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Double resonance spectroscopy reveals structure and dynamics near transition states

Joshua H. Baraban & Robert W. Field

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A shared ambition of molecular spectroscopy and molecular dynamics is to establish the truths of chemical intuition on solid physical bedrock. Experimental characterization of the transition state was thought unattainable, but modern techniques have begun to achieve the incredible.

What is meant by direct observation of a transition state? For a dissociation reaction, it is characterization of the minimum energy path toward the molecular configuration at which a specific bond (to be determined) breaks, the instantaneous structure of each of the nascent fragments, and the energy of the bond-breaking transition state above the equilibrium structure. These are classical mechanical questions asked in a quantum mechanical world.

Why is this difficult? It demands mastery of four aspects: (i) spectroscopic access to (or toward) the molecular geometry of the transition state, which is inevitably far from the equilibrium structure; (ii) determination of the correlated appearances of the about-to-separate fragments; (iii) resolution and (iv) assignment of transitions in an energy region of high state-density and broken patterns as the bound vibrational mode structure evolves from that of the intact molecule to the unbound regime of fragments. "Assignment" is based on pattern-recognition and requires extension of energy level patterns (vibrational normal modes) that are well-defined at small displacements from equilibrium structure but become obscured by increases in both complexity and density as chemically relevant energies are reached. Sets of coupled states ("polyads")[1] feature prominently in this evolution. It is far from obvious that assignment-based analysis and understanding of such spectra are even possible, let alone that they would yield direct information about transition states.

Quantum chemical calculations provide guidance. They tell the experimentalist about the potential energy surface and the properties of its stationary points, and furthermore can simulate dynamics that reveal which bond will break, and which vibrational modes will be most sensitive to the approach toward the transition state. Yet, overall, they can only indicate what to look for but not how to find it.

Rigorous, small-amplitude, ball-and-spring models of molecular vibrations[2] cannot describe large-amplitude chemical dynamics. Even the most advanced quantum mechanical models fail when asked to extend the description of small amplitude intra-molecular harmonic motions at low energies to higher energies where bonds break and molecules change their shapes[1]. Nevertheless, all chemists know that, somehow, the finite number ($3N$-6 where N is the number of atoms) of vibrational normal modes must give birth to a single reaction path en route from a stable molecule to products. The recent work by Kim et al.[3] is a beautiful example of how a symbiosis of sophisticated frequency and time domain spectroscopic techniques can illuminate the behavior of molecules near transition states.

Their study concerns predissociation of deuterated methylamine ND_2CH_3 on its S_1 potential energy surface[4], where electronically excited molecules traverse a reaction barrier en route to a conical intersection that leads to dissociation on the ground potential energy surface. One-dimensional potentials for the S_1 and S_0 electronic states were computed by scanning one of the two N-D bond lengths of the molecular structure frozen at that of the minimum of the 15-dimensional S_1 potential surface. This type of reduced-dimension computation focuses attention on the region of large amplitude motions near the minimum energy path to N-D dissociation. This reduced representation is particularly valuable because it corresponds to what the Kim et al.[3] state-of-the-art experiments sample spectroscopically and dynamically. Note that the barrier on the adiabatic 1-D S_1 potential curve is only 1500 cm^{-1}. This is thus a relatively low-barrier problem in which all but the reactive vibrational mode can be treated as near-harmonic and the density of vibrational levels is sufficiently small that statistical Intramolecular Vibrational Redistribution (IVR)[5] is negligible.

The inherent complexity of molecular vibrations increases combinatorially with molecular size and exponentially with excitation energy, leading to spectra too dense and complex to assign and, eventually, to partially chaotic dynamics. Accordingly, spectroscopists have long utilized so-called double- (or multiple-) resonance (DR) techniques, by which selected combinations of transitions reveal the quantum mechanical secrets hidden in conventional single-resonance spectra. DR methods are more powerful than the sum of their single-transition ancestors. They allow access to new classes of states and to qualitatively different recognition and analysis capabilities via the tremendous simplification and assignment information inherent in DR schemes.

A classic example of the power of DR is Stimulated Emission Pumping (SEP), where an upward and downward pair of electronic transitions circumvents restrictive vibrational selection rules to yield, via strongly non-diagonal Franck-Condon factors, systematic characterization of potential energy surfaces via spectral simplification, even at high vibrational excitation[6,7]. The IR-UV DR schemes employed by Kim et al.[3] share two important advantages with SEP: (i) they provide access to vibrational levels of the final state that would otherwise be dark in a single resonance experiment; (ii) they filter the subset of spectra chosen for access, selected systematically by the choice of the initially selected IR rovibrational transition. IR-UV and SEP DR methods have enabled the exploration and decoding of complex excited electronic state dynamics in acetylene[8] and sulfur dioxide[9], for example.

Two classes of DR spectra were recorded by Kim et al. to sensitively and selectively map the vibrational levels of both electronic states needed to explore the predissociation dynamics. Both are Double Resonance Three-Photon Ionization (DR3PI) spectra: fixed-UV, scanned-IR, and fixed-IR, scanned-UV. The rotational structure of the

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S_0 $v'' = 1$ level of the antisymmetric N-D stretching mode, v_{11}'', is obtained by fixing the UV laser at the known frequency of $2+1$ photoionization of a free D atom, while the IR laser is tuned through the ND_2CH_3 v_{11}'' band. In this scheme, the fixed frequency UV laser performs two functions: N-D photodissociation of the parent molecule from the S_0 $v_{11}'' = 1$ level (the UV laser frequency is too low to photodissociate ND_2CH_3 from its S_0 zero-point level) and creating the detected D^+ ion. This scheme is vastly more sensitive than either detection by direct absorption of the pulsed IR laser or by IR-induced fluorescence. The rotational (J',K') and methyl-rotor $(14 \geq m \geq 0)$ structure of the S_1 $v' = 0$ vibronic level is recorded when the frequency-scanned UV laser excites transitions out of rotationally assigned levels of the S_0 $v_{11}'' = 1$ level and then from this assigned S_1 (J', K', m) level to produce detected $ND_2CH_3^+$ ions.

A related but distinct experimental approach led to the seminal discovery of the "roaming" reaction mechanism[10], where two experimentally chosen photon energies were combined with measured fragment kinetic energies, revealing an unexpected class of reaction dynamics that does not proceed via a transition state. In the case of H_2CO, the first photon excites the parent molecule to a predissociated vibrational level of an electronically excited rovibronic state of H_2CO. The second photon probes the rotation-vibration population distribution in the CO $X\ ^1\Sigma^+$ photofragment via $1+1$ photoionization, and the velocity distribution of each CO^+ (v,J) level (measured in a multiplexed manner by velocity map imaging (VMI)) of the CO^+ fragment determines the (v,J) population distribution in the H_2 co-fragment. The measured $[(v,J)_{CO}, (v,J)_{H2}]$ correlated population distributions sample the microscopic H_2CO predissociation dynamics, revealing a reaction mechanism for which no traditional transition state exists.

Transition states themselves were considered impossible-to-characterize extremely short-lived activated complexes. In ref. [11], building on a century of prior work on the lowest excited singlet electronic state of acetylene by several research groups, we and our collaborators succeeded in determining properties of its S_1 *trans–cis* isomerization transition state from frequency domain spectra by careful and comprehensive application of DR methods[8]. Those experiments revealed a new type of spectral pattern in which transition state information is encoded as dips in the quantum level spacings for vibrational motions with non-zero projections along the isomerization reaction coordinate. Nevertheless, this has been achieved only for two small, exhaustively studied molecules, HCN and HCCH.

Kim and co-workers have propelled the field of transition state spectroscopy forward with a leap from HCN-HNC and *trans–cis* C_2H_2 isomerization to the predissociation mechanism of a much more complex molecule. By using two classes of IR-UV DR spectroscopy, the authors obtained clear spectra sorted to reveal excitation in the -CH_3 internal rotation. These spectra reveal a dip in the methyl rotation frequency in the S_1 excited state at the same energy at which their pump-probe measurements show a sharp increase in the dissociation rate.

The anharmonic communication between the methyl rotation and the N-D dissociation (via the antisymmetric N-D stretching vibration) allows the extraction of information about the transition state. It would be interesting to juxtapose these results with the state-selected VMI studies of Bar and co-workers that probed dissociation fragments of methylamine[12,13]. What is astonishing about the work of Kim et al. is the dramatic increase in molecule size (by nearly a factor of three over the previous state-of-the-art), which forced the authors to analyze an artfully reduced data set to extract the dynamically relevant information, and then elegantly relate the spectroscopic analysis to the direct time-domain pump-probe measurements of the dissociation dynamics. This achievement demonstrates that transition states can be characterized by chemical processes in a wide range of molecules. We are convinced that the synergistic approach demonstrated by Kim et al., innovatively combining the virtues of double resonance spectroscopy with dynamics-oriented techniques, holds significant promise for expanding our physical understanding of chemical reactions.

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R.W.F. and J.H.B. co-authored this Comment.

Competing interests
The authors declare no competing interests.

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