physicochemical characterization of isomerization states


Transition state theory is central to our understanding of chemical reaction dynamics. We demonstrate the method for extracting transition state energies and properties from a characteristic pattern found in frequency-domain spectra of isomerizing systems. This pattern—a dip in the spacings of certain barrier-proximal vibrational levels—can be understood using the concept of effective frequency, . The method is applied to the cis-trans conformational change in the S3 state of C2H2 and the bond-breaking HCN–HNC isomerization. In both cases, the barrier heights derived from spectroscopic data agree extremely well with previous ab initio calculations. We also show that it is possible to distinguish between vibrational modes that are actively involved in the isomerization process and those that are passive bystanders.

The central concept of the transition state in chemical kinetics is familiar to all students of chemistry. Since its inception by Arrhenius (1) and later development in a full theory by Eyring, Wigner, Polanyi, and Evans (2–5), the idea that the thermal rate depends primarily on the highest point along the lowest-energy path from reactants to products has remained essentially unchanged. Most of chemical kinetics is now firmly based on this idea of the transition state, notwithstanding the emergence of unusual features such as one-dimensional heating (6), where a photodissociated atom wanders before abstracting from the parent fragment. Despite the clear importance of the transition state to the field of chemistry, direct experimental studies of the transition state and its properties are scarce (6).

We report the observation of a vibrational pattern, a dip in the trend of quantum level spacings, which occurs at the energy of the saddle point. This phenomenon is expected to provide a generally applicable and accurate method for characterizing transition states. Only a subset of vibrational states exhibit a dip; these states contain excitation along the reaction coordinate and are barrier-proximal, meaning that they are more

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susceptible than other states to the effects of the isomerization barrier. Experimental evidence for this concept is drawn from our studies of two prototypical systems: the HCN → HNC isomerization and the cis-trans conformational change in the first electronically excited singlet state of acetylene.

Effective frequency and the isomerization dip

The effective frequency \( \omega_{\text{eff}} \) is the central quantity in our model for the spectroscopic signature of isomerizing systems. In a one-dimensional system, the effective frequency is the derivative of the energy with respect to the quantum number \( n \),

\[
\omega_{\text{eff}}(n) = \frac{\partial E}{\partial n} - \frac{\Delta E}{\Delta n}
\]

(1)

where \( \omega_{\text{eff}} \) is evaluated discretely for quantized systems. \( \omega_{\text{eff}} \) is a dynamic quantity that can change as excitation increases, unlike quantities such as harmonic frequency, \( \omega_0 \), or fundamental frequency, \( \nu \), which are often listed as molecular constants. As such, it is a useful diagnostic of the behavior of the system.

Applications of effective frequency date back a long way. For example, the effective frequencies \( \omega_{\text{eff}}(n) \) of a state of a diatomic molecule are its vibrational intervals, which decrease to zero at the dissociation limit. The sum of the effective frequencies is therefore the dissociation energy. In most cases it is not possible to observe \( \omega_{\text{eff}}(n) \) all the way to the dissociation limit, but a linear extrapolation to \( \omega_{\text{eff}} = 0 \) allows a very good estimate of the dissociation energy, notwithstanding nonlinearities in the trend of vibrational intervals near dissociation. This is the basis of the Birge-Sponer plot (4) where the area under a graph of the vibrational intervals, \( \omega_{\text{eff}}(n) \), against \( n \) gives the dissociation energy. Leroy and Bernstein (10) have given a protocol for extrapolating the effective frequencies, which takes account of the exact long-range shape of the vibrational potential near dissociation. This procedure is found to give very accurate dissociation energies (11).

Effective frequencies also play a large part in our understanding of quasi-linear molecules. A quasi-linear molecule has a nonlinear equilibrium geometry but a comparatively small potential barrier to linearity. The pattern of the lowest vibrational levels is that of a bent molecule, but with increasing bending vibrational excitation, this changes smoothly into the pattern for a linear molecule, vibrating with large amplitude. Dixon (12) modeled a quasi-linear potential as a two-dimensional harmonic oscillator perturbed by a Gaussian hump at the linear configuration, and calculated its energy levels. These levels may be assigned vibrational (\( \nu \)) and angular momentum (\( K \)) quantum numbers (13). If the vibrational intervals (effective frequencies) for a given \( K \) value are plotted against \( \nu \), they pass through a minimum at the energy of the potential barrier, thereby allowing determination of its value. The depth of this “Dixon dip” is greatest for \( K = 0 \) and decreases with increasing \( K \). The reason is that the angular momentum results in a \( K \)-dependent centrifugal barrier at the linear configuration, which the molecule must avoid.

We now illustrate the concept of effective frequency in more detail, with the four types of potential shown in Fig. 1. For the harmonic oscillator,

\[
\omega_{\text{eff}} = \frac{\partial}{\partial n} \left[ \omega \left( n + \frac{1}{2} \right) \right] = \omega
\]

(2a)

and

\[
\frac{\partial \omega_{\text{eff}}}{\partial n} = 0
\]

(2b)

indicating that the dynamics of the system do not change as a function of energy. For a Morse oscillator, the potential is \( V(r) = D_c \left[ 1 - \exp(-a r) \right]^2 \), where \( D_c \) is the dissociation energy, \( a \) is a length parameter, and \( r \) is the bond length displacement. In this case,

\[
\omega_{\text{eff}} = \frac{\partial}{\partial n} \left[ \omega \left( n + \frac{1}{2} \right) + a \left( n + \frac{1}{2} \right)^2 \right] = \omega + x + 2 n x
\]

(3a)

and

\[
\frac{\partial \omega_{\text{eff}}}{\partial n} = 2 x
\]

(3b)

where \( x \) is always negative. This linear decrease of \( \omega_{\text{eff}} \) with \( n \) reflects the migration of the Morse wave functions toward the softer outer turning point. When \( \omega_{\text{eff}} \) reaches zero at the dissociation limit, it becomes clear that the Morse and harmonic oscillators display very different dynamics. Simple expressions for \( \omega_{\text{eff}} \) and \( \frac{\partial \omega_{\text{eff}}}{\partial n} \) cannot be derived for the other cases in Fig. 1, but these illustrate the most important feature even more clearly: The effective frequency goes to zero at the energy of each stationary point on the potential. Classically, this can be understood by imagining a ball released to roll on a double-minimum surface. If the ball starts on one side at exactly the height of a local maximum, it will reach that maximum with zero kinetic energy and stop. Because the ball never returns, the oscillation period is infinite and the frequency is therefore zero. We see immediately that this applies to the Morse oscillator as well: \( \omega_{\text{eff}} \) reaches zero at the dissociation limit, which is a horizontal asymptote of \( V(r) \). It is clear that this phenomenon is quite general and that zeros or
abrupt changes in $\omega^m$ signal important changes in the dynamics of the system.

In their quantum and semiclassical analysis of highly excited states of HCP, Jacobson and Child (14) mentioned a dip in $\omega^m$ as the signature of an approach to a saddle point. Because the HCP $\rightarrow$ HPC potential energy surface exhibits some unusual features (HPC is a saddle point rather than a second minimum) and is not a true isomerization (15), the observed $\omega^m$ trend was categorized as a peculiar “Dixon dip” rather than being recognized as the universal signature proposed here. Similarly, the onset of internal rotation in the ground state of SiC$_2$ (16) is not an isomerization, although the ideas presented here are applicable to it. More generally, the behavior of systems as they encounter stationary points has been investigated from other perspectives as well (17-20). For our purposes, it suffices that this dip in $\omega^m$ provides a marker of the chemically relevant transition state energy, as we demonstrate below.

**A model for measurement of the transition state energy**

To determine the transition state energy, we propose the following semiempirical formula for $\omega^m$ as a function of energy, $\bar{E}$, defined as the midpoint energy for each vibrational interval:

$$\omega^m(\bar{E}) = \omega_0 \left( 1 - \frac{\bar{E}}{E_{TS}} \right)^{1/m}$$

where $\omega_0$, $E_{TS} \geq 0$; $2 \leq m \leq \infty$; $\bar{E} \leq E_{TS}$ (4)

This expression is clearly similar to our effective frequency formula, but the two models treat essentially disjoint classes of potentials. For inverse power-law potentials where stationary points are local maxima and are therefore approached exponentially (i.e., faster than any power law) and is in some sense simultaneously long-range and local. Graphically, the dynamical distinction corresponds to positive curvature (LeRoy-Bernstein) versus negative curvature (our model) on a Birge-Sponer plot, with the linear plot of the Morse oscillator dividing the two distinct energy regions (19, 24).

A semiclassical analysis of long-range interatomic potentials of the form $D - (C/r^n)$ was performed by LeRoy and Bernstein (10) more than 40 years ago. They derived an expression that relates the change in energy per quantum number (i.e., the effective frequency) near the dissociation limit to a quantity proportional to $\left(1 - (E/D)^{n-2}/2m\right)$.

This expression is clearly similar to our effective frequency formula, but the two models treat dynamically and mathematically distinct regimes. For inverse power-law potentials where $n = \{1, 2, 3, 4, \ldots\}$, the corresponding $m$ values are $\{1/3, 1/5, 1/7, \ldots\}$. In the limit $n \rightarrow \infty$, the effective $m$ value approaches 2 from below. In contrast, our model has a lower limit of $m = 2$. In other words, these two similar effective frequency expressions treat essentially disjoint classes of potentials. The key difference is how the stationary point (or dissociation limit) is approached. For long-range potentials with inverse power-law forms, the stationary point at $r \rightarrow \infty$ is approached only polynomially. Our treatment considers potentials where stationary points are local maxima and are therefore approached over a finite domain. The common system, the Morse potential, has a stationary point at $r \rightarrow \infty$ but approaches it exponentially (i.e., faster than any power law) and is in some sense simultaneously long-range and local.

**Practical application**

What is the best way to extract the desired saddle point energy from spectroscopically measured quantities? From the frequency-domain spectrum we measure the energies of a series of quantized vibrational levels, and take the average $\bar{E}$ and...
The examples of S0 HCN ↔ HNC and S1 C2H2

The potential surface for the electronic ground state of the [H,C,N] system has two minima: the linear HCN and HNC isomers, separated by approximately 5200 cm\(^{-1}\). The reaction coordinate of the bond-breaking HCN-HNC isomerization corresponds mainly to the \(v_2\) bending vibration, and the barrier to isomerization is nearly 17,000 cm\(^{-1}\) above the HCN minimum. Extensive experimental term values for both isomers are available up to 10,000 cm\(^{-1}\) above the HCN minimum (26). To continue the analysis up to and beyond the barrier energy, we used spectroscopically assigned ab initio eigenenergies (26–28). In (26), levels with high bending excitation were reported to deviate unexpectedly from effective Hamiltonian predictions, reflecting the presence of the double-well potential.

The S\(_1\) state of C\(_2\)H\(_2\) supports cis and trans conformers, with the cis conformer lying about 2672 cm\(^{-1}\) above the trans. As illustrated in Fig. 3, the transition state is planar and nearly half-linear (29). The bare saddle point energy is calculated to be 4979 cm\(^{-1}\) above the trans minimum, but with an uncertainty of hundreds of cm\(^{-1}\), even for the most accurate calculations to date (30). A torsional isomerization path might have been expected on the basis of cis-trans isomerizations in other molecules, but this is not found here.

The height of the barrier relative to the fundamental frequencies leads us to expect at least some normal vibrational structure, even in the shallower cis well. Thus far, several cis vibrational levels have been identified, in reasonable agreement with ab initio calculations (31–33). In the trans well, almost all of the vibrational levels below the barrier have been assigned (33). Of the six trans conformer vibrational modes, four are fairly well behaved: the Franck-Condon active vibrations \(v_2\) (CC stretch) and \(v_3\) (trans bend) (34), and the CH stretching modes \(v_1\) and \(v_5\) (35, 36). On the other hand, a large portion of the trans vibrational manifold can only be understood within the framework of bending polyads \(\omega_{2n}\) (37), because of the Darling-Dennison and Coriolis interactions between the low-frequency ungerade bending modes, \(v_3\) (torsion) and \(v_6\) (cis bend).

Despite the success of the polyad model in reproducing the level structures associated with the bending vibrations, there are disturbing exceptions. As illustrated in figure 13 of (38), the series of \(3^4\) \(B^4\) polyads exhibits a surprising trend, with the energy of the lowest member of the polyad decreasing rapidly relative to the energies of the other polyad members. Although inexplicable by conventional models, this occurrence turns out to be intimately related to the isomerization dynamics discussed here.

Determination of the barrier height

We now apply the isomerization dip concept, and in particular Eq. 4, to the barrier proximal energy levels discussed above. Figure 4 shows the results of the pure bending \(\omega_{36}^\text{eff}\) effective frequency analysis for HCN-HNC. The barrier heights for both wells are found to be within 1% of the ab initio values. To compare \(E_{TS}\) to calculated barrier heights, either the ab initio zero point energy must be subtracted from the calculated barrier height, or an effective zero point energy must be added to the fitted \(E_{TS}\) value (see supplementary text). A consistency check of the HCN-HNC analysis stems from another dynamical parameter that affects \(\omega_{36}^\text{eff}\) and the effective barrier height: the vibrational angular momentum, \(\ell\). The fitted \(E_{TS}\) barrier heights are summarized in table S5 and, as expected, the barrier height increases approximately quadratically with \(\ell\).

Figure 5A shows plots of \(\omega_{36}^\text{eff}\) and \(\omega_{36}^\text{eff}\) for the \(3^6\) series of C\(_2\)H\(_2\) where Eq. 4 can be seen to fit the observed data very well (see tables S1 and S2 for details of the fits). The \(3^6\) levels experience the effects of the barrier most strongly, whereas the \(3^5\) levels are completely uninfluenced by it, because a combination of \(q_3\) and \(q_6\) is required to access the transition state geometry. Both \(\omega_{36}^\text{eff}\) and \(\omega_{36}^\text{eff}\) can be obtained as a function of \(v_6\) as well, reading the array of term values in table S2 horizontally rather than vertically. The same \((E, \omega_{36}^\text{eff})\) data are obtained, but in different sets.

Reaction path analysis

Several possibilities arise when the \(\omega_{36}^\text{eff}\) analysis is extended to additional vibrational progressions. The first, shown in Fig. 5C, is that of differentiating between isomerization pathways. We
have noted already that certain progressions, such as the 3" of trans-C₂H₅, show no sign of an isomerization dip. Here we see that surprising-ly, the 3" levels exhibit the same ωₓₓ as the 3', from which we conclude that the torsional cis-trans isomerization pathway is closed at these energies. This observation is consistent with the harmonic behavior in ν₄ noted in (37). Furthermore, the very strong interactions between ν₄ and ν₈ as well as the inevitable evolution of the torsion as the molecule straightens, would have led us to predict some kind of non-linear behavior of the ωₓₓ from the 3" levels. The absence of any such effects implies that the torsion is a spectator mode independent of the isomerization occurring in ν₄ and ν₈. Unlike in many other molecules, torsion does not play a role in this cis-trans isomerization. It appears that the residual π bond, despite its incomplete complement of substituents, leads to the preference for in-plane isomerization (Fig. 3).

The clear distinction between spectator modes and isomerizing modes suggests that other properties of the saddle point may be obtainable from ωₓₓ analysis. Consider a separable system that consists of an asymmetric double minimum in x and a harmonic oscillator in y: V(x, y) = V(x) + (kₚy²/2). Because the Hamiltonian is separable, E = Eₓ + Eᵧ, and therefore ωₓₓ does not depend on y, in the same way that ωₓₓ does not depend on ν₄ in trans-S₁ C₂H₅. This means that the ωₓₓ of the transition state is unchanged from that of the minimum. We can then imagine a case where (x²∂²V(x, y)/∂y²) varies with x. In such a case it is possible to extract a value for ωₓₓ of the transition state from the spacing of the ωₓₓ curves, or by plotting ωₓₓ directly, including data from above the saddle point energy (39). To give a specific example from a rotational degree of freedom, a quartic fit of the ε-dependence of the ωₓₓ HCN barrier height (table S5) yields (Α - B)ₓₓ = 11.1 (±0.9) cm⁻¹ for the transition state, which agrees well with the ab initio value of 12.2 cm⁻¹. These hitherto unmeasurable transition state rotational constants and frequencies, in addition to the saddle point energy, are critical inputs to the expression for the rate constant in transition state theory (2).

The ideas about spectator modes articulated here are confirmed by analysis of the HCN-HNC stretching mode progressions; neither shows any dip up to 18,000 cm⁻¹ above the HCN minimum. Furthermore, the shifts in the fitted barrier heights for ν₄ progressions built upon excitation in ν₅ and ν₆ match well with the one-dimensional pseudo-potentials Vₓₓ(x,y) (from 40–42) and the stretching frequencies (table S4).

Implications and outlook
The method described here provides qualitative and quantitative information about the isomerization mechanism and the transition state solely on the basis of experimental data. The reaction coordinate can be identified from the isomerization dips shown by active vibrations, and quantitative information about the energy, vibrational frequencies, and rotational constants of the transition state becomes available. It is especially promising that this analysis stems entirely from a small subset of the vibrational levels; in other words, a full vibrational analysis is not necessary. Special states exist that encode chemically important information, although it may not always be easy to recognize them.

The most exciting outcome of the excellent fits using Eq. 4 is the determination of the transition state energies. The uncertainties in Eₜₛ are at least as good as what is currently available from theory. In many cases, experiments might only confirm theoretical predictions, but we expect them to sharpen our understanding, and the potential value of our method goes well beyond validating theory. For example, we envision that this approach is a step toward establishing kinet-ics on the same firm experimental foundation as that already enjoyed by thermochemistry, where precise information is broadly available. This could aid in modeling complex reaction net-works as well as provide benchmarks for theoretical calculations.

The next stages in developing the concepts of isomerization dip and effective frequency will require more experimental data for model sys-tems as well as refinement of the basic ideas. For example, it is clear that ωₓₓ is a multidimensional quantity, which could be treated by suitable mul-tidimensional analysis. However, it is not yet clear how to define E in many dimensions. On the experimental side, the MgNC ↔ MgCN isomerization (43) is similar to HCN ↔ HNC, although with a much lower barrier; with higher resolution and a harmonic oscillator in x, one could more easily recognize the important information, although it may not always be learned, and partly it is because the spectra rapidly become very complicated at such ener-gies, so it is difficult to recognize the important patterns. In time it is likely that new classes of experiments will sample the information about isomerization that is encoded in time- or frequency-domain spectra of larger molecules. Our hope is that the concepts and examples described here will be viewed as templates for the characterization of isomerizing systems, thereby challenging and guiding spectroscopists to attack similar problems of chemical interest.

REFERENCES AND NOTES
13. The angular momentum quantum number K plays two roles here: that of the asymmetric top rotational quantum number and the linear molecule vibrational angular momentum quantum number, K. The most exciting outcome of the excellent fits using Eq. 4 is the determination of the transition state energies. The uncertainties in Eₜₛ are at least as good as what is currently available from theory. In many cases, experiments might only confirm theoretical predictions, but we expect them to sharpen our understanding, and the potential value of our method goes well beyond validating theory. For example, we envision that this approach is a step toward establishing kinet-ics on the same firm experimental foundation as that already enjoyed by thermochemistry, where precise information is broadly available. This could aid in modeling complex reaction net-works as well as provide benchmarks for theoretical calculations.

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Spectroscopic characterization of isomerization transition states

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Shaking out details of transition states
Chemists liken reaction energetics to a landscape with hills and valleys. In this context, the transition state represents the highest barrier that reagents must pass over en route to forming products. Baraban et al. introduce a framework for extracting details about the transition state of rearrangement reactions directly from vibrational spectral data. They identified a characteristic pattern in the spacing between vibrational energy levels near the transition state, which revealed its energy as well as the specific motions involved in surmounting the barrier.

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