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Complete determination of the photoionization dynamics of a polyatomic molecule. II. Determination of radial dipole matrix elements and phases from experimental photoelectron angular distributions from $\tilde{A}^{1}A_{u}$ acetylene

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We present a fit to photoelectron angular distributions (PADs) measured following the photoionization of rotationally selected $\tilde{A}^{1}A_{u}$ state acetylene. In the case of the $4^{12}\Sigma_{u}^{-}$ vibronic state of the ion, we are able to use this fit to make a complete determination of the radial dipole matrix elements and phases connecting the prepared level to each photoelectron partial wave. We have also investigated other Renner-Teller subbands with a view to disentangling geometrical and dynamical contributions to the resulting PADs. © 2007 American Institute of Physics. [DOI: 10.1063/1.2790443]

I. INTRODUCTION

The application of a "complete experiment" methodology to the photoionization of polyatomic molecules appears as a challenging problem because of the large number of radial dipole matrix elements connecting an initial state to components of the photoelectron wavefunction that have to be determined. A successful experiment must allow *at least* a comparable number of independent experimental measurements to be recorded. Only if this can be achieved does the possibility arise of combining calculations of geometric factors with a fitting procedure to the experimental data in order to elucidate the radial dipole matrix elements.

In all photoionization events, the partial wave contributions to the photoelectron wavefunction are severely limited by the symmetry of the electron-ion potential function. For atomic photoionization, the photoelectron emanating from an orbital of well-defined angular momentum labeled by l_i will have a wavefunction that is simply described by a superposition of the spherical harmonic functions $Y_{l_i-1,m}(\theta,\phi)$ and $Y_{l+1,m}(\theta,\phi)$.¹ In the case of a diatomic molecule, the initial orbital has only cylindrical, not spherical symmetry. The partial wave orbital angular momentum defined by the quantum number l will have a projection on the molecular axis defined by the quantum number λ ,² and for a heteronuclear diatomic molecule, *l* is not restricted by symmetry, although in practice will be small. For a homonuclear diatomic molecule inversion symmetry will ensure that only odd -or even-l partial waves can be formed, depending on the symmetry of the orbital from which the electron is ejected. Therefore, the number of experimental measurements needed for a complete experiment is much reduced compared with the heteronuclear case. Molecular symmetry may have additional benefits in limiting the ion rotational states that can be formed following ionization from a given initial rotational state. Similar principles affect the photoionization of polyatomic molecules, where restrictions on vibronic angular momenta and the molecular-fixed projections of rotational angular momenta can also be used to advantage in highly symmetric molecules. In an earlier work from our group, we have illustrated the benefits of molecular symmetry with reference to the photoionization of $\tilde{B}^{1}E''$ state ammonia,³ in which we were able to make a partial determination of the radial dipole matrix elements from relatively few experimental observables.

Further simplifications can occur as a consequence of sensitivity of photoelectron angular distributions (PADs) to an initially prepared alignment.⁴ Such a sensitivity can therefore be exploited by the experimentalist by the preparation of a range of different initial alignments. This principle has been known for many years and was originally used in the determination of the photoionization dynamics of alkali atoms.^{5,6} More recent experiments have reached high sophistication and enabled the determination of even the signs of the phase differences between partial waves.⁷⁻¹⁰ The sensitivity of PADs to alignment can be particularly acute for the ejection of photoelectrons from Rydberg orbitals with l > 0.3In other cases, a sensitivity in molecular photoionization is only observed when ion rotational states are resolved,⁹ limiting the utility of this phenomenon to situations where such resolution can be achieved.

In Paper I (Ref. 11), we showed that PADs from $\tilde{A}^{-1}A_u$ state acetylene are sensitively dependent on the rotational level out of which photoionization occurs. In addition, inversion symmetry ensures that only photoelectron partial waves with *odd l* can be formed. Thus, the measurement of PADs as a function of prepared rotational level has provided a data set that is sufficiently large for a complete determination of the photoionization dynamics corresponding to the formation of the $4^{12}\Sigma_u^{-1}$ ion vibronic state to be made. In the work described here, we present a fit to data shown in Paper I and

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show that we are able to determine the full set of expected radial dipole matrix elements and phases. We also discuss how our methodology can be used to understand the ionization dynamics relevant to the formation of the other ion vibronic states.

II. BACKGROUND

A. Photoelectron angular distributions

The ground state of the acetylene ion $(\tilde{X}^2 \Pi_u)$ is linear. The Renner-Teller (RT) effect splits the vibrational states into vibronic levels designated by K_+ , the quantum number describing the molecular frame projection of the vibronic angular momentum. The vibronic states are labeled as $\Sigma, \Pi, \Delta, ...,$ according to $K_+=0, 1, 2, ...,$ and are preceded by X^m to denote the parent vibrational state. In this work, the bands discussed all involve ν_4 , the *trans*-bending mode of the ion, for example, $4^3 {}^2\Delta_u$ denotes the $K_+=2$ vibronic component of the $\nu_4=3$ vibrational level. Further discussion of the structure of the $\tilde{X} {}^2\Pi_u$ cation and $\tilde{A} {}^1A_u$ intermediate state can be found in our previous paper and references therein.¹¹

The rotational structures of the subbands differ according to the relative magnitudes of the RT and spin-orbit coupling constants. In particular, the $K_+=0$ levels are well described by Hund's case (b), while the $0 < K_+ \le \nu_4$ levels are best described as intermediate between Hund's cases (a) and (b), and the $K_+=\nu_4+1$ levels can be described as Hund's case (a).¹² These considerations mean that it is possible to use expressions for photoelectron angular distributions that have been developed for diatomic molecules well described by Hund's case (a) or (b). Our formalism is primarily based on the work of Reid *et al.*,¹³ which itself built on work by Dixit and McKoy.¹⁴ In addition, the effects of a nonlinear intermediate state and the nonzero spin of the ion have also been taken into account, as shown in the Appendix.

In general terms, the photoelectron angular distribution arising from population of an ion rotational level labeled by N_+ (total angular momentum quantum number, excluding spin) following ionization of an intermediate rotational level N_i can be cast in the following form:¹³

$$I(\theta,\phi) = \sum_{ll'} \sum_{\lambda\lambda'} \sum_{mm'} \gamma_{N_{+}l\lambda l'\lambda'} r_{l\lambda} r_{l'\lambda'}$$
$$\times \cos(\eta_{l\lambda} - \eta_{l'\lambda'}) Y_{lm}(\theta,\phi) Y^{*}_{l'm'}(\theta,\phi), \qquad (1)$$

in which geometrical terms (the $\gamma_{N_{+}l\lambda l'\lambda'}$ coefficients) and dynamical terms (the magnitude $r_{l\lambda}$ and the phase $\eta_{l\lambda}$ of the radial dipole matrix element connecting the initially prepared state to each photoelectron partial wave) are clearly separated. The quantum numbers l, λ , and m describe the photoelectron partial waves, denoting the orbital angular momentum, molecular frame projection, and laboratory frame projection, respectively. The radial dipole matrix elements and phases depend on l and λ (molecular frame), while the spherical harmonics depend on l and m (laboratory frame). The primes denote coherent terms which can interfere, and the observed PAD is formed from the coherent summation over all contributing partial waves. The form of the $\gamma_{N_{\mu}l\lambda l'\lambda'}$ coefficients relevant to the ionization of $\tilde{A}^{1}A_{u}$ state acetylene is discussed further in the Appendix.

An important point regarding this formalism is that the radial dipole matrix elements are integrated over the internuclear coordinates in the initial and ion states¹⁴ (see Appendix) and will therefore depend on the vibrational states involved, as well as on the continuum energy. These dependences are, however, expected to be small provided that states with widely differing internuclear separations are not studied, and that there are no resonances in the continuum. In the experimental data considered here,¹¹ it is a very reasonable assumption that the dynamical parameters will be constant across a vibrational band because only tiny changes in the continuum energy result from the preparation of different rotational levels. Previous photoelectron studies,¹⁵ as well as our own resonance-enhanced multiphoton ionization spectra, have shown no evidence for resonant features in the continuum in this energy range. Thus, we can assume that changing the angular momentum characteristics of the intermediate and ion states for a given band will affect the $\gamma_{N,l\lambda l'\lambda'}$ coefficients but not the dynamical terms. It is this separation which allows the application of a fitting methodology based on data recorded via different intermediate rotational states.

Comparing Eq. (1) with the generic expression for a photoelectron angular distribution,

$$I(\theta,\phi) = \sum_{L} \sum_{M} \beta_{LM} Y_{LM}(\theta,\phi), \qquad (2)$$

we can write

$$\beta_{LM} = \sum_{ll'} \sum_{\lambda\lambda'} \sum_{mm'} (-1)^m \\ \times \sqrt{\frac{(2l+1)(2l'+1)(2L+1)}{4\pi}} \begin{pmatrix} l & l' & L \\ m & -m' & M \end{pmatrix} \\ \times \begin{pmatrix} l & l' & L \\ 0 & 0 & 0 \end{pmatrix} \gamma_{N_+ l\lambda l'\lambda'} r_{l\lambda} r_{l'\lambda'} \cos(\eta_{l\lambda} - \eta_{l'\lambda'}).$$
(3)

The β_{LM} coefficients can be determined experimentally by fitting photoelectron angular distributions to a superposition of spherical harmonic functions, $Y_{LM}(\theta, \phi)$, as shown in Paper I.¹¹ For the data presented in Paper I (Ref. 11), the single-photon excitation and ionization polarization vectors were parallel. In this instance, Eq. (2) is restricted to give terms with L=0, 2, and 4 and M=0 terms.⁴ Thus, the photoelectron angular distributions are cylindrically symmetric and have an inversion symmetry.

B. Photoionization propensity rules

Detailed discussion of photoionization propensity rules for diatomic and polyatomic cases can be found in Refs. 16–18; we discuss here relevant points for acetylene. Various constraints can be placed on the angular momenta of the ejected photoelectron partial waves by consideration of the intermediate and ion state symmetries. Because acetylene has an inversion symmetry in all states relevant here, the $\tilde{X}^2 \Pi_u \leftarrow \tilde{A}^1 A_u$ transition must rigorously involve the emis-



FIG. 1. Photoelectron angular distributions corresponding to formation of the ion in the $4^{12}\Sigma_{u}^{-}$ vibronic state. R_{x} and Q_{x} denote the rotational lines of the $\tilde{A}^{1}A_{u}(\nu_{4}=4 \text{ and } K=1) \leftarrow \tilde{X}^{1}\Sigma_{g}^{+}(\nu=0 \text{ and } K=0)$ transition used to prepare the intermediate state. Solid lines show experimental PADs with associated error bars, dashed lines show the simulated PADs resulting from our fit of the experimental data of Eq. (1). All PADs are shown as polar plots (I, θ) . The laser polarization direction is shown by **E**, the electric vector.

sion of a photoelectron whose wavefunction is a superposition of partial waves with l odd only.^{12,17} This symmetry condition presents a huge simplification to the ionization dynamics.

The set of accessible ion rotational levels is determined by conservation of angular momentum and, for Hund's case (b), is given by 16

$$N_i - l - 1 \le N_+ \le N_i + l + 1. \tag{4}$$

This can be recast in terms of $\Delta N(=N_+-N_i)$ to give

$$|\Delta N| \le l+1. \tag{5}$$

The zero electron kinetic energy (ZEKE) data obtained by Pratt *et al.*¹² and Tang *et al.*¹⁹ show population of levels according to $|\Delta N| \leq 4$; this suggests a maximum partial wave with l=3. This observation also conforms to the general expectation in photoionization of a predominance of partial waves with low l values.

In the general case, there are no further strict selection rules on ΔN . $K_{+}=0$ vibronic levels are, however, an exception. In these cases, as discussed in Paper I (Ref. 11) and by previous authors,^{12,19} nuclear spin considerations place further limitations on ΔN . For ionization following an *R*-branch pumped excitation $\Delta N = \pm 1$ and ± 3 , while ionization following a Q-branch pumped excitation yields $\Delta N=0$ and ± 2 . This limitation on the populated N_+ states greatly improved the effective resolution of our photoelectron images by reducing spectral congestion and allowed us to obtain partial rotational resolution for the $4^{1} {}^{2}\Sigma_{u}^{-} (K_{+}=0)$ vibronic state.¹¹ In addition, the selection rule on λ that results for the $K_i = 1$ levels studied here gives $|\lambda|=0,1,\ldots,K_++1$, i.e., for K_+ =0 $|\lambda|$ is restricted to 0 or 1 only. Experimental data corresponding to this vibronic state thus offer the best chance for complete determination of the radial dipole matrix elements and phases.

C. Simulation and fitting procedure

The energy level structure for $\tilde{A} {}^{1}A_{u}$ state acetylene was taken from Watson *et al.*,²⁰ and calculation of the $\gamma_{N_{+}l\lambda l'\lambda'}$ parameters in Eq. (3) was performed according to the formalism given in the Appendix using the code written in C and the Racah 3*j* formalism.²¹ Fitting to the experimental data

was then carried out in MATLAB (RELEASE 2006B), using the LSQCURVEFIT algorithm from the Optimization Toolbox. The approach of separating the calculation of $\gamma_{N_{+}l\lambda l'\lambda'}$ values from the determination of the radial dipole matrix elements and phases meant that the $\gamma_{N_{+}l\lambda l'\lambda'}$ calculation only needed to be performed once, effectively creating a set of basis files for different N_{+} states which could then be read by the MATLAB code as appropriate.

III. RESULTS

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

The acetylene ion in its 4¹ $^{2}\Sigma_{u}^{-}$ vibronic state can be well described by Hund's case (b). Ion rotational states are therefore labeled by N_+ , and the structure of the PADs within a vibronic subband will be determined by ΔN . The fit was initially carried out using photoelectron partial waves with l=1 and 3 only, based on the propensity rules discussed in Sec. II B. Additionally, as explained above, for a Σ ion state, the projection of l onto the molecular axis λ is restricted to $|\lambda|=0$ and 1 (σ and π), resulting in eight fitting parameters in total. Because only the *relative* values of the phases can be determined, $\eta_{p\sigma}$ was set to zero and fixed for the fitting procedure to provide a reference phase. A weighting factor was applied to the data to allow for difference in image fidelity over the dataset. Each observed PAD was fitted by summation of the PADs pertaining to population of different N_{+} states, which are unresolved in the experimental data. The fitting procedure was repeated several times with random seed values in order to ensure the uniqueness of the fit. Different absolute values of $r_{l\lambda}$ could be found, but reducing these to the relative terms $F_l = r_{l\sigma}^2 + 2r_{l\pi}^2$ (*l*-wave cross section, further normalized such that $F_p + F_f = 1$ and Γ_l $=r_{l\sigma}^{2}/(r_{l\sigma}^{2}+2r_{l\pi}^{2})$ (degree of parallel character) yielded the same result. Similarly, different $\eta_{l\lambda}$ values could arise from the fit but were always due to a 2π phase shift. These results show that a large solution space was searched by the algorithm, and that the final F_l and Γ_l are unique.

The results of the fit to the experimental PADs corresponding to the 4¹ ${}^{2}\Sigma_{u}^{-1}$ ion state (as presented in Paper I)¹¹ are shown in Fig. 1 and Table I. The PADs in Fig. 1 are labeled according to the $\tilde{A}^{-1}A_{u}(\nu_{4}=4, K=1) \leftarrow \tilde{X}^{-1}\Sigma_{g}^{-1}$

TABLE I. Partial wave cross sections F_l , degree of parallel character Γ_l , and phases $\eta_{l\lambda}$. The sign of the phases cannot be deduced in this work.

l	F_l	Γ_l	λ	$\eta_{l\lambda}$
p	0.78 (1)	0.12 (3)	$\sigma \ \pi$	0° ^a 117° (1)
f	0.22 (1)	0.43 (2)	$\sigma \ \pi$	175° (3) 250° (1)

^aDenotes the phase fixed as reference phase.

 $(\nu=0, K=0)$ rotational transition used to prepare the intermediate state. The simulated PADs show excellent agreement with the experimental PADs for the R_1 , R_5 , R_9 , Q_3 , and Q_5 transitions, with slightly poorer agreement for the R_3 , R_7 , and Q_7 transitions. For the R_7 , R_9 , and Q_7 transitions there is a loss in signal intensity in the photoelectron images as a consequence of reduced intermediate state populations at higher J_i . This is allowed for by weighting the fit in favor of the lower J_i cases, and it is not therefore surprising that the higher J_i cases show differences from the fitted PADs. This loss in image fidelity is clearly seen in the photoelectron images, as shown in Fig. 3 of the previous paper.¹¹ In the case of the R_3 transition, the reasons for disagreement between the fitted PAD and the experimental PAD are unclear, although the fit is still acceptable. The observed trend toward a more isotropic PAD with increasing J_i across the R branch is reproduced in the simulations and attributed to the effect of a reducing intermediate state alignment. The effect of this alignment on PADs is illustrated in Fig. 2, in which comparisons can be made between the simulated PADs resulting from lower and higher selected J_i values and from R and Q transitions. Although loss of PAD anisotropy appears to correlate with reduced intermediate state alignment at high J_i for the *R* branch [Fig. 2(a) versus Fig. 2(b)], this is not seen for the Q branch [Fig. 2(c) versus Fig. 2(d)]. The apparent loss in observed anisotropy for the Q_7 PAD seems likely therefore to be caused by experimental uncertainties. The fact that this does not appear to be reflected by the error bars in Fig. 1 is a consequence of the way in which the error bars are derived (see Sec. 4.2 in Ref. 11). Both the experiment and the simulation show a similarity between the PADs recorded via *R*-and *Q*-branch transitions, despite the very different intermediate state alignments prepared in each case [Fig. 2(a) versus Fig. 2(c) and Fig. 2(b) versus Fig. 2(d)]. This illustrates the fact that the relationship between alignment and PADs sometimes defies intuition, and only a calculation can fully explain results (see Appendix).

The radial dipole matrix elements deduced from the fit (Table I) show that the photoelectron wavefunction is largely $p\pi$ wave in character (69%), with small (~10%) $p\sigma$ -, $f\sigma$ -, and $f\pi$ -wave contributions. The predominantly perpendicular nature of the ionization is indicative of the molecular character of the $\tilde{A}^{1}A_{u}$ state and would not be observed for the ionization of an atomiclike state in which equal contributions of σ and π waves would be expected. However, we show later that we can eliminate any significant contributions from l=5 waves, suggesting that an analogy can be drawn between the outermost π_{u} molecular orbital and an atomic d



FIG. 2. Calculated PADs arising from the (a) R_1 , (b) R_5 , (c) Q_2 , and (d) Q_6 rotational lines of the $\tilde{A} \,{}^1A_u(\nu_4=4 \text{ and } K=1) \leftarrow \tilde{X} \,{}^1\Sigma_g^{+}(\nu=0 \text{ and } K=0)$ transition, and formation of the $K_+=0$ state of the ion. The accompanying plots show the intermediate state M_i populations in each case. Radial dipole matrix elements and phases as deduced from our fit are used in these calculations. All PADs are shown as polar plots (I, θ) . The laser polarization direction is shown by **E**, the electric vector.

orbital. The largely perpendicular character of the photoelectron wavefunction tells us, therefore, that this *d*-like orbital is pinned strongly to the molecular frame. The observed fourfold PADs are highly sensitive to the phase lag between the $f\sigma$ and $f\pi$ partial waves, and this enables us to be very confident that they are close to $\pi/4$ out of phase. Because our experiment has been undertaken with linearly polarized light we are insensitive to the sign of this phase difference.⁸

The β_{00} values are proportional to the angle-integrated cross sections and therefore can be used to predict branching ratios between different ΔN transitions corresponding to a given ion vibronic state. Accessible ion rotational levels are determined by the rule $\Delta N = \pm 1$ and ± 3 for an *R*-branch pumped intermediate state and $\Delta N=0$ and ± 2 for a *Q*-branch pumped intermediate state, as discussed in Sec. II B. *R*-branch pumped transitions show preferential population of $\Delta N = +1$ at low J_i . At higher J_i the N_+ levels resulting from $\Delta N = \pm 1$ transitions become more evenly populated. As an independent test of the predicted branching ratios we show in Figs. 3(a) and 3(b) a comparison of the ZEKE results from Tang *et al.*¹⁹ with simulated spectra for the R_1, R_3, R_5 , and R_7 pumped cases. Good agreement is seen between the spectra, and the simulations match the ZEKE spectra particularly well for the R_1 and R_3 cases. The R_1 result is also consistent with the partially resolved spectrum shown in Fig. 6 of Ref.



FIG. 3. Rotationally resolved photoelectron energy spectra corresponding to the formation of the $4^{12}\Sigma_{u}^{-}$ vibronic state. (a) Experimental ZEKE spectrum obtained by Tang *et al.* (Ref. 19), plotted using the data kindly provided by Dr. Y-C Hsu. (b) Calculated spectrum allowing *l*=1 and 3 partial wave contributions. (c) Calculated spectrum allowing *l*=1, 3, and 5 partial wave contributions.

12. The slight discrepancies at higher J_i could be due to the decrease in signal to noise as the pump transitions become weaker and the intermediate state population decreases. This is the same problem found in our photoelectron images recorded from these high J_i intermediate states. Interestingly, the ZEKE data do not show the $\Delta N = +3$ peaks, although these are seen as shoulders on the high-energy side of the rotational contours extracted from our images for high J_i (Fig. 2 of Ref. 11). Broadening the linewidths of the Lorentzians used to produce the simulated spectra reproduced the qualitative features of the ion rotational contours observed in Paper I and confirmed that the observed shoulders arise from the $\Delta N = +3$ transitions. A more quantitative assessment could also be made by fitting Lorentzians to the experimental data shown in Ref. 11, while constraining the rotational level separations [determined as $E(N_+) = BN_+(N_++1)$ with B =1.1 cm⁻¹],¹² yielding experimental branching ratios. This procedure worked well for high $J_i(>5)$ and produced branching ratios in good agreement $(\pm 5\%)$ with the calculated ratios; for low J_i , this method did not produce reliable results because the lack of rotational resolution in our images led to ambiguous Lorentzian fits.

Calculations for the data obtained via Q-branch pump transitions show preferential population of $\Delta N=0$ at low J_i . At high J_i , $\Delta N=+2$ becomes the preferential transition. In these cases, our experimentally derived branching ratios show relatively poor agreement with the results of our simulation. As with the low J_i *R*-branch case, this is the result of a lower effective experimental resolution for the Q-branch transitions. Unfortunately there is no equivalent Q-branch pumped ZEKE data in the literature for further comparison.

A further use of the branching ratios as a diagnostic is shown in Fig. 3(c). In this example, we show the result of allowing l=5 to contribute to the PAD in order to test the propensity rule l=1 and 3. In this case, we performed a fit to the experimental PADs shown in Fig. 1 as before but allowed the fit to include an h wave. A good fit to the experimental PADs could still be found, with only the R_9 case showing a poorer result than the l=1 and 3 only fit shown in Fig. 1. This fit produced a very different parameter set, with l-wave cross sections $F_p=0.52$, $F_f=0.10$, and $F_h=0.38$. Although the shift in partial wave contribution from f wave to h wave, relative to the previous results, seemed unlikely, the fitted PADs alone cannot rule out this possibility. However, consideration of the branching ratios arising from this fit shows very clear evidence for the lack of an h-wave contribution. The ratios of the $\Delta N = \pm 1$ peaks remain similar to the examples shown in Figs. 3(a) and 3(b), but the intensities of the $\Delta N = +3$ features show a large increase. This is not consistent with any of the experimental data. Furthermore, by constraining the contribution of the *h* wave, we find that even an *h*-wave cross section as small as $F_h=0.01$ has a large effect on the branching ratios. For the R_1 case the inclusion of this small *h*-wave contribution yields 31% population of $\Delta N = +3$ vs 16% without this contribution. We can thus conclude that the branching ratios show a very high sensitivity to the presence of high-order partial waves, and that any l=5 partial wave contribution is negligible, with a cross section $\ll 1\%$.

B. Ion states with $K_+>0$

The magnitudes and phases of the radial dipole matrix elements corresponding to the formation of the $K_{+}=0$ vibronic state of the ion have been determined, as described in Sec. III A. As explained above, the radial dipole matrix elements are expected to have a small dependence on vibrational state and on continuum energy. In the case of the K_{+} >0 levels, additional considerations arise in applying the fitting methodology. First, there are further dynamical parameters to be determined because partial wave components with $|\lambda| > 1$ are permitted, as governed by the selection rule $|\lambda| \leq K_+ + 1$. Thus, for a Π vibronic state the dynamical parameters $r_{f\Delta}$ and $\eta_{f\Delta}$ are required in addition to those already considered, while for a Φ vibronic state the full set of *f*-wave components including $r_{f\Phi}$ and $\eta_{f\Phi}$ are necessary. Second, the change from Hund's case (b) to an intermediate (a)/(b) case (Sec. II A) means that spin-orbit effects need to be considered. Third, the loss of the ΔN selection rule (Sec. II B) means that all N_+ states allowed by conservation of angular momentum [Eq. (5)] can be accessed upon ionization. In addition, the images in which the $K_+>0$ levels appear were recorded with $\sim 2600 \text{ cm}^{-1}$ maximum ion internal energy, compared with only $\sim 650 \text{ cm}^{-1}$ maximum ion internal energy required to access the $4^{1/2}\Sigma_u^-$ vibronic state. This increase in available energy leads to lower resolution in our images, and although we still obtain vibronic subband resolution [with occasional overlap, see Fig. 1(b) of the previous paper¹¹], we cannot obtain any information on the spin-orbit or rotational structure within a subband.

The decrease in resolution of our images, combined with the other considerations outlined above, means that the fits to



FIG. 4. Experimental and calculated PADs for different K_+ states. Panel (a) shows the experimental PADs recorded via the R_1 line of the $\tilde{A}^{-1}A_u(\nu_4 = 5 \text{ and } K=1) \leftarrow \tilde{X}^{-1}\Sigma_g^{-+}(\nu=0 \text{ and } K=0)$ transition. Calculated PADs are shown for (b) all $r_{l\lambda}=1$, $\eta_{l\lambda}=0$, and (c) all $r_{l\lambda}=1$, $\eta_{l\lambda}=0$ except $\eta_{f\pi}=\eta_{f\Delta}=180^\circ$. All PADs are shown as polar plots (I, θ) . The laser polarization direction is shown by **E**, the electric vector.

the $K_+>0$ levels will not be as robust as the fit presented for the $K_+=0$ (4^{1 2} Σ_u^-) level, with increasing uncertainties as K_+ increases. A successful determination of the radial dipole matrix elements for these vibronic states, therefore, will rely on either independent methods of assessing the validity of the results or further experimental measurements in, for example, alternative polarization geometries. A preliminary fit to the PADs corresponding to the formation of the 4² ² Π_u vibronic state, however, leads us to cautiously conclude that only small changes in radial dipole matrix elements result as compared with those deduced for the 4¹ ² Σ_u^- vibronic state.

Despite the problems associated with elucidating the radial dipole matrix elements and phases, our simulation still allows us to consider the behavior of the PADs with K_+ in a more qualitative manner. The experimental PADs shown in the previous paper¹¹ reveal a rotation in the PAD orientation between odd and even K_+ levels, with the maximum intensity lying parallel to the laser polarization axis for K_+ odd and perpendicular to the laser polarization axis for K_+ even. Figure 4(a) shows experimentally recorded PADs for different K_+ levels. Changes in both the geometrical $(\gamma_{N_+l\lambda l'\lambda'})$ and dynamical $(r_{l\lambda}$ and $\eta_{l\lambda})$ parameters may be responsible for the observed changes in the PADs. However, given that only small changes in the dynamical parameters are expected, it is instructive to calculate the geometrical parameters for different K_{+} levels, by taking a fixed set of dynamical parameters, and observe the resulting behavior of the PADs. Figure 4(b) shows the results of such a calculation. The matrix elements are set as $r_{l\lambda}=1$ and $\eta_{l\lambda}=0$ for l=1 and 3 and for all allowed λ . PADs arising from population of all accessible N_+ states are calculated for both spin-orbit components of a given K_+ level, and this set of PADs is then summed to produce a single PAD comparable to those recorded experimentally with vibronic resolution. Under these constraints, the relative rotation of the PADs corresponding to states with $K_{+}=0, 1,$ and 2 is predicted by the calculation. However, the relative rotation of the $K_{+}=3$ PAD can only be predicted by setting the phases $\eta_{f\Delta}$ and $\eta_{f\Phi}$ to 180°, as shown in Fig. 4(c). This illustrates how very sensitive PADs are to the values of the phase differences between partial waves. With more experimental data it seems certain that a complete determination of the photoionization dynamics corresponding to the formation of the $K^+ > 0$ ion states can be achieved.

IV. DISCUSSION

We consider the outcomes of this study when compared with similar experiments conducted on NO (A ${}^{2}\Sigma^{+}$) (Ref. 22) and NH₃ $(\tilde{B} \ ^1 E'')$.³ In Ref. 22, photoelectron angular distributions corresponding to resolved ion rotational states were obtained following the ionization of a single selected intermediate level with N_i =22. The PADs depended sensitively on ΔN , allowing determination of all the radial dipole matrix elements and phases when three different experimental polarization geometries were used. However, when the PAD was averaged over ion rotational states, the result was insensitive to intermediate rotational level and to alignment. Because by far the most probable transition was to the $N_{+}=N_{i}$ rotational level of the ion, the rotationally summed PAD looked equivalent to the one determined for the $\Delta N=0$ transition. Because the $A^{2}\Sigma^{+}$ state of NO is well described as an s-Rydberg orbital, the $\Delta N=0$ transition is associated almost exclusively with atomic-like p-wave photoelectrons which have no alignment sensitivity, and only by observing the small $\Delta N \neq 0$ transition could the contributions of other partial waves be deduced. In addition, the chosen value of N_i does not restrict the allowed ΔN values, and so no additional information could be obtained by varying N_i . In the case of $A^{2}\Sigma^{+}$ state NO, therefore, the resolution of ion rotational levels was essential to the complete determination of the photoionization dynamics. In the ammonia work described in Ref. 3, ion rotational states were not resolved, and PADs were measured for a set of low values of N_i and K_i and shown to depend sensitively on these. This occurred because (i) the $\tilde{B}^{1}E''$ state of ammonia is well described as a p-Rydberg state which is strongly alignment sensitive and (ii) nuclear spin selection rules restrict the subset of ion rotational states that can be formed from a given intermediate rotational state. Therefore, a semi-complete determination of photoionization dynamics could be made without needing to resolve ion rotational levels. The case of $\tilde{A}^{1}A_{\mu}$ state acetylene, as presented here, has turned out to be even more advantageous than that of $\tilde{B}^{1}E''$ state ammonia because of the strong parity selection rule controlling the photoelectron orbital angular momentum *l*. This has enabled us to make a complete determination of the photoionization dynamics relevant to the formation of the $4^{1} {}^{2}\Sigma_{u}^{-}$ vibronic state of the ion, with incomplete resolution of ion rotational levels. In the case of acetylene, additional interest results from the formation of other ion vibronic states.

V. CONCLUSIONS

We have used photoelectron angular distributions measured following the ionization of selected rotational levels in the $A^{-1}A_{\mu}$ state of acetylene to make a complete determination of the photoionization dynamics corresponding to the formation of the $4^{12}\Sigma_{u}^{-}$ vibronic state of the ion ground state. This process has been expedited by the strict selection rules determining the allowed ion rotational levels and photoelectron partial wave orbital angular momenta. The photoelectron wavefunction has been determined to be $\sim 78\% p$ and $\sim 22\% f$, with < 1% h. We have observed changes in the PADs corresponding to the formation of other ion vibronic states and have been able to account for these qualitatively. For these states more experimental data taken in different polarization geometries are needed in order to achieve a complete determination of the relevant photoionization dynamics.

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APPENDIX: THE γ COEFFICIENTS

Following Reid *et al.*,¹³ the γ coefficients introduced in Eq. (1) can be expressed as

$$\gamma_{N_{+}l\lambda l'\lambda'} = (2N_{i}+1)(2N_{+}+1)$$

$$\times (-i)^{l'-l} \sum_{M_{+}} \sum_{M_{i}} \sum_{N_{i}N_{i}'} \sum_{\mu_{\lambda}\mu_{\lambda}'} {}^{J_{i}K_{i}} \rho_{M_{i}M_{i}}$$

$$\times C(l'\lambda'N_{i}'\mu_{\lambda}')C(l\lambda N_{i}\mu_{\lambda}), \qquad (A1)$$

where ${}^{J_iK_i}\rho_{M_iM_i}$ represents the intermediate state density matrix and describes the population of M_i levels,

$${}^{J_i K_i} \rho_{M_i M_i} \propto S(J_g K_g, J_i K_i) \sum_{M_g} \begin{pmatrix} J_g & 1 & J_i \\ M_g & \mu_0 & M_i \end{pmatrix}^2.$$
 (A2)

Here, $S(J_gK_g, J_iK_i)$ is the rotational line-strength factor connecting the ground and intermediate rotational levels. $S(J_gK_g, J_iK_i)$ terms are calculated using a linear rotor model for the ground state and the effective Hamiltonian of Watson *et al.*²⁰ to model the *trans*-bent intermediate state.

The C coefficients in Eq. (A1) are angular momentum coupling factors,

$$C(l\lambda N_{t}\mu_{\lambda}) = (2N_{t}+1)(-1)^{M_{+}+\mu_{\lambda}} \binom{N_{t} \ 1 \ l}{M_{t} \ 0 \ m} \times \binom{N_{+} \ N_{i} \ N_{t}}{-K_{+} \ K_{i} \ K_{t}} \binom{N_{t} \ 1 \ l}{-K_{t} \ \mu_{\lambda} \ -\lambda} \times \binom{N_{+} \ N_{i} \ N_{t}}{-M_{+} \ M_{i} \ M_{t}} \binom{N_{+} \ J_{+} \ S_{+}}{M_{+} \ M_{J+} \ M_{S+}} \times \binom{N_{+} \ J_{+} \ S_{+}}{K_{+} \ P_{+} \ \Sigma_{+}}.$$
(A3)

Here, l, λ , and m denote the photoelectron orbital angular momentum quantum numbers with projections λ in the molecular frame and m in the laboratory frame. The incident photon is denoted as 1, μ_{λ} , and 0, reflecting one unit of angular momentum with a molecular frame projection μ_{λ} and laboratory frame projection of zero as applicable for linearly polarized light. Rotational levels are labeled in Hund's case (b), with N_{+} and N_{i} denoting the total angular momenta in the ion and intermediate states, respectively, excluding spin. K and M denote the molecular frame and laboratory frame projections of N, the terms N_t , K_t , and M_t are dummy parameters. The final two 3j symbols allow for nonzero spin in the ion, they couple N_+ to J_+ and its projections P_+ (molecular frame) and M_{I+} (laboratory frame) via the total spin S_{+} and its components Σ_{+} (molecular frame) and $M_{S_{+}}$ (laboratory frame). In the case of the $K_{+}=0$ levels, these final two terms can be omitted due to the weak spin-orbit interactions in the state. In the $K_+>0$ case, spin must be included, but rotational levels within a spin-orbit band can still be uniquely labeled by N_{\perp} .

Apart from the inclusion of S_+ this formalism is equivalent to that given in Refs. 13 and 14. The treatment of spin is similar to that of Braunstein *et al.*,²³ except that here, we do not sum over the spin-orbit states. In this way, the final PAD can be calculated for each unique N_+/J_+ level in a given spin-orbit band; these PADs can then be further summed as appropriate to the experimental resolution. Equation (A3) is the origin of the selection rules placed upon both ΔN and $|\lambda|$ in the text. It also indicates the routes through which the various angular momenta present in the molecule couple to each other.

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