Studies of intersystem crossing dynamics in acetylene

Ryan L. Thom, Bryan M. Wong, and Robert W. Field
Department of Chemistry, Massachusetts Institute of Technology, Cambridge, Massachusetts 02139

John F. Stanton
Department of Chemistry and Biochemistry, The University of Texas at Austin, Austin, Texas 78712

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We report a new ab initio study of the acetylene $T_3$ potential energy surface, which clarifies the nature of its energy minimum, and present computed equilibrium geometries and diabatic frequencies. This information enables the computation of harmonic vibrational overlap integrals of $T_3$ vibrational levels with the $S_1$ $3\nu_3$ state. The results of this calculation support the interpretation of two local perturbations of $S_1$ $3\nu_3$, revealed in ultraviolet laser-induced fluorescence/surface electron ejection by laser excited metastables spectroscopy and Zeeman anticrossing measurements, respectively, as arising from two rotational submanifolds of a single $T_3$ vibrational state. We present plausible assignments for this state as a guide for future experimental work. © 2007 American Institute of Physics. [DOI: 10.1063/1.2730832]

I. INTRODUCTION

The mechanism of intersystem crossing in the acetylene molecule has attracted considerable experimental and theoretical attention for many years. Attention has focused on particular vibrational modes of the $S_1 \tilde{A}_1 \rightarrow \tilde{A}_u$ electronic state, the $\nu_3$ symmetric CCH bending vibration, as a promoter of coupling to the triplet manifold. Several lines of experimental evidence reveal a monotonic increase in coupling to triplet levels with increasing quantum of $\nu_3$. One measure of such coupling is the density of Zeeman anticrossings (ZAC) (described further below), which was found to increase steadily with $\nu_3$ until, in $4\nu_3$, the anticrossings became too densely spaced to resolve.\(^1\) This increase in coupling to triplets is much more rapid than the increase in density of triplet vibrational states. Thus it is a matrix element rather than a density of states effect. But why should the $S_1 \rightarrow T_3$ matrix element increase rapidly with excitation in $S_1$ $\nu_3$? This is a vibrational overlap effect associated with the near-linear turning point of vibrational levels on the $S_1$ and $T_3$ potential surfaces.

In 1987, Ochi and Tsuchiya\(^2,3\) recorded the laser-induced fluorescence (LIF) spectra of the $\tilde{A}_1^+A_u^- \rightarrow \tilde{X}_1\Sigma^+_g \tilde{X}_1\Sigma^+_g$, $\tilde{V}_0^2K_0^1$, $\tilde{V}_0^2K_0^0$, and $\tilde{V}_0^2K_1^1$ subbands in a molecular beam at moderate (0.1 cm\(^{-1}\)) resolution. (Here V denotes the trans-bend mode, $\nu_3^v$ in the $\tilde{X}_1\Sigma^+_g$ ground electronic state and $\nu_3^v$ in the $\tilde{A}_1^+A_u^-$ excited state, and $K$ denotes the projection of total angular momentum $J$ along the a axis, $K^m$ in the $\tilde{X}_1$ state, and $K_0^p$ in the $\tilde{A}_1$ state. The subscript is the lower state quantum number, and the superscript is the upper state quantum number; i.e., $V^m$ refers to a transition that connects the $mv_2$ and $nv_3^v$ vibrational levels.) In the spectra of Ochi and Tsuchiya, an especially large degree of $v_3$ fractionation was observed in the rotational lines of $V^0_0K^1_0$. Quantum beats were also seen in the fluorescence decay of some of these levels, the frequency and intensity of which were modified in the presence of magnetic fields. These authors proposed both that the $\tilde{A}_1^+A_u^- 3\nu_3$ level is strongly mixed with a bath of triplet vibrational states, and that a specific rovibrational level of the $T_3$ state is likely to play a key role in this coupling. They noted that the energy minimum of the seam of intersection between $S_1$ and $T_3$ had been predicted to occur in the energy vicinity of $\tilde{A}_1^+A_u^- 3\nu_3$ (Refs. 4–6) and at a geometry close to that of the near-linear turning point of the $S_1$ $3\nu_3$ level. They also pointed out that $T_3$ does not possess sufficient vibrational state density at the energy of $\tilde{A}_1^+A_u^- 3\nu_3$ to account for the observed degree of fractionation, and thus hypothesized that the role of $T_3$ is to mediate the coupling of the $\tilde{A}_1^+A_u^- 3\nu_3$ level to the bath of $T_{1,2}$ states—the doorway-mediated coupling hypothesis.

In 1994, Drabbels et al.\(^7\) recorded a high resolution (18 MHz) LIF spectrum of the $V^0_0K^1_0$ and $V^2_0K^0_0$ subbands. They observed a background dark-state density on the order of $10^{-4}$ cm\(^{-1}\), which was approximately consistent with the expected density of $T_3$ states in this energy region. A later work\(^8\) reconsidered this density of states calculation and showed the properly symmetry-sorted $T_1 + T_2$ state density to be in good agreement with the observed value. On the assumption of a direct singlet-triplet coupling model, Drabbels et al. used the Lawrance-Knight deconvolution algorithm\(^9\) to extract the zeroth-order energies of the dark states and their coupling strengths to the bright $S_1$ state.

In addition to laser-induced fluorescence-based measurements, another class of experiments has exploited the magnetic properties of the dark triplet states not directly accessible by zero-field techniques. Dupré et al.\(^10\) reported ZAC experiments, exciting the $\nu_3=0–3$ levels of the $\tilde{A}_1^+A_u^-$ state. In a ZAC measurement, a single $S_1$ rovibrational level is excited and the intensity of the resulting fluorescence is monitored, while the strength of an external magnetic field is scanned (typically over a range of 0–8 T). States containing triplet electronic state character and therefore possessing a magnetic dipole moment are tuned in energy; when such a
state is tuned into degeneracy with the fluorescing bright state, it mixes appreciable dark-state character into the bright state, resulting in a decrement to the fluorescence signal (due mainly to enhanced collisional quenching of the longer-lived eigenstate). The resulting anticrossing spectrum gives a panoramic view of the nearby (within up to ~7.5 cm⁻¹ for a maximum field strength of 8 T) triplet spin-rovibronic states capable of being Zeeman-tuned into resonance with the optically populated S₁ level. These acetylene ZAC spectra also showed a dramatic increase in the number of anticrossings with increasing excitation of the A₁ N₁ v₁ mode; but with the possible exception of a single very broad anticrossing, which will be reconsidered later in this paper, none of the observed anticrossings could be assigned to triplet states of definite vibrational and rotational (Kₐ, N) quantum numbers.

Finally, a third type of experiment, surface electron ejection by laser excited metastables (SEELEM),¹¹ has been performed. This technique offers direct sensitivity to both triplet and singlet fractional basis state characters. SEELEM spectra of the V₁ K₀ band, recorded simultaneously with UV-LIF spectra,¹² revealed a dense manifold of predominantly triplet-character eigenstates. Subsequently, various statistical measurements were devised¹³ to characterize the intensity contours of the SEELEM lines. These statistical measurements confirmed a doorway mediated as opposed to a direct mechanism of intersystem crossing.

II. ASSIGNED T₃ ∼ S₁ PERTURBATIONS

Reference 8 contains the most exhaustive analysis yet attempted of a simultaneously recorded UV-LIF and SEELEM data set in the region of the V₂ K₀ band (around 45 300 cm⁻¹). The UV-LIF data set displayed a very large (~10⁴) dynamic range of intensity, and numerous assignments of singlet and triplet perturbers of S₁ 3v₁ were made. One of the key results of that work is the identification of a rotational series of triplet levels that, as a function of J, tune through a ΔJ=0, ΔKᵣ=0 energy resonance with rotational levels of 3v₁. This “local perturbation” was fitted using an effective Hamiltonian model, based on the well-known¹⁴,¹⁵ rotational quantum number dependence of spin-orbit matrix elements in a Hund’s case-b basis. The rotation-independent matrix element extracted from this deperturbation was found to be 0.126 cm⁻¹.

It should be noted that a key observation reported in Ref. 8 must be reinterpreted in light of recent experimental results.¹⁶ Specifically, the lines in Table II assigned to the O branch of the T₃ → S₀ transition have been shown to terminate on states of insufficiently long lifetimes to be triplets; moreover, the temperature dependence of their intensities is suggestive of a singlet-singlet hot band. This in turn casts doubt on the validity of the T₃ → S₀ Q branch rotational assignments, which should be carefully subjected to similar measurements. In any event, on account of the difficulties in obtaining unambiguous assignments of the highly congested Q branch, these transitions were not included in the present implementation of the deperturbation fit model of Ref. 8, and so the result for the spin-orbit perturbation matrix element, obtained from the reliably assigned R- and P-branch transitions, remains unaffected.

In addition to this local perturbation between the T₃ doorway state and low-J values of S₁ 3v₁ (K=1), probably the strongest isolated singlet-triplet interaction observed to date in acetylene is a very broad Zeeman anticrossing in fluorescence from the rotationless (J=K=0) level of the same S₁ vibrational state (3v₁).¹¹⁷ From the reported ZAC spectrum,¹⁸ the position of this anticrossing is observed to be at 7.14 T, with a width of 0.66 T. The corresponding energy shift is calculated from the magnetic field strength using the Zeeman relation¹⁷

$$\Delta E = M_S g \mu_B \Delta B,$$

where Mₛ is the electron-spin space-fixed projection quantum number (±1 for a pure triplet, assuming the limit of Paschen-Back decoupling), g is the effective g factor (assumed to equal the approximate “bare-electron” value of 2), and \(\mu_B = 9.274 \times 10^{-24} \text{ J T}^{-1}\) is the Bohr magneton. Thus we find a zero-field S₁, T₃ energy difference for this anticrossing of |ΔE| = 6.67 cm⁻¹. The energy of 3v₁ J=K=0 is 45 285.7 cm⁻¹, thus the zeroth-order energy of the triplet perturber must lie at either 45 279.0 or 45 292.4 cm⁻¹. In the presence of the magnetic field, the J=0 singlet can mix with a triplet of either J=1 or 0, implying N=2, 1, or 0, and therefore a priori K for the triplet could assume any of the values 2, 1, or 0.

The strength of the singlet-triplet interaction is reflected in the width of the anticrossing; in the classic analysis of Wieder and Eck,¹⁹ it is shown that an isolated anticrossing in the “strong coupling” limit (singlet-triplet coupling element much larger than mean depopulation rates) has a Lorentzian line shape with a full width half maximum given by

$$\Gamma = \frac{1 + \gamma_S / \gamma_T}{(\gamma_S / \gamma_T)^{1/2} M_S g \mu_B},$$

where \(\gamma_S\) and \(\gamma_T\) are the total (radiative plus collisional) depopulation rates of the singlet and triplet states, respectively. Under the simplifying approximation \(\gamma_S ≈ \gamma_T\), the prefactor reduces to 2, and the singlet-triplet coupling element is given by one-fourth of the anticrossing width, converted to units of energy. Thus the measured width of 0.66 T gives an interaction strength of 0.17 cm⁻¹. This measured coupling matrix element can be related to the corresponding zero-field matrix element by the equation²⁰

$$V_{ST}(N_S) = V_{ST}^{B=0}(v_ν, K_S, N_S; v_ν, K_T, N_T) \sqrt{2N_S + 1} \times \left( \begin{array}{ccc} N_S & 1 & N_T \\ -M_{N_S} & M_{N_T} & M_{N_ν} \end{array} \right),$$

where Nₛ=Mₙₛ=0, so that Nₜ=1 is fixed by the triangle rule. Evaluating the Wigner coefficient with Mₙₜ=-Mₙₛ=±1, we find that

$$|V_{ST}^{B=0}| = \sqrt{3} |V_{ST}| = 0.29 \text{ cm}^{-1}.$$
in the zero-field matrix element is equal to unity, and so the non-rotating-molecule matrix element is in fact 0.29 cm\(^{-1}\) (under the assumption of \(K_s=1\), the result would have to be multiplied by a factor of 2).

This is roughly similar in magnitude to the coupling matrix element between \(S_3\) and the \(K=1\) component of the \(T_3\) perturber, extracted from the UV-LIF spectrum. This suggests that these \(K=0\) and 1 \(S_1\) \(2\nu_5\)--\(T_3\) interactions are two local perturbations by the \(K_s=0\) and 1 rotational submanifolds of the same \(T_3\) vibrational state. The smaller possible value of the zeroth-order energy falls approximately 21 cm\(^{-1}\) below the energy of \(S_1\) \(2\nu_5\); thus it is plausible to assign the anticrossing triplet perturber as the \(K=0\) component of the same \(T_3\) vibrational level that appears in our UV-LIF spectrum, provided that we can show this to be a reasonable \(K=0, K=1\) energy separation for a vibrational level of the \(T_3\) state.

The relationship between the measured two-level \(T_3 \sim S_1\) interaction matrix element and the derived nonrotating molecule vibrational matrix element could be distorted by unknown factors, such as dilution of \(S_1\) \(2\nu_5\) and \(T_3\) perturber characters into the quasicontinuum of the same \(T_3\) vibrational level. The decisive factor with respect to the likelihood of additional \(T_3 \sim S_1\) vibrational near degeneracies is the magnitude of the \(A\)-rotational constant, which governs the coarse rotational spacings between subbands associated with different values of \(K\), the magnitude of the projection of rotational angular momentum along the \(a\) (least moment of inertia) axis. It would be helpful to have a grasp of the dependence of this quantity on the \(T_3\) vibrational quantum numbers, in order to gauge the rotational spacings of the \(T_3\) excited vibrational levels. In particular, we expect that \(A_s\) will be altered in a complicated manner by excitation of the symmetric CCH bending and torsional modes (as well as by \(a\)-type Coriolis interactions).

### III. VIBRATIONAL ASSIGNMENT

#### A. New ab initio determination of the diabatic \(T_3\) minimum

Both the ZAC measurement, on the one hand, and the deperturbation model used to interpret the UV-LIF/SEELEM data set, on the other, provide estimates of spin-orbit matrix elements between \(S_1\) and \(T_3\) perturbers. To an excellent approximation, this matrix element factors into the product of a purely electronic matrix element of the spin-orbit operator and a vibrational overlap integral. The latter can be estimated if something is known about the equilibrium structures and the force fields near the equilibrium geometry of the respective electronic states. The equilibrium geometry and force field can be computed by \(ab\) initio methods. Precisely such a calculation has already been carried out for \(T_3\) acetylene by Cui and Morokuma,\(^6\) who computed \(H^{SO}\) between \(S_1\) and \(T_3\) at several nuclear configurations. At minimum of the seam of intersection in \(C_2\) symmetry between the \(S_1\) and \(T_3\) surfaces, this matrix element (i.e., \(\langle \Psi(S=0,M_S=0)|H^{SO}|\Psi(S=1,M_S=1)\rangle\)) is 13.7 cm\(^{-1}\). This in turn implies a vibrational overlap integral for the \(T_3\) perturber of 0.126/13.7=0.01.

This raises two questions: Can we compute a vibrational overlap of this magnitude with \(S_1\) \(2\nu_3\) for any low-lying vibrational level of \(T_3\)? Do the overlaps computed for the lowest-lying levels show any diagnostic trends with vibrational quantum numbers that might aid in proposing or at least narrowing down the vibrational assignment possibilities for the \(T_3\) perturber? To answer these questions, we must examine the complicated \(T_3\) potential energy surface in more detail.

\(Ab\) initio electronic structure calculations have been slow in arriving at a consensus regarding the location and nature of the minimum of the \(T_3\) potential energy surface. Cui and Morokuma\(^6\) were only able to locate a transition state (saddle point), with one imaginary normal mode frequency along an antisymmetric CCH bending coordinate. More recently, Ventura et al.,\(^21\) performed extended multireference electron correlation calculations on all four of the lowest-lying acetylene triplet potential energy surfaces. These authors were able to find a genuine minimum (no imaginary frequencies) belonging to the \(T_3\) surface and described its equilibrium structure, although they provided no normal mode vibrational frequencies or eigenvectors. Ventura et al. describe two seams of \(T_2\) \(\sim T_3\) conical intersections that lie very close to the predicted \(T_3\) stationary point. This complicated topography accounts for the difficulties encountered in locating stationary points.

In order to shed light on the nature of the \(T_3\) potential energy surface, with a view of producing an accurate estimate of this crucial vibrational overlap integral, we have carried out new \(ab\) initio calculations. To treat the interactions between \(T_2\) and \(T_3\), we employ a simple diabatic model in which the \(T_1\) and \(T_2\) electronic states are coupled by the two nontotally symmetric modes, \(\nu_5\) (antisymmetric CCH stretch) and \(\nu_6\) (antisymmetric CCH bend). To estimate the adiabatic couplings, we write the diabatic electronic Hamiltonian matrix \(U\) in the basis spanned by \(\phi_1\) and \(\phi_2\), which are the diabatic wave functions associated with \(T_3\) and \(T_2\), respectively. Within the harmonic approximation, the diabatic potential energy curves \(U_{11}\) and \(U_{22}\) expressed in the dimensionless normal coordinates \(q=(\omega/\hbar)\xi^2Q\) are given by

\[
U_{11}=\langle \phi_1|U|\phi_1\rangle = \frac{1}{2}\omega_5q_5^2 + \frac{1}{2}\omega_6q_6^2, \tag{5}
\]

\[
U_{22}=\langle \phi_2|U|\phi_2\rangle = \frac{1}{2}\omega_5q_5^2 + \frac{1}{2}\omega_6q_6^2 + \Delta, \tag{6}
\]

where \(\Delta\) is the vertical excitation energy between the \(T_3\) and \(T_2\) states at the reference \(C_2\) saddle point on the \(T_3\) surface. In Eqs. (5) and (6) we have assumed that modes \(\nu_5\) and \(\nu_6\) have the same frequencies (\(\omega_5\) and \(\omega_6\), respectively) in the \(T_3\) and \(T_2\) diabatic states.\(^22,23\) Since the two states are diabatic, they are coupled by the adiabatic vibronic coupling operator \(U_{12}\) which can be expanded in a Taylor series in \(q_5\) and \(q_6\).\(^24,25,26\)
Using Eqs. batic energy curves, are
\[ E = \lambda_5 q_5 + \lambda_6 q_6 + \lambda_5' q_5^2 + \lambda_6' q_6^2 + \cdots \]
where we retain only the linear terms in \( q_5 \) and \( q_6 \) in Eq. (7).

To make contact with properties obtained from quantum chemistry methods, the following adiabatic quantities: \( \Delta, \Omega_5^\pm, \) and \( \Omega_6^\pm. \) We employed the equation of motion coupled cluster with singles and doubles (EOM-CCSD) method for all geometry optimizations and harmonic frequency calculations. The correlation-consistent basis sets of Kendall et al.\textsuperscript{25} denoted by cc-pVXZ, where \( X \) stands for \( D \) (double), \( T \) (triple), or \( Q \) (quadruple) zeta quality, were used. All EOM-CCSD calculations were performed using the ACES II set of programs\textsuperscript{28} with analytic gradients for both geometry and harmonic frequency calculations.

The geometries for the \( C_2 \) saddle point on the \( T_3 \) surface are collected in Table I, with previous results from the literature for comparison. A general decrease in bond lengths and increase in bond angles is observed with larger basis set size. However, when the basis set increases from cc-pVTZ to cc-pVQZ, the difference in geometry is relatively small within the EOM-CCSD approach. The pVQZ results of Table I agree well with the MR-AQCC (TQ)-extrapolated values from Ventura et al.\textsuperscript{21}

### Table I. Computed structures at the diabatic \( T_1 \) minimum.

<table>
<thead>
<tr>
<th></th>
<th>pVDZ</th>
<th>pVTZ</th>
<th>pVQZ</th>
<th>Ventura et al.\textsuperscript{1}</th>
</tr>
</thead>
<tbody>
<tr>
<td>( r_{CC} (\text{Å}) )</td>
<td>1.381</td>
<td>1.349</td>
<td>1.347</td>
<td>1.352</td>
</tr>
<tr>
<td>( R_{CCH} (\text{Å}) )</td>
<td>1.101</td>
<td>1.075</td>
<td>1.077</td>
<td>1.079</td>
</tr>
<tr>
<td>( \theta_{CCH} (\text{°}) )</td>
<td>132.6</td>
<td>137.4</td>
<td>137.3</td>
<td>138.7</td>
</tr>
<tr>
<td>( \tau_{HCCH} (\text{°}) )</td>
<td>104.7</td>
<td>104.6</td>
<td>104.5</td>
<td>106.1</td>
</tr>
</tbody>
</table>

\textsuperscript{1}Reference 21.

B. Harmonic overlap integrals

The computed parameters for the adiabatic vibronic couplings between \( T_3 \) and \( T_2 \) were obtained using Eqs. (14) and (15) and are listed in Table II. The diabatic frequencies of \( T_3 \), \( \omega_5 \), and \( \omega_6 \) (rescaled to conventional mass-weighted normal coordinates) are also listed. Within all basis sets, the \( \nu_6 \) mode, which corresponds to the antisymmetric CCH bend, provides the stronger coupling between \( T_3 \) and \( T_2 \).

Now the harmonic frequencies and force constants about the “diabatized” \( T_3 \) minimum can be used to compute vibrational overlap integrals with \( S_1, S_3 \). In order to minimize the error of this calculation, we have also recomputed harmonic frequencies and force constants for \( S_1 \). Tables III and IV list the normal modes and calculated frequencies for \( S_1 \) and \( T_3 \), respectively. The calculation also establishes an electronic energy separation (\( T_3(S_1) - T_3(S_3) \)) of 0.001 2211 hartree = 270 cm\(^{-1}\).

The vibrational overlap integrals are straightforwardly calculated within the harmonic oscillator approximation using the multidimensional generating function formalism developed by Sharp and Rosenstock\textsuperscript{31} and extended by several other authors.\textsuperscript{32,35} The required inputs are the respective nor-
normal mode frequencies and $L$ matrices, which contain the normal mode eigenvectors expanded in a basis of internal stretch and bend angle coordinates.\(^3\)\(^4\)

Table V lists the $T_3$ vibrational states, the harmonic energies of which are predicted to fall within approximately 100 cm\(^{-1}\) of $S_1$ $3\nu_3$, along with their calculated overlaps with $S_1$ $3\nu_3$.

### C. A-rotational constants

We are now in a position to make some quantitative predictions concerning the vibrationally averaged (diabatic) A-rotational constants discussed earlier. A straightforward calculation determines $A_v$ (the value of $A$ corresponding to our computed equilibrium geometry) as 19.95 cm\(^{-1}\), considerably larger than the value observed for vibrational levels of $S_1$ (typically $\sim$14–15 cm\(^{-1}\)). As is the case for $S_v$, the $a$-inertial axis is tilted away from the C–C bond axis by a slight angle ($\sim 6^\circ$). The increase in $A_0$ for $T_3$ is explained largely by the significantly wider (i.e., less bent) CCH bond angle at the $T_3$ minimum, which brings the structure closer to linearity and consequently reduces the $a$-axis moment of inertia. In order to estimate the vibrational dependence of the $A$-rotational constant for $T_3$, we make use of the results of a second-order perturbative treatment, by which one can calculate the vibration-rotation interaction constants $\alpha$, defined by the power series

$$A_v = A_e - \sum \alpha_r (v_r + 1/2) + \cdots .$$

The result for $\alpha_r^A$ in the harmonic limit is\(^3\)\(^5\)

$$-\alpha_r^A = \frac{2A_e^2}{\omega_r} \left[ \sum_{\xi} \frac{3(\omega_r^A)^2}{4\xi^2} + \sum_{s+r} (\xi_s - \xi_r)^2 \left( \frac{3\omega_s^A + \omega_r^A}{\omega_s^A - \omega_r^A} \right) \right],$$

where

### TABLE IV. Computed diabatic $T_3$ vibrational frequencies.

<table>
<thead>
<tr>
<th>Mode</th>
<th>Predominant character</th>
<th>Calc. (cm(^{-1}))</th>
</tr>
</thead>
<tbody>
<tr>
<td>$v_1$ ($a_v$)</td>
<td>Symmetric CH stretch</td>
<td>3225.88</td>
</tr>
<tr>
<td>$v_2$ ($a_v$)</td>
<td>Torsion</td>
<td>1626.90</td>
</tr>
<tr>
<td>$v_3$ ($a_v$)</td>
<td>CC stretch</td>
<td>1411.96</td>
</tr>
<tr>
<td>$v_4$ ($a_v$)</td>
<td>Symmetric CCH bend</td>
<td>653.04</td>
</tr>
<tr>
<td>$v_5$ ($a_v$)</td>
<td>Antisymmetric CH stretch</td>
<td>3036.48</td>
</tr>
<tr>
<td>$v_6$ ($a_v$)</td>
<td>Antisymmetric CCH bend</td>
<td>397.56</td>
</tr>
</tbody>
</table>

The constants denoted $\epsilon_{\gamma \delta}$ are the Coriolis coefficients that define the components of vibrational angular momentum in terms of the normal coordinates and their conjugate momenta,

$$\pi^\gamma = \sum_{r,s} \epsilon_{\gamma \delta} Q^r_s P^s_r .$$

They are listed in Table VI can be calculated directly from the $I$-matrix components as follows:

$$\pi_{\gamma \delta}^r = \sum_{r,s} \epsilon_{\alpha \beta}^r (\mu_i)^{\gamma \delta} .$$

In Eq. (17) above, the first term represents contributions in first-order perturbation theory from the quadratic dependence of the $\mu$ tensor, and therefore also of the rotational constant operator, on the normal coordinates. The second term represents the second-order contributions of Coriolis interactions diagonal in $J$, but which exchange two quanta of nonidentical normal modes. Both classes of terms contribute to the energy a term proportional to $(v+1/2)K^2$, and therefore, a term to the rotational constant linear in $(v+1/2)$.

Examining Table V, we find three $T_3$ vibrational states lying between 38 and 111 cm\(^{-1}\) from $S_1$ $3\nu_3$ with an appropriate vibrational overlap ($\sim 0.01$) with the observed triplet perturber. Of all the computed quantities, we expect the overlap integral to be the least accurate, owing both to error in the frequencies and to neglected anharmonicity. The overlap integrals are rigorously zero by symmetry.

### TABLE V. $T_3$ vibrational levels predicted to lie in the vicinity of $S_1$ $3\nu_3$.

| Vibrational level | $E-E(3\nu_3)$ (cm\(^{-1}\)) | $\langle \psi | S_1 | 3\nu_3 \rangle$ | $A_v$ (cm\(^{-1}\)) |
|-------------------|-------------------------------|-------------------------------|-------------------|
| $v_1 + 2\nu_3 + \nu_6$ | $-108$ | 0 | 24.62 |
| $v_1 + 3\nu_3$ | $-68$ | 0.12 | 28.82 |
| $v_1 + 5\nu_6$ | $-39$ | 0 | 11.25 |
| $4\nu_3 + 2\nu_6$ | $-32$ | $-0.0062$ | 26.86 |
| $v_1 + 6\nu_6$ | $-5$ | $-0.0037$ | 19.19 |
| $v_1 + 7\nu_6$ | $-3$ | 0 | 9.29 |
| $v_1 + v_2 + \nu_6$ | $-3$ | 0 | 20.05 |
| $v_1 + v_3 + \nu_6$ | $-3$ | 0 | 20.05 |
| $v_1 + v_3 + 3\nu_6$ | $+34$ | 0 | 18.09 |
| $2\nu_3 + \nu_6$ | $+38$ | 0.015 | 24.25 |
| $v_1 + 2\nu_3 + 2\nu_6$ | $+74$ | 0.011 | 22.29 |
| $3\nu_3 + 4\nu_6$ | $+110$ | 0.017 | 20.33 |
tegrals, by contrast, are expected to be much less sensitive to uncertainty in the computed frequencies. It is seen that the state $2 v_3 + v_4$, with a reasonable $A_v$ value of 24.45 cm$^{-1}$, is predicted to lie only 38.0 cm$^{-1}$ higher in energy than $S_1 3 v_3$. A still higher-energy state at 110.4 cm$^{-1}$ from $3 v_3$, $3 v_4 + 4 \nu_6$, is predicted to possess an $A_v$ value closest to that required for the observed simultaneous perturbation of $S_1 3 v_3$ $K=0$ and $K=1$. We thus tentatively propose these two vibrational levels as leading candidates for the assignment of the twice-sampled (in $K=0$ and 1) $T_3$ perturber.

IV. ADDITIONAL $T_3 \sim S_1$ NEAR DEGENERACIES

The calculation described in this work establishes a theoretical value for the energy of the $T_3$ zero-point vibrational level of 41 860 cm$^{-1}$. There are therefore, in this approximately 3500 cm$^{-1}$-wide energy region below $S_1 3 v_3$, many $T_3$ vibrational levels capable of interacting, perhaps strongly, with $3 v_3$ or with another $S_1$ vibrational level. Indeed, Table V lists one $T_3$ level, $v_3 + 3 v_4$, which, although lying roughly 100 cm$^{-1}$ in energy from our preferred candidate for the $T_3$ perturber, is predicted to interact with it in an order of magnitude more strongly. Thus this level could experience enough mixing with $S_1$ to be appreciably illuminated. Careful examination of this region by UV-LIF/SEELEM spectroscopy would be worthwhile. Within an energy region $\pm 300$ cm$^{-1}$ near each $S_1$ vibrational level, there is likely to be a $T_3$ vibrational level with vibrational overlap $\approx 0.1$, hence spin-orbit matrix element $\approx 1$ cm$^{-1}$.

V. CONCLUSION

We have undertaken a new ab initio characterization of the acetylene $T_3$ potential energy surface in the vicinity of its stationary point. After accounting for the adiabatic interactions with the $T_2$ surface, harmonic frequencies and force constants about the diabatic $T_3$ minimum have been obtained, which enable the calculation of harmonic vibrational overlap integrals with the $3 v_3$ vibrational level of $S_1$ for the entire manifold of low-lying $T_3$ vibrational states. On the basis of these quantities, a small number of $T_3$ states that lie in the energetic region of $S_1 3 v_3$ has been found to possess overlaps of the correct magnitude for the triplet perturber of this level. Two of these, the $2v_3 + 3v_4$ and $3v_4 + 4\nu_6$ levels, are predicted to possess a complete rotational structure consistent with the observed perturbations of $S_1 3 v_3$ at both $K=0$ and 1, unifying UV-LIF/SEELEM measurements with a much earlier Zeeman anticrossing observation. Experiments are in progress to locate additional $T_3$ levels with the goal of adding a few more experimental calibrations of the $T_3$ diabatic potential energy surface and $S_1 \sim T_3$ and $T_3 \sim T_{1,2}$ spin-orbit coupling strengths.

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