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On the simulation of photoelectron spectra complicated by conical intersections: Higher-order effects and hot bands in the photoelectron spectrum of triazolidide $(\text{CH})_2\text{N}_3^-$

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We report simulated photoelectron spectra for 1,2,3-triazolidide $(\text{CH})_2\text{N}_3^-$, which reveal the vibronic energy levels of the neutral radical 1,2,3-triazolyl, $(\text{CH})_2\text{N}_3$. The spectral simulation using a quasidiabatic Hamiltonian $\mathbf{H}^d$ comprised of polynomials through 4th order (thereby extending conventional quadratic expansions), is compared to both the experimental spectrum and a standard Franck-Condon (adiabatic) simulation. The quartic $\mathbf{H}^d$ is far superior to the quadratic $\mathbf{H}^d$, reproducing the main features of the experimental spectrum and allowing for their subsequent assignment. The contributions from excited anion states successfully reproduce the observed vibronic transitions to the red of the assigned band origin of the neutral species. The algorithmic extensions required for the determination of these hot band contributions to the total spectrum are discussed. Convergence of the spectral envelope with respect to the vibronic basis, including both the principal and hot bands, required more than 10^9 terms. © 2011 American Institute of Physics. [doi:10.1063/1.3587094]

I. INTRODUCTION

In molecules that exhibit symmetry-required Jahn-Teller degeneracies, it is recognized that spectral simulations must incorporate nonadiabatic effects, even for the lowest energy vibronic states.^{1–7} Although the symmetry-required nature of the degeneracy is removed for substitutional isomers of these highly symmetric molecules,^{8–16} an analogous accidental seam of conical intersection persists. Since the perturbation from the symmetry-required case may be appreciable, the role of nonadiabatic effects on the low-lying vibronic energy levels is difficult to anticipate *a priori*. Furthermore, from an experimental perspective, the presence of hot bands, that is, transitions arising from excited anionic vibrational levels, further obfuscate the assessment of the character of the low-lying vibronic energy levels.¹⁷ In situations such as these, theoretical simulations can assist in ascertaining the importance of these potentially competing factors.¹⁶

In this work, we report a simulation of the anion photodetachment spectrum of 1,2,3-triazolidide/ $(\text{CH})_2\text{N}_3^-$ revealing the vibronic energy level structure of the 1,2,3-triazolyl/ $(\text{CH})_2\text{N}_3$ radical. Interest in this molecule, and nitrogen containing five member ring compounds (azolyls), in general, results from the potential applications of these species as high energy-density materials.^{18–20} The experimental photoelectron spectrum of the 1,2,3-triazolidide anion has been recorded by Lineberger's group.²¹ In that study, it was found that single-state adiabatic simulations, determined directly from the Franck-Condon vibrational overlaps, failed to reproduce the recorded spectrum. This is not entirely surprising, since we have recently demonstrated the complexity

of the interactions coupling the low-lying electronic states in this molecule.²² However, it should be noted that the minimum energy conical intersection in 1,2,3-triazolyl is located 3737 cm^{-1} above the ground state minimum.

The 1,2,3-triazolyl molecule can be viewed as a substitutional isomer of the cyclopentadienyl radical, which has a Jahn-Teller distorted $^2E_1''$ ground state.^{1,2,23} The degenerate electronic states arise from electronic configurations involving singly occupied molecular π -orbitals.^{1,2,23} The electronic states that result from excitations between the π -orbitals ($\pi \rightarrow \pi$ excitations) will be denoted as $\pi\pi$ electronic states. For the triazolyl radical, it was established²² that the low-lying electronic states do not arise exclusively from excitations between π -type orbitals. Rather, two additional low-lying electronic states arising from excitations out of the nitrogen lone pair orbitals are also observed, and are subsequently denoted $n\pi$ states ($n \rightarrow \pi$ transitions). These states are interspersed within the $\pi\pi$ manifold. Thus, in contrast to the minimum energy conical intersections observed in cyclopentadienyl and other azolyl species investigated to date (i.e., pyrrolyl,^{10,13,24} imidazolyl,⁹ and pyrazolyl^{9,12}), which involve two $\pi\pi$ electronic states, the minimum energy conical intersection in triazolyl involves an $n\pi$ state and a $\pi\pi$ state. Additional seams of accidental two and three state conical intersections were also established at somewhat higher energies.²²

The spectral simulations reported in this work are based on the time-independent multimode vibronic coupling method,^{5,7} which was developed over a quarter century ago by Köppel, Domcke, and Cederbaum,⁷ and is a powerful theoretical tool for simulating the electron photodetachment spectra of nonadiabatically coupled electronic states. Within this formalism, the spectral simulation problem is solved in two steps.²⁵ First, the energies and interactions of N^{state} adiabatic electronic states coupled by conical intersections are

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represented by a symmetric $N^{\text{state}} \times N^{\text{state}}$ quasi-diabatic Hamiltonian, $\mathbf{H}^d$, whose matrix elements are polynomials of varying degree in a set of $N^{\text{int}} = 3N^{\text{at}} - 6$ internal coordinates. The polynomials comprising $\mathbf{H}^d$ are usually restricted to include only first- and second-order terms, resulting in the quadratic vibronic coupling model.²⁶ However, in the 1,2,3-triazolyl radical, the complicated topographical features noted above precluded the construction of a uniformly accurate quadratic $\mathbf{H}^d$. These limitations of the fully quadratic model clearly illustrated the benefits that can be obtained from incorporating higher-order terms in the expansion of $\mathbf{H}^d$, as has been noted by others^{27–29} for highly symmetric molecules exhibiting conical intersections.

Following the construction of an $\mathbf{H}^d$ that confidently represents the *ab initio* data from which it was derived, the second step involves the determination of the spectral intensity distribution function,³⁰ $I(E)$, describing transitions from an anion vibrational state into the complicated vibronic manifold of the neutral species:

$$I(E) = \sum_{\alpha} \rho(\alpha) \sum_K |A_{\alpha,K}|^2 \delta(E - (E_K^T - E_{\alpha}^T)). \quad (1a)$$

Here ρ reflects the relative population of the anion state α , and the amplitude

$$A_{\alpha,K} = \langle \Psi_{\alpha}^{\text{an}}(\mathbf{q}, \bar{\mathbf{w}}) | \mu | \Psi_K^T(\mathbf{q}, \mathbf{w}) \rangle_{\mathbf{q}, \mathbf{w}} \quad (1b)$$

connects the α th anion vibronic level to the K th level of the neutral species. Here, $\mathbf{q}$ denotes the electronic coordinates, and $\mathbf{w}$ are $\bar{\mathbf{w}}$ are sets of $N^{\text{int}} = 3N^{\text{at}} - 6$ internal coordinates for the neutral and the anion, respectively. The evaluation of $A_{\alpha,K}$ will be discussed in Sec. II.

This study has three interrelated goals. First, we consider the impact of the representation of $\mathbf{H}^d$ on the accuracy of the spectral simulation. Second, we will provide a simulation of the photoelectron spectrum of 1,2,3-triazolyl that takes into account anharmonicity and the presence of hot bands. Here, it is important to point out that simulation of the hot bands associated with excited vibrational states of the anion are computed at the same level of accuracy as the ground state spectrum. Finally, in the course of these analyses, we report two new algorithms required to execute these calculations.

The outline of the manuscript is as follows. Section II reviews the procedures used in the simulation in order to highlight the new algorithms reported here. Section III presents a numerical study of the 1,2,3-triazolide/1,2,3-triazolyl system, based on four low-lying electronic states of the triazolyl radical, $(\text{CH}_2)_2\text{N}_3$. The computational task described in Secs. II and III is summarized in Fig. 1. Section IV summarizes and presents directions for future research.

II. THEORETICAL APPROACH

In the following, we summarize our approach for determining the spectral intensity distribution function using an implementation of the time-independent formulation of multimode vibronic coupling method. As stated in the Introduction, this is accomplished in two steps. First, a quasidiabatic Hamiltonian, $\mathbf{H}^d$, is constructed which can accurately repre-

FIG. 1. Diagram of the simulation of the photoelectron experiment. Excitations from the ground and excited vibrational levels of the harmonic ground state potential energy surface of triazolide produced states of triazolyl constructed from four coupled potential energy surfaces and a scattered electron. The simulated spectrum obtained by combining the spectra of the five vibrational levels is pictured. Excitations out of the excited vibrational states of the negative ion are indicated by red dots.

sent the *ab initio* energies $E_I(\mathbf{Q})$, energy gradients $\nabla E_I(\mathbf{Q})$, and derivative couplings $\mathbf{f}^{I,J}(\mathbf{Q})$ for N^{state} adiabatic, bound electronic states over a large region of the internal coordinate space. In the second step, the $\mathbf{H}^d$ is employed to construct the vibronic Hamiltonian matrix, $\mathbf{H}^{\text{vib}}$, whose eigenvalues (E_K^T) and eigenvectors ($\Psi_K^T(\mathbf{q}, \mathbf{w})$) are used to determine the spectral intensity distribution function.

A. Nonadiabatic wave function for residual species

The wave function for the neutral species produced by electron photodetachment must be capable of describing N^{state} electronic states coupled strongly by conical intersections. This is accomplished by expanding the total wavefunction (Ψ_K^T) as a sum of products of quasidiabatic electronic states, (Ψ_I^d), and a vibrational function, (ζ_I^K), as follows:

$$\Psi_K^T(\mathbf{q}, \mathbf{w}) = \sum_{I=1}^{N^{\text{state}}} \Psi_I^d(\mathbf{q}; \mathbf{w}) \zeta_I^K(\mathbf{w}). \quad (2a)$$

The $\zeta_I^K(\mathbf{w})$ are in turn expanded in the multimode vibrational basis,

$$\zeta_I^K(\mathbf{w}) = \sum_{\mathbf{m}} d_{\mathbf{m}}^{I,K} \xi_{\mathbf{m}}(\mathbf{w}), \quad (2b)$$

where the $\xi_{\mathbf{m}}(\mathbf{w})$ are expressed as multimode products,

$$\xi_{\mathbf{m}}(\mathbf{w}) = \prod_{j=1}^{N^{\text{int}}} \chi_{m_j}^{(n),j}(w_j) \quad (2c)$$

with

$$0 \leq m_j < M_j. \quad (2d)$$

In these equations, $\mathbf{w}$ is a linear transformation of a basic set of internal coordinates, $\mathbf{Q}$, $\mathbf{w} = \mathbf{T}(\mathbf{Q} - \mathbf{Q}^0)$. In this

study, the underlying coordinate basis corresponds to the natural internal coordinates,³¹ with the choice of origin, $\mathbf{Q}^0$, for these coordinates to be discussed below. The $\mathbf{w}$ are a set of internal coordinates, or modes, chosen to describe the neutral molecule, and $\chi_m^{(n),j}$ is the m th harmonic oscillator function associated with the j th mode. This set of coordinates, $\mathbf{w}$, and vibrational functions, $\chi_m^{(n),j}$, will be referred to below as the *neutral biased basis*. From Eqs. (2a)–(2d), the size of this vibronic basis is seen to be $N^T = N^{\text{state}}N^{\text{vib}}$, where $N^{\text{vib}} = \prod_{j=1}^{N^{\text{int}}} M_j$.

B. Form of $\mathbf{H}^d$ and $\mathbf{H}^{\text{vib}}$

The Ψ_j^d , the quasi-diabatic electronic states, are specified by their matrix elements of the electronic (coulomb) Hamiltonian, $H^0(\mathbf{q}; \mathbf{Q})$, which are

$$H_{\alpha,\beta}^d = \langle \Psi_\alpha^d(\mathbf{q}; \mathbf{Q}) | H^0(\mathbf{q}; \mathbf{Q}) | \Psi_\beta^d(\mathbf{q}; \mathbf{Q}) \rangle_q, \quad (3a)$$

where

$$H_{\alpha,\beta}^d(\mathbf{Q}) = E_\alpha(\mathbf{Q}^0) + \sum_{k=1}^{N^{\text{int}}} V_k^{(1),\alpha,\beta} \bar{Q}_k + \frac{1}{2!} \sum_{k,l=1}^{N^{\text{int}}} V_{k,l}^{(2),\alpha,\beta} \bar{Q}_k \bar{Q}_l + \frac{1}{3!} \sum_{k,l,m=1}^{N^{\text{int}}} V_{k,l,m}^{(3),\alpha,\beta} \bar{Q}_k \bar{Q}_l \bar{Q}_m + \dots \quad (3b)$$

and $\mathbf{Q} = \mathbf{Q}^0 + \bar{\mathbf{Q}}$. Note that $\mathbf{H}^d$ is a symmetric $N^{\text{state}} \times N^{\text{state}}$ matrix whose elements are arbitrary order polynomials in the internal coordinates, centered at $\mathbf{Q}^0$. The determination of $\mathbf{H}^d$ has been discussed previously.^{22,26}

The $d_m^{I,K}$ in Eq. (2b) satisfy

$$(\mathbf{H}^{\text{vib}} - \mathbf{I}E_K^T)\mathbf{d}^K = \mathbf{0}, \quad (4)$$

where $\mathbf{H}^{\text{vib}}$ is the matrix representation of $H^T = T^{\text{nuc}} + H^0$ in the vibronic basis $\Psi_I^d(\mathbf{q}; \mathbf{w})\xi_{\mathbf{m}}(\mathbf{w})$, $I = 1-N^{\text{state}}$, $\mathbf{m} = \mathbf{0} - (\mathbf{M} - \mathbf{1})$, and T^{nuc} is the nuclear kinetic energy operator. Note that although $\mathbf{H}^d$ is constructed in the $\mathbf{Q}$ basis, it must be transformed to the $\mathbf{w}$ basis for use in Eq. (4) as discussed in Ref. 6. For the systems studied to date, this has not been a serious problem for $\mathbf{V}^{(1)}$ and $\mathbf{V}^{(2)}$, but this transformation can lead to computational issues as the number of nonvanishing $\mathbf{V}^{(n)}$ for $n > 2$ can become large. This point is discussed further in Sec. III.

C. Determination of E_K^T and Ψ_K^T using a Lanczos procedure

From the definition of N^{vib} , it is observed that the dimension of $\mathbf{H}^{\text{vib}}$ can become extremely large for molecules with more than a trivial number of vibrational modes, or, as the number of functions per mode increases. Thus, in practice, this matrix is not explicitly constructed. Fortunately, $\mathbf{H}^{\text{vib}}$ has three key properties that allow for its efficient implicit computation:⁵ it is highly sparse, the nonzero matrix elements are easily identified, and the matrix elements themselves are trivial to compute. The first two properties together are referred to as the structured sparsity of $\mathbf{H}^{\text{vib}}$. Exploiting these properties, we have previously developed

an open-ended, fine-grained parallel, iterative Lanczos diagonalization routine that recursively constructs a tri-diagonal matrix whose eigenspectrum approximates that of $\mathbf{H}^{\text{vib}}$, for $\mathbf{H}^d$ through quadratic terms.³⁰ Here, we report an extension of this procedure to arbitrary order $\mathbf{H}^d$. The distributed nature of the fine-grained procedure increases the N^T which is tractable and reduces the time to solution. This is essential since, although the number of nonzero terms in $\mathbf{H}^{\text{vib}}$ grows only linearly with N^T , the prefactor increases as one includes higher-order terms. A benefit of the Lanczos procedure is that it eliminates the need to retain the eigenvectors of $\mathbf{H}^{\text{vib}}$ when determining the spectral intensities. The implementation is discussed further in Appendix A.

D. Determination of the spectral amplitudes

Unlike the neutral molecule, the wave function for the negative ion is assumed to be well described in terms of the harmonic vibrational potential expanded about a minimum on an uncoupled adiabatic electronic state. The wavefunction for the anion, in its ground electronic state ($\Psi_0^{T,\text{an}}(\mathbf{q}; \bar{\mathbf{w}})$), has the following form:

$$\Psi_\alpha^{T,\text{an}}(\mathbf{q}, \bar{\mathbf{w}}) = \Psi_0^{a(\text{an})}(\mathbf{q}; \bar{\mathbf{w}}) \zeta_a^{(\text{an})}(\bar{\mathbf{w}}), \quad (5a)$$

where $\bar{\mathbf{w}} = \bar{\mathbf{T}}(\mathbf{Q} - \mathbf{Q}^{0,(\text{an})})$,

$$\zeta_a^{(\text{an})}(\bar{\mathbf{w}}) = \prod_{j=1}^{N^{\text{int}}} \chi_{a_j}^{(\text{an}),j}(\bar{w}_j), \quad (5b)$$

$\zeta_a^{(\text{an})}(\bar{\mathbf{w}})$ is the vibrational wavefunction for the anion in its ground electronic state and $\chi_m^{(\text{an}),j}$ is the m th harmonic oscillator function associated with the j th mode of the anion. Here, $\mathbf{Q}^{0,(\text{an})}$ is the ground state equilibrium geometry of the anion and the $\bar{\mathbf{w}}$ are its normal coordinates, with the ground vibrational state denoted $\mathbf{a} = (0, 0, \dots, 0) = \mathbf{0}$. This combination of $\bar{\mathbf{w}}$ and $\chi_m^{(\text{an}),j}$ will be referred to as the *anion biased basis*. We call attention to the fact that the neutral coordinates ($\mathbf{w}$) and anion coordinates ($\bar{\mathbf{w}}$) need not be the same.

The quantity of interest in this study is $I(E)$, the spectral intensity distribution function, given in Eq. (1a). Inserting Eqs. (2a) and (5a) into Eq. (1b) gives

$$A_{\alpha,K} = \sum_{I=1}^{N^{\text{state}}} \langle \zeta_a^{(\text{an}),0}(\bar{\mathbf{w}}) | \mu^{0,I}(\mathbf{w}) | \zeta_I^K(\mathbf{w}) \rangle_{\mathbf{w}}, \quad (6a)$$

where $\mu^{0,I}(\mathbf{w})$ is the electronic transition moment operator connecting the ground electronic state of the anion to the I th diabatic state of the neutral. Neglecting, as is routinely the case, the coordinate dependence of $\mu^{0,I}(\mathbf{w})$, and using Eqs. (2b), (2c), and (5b), Eq. (6a) becomes

$$A_{\alpha,K} = \sum_{I,\mathbf{m}} \mu^{0,I} s_{\mathbf{a},\mathbf{m}} d_{I,\mathbf{m}}^K, \quad (6b)$$

where

$$s_{\mathbf{a},\mathbf{m}} = \left\langle \prod_{j=1}^{N^{\text{int}}} \chi_{a_j}^{(\text{an}),j}(\bar{w}_j) \middle| \prod_{j=1}^{N^{\text{int}}} \chi_{m_j}^{(n),j}(w_j) \right\rangle. \quad (7)$$

The dot product in Eq. (6b) can be easily obtained from the Lanczos diagonalization provided the N^T dimensional vector, $\mu^{0,I} s_{\mathbf{a},\mathbf{m}}$ (indexed by I and $\mathbf{m}$), is used to start the Lanczos algorithm. The evaluation of $s_{\mathbf{a},\mathbf{m}}$ is simplified greatly if the choice $\chi_m^{(n),j} = \chi_m^{(an),j}$ is made, in which case $s_{\mathbf{a},\mathbf{m}} = \delta_{\mathbf{a},\mathbf{m}}$. However, this may be a false economy if this choice of basis requires a concomitant increase in the number of basis functions needed to obtain a converged spectral simulation. Instead, the $\chi_m^{(n),j}$ are chosen to be a neutral biased basis and the large number of the multidimensional Franck-Condon overlap integrals [Eq. (7)] are evaluated using recursion relations derived from standard generating function techniques.^{32–37} We have previously discussed³⁸ the evaluation of $s_{\mathbf{a},\mathbf{n}}$ for $\mathbf{a} = \mathbf{0}$. In Appendix B, we provide a derivation of the analytic expressions for the recursion relations and discuss their implementation for the hot band case $a_j = 1$, $a_k = 0$, $k \neq j$, required here.

Note that $s_{\mathbf{a},\mathbf{m}}$ satisfy

$$D_{\mathbf{a}}(M_1, \dots, M_{N^{\text{int}}}) = \sum_{\mathbf{m}=\mathbf{0}}^{\mathbf{M}-1} |s_{\mathbf{a},\mathbf{m}}|^2 \leq 1, \quad (8)$$

where the equality indicates that the anion vibronic state is fully described by the neutral biased basis. The condition $D_{\mathbf{a}}(M_1, \dots, M_{N^{\text{int}}}) = 1$, which as we show in Sec. IV is satisfied to a good approximation, is a necessary, but not sufficient, condition for the utility of the neutral biased basis.

III. APPLICATION: 1,2,3-TRIAZOLIDE/1,2,3-TRIAZOLYL SYSTEM

As noted in the Introduction, the triazolyl radicals fall into the class of molecules known as azolyis ($N_x(\text{CH})_y$), where $x + y = 5$, which can be thought of as substitutional derivatives of the cyclopentadienyl radical, $(\text{CH})_5$. The cyclopentadienyl radical exhibits a Jahn-Teller distorted ${}^2E_1''$ ground state that originates from incompletely filled degenerate π orbitals. The molecular point group symmetry is reduced from D_{5h} to C_{2v} upon the substitution of CH groups with nitrogen atoms, thus removing the *degeneracy required* nature of the seam of conical intersection. Previous investigations indicate that the pyrrolyl^{10,13,14,24} and pyrazolyl^{9,12} radicals exhibit low-lying conically intersecting $\pi\pi$ electronic states of symmetries 2A_2 and 2B_1 , which correlate to the components of the degenerate ${}^2E_1''$ state found in the cyclopentadienyl radical. However, the increased number of adjacent lone-pair orbitals present in the triazolyl radical produces a substantial departure from this archetype. Excitations from these lone pair orbitals give rise to two additional intertwined low-lying $n\pi$ electronic states with 2A_1 and 2B_2 symmetry. The symmetry of the four lowest electronic states in order of increasing energy are: ${}^2B_1 < {}^2A_1 < {}^2A_2 < {}^2B_2$. The intercalation of the $n\pi$ and $\pi\pi$ electronic states in the triazolyl radical indicates that comparisons to the cyclopentadienyl radical will not be particularly useful in understanding the excited-state electronic structure of this species.

Thus, it is apparent that the electronic structure of triazolyl is considerably more intricate than its azolyl antecedents. For the pyrrolyl radical,^{10,13,14,24} it was found that two-state $\mathbf{H}^d$ were adequate to accurately simulate the photoelectron spectrum. In the case of the pyrazolyl radical,^{9,12} the inclusion of interactions with a third electronic state resulting from a nitrogen lone pair excitation was essential and three-state $\mathbf{H}^d$ were used. Regardless of the number of states involved in the constructions, a quadratic $\mathbf{H}^d$ sufficiently described the relevant topographies and the resulting spectral simulations were quantitatively comparable to the experimental results. The myriad of complications present in the low-lying electronic topography of the triazolyl radical prohibited the construction of an accurate quadratic $\mathbf{H}^d$ and was the impetus for generating $\mathbf{H}^d$ including higher-order polynomials. The quartic $\mathbf{H}^d$, reported in a previous work, Ref. 22, denoted *DYS1* below, employs only a small subset of full cubic and quartic terms. Yet it exhibits a remarkable capacity to reproduce the *ab initio* data over large regions of the nuclear coordinate space, providing a uniformly accurate representation of the *ab initio* data in the regions of three isolated critical points: the ground state minimum, the minimum energy conical intersection, and a saddle point on the ground state potential energy surface. This faithful representation of the four lowest states in triazolyl could not be obtained using the more standard fully quadratic representation. Here, we quantify the improvements achieved in the spectral simulations.

A. Electronic structure treatment

The electronic structure description used in this study was presented previously in *DYS1*, and will only be summarized. While it is convenient to employ C_{2v} symmetry labels to discuss the electronic structure of triazolyl, all *ab initio* calculations were performed in the C_1 symmetry. The molecular orbitals were determined employing a polarized double zeta quality basis set in conjunction with a 4 state-averaged multiconfiguration self consistent field procedure using an 11 electron, 8 orbital complete active space. The active space includes the five π orbitals (three b_1 , two a_2) and three lone pair nitrogen orbitals (two a_1 , one b_2). Electron correlation was treated at the multireference single and double excitation configuration interaction (MR-CISD) level of theory. With the nitrogen and carbon 1s orbitals kept doubly occupied in the core, the resulting MR-CISD expansion is comprised of $\sim 2 \times 10^8$ configuration state functions (CSFs).

The anion calculations are completely independent of those for the neutral since $\mu^{0,I}$ is not computed. Two basis sets were used to construct the wave function for the negative ion. The aTZP (aDZP) bases included Dunning's aug-cc-pVTZ (aug-cc-pVDZ) (Refs. 39 and 40) bases on the carbons and nitrogens and a DZP basis on the hydrogens.⁴¹ The molecular orbitals were determined from a single configuration wave function. The CISD expansion consisted of $\sim 4 \times 10^6$ (7×10^5) CSFs. All electronic structure calculations reported in this work employed the COLUMBUS suite of electronic structure codes.^{42,43}

TABLE I. Geometric parameters of pertinent *ab initio* determined C_{2v} symmetry minima. Distances in Å, angles in degrees. The atom labeling used below and in the text is as follows: N_1 lies on the C_2 axis, while the (N_2 , N_3), (C_1 , C_2), and (H_1 , H_2) are symmetry equivalent pairs.

	min^2B_1	$min^1A_1(dz)$	$min^1A_1(tz)$	$\ \Delta(^1A_1 - ^2B_1)\ $
				$min^1A_1(dz)[min^1A_1(tz)]$
$r(N_1-N_2)$	1.3770	1.3307	1.3163	0.0463 [0.0603]
$r(N_2-C_1)$	1.3102	1.3490	1.3383	0.0388 [0.0281]
$r(C_1-C_2)$	1.4737	1.3889	1.3759	0.0848 [0.0988]
$r(C_1-H_1)$	1.0756	1.0767	1.0748	0.0011 [0.0008]
$\angle N_2N_1N_3$	111.3	111.2	111.2	0.1 [0.1]
$\angle N_1N_2C_1$	106.6	107.0	107.1	0.1 [0.1]
$\angle H_1C_1N_2$	123.1	122.0	122.0	1.1 [1.1]

B. Surface extrema

Here, we present a brief synopsis of the main electronic structure results previously reported in *DYS1* and germane to the present discussion. In the radical species, three key extrema with C_{2v} symmetry were identified: a minimum (evinced in Table I), min^2B_1 , a saddle point, ts^2A_1 on the ground state potential energy surface, and the minimum energy $^2B_1-^2A_1$ conical intersection, denoted $mex^2B_1-^2A_1$. As for the anion, the C_{2v} symmetry ground state minimum is denoted min^1A_1 and was determined using the aTZP and aDZP bases. The resultant geometries, labeled $min^1A_1(tz)$ and $min^1A_1(dz)$ respectively, are presented in Table I. The adiabatic energy at min^2B_1 (ts^2A_1) on the ground state potential energy surface relative to the $mex^2B_1-^2A_1$ energy is -3737 (-415) cm^{-1} . The curvature at all critical points was established by constructing *ab initio* Hessian matrices. The harmonic frequencies for min^2B_1 , $min^1A_1(tz)$, and $min^1A_1(dz)$ are reported in Table II. Here, the frequencies are ordered by the irreducible representation corresponding to (n_{a1} , n_{a2} , n_{b1} , n_{b2}) = (6, 2, 2, 5). The two lowest harmonic frequencies of the neutral, possessing b_1 and b_2 symmetry, correspond to

TABLE II. *Ab initio* determined harmonic frequencies (in cm^{-1}) at min^2B_1 and min^1A_1 and the vibronic basis employed in spectral simulations.

		min^2B_1	$min^1A_1(dz)$	$min^1A_1(tz)$	M_i^a
a_1	$\omega_1(a_1)$	3408.9	3372.6	3323.2	1
	$\omega_2(a_1)$	1558.0	1550.4	1544.3	4
	$\omega_3(a_1)$	1344.6	1321.4	1310.3	3
	$\omega_4(a_1)$	1099.7	1255.9	1265.2	4
	$\omega_5(a_1)$	1052.0	1147.9	1148.3	4
	$\omega_6(a_1)$	933.6	1007.6	1015.3	5
a_2	$\omega_7(a_2)$	859.3	756.7	885.5	3(4)
	$\omega_8(a_2)$	576.5	681.2	716.6	5(5)
b_1	$\omega_9(b_1)$	785.5	796.1	828.9	5(7)
	$\omega_{10}(b_1)$	204.2	764.9	786.0	7(10)
b_2	$\omega_{11}(b_2)$	3394.4	3345.0	3296.7	1
	$\omega_{12}(b_2)$	1553.3	1513.5	1507.2	3
	$\omega_{13}(b_2)$	1217.9	1263.6	1241.1	3
	$\omega_{14}(b_2)$	992.3	1165.5	1161.1	5
	$\omega_{15}(b_2)$	304.1	1001.0	1013.1	7

^a M_i denotes the number of harmonic oscillator functions for a given mode required to obtain a converged spectral simulation. The numbers in parenthesis indicate the M_i necessary to obtain a converged spectrum for the corresponding hot band.

motions that are expected to be highly anharmonic, and differ significantly from the corresponding modes of the negative ion. Furthermore, focusing on $r(N_1-N_2)$, $r(N_2-C_1)$, and $r(C_1-C_2)$ bond distances, it is seen in Table I that min^2B_1 differs significantly from $min^1A_1(tz)$ ($min^1A_1(dz)$), with the largest deviation seen to be 0.100 (0.080) Å for $r(C_1-C_2)$. On the other hand, it is also seen that the angles $\angle N_1N_2C_1$, $\angle H_1C_1N_2$, and $\angle N_2N_1N_3$ show little change, differing by no more than about a degree for min^2B_1 and $min^1A_1(x)$, $x = dz, tz$.

C. The photodetachment spectrum of the triazolidine anion

In this section, simulations of the photodetachment spectrum of the 1,2,3-triazolidine anion are reported, analyzed, and compared to the experimental spectrum of Lineberger and co-workers²¹ (subsequently denoted L1), which is shown in Fig. 2(a). We have labeled the peaks of the major vibronic transitions A-K.

1. Experimental spectrum

While the predominant spectral feature in the experimental spectrum is an intense peak at 3.447 eV, multiple intense peaks at lower binding energies between 3.55 and 3.70 eV are also observed. There is an abrupt cutoff in the spectrum at an

FIG. 2. Plate (a) Experimental photoelectron spectrum from L1. Plate (b) Simulation of triazolidine photoelectron spectrum based on the quartic H^d employing the $min^1A_1(tz)$ description of the anion. Contributions originating from five vibrational levels of the anion are included as red $a = 0$, purple $a_7 = 1$, green $a_8 = 1$, blue $a_9 = 1$, and yellow $a_{10} = 1$.

electron binding energy of 3.7 eV resulting from the ionizing photon energy. As a result, the observable spectral window is less than 2100 cm^{-1} . *L1* were unable to make any assignments other than to note that the peak labeled A was the vibrational origin of the ground electronic state. *L1* also observed that each peak exhibited an anisotropy parameter within the range of -0.2 to -0.6 . Since the calculated adiabatic energy separations of the ts^2A_1 and the $mex^2B_{1-2}A_1$, relative to min^2B_1 , are 3322 cm^{-1} and 3737 cm^{-1} , respectively, one might speculate that a single uncoupled potential energy surface would be adequate to characterize the neutral vibronic energy levels evinced in the experimental spectrum. However, as originally observed in *L1*, this is emphatically not the case.

2. Simulations: General considerations

In each of the photodetachment simulations that follow, a representation of the neutral and anion wave functions, shown in Eqs. (2a) and (5a), respectively, is required to determine $I(E)$. The normal mode basis $\chi_m^{(n),j}$, the neutral biased basis, is determined at min^2B_1 with the corresponding harmonic frequencies presented in Table II. This basis, tailored to describe the neutral species, must also be capable of describing the ground and low-lying vibrational states of the anionic species, $\chi_m^{(an),j}$, which are based on *ab initio* wavefunctions. The hot band simulations will consider excitations out of the four lowest vibrational states of the anion, which in the harmonic approximation correspond to $\omega_7(a_2) = 885\text{ cm}^{-1}$, $\omega_8(a_2) = 716\text{ cm}^{-1}$, $\omega_9(b_1) = 829\text{ cm}^{-1}$, and $\omega_{10}(b_1) = 786\text{ cm}^{-1}$. See Table II. Here, the irreducible representation carried by the mode is given in parenthesis. The populations of these levels, denoted $\rho(\alpha)$ in Eq. (1a) and shown in Table III, will be estimated assuming a thermally equilibrated (at 400 K) molecular beam so that $\rho(\alpha_i)/\rho(0) = \exp(-\omega_i/kT)$, where k is Boltzman's Constant, T is the temperature, and ω_i corresponds to the harmonic frequency for mode i . This choice of temperature provides for the reasonable reproduction of the spectrum of *L1* and is consistent with the experimental conditions.⁴⁴ Also reported in Table III are the intensity overlap factors, which correspond to the scale factor used to normalize the intensities of the individual hot band spectra. Thus, the total composite spectrum is obtained as a summation of both the ground state and the hot band spectra with each computed intensity scaled by the product of a Boltzman and an intensity scale factor.

The number of vibronic basis functions used to expand the total wave function (Ψ_K^T) in all of the simulations is de-

tailed in Table II. These bases were sufficient to converge the spectral envelopes of all the simulations presented below. For the hot band simulations, additional basis functions (see Table II) were employed to describe the mode in closest correspondence to the excited anionic vibrational state in order to ensure that the overlap $D_a(\mathbf{M})$ of the neutral biased basis with the anion vibrational state was greater than 0.99. The $D_a(\mathbf{M})$ values for each of the simulations can be found in Table III, demonstrating that the neutral biased basis capably describes the pertinent vibronic states of the anion. The residual contribution to D_a , ~ 0.01 , is likely due to the fact that $M_j = 1$ for each of the C-H stretch modes, essentially excluding them from analysis. This approximation is valid since the expected energy range of these transitions is beyond the experimental spectral window and the degree of coupling to other modes is small.

The band origin is set to 3.447 eV, the experimentally determined²¹ electron binding energy of 1,2,3-triazolide. The stick spectra from the time-independent calculations are convoluted with a Gaussian of width 10 meV ($\sim 80\text{ cm}^{-1}$) to simulate the instrumental resolution available in the experimental determination of the spectrum. For all the simulations the transition moments $\mu^{0,j}$ ($j = 1-4$) are assumed to be equal and geometry independent.

3. The adiabatic simulation

To more clearly quantify the effects of the nonadiabatic interactions on the photoelectron spectrum, a vibronic spectrum is computed in which the electronic states are uncoupled. In this adiabatic/Franck-Condon simulation, the spectrum is a superposition of the spectra for the individual adiabatic states. The line positions are given by linear combinations of the frequencies of the neutral, provided in Table II, and the intensities are determined by the Franck-Condon overlaps with the anion wavefunctions. Since the lowest energy point on the 2A_1 surface is found at 3322 cm^{-1} and is a first-order saddle point, transitions to these vibronic energy levels would not be observed in the experimental energy window and thus are not considered.

The adiabatic simulations computed using the $min^1A_1(dz)$ and $min^1A_1(tz)$ descriptions of the anion, determined without the inclusion of hot band transitions, are shown in Figs. 3(a) and 4(a), respectively. It is clear that these simulations do not reproduce the experimental spectrum very well. It is found that although the band origin for the $min^1A_1(tz)$ determined adiabatic simulation is the most intense transition (i.e., largest overlap), the most intense convoluted peak, which arises due to the small separation between two relatively intense vibronic transitions, is predicted to be observed at 3.6 eV, lying roughly 1200 cm^{-1} above the band origin. This is not the case for the $min^1A_1(dz)$ determined adiabatic simulation, which correctly has the band origin as the largest peak. However, the ability for these simulations to reproduce the intensity patterns of the observed spectrum at higher energies is unsatisfactory. Equally important in evincing the inadequacy of the adiabatic representation are the significant changes observed in the

TABLE III. $D_a(\mathbf{M})$ and contributions to the relative intensity factors for each of the spectral simulations.

	D_a	Intensity overlap factor	Boltzman factor (400 K)
GS	0.992	0.205	1.00
1 $\chi_1^{(an),8}(a_2)$	0.992	0.196	0.08
2 $\chi_1^{(an),10}(b_1)$	0.990	0.179	0.06
3 $\chi_1^{(an),9}(b_1)$	0.992	0.178	0.05
4 $\chi_1^{(an),7}(a_2)$	0.992	0.178	0.04

FIG. 3. Adiabatic, Franck-Condon (plate **a**), quadratic $\mathbf{H}^d$ (plate **b**), and quartic $\mathbf{H}^d$ (plate **c**) simulation of the triazolid photoelectron spectrum employing the $\min^1 A_1(dz)$ description of the anion.

simulated spectrum when nonadiabatic effects are included, as described below.

At this point, it is prudent to discuss the differences in the simulations stemming from the electronic structure treatment of the anion. When comparing the two adiabatic simulations in Figs. 3(a) and 4(a), it is apparent that although qualitatively similar (the spectral lines are found in exactly the same positions), there is a significant variation in the transition intensities due solely to the description of the anion. In addition, this variation is not uniform from one transition to another, a point which will be discussed further below. While the $\min^1 A_1(tz)$ based results, which correspond to a more rigorous computation of the anionic ground state are preferred *a priori*, the $\min^1 A_1(dz)$ results are included for comparison.

FIG. 4. Adiabatic, Franck-Condon (plate **a**), quadratic $\mathbf{H}^d$ (plate **b**), and quartic $\mathbf{H}^d$ (plate **c**) simulation of the triazolid photoelectron spectrum employing the $\min^1 A_1(tz)$ description of the anion.

4. Quadratic quasidiabatic Hamiltonian simulation

The quadratic $\mathbf{H}^d$ simulations based on the $\min^1 A_1(dz)$ and $\min^1 A_1(tz)$ descriptions of the anion are reported in Figs. 3(b) and 4(b), respectively. The $\mathbf{H}^d$ employed here differs slightly from that of *DYS1* in that *ab initio* data at two geometries, [displaced 0.1 a.u. along intersection adapted coordinates 10 and 15, respectively, as defined in *DYS1*], were added to the data set used in *DYS1* so that the $\mathbf{H}^d$ determined critical points exhibit the proper curvature. The simulations in Figs. 3(b) and 4(b) successfully predict that the band origin will have the largest intensity. Although this is a noted improvement over the adiabatic spectra, the reproduction of the energies and intensities of all subsequent vibronic transitions is rather poor. Both quadratic simulations predict a small

peak at about 3.525 eV and a triplet of high intensity peaks for the electron binding energy in the range 3.550–3.600 eV. At energies above 3.600 eV, the vibronic energy level density increases significantly, yielding intensity patterns that poorly reproduce the experimental spectrum.

The nonuniform intensity variation that was evident in the adiabatic simulations is again apparent when comparing the two quadratic simulations. Thus, as in the adiabatic case, the description of the anion wave function has an impact on the predicted intensity pattern.

5. Quartic quasidiabatic Hamiltonian simulation

The quartic $\mathbf{H}^d$ simulations based on $\min^1 A_1(\text{dz})$ and $\min^1 A_1(\text{tz})$ descriptions of the anion are reported in Figs. 3(c) and 4(c), respectively. These results are in reasonable agreement with the experimental spectrum, affording the opportunity to make assignments of the high intensity transitions. It is evident that the quartic $\mathbf{H}^d$ provides a significantly more accurate reproduction of the experimental results than either the adiabatic or quadratic $\mathbf{H}^d$ based simulations. As with the quadratic $\mathbf{H}^d$, both quartic $\mathbf{H}^d$ based simulations successfully predict that the band origin is the highest intensity peak. However, the reproduction of the intensities of all subsequent vibronic transitions, labeled b - k , depends somewhat on the anion representation. The $\min^1 A_1(\text{dz})$ simulation reliably reproduces the relative intensities of most of the b - k peaks but the overall intensity is uniformly underestimated. In each simulation the relative intensities of the b , c , d triplet are well-approximated; the intensity of peaks f and g are less satisfactory; and the h - k intensities resemble the experimental results. Both of the quartic simulations predict a small peak at about 3.525 eV, peak b discussed below. Peaks c and d occurring between 3.550–3.600 eV are comprised of three intense vibronic transitions. The quartic $\mathbf{H}^d$ predicted energies for these peaks b – d are in excellent agreement with the experimental results (see Table IV). The spectral simulation does an adequate job at reproducing the peaks e - k at higher energies, ranging from 3.60–3.70 eV. However, the simulated spectra extend to higher electron binding energies (eBE) than that found in the measured spectra.

A comparison of the two quartic simulations evinces the nonuniform intensity variations that were observed in the adiabatic and quadratic simulations. In fact, particular vibronic transitions differ in intensity by up to a factor of 2, with the $\min^1 A_1(\text{tz})$ results preferred. Finally, it is essential to emphasize the evolution of the simulated spectra as the quality of the representation of the coupled potential energy surfaces improves from adiabatic, to quadratic $\mathbf{H}^d$, to quartic $\mathbf{H}^d$ and is dramatically evinced by comparing the spectra in Figs. 3(a)–3(c), or Figs. 4(a)–4(c).

6. Analysis of the spectra: Assignments

The spectra are further analyzed by examining the explicit eigenvalues and eigenvectors obtained from the quartic $\mathbf{H}^d$ simulations. These quantities are compared with the rele-

FIG. 5. Pertinent normal modes vibrations of triazolyI.

vant adiabatic results in order to assess the magnitude of the nonadiabatic interactions. The eigenvectors associated with the adiabatic simulations are the multimode basis functions (products of harmonic oscillator wave functions), while the eigenvalues are the sums of the corresponding harmonic oscillator energies. These levels are denoted $[x \text{ cm}^{-1} n \omega_m[s]]$, where x is the energy in cm^{-1} of a state relative to the band origin followed by n which is the number of vibrational quanta in the m th mode. The vibrational wave function, $\chi_n^{(n),m}$, carries irreducible representation s . The more pertinent vibrational modes are pictured in Fig. 5. For this wave function analysis, it was computationally convenient to employ a smaller vibronic basis ($N^{\text{vib}} \sim 2 \times 10^7$) to determine the vibronic eigenvectors. The truncated vibronic basis used in the simulation as well as the simulation itself are found respectively in Table SI and Fig. (S1) of the supplemental data.⁴⁵ Comparing the spectra in Figs. (S1) and 4(c) demonstrates that the spectral envelope of the truncated simulation is nearly identical to that of the converged result. This provides sufficient encouragement that the analysis using the smaller basis results will be equally applicable to the final converged spectrum.

For the quartic $\mathbf{H}^d$ simulation, the analysis of the vibronic eigenvectors is complicated by the fact that although the modes (basis functions) are the same as in the adiabatic case, they now refer to diabatic electronic states, which are, to some extent, always coupled. The morphing of the spectral profile in the $\mathbf{H}^d$ based simulations, that is, changes in the intensities and energies of the vibronic transitions relative to the adiabatic representation, is the unambiguous manifestation of nonadiabatic interactions.

To facilitate the following discussion, presented in Table IV, are the energies and the principal contribution, $(d_{k_m}^{I,K})^2$ to the K th eigenvector of the low-energy vibronic transitions. The indices I, k, m in $(d_{k_m}^{I,K})^2$ refer to $I \chi_k^{(n),m}(s)$, where I denotes the I th diabatic and k_m denotes the harmonic oscillator function with k quanta in the m th mode of the neutral. s denotes the irreducible representation carried by the vibronic product. The ground vibrational state is indicated by $m = k = 0$.

As can be seen in Table IV, the vibronic transition labeled peak a in Fig. 4(c), the vibrational band origin, is

TABLE IV. Peak positions from the experimental ($L1$) spectrum along with the assignments for the low energy vibronic transitions resulting from the quartic- $\mathbf{H}^d$ simulation. Energies given in cm^{-1} . N/A indicates that these attributes were not determined. The fifth and sixth column headings are defined as follows: $(d_{lm}^{1,I})$ is the coefficient of $\Psi_1^d \chi_l^{(n),m}$ and $\Sigma_{ld}^I = \sum_{\mathbf{m}} (d_{lm}^{1,I})^2$, where Ψ_1^d is the lower diabat, $I = {}^2B_1$, and in $d_{lm}^{1,I}$ only the single $l_m > 0$ is indicated.

Experimental designation	E (exp)	$\mathbf{H}^d$ Assignment	E ($\mathbf{H}^d$)	Σ_{ld}^I	Largest $(d_{lm}^{1,I})^2$; (l, m)
A	0	a	0	0.90	0.83;(0,0)
B	685	b'	500	0.83	0.62;(1,15)
		b''	621	0.75	0.52;(2,10)
C	854	c	848	0.86	0.63;(1,6)
D	1000	d'	1026	0.89	0.68;(1,5)
		d''	1110	0.88	0.66;(1,4)
E	1266	e	1314	0.84	0.33;(1,3)
F	1492	f	1557	0.86	0.37;(1,2)
G	1560	g	1718	N/A	N/A
H	1702	h	1920	N/A	N/A
I	1871	i	2121	N/A	N/A
J	1943	j	2242	N/A	N/A
K	2000	k	2282	N/A	N/A

comprised predominantly of ${}^2B_1\chi_0^{(n),0}(b_1)$. The fact that it is not entirely ${}^2B_1\chi_0^{(n),0}(b_1)$ is a consequence of the diabatic state coupling. The peak labeled b occurring at ~ 3.500 – 3.525 eV (~ 500 – 621 cm^{-1}) results from two weak transitions, subsequently denoted b' and b'' . The b' eigenstate is found to carry the a_2 vibronic irreducible representation. Thus, given the vibronic symmetry of this level, its intensity arises solely from intensity borrowing engendered by nonadiabatic interactions. The wave function for the b'' level carries the b_1 vibronic irreducible representation. Energetically, the principal contributor to this peak, ${}^2B_1\chi_2^{(n),10}(b_1)$, is significantly shifted from its nominal adiabatic energy precursor, $[408$ cm^{-1} , $2\omega_{10}[a_1]$]. Although these peaks have low intensity, it is seen that nonadiabatic interactions are demonstrable.

The intense peak labeled c in Fig. 4(c) occurs at somewhat higher eBE, ~ 3.550 eV (848 cm^{-1}) [933 cm^{-1} $\omega_6[a_1]$], with the suggested adiabatic assignment included in the square brackets. From Table IV it is seen that the largest contributor to peak c arises from ${}^2B_1\chi_1^{(n),6}(b_1)$. It is found that no other basis function contributes more than 6% (${}^2B_1\chi_1^{(n),5}(b_1)$) to the wave function. The energy shift for this transition relative to the adiabatic transition is 86 cm^{-1} . Interestingly, the intensity of this transition is largely unaffected by nonadiabatic interactions.

Table IV describes the eigenfunctions of the intense peaks labeled d in Fig. 4(c) occurring at electron binding energies, $d \sim 3.575$ – 3.580 eV, (~ 1026 – 1111 cm^{-1}) [1052 cm^{-1} $\omega_5[a_1]$] and [1100 cm^{-1} $\omega_4[a_1]$], with the suggested adiabatic assignments again included in the square brackets. Two vibronic transitions contribute to the peak labeled d , subsequently denoted d' and d'' . For d' , Table IV shows that the basis function ${}^2B_1\chi_1^{(n),5}(b_1)$ makes the dominant contribution to the eigenvector. For the d'' transition, the basis function with the dominant contribution to the vibronic eigenvector is ${}^2B_1\chi_1^{(n),4}(b_1)$. Overall, 88% of this wavefunction is attributable to the ground state 2B_1 diabat. Large intensity

changes are observed for these peaks indicating significant nonadiabatic interactions.

Vibronic transitions occurring at energies greater than ~ 3.600 eV (~ 1200 cm^{-1}), incur an appreciably higher degree of mixing. In this range, the largest contribution of a particular multimode function is not greater than 0.5 for any vibronic transition being greater than 0.05 on the intensity scale.

7. Simulation including excited anionic vibrational levels

Examination of the experimental spectrum in the region 3.350–3.550 eV, centered around the threshold peak A, reveals several low intensity vibronic transitions, including some to the red of the origin band. The results of the quartic $\mathbf{H}^d$ simulations, in Sec. III C (5) indicate that not all of the observed transitions occurring between peaks A and B can be attributed to the ground vibrational state of the anion. This is particularly obvious for the shoulder to the red of the origin band. These additional features are likely to originate from excited vibrational states of the anion. This observation was the impetus for subjecting this molecule to further analysis through the simulation of the hot band spectra, attributable to the four low-lying vibrational levels of the anion noted previously. For this additional analysis, only the $\text{min}^1 A_1(\text{tz})$ description of the anion was used.

The composite nonadiabatic photodetachment spectrum, including hot bands from the lowest four vibrational states of the anion, is reported in Fig. 2(b), and improves the agreement with the experimental spectrum, displayed in Fig. 2(a). The composite simulation provides a far more quantitative reproduction of the experimental band origin, especially note the shoulder peak(s) discussed above. This simulation also provides an explanation for the presence of the several low intensity peaks between the band origin, peak A, and the peak labeled B in the experimental spectrum that were not evident

in either the adiabatic, quadratic, or quartic simulations that included only the ground vibrational level of the anion. Thus, as discussed in the Introduction, these computational simulations have enabled the disambiguation between weak nonadiabatic effects and hot band transitions.

8. Implications

In molecules that exhibit low-lying conical intersections, symmetry required or accidental, it is necessary to incorporate nonadiabatic interactions to account for the observed spectral features. When the separation between the seam of intersection and the pertinent critical points on the ground state potential energy surface is large, it is expected that nonadiabatic mixing will not be significant at low energies and that the single state adiabatic approximation should be adequate to account for the experimental observables in this energy range. In this work we have addressed, from a computational perspective, when it becomes necessary to consider nonadiabatic interactions. We were able to identify nonadiabatic interactions within 500 cm^{-1} of threshold (the b' transition). However, we also found that the size of the contributions from hot bands can be comparable to those of weak nonadiabatic interactions, complicating the assignment of the experimentally observed transitions.

The assignment of the hot bands can be verified by additional experimental measurements, under “colder” conditions. In this case our calculations show that the shoulder on peak A and several of the transitions occurring between peaks A and B should disappear. It is hoped that the present results will motivate such experiments.

IV. SUMMARY AND CONCLUSIONS

The photoelectron spectrum of the 1,2,3-triazolide, $(\text{CH})_2\text{N}_3^-$, including hot bands, has been simulated using a vibronic expansion of $\sim 10^9$ vibronic basis states. The spectrum has previously been measured by Lineberger's group. The simulation is based on a recently reported fourth-order quasidiabatic Hamiltonian, $\mathbf{H}^d$. To carry out these calculations two algorithmic extensions were required. The algorithm utilized in solving the secular equation that arises in the time-independent multimode expansion of the quadratic vibronic coupling problem was extended to handle arbitrary-order polynomial expansions in $\mathbf{H}^d$. The implementation of the algorithm is open-ended, achieved through the use of fine grained parallelism to partition the trial vectors. We also introduce an algorithm to reduce the size of the vibronic basis needed to describe the hot band spectra by calculating Franck-Condon overlaps of the vibronic basis functions with the excited vibrational levels of the anion. This extended our existing algorithm which was restricted to the vibrational ground state of the anion. These algorithms allow us to exploit the enhanced capability of the higher order $\mathbf{H}^d$ to reproduce the *ab initio* data, energies, energy gradients, and derivative couplings, over the relevant domain of the nuclear coordinate space, to achieve accurate simulations in computationally challenging systems.

For the triazolide photoelectron spectrum, the simulation based on the quartic $\mathbf{H}^d$ is far superior at reproducing the main features of the experimental spectrum, when compared with standard quadratic $\mathbf{H}^d$ based simulations. The improved results of the higher-order simulation allow for the assignment of the main vibronic transitions observed in the experimental spectrum. Sequence (vibrationally excited anion) band contributions, corresponding to one quantum in each of four low frequency modes of the triazolide anion, explain the observed vibronic transitions occurring to the red of the assigned band origin of the neutral species and some weak transitions to the blue of the origin band.

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APPENDIX A: OPEN ENDED, HIGHER ORDER PARALLEL LANCZOS ALGORITHM

The development of an efficient algorithm for performing the matrix-vector product $\mathbf{H}^{vib}\mathbf{d}$ is the key computational step in the Lanczos algorithm. Using its structured sparsity, and the simple rules for evaluating harmonic oscillator matrix elements, $\mathbf{H}^{vib}$ can be readily pre-processed *a priori*, in order to identify the non-zero matrix elements for each potential term in $\mathbf{H}^{vib}$. Formally, this is accomplished through the use of a simple basis set ordering scheme, where the index for the N^{int} -length vector, $\mathbf{n}$, denoting the vibrational basis function is given by

$$I_n = \sum_{i=1}^{N^{int}} \left[n_i \prod_{j=i}^{N^{int}} N_{j+1} \right] + 1, \quad \text{where} \\ \times \begin{cases} N_j = M_j, j = 1 - N^{int} \\ N_{N^{int}+1} = 1 \end{cases}, \quad (\text{A1})$$

M_j is the number of basis function for the j th mode, and I_n runs from 1 to N^{vib} . Using the standard formulae for harmonic oscillator matrix elements,⁴⁶ the strides in I_n between connected basis functions associated with each potential term in $\mathbf{H}^d$ can be pre-computed given the highly ordered manner in which the elements appear in the $\mathbf{H}^{vib}$ matrix. This circumvents the need to explicitly store the indices, which would soon result in an intractable storage problem. Each process, therefore, determines the number of non-zero elements between a contiguous set of columns, n_{left} and n_{right} , in $\mathbf{H}^{vib}$ such that $I_{n_{right}} - I_{n_{left}} + 1 = N^{vib}/n_{proc}$, where n_{proc} is the number of processors. In this way, the $N^{vib} \times N^{vib}$ problem is reduced to an $N^{vib} \times (N^{vib}/n_{proc})$ matrix-vector product. The final result is obtained via summation of the n_{proc} N^{vib} -length vectors. The determination of the index map for each potential term is completely automated and is independent of the unique number indices (i.e., polynomial order) of any given

term. Thus, the algorithm can handle $\mathbf{H}^d$ constructed employing arbitrary order polynomials.

The parallel implementation of the algorithm distributes the Lanczos vectors over multiple processors employing the Global Arrays libraries,^{47,48} where the current and previous two Lanczos vectors, required to evaluate the recursion relation, were stored in the distributed memory. Previous studies have shown³⁰ that the algorithm scales quite well up to ~ 40 processors.

APPENDIX B: ANALYTIC EXPRESSIONS FOR THE OVERLAP FACTORS

For spectral simulations involving initial states that do *not* correspond to the ground vibrational state of the anion, the evaluation of the $s_{\mathbf{a},\mathbf{m}}$ [Eq. (7)] is more complicated than for its ground state $s_{0,\mathbf{m}}$ counterpart. In this Appendix we described the formal and computational issues involved in the evaluation of these Franck-Condon overlap integrals.

The necessary overlaps are efficiently determined using established generalized Hermite polynomial generating function formalisms, which have been discussed by several authors.^{32–37} This algorithm is an extension of the one previously reported by our group for $\mathbf{a} = 0$, which could handle vibronic expansions comprised of $> 10^9$ terms. In general, the Franck-Condon overlap integrals, $s_{\mathbf{a},\mathbf{m}}$, are only difficult to determine when the $\mathbf{w}$ and $\bar{\mathbf{w}}$ represent different normal coordinate systems with different origins and orientations. For the anion and neutral species,

$$\bar{\mathbf{w}} = \mathbf{T}^{(a)}(\mathbf{X} - \mathbf{X}^{(\text{eq},a)}), \quad (\text{B1a})$$

$$\mathbf{w} = \mathbf{T}^{(n)}(\mathbf{X} - \mathbf{X}^{(\text{eq},n)}), \quad (\text{B1b})$$

where $\mathbf{X}$ is an arbitrary set of N^{int} internal coordinates, the anion[neutral] have equilibrium geometries $\mathbf{X}^{(\text{eq},a)}$ [$\mathbf{X}^{(\text{eq},n)}$] and normal coordinate transformations $\mathbf{T}^{(a)}$ [$\mathbf{T}^{(n)}$]. Expressing the anion normal coordinates, $\bar{\mathbf{w}}$, in terms of the neutral coordinate system gives the following relationship:

$$\bar{\mathbf{w}} = \mathbf{T}\mathbf{w} + \mathbf{d}, \quad (\text{B2})$$

where

$$\mathbf{T} = \mathbf{T}^{(a)}\mathbf{T}^{(n)-1} \quad \mathbf{d} = \mathbf{T}^{(a)}[\mathbf{X}^{(\text{eq},n)} - \mathbf{X}^{(\text{eq},a)}]. \quad (\text{B3})$$

From Eq. (5b) [(2c)], the multimode basis functions are the well-known harmonic oscillator wave functions, where $\chi_m^{(an),j}(\bar{w}_j)[\chi_m^{(n),j}(w_j)]$ represents the m th harmonic oscillator function for the j th mode for the anion[neutral]. For the anion and the neutral we have, respectively

$$\chi_{\alpha_i}^{(an),i}(\bar{w}_i) = \left(\sqrt{\frac{\alpha_i}{\pi}} \frac{1}{2^{n_i} n_i!} \right)^{1/2} H_{n_i}(\sqrt{\alpha_i} \bar{w}_i) \exp\left(\frac{-\alpha_i \bar{w}_i^2}{2} \right), \quad (\text{B4a})$$

$$\chi_{\beta_j}^{(n),j}(w_j) = \left(\sqrt{\frac{\beta_j}{\pi}} \frac{1}{2^{m_j} m_j!} \right)^{1/2} H_{m_j}(\sqrt{\beta_j} w_j) \exp\left(\frac{-\beta_j w_j^2}{2} \right), \quad (\text{B4b})$$

where $\alpha_i(\beta_j)$ is the $i(j)$ th harmonic frequency in atomic units and H_m is a Hermite polynomial. Now using Eqs. (B4a) and

(B4b), the overlap integral, Eq. (7), may be formally rewritten as

$$s_{\mathbf{a},\mathbf{m}} = \left\langle \prod_{j=1}^{N^{\text{int}}} \chi_{\alpha_j}^{(an),j}(\bar{w}_j) \left| \prod_{j=1}^{N^{\text{int}}} \chi_{\beta_j}^{(n),j}(w_j) \right. \right\rangle \\ = \left\langle \prod_{i=1}^{N^{\text{int}}} \left(\sqrt{\frac{\alpha_i}{\pi}} \frac{1}{2^{n_i} n_i!} \right)^{1/2} H_{n_i}(\sqrt{\alpha_i} \bar{w}_i) \exp\left(\frac{-\alpha_i \bar{w}_i^2}{2} \right) \right| \\ \times \left| \prod_{j=1}^{N^{\text{int}}} \left(\sqrt{\frac{\beta_j}{\pi}} \frac{1}{2^{m_j} m_j!} \right)^{1/2} H_{m_j}(\sqrt{\beta_j} w_j) \exp\left(\frac{-\beta_j w_j^2}{2} \right) \right\rangle. \quad (\text{B5})$$

Note that the bra and ket are normalized in different coordinate systems. Since the derivation of the analytic expressions parallels the case for $\mathbf{a} = 0$, only an outline will be presented here. The overall goal is to construct a generating function which encodes both the bra(anion) and ket(neutral) vectors of this integral, allowing for the efficient computation of the required overlaps.

As was done previously, see Ref. 38 for details, we employ the method of Karplus and Warshel^{49,50} to obtain the Franck-Condon overlaps. Within this method, the recursion relation required for the practical computation of all the Franck-Condon overlaps is obtained by differentiating the corresponding generating function. Following Karplus and Warshel we have,

$$G(\mathbf{y}, \mathbf{z}) = \tilde{G} \exp\{2\tilde{\mathbf{d}}^\dagger \mathbf{y} + \mathbf{z}^\dagger (\tilde{\mathbf{A}} - \mathbf{I})\mathbf{z} + 2\mathbf{z}^\dagger \tilde{\mathbf{A}}^T \mathbf{y} \\ - \mathbf{z}^\dagger \tilde{\mathbf{A}}^T \tilde{\mathbf{d}} - \tilde{\mathbf{d}}^\dagger \tilde{\mathbf{A}}^T \mathbf{y} + \mathbf{y}^\dagger (\tilde{\mathbf{A}}^{TT\dagger} - \mathbf{I})\mathbf{y}\} \\ = \sum_{\mathbf{m},\mathbf{n}} \prod_j y_j^{m_j} \prod_i z_i^{n_i} \frac{C(\mathbf{m};\mathbf{n})}{\prod_{k,l} (m_k!)(n_l!)}, \quad (\text{B6})$$

which has the form of a multidimensional Hermite polynomial generating function for the $C(\mathbf{m};\mathbf{n})$ and consequently the $s_{\mathbf{m},\mathbf{n}}$, since

$$s_{\mathbf{m},\mathbf{n}} = \tilde{G} \frac{C(\mathbf{m};\mathbf{n})}{\left[\prod_{i,j} (2^{n_i})(2^{m_j})(n_i!)(m_j!) \right]^{1/2}}. \quad (\text{B7})$$

The quantities in Eq. (B6), the matrices $\mathbf{A}$, $\tilde{\mathbf{A}}$, $\tilde{\mathbf{A}}^{T\dagger}$, and $\tilde{\mathbf{A}}^{TT\dagger}$, the vector $\tilde{\mathbf{d}}$, and the scalar $\tilde{G}$ are defined as follows:

$$A_{k',k} = \frac{1}{2}[\beta_k \delta_{k,k'} + \sum_j (T_{j,k'} \alpha_j T_{j,k})], \quad (\text{B8})$$

$$\tilde{G} = \left(\frac{(\det \mathbf{T}) \sqrt{\prod_i \beta_i \alpha_i}}{\det \mathbf{A}} \right)^{1/2} \exp \left\{ - \sum_j \frac{\alpha_j d_j^2}{2} + \frac{\tilde{\mathbf{d}}^\dagger \tilde{\mathbf{A}}^{TT\dagger} \tilde{\mathbf{d}}}{4} \right\}, \quad (\text{B9})$$

and

$$\tilde{A}_{k',k} = \sqrt{\beta_{k'}} A_{k',k}^{-1} \sqrt{\beta_k}, \quad (\text{B10})$$

$$\tilde{A}_{k',j}^{T\dagger} = \sqrt{\beta_{k'}} \sum_k A_{k',k}^{-1} T_{k,j}^\dagger \sqrt{\alpha_j}, \quad (\text{B11})$$

$$\tilde{A}_{j',j}^{TT\dagger} = \sqrt{\alpha_{j'}} \sum_{k,k'} T_{j',k'} A_{k',k}^{-1} T_{k,j}^\dagger \sqrt{\alpha_j}, \quad (\text{B12})$$

$$\tilde{d}_j = d_j \sqrt{\alpha_j}. \quad (\text{B13})$$

Taking the partial derivatives $\partial/\partial z_i$ to index $\mathbf{n}$ and $\partial/\partial y_k$ to index $\mathbf{m}$, matching the coefficients of $\prod_i z_i^{n_i}$ and $\prod_i y_i^{m_i}$, and setting equal to zero gives the first recursion relation:

$$\begin{aligned} C(\mathbf{m}; \mathbf{n}, n_j + 1) = & 2 \sum_i (\tilde{\mathbf{A}} - \mathbf{I})_{j,i} n_i C(\mathbf{m}; \mathbf{n}, n_i - 1) \\ & + 2 \sum_i \tilde{A}_{j,i}^{T\dagger} m_i C(\mathbf{m}, m_i - 1; \mathbf{n}) \\ & - \sum_i (\tilde{A}_{j,i}^{T\dagger} \tilde{d}_i) C(\mathbf{m}; \mathbf{n}), \end{aligned} \quad (\text{B14})$$

where $C(\mathbf{0}, \mathbf{0}) = 1$ and $C(\mathbf{m}; \mathbf{n}, n_j + 1)$ is the C for which the j th index in the vector $\mathbf{n}$ is increased by 1. If it is assumed that the bra state is the ground vibrational state, Eq. (B14) simplifies to the expression

$$\begin{aligned} C(\mathbf{0}; \mathbf{n}, n_j + 1) = & 2 \sum_i (\tilde{\mathbf{A}} - \mathbf{I})_{j,i} n_i C(\mathbf{0}; \mathbf{n}, n_i - 1) \\ & - \sum_i (\tilde{A}_{j,i}^{T\dagger} \tilde{d}_i) C(\mathbf{0}; \mathbf{n}) \end{aligned} \quad (\text{B15})$$

for $j = 1 - N^{\text{int}}$. With this result in hand, the *second recursion* relation is easily determined to be

$$\begin{aligned} C(\mathbf{m}, m_j + 1; \mathbf{n}) = & 2 \sum_i (\tilde{A}_{i,j}^{TT\dagger} - \mathbf{I})_{j,i} m_i C(\mathbf{m}, m_i - 1; \mathbf{n}) \\ & + 2 \sum_i \tilde{A}_{i,j}^{T\dagger} n_i C(\mathbf{m}; \mathbf{n}, n_i - 1) \\ & + 2 \sum_i \tilde{d}_i \left(\delta_{i,j} - \frac{\tilde{A}_{i,j}^{TT\dagger}}{2} \right) C(\mathbf{m}; \mathbf{n}) \end{aligned} \quad (\text{B16})$$

for $j = I - N^{\text{int}}$. For this application, the efficient implementation of the Lanczos algorithm requires that there should be sufficient storage to keep the entire N^{vib} vector (in fact, $3N^{\text{vib}}$) in memory. Since all overlaps for a given $\mathbf{m}$ are required for the construction of the initial Lanczos vector, a “compute once” table approach is employed here. Accordingly, the $C(\mathbf{m}, \mathbf{n})$ terms are determined in two stages. First, the $C(\mathbf{0}, \mathbf{n})$ are computed in batches corresponding to increasing values of the phonon counter $\kappa(\mathbf{0}, \mathbf{n}) = \sum_{i=1}^{N^{\text{int}}} n_i$, thereby ensuring that each $C(\mathbf{0}; \mathbf{n}, n_l - 1)$ required to compute $C(\mathbf{0}; \mathbf{n})$ has already been calculated from the recursion relation. Once the $C(\mathbf{0}; \mathbf{n})$ are in hand, the $C(\mathbf{m}; \mathbf{n})$ terms can then be determined in a similar fashion, accordingly guaranteeing that each $C(\mathbf{m}, m_l - 1; \mathbf{n})$ overlap has already been tabulated. However, this method is limited to *bra* states with $\kappa(\mathbf{m}) \approx 2$, since each value of $\kappa(\mathbf{m})$ requires $\kappa(\mathbf{n})$ and $\kappa(\mathbf{n}, n_l - 1)$ in the *ket*

state. This results in an untenable storage problem for large values of N^{vib} . In these cases, where Franck-Condon overlaps are required for arbitrary *bra* and *ket* states, tree-based methods³⁵ will be more appropriate.

As has been previously demonstrated,³⁸ the introduction of a neutral biased basis allows for a more compact representation of the relevant vibronic states and accordingly reduces the computational demands required to obtain a converged spectral simulation. These savings invariably outweigh the one-time cost of evaluating a large number of Franck-Condon overlaps necessary to generate the initial state wavefunction.

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