Eigenstates of Thiophosgene Near the Dissociation Threshold: Deviations From Ergodicity

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ABSTRACT: A subset of the highly excited eigenstates of thiophosgene (SCCl$_2$) near the dissociation threshold are analyzed using sensitive measures of quantum ergodicity. We find several localized eigenstates, suggesting that the intramolecular vibrational energy flow dynamics is nonstatistical even at such high levels of excitations. The results are consistent with recent observations of sharp spectral features in the stimulated emission spectra of SCl$_2$.

INTRODUCTION

The statistical Rice–Ramsperger–Kassel–Marcus (RRKM) theory of reaction rates occupies a central place in the field of reaction dynamics both for its elegance and simplicity. Indeed, within the RRKM approximation, reaction rates can be calculated irrespective of the intricate intramolecular dynamics that happen prior to the reaction. In recent years, however, the appearance of several examples of intrinsically non-RRKM reactions has mostly come from answering the question requires understanding the nature of the molecular eigenstates near reaction thresholds. In particular, the situation wherein all the eigenstates are sufficiently delocalized seems ideal for the validity of the statistical approximation. However, existence of localized eigenstates at the reaction threshold would suggest strong deviations from the RRKM regime. Consequently, there have been many studies aiming to characterize the nature of highly excited eigenstates in different systems. Recent reviews highlight the relationship between eigenstate assignments based on classical phase space structures and deviations from the RRKM regime.

The above arguments, more precisely, are connected to a question that has confounded researchers for nearly a century: what constitutes a quantum analog of the classical ergodic hypothesis in an isolated many-body quantum system? Progress toward answering this question has mainly come from semiclassical analysis of quantum chaotic models giving rise to the notions of weak quantum ergodicity and quantum unique ergodicity. Recently, an approach that has attracted substantial attention is the so-called eigenstate thermalization hypothesis (ETH). According to ETH, for an isolated quantum system governed by the Hamiltonian $\hat{H}$ with eigenstates $|\alpha\rangle$, the eigenstate expectation value $V_{\alpha\alpha} \equiv \langle \alpha | \hat{\mathcal{O}} | \alpha \rangle$ of an observable $\hat{\mathcal{O}}$ changes slowly and smoothly with the state. Specifically,

$$\langle \alpha | \hat{\mathcal{O}} | \beta \rangle \equiv V_{\alpha\beta} = \mathcal{V}(E_{\alpha}) \delta_{\alpha\beta} + O(H^{(-1)/2})$$

with the $O(H^0)$ leading term of $\mathcal{V}(E_{\alpha})$ being the classical microcanonical average:

$$\langle V \rangle_{\text{mc}}(E_{\alpha}) = \frac{\int \hat{V}(\mathbf{q}, \mathbf{p}) \delta[H(\mathbf{q}, \mathbf{p}) - E_{\alpha}] d\mathbf{q} d\mathbf{p}}{\int \delta[H(\mathbf{q}, \mathbf{p}) - E_{\alpha}] d\mathbf{q} d\mathbf{p}}$$

In the above equation, $f$ is the number of degrees of freedom and $V(\mathbf{q}, \mathbf{p})$ is the classical symbol corresponding to the quantum $\hat{\mathcal{O}}$. Furthermore, consider the long-time average of the time-dependent expectation value $\langle \langle j(t) | \hat{\mathcal{O}} | j(t) \rangle \rangle \equiv \langle \mathcal{V}(t) \rangle$

$$\mathcal{V} \equiv \lim_{t \to \infty} \langle \mathcal{V}(t) \rangle = \sum_{\alpha} |C_{\alpha j}|^2 V_{\alpha\alpha}$$

in some initial nonstationary state $|j\rangle = \sum_{\alpha} C_{\alpha j}|\alpha\rangle$ with mean energy $\bar{E}_j$. Since ETH implies that $V_{\alpha\alpha}$ is approximately constant in an appropriately chosen energy window of width $\Delta E$, one can write

$$\mathcal{V} = \langle V \rangle_{\text{mc}}(E_j) \equiv \frac{1}{N_{\Delta E}} \sum_{\alpha} V_{\alpha\alpha}$$

with $N_{\Delta E}$ being the number of eigenstates within the energy window. These predictions of ETH, along with the effect of finite state space, have been tested in a variety of systems like...
interacting hard core bosons and fermions on lattices and one-dimensional interacting spin chains.

The issue of whether all classically nonintegrable quantum systems obey ETH is still under debate. In particular, many-body Anderson localization can lead to systems showing both thermalized and localized phases. Recent studies show that ETH can still hold as long as the various perturbations act homogeneously, i.e., do not have any specific selection rules, leading to ergodicity over the entire relevant Hilbert space. Interestingly, the phenomenon of intramolecular energy redistribution (IVR) dynamics near the dissociation energy (~600 THz). The motivation for this study comes from the recent work by Chowdary and Gruebele wherein they observed sharp assignable features near and above the dissociation energy in the stimulated emission pumping spectra. Previous works have focused on the nature of the eigenstate and IVR dynamics near the threshold for the onset of IVR (~240 THz) and have already established the existence of different classes of localized eigenstates and hence nonstatistical IVR dynamics. Employing a model spectroscopic Hamiltonian, it is shown that localized states do persist at energies close to the dissociation energy. Moreover, it is shown that there are special initial states that are robust despite the increased density of states and strong anharmonic couplings.

### MODEL HAMILTONIAN

The Hamiltonian used for the current study is a fairly accurate effective Hamiltonian for SCCl constructed by Sibert and Gruebele using canonical Van Vleck perturbation theory and can be expressed as

$$H_0 = \sum_i \alpha_i(\nu_i + \frac{1}{2}) + \sum_{ij} x_{ij}(\nu_i + \frac{1}{2})(\nu_j + \frac{1}{2}) + \sum_{ijk} x_{ijk}(\nu_i + \frac{1}{2})(\nu_j + \frac{1}{2})(\nu_k + \frac{1}{2})$$

being the zeroth-order anharmonic Hamiltonian and the various anharmonic resonances, coupling the zeroth-order states, are contained in

$$V_{res} = k_3\alpha_2^\dagger\alpha_2\alpha_6^\dagger + k_3\alpha_4^\dagger\alpha_4\alpha_6^\dagger + k_3\alpha_5^\dagger\alpha_5\alpha_6^\dagger + k_3\alpha_5^\dagger\alpha_5\alpha_6^\dagger + k_3\alpha_6^\dagger\alpha_6\alpha_6^\dagger + k_3\alpha_6^\dagger\alpha_6\alpha_6^\dagger + \ldots$$

In the above expression, the operators \(\alpha_k\) and \(\alpha_k^\dagger\) are lowering and raising operators for the \(s\)th mode, respectively, with \(\{\alpha_k, \alpha_k^\dagger\} = 1\), in analogy to the usual harmonic oscillator operators. Note that there are other much weaker resonances in the Hamiltonian, which are ignored in the current study. The above Hamiltonian has effectively three degrees of freedom due to the existence of three, approximately, conserved quantities or polynomials

$$K = \nu_1 + \nu_2 + \nu_3$$
$$L = 2\nu_1 + \nu_2 + \nu_6$$
$$M = \nu_4$$

Therefore, \(H\) is block diagonal, and in the present work, the focus is on \((K,L,M) = (13, 25, 14)\) block, which has a total of 1365 eigenstates spanning an energy range of about (18099, 20841) cm\(^{-1}\). Note that Chowdary and Gruebele used the above Hamiltonian to perform an extensive study of the vibrational state space and concluded that about 1 in 10\(^3\) zeroth-order states are localized near the dissociation energy. In what follows, for convenience, we will refer to the resonances by highlighting the modes involved. Thus, the first term in eq 6 will be referred to as the 526-resonance.
The classical Hamiltonian corresponding to eq 6 can be expressed in terms of action-angle variables as $H(\mathbf{j}, \mathbf{\psi}) = H_0(\mathbf{j}) + V_m(\mathbf{j}, \mathbf{\psi})$ where

$$H_0(\mathbf{j}, \mathbf{\psi}) = C + \sum_{i=1,3} \alpha_i J_i + \sum_{ij} \alpha_{ij} J_i J_j + \sum_{ijk} \beta_{ijk} J_i J_j J_k$$  

(8)

is the zeroth-order Hamiltonian and the resonant perturbations given by

$$V_m(\mathbf{j}, \mathbf{\psi}) = v_{36}(\mathbf{j}; K, L) \cos \psi_1 + v_{326}(\mathbf{j}; K, L) \cos \psi_2 + v_{125}(\mathbf{j}; K, L) \cos(\psi_1 + \psi_2) + v_{36}(\mathbf{j}; K, L) \cos(2\psi_3) + v_{133}(\mathbf{j}; K, L) \cos(\psi_1 - \psi_2) + v_{260}(\mathbf{j}; K, L) \cos(2\psi_3)$$

(9)

In the above equations, the actions ($K = K + 3/2$, $L = L + 3/2$, and $M = M + 1/2$) are conserved, being the classical analogs of the quantum polyads, and hence, $H(\mathbf{j}, \mathbf{\psi})$ is ignorable in the conjugate angles ($\psi_1$, $\psi_2$, and $\psi_3$). The parameters ($C, \phi, \alpha$, and $\beta$) of the reduced Hamiltonian (not given here) are related to the original parameters via the canonical transformation, and the reader is referred to a previous work for details. It is important to note that the overlap of nonlinear resonances in eq 9 render the classical system nonintegrable with the possibility of extensive chaos in the classical phase space.

### RESULTS AND DISCUSSION

We begin this section by computing two measures for eigenstate delocalization that are well-known. The first quantity is the participation ratio

$$L_n = (\sum_n |\langle n|n\rangle|^4)^{-1} \equiv (\sum_n p_{\text{tot}}^{-2})^{-1}$$  

(10)

which is a measure of the total number of basis states $\{|n\rangle\}$ that participate in making up the eigenstate $|n\rangle$. A second quantity is the information or Shannon entropy of an eigenstate given by the expression

$$S_n = -\sum_n p_{\text{tot}} \ln p_{\text{tot}}$$  

(11)

Note that the maximal $S_n \approx \ln(0.48N)$ for a Gaussian orthogonal ensemble, which has the value of $\sim 6.5$ since in our case $N = 1365$. It is also useful to observe that in eq 4 if we choose $V = \ln(nl)$, then $V = \sigma_0 = \sum_i C_{i\alpha}^2$ is the dilution factor associated with $\ln(nl)$ and assuming ETH has $\sigma_0 = N^{1/4}$. In Figure 1, the measures $L_n$ and $S_n$ are shown for all the eigenstates computed in the basis of the zeroth-order states, i.e., eigenstates of $H_0$. As expected both measures agree and indicate localized states at the low and high end of the spectrum. The middle part (19250, 19750) cm$^{-1}$ of the spectrum has states exhibiting large values for both the measures. However, note that $S_n$ in particular does not become maximal even in this complicated energy range. Thus, although one expects that even at this high energy the eigenstates are not maximally delocalized, the origin of such partial localization are not apparent from the results.

In order to gain more detailed insights, we compute the eigenstate expectation values of the various resonance operators in eq 6 and compare them to the classical microcanonical average computed in the $(\mathbf{j}, \mathbf{\psi})$ reduced representation using the expression

$$\langle V \rangle_{\text{mic}}(E) = \frac{\int \langle V(\mathbf{j}, \mathbf{\psi}) | \delta[H(\mathbf{j}, \mathbf{\psi}) - E] | d\mathbf{j} d\mathbf{\psi} }{\int \delta[H(\mathbf{j}, \mathbf{\psi}) - E] | d\mathbf{j} d\mathbf{\psi} }$$  

(12)

The results, shown in Figure 2, clearly show considerable fluctuations of the $V_m$ about the $\langle V_m \rangle(E)$ and imply the existence of several localized eigenstates. Note that strongly localized states are seen, in agreement with Figure 1, at both the low and high energy regions of the polyad. However, now it is possible to ascribe the low and high energy localized states with the 36-resonance and a combination of the 156 and 526 anharmonic resonances, respectively. Particularly striking is the 36-resonance case at low energies exhibiting rather large quantum expectation values. In fact, following previous works, one can analyze the single integrable 36-nonlinear resonance term in eq 9

$$v_{36}(\mathbf{j}; K, L) \cos 2\psi_3 \equiv 2J_0(L_1 - K_2 - J_3) \cos 2\psi_3$$  

(13)

with $L_1 \equiv L - J_1$ and $K_2 \equiv K - J_3$ being constants. The analysis yields the extremal values for the quantum expectations as

$$\langle \alpha a_\alpha^\dagger a_\alpha a_\beta^\dagger a_\beta^\dagger + c.c. \rangle = \pm \frac{1}{2} (L_1 - K_2)^2$$  

(14)

with $\pm$ corresponding to $\psi_3 = 0$ and $\psi_3 = \pi/2$, respectively. Decent agreement of the above estimate with the computed values for the first few states shown in Figure 2 suggests that even around $\sim 540$ THz above the ground state the classical phase space of SCCl$_3$ has a large regular region capable of supporting several regular quantum states. By using previously established techniques, it is possible to provide dynamical...
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Figure 1 in order to check the extent of deviation from ETH in this region.

**DEVIATION FROM ERGODICITY**

The results in Figure 2 show the strong fluctuations about the classical microcanonical average suggesting deviations from ergodicity. However, as suggested by Pechukas,\(^5\) the diagonal matrix elements V\(_{\alpha\alpha}\) are expected to have quantum fluctuations, which are of the same order of magnitude as the off-diagonal matrix elements V\(_{\alpha\beta}\). It is therefore interesting to see if the deviations seen in the complicated (19250,19750) cm\(^{-1}\) part of the polyad shown in Figure 2 are essentially the expected quantum fluctuations. As discussed by Feingold and Peres, the computation of the quantum fluctuations in V\(_{\alpha\alpha}\) is rather involved and related to the classical autocorrelation of the relevant observables.\(^9\) One approach is to model the distribution of V\(_{\alpha\beta}\) by a Gaussian as in the earlier work.\(^9\) However, in this work we take a more stringent constraint and associate the extent of quantum fluctuation of V\(_{\alpha\alpha}\) with the largest off-diagonal matrix element V\(_{\alpha\beta}\). Typically, the largest such element is found to be close to the diagonal.

In Figure 3 we show the complicated region of the polyad with the expected quantum fluctuations in V\(_{\alpha\alpha}\) at specific points. It is clear from Figure 3 that, despite the near constant values for the various V\(_{\alpha\alpha}\) there are several states (highlighted by boxes) that indeed deviate strongly from the microcanonical average. Interestingly, many of these states are not easily identifiable from Figure 1 since both I\(_{\alpha}\) and S\(_{\alpha}\) are not capable of identifying localization in the phase space. Hence, Figure 3 clearly establishes the power of the approach based on eigenstate expectation values. Note that different resonance operators reveal different localized eigenstates in a complementary fashion. For instance, a localized state with large negative expectation value for the 36-resonance in Figure 3 is not easily identifiable from any of the other expectation values. Although not shown here, we have further confirmed the predictions of Figure 3 by studying the semiclassical angle space representation \(\langle \psi | \alpha \rangle \equiv \sum c_n \exp (i n \psi) \) of the eigenstates.

The ETH result in eq 4 essentially depends on the lack of correlation between the intensities p\(_{\alpha\alpha}\) and the expectation values V\(_{\alpha\alpha}\). Thus, are the results in Figure 3 contrary to the ETH expectations? In this context, it is interesting to note that a sensitive measure for violations from ergodicity called as the intensity–velocity correlator was introduced earlier by Tomsovic.\(^6\) and has been applied to several paradigmatic systems.\(^7\) This measure correlates the intensity p\(_{\alpha\alpha}\) with the parametric evolution of the eigenvalues (level velocities) as

\[
C_\zeta(\lambda) = \frac{1}{\sigma_\kappa \sigma_\zeta} \left\langle p_{\alpha\alpha} \frac{\partial E_\alpha(\lambda)}{\partial \lambda} \right\rangle_{\alpha \in \Delta E} \equiv \left\langle \frac{\partial E_\alpha(\lambda)}{\partial \lambda} \right\rangle_{\alpha \in \Delta E}
\]

where \(\lambda\) is a Hamiltonian parameter of interest. In the second part of eq 15, the quantities are scaled to unit variance, and the level-velocities are zero centered to remove any net drift. The averaging above is done over a window \(\Delta E\) consisting of N\(_{\Delta E}\).
To make contact with ETH, we choose the parameter in eq 6, say \( k_{36} \), and the initial state as the zeroth-order number state \( |n\rangle \). Then, using the Hellman–Feynman theorem, the covariance can be written down as

\[
Cov_n(k_{36}) = \left\langle \left[ \left\langle \sum_{aa} \left( V_{aa}^{(36)} - \bar{V}_{aa}^{(36)} \right) \right\rangle \right]_{\lambda \in \Delta \lambda} \right\rangle
\]

(16)

where \( \bar{V}_{aa}^{(36)} \) is the window average of \( V_{aa}^{(36)} \). Similarly, one has measures for every anharmonic resonance in the Hamiltonian.

Thus, as the expectations are zero-centered, ETH, as in eq 4, implies that \( Cov_n(k_{36}) = 0 \) for every choice of \( \ln \). On the contrary, nonzero values for \( Cov_n \) yield a quantitative measure of the deviations from ergodicity. We now choose two zeroth-order states \( |5,8,15,14,0,0\rangle \) and \( |6,7,13,14,0,0\rangle \) with energies \( E_n^0 = 19388.3 \) and 19574.7 cm\(^{-1}\), respectively, in the range appropriate to Figure 3 and compute the intensity–velocity covariance for each resonance operator. The energy windows are centered at their respective \( E_n^0 \) with widths \( \Delta E = 2\delta E_n^0 \) determined by the energy uncertainty \( \delta E_n^0 (\approx 50 \text{ cm}^{-1} \text{ for both states}) \). Within the selected window, there are about 80 eigenstates, and the respective classical microcanonical expectations are nearly constant (cf. Figure 3). Hence, the classical phase space is not expected to change much over the averaging window. The results are shown in Figure 4 and clearly indicate deviations from ergodicity. As expected, the 36-resonance plays an important role for both states. However, localization due to the 526 and the 125 resonances are also observed. The dominance of the 36-resonance can be understood from the parametric evolution of the eigenvalues shown in Figure 4 with varying resonance strength. Several states exhibiting linear parametric motion (solitonic states \( |54,58\rangle \)) can be seen amidst a sea of avoided crossings. Such solitonic states are the robust localized states, also seen exhibiting large fluctuations in Figure 3, resulting in the strong deviations from ergodicity as measured by the covariance.

A final remark is in order at this stage regarding the choice of the two specific zeroth-order states chosen in Figure 4. In their recent work, \( ^{54,58} \) Chowdary and Gruebele associated the sharp fluctuations and hence partially localized, are highlighted by blue boxes.
perturbations do have specific selection rules and hence testing the ETH in a more complex situation.\(^\text{56}\)

The techniques used here are very general and not limited by the dimensionality of the system. The intensity–velocity correlator used in this study is not only capable of identifying localized states but also singles out the relevant perturbations that lead to localization. Note that the eigenstate expectation values play a key role in both ETH and the matrix fluctuation–dissipation (MFD) approach\(^\text{63}\) of Gruebele. Hence, a better understanding of the connection between the two should be useful in gaining fundamental classical–quantum correspondence insights into the dynamics and control of IVR. Finally, it would be of some interest to determine the exact nature of the relationship between ETH, on one hand, and the Logan–Wolynes transition criterion\(^\text{57}\) and the Leitner–Wolynes quantum ergodicity criterion\(^\text{40}\) which includes the dynamical tunneling effects, on the other hand.

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**CONCLUSIONS**

In this work, we have shown that several eigenstates of SCCl\(_3\) exhibit localization even near the dissociation threshold. Such nonthermalized states are identified using sensitive and quantitative measures for deviations from ergodicity. Consequently, the dynamics at these energies should exhibit deviations from RRKM predictions. However, as pointed out in an earlier work\(^\text{58}\) observing the deviations from RRKM depends on whether the optically accessible states have sufficient overlaps with the partially localized eigenstates or not. In other words, experimentally prepared initial states that have significant overlaps with partially localized eigenstates are bound to have nonstatistical dynamics since the eigenstates encode the infinite time energy flow dynamics of the system.

Although the converse statement, i.e., validity of ETH implies RRKM is yet to be established, the important studies\(^\text{59}\) by Nordholm and Rice do lead us to believe that it is reasonable to expect so. It is also relevant to note that the present work is an example of a system wherein the integrability breaking

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**REFERENCES**


