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A new technique to study Rydberg states by multiphoton ionization spectroscopy
Gerade Rydberg states of acetylene studied by multiphoton ionization and photoelectron spectroscopy

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The lowest few gerade Rydberg states of C\(_2\)H\(_2\), C\(_2\)HD, and C\(_2\)D\(_2\) have been observed as two-photon resonances in the multiphoton ionization (MPI) spectra of these isotopic species. Analysis of the two-photon excitation spectra of these molecules, and of the accompanying MPI-photoelectron spectra for C\(_2\)H\(_2\), enable characterization of the \(^1\Sigma^+\) and \(^1\Delta_g\) Rydberg states arising from the electronic promotion \(\pi^*_{1\Sigma} 3\pi\pi^*_{1\Sigma} \rightarrow \pi^*_{1\Sigma}\) and reveal extensive vibronic interaction in this energy region. A search was made for higher gerade Rydberg states at energies up to 90 000 cm\(^{-1}\). Weak, diffuse signal is observed for the 4p complex. No ionization signal was observed in the energy range where the \(np\) (\(n = 5-7\)) Rydberg states are expected to appear. This is taken as evidence for opening of a facile nonradiative decay channel at high excitation energies.

I. INTRODUCTION

Much is already known about the vertical electronic spectrum of the acetylene molecule from numerous experimental investigations of its one-photon vacuum ultraviolet (VUV) absorption spectrum\(^{1-16}\) and \textit{ab initio} calculations of key sections of the potential functions for many of its excited states.\(^{17-20}\) To this extensive body of data has recently been added the results of spectroscopic studies using resonance enhanced multiphoton ionization (MPI),\(^{21-23}\) in which several of the more stable Rydberg states have been identified as three-photon resonances in an overall four-photon ionization process.

Acetylene is a centrosymmetric molecule (point group \(D_{\text{sh}}\)) with a \(^1\Sigma^+\) electronic ground state. The \(\pi-\pi\) selection rule applies to excitations brought about using any odd number of photons, thus both the one- and three-photon studies are able to provide information about its ungerade excited states. Consequently, our knowledge of the gerade Rydberg states of acetylene (notably those arising from the electronic promotions \(\pi^*_{1\Sigma} 3\pi\pi^*_{1\Sigma} \rightarrow \pi^*_{1\Sigma}\)) is restricted to the findings of \textit{ab initio} theory\(^{20}\) and to the somewhat tentative conclusions of one study of the electron energy loss spectrum of this molecule.\(^{24}\)

The present work, which describes the joint findings of two research groups, partly rectifies this deficiency. The gerade states of interest are populated via a coherent two-photon excitation process and detected by the resonance enhancement they provide to the overall three-photon ionization process. In the Bristol experiments the resulting ions are mass discriminated by time-of-flight mass spectrometry (TOFMS). Using such methods it is straightforward to record separate excitation spectra for each of the isotopic species C\(_2\)H\(_2\), C\(_2\)HD, and C\(_2\)D\(_2\).

Complementary information is provided by the Stony Brook experiments, in which the kinetic energy distributions of the photoelectrons resulting from the ionization process are measured. The utility of resonance enhanced multiphoton ionization-photoelectron spectroscopy (REMPI-PES) as a spectroscopic tool is now well established.\(^{25,26}\) When, as in the present case, the ionization of the Rydberg intermediate requires absorption of but a single photon, the distribution of ion vibrational states produced is determined by the matrix elements coupling the intermediate (Rydberg) and final (ion) states. Given a certain minimum spectroscopic knowledge of the parent ion, analysis of the resulting REMPI-PES can thus provide useful information about the structure and dynamics of the neutral intermediate state. This is the case in the present study. Band contour analysis of the wavelength resolved 2 + 1 MPI excitation spectra provide an unambiguous determination of the vibronic symmetries of the resonant intermediate levels, but state assignments and in particular, the role of vibronic interaction would have been very hard to establish without the complementary MPI-PES data.

II. EXPERIMENTAL

A. Two-photon excitation spectroscopy

Mass resolved two-photon resonance enhanced MPI spectra of C\(_2\)H\(_2\), C\(_2\)D\(_2\), and C\(_2\)HD were obtained in Bristol using a home built time-of-flight mass spectrometer of conventional design.\(^{27}\) The gases were prepared by the action of, respectively, H\(_2\)O, D\(_2\)O, and 50/50 H\(_2\)O/D\(_2\)O mixture on CaC\(_2\), and purified by low temperature trap-to-trap distillation. A "C\(_2\)HD" sample prepared in this way consists of a mixture of all three isotopic variants. The sample of interest (typically ~20% seeded in argon, stagnation pressure <500 Torr) was expanded through a pulsed valve and then constrained to flow through a stainless steel capillary of length 5 mm and inside diameter 1 mm before emerging into the first acceleration stage of the TOF mass spectrometer. In operation the mean pressure in this chamber was maintained at ~10\(^{-5}\) Torr while that in the differentially pumped drift
region is estimated to be one order of magnitude lower. The rotational temperature of the acetylene molecules under these mild expansion conditions was established as 180 ± 20 K by recording and analyzing the 3 + 1 MPI excitation spectrum of the previously documented \( 1^3\Phi_u (\pi_u^0 3d\delta_g^0) \rightarrow 1^3\Sigma_u^+ \) transition.\(^{21}\)

The gas pulse is crossed at right angles by the frequency doubled output of an excimer pumped dye laser (Lambda-Physik EMG 201 and FL 2002) operating with the dyes coumarin 153 and 307. The wavelength was calibrated using optogalvanic spectroscopy of neon. Frequency doubled radiation in the wavelength range 257–285 nm was produced using a servotuned harmonic generator (Inrad model 5-12), and was linearly polarized such that its E vector was aligned parallel to the axis of the time-of-flight spectrometer. When needed, circularly polarized light was produced by insertion of a Fresnel rhomb (Karl Lambrecht, fused quartz, optimized for 272 nm). The ultraviolet pulse energies were maintained at <200 \( \mu \)J; at higher pulse energies the resolution of the time-of-flight spectrum was degraded.

The laser is triggered and focused (27 cm f.l. lens) so as to interact with each gas pulse at the point of maximum flux. Ions formed via MPI in the focal volume are subject to two stages of acceleration prior to entering the field-free drift region and eventual detection by a channel electron multiplier (Mullard X919 CL, typical operating voltage = 1600 V). Time-of-flight spectra were recorded by feeding the amplified output from the channel electron multiplier into a fast digital oscilloscope (LeCroy 9400, 125 MHz bandwidth), the sweep of which was pretriggered by the signal from a fast photodiode coincident with the dye laser pulse. An Apple II microcomputer with IEEE-488 interface was used for signal averaging of these transients and data storage. MPI spectra associated with one particular ion mass were obtained using a boxcar (PAR 162/165, operating in its linear gate mode with a 50 ns time window) to sample just that fraction of the total ion yield which showed the appropriate time-of-flight, as a function of the laser excitation wavelength. The analog output of the boxcar was fed through a voltage to frequency converter and recorded digitally on the Apple II.

B. Photoelectron spectroscopy

The photoelectron spectra were taken using a molecular beam mass/photoelectron spectrometer at Stony Brook. Ionization occurs at the intersection of the laser focus and a pulsed, differentially pumped, molecular beam of acetylene. The acetylene was purified by passage through a dry ice trap and the pulsed valve was operated to give a time averaged pressure of acetylene in the main chamber of \( \sim 4 \times 10^{-5} \) Torr. The ionization region is midway between a pair of electrodes which form the first elements of the injection optics for the mass and photoelectron spectrometers. The ions produced are accelerated up through a set of electrostatic lenses, mass analyzed by a quadrupole mass filter (Extral—0.75 in. rods), and detected with a Daly detector/gated integrator combination.

In photoelectron spectroscopy mode, the acceleration field in the ionization region is reduced to \( \sim 0.5 \) V/cm. A small fraction of the photoelectrons is collected and focused by an einzell lens through the entrance slit of a hemispherical electron energy analyzer (Comstock) operated in constant pass energy mode. Transmitted electron signal is measured with a CEMA/preamplifier/gated integrator combination. For these experiments, 1 mm analyzer slits were used, yielding energy resolution of \( \sim 65 \) meV. The ionization region and the photoelectron energy analyzer are enclosed in a \( \mu \)-metal shielding box. Mounted just outside the box are a pair of high voltage electrodes which collect electrons produced by UV photoemission from the box, and an electron gun which is used for tuning up.

The photon source is a Quantel Nd:YAG pumped dye laser system. Using a combination of doubling and mixing-after-doubling, the wavelength range from 222.64 to 311.3 nm was examined. Pulse energies varied from 0.6 to 2.5 mJ, and the laser was focused on the molecular beam with either a 10 or 20 cm focal length lens. The laser linewidth (\( \sim 0.18 \) cm\(^{-1} \)) is similar to that of the system at Bristol, except at wavelengths below 260 nm where the linewidth is \( \sim 0.7 \) cm\(^{-1} \) due to mixing with the Nd:YAG fundamental. The 2 + 1 photon ionization spectra closely match those obtained at Bristol except that a few additional bands were observed at Stony Brook due to higher laser intensities and wider tuning range.

Calibration of the photoelectron spectra was done using a mixed acetylene–xenon beam, which allowed us to switch quickly between the xenon calibrant and acetylene without changing dye or experimental conditions. 2 + 1 photon ionization of xenon through the \( 6p [2\pi]_1^3 \) level at 256.02 nm...
was used to calibrate PES of C₂H₂ obtained at 261.97, 262.86, and 263.97 nm. These three acetylene spectra were then used to calibrate the acetylene PES obtained at longer wavelengths. The PES of acetylene bands at 241.97 and 242.04 nm were calibrated against xenon excited through the 6p₁/₂ state. Once calibrated, many of the bands in the acetylene PES are easily assigned to cation states of known energies. These provide a test of the accuracy of the xenon calibration which appears to vary from +0.008 to −0.018 eV; i.e., within the resolution of the spectra.

Data acquisition is controlled by a PDP-11 computer and CAMAC interface. The reported photoelectron spectra are averages of three to four independent runs.

III. RESULTS AND DISCUSSION

Figure 1 displays representative TOF spectra obtained following excitation of C₂H₂ at 274.70, 268.25, and 262.78 nm, respectively. These illustrate the fact that under our experimental conditions the parent ion is always a major contributor to the observed TOF spectra, but that fragment ion formation gains in importance as the excitation wavelength is decreased. Figure 2 shows excitation spectra obtained using samples of C₂D₂, “C₂HD,” and C₂H₂, while monitoring the TOF signal corresponding to the respective parent ion peaks (m/e = 28, 27, and 26, respectively). Measurements of the magnitude of the parent ion signal as a function of laser pulse energy showed the expected quadratic dependence over more than an order of magnitude variation in energy. Observed band positions are listed in Table I. No 2+1 MPI signals were observed at excitation wavelengths longer than those included in Fig. 2 or below 241.9 nm.

A representative set of photoelectron spectra are displayed in Figs. 3–6. In each figure, photoelectron intensity is plotted against electron kinetic energy. The label at the top of each figure gives the assignment for the intermediate state pumped in the MPI process. The label for each panel gives ν′, the vibrational level excited in the intermediate state. Finally, the assignments for the ion vibrational states are given by superimposed bars.

The asymmetry of the acetylene core ensures (at least for low principal quantum number n) that a given πₙ⁺np⁺π⁺ excitation will give rise to four singlet and four triplet states. Ab initio calculations indicate that the singlet members of the “3p complex” will be ordered 1Π₉(πₙ⁺3pπ⁺), 1Δ₉(πₙ⁺3pπ⁺), 1Σ⁻(πₙ⁺3pπ⁺), 1Σ⁺(πₙ⁺3pπ⁺) in order of increasing energy. As with all other documented Rydberg states belonging to series that converge to C₂H₂⁺(X 2nu), these excited states may be expected to have linear equilibrium geometries with a C≡C bond length somewhat greater than in the neutral ground state. One color multiphoton ex-
TABLE I. Frequencies and possible assignments of two-photon resonances observed in the multiphoton ionization spectra of C$_2$H$_2$, C$_2$HD, and C$_2$D$_2$.

<table>
<thead>
<tr>
<th>Two-photon transition</th>
<th>C$_2$H$_2$</th>
<th>C$_2$HD</th>
<th>C$_2$D$_2$</th>
<th>$n^* = (n - \delta)^b$</th>
<th>Zero-order assignment</th>
</tr>
</thead>
<tbody>
<tr>
<td>Frequency$^a$/cm$^{-1}$</td>
<td>72 753</td>
<td>72 764</td>
<td>72 780</td>
<td>2.39</td>
<td>$^1\Delta_g, ^2\Sigma^+_g$</td>
</tr>
<tr>
<td></td>
<td>73 350</td>
<td></td>
<td></td>
<td></td>
<td>$^1\Delta_u, ^4\Pi_u$</td>
</tr>
<tr>
<td></td>
<td>73 906</td>
<td>73 866</td>
<td>73 759</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>73 976</td>
<td>73 906</td>
<td>73 868</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>74 286</td>
<td>74 267</td>
<td>74 267</td>
<td>2.49</td>
<td>$^1\Sigma^+_g, ^2\Pi^+_g$</td>
</tr>
<tr>
<td></td>
<td>74 347</td>
<td>~74 328</td>
<td>74 348</td>
<td></td>
<td></td>
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<td></td>
<td>74 390</td>
<td></td>
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<tr>
<td></td>
<td>74 559</td>
<td>74 486</td>
<td>74 433</td>
<td></td>
<td>$^1\Delta_u, ^2\Pi_u$</td>
</tr>
<tr>
<td></td>
<td>75 188</td>
<td></td>
<td></td>
<td></td>
<td>$^1\Delta_u, ^2\Pi_u$</td>
</tr>
<tr>
<td></td>
<td>75 767</td>
<td>75 621</td>
<td>75 512</td>
<td></td>
<td></td>
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<td></td>
<td>75 786</td>
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<td>75 562</td>
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<td>76 086</td>
<td>75 977</td>
<td>75 906</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>76 182</td>
<td>76 062</td>
<td>75 977</td>
<td>$^1\Sigma_g^+, ^2\Sigma^+_g$</td>
<td></td>
</tr>
<tr>
<td></td>
<td>76 344</td>
<td>76 205</td>
<td>76 072</td>
<td>($^1\Sigma_u^+, ^2\Sigma^+_g$)</td>
<td></td>
</tr>
<tr>
<td></td>
<td>77 557</td>
<td></td>
<td></td>
<td></td>
<td>$^1\Delta_u, ^2\Pi_u$</td>
</tr>
<tr>
<td></td>
<td>82 630</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>82 654</td>
<td></td>
<td></td>
<td>3.43 ($^4\Pi$ Rydbergs)</td>
<td></td>
</tr>
</tbody>
</table>

$^a$Quoted frequencies represent "center-of-gravity" of the various bands; uncertainty $\pm$ 10 cm$^{-1}$.

$^b$Quantum defect $\delta$, defined for C$_2$H$_2$, via the equation $\delta = IP - R / (n - \delta)^2$, where $R = 109 737$ cm$^{-1}$ and IP = 91 975 cm$^{-1}$ (Ref. 15).

Tentatively assigned to hot band transitions—see the text.

Citations in acetylene using identical photons are restricted by the same spin and $+ / -$ parity conservation requirements that accompany conventional electric dipole transitions, but the selection rule on $\Delta$ is relaxed to the extent that $\Delta\lambda < n$ for $n$-photon excitation and, as discussed previously, the overall transition symmetry must be gerade (ungerade) for $n =$ even (odd). Thus using two-photon excitation methods it should be possible to excite transitions to the $^1\Pi_u$, $^1\Delta_g$, and $^1\Sigma_g^+$ members of the $3p$ complex and, by analogy with the other documented Rydberg transitions in acetylene, we should expect a short progression in $v_2$ (the excited state $C \equiv C$ stretching vibration) to accompany each excitation.

On this basis we can begin to interpret the spectra shown in Fig. 2. The longest wavelength feature we assign as an electronic origin band because:

(i) it is the longest wavelength observed,

(ii) its frequency is insensitive to isotopic substitution, and

(iii) the associated MPI-PES of C$_2$H$_2$ (Fig. 3) shows a single sharp peak with kinetic energy 2.109 eV.

Given a value of 11.406 eV$^{29}$ for the first ionization potential (IP) of C$_2$H$_2$, the energy of this photoelectron peak indicates that ions formed via this intermediate state are in the ground vibrational state. (The broad hump at $\sim$0.6 eV is from scattering.) The fact that the photoelectron kinetic energy distribution shows but a single peak is expected for a Rydberg intermediate state, which should have diagonal ($\Delta v = 0$) Franck-Condon factors for ionization. Thus we conclude that the intermediate state is in its zero-point level. Similar behavior has been observed previously for the $G^1\Pi_u (\pi_u^2 3s\sigma_u^0)$, $\tilde{I}^1\Pi_u (\pi_u^2 5s\sigma_u^0)$, and $^1\Phi_u (\pi_u^2 3d\delta_u^0)$ Rydberg states of C$_2$H$_2$.23

Two additional bands with rotational contours and polarization behavior similar to the first, appear to higher frequency in the two-photon excitation spectra of each of the three isotopic species. The energy separations between these features (see Table I) accord closely with previous measurements of the, weakly isotope dependent, $v_2$ quanta in other Rydberg states of C$_2$D$_2$, C$_2$DH, and C$_2$D$_2$.15 The $2 + 1$
MPI-PES of C₂H₂ obtained following excitation through these two intermediate states each show single sharp peaks (Fig. 3). The measured photoelectron kinetic energies (2.229 and 2.334 eV, respectively) are consistent with assignment of these features in the MPI-PES to production of ions with one and two quanta of C=C stretch excited. We thus infer that the intermediate levels correspond to the 2Σ⁺ and 2Σ⁻ transitions built on the origin at 72 753 cm⁻¹.

Reference to Fig. 2 reveals that all other major features appearing in the two-photon resonance enhanced MPI spectra of all three isotopic species exhibit a significantly different, narrower band contour; Figs. 4 and 5 demonstrate that the photoelectron kinetic energy distributions associated with these features are also characteristically different in that they no longer consist of a single peak. Before discussing the interpretation of these spectral features, however, it will prove useful to consider the symmetry assignment of the excited electronic state responsible for the progression starting from the long wavelength origin (72 753 cm⁻¹ in C₂H₂).

The classic route to symmetry determination involves rotational analysis. Unfortunately these vibronic bands exhibit such compact structure that, in the present experiments, only their overall band contours may be resolved. Multiphoton transition probabilities are sensitive to the polarization state of the exciting radiation. This fact can be used to provide some additional clues as to the excited state symmetry. The cross section for coherent two photon excitation of a ΔΛ = 0 transition (e.g., 1Σ⁺ → 1Σ⁻) could contain contributions from both zeroth and second rank compo-
components of the one color, two-photon transition tensor. If present, both would contribute when using linearly polarized excitation, but upon changing to circularly polarized excitation, the former [carried by the $T^0_0(A)$ component] is forbidden while the contribution from the latter [ $T^0_0(A)$] would be enhanced by a factor of 3/2 for the same light intensity. In contrast, only second rank components of the two-photon transition probability can contribute to excitations involving $\Delta \Lambda = \pm 1, \pm 2$. Thus any features associated with $^1\Pi_u - ^1\Sigma^+$ or $^1\Delta_g - ^1\Sigma^+$ transitions in the two-photon excitation spectrum of acetylene must show enhanced signal strength with otherwise identical band structures on changing to circularly polarized excitation.

Difficulties in matching linearly vs circularly polarized laser pulse intensities, the beam displacement introduced by using a Fresnel rhomb as an achromatic circular polarizer, and the impurity of the circularly polarized light so produced, all conspire to prevent quantitative measurement of the polarization ratio associated with these two-photon resonance enhanced MPI signals. Qualitatively however, it is clear that the relative importance of the vibronic features observed in the spectrum of C$_2$H$_2$ following excitation at 274.82, 268.16, and 261.90 nm (and their counterparts in the spectra of C$_2$HD and C$_2$D$_2$) increases when using (imperfectly) circularly polarized light, though their band contours show no appreciable change. This is illustrated in Fig. 7 which shows a portion of the $2 \rightarrow 1$ MPI spectrum taken using linearly (a) and circularly (b) polarized laser light. The latter is displayed on a ten times expanded vertical scale and reveals clearly the relative enhancement of the feature centered at 268.16 nm with circularly polarized excitation. Such behavior implies predominant (if not exclusive) second rank character for the two-photon transition tensor and thus suggests assignment of the excited state vibronic symmetry for the enhanced bands as either $^1\Pi_u$ or $^1\Delta_g$. This conclusion is in accord with theory, which places both these states below the $^1\Sigma^+ (\pi^0_u 3p\pi_u^0)$ state and, in the case of
C\textsubscript{2}H\textsubscript{2}, with the tentative conclusions of one previous electron energy loss study\textsuperscript{24}.

Band contour analysis provides a possible means of distinguishing between these two possible assignments. The length of the observed \( \nu_3 \) progression, and the magnitude of the \( \nu_1 \) quanta identified for C\textsubscript{2}H\textsubscript{2}, C\textsubscript{2}HD, and C\textsubscript{2}D\textsubscript{2}, are reminiscent of those observed previously for other “good” Rydberg states (e.g., the \( \tilde{G} \) \( ^3\Pi_u \) state\textsuperscript{15}) of these isotopic species. On this basis it is likely that the state we wish to assign has rotational constants similar to those of the \( \tilde{G} \) state.

Figure 8 shows the predicted form of C\textsubscript{2}H\textsubscript{2} spectra carried by each of the various possible nonzero components of the two-photon transition tensor, assuming a beam rotational temperature of 180 K. Comparison with experiment (Fig. 9) encourages assignment of the excited state whose origin lies \( \sim 72 \) 753 cm\textsuperscript{-1} as \( ^1\Delta_g (\pi^2_2 \pi^1_4) \).

Further consideration of the calculated band contours displayed in Fig. 8 suggests that all of the other major features observed in this region of the MPI spectrum of acetylene are simple \( Q \) branches associated with excitations to states of \( ^1\Sigma^+_g \) vibronic symmetry, carried predominantly by the \( T_g^0 (\text{A}) \) component of the two-photon transition tensor. Such a conclusion is consistent with the polarization studies (Fig. 7); the cross section associated with the zeroth rank component of the transition tensor should fall to zero when using perfectly circularly polarized light.

Theory\textsuperscript{20} predicts only one \( ^1\Sigma^+_g \) electronic state in this energy region, yet for each isotopic species, the MPI spectra displayed in Fig. 2 and the band energies listed in Table I appear to divide into three pairs of features, each separated

FIG. 8. Calculated form of the rotational structure accompanying the (a) \( T_g^0 (\text{A}) \), (b) \( T_g^2 (\text{A}) \), (c) \( T_g^1 (\text{A}) \), and (d) \( T_g^2 (\text{A}) \) components of the two-photon transition tensor in C\textsubscript{2}H\textsubscript{2}. Each simulation assumes a band origin at zero, rotational constants for the excited states identical to those of the \( \tilde{G} \) \( ^3\Pi_u \) state (Ref. 15), ground state spectroscopic parameters from Ref. 36, a rotational temperature of 180 K, and a spectral linewidth of 1.5 cm\textsuperscript{-1}.

FIG. 9. (a) Resonance enhanced MPI spectrum of C\textsubscript{2}D\textsubscript{2} following circularly polarized photoexcitation at wavelengths around 274.85 nm together with (b) a calculated band contour that assumes that the transition is \( \Delta_g \rightarrow \Sigma^+_g \) [i.e., carried by the \( T_g^2 (\text{A}) \) component of the two-photon transition tensor], excited state constants as for the \( \tilde{G} \) \( ^3\Pi_u \) state of C\textsubscript{2}D\textsubscript{2} (Ref. 15), ground state parameters from Ref. 37, a rotational temperature of 180 K, and a spectral linewidth of 1.5 cm\textsuperscript{-1}.
by the relevant \( \nu_3 \) stretching frequency. The MPI-PES (Figs. 4 and 5) associated with each of these features in the spectrum of C\(_2\)H\(_2\) are double peaked (mean separation \( \approx 1340 \text{ cm}^{-1} \)), indicating a breakdown of the \( \Delta \nu = 0 \) ionization propensity rule expected for a Rydberg state.

In what follows we will argue that the most intense feature appearing around 74 270 cm\(^{-1}\) in the 2 + 1 MPI spectrum of each species should be associated with the \( ^1\Sigma_g^+ (\pi_u^2 3\pi_p^1) \) origin, but that this state is affected (in an isotope dependent manner) by vibronic interaction with (at least) one excited level of the \( ^1\Delta_g \) state. As a result these origins are shifted from the unperturbed, zeroth-order energies; the interacting level in each case gains transition strength it would not otherwise have had on simple Franck-Condon grounds, and the resulting MPI-PES show more complicated structure because of the “mixed” vibronic composition of the resonant intermediate level. In reaching this assignment it has been necessary to eliminate various other possible assignments for the interacting vibronic level.

The proposed \( ^1\Sigma_g^+ (\pi_u^2 3\pi_p^1) \) origin lies just below the presumed origins of the still poorly understood \( D, E, \) and \( F \) systems that appear in one-photon absorption.\(^{14} \) In 3 + 1 MPI only the origin bands of the \( E \) and \( F \) states are observed, and these are weak and diffuse.\(^{23} \) This and the fact that the MPI-PES\(^{23} \) of these origin bands show very complex vibrational structure suggests that vibronic mixing is important in this highly congested region of the spectrum. \textit{Ab initio} theory\(^{20} \) has difficulty in placing three ungerade states in this narrow energy range, and previously suggestions have appeared\(^{11} \) that at least one of these (the so-called \( D \) system) might actually involve levels of a \( ^1\Pi_g \) state carrying an odd number of quanta of \( \nu_5 (\pi_u) \). Though the picture remains unclear, subsequent work\(^{14} \) appears to have refuted this particular proposal. We have been able to establish only limited correlation between the pattern of gerade states observed in the present work and the complex vibronic structure seen at these energies in one-photon absorption (see below), and thus look to other members of the \( 3\pi \) complex for the source of the vibronic interaction with the \( ^1\Sigma_g^+ \) origin.

Spin is presumed to be a conserved quantity; we thus restrict discussion to singlet vibronic states. The \( ^1\Sigma_g^- (\pi_u^2 3\pi_p^1) \) state can be rejected outright, since none of the normal vibrations of acetylene are of the appropriate symmetry to generate \( ^1\Sigma_g^+ \) vibronic levels from this electronic state. The \( ^1\Pi_g (\pi_u^2 3\pi_p^1) \) state is calculated\(^{20} \) to be considerably removed in energy (\( T_0 \approx 67 900 \text{ cm}^{-1} \)) and is thus unlikely to interact strongly. This lowering of energy probably reflects substantial Rydberg (\( \pi_u^2 3\pi_p^1 \))–antibonding valence (\( \pi_u^2 \sigma_u^* \)) configuration mixing. We expect this state to be unstable with respect to the products \( \text{H} \rightleftharpoons \text{C}_2\text{H}_2 \rightarrow \text{H} \left( ^2\Sigma^+ \right) + \text{C}_2\text{H} \left( ^2\Pi \right) \)–with which it directly correlates. Consistent with this expectation is the fact that extensive investigations to longer excitation wavelengths than those shown in Fig. 2 have failed to reveal any other resonance enhanced MPI signals. Thus, although the normal coordinate \( q_3 \) is of the appropriate symmetry (\( \pi_u \)) to couple \( ^1\Pi_g \) to \( ^1\Sigma_g^+ \), we do not expect the \( ^1\Pi_g \) state to show sharp vibronic structure.

Almost by default therefore we are left with levels of the \( ^1\Delta_g (\pi_u^2 3\pi_p^1) \) state as the source of the vibronic interaction. This is wholly plausible, since the proposed \( ^1\Delta_g (\pi_u^2 3\pi_p^1) \) separation is small (\( \approx 1500 \text{ cm}^{-1} \)), and both of the bending vibrations, \( \nu_4 \) and \( \nu_5 \), are of appropriate symmetry (\( \pi_u \) and \( \pi_u \), respectively) that these two electronic states may be coupled via matrix elements involving \( q_4^2 \) or \( q_5^2 \). We consider the case of C\(_2\)H\(_2\) further, and assume that the two photon resonances at \( \approx 73 976 \text{ and } 74 286 \text{ cm}^{-1} \) are associated with \( ^1\Sigma_g^+ \) levels which, in zeroth order, may be described as \( ^1\Delta_g (\nu_{\text{bend}} = 2) \) and \( ^1\Sigma_g^+ \) electronic origin, respectively. For this two state problem first order perturbation theory, together with the observed separation (\( 310 \text{ cm}^{-1} \)) and relative band intensities (\( \approx 0.44 \text{ or } 0.56 \)) yields a measure of the strength of the vibronic interaction (\( H_{12} = 154 \text{ cm}^{-1} \)) and enables estimation of “deperturbed” zeroth-order energies for these two levels in C\(_2\)H\(_2\), viz., 74 112 and 74 150 cm\(^{-1}\) and hence \( 2\nu_{\text{bend}} \sim 1359 \text{ cm}^{-1} \) in the \( ^1\Delta_g \) state.

While recognizing the approximations inherent in this simple two level treatment of what must in reality be a many level interaction, the foregoing analysis provides a plausible qualitative interpretation for most of the remaining strong features in the spectra of all three isotopic forms. It also provides an explanation for the unexpectedly structured MPI-PES obtained when exciting via the \( ^1\Sigma_g^+ \) levels in C\(_2\)H\(_2\). The “mixed” vibronic parentage of these intermediate levels is reflected in the range of final ion states produced; the “fast” and “slow” electron peaks appear at energies appropriate to ion formation in the level \( n\nu_2 \) (\( n = 0, 1 \)) and the level \( n\nu_2 2\nu_{\text{bend}} \) (\( n = 0, 1 \)), respectively. The frequency obtained from the PES for the cation bending overtone (\( 2\nu_{\text{bend}} \approx 1340 \text{ cm}^{-1} \)) agrees well with the deperturbed frequency in the intermediate state (\( 1359 \text{ cm}^{-1} \)), and the relative intensities of the peaks in the various MPI-PES of C\(_2\)H\(_2\) accord well with the degree of mixing deduced from the two state perturbation analysis of the relevant features in the MPI excitation spectrum.

A more quantitative development of this model to include the other isotopic forms of acetylene is almost certainly not appropriate. Even if it remained reasonable to neglect the interaction of the zeroth-order \( ^1\Delta_g \) state with all vibronic levels other than \( ^1\Delta_g (2\nu_{\text{bend}}) \)–which is unlikely since the isotope shift of \( 2\nu_{\text{bend}} \) would reduce the closeness of this particular resonance—the analysis would require more information about the identity of \( \nu_{\text{bend}} \). Nevertheless, the lowering of the bending frequency on isotopic substitution should increase the zeroth-order separation, and thus weaken the vibronic mixing between the analogous pairs of levels in the substituted molecules in qualitative agreement with experiment. The Renner effect that accompanies both cis and trans bending lifts the degeneracy of the \( ^1\Delta_g \) state of the neutral, and of the \( ^2\Pi_g \) state of the molecular ion; each of the resulting components will support its own manifold of bending vibronic levels. Thus there are two zeroth-order vibronic levels of \( ^1\Sigma_g^+ \) symmetry derived from \( ^1\Delta_g (2\nu_{\text{bend}}) \) associated with, respectively, the upper component state arising from the trans-bent configuration and the lower component state of the cis-bent structure. Evidence in support of the latter assignment is provided by \textit{ab initio} calculations\(^{30} \) involving the C\(_2\)H\(_2\) \( ^1\Delta_g \) state which predict a vibrational fre-
quency for the lower component ($2\nu^{-}_s$) similar to that deduced in the present experiment; other recent calculations predict vibrational frequencies for the C$_2$H$_4$\(^+\) (\(\tilde{X}\)) molecular ion that are consistent with the observed MPI-PES given the assumption that the ionization step is vibrationally adiabatic in \(\nu_s\). The $2\nu^{-}_s-2\nu^{-}_s$ Renner splitting and spin-orbit coupling in the ion may account for the consistently greater energy breadth observed for the slow electron peak in these spectra.

However, such an assignment begs the question as to why \(q_4\) is calculated\(^{29,30}\) to cause such a large Renner splitting in the \(\Delta_g\) state. \(\Delta\) states show no first-order quadratic Renner splitting and, given the close energetic proximity of the \(1\Delta_g\), \(1\Sigma^+_g\), and \(1\Sigma^+_g\) (\(\pi\Sigma\)\(3\pi\)) Rydberg states, it is tempting to speculate that \(q_4\) promotes a strong second-order vibronic interaction between the \(\Delta\) and \(\Sigma\) states, and that it is this (rather than the normally weak first-order quartic term) that is responsible for the substantial splitting of the \(1\Delta_g\) state induced by trans bending (\(\nu^+_b-\nu^{-}_s\approx 170 \text{ cm}^{-1}\) in C$_2$H$_4$\(^+\)). Such an interpretation does not fit well with the present experimental data, since the values we derive for \(2\nu^\text{bend}\) both in the \(\Delta_g\) intermediate state and in the ground state ion are significantly less than previous estimates of \(2\nu^\text{bend}\) in these states.\(^{32,33}\) However, the very weak features discovered at higher laser powers in the MPI spectrum of C$_2$H$_2$ at \(-272.55\) and \(-265.89\) nm may plausibly be attributed to vibronically induced transitions involving the levels \(1\Delta_g\) (\(4^{-}\)) and \(1\Delta_g\) 2\((4^{-})\), respectively. Further speculation concerning the identity of \(\nu^\text{bend}\) is probably unwarranted in view of the numerous vibronic interactions and perturbations conceivable in this region of the vertical electronic spectrum of acetylene once bending vibrations are considered to be active. Indeed close inspection of Fig. 2 reveals a number of additional weak features in the MPI spectra of the three isotopic species. For completeness these are also listed, together with some tentative assignments in Table I.

The sharp feature appearing most notably in the spectra of C$_2$H$_2$ and C$_2$D$_2$ immediately to the high frequency side of the presumed \(1\Sigma^+_g\) electronic origin is worthy of additional comment. It appears with the greatest relative intensity in the spectrum of C$_2$D$_2$, and in C$_2$H$_2$, the associated PES is extremely similar to that obtained following excitation via the intense origin feature at \(-74 286 \text{ cm}^{-1}\). Its comparative insensitivity to isotopic substitution precludes assignments involving a vibronic level of \(1\Delta_g\). The close resemblance between its MPI-PES and that involving the band assigned to the (zeroth-order) \(1\Sigma^+_g\) origin, suggests that it may be due to a \(4\)\(^1\) \(\nu^\text{bend}\) band excitation. Such an assignment [which implies that excitation of one quantum of \(\nu^\text{bend}\) must have minimal effect on the vibronic mixing between the \(1\Sigma^+_g\) electronic origin and the \(2\Sigma^+_g\) state arising from \(1\Delta_g\) (\(2\nu^\text{bend}\)) is consistent with the relative band intensities found in the MPI spectra of C$_2$H$_2$ and C$_2$D$_2$, and with the observed blue shifts].

A search for MPI resonances in C$_2$H$_2$ at excitation energies higher than those shown in Fig. 2 revealed just two closely spaced, diffuse, weak features around 242 nm. Assuming that these are associated with one or more Rydberg states in series converging on the first IP implies a quantum defect \(\delta=0.57\), consistent with their assignment as origin bands associated with the \(4\)\(^p\) complex. The small peak-to-peak separation (\(\sim 24 \text{ cm}^{-1}\)) matches well with the calculated band contour for a \(1\Delta_g-1\Sigma^+_g\) transition [Fig. 8(d)]. Assignment of these features to the \(1\Delta_g\) (\(4\)\(^p\)) origin band is further supported by the photoelectron spectrum (lower panel of Fig. 6) obtained when pumping via the lower energy feature. This PES shows a single band corresponding to production of C$_2$H$_4$\(^+\) in the ground vibrational level; behavior analogous to that seen with the \(1\Delta_g\) member of the \(3\)\(^p\) complex. The photoelectron spectrum obtained when pumping through the higher energy feature (top panel of Fig. 6) provides evidence which contradicts this simple picture. This PES shows two bands, reminiscent of those obtained when pumping through intermediate states of mixed character, and implies involvement of an additional (vibronically mixed) resonant intermediate state.

The wavelength region examined (down to \(-222 \text{ nm}\)) is expected to contain the origins of the \(4\)\(^p\), \(5\)\(^p\), \(6\)\(^p\), and \(7\)\(^p\) Rydberg states, as well as a large number of vibronic bands. We presume that the weakness or absence of these bands, as well as the absence of higher \(n\)\(\nu_2\) (\(n > 1\)) members of either the electronic or the vibronically induced \(2\Sigma^+_g\) progression associated with the \(3\)\(^p\) complex (which by analogy with other Rydberg states of C$_2$H$_2$ should be Franck–Condon allowed) implies the onset of an efficient decay channel at energies \(>76 000 \text{ cm}^{-1}\). The observation by Suto and Lee\(^{16}\) of a threshold at \(-133 \text{ nm}\) for production of electronically excited C$_2$H in single photon excitation of acetylene suggests that the high Rydbergs are dissociated too rapidly to be efficiently ionized. In our earlier \(3 + 1\) photon ionization study of the unterade Rydberg states of acetylene,\(^{29}\) similar behavior was observed, although in that case signal was obtained for Rydberg states up to \(n = 5\) due to the higher laser power densities used in the three photon excitation.

Finally we wish to discuss the observation that fragment ion formation gains in importance as the excitation wavelength decreases (Fig. 1). The energetics for \(2 + 1\) photon ionization of C$_2$H$_2$, and various fragmentation channels for the ion are shown in Fig. 10. The lowest energy dissociation threshold for the acetylene cation, process (1), has been placed at 17.44 eV above the neutral ground state.\(^{23,34}\) This is well above the energies reached by the third photon in our \(2 + 1\) ionization process; and thus the ions produced should be stable with respect to dissociation:

\[
\begin{align*}
\text{C}_2\text{H}_2 + h\nu \rightarrow & \text{C}_2\text{H}^+ + \text{H} + e^- , \quad E \geq 17.44 \text{ eV}, \\
& \text{C}_2^+ + \text{H}_2 + e^- , \quad E \geq 18.2 \text{ eV}, \\
& \text{CH}^+ + \text{CH} + e^- , \quad E \geq 20.53 \text{ eV}.
\end{align*}
\]

The MPI-photoelectron spectra (Figs. 3–6) show that essentially all ionization initially results in production of parent ions with low levels of vibrational excitation, and that channels due to ionization of neutral fragments (C$_2$H for example) are minor. Figure 10 demonstrates that these parent ions must absorb at least two photons to dissociate. The experimental observation that (i) there is essentially no fragment ion production following excitation of any of the isotopic forms of acetylene at wavelengths longer than \(-270 \text{ nm}\) but (ii) extensive fragmentation occurs when the excitation
tion wavelength is ~260 nm, suggests that the two-photon fragmentation of the parent ions is improbable unless it is resonance enhanced at the one-photon level by the ionic C=C and H+ fragments which are also observed in the TOF mass spectra.

IV. CONCLUSIONS

Two-photon resonant multiphoton ionization together with photoelectron spectroscopy have been used to provide the first clear insight into the gerade excited states of acetylene. The \( n = 3 \) member of the \( \Delta g (\sigma_u^* \pi pm_u^*) \) series is observed with laser limited resolution; it behaves as a "good" Rydberg state, shows a short progression in the excited state C=C stretching vibration, and follows a \( \Delta E = 0 \) propensity rule for ionization. The corresponding \( \Sigma_g^+ (\pi_u^* 3p \rho m_u^*) \) state also shows a sharp spectrum but is observed to undergo substantial vibronic interaction with an excited level of the \( \Delta g \) state carrying two quanta of bending vibration (probably \( \nu_3^* \)). The location of these origin bands allows some assignments (and reassignments) of features observed previously in the one-photon VUV absorption spectrum. The partial reanalysis, presented in Table II, raises further questions regarding the reality of the \( \tilde{E} \) valence state of acetylene. However, a fully self-consistent interpretation of the acetylene spectrum in the troublesome energy range 72 000–78 000 cm\(^{-1}\) remains some ways off, and will almost certainly require knowledge of the unobserved \( \Sigma_g^+ (\pi_u^* 3p \rho m_u^*) \) Rydberg state and its attendant vibronic structure.

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**TABLE II. Reassignments of vibronic features observed in one-photon absorption spectrum of acetylene.**

<table>
<thead>
<tr>
<th>Molecule</th>
<th>Old assignment (Refs. 8 and 14)</th>
<th>Probable new assignment</th>
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<tr>
<td>( \text{C}_2\text{D}_2 )</td>
<td>( \tilde{E} )-( \Xi_4^b ) ( \Delta_g ) ( \Sigma_g^+ ) ( \Sigma_g^+ ) ( \Sigma_g^+ ) ( \Sigma_g^+ ) ( \Sigma_g^+ )</td>
<td>( \tilde{E} )-( \Xi_4^b ) ( \Delta_g ) ( \Sigma_g^+ ) ( \Sigma_g^+ ) ( \Sigma_g^+ ) ( \Sigma_g^+ ) ( \Sigma_g^+ )</td>
</tr>
<tr>
<td>( \text{C}_2\text{H}_2 )</td>
<td>( \tilde{E} )-( \Xi_4^b ) ( \Delta_g ) ( \Sigma_g^+ ) ( \Sigma_g^+ ) ( \Sigma_g^+ ) ( \Sigma_g^+ ) ( \Sigma_g^+ )</td>
<td>( \tilde{E} )-( \Xi_4^b ) ( \Delta_g ) ( \Sigma_g^+ ) ( \Sigma_g^+ ) ( \Sigma_g^+ ) ( \Sigma_g^+ ) ( \Sigma_g^+ )</td>
</tr>
<tr>
<td>( \text{C}_2\text{H}_3 )</td>
<td>( \tilde{E} )-( \Xi_4^b ) ( \Delta_g ) ( \Sigma_g^+ ) ( \Sigma_g^+ ) ( \Sigma_g^+ ) ( \Sigma_g^+ ) ( \Sigma_g^+ )</td>
<td>( \tilde{E} )-( \Xi_4^b ) ( \Delta_g ) ( \Sigma_g^+ ) ( \Sigma_g^+ ) ( \Sigma_g^+ ) ( \Sigma_g^+ ) ( \Sigma_g^+ )</td>
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