(v_6\) and \(v_7\) in going from the ground state through \(\Delta_2\) to the ion, the features are labeled \(v_{6/7}\). [FCFs for transitions from the \(|v_2^+=1, v_6^+=1\rangle\) and \(|v_2^+=1, v_7^+=1\rangle\) were also calculated which produced the same bands, but with different intensities.] A Gaussian function with a width of 25 cm\(^{-1}\) has been added to the stick spectra for better visualization of the transitions. The dashed lines in the figure indicate the maximum ion internal energy reached in one-color, resonant two-photon ionization.

The calculated photoelectron spectrum out of the \(|v_2^+=1, v_6^+=1\rangle\) level of the \(\Delta_u\) state [Fig. 7(a)] is consistent with certain aspects of the experimental spectrum [Fig. 6(a)], but inconsistent with others. The calculated spectrum correctly predicts a FC progression in \(v_2^+\) that has substantial intensity in both the \(v_2^+=0\) and \(v_2^+=1\) levels, as observed. In addition, the calculation confirms a lack of intensity in the transition to the zero point level of the cation, with a false origin appearing at \(v_{6/7}=1\). However, the fundamental frequencies of \(v_6\) or \(v_7\) are expected to be much smaller than 1230 cm\(^{-1}\), even in the presence of Renner-Teller coupling. In direct ionization out of the linear \(\Delta_u\) state to the linear ion, the FC overlap integrals require that the symmetries of the vibrational levels accessed in the ion are the same as those in the neutral. Since \(\pi_g\) vibrational levels are needed to induce vibronic coupling in the \(S_0\Delta_u\) transition, \(\pi_g\) sym-

FIG. 8. Calculated Franck-Condon profiles for the transitions originating in the (a) \(|v_2^+=1, v_6^+=1\rangle\), (b) \(|v_2^+=2, v_6^+=1\rangle\), and (c) \(|v_2^+=2, v_7^+=1\rangle\) levels in the \(\Delta_u\) state. The stick spectra have been convoluted with a Gaussian function with a width of 25.0 cm\(^{-1}\) for better visualization of the transitions. The dashed lines in the figures indicate the maximum ion internal energy available following two-photon ionization. Spectrum (b) was calculated with a change in the C≡C bond length of 0.018 Å between the \(\Delta_u\) state of the neutral and the \(\Delta_u\) state of the C_2H_2 cation.
metry vibrational levels in the ion will be produced.

Since there are no πg vibrational fundamentals at 1230 cm\(^{-1}\), one anticipates that a πc combination band is responsible for the observed feature. A plausible assignment for the 1230 cm\(^{-1}\) band would be as the \(|v_h^e=1, v_{\delta}\!\!\gamma^e=1\rangle\) level, since the frequency of the C–C symmetric stretch (ν\(_s\), \(\alpha^e_s\) symmetry) is known to be 860 cm\(^{-1}\)\(^{14}\) leaving 370 cm\(^{-1}\) for the Renner-Teller active \(v_{\delta}\!\!\gamma^e\) = 1 level. However, the dominance of this band in the spectrum is hard to reconcile with the assignment of the intermediate state as \(|v_h^e=1, v_{\delta}\!\!\gamma^e=1\rangle\). Presumably, there would need to be Fermi resonant mixing in the intermediate state between the \(|v_h^e=1, v_{\delta}\!\!\gamma^e=1\rangle\) and a level that contains \(v_3^c\) character. A 2:1 Fermi resonance between \(v_2\) and \(2v_3\) is the most likely possibility. Figure 7(b) shows the calculated photoelectron spectrum from the \(|v_h^e=2, v_{\delta}\!\!\gamma^e=1\rangle\) intermediate state (with a change in the C=C bond length upon ionization of 0.018 Å\(^{29}\)) which has as its most intense band the transition to the \(|v_h^e=1, v_{\delta}\!\!\gamma^e=1\rangle\) level of the ion. The actual spectrum would then be a composite of Figs. 7(a) and 7(b).

The computed photoelectron spectrum from the \(|v_h^e=2, v_{\delta}\!\!\gamma^e=1\rangle\) state [Fig. 7(c)] also reproduces experiment only in part. Building off the false origin, the progression in \(v_h^e\) is qualitatively consistent with experiment, showing a strong transition to \(v_h^e=1\) (12100 cm\(^{-1}\)), and much weaker transitions to \(v_h^e=0\) and 2. However, the calculation predicts a rather intense transition at \(v_h^e=3\), that is not observed experimentally, even though this level should be below the high energy cut-off in the experimental spectrum (8566 cm\(^{-1}\)). Taken as a whole, the match-up between experiment and calculation is less than satisfactory, and no simple, harmonic picture of the intermediate and ionic states seems to be capable of reproducing the observed photoelectron spectra out of the \(|v_h^e=2, v_{\delta}\!\!\gamma^e=1\rangle\) and \(|v_h^e=1, v_{\delta}\!\!\gamma^e=2\rangle\) levels, even if the Renner-Teller splittings in the ion are considered.

The unusual Franck–Condon profiles of Figs. 7(a) and 7(b) suggest the possibility that the observed intensities reflect the presence of another electronic state that is mixing with the \(21^6\!\!\gamma^e\) and \(21^6\!\!\delta^e\) levels of the \(1^3\Delta_u^e\) state. This possibility is also consistent with the inherent broadening of the transitions in the resonant two-photon ionization spectrum and the high quantum efficiency of intersystem crossing out of these levels into the triplet manifold. If this second state can also be ionized by absorbing an additional photon, the photoelectron spectrum would reflect the photoionization branching ratios for both the \(1^3\Delta_u\) and the perturbing state. (Indeed, these experiments were originally intended as the first step in an attempt to record photoelectron spectra for these other states.) The \(S_1\) state is a likely candidate for this perturbing level, which could serve as an intermediary to the triplet manifold in the intersystem crossing. However, the electronic origin of the \(S_1\) state\(^{30}\) is approximately 8323 cm\(^{-1}\) below that of the \(1^3\Delta_u\ 21^6\!\!\gamma^e\) level, and in the radiationless transition, this difference must be converted into vibrational energy in the \(S_1\) level. This process will thus result in the population of relatively high vibrational levels of the \(S_1\) state. In general, it would be somewhat surprising if the Franck–Condon factors between such levels and the low vibrational levels of the ion were substantial. In addition, relatively long Franck–Condon progressions would be expected in the bending modes, counter to observation. The triplet manifold itself offers a second possibility, but is also hard to reconcile with the comparatively sparse photoelectron spectra observed, for instance, from the \(21^6\!\!\delta^e\) level.

A second alternative worth mentioning is that of electronic autoionization. The \(CH_2^+\) cation has an excited state (\(A^2\Pi_u\)) that is 19276 cm\(^{-1}\) above the \(X^2\Pi_g\) ground state. The two-photon energy thus has the potential for accessing Rydberg states converging to this excited threshold. These states would decay by electronic autoionization, and the resulting vibrational state distribution would be expected to reflect the Franck–Condon factors between the autoionizing state and the ground electronic state of the ion. The one difficulty with this explanation comes from a consideration of the excitation process. The dominant configuration in the \(1\Delta_u\) level is ...(1 \(\pi_{\mu\gamma}\))\(^{(1)}\)(1 \(\pi_{\nu\gamma}\))\(^{(1)}\)(1 \(\pi_{\gamma\gamma}\))\(^{(1)}\)(1 \(\pi_{\mu\gamma}\))(2 \(\pi_{\mu\mu}\))\(^{(1)}\) or ...(1 \(\pi_{\mu\gamma}\))\(^{(2)}\)(1 \(\pi_{\nu\gamma}\))\(^{(1)}\)(1 \(\pi_{\gamma\gamma}\))\(^{(1)}\)(1 \(\pi_{\mu\gamma}\))(2 \(\pi_{\mu\mu}\)). One electron transitions from these configurations would result in either excitation of the outer electron or one of the inner electrons. Excitation of the outer electron would produce Rydberg series converging to the ground state of the ion. Excitation of a 1 \(\pi_{\mu\gamma}\) electron into the singly occupied 1 \(\pi_{\mu\gamma}\) orbital (or equivalently, excitation of a 1 \(\pi_{\nu\gamma}\) electron into the singly occupied 1 \(\pi_{\nu\gamma}\) orbital) would produce a Rydberg state with an \(A^2\Pi_u\) core that could autoionize into the ground state configuration. However, given that the difference in the electronic energies of the \(A^2\Pi_u\) and \(X^2\Pi_g\) states\(^{17,18}\) is only 19276 cm\(^{-1}\) and that the photon energy is greater than 40000 cm\(^{-1}\), this would require a substantial amount of vibrational excitation in the autoionizing Rydberg state. The Franck–Condon factors for such a transition would be expected to be quite poor, especially in view of the relatively similar geometries of the \(A^2\Pi_u\) and \(X^2\Pi_g\) states. In principle, excitation from a deeper core orbital to autoionizing states converging to a higher excited state of the cation is possible, but there is insufficient information to assess this possibility.

V. CONCLUSIONS

The present photoelectron spectra provide new information on the assignments of the observed bands in the \(1^3\Delta_u^e\) \(\rightarrow\) \(X^2\Sigma_g^+\) transition, and on the energetics of the low-lying vibrionic levels of the \(CH_2^+\) cation. The present analysis is most successful for the lowest vibrionic levels of the \(CH_2^+\) \(X^2\Pi_g^e\) state. In particular, the three components of the \(v_h^e=1\) Renner-Teller multiplet were observed, yielding Renner-Teller parameters of \(a_h^e=670\) cm\(^{-1}\) and \(\epsilon^e_h=0.32\). These values are quite close to those obtained for the trans-bending \(\nu_5^e\) vibration in the ground state of the acetylene cation.\(^ {22,23}\) The analysis of the higher vibrionic levels of the diacetylene cation is complicated by the presence of four low-frequency vibrational modes and the correspondingly large number of potential assignments. Ultimately, however, the data indicate that vibrionic selection rules and Franck–Condon factors for the ionizing transition play a large role in determining the appearance of the spectra. More detailed calculations of the potential surfaces of the \(1^3\Delta_u^e\) and \(X^2\Pi_g^e\)
states would allow more quantitative calculations of the Franck–Condon factors, and provide a good test of the present interpretation of the photoelectron spectra from the $1^1\Delta_u$ state.

The present experiments suggest a number of future studies that may ultimately help address some of the questions raised here. In particular, double-resonance spectroscopy in which different vibronic levels of the $1^1\Delta_u$ state are pumped and a second laser is scanned through selected portions of the ionization continuum would be useful in identifying any electronically or vibrationally autoionizing levels in the energy region of interest. In addition, two-color ZEKE or MATI spectroscopy via the same intermediate states would provide a more accurate and much higher resolution determination of the vibronic structure in the $X^2\Pi_g$ state of the $C_4H_2^+$ cation, which would be a great help in the assignment and analysis of the photoelectron spectra presented here. Ultimately, such studies are expected to provide a considerably more complete understanding of the energetics of the $C_4H_2$ ground state, the photoionization dynamics of the $1^1\Delta_u$ state, and the energetics and perturbations of the vibronic structure in the $1^1\Delta_u$ state.

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