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ring. It seems that, in both the parent compounds and the cation radicals derived from them, the effect of lowering the pK by increasing the number of sulfonate groups on the benzene ring is simply an effect of increasing negative charge in the molecule or the radical.

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COMMENTS

Comment on "Direct Deconvolution of Extensively Perturbed Spectra: The Singlet-Triplet Molecular Eigenstate Spectrum of Pyrazine"

Str: High-resolution laser spectroscopy allows the eigenstate-resolved study of intramolecular dynamics, where the dynamics may be intersystem crossing, internal conversion, intramolecular vibrational energy distribution, or isomerization. In these studies one is often in the "intermediate case limit" where transitions to expected isolated states are broken up into small to large numbers of resolved eigenstates due to the dynamics. The basis states that carry absorption strength from a given initial state are known as bright states, and the other basis states are known as dark states. In cases where absorptions from different bright states do not overlap, it is possible to analyze the spectrum in terms of a phenomenological relaxation Hamiltonian for each individual bright state

$$H = e_b|b\rangle\langle b| + \sum_{d=1}^{N-1} e_d|d\rangle\langle d| + f_d(|d\rangle\langle b| + |b\rangle\langle d|) \quad (1)$$

This Hamiltonian has the dark states "prediagonalized" and thus has zero coupling between dark states. One is always free to choose such a basis, and since an absorption spectrum is directly sensitive only to the character of the bright state, this is a convenient starting point. This form of the Hamiltonian has been widely used and has been called the "canonical form" by Robinson and Langhoff.¹ If in a spectrum one observes a set of lines to N eigenstates, then one knows N eigenenergies (ν_i) and N intensities (I_i). The absolute intensity depends upon the absorption strength of the bright state, and thus only the $N - 1$ relative intensities are relevant to the dynamics. The relaxation Hamiltonian for one bright state interacting with $N - 1$ dark states has exactly $2N - 1$ free parameters, and thus one may in principle invert the problem to determine the N unperturbed energies and $N - 1$ coupling matrix elements. It is clear that the solution will be indeterminate as to the sign of the matrix elements, but it was not obvious until recently that a unique solution exists beyond that ambiguity or how to construct any solution.

Berg² provided a general solution to this problem, for the case where the dark states can be considered a continuous set $d(E)$. She showed how the product $f_d^2(E) \rho(E)$, where $\rho(E)$ is the density of dark states, could be calculated from the matrix element $G_{bb}(E)$, where $G(E)$ is the Green's function. $\text{Im } G_{bb}(E)$ can be directly calculated from the absorption spectrum, and $\text{Re } G_{bb}(E)$ can be calculated from $\text{Im } G_{bb}(E)$ by the Kramers-Kronig integral relation.

Lawrance and Knight³ (LK) reformulated Berg's procedure and showed how it could be simplified in the case of fully resolved spectra to avoid the calculation of the singular Kramers-Kronig integral. This method is based upon expressing the energy Green's

function $G(E)$, in both the eigenvector and initial basis sets. By equating the $G_{bb}(E)$ matrix element in both basis sets, one gets

$$G_{bb}(E) = \sum_{k=1}^N \frac{I_k'}{\nu_k - E} = \left[e_b - E - \sum_{d=1}^{N-1} \frac{f_d^2}{e_d - E} \right]^{-1} \quad (2)$$

where the reduced intensities are given by

$$I_k' = I_k / \sum_{j=1}^N I_j$$

This can be rearranged to give

$$\sum_{d=1}^{N-1} \frac{f_d^2}{e_d - E} = e_b - E - \left[\sum_{k=1}^N \frac{I_k'}{\nu_k - E} \right]^{-1} \quad (3)$$

LK suggested putting in the experimental data (I_k' and ν_k) with some arbitrary damping width (ν_k replaced by $\nu_k + i\Gamma$) and evaluating the right-hand side of eq 3 as a function of E to find resonances corresponding to each of the e_d . This is somewhat problematic in that one must use a damping width Γ (and thus a calculated point spacing) much smaller than any of the observed energy level spacings to be sure the individual resonances are nonoverlapping and thus independent. The long tails of Lorentzian lines are particularly troublesome, causing shifts in the calculated peaks on the order of $\Gamma^2/(e_d - e_d')$. States with small f_d will require particularly small Γ not to be lost in the tails of other states since the intensity of the resonance scales as f_d^2 .

We note that the third term on the right-hand side of eq 3 must diverge in order that the left-hand side have a pole at $E = e_d$. Thus, the energies of the dark states e_d are the roots of the function $h_1(E)$ where in general

$$h_n(E) = \sum_{i=1}^N \frac{I_i'}{(\nu_i - E)^n} \quad (4)$$

This function has poles at each observed eigenvalue ν_i and is monotonically increasing in each interval $[\nu_i, \nu_{i+1}]$, and thus has one root in each of these $N - 1$ intervals, and these are the only roots. These roots can be found easily by the method of bisection. Referring to eq 3, it is clear that the residual of the pole at e_d is just f_d^2 ; thus

$$\frac{1}{f_d^2} = h_2(e_d) = \sum_{i=1}^N \frac{I_i'}{(\nu_i - e_d)^2} \quad (5)$$

The bright state energy can be calculated from the center of gravity of the observed transitions.

$$e_b = \sum_{k=1}^N I_k' \nu_k \quad (6)$$

The root mean coupling matrix element can be evaluated directly from

$$\sum_{d=1}^{N-1} f_d^2 = \sum_{k=1}^N I_k' (\nu_k - e_b)^2 \quad (7)$$

(1) Robinson, G. W.; Langhoff, C. A. *Chem. Phys.* 1974, 5, 1.

(2) Berg, J. O. *Chem. Phys. Lett.* 1976, 41, 547.

(3) Lawrance, W. D.; Knight, A. E. W. *J. Phys. Chem.* 1985, 89, 917.

We believe this formulation has a significant computational advantage over that suggested by LK. While either method can be used in practice, the present method is more robust, and the time required scales only logarithmically with required precision while that of LK scales linearly. Moreover, the present method allows one to propagate estimated errors and thus obtain uncertainties for the parameters. Since this is an exact inversion of the data, there is no redundancy, as in a least-squares fit, by which to estimate parameter uncertainty.

If we assume that the errors in the energies and intensities are independent, we can estimate the errors in the Hamiltonian parameters p_k by using

$$\sigma^2(p_k) = \sum_{i=1}^N \sigma^2(\nu_i) \left(\frac{\partial p_k}{\partial \nu_i} \right)^2 + \sigma^2(I_i) \left(\frac{\partial p_k}{\partial I_i} \right)^2$$

A reasonable model is for $\sigma^2(\nu_i) = \sigma^2(\nu)$ (i.e., constant), and $\sigma^2(I_i) = \sigma_1^2(I) + \sigma_2^2(I)I_i^2$ (due to a noise level, σ_1 , and an amplitude instabilities, σ_2). Thus, to first order one needs only the partial derivatives, which are

$$\begin{aligned} \frac{\partial e_b}{\partial \nu_k} &= I_k' & \frac{\partial e_b}{\partial I_k} &= \frac{\nu_k - e_b}{\sum I_i} \\ \frac{\partial \sum f_d^2}{\partial \nu_k} &= 2I_k'(\nu_k - e_b) & \frac{\partial \sum f_d^2}{\partial I_k} &= \frac{(\nu_k - e_b)^2 - \sum f_d^2}{\sum I_i} \\ \frac{\partial e_d}{\partial \nu_k} &= \frac{f_d^2 I_k'}{(\nu_k - e_d)^2} & \frac{\partial e_d}{\partial I_k} &= \frac{-\sum f_d^2}{(\sum I_i)(\nu_k - e_d)} \\ \frac{\partial f_d}{\partial \nu_k} &= f_d^3 \left[\frac{I_k'}{(\nu_k - e_d)^3} - \frac{f_d^2 I_k'}{(\nu_k - e_d)^2} h_3(e_d) \right] \\ \frac{\partial f_d}{\partial I_k} &= \frac{f_d^3}{2(\sum I_i)} \left[\frac{2f_d^2 h_3(e_d)}{\nu_k - e_d} + \frac{1}{f_d^2} - \frac{1}{(\nu_k - e_d)^2} \right] \quad (8) \end{aligned}$$

These first-order estimates for the errors are expected to be valid as long as the error bars for different dark states do not overlap. If that situation should occur, one has an avoided crossing inside the experimentally allowed parameter space, and perturbation estimates will not be valid. The errors for the mean square matrix element, however, will be only weakly affected since when two dark states cross, the individual matrix elements change rapidly, while the sum of the squares of the matrix elements do not.

A FORTRAN routine to perform the LK deconvolution and error estimation is available on request from the author.

In their reply to this Comment, Lawrance and Knight raise to important question as to what has been learned by this deconvolution procedure. I would like to add my own comments on this point. (a) The $\sum f_d^2$ is independent of a prediagonalization of the dark states and thus can in principle be compared with the same quantity calculated in any basis. In practice, one must be careful of states that have large f_d but are sufficiently off-resonance that they are not observed in the spectrum. (b) When one observes a spectrum as a function of rotational quantum number, and the tuning of states with J is sufficiently slow that the same dark states can be observed for several J 's, it is then possible to observe avoided crossings of the prediagonalized dark states and thus get information on the matrix elements between dark states. In our own work,⁴ we have found that running the deconvolution for each J provides a method to assign weak lines in the spectrum. (c) Work in the nuclear physics literature⁵ has shown that spectral statistics can be distorted near a resonance. Deconvolution, therefore, should be done prior to computing level spacing or other statistical properties of the spectrum.

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Reply to Comment on "Direct Deconvolution of Extensively Perturbed Spectra: The Singlet-Triplet Molecular Eigenstate Spectrum of Pyrazine"

Sir: The Comment by Lehmann concerning our method for the deconvolution of perturbed spectra via a Green's function inversion procedure suggests using a slightly different numerical procedure that leads to a useful formula for error estimation and hence the uncertainties in the model parameters. While we are supportive of this optional alternative method proposed by Lehmann, we are conscious that users of the Lawrence-Knight deconvolution procedure, with or without the Lehmann extension, be cognizant of its inherent limitations. We thus take the opportunity here to clarify the knowledge that one might hope to obtain by application of the procedure.

Lehmann points out correctly that one is quite free to choose a basis in which one has a single bright state coupled to a set of dark states that have been "prediagonalized". Thus, one is usually free to phrase the problem in such a way that the Hamiltonian suits the form required for the Green's function deconvolution. The issue of paramount concern, however, is to gauge *what has been learnt* by performing the deconvolution in such a case. In the case of intramolecular vibrational redistribution (IVR), for example, a natural factoring of the Hamiltonian separates it into (i) a harmonic part, (ii) an anharmonic part, and (iii) terms involving vibration-rotation coupling (e.g., Coriolis interactions). A bright state $|b\rangle$ would thus be coupled to the dark states $\{|d\rangle\}$ through anharmonic and vibration-rotation terms. Furthermore, the dark states would themselves be coupled together by these same kinds of terms.

Consider first a hypothetical procedure that would lead to a prediagonalized set of dark states $\{|f\rangle\}$ from a molecular manifold of states and a set of known coupling matrix elements. One would have to first remove the coupling elements V_{bd} of the dark states with the bright state (via anharmonic and vibration-rotation interaction terms) and then diagonalize the corresponding dark states Hamiltonian that would include the anharmonic and vibration-rotation interaction terms V_{df} coupling just the dark states with each other. From this procedure, one would obtain a set of "prediagonalized" dark states together with a transformation matrix for converting the original coupling terms V_{bd} between the bright and dark states to those appropriate to this new basis, i.e., V_{bf} .

Now consider what we learn from the reverse process, i.e., a deconvolution of the observed molecular eigenstate spectrum. One obtains the zero-order energy of the bright state, $|b\rangle$ the zero-order energies of the "prediagonalized" dark states $\{|f\rangle\}$, and the magnitudes of the coupling matrix elements V_{bf} connecting the bright state with each of the "prediagonalized" dark states. However, one cannot identify the coupling terms V_{bf} derived from the deconvolution procedure with particular terms V_{bd} (e.g., Coriolis or anharmonic, etc.) in the original Hamiltonian, since one does not know, and indeed cannot determine from the molecular eigenstate spectrum alone, the transformation from the original Hamiltonian to the one appropriate for the prediagonalized dark states. Furthermore, the original set of dark states $\{|d\rangle\}$ cannot be identified for the same reason.

(4) Pate, B. H.; Lehmann, K. K.; Scoles, G. *J. Chem. Phys.*, in press.

(5) Brody, T. A.; Mello, P. A.; Flores, J.; Bohigas, O. *Lett. Nuovo Cimento* 1973, 7, 707.