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# Complete determination of the photoionization dynamics of a polyatomic molecule. I. Experimental photoelectron angular distributions from $\tilde{A}^{1}A_{u}$ acetylene

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Angle-resolved photoelectron spectra from rotationally selected  $\tilde{A}^{1}A_{u}$  state acetylene have been recorded using velocity-map imaging. Several Renner-Teller split vibrational bands have been observed and assigned, showing good agreement with previous zero kinetic energy photoelectron (ZEKE) work [S. T. Pratt, P. M. Dehmer, and J. L. Dehmer, J. Chem. Phys. **99**, 6233 (1993); S.-J. Tang, Y.-C. Chou, J. J.-M. Lin, and Y.-C. Hsu, *ibid.* **125**, 133201 (2006).] The extracted photoelectron angular distributions (PADs) corresponding to these bands show a strong dependence on the vibronic angular momentum projection quantum number  $K_{+}$ . Subbands with odd  $K_{+}$  show PADs with maximum intensity along the polarization vector of the ionizing laser beam, while those with even  $K_{+}$  show PADs with maximum intensity perpendicular to this direction. Velocity-map images recorded at low photoelectron energies approach rotational resolution of the ion, and the evolution of the PADs with increasing rotational level prepared in the  $\tilde{A}^{-1}A_{u}$  state indicates the potential of a "complete" determination of the photoionization dynamics of the  $\tilde{A}^{-1}A_{u}$  state. This is further investigated in the following paper. © 2007 American Institute of Physics. [DOI: 10.1063/1.2790442]

### I. INTRODUCTION

The Holy Grail in photoionization studies is the determination of all the radial dipole matrix elements and phases connecting a selected quantum state to each of the partial wave components of the photoelectron wavefunction. Such a determination is termed a "complete" experiment<sup>1</sup> and has been achieved for only a limited number of atomic and diatomic systems.<sup>2–7</sup> The extension to polyatomic systems relies ideally on the ability to measure photoelectron angular distributions (PADs) either corresponding to resolved internal energy states of the ion or, in the case of dissociative photoionization, relating to the molecular frame.<sup>7</sup> In this work we are concerned with the former. The resolution of polyatomic ion rotational levels in photoelectron spectroscopy is a serious challenge; however, in previous work<sup>8</sup> using a field-free time-of-flight method we have shown that, as a consequence of symmetry restrictions, the measurement of PADs following the preparation of resolved rotational levels in the  $\tilde{B}^{1}E''$  state of NH<sub>3</sub> can yield quite detailed information on photoionization dynamics, albeit short of the goal of completeness, even when the ion is not rotationally resolved.

As a small molecule that undergoes interesting dynamics upon excitation, acetylene has been of spectroscopic interest for many years. Early work on the  $\tilde{A} {}^{1}A_{u} \leftarrow \tilde{X} {}^{1}\Sigma_{g}^{+}$  band system was carried out by Ingold and King,<sup>9</sup> who conclusively established the geometry change from linear to *trans*-bent upon excitation. Extensive work on the characterization of the  $\tilde{A} {}^{1}A_{u}$  state was performed by Watson *et al.*,<sup>10,11</sup> whose focus was on the rotational structure of the  $\tilde{A} {}^{1}A_{u}$  state. This state is of particular interest because of the geometry change upon excitation from a linear to near-prolate asymmetric top, and effective Hamiltonians describing the  $\tilde{A} {}^{1}A_{u}$  state were developed. The dynamics of the molecule in its  $\tilde{A} {}^{1}A_{u}$  state have also provoked interest. The *trans*-bent state can undergo isomerization to the *cis*-bent state if >47 400 cm<sup>-1</sup> internal energy (lying between 5 and 6 quanta in the *trans*-bending mode) is present.<sup>12,13</sup> There is also the possibility of predissociation, mediated by intersystem crossing to nearby triplet states.<sup>14,15</sup> The  ${}^{2}\Pi_{u}$  ground state of the acetylene cation is a prototypical system for the study of the Renner-Teller effect in a tetra-atomic molecule.<sup>16</sup>

A number of previous photoelectron studies of acetylene have been undertaken; of particular note are two studies via the  $\tilde{A} {}^{1}A_{u}$  state by Pratt *et al.*<sup>17,18</sup> and the more recent zero kinetic energy photoelectron (ZEKE) work of Tang *et al.*<sup>19</sup> In these studies, assignments were made of various vibrational frequencies of the ion in its  ${}^{2}\Pi_{u}$  ground state, and observations made of Renner-Teller splittings and rotational structure. In the work presented here, we use photoelectron velocity-map imaging (VMI) as a means of simultaneously acquiring photoelectron spectra and angular distributions (PADs) and concentrate our analysis on the latter. In the following paper,<sup>20</sup> we show how we are able to fit the experimentally determined PADs in order to determine the radial dipole matrix elements and phases for the ionization event.

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## **II. EXPERIMENT**

UV radiation in the range of 207–216 nm was produced using the frequency tripled output from a dye laser (Sirah Cobra-Stretch) with DCM in methanol dye solution, giving an output pulse energy of 2–3 mJ. The dye laser was pumped with the second harmonic output from a 10 Hz Nd:YAG (yttrium aluminum garnet) (Continuum Powerlite Precision II 8010) with a pulse energy of 600 mJ and a pulse duration of 5–7 ns. The UV beam was focused into the VMI spectrometer using a 30 cm focal length lens and crossed with a beam of acetylene. The acetylene was prepared in its  $\tilde{A}^{-1}A_u$  excited state, and subsequently ionized, using two photons from the same laser beam.

Our VMI spectrometer follows the now standard Eppink and Parker design<sup>21,22</sup> and has been described in detail elsewhere.<sup>23</sup> Acetylene (BOC, >98.5% pure) was introduced into the spectrometer via a pulsed nozzle, creating a supersonic jet expansion. Neat acetylene was used in the expansion to enable the population of a range of rotational levels. The rotational temperature was characterized by the recording of (1+1) resonance-enhanced multiphoton ionization (REMPI) spectra, which were compared with simulated absorption spectra based upon the effective Hamiltonians of Watson *et al.*<sup>10</sup> Rotational temperatures in the range of 20–30 K were typically achieved with a 2 bar acetylene gas backing pressure. Additionally these one-color (1+1) REMPI spectra offered a method of calibration of the laser wavelength.

Ionization occurred where the laser was crossed with the molecular beam. Ejected photoelectrons were focused by an electrostatic lens onto a position sensitive detector (Photek) comprising two microchannel plates and a phosphor screen. The electrostatic lens enables 100% photoelectron collection efficiency, and the correct voltage ratios create the velocity-mapping condition.<sup>21</sup> The phosphor emission was imaged using a charge coupled device (CCD) camera (Basler A320f). The detector was controlled by a Photek GM1KV gate module and gated on for a period of 1  $\mu$ s.

The laser polarization was vertical with respect to the detector; the north-south direction in the final image corresponds to the axis of polarization. In this way cylindrical symmetry was maintained, as required for the inversion procedures used to process our images.<sup>22</sup> The images were typically accumulated over a period of 1 h, corresponding to 36 000 laser shots. Photek ISF32 software, running on a standard personal computer (PC) under Windows XP, was used for image acquisition.

Image analysis was primarily performed using the pBasex inversion method.<sup>24</sup> A representative sample of the results was also cross-checked using the inverse Abel transformation algorithm used in our previous imaging work.<sup>23</sup> In all cases good agreement was found between the two methods, with pBasex providing more comprehensive data output including error bounds.

The photoelectron energy spectra presented in this paper have been extracted from the radial component of our inverted photoelectron images, averaged over the angular coordinate. The raw radial spectra, as obtained from the radial component of pBasex or Abel inverted images, are a function of photoelectron speed. These radial spectra can be mapped quadratically onto an arbitrary energy scale which can then be calibrated to an ion internal energy scale using two known energies. The acetylene ionization potential is well known to be 91 953.5(5) cm<sup>-1</sup>,<sup>25,26</sup> thus the greatest photoelectron energy (outmost ring of the photoelectron image) for a given ionization frequency can be calculated, and the definition of the image center as zero photoelectron energy gives a second fixed point for calibration. An alternative approach involving the assignment of energies to two known bands in the spectrum can also be used for calibration; this method provided equivalent spectra to within the resolution limit of the photoelectron images.

A major factor governing the overall resolution of the images is the maximum photoelectron kinetic energy. This arises from the necessity of compressing the radial component of the ejected photoelectron distribution onto the finite sized position sensitive detector; a larger photoelectron energy spread results in a lower absolute resolution as a greater energy range must be focused onto the detector. A solution to this problem is slow photoelectron velocity-map imaging (SEVI), which was developed by Osterwalder et al.<sup>27</sup> In this technique, the photoelectron distribution is focused with much lower voltages than normally used, such that only the central portion falls onto the detector, providing an increase in resolution at the cost of dynamic range. An energy spectrum over an extended range can then be recorded in steps by using a two-color (1+1') REMPI scheme and incrementally increasing the probe frequency. In this work we have not employed the full SEVI technique, but our photoelectron images recorded at low total energies are analogous to those obtained via SEVI and provide us with energy resolution of  $\sim$  30 cm<sup>-1</sup>. A final point of note concerning energy resolution arises from the quadratic mapping of photoelectron velocity to energy. The resulting energy spectra show a decrease in resolution with increasing photoelectron velocity, while a spectrum in velocity space will show a constant velocity resolution across the image (see, for example, Fig. 3 of Ref. 27).

## **III. BACKGROUND AND THEORY**

Throughout this paper, and the one that follows,<sup>20</sup> we use the subscripts g and i for ground and intermediate states, respectively, and the subscript + for cation states. The ground states of neutral  $(\widetilde{X}\ ^1\Sigma_g\ ^+)$  and cationic  $(\widetilde{X}\ ^2\Pi_u)$  acetylene are both linear ( $D_{\infty h}$  symmetry); the  $\tilde{A}^{-1}A_{\mu}$  excited state is *trans*-bent ( $C_{2h}$  symmetry). The geometry changes in the  $\widetilde{A}^{1}A_{\mu} \leftarrow \widetilde{X}^{1}\Sigma_{\rho}^{+}$  and  $\widetilde{X}^{2}\Pi_{\mu} \leftarrow \widetilde{A}^{1}A_{\mu}$  transitions excite long progressions in the *trans*-bending mode  $(v_4, \pi_g$  symmetry in the linear geometry;  $v_3, a_g$  symmetry in the *trans*-bent geometry).<sup>10,18</sup> Standard practice<sup>10</sup> for labeling transitions involving this key mode is  $V_n^m$ , where the transition is from  $v_4=n$  to  $v_3=m$ . In the work reported here pump transitions within the bands  $V_0^4 K_0^{-1} (46\ 288.29\ \text{cm}^{-1})$ and  $V_0^{5}K_0^{-1}(47\ 259.96\ \text{cm}^{-1})$  were used, where  $K_0^{-1}$  denotes the change in the quantum number K which labels the molecular frame component of the total angular momentum labeled by

the quantum number *J*. The rotational structure of these bands is well known and can be calculated using the effective Hamiltonians of Watson *et al.*<sup>10</sup> Low *J* rotational lines are typically separated by several  $\text{cm}^{-1}$ , allowing the selection of an individual rotational line for the pump transition.

A consequence of the geometry change upon excitation is the change from a linear rotor to near-prolate asymmetric top. In the ground state the axial angular momentum quantum number  $K_g$  is equated with  $l_4$ , the quantum number describing the vibrational angular momentum of  $v_4$ , while in the  $\tilde{A}^{-1}A_u$  state  $K_i=K_a$ , the asymmetric top (or total) axial angular momentum quantum number. For a vibrationally cold molecular beam (<100 K)  $v_4=0$ , so in all cases considered here  $l_4=0$ . The strongest subbands in the  $\tilde{A} \leftarrow \tilde{X}$  transition are those with  $\Delta K=\pm 1$ , although subbands with  $\Delta K$ =0,  $\pm 2$  are also observed due to axis-switching upon excitation.<sup>10</sup> As a result of the  $\Delta K$  propensity rule, we concentrated in this work on the preparation of K=1 levels within the  $\tilde{A}^{-1}A_u$  state in order to obtain sufficient intermediate state population.

In the acetylene ion  $(\tilde{X}^2\Pi_{\mu})$  the magnitude of the axial component of the total angular momentum, labeled by the quantum number  $K_+$ , arises from the coupling of the vibrational  $(l_{+})$  and electronic  $(\Lambda_{+})$  angular momenta,  $K_{+} = |l_{+}|$  $+\Lambda_+|$ . The quantum number  $K_+$  therefore describes a vibronic angular momentum, while  $K_i$  describes a purely rotational angular momentum. As in the  $\widetilde{A} \leftarrow \widetilde{X}$  transition the selection rules for  $\Delta K$  are not strict; a propensity for  $\Delta K = \pm 1$ is expected,<sup>18</sup> but transitions with  $\Delta K=0,\pm 2,...$ , may also be observed.<sup>18,19</sup> The value of  $K_+$  determines the Renner-Teller (RT) structure of the ion. This vibronic structure dominates both the rotational structure  $(B_0=1.10463(2) \text{ cm}^{-1})^{18}$ and the spin-orbit splitting  $(|A_0|=30.91(2) \text{ cm}^{-1})$ .<sup>28</sup> The RT parameter  $\varepsilon_{4+}=0.30$  (Ref. 18) for a  $K_{+}=0$  level with  $v_{4+}=1$ and  $v_{5+}=0$ , resulting in a splitting between the subbands of approximately 400 cm<sup>-1</sup> (Ref. 19). A fuller discussion of the Renner-Teller structure can be found in Refs. 16, 18, 19, and 29; for the purposes of this work it is sufficient to be able to assign the RT states in the photoelectron energy spectra. RT states are labeled according to their value of  $K_+$ , i.e.,  $\Sigma, \Pi, \Delta, \ldots$ , and are preceded by  $X^m$  which denotes the parent vibrational level. For example,  $4^{3}\Delta$  denotes the  $K_{+}=2$ component of the  $v_4=3$  vibrational level. The ungerade symmetry of the  $\tilde{X}^2 \Pi_{\mu}$  state means that only RT states with  $K_+$  $+v_{4+}$  = odd are observed, hence for even  $v_{4+}$  only odd  $K_{+}$ levels exist, and vice versa.<sup>29</sup>

In this work we concentrate on the analysis of photoelectron angular distributions (PADs). If cylindrical symmetry is maintained, then in a (1+1) REMPI scheme the intensity of photoelectrons emitted into the solid angle defined by  $\theta$  and  $\phi$  is given by

$$I(\theta,\phi) \propto \beta_{00} Y_{00}(\theta,\phi) + \beta_{20} Y_{20}(\theta,\phi) + \beta_{40} Y_{40}(\theta,\phi), \quad (1)$$

where the  $Y_{LM}$  are spherical harmonics, the  $\beta_{LM}$  parameters are coefficients, and Eq. (1) has no dependence on the angle  $\phi$ . The coefficient  $\beta_{00}$  gives a measure of the angleintegrated intensity, and it is common to quote the other  $\beta_{LM}$ parameters normalized to  $\beta_{00}$  to facilitate the comparison of



FIG. 1. Ion internal energy spectra extracted from the photoelectron images recorded via (a) the  $R_1$  transition of the  $V_0^4 K_0^{-1}$  band and (b) the  $R_1$  transition of the  $V_0^5 K_0^{-1}$  band. The ion vibrational bands and Renner-Teller subbands are labeled as described in the text.

different angular distributions. The forms of the  $\beta_{LM}$  parameters are considered in some detail in the following paper.<sup>20</sup>

## **IV. RESULTS**

#### A. Overview: Ion internal energy spectra

We consider in this paper photoelectron images recorded following the excitation of two different vibrational bands in the  $\tilde{A} {}^{1}A_{u}$  state:  $V_{0}{}^{4}K_{0}{}^{1}(46\ 288.29\ \text{cm}^{-1})$  and  $V_{0}{}^{5}K_{0}{}^{1}(47\ 259.96\ \text{cm}^{-1})$ . In both cases images were recorded after a selection of P-, Q-, and R-branch transitions. The R-branch transitions were strongest and best resolved in the  $\tilde{A} {}^{1}A_{u}$  state, with no overlapping lines at low temperature. They therefore represent the majority of the pump transitions used. In all cases levels with the rotational projection quantum number  $K_{i}=1$  were prepared, as a consequence of their greater transition intensity.<sup>10</sup>

Figure 1 shows representative photoelectron spectra from the two  $\tilde{A} {}^{1}A_{u}$  vibrational bands studied, and Table I lists the vibronic level positions and comparison with literature values. The Renner-Teller assignments shown have been based upon previous photoelectron<sup>17</sup> and ZEKE (Refs. 18 and 19) studies, as well as on calculations.<sup>16,30</sup> Further support for the  $K_{+}$  assignments was also provided by the PADs; this will be discussed later.

In Fig. 1(a) ionization is via the  $V_0^4 K_0^{-1}$  band  $(R_1)$ , the lowest energy vibrational band accessible in a one-color ionization scheme. The laser wavelength was approximately 216 nm giving a maximum ion energy of ~650 cm<sup>-1</sup> and best energy resolution of ~30 cm<sup>-1</sup> (for further discussion of resolution see Sec. II). The photoelectron signal was very weak due to the low Franck-Condon factors corresponding to the formation of the accessible  $v_+=0({}^2\Pi_u)$  and  $v_{4+}=1({}^2\Sigma_u^{-})$  ion states, but the low total energy provided the best experimental resolution. As will be shown in the follow-

TABLE I. Vibronic state assignments.  $E_{vib}$  values are averaged over our experimental results, values in parentheses represent the error assigned from the standard deviation in the peak position.

Vibronic	F	Literature		
assignment	$(cm^{-1})$	Pratt et al. <sup>a</sup>	Tang et al. <sup>b</sup>	Peric et al. <sup>c</sup>
$0^{0} {}^{2}\Pi_{\mu}$	0		0	
$4^{1} \Sigma_{u}^{-}$	499(12)	485	487.3	485
$4^{1} \Delta_u^2$	686(19)	668	665.7	661
$4^{2}  {}^{2}\Pi_{u}$	1114(7)	1098	1095.2	1095
$5^{2} {}^{2}\Pi_{u}$	1381(20)		1379.5	1452/1488
$4^{3} {}^{2}\Sigma_{u}^{-}$	1711(21)	1672	1672.9	1702
$4^{3} {}^{2}\Delta_{u}$	1752(19)	1738	1732.8	
$4^{1}5^{2} {}^{2}\Gamma_{u}$	2101(10)	2025	2103.6	
$4^{4} {}^{2}\Pi_{u}$	2202(30)		2288.2	2358
$4^{4} {}^{2} \Phi_{u}$	2333(5)	2320 <sup>d</sup>	2387.1	2436
$4^{3} {}^{2}\Delta_{u}$	2426(4)			2481
$4^{3} {}^{2}\Sigma_{u}^{+}$	2455(3)			2555
?	2529(6)		2507.6/2524.2 <sup>e</sup>	2554/2565 <sup>e</sup>

<sup>a</sup>Reference 18.

<sup>b</sup>Reference 19. <sup>c</sup>Reference 20.

dp c 17

<sup>d</sup>Reference 17.

<sup>e</sup>Possible assignment as  $4^2 + 5^2 \prod_u$  or  $\Phi_u$  state.

ing section, partial rotational resolution of the ion in its  $4^{12}\Sigma_u^-$  state has been achieved from the photoelectron images recorded in this energy range, following the excitation of intermediate rotational states with  $J_i > 5$ . Photoelectron energy resolution in the region of the  $0^{02}\Pi_u$  state is least good because the formation of this state correlates with higher energy photoelectrons (see Sec. II). The increased width of the feature relative to the  $4^{12}\Sigma_u^-$  feature indicates the presence of unresolved spin-orbit splitting in this band. As discussed in Sec. IV B the spin-orbit splitting in the  $\Sigma$  subbands is small, and so in the case of the  $4^{12}\Sigma_u^-$  feature neither resolved spin-orbit bands nor broadening due to unresolved spin-orbit splitting are observed.

Figure 1(b) shows the spectrum recorded via  $V_0^{5}K_0^{-1}(R_1)$ . Here a one-color ionization scheme required wavelengths in the region of 211.5 nm, resulting in a maximum ion internal energy of ~2600 cm<sup>-1</sup>. Many more vibronic bands are accessible in the ion at these higher total energies. The Franck-Condon factors for population of these states are much enhanced versus those corresponding to the formation of the  $4^{1} {}^{2}\Sigma_{u}^{-}$  vibronic state. The move to higher total energy reduces the resolution of the photoelectron images, giving typical peak widths [full widths at half maximum (FWHMs)] of the order of 50–80 cm<sup>-1</sup>. The vibronic bands are still well resolved, but no information on the ion rotational states lying under a feature can be inferred.

## B. The $4^{1} {}^{2}\Sigma_{\mu}^{-}(K_{+}=0)$ vibronic state

The  $\Sigma_u^{-/+}$  vibronic states are unique in that the spin-orbit splitting is very small (<1 cm<sup>-1</sup>), and the rotational structure is well described by Hund's case (b).<sup>18</sup> In addition, the overall parity of the  $\Sigma_u^{-/+}$  vibronic states places constraints on the allowed combinations of nuclear spin state and ion rotational level. For the  $\Sigma_u^{-}$  state, rotational levels with odd  $N_+$  (total



FIG. 2. Ion internal energy spectra in the region of the  $4^{12}\Sigma_{u}^{-}$  vibronic subband. These spectra were extracted from photoelectron images recorded via *R*-branch transitions of the  $V_0^4 K_0^{-1}$  band.

angular momentum quantum number excluding spin) must be associated with nuclear spin states which are antisymmetric with respect to exchange of nuclei, while rotational levels with even  $N_+$  must be associated with nuclear spin states which are symmetric with respect to exchange of nuclei.<sup>18</sup> The consequence of this rotational level structure is that the  $\Delta N(=N_+-N_i\equiv N_+-J_i)$ allowed transitions for the  $\tilde{X}^2 \Pi_u (4^{12} \Sigma_u) \leftarrow \tilde{A}^{1} A_u$  ionization are dependent on the nuclear spin of the prepared  $\tilde{A}^{1}A_{\mu}$  state. This nuclear spin state is in turn dependent on the nuclear spin of the molecule prior to excitation and, therefore, the pump transition used. For an *R*- or *P*-branch excitation the intermediate state populated will have an antisymmetric nuclear spin state for  $J_i$ = even and a symmetric nuclear spin state for  $J_i$  = odd; ionization will then follow the selection rule  $\Delta N = \pm 1, \pm 3$  in order to conserve nuclear spin state. Similarly, pumping via a Q-branch transition will lead to a correlation of  $J_i$  = even with symmetric nuclear spin state and  $J_i$  = odd with antisymmetric nuclear spin state, with a selection rule upon ionization of  $\Delta N=0,\pm 2.^{18}$  The rotational selection rule for the *R*-branch case is illustrated in the ZEKE work of Tang et al.,<sup>19</sup> where ionization via  $V_0^{3}K_0^{-1}(J_i=1-8)$  *R*-branch transitions showed preferential population of rotational states with  $\Delta N = \pm 1$  in the  $4^{1} \Sigma_{\mu}^{2}$  vibronic state. Pratt *et al.*<sup>18</sup> provide schematic diagrams of the rotational structures discussed here, although they were only able to partially resolve  $N_+$  states in their ZEKE work.

Energy spectra extracted from photoelectron images recorded via the  $R_1$ ,  $R_3$ ,  $R_5$ ,  $R_7$ , and  $R_9$  transitions of the  $V_0^4 K_0^{-1}$ band are shown in Fig. 2. The trend in these spectra is clear: the  ${}^2\Sigma_u^{-}$  vibronic state initially appears as one feature which then decreases in total intensity and broadens into two partially resolved features at high  $J_i$ . This broadening is consistent with the ionization event populating two ion rotational levels with  $N_+=J_i\pm 1$ . As  $J_i$  increases, higher  $N_+$  levels are accessed, and a larger rotational spacing is observed in the spectrum. For large  $N_+$  the line spacing is large enough (~30 cm<sup>-1</sup>) that partial rotational resolution is observed in the images. The small features at ion energies above



FIG. 3. (a) Raw photoelectron images obtained via *R*-branch transitions of the  $V_0^4 K_0^{-1}$  band. (b) Photoelectron angular distributions (PADs) extracted and averaged across the inner ring of the images shown in (a); this ring correlates with formation of the ion in the  $4^{12}\Sigma_u^{-1}$  vibronic state. All PADs are shown as polar plots  $(I, \theta)$ . The laser polarization direction is shown by **E**, the electric vector.

600 cm<sup>-1</sup> do not appear in the ZEKE data<sup>19</sup> but can be attributed to  $\Delta N$  = +3 peaks as shown in the following paper.<sup>20</sup>

Figure 3(a) shows the raw images from which the  ${}^{2}\Sigma_{\mu}$ photoelectron spectra were extracted. In these images the outer ring, corresponding to maximum photoelectron speed, correlates with the population of the vibrationless ground state of the acetylene cation (labeled  $0^{0} {}^{2}\Pi_{u}$  in Fig. 1). The inner ring in the images arises from the population of the  $4^{12}\Sigma_{\mu}^{-}$  vibronic state. Extraction of the angular data from the inner ring for each of the images in Fig. 3(a) yields the PADs plotted in Fig. 3(b). In all cases the extracted PADs are the intensity-weighted sum of the  $N_+$  ion states formed by ionization. These PADs are then fitted to Eq. (1) in order to deduce values for  $\beta_{20}$  and  $\beta_{40}$ . Error bounds on the PADs are also shown, these are derived from the errors in the  $\beta_{20}$  and  $\beta_{40}$  parameters, as calculated by the pBasex inversion technique,<sup>24</sup> and generally increase with the loss of subband intensity in the photoelectron image. It should be noted that although the images recorded via high  $J_i$  show partial rotational resolution, it was found that PADs for individual  $N_{+}$ states could not be reliably extracted from this data. This was due to the low intensities of these features causing excessive noise in the angular data extracted over a small energy range.

TABLE II. Normalized  $\beta_{20}$  and  $\beta_{40}$  values deduced by fitting PADs recorded after pumping on various rotational lines in the  $V_0^4 K_0^{-1}$  band to Eq. (1). Values in parentheses indicate error values as derived from the fitting algorithm used by pBasex. Cases where the  $\beta_{LM}$  value is close to zero with greater than 50% error are shown in italics.

Pump line	$J_1$	$eta_{20}$	$eta_{40}$
$R_1$	2	0.07(1)	-0.15(1)
$R_3$	4	0.00(1)	-0.11(1)
$R_5$	6	0.04(2)	-0.06(2)
$R_7$	8	0.13(2)	-0.04(2)
$R_9$	10	0.03(2)	-0.03(2)
$Q_3$	3	-0.02(1)	-0.08(1)
$Q_5$	5	-0.02(1)	-0.07(1)
$Q_7$	7	0.08(1)	-0.05(1)

Only by averaging over a larger energy range could reliable PADs be obtained, with consequent loss of  $N_+$  selectivity.

The PADs show a clear change over the sequence. The PAD that results following the  $R_1(J_i=2)$  excitation is most striking, with clear fourfold structure. For PADs recorded via higher  $J_i$  intermediate levels a reduction in this anisotropy can be seen, with the  $R_0(J_i=10)$  PAD showing very little angular structure. Normalized  $\beta_{20}$  and  $\beta_{40}$  values for these PADs are listed in Table II. The fourfold structure seen in the PADs indicates a significant contribution from the  $Y_{40}$ spherical harmonic [Eq. (1)], and in fact the normalized magnitudes of the  $\beta_{40}$  coefficients are greater than those of the  $\beta_{20}$  coefficients. The more isotropic PADs seen for high  $J_i$ are reflected in the decrease in magnitude of the  $\beta_{40}$  values for these PADs, while the loss in image fidelity correlates with the increase in the errors attributed to the extracted  $\beta_{40}$ parameters. The  $\beta_{20}$  parameters fluctuate over the sequence but remain small throughout and thus make little contribution to the anisotropy observed. The  $R_7$  and  $Q_7$  cases are the only exceptions, with  $|\beta_{20}| > |\beta_{40}|$ . Further analysis of these parameters is made in the following paper.<sup>20</sup>

#### C. $K_+>0$ vibronic states

The photoelectron spectra corresponding to vibronic state with  $K_+ > 0$  have been extracted from photoelectron images recorded via pump transitions of the  $V_0^{5}K_0^{-1}$  band as discussed in Sec. IV A. The energy resolution is much lower than that obtained from the images discussed in Sec. IV B, with typical feature widths (FWHM) of around  $50-80 \text{ cm}^{-1}$ . The Renner-Teller structure of the ion allows  $K_+$  levels to be resolved in most cases (with the exception of some overlapping subbands), but we have not resolved  $J_+/N_+$  levels. Additionally, it should be noted that the  $0 < K_+ \le v_{4+}$  levels exhibit a different rotational structure from the  $\Sigma_u^{-/+}$  vibronic states previously discussed. These states show spin-orbit splitting of a similar magnitude to the rotational line spacing  $(A_0=30.91(2) \text{ cm}^{-1})$ ,<sup>18</sup> and are therefore described as intermediate between Hund's cases (a) and (b) and labeled with the total angular momentum quantum number, including spin,  $J_{+}$ . The nuclear spin state restriction that occurs for the  $\Sigma$  vibronic states is also removed by the presence of two  $K_+$ components for each  $J_{+}$  level which allows both nuclear spin states to exist for each ion rotational level.<sup>18</sup> Therefore, all



FIG. 4. PADs extracted from the photoelectron image recorded via *R*-branch transitions of the  $V_0^5 K_0^{-1}$  band. Ion vibrational level and Renner-Teller subbands are labeled. The left-hand column shows PADs arising from the population of  $K_+$ =odd levels, the right-hand column shows PADs arising from population of  $K_+$ =even levels. All PADs are shown as polar plots  $(I, \theta)$ . The laser polarization direction is shown by **E**, the electric vector.

 $J_+/N_+$  levels can be accessed upon ionization within the angular momentum confines imposed by the selection rule<sup>31</sup>  $|\Delta N| \leq l+1$ , where *l* is the photoelectron orbital angular momentum quantum number. The selection rules that constrain the photoelectron partial waves that can be formed are further discussed in the following paper,<sup>20</sup> but we note here that the ZEKE works of Pratt *et al.*<sup>18</sup> and Tang *et al.*<sup>19</sup> have been consistent with the assumption that l=1,3 are the dominant partial wave components, yielding  $|\Delta N| \leq 4$ . This is also confirmed in the analysis of our data.<sup>20</sup>

In Fig. 4 we show examples of the PADs corresponding to the population of different vibronic states of the acetylene ion. Error bounds on the PADs are also shown; as before they are derived from the errors in the  $\beta_{20}$  and  $\beta_{40}$  parameters as calculated by the pBasex inversion technique. It can be seen that, in the case of the intense features arising from the 4<sup>3</sup> and 4<sup>4</sup> vibrational states, the errors in the extracted  $\beta_{20}$ and  $\beta_{40}$  parameters are negligible. The PADs show a behavior that is dependent on the value of  $K_+$ . For  $K_+$ =even the PAD is horizontally oriented, i.e., the maximum intensity lies perpendicular to the laser polarization (defined as northsouth in all our images and PADs). For  $K_{+}$ =odd the PAD is vertically oriented, i.e., parallel to the laser polarization axis. Furthermore, we observe changes in the PAD according to the prepared  $J_i$  state, although unlike the PADs discussed in Sec. IV B these cannot be easily categorized into a trend.

### **V. DISCUSSION**

The form of a photoelectron angular distribution depends on geometrical factors (angular momentum coupling) and dynamical factors (radial dipole matrix elements connecting the ionized state to each photoelectron partial wave and their relative phases). The former will be influenced by the prepared rotational level, the ion rotational level formed, and the alignment generated in the excitation step. This alignment can be varied by using different polarization geometries,<sup>32,33</sup> but otherwise is determined by the selected transition, the number of photons required for excitation, and whether the experiments are conducted in the weak-field and electric dipole limits. In the experiments presented here, a fixed polarization geometry was used (excitation and ionization beam polarization parallel), and the power levels were such that the weak-field and electric dipole approximations could be applied. Within this framework, the geometrical factors can be calculated as we show in the following paper.<sup>20</sup> When the geometrical factors are known the possibility of fitting the experimental PADs in order to determine the dynamical factors arises; this is the essence of the "complete" experiment. As illustrated above, the observed PADs depend strongly on the selected intermediate rotational level. This was also observed in the case of the ionization of ammonia in its  $\tilde{B}^{1}E''$  electronic state<sup>8</sup> but was not observed for the ionization of nitric oxide in its  $A^{2}\Sigma^{+}$  electronic state.<sup>33</sup> It is, in fact, a feature of the ionization of polyatomic molecules which can be used to advantage in the pursuit of a complete experiment. In the following paper,<sup>20</sup> we show that we are able to quantitatively account for the behavior of the PADs presented here and also to extract the radial dipole matrix elements and phases that give rise to them for the case of the  $4^{1} \Sigma_{\mu}^{2}$  vibronic state.

## **VI. CONCLUSIONS**

We have reported experimental observation of photoelectron spectra and angular distributions recorded from acetylene using a (1+1) resonance-enhanced multiphoton ionization scheme, following the preparation of various intermediate rovibrational levels of the  $\tilde{A}^{-1}A_u$  excited state manifold. In the instance where ion states with  $K_+=0$  are formed we have achieved partial rotational resolution in our images by ionizing at just above threshold and observed fourfold symmetric PADs which evolve with the  $J_i$  intermediate level populated by the pump laser pulse. These data are sufficient to enable us to achieve a "complete" determination of the relevant photoionization dynamics; in the following paper<sup>20</sup> we show how we are able to simulate the PAD behavior and elucidate the radial dipole matrix elements and phases from this partially resolved experimental data.

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