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Chapter 5

HIGH RESOLUTION VISIBLE OVERTONE SPECTROSCOPY: A SEARCH FOR INTRAMOLECULAR VIBRATIONAL RELAXATION

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A. INTRODUCTION

There is currently an intense interest in the character of highly excited vibrational states of polyatomic molecules. While understanding such states is a challenging problem in its own right, a description of such states is also an important contribution towards a deeper understanding of much of molecular dynamics. The most direct way to study highly excited vibrational states is by observing the overtone absorption spectra of hydrides. Transitions to states with 5–7 quanta of X–H vibration typically occur in the spectral range of currently available cw dye lasers and involve excitation to levels with about ~40% of an X–H dissociation energy. In this paper we will present a survey of results we have obtained in the high resolution spectroscopic study of several small hydrides. We will try to distill from these results some general conclusions about the nature of intramolecular vibrational relaxation in general. Before doing that, however, a digression into the meaning of intramolecular vibrational relaxation is necessary.

B. MODEL FOR INTRAMOLECULAR VIBRATIONAL RELAXATION (IVR)

We will now present a qualitative model for IVR. Although this problem has been treated in considerable detail in the literature, explanations based upon simple physical arguments have not been emphasized. The approach used here is virtually identical to qualitative treatments of intersystem crossing in excited electronic states. In particular, the review article by Freed [1] has been heavily relied upon, and is recommended to all interested readers. The analysis forms the basis for our claim that detailed spectroscopic study of small molecules is relevant to the problem of IVR in larger molecules.

Consider a state $<\alpha|$ that has a non-zero transition matrix element from the ground state. In an overtone transition, $<\alpha|$ will be a state with n quanta

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in the X–H stretch, and with perhaps a small number of quanta in some other mode for a combination band. The state $<\alpha|$, often called the doorway state or the bright state, is not an eigenstate of the Hamiltonian H for the molecule. It is nearly degenerate with a set of states labeled $<m|$. For convenience, we will choose the states $<m|$ such that they diagonalize H neglecting $<\alpha|$. Thus we may write

$$\left.\begin{aligned} H|\alpha> &= E_\alpha|\alpha> + \sum_m e_{\alpha m}|m> \\ H|m> &= E_m|m> + e_{\alpha m}|\alpha> \end{aligned}\right\} \qquad (1)$$

E_α and E_m are the expectation values for H in states $<\alpha|$ and $<m|$ respectively. This special choice of $<m|$ removes the complications of coupling between different dark states $<m|$ and $<m'|$. As long as we stay formal, and do not have to generate the states $<m|$, we are free to choose them however we wish. The effect of the couplings $e_{\alpha m}$ produce a set of eigenstates labeled $<\varphi|$. The absorption strength of a state $<\varphi|$ will be proportional to $|<a|\varphi>|^2$.

If all the couplings $e_{\alpha m} << |E_\alpha - E_m|$, then the couplings can be treated accurately by perturbation theory. One eigenstate will be essentially $<\alpha|$, and the other eigenstates will be essentially states $<m|$. The small amount of mixing will allow the eigenstates corresponding to $<m|$ to steal intensity proportional to $(e_{\alpha m}/(E_\alpha - E_m))^2$.

If a small number of states $|m>$ have $e_{\alpha m} \gtrsim |E_\alpha - E_m|$ then we have the situation depicted in Fig. 1a. Spectroscopists refer to such situations as a resonance between N levels. It is well known that perturbation expansions diverge in such cases and that one must diagonalize a N×N matrix of the N interacting states. If the interaction energy is less than the difference between rotational energy for the interacting states, then the states will only be in resonance over a small number of J,K values. This produces rotational perturbations in the spectrum. If the interaction energy is much larger than the difference in rotational energy, then the levels will interact by about the same amount for all J,K levels, and each eigenstate $<\varphi|$ will have a well behaved rotational structure. Thus we have extra complete vibrational bands, and this is referred to as a vibrational or Fermi perturbation. Intermediate cases are quite common. If all the eigenstates $<\varphi|$ involved in a resonance are measured, as well as the relative intensities, then it is, in principle, possible to 'deperturb' the levels, i.e. to recover the energies E_α, E_m, *and* $e_{\alpha m}$ from the experimental data. This becomes rapidly more difficult as N becomes larger than 2 because: (1) the number of constants to be determined increase and have a strongly non-linear dependence on the data; and (2) the simple spectroscopic patterns used to assign spectra break down and the spectroscopist does not know which quantum numbers to assign to the observed lines.

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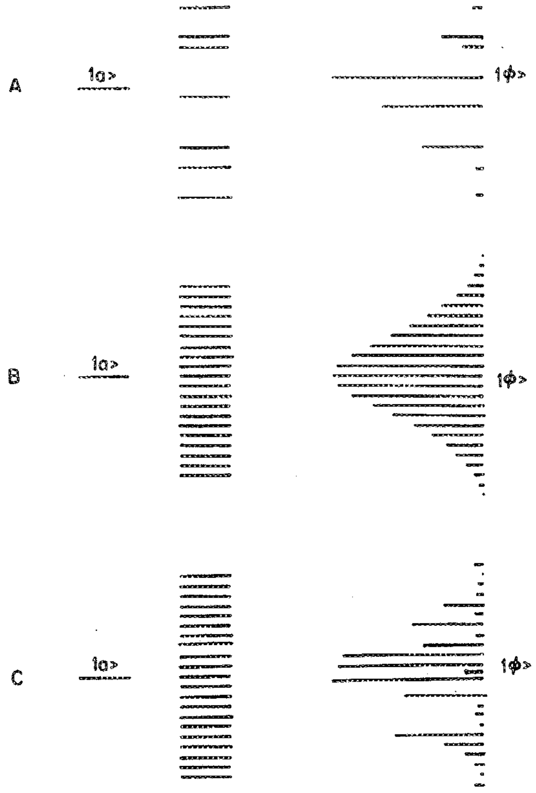

Figure 1 Intermolecular vibrational relaxation in the (A) small, (B) large, and (C) intermediate molecule cases as discussed in the text.

In the parlance of intramolecular relaxation, this limit of N strongly interacting states is referred to as the small molecule limit. As long as the density of strongly interacting states remains small enough that one can excite individual eigenstates of the system, the situation is referred to as the small molecule limit. In the field of electronic relaxation, NO_2 and SO_2 are standard examples of this type of behavior.

When the density of strongly interacting states exceeds the available resolution, then individual eigenstates cannot be prepared. This is referred to as the large molecule limit. In this limit, the full spectroscopic problem cannot be solved, so people resort to simple models. The Bixon–Jortner [2] (B–J) model has been widely used because of its analytic solution as well as its applicability in the case of spontaneous emission, a familiar example of relaxation. In this model, the states $<m|$ are taken to be equally spaced with a density of states ϱ. The coupling matrix elements are taken as a

constant e over the range of states that couple. By extending this constant density of states to $E_m = \pm\infty$, the eigenstates can be found exactly. The transition moments $|<a|\varphi>|^2$ are found to be distributed according to a Lorentzian curve with full width $e^2\varrho$. The absorption spectrum will be a smooth, structureless curve until the resolution exceeds the inverse of the density of states. The behavior of the B-J model is shown qualitatively in Fig. 1b.

The elegance of the B-J model hides its seriously unphysical assumptions. The extension of E_m to $\pm\infty$ results in a curve with an infinite second moment. Correcting this assumption would presumably only effect the far wings, not the important center of the curve. More important, the assumption of a constant $e_{\alpha m}$ is clearly incorrect. It is usually assumed that if the density of states is high enough, that some average $2\pi e^2(E_m)$ can be defined which will be a slowly varying function over the width of the resonance. We are unaware of any evidence that such a well behaved limit should be expected.

If we abandon the B-J model, we are left with the possibility as represented in Fig. 1c. A few states couple strongly to $<\alpha|$, a still larger class couple with a smaller magnitude, a still larger class with a still smaller coupling, etc. We can imagine that the ideal absorption curve, without inhomogenous broadening and with infinite resolution, would have an erratic shape up to arbitrary resolution until the intrinsic width of the states $|\varphi>$ is reached. Such a curve would be almost a fractal! We refer to this as the intermediate molecule case. It is our belief, based upon the results described later, that IVR in real molecular systems is probably much closer to this qualitative picture than that given by the B-J model.

Even in the general case, where no analytic solution exists, we can appeal to the theory of moments to gain insight. The absorption feature due to $<\alpha|$ will be centered around E_a. The next question to ask is: 'What is the variance of the absorption curve, which gives us the best general measure of its width?' The absorption curve is just a spectral distribution of the energy of state $<\alpha|$, so we can calculate the variance of the absorption curve by computing the uncertainty of the energy of state $<\alpha|$ by:

$$(\Delta H)^2 \equiv <\alpha|H^2|\alpha> - <\alpha|H|\alpha>^2 \tag{2}$$

Inserting a decomposition of unity in the middle of H^2 gives

$$(\Delta H)^2 = \Sigma e^2_{\alpha m} = \int_E e^2_{\alpha m}\varrho\,(E)\;\mathrm{dE} \tag{3}$$

For a given type of initial state, the expectation values of H and H^2 will be insensitive to the size of the molecule, but the density of states will increase exponentially with the number of degrees of freedom. Thus we have the result that the average $e^2_{\alpha m} \sim \varrho(E)^{-1}$ as the degrees of freedom increase. The

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expression for the linewidth of the B-J model have led many to assume that the rate of IVR must be fast for molecules with astronomical values for the density of states.

The above analysis shows that the width over which an absorption feature is spread (as defined by the second moment) is insensitive to the size of the molecule. Thus by characterizing the width over which appreciable mixing occurs for small polyatomics, we can characterize the magnitude that we expect for larger molecules. Furthermore, we can test whether or not there is any evidence that the coupling to the dark states $<m|$ can be meaningfully approximated by some type of average coupling.

It is important to perform these tests because large molecules do not yield much information directly, since they have tremendous inhomogenous broadening from the large number of vibration–rotation energy levels populated at ambient temperature. The high overtone transitions have been too weak to be seen in a supersonic expansion, but for one exceptional case.[3] When one convolutes a broad inhomogenous lineshape with the ideal absorption spectrum, one loses any ability to tell whether the molecule is a small, intermediate or large limit case.

The question of which case is appropriate to use for a particular molecule is not a matter of merely academic concern. For a molecule in the small, and to a lesser extent intermediate limit, the excitation will stay localized predominantly in the region of phase-space that characterizes the state $<\alpha|$. This will be especially the case if, as we believe, the states that couple strongly to $<\alpha|$ are those $<m|$ that are near to $<\alpha|$ in phase-space. This implies that the molecule may behave in a state specific way long after excitation for an intermediate case molecule, and indefinitely for a small case molecule.

In the large molecule limit, as pictured by the B-J model, the initially prepared state decays into the quantum analog of a classical microcanonical average over an energy surface at E_α. This implies that after excitation of $<\alpha|$, this nonstationary state will decay into something that behaves like a statistical distribution in phase-space.

The extensive work by Berry and co-workers[4] on benzene and its derivatives has become the standard for much of the experimental work on overtone spectroscopy. In these experiments, the linewidth of the overtone absorption features was observed to increase and then decrease with overtone number, with a maximum width of $\sim 100\,\mathrm{cm}^{-1}$ for the $\Delta v = 6$ transition. The results displayed very little sensitivity to either deuterium or fluorine substitution. This led those workers to assign the overtone linewidth as due to IVR into a dense 'heat bath' of other vibrational levels with a characteristic time of ~ 50 fs. This argument was supported by the initial observation of Lorentzian lineshapes, as predicted by the B-J model. Later observations, however, revealed that the lineshapes were in fact strongly non-Lorentzian. The observation that benzene does not have resolved rotational structure in its overtone bands is not surprising; even the fundamentals of benzene are not fully resolved in a Doppler broadened experiment. The observed overtone linewidths are much broader than expected for the unresolved rotational contours. Recently, Reinhard *et al.*[5] have been able to reproduce the observed benzene lineshapes as a function of overtone number by invoking a simple vibrational resonance between the overtone state, and a small number of other states. It still remains to be seen if the same simple mechanism also reproduces the lineshapes of the substituted benzenes that have been observed. It is clear, however, that the observations on benzene do not determine the character of the states into which the overtone state relaxes. Many other molecules have also been studied by low resolution overtone spectrosopy. Linewidths of $\sim 100\,\mathrm{cm}^{-1}$ appear almost universally. It is common to ascribe these linewidths to IVR, but since these molecules have been much less thoroughly studied than benzene and its derivatives, this interpretation is open to question. We have therefore chosen to study small molecules, which can be examined in very fine detail, in order to obtain a deeper understanding of the nature of IVR of the states prepared by overtone spectroscopy.

C. SPECTROSCOPY

We have examined the highly forbidden visible overtone spectra of simple hydrides by utilizing the great sensitivity of intracavity photoacoustic detection of the absorbed power of a cw dye laser. The laser spectrometer has been described in detail[6] so we will only summarize its features here. The spectrometer can obtain spectra of gas phase samples at a resolution limited by Doppler broadening, typically $\sim 0.04\,\mathrm{cm}^{-1}$ for the molecules we have studied. Unblended spectroscopic line centers can be determined with a precision of $\sim .001\,\mathrm{cm}^{-1}$, which corresponds to a fractional accuracy of 1 part in 10^7. The spectrometer is fully computer controlled and can take spectra over regions of hundreds of wavenumbers with almost no human intervention. Our noise equivalent absorption sensitivity is $\sim 10^{-9}$/cm of pathlength, letting us observe the $\nu_{C-H} = 5$ transition of acetylene with a signal-to-noise ratio of over one thousand to one.

We will now discuss the qualitative results for some of the molecules that we have studied.

1. HCN Results

We have observed spectra[6,7] of $H^{12}C^{14}N$, $H^{13}C^{14}N$ and $H^{12}C^{15}N$, detecting about five spectroscopic bands for each isotopically substituted molecule. All the observed bands can be fitted to a distortable rotor energy level expression to within the experimental uncertainty. The observed spectroscopic constants (ν_0B,D) for the upper vibrational states are in good agreement with those predicted by a simple anharmonic expansion. Calculations of the density of states reveals that each spectrally bright vibrational state crosses dark vibrational states approximately one hundred times as J varies over the range observed. The lack of any detectable rotational perturbations implies that the coupling matrix elements ($e_{\alpha m}$) must be less than 0.1 cm^{-1} for those $<m|$ that cross. Almost all the crossing levels have considerable excitation of the bending degrees of freedom. One vibrational resonance is observed in one isotope, with a coupling matrix element of ~ 20 cm^{-1}. This resonance is due to the fact that two quanta of C–H vibration is approximately equal in energy to three quanta of C–N vibration. This 2:3 resonance causes vibrational perturbations to appear sporadically throughout the HCN spectrum.

2. Acetylene Results

We have observed spectra of four isotopic species of acetylene,[8] $^{12}C_2H_2$, $^{13C}C_2H_2$, $^{12}C^{13}CH_2$, and $^{12}C_2HD$. In contrast to the results for HCN, almost every vibrational band of acetylene is perturbed at least once in its rotational progression. The density of levels of acetylene is such that the bright states must cross several thousand other states over the range of J observed. Thus the states causing the detected perturbations are a small fraction of the total set of states. We have reliable estimates of the energy for states with only stretching excitation, and we can rule them out as the cause of the perturbations. In those few cases where enough data exist to deperturb the spectra, we establish that the coupling strengths are 0.1 cm^{-1} or less, and that the rotational constants for the perturbing levels are close to that of the bright levels. This implies that the perturbing levels have only a small number of quanta of excitation in the bending modes. There are also many weak vibrational bands observed for which we have no vibrational assignments. These states must also have some amount of bending excitation, and are thus believed to obtain their intensity by stealing intensity from the strong stretching-only states. The fact that these levels are on the order of tens of wavenumbers away from stretching states and still have detectable intensity implies that the coupling strength for these small number of states must be much greater than 1 cm^{-1}.

3. Methane Results

We have observed spectra of CH_4 and CD_3H in the region where the $\nu_{C\text{-}H} = 6$ transition is expected. Both of these molecules have been studied before in this region,[9,10] but not with the resolution available with our spectrometer. For CD_3H we expected to find one band, but instead two almost equally intense bands are observed with origins at 16230 and

16156 cm^{-1}. The transitions are assigned as a strong vibrational resonance between the states $6\nu_1$ and $5\nu_1+2\nu_5$. At ambient temperature, the bands are badly overlapped and show poorly resolved K sub-band structure. Spectra were also taken at 77°K, greatly simplifying the spectra (see Fig. 2) by reducing the overlap of the bands and by lowering the Doppler width by a factor or two. Fits of the upper state rotational energies gave standard deviations of 0.020 and 0.008 cm^{-1}, much higher than the experimental uncertainties. The poor fits are due to the large number of weak rotational perturbations. Many of the observed lines show evidence for splitting at 77°K, as one line in Fig. 2 does.

The rotational constants for the two states are very different. Traditional arguments [11] state that when two states are in strong vibrational resonance, the observed rotational constants will be weighted averages of the rotational constants for the two unperturbed levels. Since the observed intensities imply almost 50–50 mixing of the two states, the observed rotational constants should be almost identical. The traditional argument assumes that the effective rotational constant operators have negligible matrix elements between the two unperturbed states. This obviously cannot be true in this case. The other striking thing about the observed rotational constants is that they are inconsistent with the known vibration-rotation interaction constants of CD_3H, suggesting that both states are involved in Coriolis resonance with some third unseen state or states lower in energy.

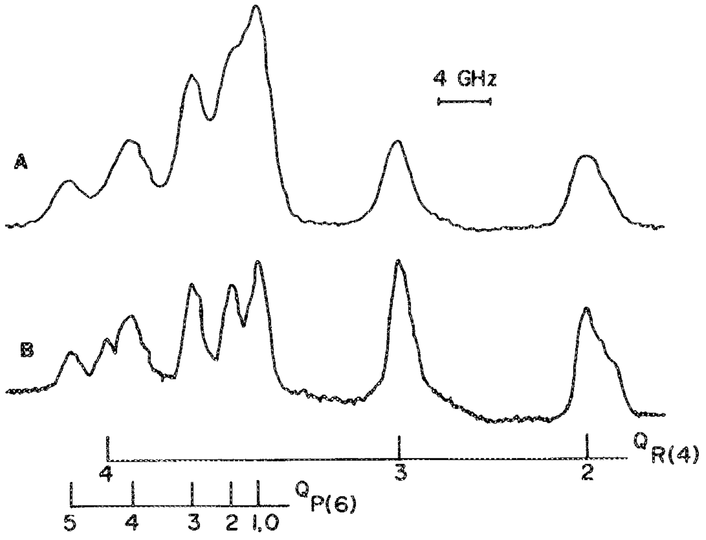

Figure 2 High resolution photoacoustic spectrum of CD_3H in region of 6 quanta of C–H vibration. The top trace is at room temperature and the bottom trace is at 77°K. The resolution in both spectra is dominated by Doppler broadening. *Reproduced from Scherer, Lehmann and Klemperer*, Journal of Chemical Physics, *1984, 81*, by permission of the American Institute of Physics.

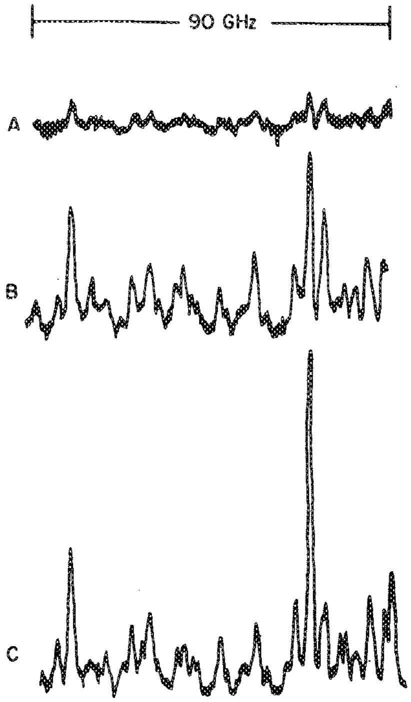

Figure 3 High resolution photoacoustic spectrum of CH_4 in region of 6 quanta of C–H vibration. Conditions are (A) room temperature, (B) 196 °K, (C) 77°K. *Reproduced from Scherer, Lehmann and Klemperer*, Journal of Chemical Physics, *1984, 81, by permission of the American Institute of Physics.*

At 300°K, the spectrum of CH_4 in this region is a bumpy continuum, with a few sharp features sticking above the baseline. At 77°K, the spectrum simplifies greatly and is almost fully resolved. Fig. 3 shows a small portion of the observed spectrum at three temperatures—77, 200° and 300°K. Attempts are currently under way to assign the 77°K spectrum. It is clear that many vibrational bands are overlapping in this region but that this number of interacting states is insignificant compared to the number of CH_4 states in the energy region covered by the bands, $\sim 100\,\mathrm{cm}^{-1}$. A final comment on the CH_4 spectrum is that it simplifies drastically in going from 300° to 200°K. This is suggestive that the high J states contribute disproportionately to the complexity. This is reasonable if Coriolis interactions dominate the state to state couplings since these interactions increase with J.

4. Hydrazoic Acid Results

We have examined spectra of the molecule HN_3 in the region of 5 and 6 quanta of ν_{N-H}. At high resolution the spectra are very complicated and we have only assigned part of the K = 0 subband. This is in large part due to rotational congestion, but many small perturbations are evident in the spectrum. At a resolution of 0.3 cm^{-1}, the overtone bands display regular rotational band contours, implying that the perturbations are small. The $6\nu_{N\text{-}H}$ state is above the best estimate[12] for the dissociation energy into NH ($^1\Delta$) and N_2. In contrast to this work, HN_3 has been shown to undergo collisionless multiphoton dissociation when pumped by a CO_2 laser.[13] The quasicontinuum model for multiphoton absorption assumes rapid IVR in the pumped molecule as it climbs the vibrational ladder. The overtone spectra imply that for at least some of the high lying states of HN_3, rapid IVR does not occur.

D. CONCLUSIONS

The results we have obtained on small molecules are strongly suggestive that the Bixon–Jortner model of IVR is not appropriate for understanding the relaxation of states produced when high lying hydrogen stretching overtones are pumped. The interactions of the overtone state with the manifold of other vibrational states display very strong selection rules. Very large interactions (~ 100 cm^{-1}) occur only for states that have similar quantum numbers. As we decrease the magnitude of the coupling, the density of perturbations grows but still a small fraction of the available states is involved. This implies that statistical pictures for the interactions will be misleading and can therefore lead to incorrect predictions. We close by stating that we believe this work makes the prospects of state specific chemistry much more favorable than it has appeared to be, based upon the interpretation of previous experiments.

E. POST-SCRIPT (AUGUST 1985)

This article was written in August, 1983, and reflects our thinking as of that date. In the last 2 years, new experimental evidence has shown that the simple behavior that we observed in the overtone experiments just discussed is but one of the many behaviors that real molecules display in highly excited vibrational states. We believe the most important experiments in this field have been done by Field, Kinsey and co-workers[14] who were the first to document statistical types of IVR. They used the technique of stimulated emission pumping to selectively populate highly excited vibrational states of C_2H_2 and H_2CO. KKL is currently using the newly developed technique of microwave detected, microwave-optical double resonance to assign the overtone bands of NH_3.[15] This technique is also being used to characterize IVR in the spectrum of NO_2.[16] The results on NH_3 overtones indicate that almost every optical transition is broken up into several lines spread over one or two wavenumbers. The density of observed perturbing levels is larger than the harmonic prediction for the total density of vibrational states. Therefore, we conclude that no selection rules hold in the perturbations, and that the eigenstates are spread over phase-space in a statistical fashion. The width over which lines are spread, the 'homogeneous' broadening for this small molecule, is a factor of 50 less than has been routinely attributed to the homogeneous width of many larger molecules. It is interesting to note that the overtone spectrum of NH_3 displays statistical behavior while the overtone spectra of C_2H_2 and CD_3H display regular behavior and yet these molecules have densities of vibrational states much higher than that of NH_3. We also note that the line density and width of the observed transitions increase only weakly with J, implying that the dominant coupling is due to anharmonicity, not Coriolis or centripital interactions which increase rapidly with J.

These, and other experiments continue to mature our understanding of highly excited vibrational states. It is clear at this point that no single model will be adequate for all molecules, and that the many subtle behaviors that molecules may display require sensitive and selective experimental techniques to unravel. Double resonance methods hold the most promise for accomplishing these goals.

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