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Deconvolution of spectral data using a doorway-coupling model Hamiltonian

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The doorway-mediated mechanism for dynamical processes represents the first step beyond statistical dynamics toward an explicit mechanism. A bright state $\rightarrow$ doorway state $\rightarrow$ dark bath doorway-coupling model Hamiltonian characterizes the small molecule limit behavior of the doorway state in mediating the interaction with other dark states in the large molecule limit. Established methods of spectral deconvolution are extended to determine the parameters of a doorway-coupling model Hamiltonian from the energies and intensities of eigenstates in a high-resolution spectrum. The most important parameters of the Hamiltonian, including the doorway state energy and bright $\sim$ doorway matrix element, may be computed directly from moments of the spectral intensity distribution. We demonstrate that these parameters can be recovered accurately even when some eigenstates are unresolved. The deconvolution procedure is applied to the spectrum of the $3\nu_3$ $K_a=1$ vibrational level of S_1 acetylene, where a single, local, T_3 doorway level mediates coupling to the $T_{1,2}$ manifold. Previous studies of this $S_1 \sim T_3$ perturbation are discussed in light of the doorway state energies and matrix elements obtained by inversion of the spectral data. © 2010 American Institute of Physics. [doi:10.1063/1.3357311]

I. INTRODUCTION

Spectral deconvolution is a method for local deperturbation of a high-resolution spectrum. It is used to determine, from a spectrum, the parameters that define a model Hamiltonian. The standard statistical limit model Hamiltonians derived from the deconvolution procedure consist of a single, optically bright zero-order state that is coupled directly to a set of prediagonalized, optically dark zero-order states. In this article, we describe how spectral deconvolution may be extended to another class of model Hamiltonians, which characterize doorway-mediated dynamical processes. Doorway-coupling model Hamiltonians are the simplest variety of model Hamiltonians that explicitly parameterize interactions among zero-order dark states. In the study of intersystem crossing (ISC) and intramolecular vibrational redistribution (IVR), the characterization of interactions between zero-order dark states is a prerequisite for experimental characterization of explicit mechanisms that extend beyond a statistical, direct-coupling picture.

Spectral deconvolution has been used to study IVR in many small molecules, including NO_2 , allene, and several substituted propynes.^{1–4} It was originally developed for the study of ISC, where it has been applied to the spectra of intermediate case molecules such as acetylene, naphthalene, and pyrazine.^{1,5,6} The technique for deconvolution of continuous spectra was described by Berg⁷ and independently, in a more general form, by Ziv and Rhodes.⁸ Both methods make use of a Green's function formalism. A discrete formulation of spectral deconvolution was presented by Lawrance and Knight,⁶ and afterward simplified by Lehmann.⁹ Leh-

mann's refinement of the technique obviates the need to compute any Green's function from the spectrum—we refer to this method as Lawrance–Knight–Lehmann (LKL) deconvolution. Interestingly, the LKL method had been used in 1977 by Brand and Hoy¹⁰ to deperturb portions of the NO_2 electronic spectrum. That work was cited by Cable and Rhodes,¹ who artificially rebroadened the same spectrum to demonstrate their continuous deconvolution technique.

In its discrete state formulation, spectral deconvolution returns a set of dark state energies and squared bright $\sim$ dark matrix elements. In its continuous formulation, the procedure returns a zero-order dark state spectral density function for coupling to the bright state. A diagram of a direct-coupling Hamiltonian returned by LKL deconvolution is shown in Fig. 1(a).

The ability to generate a set of prediagonalized dark states by LKL deconvolution loses its luster when an interaction of explicit dynamical interest occurs within the set of dark states. This is exemplified by sequential coupling among tiers of dark states, a common situation in small polyatomic molecules.¹¹ Although dark state $\sim$ dark state interactions can play a central role in the redistribution of molecular energy, the traditional deconvolution procedure does not directly yield information pertaining to their dynamics.

To this end, several efforts have been made to investigate perturbations within the block of prediagonalized dark states returned by LKL deconvolution. Pate *et al.*¹² used a method of matrix rotation to obtain a qualitative explanation of a J -dependent Coriolis interaction between two dark states in their deperturbation of the trifluoropropyne spectrum. Altunata and Field¹³ derived a parameter to predict the relative energy of a single “doorway” state, a unique dark state that mediates all coupling between the bright state and the re-

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$$\begin{aligned}
\mathbf{H}_{\text{direct}} &= \begin{bmatrix} E_s & H_{s1} & H_{s2} & H_{s3} & H_{s4} & \cdots \\ & E_1 & & & & \\ & & E_2 & & & \\ & & & E_3 & & \\ & & & & E_4 & \\ & & & & & \ddots \end{bmatrix} \\
\mathbf{H}_{\text{doorway}} &= \begin{bmatrix} E_s & H_{s\ell} & & & & \\ & E_\ell & H_{\ell 1} & H_{\ell 2} & H_{\ell 3} & \cdots \\ & & E_1 & & & \\ & & & E_2 & & \\ & & & & E_3 & \\ & & & & & \ddots \end{bmatrix} \\
\mathbf{H}_{\text{doorway}} &= \begin{bmatrix} E_\ell & H_{\ell s} & H_{\ell 1} & H_{\ell 2} & H_{\ell 3} & \cdots \\ & E_s & & & & \\ & & E_1 & & & \\ & & & E_2 & & \\ & & & & E_3 & \\ & & & & & \ddots \end{bmatrix}
\end{aligned}$$

FIG. 1. Top: direct-coupling model Hamiltonian. One vector of matrix elements connects a single bright state, $|s\rangle$, to a prediagonalized set of dark basis states, $\{|m\rangle\}$, which are enumerated in the figure. Middle: doorway-coupling Hamiltonian. A single bright basis state, $|s\rangle$, is connected to a single doorway basis state $|\ell\rangle$, which is connected in turn to a prediagonalized block of dark states, $\{|m\rangle\}$. Bottom: doorway-coupling Hamiltonian in the embedded bright state arrangement. The form of the matrix is equivalent to the direct-coupling model, without the need for a matrix rotation. All model Hamiltonians in the figure are symmetric and real; only nonzero elements above the diagonal are shown.

remaining dark states. A method to determine the energy and squared matrix element of a doorway state from the spectrum allows the construction of a new doorway-coupling model Hamiltonian. Such a Hamiltonian is shown in Fig. 1(b).

The parameters in a direct-coupling Hamiltonian are uniquely determined by the spectrum; the total number of energies and relative intensities in the spectrum is equal to the number of free parameters in the model Hamiltonian. For a spectrum consisting of $N+1$ transitions, the number of free parameters after normalization is $2N+1$ ($N+1$ energies and N normalized intensities).⁶ A direct-coupling Hamiltonian contains one bright state energy, N dark state energies, and N bright~dark coupling matrix elements, totaling $2N+1$. A doorway-coupling Hamiltonian also contains $2N+1$ free parameters: one bright state energy, one bright~doorway matrix element, one doorway state energy, $N-1$ dark state energies, and $N-1$ doorway~dark coupling matrix elements.

The equal number of parameters in the direct and doorway-coupling Hamiltonians suggests that a doorway-coupling Hamiltonian can also be derived uniquely from the experimental data. Such a technique was described for the continuous case by Ziv and Rhodes⁸ in their original paper. The authors introduce the concept of a “spectroscopic channel basis” to describe a sequence of model Hamiltonians available through recursive application of spectral deconvolution. The spectroscopic channel basis includes model Hamiltonians with any number of sequential doorway states, from 0 to $N-1$. Three examples are shown in Fig. 2.

After a brief review of the continuous and discrete forms of spectral deconvolution, we demonstrate how to extend the discrete deconvolution method to determine experimentally the parameters of a doorway-coupling model Hamiltonian.

FIG. 2. Diagrams of model Hamiltonians containing (a) a single bright state, (b) one bright state and one doorway state, and (c) one bright state with two sequential doorway states. Dotted lines indicate basis states connected via off-diagonal matrix elements.

Moreover, we show that the most important parameters of the model Hamiltonian may be computed directly from moments of the spectral intensity, and thus are available from spectra where poor resolution prevents a full deconvolution. We discuss the effects of level trapping and broadened line shapes in the extended deconvolution results. Finally, we apply our method to the spectrum of acetylene, and show that the most important parameters of the model Hamiltonian may be recovered from spectra of drastically different resolution and signal-to-noise.

II. LKL DECONVOLUTION: CONSTRUCTION OF A DIRECT-COUPLING MODEL HAMILTONIAN

Using the standard spectral deconvolution method, the parameters that define a direct-coupling Hamiltonian are extracted from an absorption spectrum. The basis for this Hamiltonian consists of a single bright basis state, $|s\rangle$, which is coupled to a set of N prediagonalized dark states, $\{|m\rangle\}$, through a set of bright~dark matrix elements, $\{H_{sm}\}$

$$\mathbf{H}_{\text{direct}} = E_s |s\rangle\langle s| + \sum_{m=1}^N E_m |m\rangle\langle m| + \sum_{m=1}^N H_{sm} (|s\rangle\langle m| + |m\rangle\langle s|). \quad (1)$$

This Hamiltonian is illustrated in Fig. 1. The technique of spectral deconvolution requires that a single bright basis state provides all oscillator strength from the initial state for the spectrum in question.

We briefly review the continuous formulation of spectral deconvolution, following the notation of Cable and co-workers.^{1,8} The Green's function for the direct-coupling Hamiltonian

$$\mathcal{G}_s(E) = \lim_{\gamma \rightarrow 0} [\mathbf{H}_{\text{direct}} - (E + i\gamma)\mathbf{I}]^{-1} \quad (2)$$

has an imaginary component proportional to the absorption spectrum

$$\text{Im}[\mathcal{G}_s(E)] \propto \sigma_A(E). \quad (3)$$

The normalization condition for the imaginary part of the Green's function is

$$-\frac{1}{\pi} \int_{-\infty}^{\infty} \text{Im}[\mathcal{G}_s(E)] = 1. \quad (4)$$

Dispersion relations connect the real part of the Green's function to the imaginary part. The real part of the Green's function may be derived by applying a Hilbert transformation to $\text{Im}[\mathcal{G}_s(E)]$

$$\text{Re}[\mathcal{G}_s(E)] = \frac{1}{\pi} \mathcal{P} \int_{-\infty}^{\infty} \frac{\text{Im}[\mathcal{G}_s(E')]}{E' - E} dE', \quad (5)$$

where the symbol $\mathcal{P}$ indicates the principal value of the integral.

Using projection operators, another Green's function, $\mathcal{F}_s(E)$, may be defined for the subspace of dark states in the Hamiltonian.^{1,8} It is related to the Green's function for the full Hamiltonian by

$$\mathcal{G}_s(E) = [E - E_s - \mathcal{F}_s(E)]^{-1}. \quad (6)$$

The imaginary part of $\mathcal{F}_s$

$$\text{Im}[\mathcal{F}_s(E)] = -\text{Im} \left[\frac{1}{\mathcal{G}_s(E)} \right] \quad (7)$$

is the desired zero-order density function for coupling to the bright state. This is called the “interaction density spectrum” by Ziv and Rhodes,⁸ and the “weighted density function” by Berg and others.⁷ The magnitude of this function is related to the local bright~dark squared matrix element, $H_{sm}^2(E)$, and the density of dark states, $\rho_m(E)$, by the golden rule⁷

$$\text{Im}[\mathcal{F}_s(E)] = \pi H_{sm}^2(E) \rho_m(E). \quad (8)$$

The bright state energy, E_s , is obtained from the first moment of spectral intensity (the “center of gravity” of the spectrum)

$$E_s = \int \sigma_A(E) \times E dE = -\frac{1}{\pi} \int \text{Im}[\mathcal{G}_s(E)] \times E dE \quad (9)$$

a result of expanding the eigenstate absorption intensities in the direct-coupling basis.

If all transitions in the spectrum are fully resolved, the procedure for deconvolution is simplified greatly. A method for deconvolution of discrete transitions was presented by Lawrance and Knight,⁶ who modified Berg's⁷ method for the continuous case. A simpler and better algorithm was later put forth by Lehmann.⁹ The result of discrete deconvolution is a set of zero-order dark state energies $\{E_m\}$ and squared matrix elements $\{H_{sm}^2\}$. The phases of the matrix elements are not determined by the procedure, and indeed do not affect the energies or spectral intensities of the eigenstates. Interference effects among dark states do not arise in the direct-coupling Hamiltonian because one and only one coupling pathway connects each dark state to the single bright state.

We briefly review the deconvolution formulas for a discrete spectrum of transitions at frequencies $\{\nu_i\}$ with normalized intensities $\{I_i\}$, following Lehmann.⁹ The bright state energy, E_s , coincides with the first moment of the spectral intensity

$$E_s = \sum_i I_i \times \nu_i \quad (10)$$

as for the continuous formulation. The zero-order dark state energies, $\{E_m\}$, in the direct-coupling basis are the zeroes of the function

$$f_s(E) = \sum_i \frac{I_i}{\nu_i - E} \quad (11)$$

which may be found numerically. After the set of zero-order dark state energies $\{E_m\}$ is obtained, the set of squared bright~dark matrix elements $\{H_{sm}^2\}$ is determined by successive substitution of each dark state energy, E_m , into the equation

$$H_{sm}^2 = \left[\sum_i \frac{I_i}{(\nu_i - E_m)^2} \right]^{-1}. \quad (12)$$

The sum of the squared bright~dark coupling matrix elements is equal to the second moment of spectral intensity about the mean

$$\sum_m H_{sm}^2 = \sum_i I_i \times (\nu_i - E_s)^2. \quad (13)$$

This quantity, as well as the quantity in Eq. (10), is invariant to matrix rotations, thus it is conserved for any choice of basis.⁹

Because the function $f_s(E)$ has one root between each pair of consecutive eigenvalues, one dark state energy in the direct-coupling Hamiltonian is “trapped” between each pair of consecutive eigenstate energies observed in the spectrum. This effect places a limit on the degree to which coupling to a single bright state can influence the nearest-neighbor level spacings among a set of dark states.¹⁴

III. EXTENDED DECONVOLUTION: CONSTRUCTION OF A DOORWAY-COUPLED MODEL HAMILTONIAN

We wish to go a step beyond the LKL deconvolution procedure and construct a Hamiltonian in which only a single dark basis state, $|\ell\rangle$, is coupled to the bright state. This “doorway” state mediates all coupling between the bright state and the set of remaining dark states $\{|n\rangle\}$

$$\begin{aligned} \mathbf{H}_{\text{doorway}} = & E_s |s\rangle\langle s| + E_\ell |\ell\rangle\langle \ell| + H_{s\ell} (|s\rangle\langle \ell| + |\ell\rangle\langle s|) \\ & + \sum_{n=1}^{N-1} E_n |n\rangle\langle n| + \sum_{n=1}^{N-1} H_{\ell n} (|\ell\rangle\langle n| + |n\rangle\langle \ell|). \end{aligned} \quad (14)$$

A diagram of a doorway-coupling Hamiltonian is shown in Fig. 1(b).

A continuous formulation for constructing a doorway-coupling Hamiltonian from the spectrum was presented by Ziv and Rhodes.⁸ They begin with the Green's function, $\mathcal{F}_s(E)$, for the subspace of dark states in the direct coupling Hamiltonian. This diagonal block of states is partitioned into a single doorway state, $|\ell\rangle$, and a new subspace of zero-order dark states, $\{|n\rangle\}$, which determine the doorway-coupling Hamiltonian. The Green's function, $\mathcal{G}_\ell(E)$, for the doorway~dark block is determined by $\mathcal{F}_s(E)$

$$\mathcal{F}_s(E) = V_{s\ell}^2 \mathcal{G}_\ell(E) - i\Gamma_s/2, \quad (15)$$

where $i\Gamma_s/2$ is the width of the bright state, and $V_{s\ell}$ is the bright~doorway matrix element. The change-of-basis from a direct-coupling model Hamiltonian to a doorway-coupling model Hamiltonian is isolated within the block of dark states, thus the bright basis state is identical in both models.

Aside from a constant offset, the function $\text{Im}[\mathcal{G}_\ell(E)]$ is proportional to the interaction density spectrum, $\text{Im}[\mathcal{F}_s(E)]$, just as the function $\text{Im}[\mathcal{G}_s(E)]$ is proportional to the absorption spectrum. This illustrates clearly that *the problem of deriving a doorway-coupling Hamiltonian from a direct-coupling Hamiltonian is, in essence, identical to the problem of deriving a direct-coupling Hamiltonian from the spectrum*. In both cases, our task is to create, from a diagonal set of states, a new basis in which a single state carries all oscillator strength.

Following Cable and Rhodes,¹ we proceed by rewriting Eqs. (6)–(9) for the doorway-coupling Hamiltonian. The Green's function for the subspace of dark states in the doorway-coupling Hamiltonian is

$$\mathcal{G}_\ell(E) = [E - E_s - \mathcal{F}_\ell(E)]^{-1} \quad (16)$$

which leads to an equation that describes the interaction density spectrum for coupling to the doorway state

$$\text{Im}[\mathcal{F}_\ell(E)] = -\text{Im}\left[\frac{1}{\mathcal{G}_\ell(E)}\right]. \quad (17)$$

The doorway state energy is the first moment of $\text{Im}[\mathcal{F}_s(E)]$, the interaction density spectrum for coupling to the bright state

$$E_\ell = -\frac{1}{\pi} \int \text{Im}[\mathcal{F}_s(E)] \times E \, dE. \quad (18)$$

Since the integral of $\text{Im}[\mathcal{G}_\ell(E)]$ over energy is normalized to $-\pi$, the magnitude of $V_{s\ell}$ may be obtained by integrating the energy-dependent part of the interaction density spectrum for coupling to the bright state. Using Eq. (15)

$$V_{s\ell}^2 = -\frac{1}{\pi} \int (\text{Im}[\mathcal{F}_s(E)] + i\Gamma_s/2) \, dE. \quad (19)$$

We have derived all desired properties of the doorway-coupling Hamiltonian for the continuous case. At this point, it is clear that one could, in principle, solve the system for a second or third tier doorway. However, we choose to focus only on the single doorway-coupled Hamiltonian because that model is most readily applied to several examples of experimental spectra.

In the discrete case, a doorway-coupling Hamiltonian may be derived from the direct-coupling Hamiltonian by applying the LKL deconvolution procedure recursively to the prediagonalized block of dark states. The deconvolution algorithm dedagonalizes this block by projecting out a single state that contains all coupling to the bright state. Dark state energies and squared bright~dark matrix elements from the direct-coupling Hamiltonian replace spectral frequencies (ν_i) and intensities (I_i) as input to the algorithm that is outlined in Sec. II.

The doorway state energy is the first moment of the distribution of $\{H_{sm}^2\}$ in the direct-coupling Hamiltonian. Using a normalized set of dark state matrix elements

$$h_{sm}^2 = \frac{H_{sm}^2}{\sum_m H_{sm}^2} \quad (20)$$

we may write the doorway state energy as

$$E_\ell = \sum_m h_{sm}^2 \times E_m. \quad (21)$$

The new set of zero-order dark state energies, $\{E_n\}$, for the doorway-coupling Hamiltonian is given by the roots of

$$f_\ell(E) = \sum_m \frac{h_{sm}^2}{E_m - E} \quad (22)$$

which places a single E_n between each consecutive pair of dark state energies in the direct-coupling Hamiltonian. The new set of doorway~dark matrix elements is found from the dark state energies, $\{E_n\}$, by substitution into

$$H_{sn}^2 = \left[\sum_m \frac{h_{sm}^2}{(E_m - E_n)^2} \right]^{-1}. \quad (23)$$

The bright~doorway matrix element may be determined by considering the properties of the direct-coupling Hamiltonian. The quantity $\sum_m H_{sm}^2$ is invariant under matrix rotations, thus it is conserved for any basis set that includes a single bright state.⁹ Since the bright state is coupled exclusively to the doorway state in this model Hamiltonian, it follows that

$$H_{s\ell}^2 = \sum H_{sm}^2. \quad (24)$$

The four equations above allow calculation of all parameters in the doorway-coupling Hamiltonian.

The key parameters of the doorway-coupling model Hamiltonian, E_s , $H_{s\ell}$, E_ℓ , and $\sum H_{\ell m}$, may be written directly in terms of moments of the absorption spectrum. This allows them to be derived directly from the spectrum without deconvolution. Equation (10) equates the bright state energy and the first moment (center of gravity) of the spectral intensity. The second central moment (variance) of the spectral intensity is equal to the squared bright~doorway matrix element

$$H_{s\ell}^2 = \sum_i I_i \times (\nu_i - E_s)^2 \quad (25)$$

which follows (in the discrete case) from Eqs. (24) and (13). The doorway state energy is the ratio of the third and second central moments of the absorption spectrum. In the discrete formulation, this is

$$E_\ell = \frac{\sum_i I_i \times (\nu_i - E_s)^3}{\sum_i I_i \times (\nu_i - E_s)^2}. \quad (26)$$

To determine the sum of squared matrix elements between the doorway state and the remaining dark states, we must subtract the second moment of intensity about the doorway state energy from the ratio of the fourth and second central moments of spectral intensity

TABLE I. Key parameters of the doorway-coupling model Hamiltonian may be calculated directly from the absorption spectrum without LKL deconvolution. The bright state energy, bright $\sim$ doorway matrix element, and doorway state energy have simple relationships to moments of the spectrum. For clarity, moments of the absorption spectrum are defined explicitly in the table.

Parameter	Equivalent moments of absorption spectrum	
E_s	μ	
$H_{s\ell}^2$	μ_2	
$E_\ell - E_s$	μ_3 / μ_2	
$\Sigma H_{\ell m}^2$	$\mu_4 / \mu_2 - \mu_2(E_\ell)$	
Moment	Continuous case	Discrete case
μ	$\int \sigma_A(E) \times E \, dE$	$\sum_i I_i \times \nu_i$
μ_n	$\int \sigma_A(E) \times (E - \mu)^n \, dE$	$\sum_i I_i \times (\nu_i - \mu)^n$
$\mu_n(c)$	$\int \sigma_A(E) \times (E - c)^n \, dE$	$\sum_i I_i \times (\nu_i - c)^n$

$$\Sigma H_{\ell m} = \frac{\sum_i I_i \times (\nu_i - E_s)^4}{\sum_i I_i \times (\nu_i - E_s)^2} - \Sigma_i I_i \times (\nu_i - E_\ell)^2. \quad (27)$$

Table I summarizes the relationships between the moments of the spectrum and the parameters of the doorway-coupling Hamiltonian, for both the continuous and the discrete formulations.

To demonstrate the method of obtaining a doorway-coupling model Hamiltonian from a discrete spectrum, we apply our procedure to a NO₂ spectrum reported by Smalley *et al.*¹⁵ Our purpose here is only to demonstrate the procedure, not to address the dynamics of the NO₂ molecule. This

FIG. 3. Thick vertical lines indicate zero-order dark state energies and matrix elements obtained by discrete LKL deconvolution of a portion of the NO₂ spectrum reported by Smalley *et al.* (Ref. 15). The single bright state energy obtained from deconvolution is displayed as a vertical line in the negative direction. The original absorption spectrum is shown as a set of Gaussian line shapes superimposed on the deconvolution results.

FIG. 4. Thick vertical lines indicate zero-order dark state energies and matrix elements obtained by an extended LKL deconvolution of a portion of the NO₂ spectrum reported by Smalley *et al.* (Ref. 15). The bright state energy obtained from the first stage of deconvolution is displayed as a dashed vertical line in the positive direction, scaled to the bright $\sim$ doorway matrix element. The energy of the single doorway state is displayed as a vertical line in the negative direction. The original absorption spectrum is shown as a set of Gaussian line shapes superimposed on the deconvolution results. Note that the energies for the combined set of bright and dark states in the doorway-coupled basis satisfy the usual level trapping rules for dark states in a direct-coupled basis.

portion of spectrum was also used by Cable and Rhodes¹ to demonstrate their continuous deconvolution method, so it provides a basis for comparison with their published results.

Figure 3 displays the parameters of a direct-coupling Hamiltonian obtained from a single LKL deconvolution. We include the original spectrum along with the zero-order energies to illustrate the level trapping phenomenon. Two eigenstates in the spectrum are nearly degenerate at about 15 000 cm⁻¹, thus trapping one of the zero-order dark states in the narrow energy range between these two eigenstates. Figure 4 shows the parameters of a doorway-coupling Hamiltonian obtained by the extended deconvolution procedure. This figure illustrates that, in the doorway-coupling model Hamiltonian, all members of the combined set of zero-order energies plus the bright state energy are trapped between the eigenstates of the spectrum.

This level-trapping property exists for the doorway-coupling Hamiltonian because this Hamiltonian can be rearranged, without a matrix rotation, to have the same form as a direct-coupling Hamiltonian. Simply by reordering the columns so that the bright state is embedded into the manifold of dark states, the doorway-coupling Hamiltonian becomes identical in form to the direct-coupling Hamiltonian. This arrangement is shown in Fig. 1(c). With the Hamiltonian arranged in this form, it is clear that the distribution of doorway state amplitude among the dark states is equivalent to the distribution of bright state amplitude in a direct-coupling

FIG. 5. Interaction density spectrum for coupling to the doorway state, computed from a portion of the NO₂ spectrum reported by Smalley *et al.* (Ref. 15). These results are in agreement with those of Cable and Rhodes (Ref. 1) (compare to their Fig. 11).

model. As a consequence, the phenomenon of level trapping still applies to a doorway-coupled system, though the bright state and doorway state have swapped roles.

In the doorway-coupling Hamiltonian, the zero-order bright state and the $N-1$ zero-order dark states are trapped between the eigenstate energies, in the same manner as the N dark states of the direct-coupling Hamiltonian. Doorway-coupling models with two or more successive doorway states do not share this level trapping property. The models require a change in basis to bring them into the form of the direct-coupling Hamiltonian. In this respect, the doorway-coupling Hamiltonian with a single doorway state is unique among the set of doorway-coupling Hamiltonians in the spectroscopic channel basis of Ziv and Rhodes.⁸

To compare the discrete and continuous formulations, we have used the methods detailed by Cable and Rhodes¹ to re-evaluate the interaction density spectrum for coupling to the doorway state. Our results are presented in Fig. 5; agreement with Fig. 11 of Ref. 1 is within acceptable limits given that the computation involves numerical evaluation of principal value integrals.

Figure 6 compares the discrete and continuous deconvolution results for the doorway-coupling Hamiltonian. The Lorentzian peaks in the interaction density spectrum coincide exactly with the dark state energies in the discrete formulation. Lorentzian line shapes transform correctly under the Hilbert transformation of Eq. (5), producing smooth poles in the real part of the Green's function derived from the absorption spectrum.

Because the continuous formulation is exact for Lorentzian line shapes, a continuous deconvolution of unresolved, homogeneously broadened spectral lines will have the correct functional form, although some peaks may remain unresolved in the resulting interaction density spectrum. Thus, for a spectrum with homogeneous width γ , the interaction density spectrum, $\mathcal{F}(E)$, for the doorway state is equal to

$$\mathcal{F}_\ell(E) = \mathcal{L}_\gamma * \sum_m H_{\ell m}^2 \delta(E_m - E), \quad (28)$$

where the symbol $*$ denotes convolution, $\mathcal{L}_\gamma$ is a Lorentzian function with full width at half maximum (FWHM) γ , and the index m runs over the diagonal block of dark states coupled to $|\ell\rangle$. A comparison of discrete and continuous deconvolution results is shown in Fig. 7, where the original discrete spectrum has been convoluted with a Lorentzian function with a FWHM of 6 cm⁻¹. The rising far wings of the interaction density spectrum arise from the nonzero tails of the Lorentzian peaks, which cause the inverse of the

FIG. 6. Comparison of discrete and continuous extended deconvolution results for the same spectrum. The dark state energies and squared matrix elements in the discrete formulation correspond to the peaks of the interaction density spectrum in the continuous formulation. The (unphysical) rising edges of the interaction density spectrum arise from the nonzero tails of the Lorentzian peaks, which cause the inverse of the Green's function to accumulate at the edges of the computed spectrum.

FIG. 7. Continuous deconvolution carried out for Lorentzian broadened line shapes of 6 cm^{-1} FWHM, corresponding to $1/2$ the average level spacing of the spectrum. The continuous deconvolution result is consistent with the discrete result to a resolution of 6 cm^{-1} . The rising wings of the interaction density spectrum arise from the nonzero tails of the Lorentzian peaks, which cause the inverse of the Green's function to accumulate at the edges of the computed spectrum.

Green's function to accumulate at the edges of the computed spectrum.

Doppler broadening, an *inhomogeneous* effect, is the dominant broadening mechanism in most gas phase high-resolution spectroscopy experiments. In the limit of inhomogeneous broadening, the continuous form of the deconvolution fails, because Gaussian line shapes do *not* transform correctly under the Hilbert transformation of Eq. (5). If the deconvolution procedure is carried out regardless, the resulting interaction density spectrum will contain peaks at incorrect energies and intensities.

In such a situation, the experimentalist is faced with two choices: Discretize the spectrum and miss dark state~dark state spacings smaller than the resolution, or convolve the spectrum with a Lorentzian line shape to obtain an unresolved but functionally correct interaction density spectrum. In practice, the additional linewidth contributed by convolution with a Lorentzian line shape degrades much of the structure in the interaction density spectrum. If a spectrum is discretized before deconvolution, the level-trapping properties of direct and doorway-coupling model Hamiltonians guarantee that no undetected zero-order dark state will exist outside the bounds of an unresolved cluster. We emphasize that the most important parameters of the model Hamiltonian, E_s , $H_{s\ell}^2$, E_ℓ , and $\Sigma H_{\ell m}^2$, will remain correct for any symmetric line shape in the spectrum because they can be computed directly from moments of the spectral intensity. In the next section, we demonstrate that estimates for these parameters are valid even if some eigenstates are unresolved.

IV. APPLICATION TO HIGH-RESOLUTION SPECTRA OF ACETYLENE

In 1994, Drabbels *et al.*⁵ recorded the laser-induced fluorescence (LIF) spectrum of the $3_0^3K_0^1$ vibronic subband of S_1

acetylene at a resolution of 18 MHz. The authors used the LKL method to generate a set of direct-coupling matrix elements from the spectral data. However, several subsequent investigations of this band have found strong evidence that a near-degenerate vibrational level of the T_3 electronic state mediates coupling between the S_1 level and the remaining levels, which are classified as high-lying vibrational levels of the T_1 and T_2 electronic states.

Using the methods described above, we have calculated the parameters of a doorway-coupling model Hamiltonian for each rotational transition of the $3_0^3K_0^1$ subband reported by Drabbels *et al.*⁵ The results are shown in Table II. Note the near-linear change in bright state-doorway state energy difference with increasing J . This result is consistent with the observation of a local T_3 vibrational level with a rotational constant slightly different from that of the singlet.

To investigate the effects of intensity noise and unresolved eigenstates in the spectrum, we generated a series of inhomogeneously broadened spectra from the discrete data set of Drabbels *et al.*⁵ For each line in the series $R(0)$ – $R(3)$, the discrete spectrum was convolved with a Gaussian line shape of standard deviation 0.06 cm^{-1} and sampled at energy intervals of 0.01 cm^{-1} . Baseline noise was introduced to each spectrum by adding an intensity pulled from a random normal distribution with a standard deviation of 1% of the average eigenstate intensity in the cluster. Intensity noise was introduced with a standard deviation of 5% of the true intensity at each point. The model Hamiltonian parameters, E_s , E_ℓ , and $H_{s\ell}$, were computed directly from moments of the spectral intensity without an explicit deconvolution. The results from 100 trials are presented in Table II for comparison with the parameters determined from the discrete spectrum. The errors for doorway state energy are roughly an

TABLE II. Parameters of a doorway-coupling model Hamiltonian for the S_1-S_0 $3^3_0K_0^1$ vibrational subband of acetylene. The energy of the zero-order bright state, E_s , the relative energy of the zero-order doorway state, $E_\ell-E_s$, and the bright $\sim$ doorway matrix element, $H_{s\ell}$, are shown. The discrete spectrum parameters were obtained by applying the extended deconvolution method to the discrete spectrum of Drabbels *et al.* (Ref. 5). For each line in the R branch, 100 artificially broadened spectra were derived from the discrete spectrum, as described in the text. The broadened spectrum parameters were computed from moments of spectral intensity, without an explicit deconvolution. All values are in units of cm^{-1} , and errors indicate one standard deviation from the mean.

Line	E_s	$E_\ell-E_s$	$H_{s\ell}$
Discrete spectrum			
$R(0)$	45 303.1255	-0.2731	0.1418
$R(1)$	45 305.2210	-0.1120	0.1206
$R(2)$	45 307.1738	0.0272	0.1188
$R(3)$	45 308.9133	0.0990	0.1704
$Q(1)$	45 300.6503	0.0418	0.1980
$Q(2)$	45 300.1678	-0.0508	0.1245
$Q(3)$	45 299.4414	-0.2272	0.1785
$Q(4)$	45 298.4825	-0.1753	0.1695
Broadened spectrum			
$R(0)$	45 303.127 $\pm$ 0.003	-0.27 $\pm$ 0.01	0.144 $\pm$ 0.003
$R(1)$	45 305.216 $\pm$ 0.002	-0.15 $\pm$ 0.03	0.125 $\pm$ 0.003
$R(2)$	45 307.179 $\pm$ 0.006	0.04 $\pm$ 0.03	0.116 $\pm$ 0.007
$R(3)$	45 308.912 $\pm$ 0.005	0.12 $\pm$ 0.03	0.179 $\pm$ 0.005

order of magnitude larger than those for the bright state energy and bright state $\sim$ doorway state matrix element, reflecting the higher moments of spectral intensity used in the computation. The parameters derived from inhomogeneously broadened spectra agree with those from the discrete spectra, although some eigenstates are unresolved.

This band of acetylene was considered by Altunata and Field,¹³ who derived a parameter that is proportional to the product $E_\ell \times H_{s\ell}^2$. The “skewness” parameter of Altunata and Field¹³

$$S = \sum_m I_m^2 \times (E_m - E_0) \quad (29)$$

is computed from the results of a single deconvolution, using the quasicontinuous formulation of Lawrance and Knight.⁶ The intensity factor, I_m , is proportional to the matrix element squared, H_{sm}^2 , in the discrete formulation. The authors identify E_0 with the “midpoint of the energy axis of the LK output.” Because this skewness parameter scales as energy to the first power, it may more accurately be considered an expression for the center-of-gravity of the distribution of $\{H_{sm}^4\}$ in the direct-coupling Hamiltonian.

The authors of Ref. 13 applied their S parameter to the $3^3_0K_0^1$ spectrum reported by Drabbels *et al.*⁵ and reported the product $E_\ell \times H_{s\ell}^2$ for the $R(0)$ through $R(4)$ transitions. We compare these results with the deconvolution method described in the present paper by normalizing the S parameter to the quantity $H_{s\ell}^2$, computed from the variance of the spectrum [Eq. (25)]. Figure 8 compares the doorway state energy computed from deconvolution to the normalized values obtained from the S parameter, as reported in reference 13. The small (0.03 cm^{-1}) discrepancies presumably result from in-

FIG. 8. Comparison between the Altunata and Field¹³ S parameter and the bright state-doorway state energy difference ($E_\ell-E_s$) obtained from extended LKL deconvolution. The S parameter results are scaled by the squared bright $\sim$ doorway matrix element, which is equal to the variance of spectral intensity.

tegration of the interaction density spectrum [Lawrance and Knight's⁶ $B(E)$] used to compute the S parameter.

The most complete description of the doorway level in $3^3_0K_0^1$ is given by Mishra *et al.*,¹⁶ who used the complementary spectroscopic techniques of LIF and SEELEM to record the spectrum of long-lived states coupled weakly to S_1 . To analyze this local T_3 perturber, they constructed reduced term value plots and fit the experimental energies to a model Hamiltonian.

The results of the Hamiltonian fit by Mishra *et al.*¹⁶ yielded a bright $\sim$ doorway matrix element of $H_{s\ell} = 0.126 \text{ cm}^{-1}$ for the e -symmetry components (the authors do not give an uncertainty for this value).¹⁶ We compare the deconvolution results with the Hamiltonian fit by averaging the value of $H_{s\ell}$ obtained from extended deconvolution over the rotational quantum number J . The average bright $\sim$ doorway matrix element from deconvolution is $\langle H_{s\ell} \rangle = 0.138 \pm 0.021 \text{ cm}^{-1}$, in agreement with the previous results. The bright state and doorway state energies obtained from deconvolution are compared to the reduced term values of Ref. 16 in Fig. 9. As expected, the deperturbed energies lie between the nominal S_1 and T_3 eigenstate energies inferred from the spectrum.

The use of LIF intensities in the deconvolution procedure instead of absorption intensities rests on the assumption that only the bright state character of an eigenstate contributes to the fluorescence intensity. This is indeed the case for the low-lying triplet basis states of acetylene, from which transitions to the ground state are spin forbidden.

Recently, de Groot *et al.*¹⁷ investigated the spectrum of S_1 $3^3_0K_0^1$ by resonance enhanced multiphoton ionization photoelectron spectroscopy (REMPI-PES). A comparison of the REMPI-PES spectrum in the local crossing region, $J'=1-4$, to that in the region near the bandhead, $J'=11-15$, indicates the presence of a second, more energetically remote T_3 doorway state. The two doorway states are arranged in a parallel configuration; nonzero matrix elements connect both T_3 doorway states to the S_1 bright state and to the set of $T_{1,2}$ dark states. The second doorway state is observed through an

FIG. 9. The S_1 and T_3 basis state energies obtained from extended LKL deconvolution are shown together with the reduced term values of Mishra *et al.* (Ref. 16). Top: e -symmetry basis state energies obtained from R -branch transitions. Bottom: f -symmetry basis state energies obtained from Q -branch transitions. The deperturbed energies from deconvolution lie between the nominal S_1 and T_3 eigenstate energies inferred from the spectrum, as they must.

interference effect, which is manifested in a J' -dependence of the relative fraction of S_1, T_3 versus T_1, T_2 electronic character.

To a reasonable approximation, the interference effect results from a loss of T_3 , rather than S_1 , electronic character. The total T_3 character of a nominal $T_{1,2}$ eigenstate, $|m\rangle$, may be evaluated by perturbation theory, yielding the result

$$|\langle T_3 | m \rangle|^2 = \frac{H_{\ell m}^2}{\Delta E_{\ell m}^2} + \frac{H_{\ell' m}^2}{\Delta E_{\ell' m}^2} + \frac{H_{\ell m} H_{\ell' m}}{\Delta E_{\ell m} \Delta E_{\ell' m}}, \quad (30)$$

where $|\ell\rangle$ and $|\ell'\rangle$ are the two parallel T_3 doorway states. The final term in Eq. (30) may give rise to the destructive interference between the doorway states observed by de Groot *et al.*¹⁷ To find a comparable term in the expression for S_1 electronic character, the perturbation theory must be extended to much higher order.

Regardless, we expect that the quantity, $H_{\ell' m}/\Delta E_{\ell' m}$, will be approximately constant for the remote doorway at

low J' , because of the large energy difference relative to the local doorway. This is confirmed by the spectrum of de Groot *et al.*,¹⁷ in which the S_1, T_3 versus T_1, T_2 electronic character is approximately constant in the range $J'=1-4$. The consistency of the matrix elements between the bright state and the local doorway state obtained from the deconvolution procedure also lends credence to the approximation that the remote doorway does not have a significant impact on the local deperturbation at $J'=1-4$, apart from a constant contribution to the matrix element between the bright state and the local doorway.

V. CONCLUSION

We have shown how to extend established methods of spectral deconvolution to determine uniquely the parameters of a doorway-coupling effective Hamiltonian. The most important parameters of the effective Hamiltonian, the doorway state energy and the bright $\sim$ doorway matrix element, are related to moments of the spectral intensity distribution. By generating artificially broadened spectra, we show that these parameters may be recovered when some eigenstates are unresolved.

We have applied this technique to the spectrum of the $3\nu_3 K=1$ vibrational level of S_1 acetylene, where a local, T_3 doorway level mediates coupling to the $T_{1,2}$ manifold. The T_3 energies and matrix elements obtained from the deconvolution are consistent with the deperturbation of Mishra *et al.*¹⁶ The extended deconvolution results verify that the S parameter of Altunata and Field¹³ is proportional to the product $E_\ell \times H_{\ell' m}^2$.

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