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THE ROLE OF STATE SPECIFICITY IN UNIMOLECULAR RATE THEORY

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Molecules with isolated compound state resonances decompose with state specific unimolecular rate constants. In some cases, this state specificity can also be identified as mode specific decomposition. *Mode specificity* means there are exceptionally large or small state specific rate constants depending on which internal modes are excited in forming the resonance state. The ability to establish the modes excited requires that the energies, for resonance states yielding mode specific behavior, can be predicted by finding patterns in the positions of these states in the spectrum. Such patterns allow a zero-order Hamiltonian and basis set to be used to assign quantum numbers to the resonances and to define the type of mode specificity. A situation contrary to one where *all* the resonance states exhibit mode specificity is *statistical state specificity*. For this case there are *no* patterns in the positions of the resonances in the spectrum, so that *all* the resonance states are intrinsically unassignable. Small and large fluctuations of the state specific rate constants are simply random occurrences, and cannot be associated with any pattern. Statistical inaccuracies make it difficult to identify mode specificity from a distribution of nearest neighbor energy levels. For all types of state specificity (including mode specificity and statistical state specificity), a microcanonical ensemble of compound state resonances will usually not decay exponentially. However, a corresponding result is often not obtained by classical mechanical simulations. The nonexponential decay of a microcanonical ensemble of resonance states results in monoenergetic chemical activation and thermal Lindemann–Hinshelwood rate constants which deviate from those of RRKM theory.

1. Introduction

For some time RRKM (Rice–Ramsperger–Kassel–Marcus) theory has formed the basis of unimolecular rate theory [1–3]. RRKM theory assumes molecules, excited with a microcanonical distribution of energy states in the energy interval $E \rightarrow E + dE$, decompose with random probabilities so that

$$N(E, t)/N_0 = \exp[-k(E)t], \quad (1)$$

where $k(E)$ is the RRKM unimolecular rate constant. RRKM theory has been successful in interpreting many studies of unimolecular decomposition [1–3].

If a unimolecular reactant has a small number of degrees of freedom, a small value of rotational angular momentum, and/or a low unimolecular threshold, the reactant will have a low density of states for internal energies near the unimolecular threshold. Such a reactant molecule, excited above the unimolecular threshold, is expected to decompose via isolated compound-state resonances [4,5]. These resonance states are the natural extension of the bound vibrational/rotational eigenstates into the dissociative continuum. While the former states are trapped forever in a region of finite extent, the latter states leak towards product space after characteristic times. The energy for a resonance state $|n\rangle$ is a complex sum, consisting of the eigenvalue and width, i.e.

$$E_n = E_n^r - i\Gamma_n/2, \quad (2)$$

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where the real component of the energy E_n^r gives the position of the resonance in the spectrum.

The absorption width Γ_n for the resonance state $|n\rangle$ is related to the state's lifetime τ_n by $\tau_n = \hbar/\Gamma_n$. The random (i.e. exponential) probability for a resonance state to decay to products depends on the rate constant k_n , which is equal to the inverse of τ_n . The k_n are called *state specific* unimolecular rate constants. A microcanonical ensemble of compound-state resonances will decay according to

$$N(E, t) = \sum_n \exp(-k_n t). \quad (3)$$

If each of the *state specific* rate constants k_n equal the RRKM rate constant $k(E)$, the decay of a microcanonical ensemble of compound-state resonances will be identical to that predicted by RRKM theory. In contrast, if each resonance state has a unique rate constant, the decay of the microcanonical ensemble will not be exponential.

Both experimental [6–10] and theoretical [11–15] studies have shown that many van der Waals molecules dissociate with state specific rate constants which differ significantly from the RRKM values. However, there have been substantially fewer studies of state specific decomposition for molecules with covalent intramolecular potentials. Some of the earliest theoretical studies of state specific decay for the latter class of molecules were by Mies and Krauss [16,17] and Rice [18], and, since this work, the number of theoretical studies outnumber the experimental ones. A survey of the theoretical work [4,19–47] is given in table 1. Extensive experimental studies of state specific decay have been performed for H_2CO [48–50] and H_3^+ [51] decomposition.

An important finding from the above experimental and theoretical studies of molecules with covalent intramolecular potentials is that there may be significant fluctuations in the state specific rate constants. This is illustrated in fig. 1, where preliminary results [46] for the dissociation reaction $\text{H}-\text{C}=\text{O} \rightarrow \text{H} + \text{C}=\text{O}$ are given. Resonance states, within a small energy interval, may have rate constants which vary by several orders of magnitude. Clearly, for such a case a microcanonical ensemble of resonance states will not decay exponentially. For most systems investigated, there are extensive fluctuations in the state specific rate constants and agreement with RRKM is not ob-

Table 1
Quantum mechanical and semiclassical studies of state specific unimolecular decomposition ^{a)}

| System ^{b)} | Ref. |
|--|-----------|
| $\text{ABC} \rightarrow \text{AB} + \text{C}$ | [4,19,20] |
| Barbanis | [21] |
| Hénon–Heiles | [22–24] |
| model isomerization | [25] |
| $\text{ABA} \rightarrow \text{AB} + \text{A}$ (H_2O , CH_2) | [26–26] |
| ($\text{C}^1\text{A}'$) $\text{DCN} \rightarrow \text{D} + \text{CN}$ | [37] |
| $\text{H}_2\text{CO} \rightarrow \text{H}_2 + \text{CO}$ | [38–40] |
| $\text{H}-\text{C}-\text{C} \rightarrow \text{H} + \text{C}=\text{C}$ | [41,42] |
| $\text{H}_2\text{C}=\text{C} \rightarrow \text{HC}=\text{CH}$ | [43] |
| $\text{HCO} \rightarrow \text{H} + \text{CO}$ | [44–46] |
| $\text{H}_3^+ \rightarrow \text{H}^+ + \text{H}_2$ | [47] |

^{a)} The calculations are for potentials with covalent intramolecular potentials.

^{b)} Each of the following studies is a two-dimensional calculation, except the three-dimensional calculations for HCO and H_3^+ .

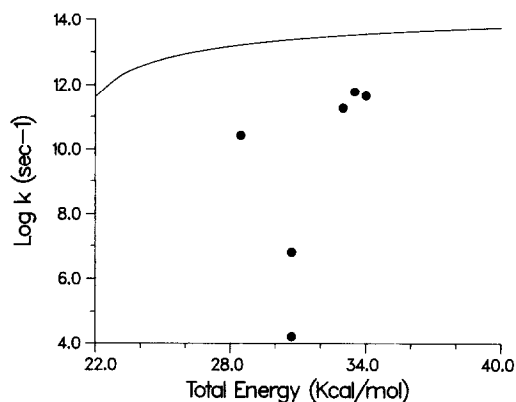


Fig. 1. Quantum mechanical state specific rate constants for the three-dimensional ($J=0$) decomposition reaction $\text{H}-\text{C}=\text{O} \rightarrow \text{H} + \text{C}=\text{O}$. The rate constants are determined by the stabilization graph plus analytic continuation method described in ref. [42]. Details of the calculations for HCO are given in ref. [46]. The solid curve is the classical harmonic RRKM rate constant. For energies in excess of 25 kcal/mol, the quantum and classical harmonic RRKM rate constants agree to within 10%.

served. A striking counter example is the quantum mechanical study by Waite and Miller [22] for the Hénon–Heiles Hamiltonian. Here, state specific rate constants are found to be well described by RRKM theory. However, if the parameters for the Hénon–Heiles Hamiltonian are changed so that the density of states is increased, substantial fluctuations in the state specific rate constants are found [24].

Understanding state specific unimolecular decom-

position is an important component of unimolecular rate theory. In the following sections different aspects of state specific decomposition are discussed. Section 2 considers the relationship between state specific and mode specific dissociation. The incompleteness (and possible inaccuracy) of the classical mechanical description of state specific decomposition is discussed in section 3. In section 4 the ability to distinguish mode versus state specific decomposition by studying regular and irregular spectra is considered. The unimolecular lifetime distribution $P(E, t)$ and Lindemann–Hinshelwood thermal unimolecular rate constant $k_{\text{uni}}(\omega, T)$ are integral components of unimolecular rate theory. Their relationship is reviewed in section 5 for state specific decomposition. Section 6 is a summary.

2. Mode specific versus state specific unimolecular decomposition

State specific unimolecular decomposition from isolated compound state resonances does not necessarily imply mode specific unimolecular decomposition^{#1}. Nor is mode specificity established by the presence of fluctuations in state specific rate constants for resonances within a narrow energy interval. What is required for mode specific unimolecular decomposition is a distinguishable and, thus, assignable pattern (or patterns) in the positions of resonance states in the spectrum. Identifying such patterns in a spectrum allows one to determine which modes in the molecule are excited when forming the resonance state. It is, thus, possible to interpret particularly large or small state specific rate constants in terms of mode specific excitations. Therefore, mode specificity means there are exceptionally large or small state specific rate constants depending on which modes are excited and that the energies, for the resonance states yielding mode specific behavior, can be predicted by finding patterns in the positions of these resonance states in the spectrum.

Fluctuations in state specific rate constants can also arise from resonance state wave functions which are randomly distributed in coordinate space. Here, the

random characteristics of the wave functions may give rise to particularly large or small state specific rate constants. However, in contrast to the above mode specific states, there are no patterns in the spectrum for these states and, as a result, they are intrinsically unassignable (i.e. they have no good quantum numbers apart from the total energy). Thus, energies for these resonance states do not fit into a pattern, and states with particularly large or small rate constants are simply random occurrences in the spectrum.

The ability to assign a group of resonance states, as required for mode specific decomposition, implies that the complete Hamiltonian for these states is well approximated by a zero-order Hamiltonian with eigenfunctions $\phi_i(m)$ [55]. The ϕ_i are product functions of a zero-order orthogonal basis for the reactant molecule, or, more precisely, product functions in a natural basis representation of the molecular states [56], and the quantity m represents the quantum numbers defining ϕ_i . The wave functions ψ_n for the compound state resonances, before they begin to leak towards products, are approximately given by

$$\psi_n = \sum_i c_{ni} \phi_i(m) . \quad (4)$$

Resonance states in the spectra, which are assignable in terms of the zero-order basis $\phi_i(m)$, will have a predominant expansion coefficient c_{ni} . Hose and Taylor [55] have argued that for an assignable level $c_{ni}^2 > 0.5$. More than one zero-order Hamiltonian may be necessary to assign resonance states for an excited molecule. For the Hénon–Heiles Hamiltonian Hose and Taylor used two zero-order Hamiltonians to identify assignable resonances as either restricted precessors (Q^I) or quasiperiodic librators (Q^{II}) [24,55]. Similarly, Manz and co-workers [28–36] assigned many stretching resonances of ABA molecules as either hyperspherical mode or local mode states.

Assignable resonance states give rise to mode specific unimolecular decomposition if the resonance states exhibit characteristic rate constants dependent on the type of mode(s) excited. It should be noted that the ability to assign quantum numbers to resonance states does not necessarily mean the unimolecular decomposition will be mode specific. For example, consider the calculations by Waite and Miller [22] for the Hénon–Heiles Hamiltonian. All reso-

^{#1} Some of the issues considered in this section are discussed in refs. [52–54].

nance states in the spectrum are assignable. However, the rate constants k_n are not mode specific and, instead, are in good agreement with those predicted by RRKM theory. This result is apparently related to the symmetry of the Hamiltonian and the density of states [24].

In contrast to resonance states which can be assigned quantum numbers and which may exhibit mode specific decomposition are states which are intrinsically unassignable. Because of extensive couplings, a zero-order Hamiltonian and basis cannot be found to represent the wave functions ψ_n for these states. The spectrum for these states is irregular without patterns, and fluctuations in the k_n are related to the manner in which the ψ_n are randomly distributed in coordinate space. For the most statistical (i.e. nonseparable) situation, the expansion coefficients in eq. (4) are random variables, subject only to the normalization and orthogonality conditions

$$\sum_n c_{ni}^2 = 1 \quad \text{and} \quad \sum_i c_{ni} c_{mi} = 0. \quad (5)$$

To date, unambiguous examples of mode specific decay from isolated resonance states have not been established from experimental studies of molecules with covalent bonds (in contrast with van der Waals molecules [6–10]). Examples of mode specificity have come from quantum mechanical calculations of resonance energies and lifetimes. Bai et al. [24] found that, if the density of states for the Hénon–Heiles Hamiltonian is sufficiently large, at the same energy the Q^{II} states decay about an order magnitude faster than the Q^I states. At low excitation energies resonance stretching states of ABA molecules identified as hyperspherical modes decay at slower rates than do the local mode resonances [29,35]. However, for

higher energies such a rule cannot be established for the ABA resonance states [35]. Mode specific decomposition has been illustrated for the $H-C-C \rightarrow H+C=C$ model Hamiltonian [42]. Lifetimes for different resonance states are given in table 2. The states are listed according to the quantum number for the HC stretch mode. The progression of resonance states with zero quantum in the HC stretch has the longest lifetimes, while the progression with two quanta in the HC stretch has the shortest lifetimes. Such a finding is characteristic of mode specific decomposition. A similar type of mode specific behavior is expected for the $H-C=O \rightarrow H+C=O$ reaction [44–46], which has a Hamiltonian similar to that for the $H-C-C$ system.

If all the resonance states which form a microcanonical ensemble have random ψ_n and are intrinsically unassignable, a situation arises which we will refer to as *statistical state specific* behavior. Since each ψ_n is projected randomly onto the ϕ_i basis functions for any zero-order representation, the distribution of the state specific rate constants k_n will be as statistical as possible. If these k_n within the energy interval $E \rightarrow E + dE$ form a continuous distribution, Levine [57,58] has argued that the probability of a particular k is given by the Porter–Thomas [59] distribution

$$P(k) = \frac{\nu}{2\bar{k}} \left(\frac{\nu k}{2\bar{k}} \right)^{\nu/2-1} \frac{\exp(-\nu k/2\bar{k})}{\Gamma(\frac{1}{2}\nu)}, \quad (6)$$

where \bar{k} is the average state specific unimolecular rate constant within the energy interval $E \rightarrow E + dE$,

$$\bar{k} = \int_0^\infty k P(k) dk \quad (7)$$

and ν is the “effective number of decay channels”.

Table 2

Compound-state resonance lifetime for the $H-C-C \rightarrow H+C=C$ model system [42]

| State ^{a)} | Energy ^{b)} | Lifetime ^{c)} | State | Energy | Lifetime | State | Energy | Lifetime |
|---------------------|----------------------|------------------------|-------|--------|-----------|-------|--------|-----------|
| 0,12 | 16195 | 1.28(–10) | 1,9 | 15803 | 4.90(–11) | 2,7 | 16209 | 1.34(–12) |
| 0,13 | 17221 | 1.50(–8) | 1,10 | 16894 | 1.36(–10) | 2,8 | 17357 | 2.13(–13) |
| 0,14 | 18223 | 1.19(–8) | 1,11 | 17963 | 5.38(–11) | 2,9 | 18419 | 1.90(–13) |
| 0,15 | 19205 | 4.33(–10) | 1,12 | 19009 | 1.33(–10) | 2,10 | 19536 | 1.55(–13) |
| 0,16 | 20167 | 4.03(–10) | 1,13 | 20032 | 2.48(–11) | | | |

^{a)} In the identification of the state (n_1, n_2) , n_1 and n_2 are the HC and CC stretch quantum numbers, respectively.

^{b)} Energy is in cm^{-1} . ^{c)} Lifetime is in s.

This distribution is borrowed from the field of nuclear physics where it was used to represent the probability of a channel width. If ν equals 1 or 2 the most probable k is a value of zero. For $\nu > 2$ there is a maximum in $P(k)$ located at [60]

$$k_{\max} = \frac{\nu-2}{\nu} \bar{k}. \quad (8a)$$

(See fig. 4 in ref. [58] for a depiction of the different $P(k)$.) The extent of fluctuations in k for $\nu > 2$ may be studied by considering the second moment

$$\begin{aligned} & \langle [(k - k_{\max})/k_{\max}]^2 \rangle \\ &= \int_0^{\infty} [(k - k_{\max})/k_{\max}]^2 P(k) dk \\ &= \frac{2(\nu+1)}{(\nu-2)^2}. \end{aligned} \quad (8b)$$

As ν becomes large this moment approaches zero.

The population of reactant molecules decays non-exponentially for the Porter–Thomas distribution and is given by [60,61]

$$N(E, t)/N_0 = (1 + 2\bar{k}t/\nu)^{-\nu/2}. \quad (9)$$

Thus, for state specific decay and the most statistical (or nonseparable case), a microcanonical ensemble does *not* decay exponentially as predicted by RRKM theory. It is worthwhile noting that when $\frac{1}{2}\nu$ becomes very large, the rhs of eq. (9) approaches $\exp(-\bar{k}t)$ [61], since $\lim (1 + x/n)^{-n} = \exp(-x)$, when $n \rightarrow \infty$.

Possible forms of $P(k)$ have not been established for groups of resonance states which are mode specific or groups which contain both mode specific and non mode specific resonances. More work is required to determine $P(k)$ for systems that are not statistical state specific. Levine [53] has found that the ABA resonances studied by Manz and co-workers [29,35] can be fit by eq. (6) with $\nu \approx 1.8$. These ABA resonances include a large number of mode specific states and the ABA system is certainly not statistical state specific. The inference to be made, in light of this result, is that the ability to fit a collection of resonance widths to eq. (6) does not prove the system is statistical state specific. As discussed above, the evidence for statistical state specificity is the absence of *any*

patterns in the positions of the resonances in the spectrum so that all the resonance states are intrinsically unassignable.

To conclude this section, for many reactant molecules it is expected that a microcanonical ensemble of resonance states will contain states which exhibit mode specific decay and can be identified by patterns (i.e. progressions) in the spectrum, as well as unassignable states with random ψ_n and, thus, state specific rate constants with random fluctuations. In general, it is not expected that the ψ_n which form a microcanonical ensemble will have identical k_n which equal the RRKM $k(E)$.

3. Classical mechanical dynamics and state specific decomposition

A number of studies have shown there is an acceptable correspondence between the classical intramolecular motion of a bound molecule and the nature of vibrational/rotational energy levels [55,62,63]. In general, energy levels are assignable if the classical motion for the level is regular (i.e. quasiperiodic). Energy levels which appear to be intrinsically unassignable are associated with classical irregular (i.e. chaotic) motion. An exception to the above correspondence is the finding of chaotic classical trajectories for energy levels which are assignable but have regular wave functions [64–66]. This occurs when the trajectory traverses chaotic regions of phase space which have volumes smaller than \hbar and, thus, are not relevant to quantum mechanics [67].

The correspondence between classical and quantum mechanical state specificity appears to be more uncertain than the correspondence described above for energy levels [68]. To illustrate, consider two different types of microcanonical ensembles of reactant molecules, each having energy in excess of the unimolecular threshold. One ensemble consists of classical quasiperiodic trajectories trapped in the reactant region of phase space and the other consists of chaotic trajectories which decompose to products. The classical/quantal correspondence is well defined for the ensemble of quasiperiodic trajectories. Applying semiclassical mechanics to the trajectories will give the energy E_n^r , eq. (2), and wave function ψ_n for

the compound-state resonances. The spectrum will be assignable and the rate constants k_n are expected to exhibit mode specificity. To determine k_n semiclassically the wave function ψ_n for the trapped molecule is connected with the wave function in the exit channel [4]. Since the trajectories are quasiperiodic and trapped in the reactant region of phase space, the classical microcanonical ensemble will not decompose, i.e. the classical rate is zero. However, the semiclassical and quantal $N(E, t)$, eq. (3), are expected to be nonexponential and in agreement.

The classical/quantal correspondence is not as pleasing for the microcanonical ensemble of chaotic trajectories. If the density of states is sufficiently small, this ensemble is expected to exhibit statistical state specific, but not mode specific, decomposition. However, except for a few successes [63], it has not been possible to determine semiclassical resonance energies E_n^r and wave functions ψ_n from chaotic trajectories. Thus, in general, semiclassical k_n cannot be evaluated and a comparison cannot be made between the quantum and semiclassical $N(E, t)$ for the microcanonical ensemble. Since the chaotic trajectories decompose to products the classical $N(E, t)$ can be determined. However, because of zero-point energy effects and the improper treatment of resonances by chaotic classical trajectories, the classical and quantal $N(E, t)$ are not expected to agree [68]. For example, if the classical motion is sufficiently chaotic so that a microcanonical ensemble is maintained during the decomposition process, the classical $N(E, t)$ will be exponential with a rate constant equal to the classical (not quantal) RRKM value [69–71]. However, the quantal decay is expected to be *statistical state specific*, where the random ψ_n give rise to statistical fluctuations in the k_n and a nonexponential $N(E, t)$. This distinction between classical and quantum mechanics for Hamiltonians, with classical $N(E, t)$ which agree with classical RRKM theory, is expected to be evident for numerous systems, including the $\text{H-C-C} \rightarrow \text{H} + \text{C}=\text{C}$ models [72–74].

The above are two extreme cases. Many examples are known where the complete microcanonical ensemble of trajectories is chaotic, but the situation where all the microcanonical motion above the classical threshold is quasiperiodic is more of an idealization (the latter is more likely if the unimolecular process is barrier tunnelling). A common classical

microcanonical ensemble is one which consists of both quasiperiodic and chaotic trajectories [72–75]. There also may be “vague tori” trajectories [67] which, in some cases, may yield correct k_n for resonance states [68]. However, the point to be emphasized is that, if the quantum mechanical decomposition occurs via isolated compound-state resonances, only in anomalous cases are the classical and quantal $N(E, t)$ the same for a microcanonical ensemble.

4. Determination of mode specific versus state specific decomposition from energy level spacings

Spectra comprised of vibrational/rotational eigenvalues are often classified as regular or irregular [62,63]. For a regular spectrum there is a good zero-order representation of the Hamiltonian and quantum numbers can be assigned to the energy levels. The usual occurrence is for the corresponding classical trajectories to be quasiperiodic. The sequence of energy levels is random for an irregular spectrum, since there is strong mixing in any zero-order representation. The only good quantum number is the total energy. The classical motion is chaotic for an irregular spectrum. A criterion proposed for identifying regular and irregular spectra is the distribution of nearest neighbor energy level spacings [76,77]. Regular spectra are characterized by the Poisson level spacing distribution

$$P(s) = 1/\langle s \rangle \exp(-s/\langle s \rangle), \quad (10)$$

where $\langle s \rangle$ is the average spacing. From studies of strongly coupled systems, it is suggested that the level distribution is of the Wigner form,

$$P(s) = \pi s/2 \langle s \rangle^2 \exp(-\pi s/4 \langle s \rangle^2), \quad (11)$$

for irregular spectra. Spectra which are neither regular or irregular, but intermediate between these two limiting cases, can be fit by a weighted superposition of the above Poisson and Wigner distributions [76], or by the distribution function proposed by Brody [78].

Following the discussion in the previous sections, an ensemble of quasiperiodic trajectories, which exhibits mode specific quantum mechanical decomposition, is expected to have a regular spectrum of resonance energy level with spacings given by the Poisson distribution. A spectrum of resonance levels

with statistical state specific decomposition should be irregular with a Wigner energy spacing distribution. If the ensemble of resonances consists of levels which exhibit mode specific decomposition and levels which do not, the distribution of energy level spacings should be intermediate of the Poisson and Wigner forms. Thus, studying the nature of the distribution of nearest neighbor energy level spacings for compound state resonances is one potential approach for detecting mode specific unimolecular decomposition. An apparent successful example of comparing nearest neighbor energy level spacings and state specific rate constants are calculations for ABA models with $m_B/m_A \approx 10$. As discussed above, for low excitation energies Manz and co-workers [29,35] found that most of the unimolecular decomposition is mode specific with a small fraction of the resonance states exhibiting characteristics consistent with random wave functions. The distribution of nearest neighbor energy level spacings for such models is well fit by the Poisson distribution (i.e. a regular spectrum) [79,80], a result consistent with mode specific decomposition. It should be noted that from very early trajectory calculations, Bunker [69,70] suggested that ABA models with large B/A mass ratios have metrically decomposable phase spaces, which is consistent with the mode specific rate constants.

Some inconsistencies have been noted [81,82] in comparing the spectrum (regular versus irregular), transition rates, and $P(s)$ for NO_2 . The absorption spectrum of NO_2 represents a problem of outstanding complexity. There are a number of electronic states which interact with one another. The spectrum looks irregular (chaotic) with no discernable patterns. An unambiguous assignment and interpretation of the observed spectrum has not been made. In particular, it has not been possible to assign quantum numbers to the levels of the excited electronic states. On all counts, the spectrum appears to be irregular and intrinsically unassignable. Such a conclusion is supported by the statistics of the transition rates [81]. In apparent conflict with such a finding is the report by Lehman and Coy [81] that $P(s)$ is of the Poisson form, consistent with a regular spectrum. In another study, Persch et al. [82] find that $P(s)$ for NO_2 is well represented by the Wigner surmise. They stress the difficulty in determining the correct $P(s)$ from the experimental spectrum as a result of missing lines,

spurious lines of the wrong symmetry, etc. It seems clear that more work, both experimental and theoretical, is needed and will be performed for the NO_2 system to compare different approaches for identifying the form of the spectrum.

One practical problem, associated with using $P(s)$ to identify regular versus irregular spectra and the possible presence of mode specific decomposition, is the difficulty in determining a large, statistically meaningful number of resonance (and/or bound) energy levels [83–85]. As an illustration of this difficulty, quantum mechanical calculations are reported here for the three-dimensional $\text{H}-\text{C}-\text{C} \rightarrow \text{H} + \text{C}=\text{C}$ Hamiltonian studied previously by the approximate Sorbie–Handy [86] and DeLeon–Heller–Miller [87] semiclassical methods. The Hamiltonian consists of Morse CH and CC stretches and a harmonic HCC bend which are coupled through both kinetic and potential energy terms. The classical energy difference between $\text{H} + \text{C}=\text{C}$ and $\text{H}-\text{C}-\text{C}$ is 40.0 kcal/mol. Eigenvalues for the $\text{H}-\text{C}-\text{C} \rightarrow \text{H} + \text{C}=\text{C}$ quantum mechanical Hamiltonian were obtained by solving the vibrational secular equation. To evaluate matrix elements for the vibrational secular equation, CH and CC stretch coordinate integrations were performed with 64-point Gauss quadrature. For integrations over the HCC bend coordinate 60-point Gauss–Hermite quadrature was used. The calculations were performed on the IBM 3090 Vector Facility in Kingston, New York. The matrix diagonalization was performed using the Engineering and Scientific Subroutine Library (ESSL) routine DSLEV.

The vibrational secular equation was solved using Morse functions for the CH and CC stretches and harmonic oscillator functions for the HCC bend. The quantum mechanical energies, for the 87 levels with energy less than 35 kcal/mol, are sufficiently converged for one to compare eigenvectors for the levels, to calculate nearest neighbor energy spacings, and to

compare with the previous semiclassical results^{#2}. Hose and Taylor [55] have suggested, that if the principal component of a level's eigenvector is greater than $(0.5)^{1/2}$ for a natural basis representation, the level could be classified as regular. Though the basis set used here is not a natural representation, each one of the 87 levels has a principal eigenvector component greater than $(0.5)^{1/2}$. The same result would be found if a natural basis set representation was used. Thus, all the H-C-C levels with energy less than 35 kcal/mol are characterized as regular and can be assigned quantum numbers. In previous work [86,87] semiclassical eigenvalues were obtained from trajectories with regular (i.e. quasiperiodic) intramolecular motion. For 28 of the 87 levels, with energy less than 35 kcal/mol, semiclassical eigenvalues were not determined because no attempt was made to quantize all the levels with regular motion. The above analysis of the eigenvector components indicates that it should be possible to semiclassically quantize all of the 87 levels.

The distribution of nearest neighbor energy spacings is plotted in fig. 2 for levels 2–87 of the H-C-C Hamiltonian. (The spacing between levels 1 and 2 is quite large, 2.817 kcal/mol, and is not included.) The distribution in fig. 2 appears to be intermediate of the Poisson distribution which is exponential and the Wigner distribution which has an intercept of zero. A more objective way to identify the form of the distribution in fig. 2 is to compare the distribution's ratios $\langle s^2 \rangle / \langle s \rangle^2$ and $\langle s^3 \rangle / \langle s \rangle^3$ with the corresponding ratios for the Poisson and Wigner distributions [77,83]. The second and third moment ratios are 2 and 6 for the Poisson distribution, and $4/\pi \approx 1.27$ and $6/\pi \approx 1.91$ for the Wigner distribution. For comparison, the second and third moments for the distribution of energy spacings in fig. 2 (levels 2–87) are 2.00 and 6.63 respectively. (The moments were not cal-

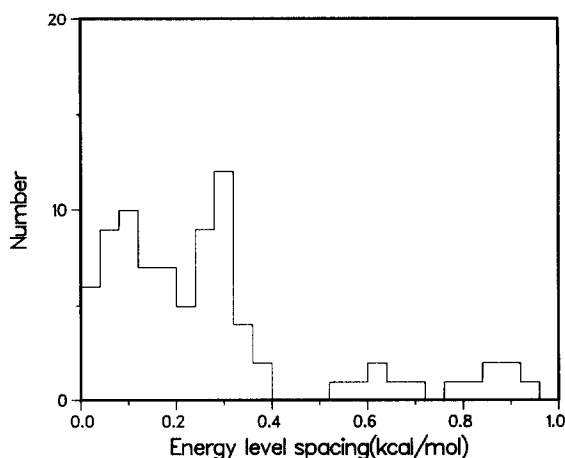


Fig. 2. Distribution of nearest neighbor energy level spacings for the coupled H-C-C Hamiltonian. The levels have energy below 35 kcal/mol.

culated from the histogram, but from the actual values of the nearest neighbor energy level spacings (see footnote 2).) Though the agreement with the Poisson moments is quite good, it is somewhat misleading. If the distribution is divided, so the energy spacings for levels 2–45 and 45–87 are treated separately, some uncertainty arises in the nature of the distribution. The second and third moments, for the distribution from levels 2–45, are 1.71 and 4.22, respectively, and are intermediate of those for the Poisson and Wigner distributions. The distribution for levels 45–87 has second and third moments equal to 1.33 and 2.05. These are nearly the same as those for the Wigner distribution.

To compare with fig. 2, the distribution of nearest neighbor energy level spacings was calculated for the uncoupled H-C-C \rightarrow H+C=C Hamiltonian. The energy for an uncoupled level is a sum of the HC Morse stretch, CC Morse stretch, and HCC harmonic bend eigenvalues. As for the coupled case, all the level spacings for energy less than 35 kcal/mol are considered, except the one between levels 1 and 2 which is quite large. The resulting distribution is given in fig. 3. There are 79 uncoupled levels with energy less than 35 kcal/mol. The second and third moments for the uncoupled distribution in fig. 3 are 2.04 and 6.57, and are similar to those given above for the coupled distribution. The moments also agree with those for the Poisson distribution. However, if the distribution is divided as done above for the coupled case, its

^{#2} For most levels the previous semiclassical [86,87] and current quantum mechanical eigenvalues agree to within ≈ 5 cm (i.e. 0.01–0.02 kcal/mol). However, for some cases the difference is greater. The largest difference is 39 cm^{-1} . However, the extensive differences between Sorbie–Handy semiclassical and quantum mechanical vibrational eigenvalues, found for the hydrocarbon fragment with a coupled CH stretch and CCH bend [88] are not present for the H-C-C \rightarrow H+C=C system studied here. The quantum mechanical eigenvalues for the H-C-C \rightarrow H+C=C system are available from the authors on request.

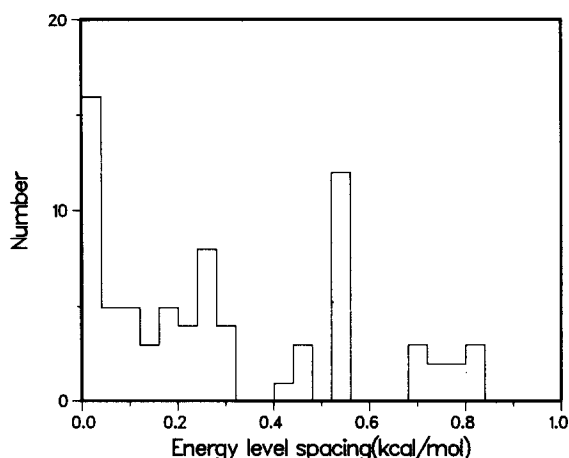


Fig. 3. Distribution of nearest neighbor energy level spacings for the uncoupled H-C-C Hamiltonian. The levels have energy below 35 kcal/mol.

identification is not as certain. The second and third moments for the energy spacings of levels 2–41 are 1.71 and 4.29, respectively. For levels 41–79 the moments are similar, and equal 1.85 and 4.26. The moments determined with the distribution subdivided are intermediate between the Poisson and Wigner values. Thus, though the uncoupled Hamiltonian clearly has a regular spectrum, an unequivocal identification cannot be made by analyzing the distribution in fig. 3.

What one concludes is that the distributions in figs. 2 and 3 do not have a high degree of statistical accuracy and a precise identification of their form cannot be made. This contrasts to previous work for KCN/KNC [84], LiCN/LiNC [83,85], HCN/HNC [87] and H₂O [89] ^{#3} Hamiltonians, where nearest neighbor energy level spacings have been analyzed for 72, 131, 106, and 109 states, respectively. These numbers of states do not differ significantly from the 78 and 86 states considered here for the uncoupled and coupled H-C-C Hamiltonians. However, it was possible to identify the energy spacing distributions for KCN/KNC, LiCN/LiNC, and H₂O as Wigner, and that for HCN/HNC as Poisson.

The principal conclusion to be drawn from this work is quite evident. The spectrum for the uncoupled H-C-C Hamiltonian is clearly regular. The ei-

genvectors found from the solution to the vibrational secular equation and the extensive regular classical motion observed in determining the semiclassical eigenvalues strongly suggest that nearly all 87 levels with total energy less than 35 kcal/mol for the coupled H-C-C Hamiltonian should also be identified as regular. However, because of a lack of statistical accuracy, neither the spectrum for the uncoupled or coupled H-C-C Hamiltonian can be correctly identified as regular from the distribution of nearest neighbor energy level spacings. Thus, some care should be taken in attempting to identify mode specific unimolecular decomposition from a distribution of nearest neighbor energy level spacings for compound-state resonances.

Our feeling at this time is that the finding reported here for H-C-C, that the lower or upper half of states in a regular system do not obey Poisson statistics, even though the whole set does, is simply an exceptional incident. However, it is possible that this finding is more profound. We are unaware of a similar finding by other investigators. To pursue this matter in more detail will require determining the number of states needed for "statistical accuracy". This is currently unknown.

5. From the lifetime distribution to the Lindemann-Hinshelwood thermal unimolecular rate constant

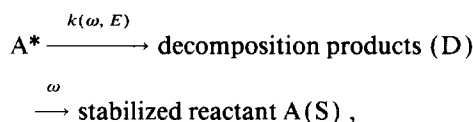
As discussed by Slater [90] and Bunker [70], the lifetime distribution $P(E, t)$ provides a link between microscopic and macroscopic unimolecular kinetics. The lifetime distribution is related to $N(E, t)$, eq. (3), according to

$$P(E, t) = -\frac{1}{N_0} \frac{dN(E, t)}{dt} = \sum_n k_n \exp(-k_n t) \left(\sum_n 1 \right)^{-1}, \quad (12)$$

where $N_0 = \sum_n 1$ is the number of resonances in the energy interval $E \rightarrow E + dE$.

Studies of unimolecular reactions involving chemical activation [91], radiationless transitions [92] and overtone excitation [93] are often interpreted by the mechanism [91]

^{#3} In the analysis of energy level spacings for H₂O, 70 symmetric and 39 antisymmetric states were analyzed.



where A^* is monoenergetically excited. The phenomenological collision-averaged monoenergetic unimolecular rate constant $k(\omega, E)$ is given by

$$k(\omega, E) = \omega D / S \quad (13)$$

and is often determined experimentally from a Stern-Volmer plot. If one makes the strong-collision assumption of unimolecular rate theory [1-3], D is given by [2, p.228; 3, p.150; 94]

$$D = \int_0^\infty W(t) P(E, t) dt, \quad (14)$$

where $P(E, t)$ is the lifetime distribution and $W(t) = \exp(-\omega t)$ is the probability the reactant avoids a collision for time t [85, p.19]. S is simply equal to $1 - D$. Inserting these expressions for D and S into eq. (13) yields

$$k(\omega, E) = N_0 / \left(\int_0^\infty N(E, t) \exp(-\omega t) dt \right) - \omega. \quad (15)$$

The $N(E, t)$ for the isolated compound-state resonances, eq. (3) gives

$$k(\omega, E) = N_0 / \left(\sum_n 1 / (k_n + \omega) \right) - \omega. \quad (16)$$

The $\omega \rightarrow \infty$ and $\omega \rightarrow 0$ limiting values of $k(\omega, E)$ are

$$k(\infty, E) = \sum_n k_n / N_0 = \langle k_n \rangle \quad (17)$$

and

$$k(0, E) = N_0 / \sum_n (1/k_n) = \langle 1/k_n \rangle^{-1}. \quad (18)$$

Thus, in the high-pressure limit $k(\omega, E)$ equals the average of the state specific rate constants within the energy interval $E \rightarrow E + dE$, while $k(\omega, E)$ for the low-pressure limit is one divided by the average of the inverse of the state specific rate constants. If all the k_i are equal, $k(\infty, E) = k(0, E)$ and normal RRKM behavior is observed. However, for *statistical state specificity*, where there are random fluctuations in the k_n , $k(\omega, E)$ will be pressure dependent.

The Lindemann-Hinshelwood unimolecular rate constant $k_{\text{uni}}(\omega, E)$ is related to the lifetime distribution $P(E, t)$ according to [70,90]

$$k_{\text{uni}}(\omega, E) = \omega D = \omega \int_0^\infty W(t) P(E, t) dt. \quad (19)$$

By comparing eqs. (13) and (19), it is seen that the relationship between $k_{\text{uni}}(\omega, E)$ and $k(\omega, E)$ is given by

$$k_{\text{uni}}(\omega, E) = \frac{\omega k(\omega, E)}{k(\omega, E) + \omega}. \quad (20)$$

If the isolated compound-state resonance expression for $P(E, t)$ is used, $k_{\text{uni}}(\omega, E)$ becomes

$$k_{\text{uni}}(\omega, E) = \frac{\omega}{N_0} \sum_n \frac{k_n}{k_n + \omega}, \quad (21)$$

where the summation is over the resonance states within $E \rightarrow E + dE$. If the energy E can be assumed to be continuous, one obtains the thermal Lindemann-Hinshelwood unimolecular rate constant by Boltzmann weighting the $k_{\text{uni}}(\omega, E)$ given by eq. (20), i.e.

$$k_{\text{uni}}(\omega, T) = \int_0^\infty \frac{k_{\text{uni}}(\omega, E) \rho(E) \exp(E/k_B T) dE}{Q}$$

$$= \frac{\omega}{Q} \int_0^\infty \frac{k(\omega, E) \rho(E) \exp(-E/k_B T) dE}{k(\omega, E) + \omega}, \quad (22)$$

where E_0 is the unimolecular threshold energy, and $\rho(E)$ and Q are the density of states and partition function for the reactant molecule's internal degrees of freedom. Eq. (22) is a further extension of the standard thermal Lindemann-Hinshelwood unimolecular rate constant [1-3]. If energy cannot be assumed to be continuous, one obtains $k_{\text{uni}}(\omega, T)$ by Boltzmann weighting the $k_{\text{uni}}(\omega, E)$ in eq. (21) to give

$$k_{\text{uni}}(\omega, T) = \frac{\omega \sum_n k_n \exp(-E_n/k_B T) / (k_n + \omega)}{Q}. \quad (23)$$

Here, the summation is over all the resonance states, not only those within $E \rightarrow E + dE$. An equation similar to eq. (23) has been used to interpret thermal unimolecular rate constants for the formyl radical [95].

For some situations a continuous distribution of

state specific rate constants $P(k)$ can be assumed for an energy interval $E \rightarrow E + dE$. As discussed above, for statistical state specificity $P(k)$ is thought to be given by the Porter–Thomas distribution. Analytic expressions for $k(\omega, E)$ and $k_{\text{uni}}(\omega, E)$ have been determined for the Porter–Thomas $P(k)$ distribution [60,61]. Other types of distributions have also been considered [60].

6. Summary

In this paper we have considered the unimolecular kinetics of molecules which decompose via isolated compound-state resonances. One of the most important points to recognize is that state specific decomposition does not necessarily imply mode specific decomposition. The latter requires: (1) a distinguishable and, thus, assignable pattern(s) in the positions of the resonances in the spectrum so that quantum numbers may be assigned to the resonance states and one may establish which modes are excited in forming the resonance; and (2) a relationship between the size of the unimolecular rate constant (large or small) and the modes excited. However, state specificity does not require the above behavior. For example, the wave functions for some or all of the resonances may be randomly distributed over the coordinate space so that the resonances are intrinsically unassignable. Here, the random attributes of the resonance wave functions can lead to random fluctuations in state specific rate constants. If all the resonances within a microcanonical ensemble have such random attributes, a condition referred to as statistical state specificity exists. A microcanonical ensemble exhibiting statistical state specificity is expected to decay non-exponentially in disagreement with RRKM theory.

There is not an exact correspondence between the classical and quantum mechanics of state specific decomposition. For many cases mode specific quantum mechanical decomposition corresponds to quasiperiodic trajectories which are trapped in the reactant region of phase space. The classical analogue of state specific, but not mode specific, decomposition is chaotic classical motion. A microcanonical ensemble of chaotic classical trajectories will usually decompose exponentially, while the corresponding microcanonical ensemble of quantum mechanical com-

pound state resonances is expected to exhibit statistical state specificity and will not decay exponentially.

Determining the distribution of nearest neighbor energy level spacings may provide one means to diagnose mode specific decomposition. For mode specificity the distribution should be of the Poisson form. However, because of statistical inaccuracies this diagnosis may be hard to make for some reactions. The nonexponential decay of a microcanonical ensemble of compound state resonances affects the pressure dependence of both the monoenergetic chemical activation and thermal Lindemann–Hinshelwood unimolecular rate constants. However, it is not known whether mode specificity and statistical state specificity have uniquely different effects on these rate constants.

Finally, additional research seems to be needed for several topics related to state specificity. For mode specific decomposition, it would be useful to know the form (or forms) for the distribution $P(k)$ of rate constants for resonance states which lie within $E \rightarrow E + dE$. The decomposition of isolated compound-state resonances is not in accord with RRKM theory. However, as the resonances broaden and begin to overlap, the decay of a microcanonical ensemble may also begin to agree with RRKM theory. Calculations are needed to see if this is indeed the case. With respect to the study of compound state resonances, experiment may have advanced more than theory. Most theoretical calculations of resonances have involved two-dimensional models, while experiments have considered highly excited resonance states of formaldehyde, which is a six-dimensional problem for angular momentum equal to zero. Clearly, advances must be made in both the application and development of theoretical methods for treating unimolecular compound state resonances.

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