Pathways for Energy Redistribution and Phase Space Bottlenecks in Many–Dimensional Systems

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Abstract

The method of Local Frequency Analysis (see C. C. Martens, M. J. Davis and G. S. Ezra, Chem. Phys. Lett. 142, 519 (1987)) is used to study intramolecular energy transfer in a rotationless planar (3 degree of freedom) model for OCS. LFA is also applied to the standard map, and to a 4-dimensional symplectic mapping consisting of two coupled standard maps.

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I. INTRODUCTION

Statistical theories, such as the well-known transition state and RRKM theories, are widely used to predict and correlate rates of chemical processes [1]. These approaches replace the difficult dynamical problem of large amplitude nonseparable anharmonic nuclear motion in polyatomic molecules with a much simpler statistical mechanical calculation. This replacement is commonly justified by assuming that the motion is of such a complicated and irregular character that it is effectively random: regions of phase space with equal measure are accessed with equal probability, and nonequilibrium distributions relax to equilibrium at a rate that is much faster than other processes of interest, such as unimolecular dissociation. Recent results from the theory of nonlinear dynamics [2] suggest the “intrinsic stochasticity” of Hamiltonian chaos as a dynamical basis for this assumption. The presence of classical chaos, however, is not in itself sufficient to guarantee that a system will behave in the fashion required by statistical theories. Typically, the phase space of a highly excited nonlinear system is made up of coexisting regions of regular and chaotic motion [2]. Long-time correlations may exist [3–6], which lead to disagreement between dynamical and statistical calculations, and deviations from transition state or RRKM behavior [7–15].

In this paper, we investigate the dynamical origins of nonstatistical behavior in highly excited polyatomic molecules. We study the phase space structures responsible for both facile energy redistribution and long-time correlations in the dynamics of a classical three degree of freedom model of the triatomic molecule OCS.

The work described in this paper was motivated by previous results on the intramolecular dynamics of a classical model of OCS constrained to vibrate in a plane (“planar OCS”). The three degree of freedom Hamiltonian for planar OCS investigated here was originally studied by Carter and Brumer [7]. They characterized the motion of this system at a number of energies, extending up to 20,000 cm$^{-1}$ (90 percent of the dissociation energy). From numerically integrated trajectories of 2.4 ps duration, Carter and Brumer determined the maximal Lyapunov exponent $\lambda$, which gives the average rate of exponential divergence of nearby trajectories: if $\lambda$ is greater than zero, then closely spaced initial conditions separate exponentially on average [2]. The associated sensitivity to initial conditions is a fundamental characteristic of Hamiltonian chaos [2].

Based on this diagnostic, Carter and Brumer found that the phase space of OCS under-
goes a transition from primarily regular to primarily chaotic behavior at an energy of around 14,000 cm$^{-1}$. They discovered, however, that localized ensembles of trajectories do not relax to microcanonical equilibrium after 2.4 ps, even at 20,000 cm$^{-1}$, the highest energy studied. This result was inconsistent with their estimation of the local relaxation time, determined from the rate of exponential divergence [16], of 0.17 ps at 20,000 cm$^{-1}$.

This interesting result led Davis and Wagner to reinvestigate the dynamics of OCS [9]. Instead of integrating for 2.4 ps, Davis and Wagner numerically solved Hamilton’s equations for 45 ps. These much longer integration times revealed two distinct timescales for relaxation, the longer of which characterized energy redistribution that was not complete, even after 45 ps.

Fig. 1 shows the time dependence of normal mode energies for a single planar OCS trajectory at 20,000 cm$^{-1}$. The labels (CO, CS, and Bend) indicate the internal coordinates approximated by these normal modes. Cursory inspection suggests that these timeseries are chaotic, due to their irregular, aperiodic appearance. This is in fact the case, as verified by the trajectory’s positive Lyapunov exponent [9]. Careful examination, however, reveals apparent nonstatistical behavior on the picosecond timescale: instead of an unrestricted transfer of energy between modes, sudden transitions between relatively long–lived regions of localized mode energies are observed. (These transitions are marked by arrows in the Figure.) The long–time correlations resulting from this apparent trapping are responsible for the very slow energy relaxation rates observed for ensembles of trajectories by Davis and Wagner [9].

To gain a better understanding of the origins of nonstatistical behavior in this system, Davis and Wagner studied a simplified collinear version of the OCS model, with the O–C–S bending angle fixed at 180 degrees. The resulting Hamiltonian has two degrees of freedom, and its phase space structure can therefore be studied by constructing Poincaré surfaces of section [2]. The sections obtained indicate that at an energy of 20,000 cm$^{-1}$, the system has a “divided phase space”, with coexisting quasiperiodic and chaotic regions [2]. Davis and Wagner found that collinear OCS trajectories could be trapped in restricted regions of phase space for many vibrational periods, and infrequently undergo sudden transitions to other regions of phase space, where they again could become localized [9].

Fig. 2 shows two surfaces of section for collinear OCS resulting from two sequential segments of a single trajectory. Fig. 2(a) gives the first 24.6 ps of the trajectory, while (b)
shows the next 4.5 ps. The areas on the surface of section visited by the trajectory during these two segments are distinct, and it is clear from the Figure that long-time trapping in two disjoint regions indeed occurs for this system, along with abrupt transitions between regions.

It was recognized by Davis [10] that results of MacKay, Meiss, and Percival [4] and Bensimon and Kadanoff [5], obtained in the context of area-preserving maps, were relevant to understanding the mechanism by which barriers to relaxation such as that apparent in Figure 2 originate in the chaotic phase space of two degree of freedom nonlinear Hamiltonian systems. As the nonintegrable perturbation strength of a two degree of freedom system is increased, the invariant tori of the unperturbed system break apart by developing an infinity of gaps. These invariant cantor sets, or “cantori” [4], form leaky barriers which can act as bottlenecks to fast relaxation. These bottlenecks are associated with vestiges of zeroth-order tori having winding numbers (i.e., frequency ratios) given by highly irrational numbers; such invariant tori are the most resistant to destruction by nonintegrable perturbations. The highly irrational “noble” numbers are those which are approximated most poorly by rationals [17], and motion on a torus with such a winding number is therefore as far as possible from a resonance condition between the two mode frequencies [2].

Davis found that this general picture describes the dynamics of collinear OCS [10]. Fig. 3 highlights important structure in the OCS phase space as it appears on the \((Q_{CS}, P_{CS})\) surface of section. Two resonance zones are visible: the \((\omega_{CO}/\omega_{CS}) = 3/1\) zone and the \((\omega_{CO}/\omega_{CS}) = 5/2\) zone, associated with the rational winding numbers 3/1 and 5/2, respectively. The 3:1 resonance zone is located in the outer chaotic region occupied by the trajectory segment shown in Fig. 2(a), while the 5:2 resonance zone is within the inner region, visited by the segment of Fig. 2(b). As suggested by Fig. 2, a barrier to rapid chaotic transport exists between these two resonances.

The noblest irrational number between the rationals 5/2 and 3/1 is \(2 + \gamma\), where \(\gamma = (\sqrt{5} - 1)/2\) is the golden mean [4, 17]. This number is considered to be the most irrational in the range considered, as its continued fraction expansion:

\[
\gamma = \frac{1}{1 + \frac{1}{1 + \frac{1}{1 + \frac{1}{1 + \ldots}}}}
\]

(1.1)

consists of an infinite sequence of 1’s. \(\gamma\) is thus the number between 0 and 1 which is the most
poorly approximated by rationals. More generally, the noble numbers are those irrationals whose continued fraction expansions terminate with an infinite sequence of 1’s [4]. Fig. 3 shows an approximation to the cantorus with winding number $2 + \gamma$, constructed using a convergent sequence of periodic orbits, as described by Davis [10]. Comparison of Figs 2 and 3 strongly suggests that this remnant of an irrational invariant torus is indeed acting as an intramolecular bottleneck [18], as can be verified by calculating the flux across families of dividing surfaces [4]: an absolute minimum occurs at a frequency ratio of $2 + \gamma$. Generically, noble cantori are thought to form intramolecular transition states for two degree of freedom systems in the sense that the noninvariant tori constructed by closing the gaps in the cantori are surfaces of minimum flux [4] (cf. Ref. 19).

Long–time correlations in nonlinear systems also occur in the vicinity of resonant quasiperiodic regions of phase space [6, 20]. In this case, the broken separatrix of a resonance zone forms the partial barrier; trajectories entering resonance zones [20] can be trapped for many vibrational periods as described, again in the context of area preserving maps, by Channon and Lebowitz [21]. Davis noted the role of trapping inside of resonance zones in collinear OCS, with the 3:1 and 5:2 resonances shown in Fig. 3 being the most important [10].

Trapping by broken separatrices and suppressed transport across noble cantori are distinct mechanisms, both leading to long–time correlations in nonlinear systems. In collinear OCS, a typical chaotic trajectory with 20,000 cm$^{-1}$ of vibrational energy occasionally crosses the $2 + \gamma$ bottleneck between the inner and outer chaotic regions. While in the outer region, the trajectory may pass through the partial separatrix, in and out of the 3:1 resonance zone; a similar transition can occur involving the 5:2 resonance zone of the inner chaotic region. Four distinct regions can thus be identified. By considering other resonances (trapping in the 8:3 resonance is also observed, see below) and noble numbers, the phase space can be segmented into arbitrarily many regions. In practice, though, only a few resonances are large enough to be important, and most cantori are so broken up that they do not act as significant barriers to chaotic flow.

The generalization of the above analysis to three degree of freedom planar OCS, and to systems with many dimensions in general, is a difficult open problem. The structure of phase space for $N \geq 3$ degree of freedom nonintegrable systems is qualitatively different from that of the two degree of freedom case. Comparatively little is known at present about
the details of relaxation pathways and origins of long–time correlations in such systems, and
the study of many dimensional Hamiltonian systems and associated symplectic maps is an
area of current research interest and activity [15, 22–35]. Obtaining an understanding of the
phase space structure of multimode systems is clearly of great importance for the theory of
intramolecular dynamics [15, 28, 30, 31, 36–39].

The essential difference between \( N = 2 \) and \( N \geq 3 \) degree of freedom systems lies in
the fact that in the latter case invariant tori do not divide the energy shell into disjoint
regions, as they do in the former. Invariant tori for \( N \) degree of freedom systems are \( N \)
dimensional manifolds, whereas the constant energy surface is \( 2N - 1 \) dimensional. For
\( N > 2 \), tori do not have the correct dimensionality to form absolute barriers to transport on
the energy shell, as a chaotic trajectory can simply “go around” an invariant torus without
leaving the energy shell [2]. In many–dimensional nonlinear systems, the phase space is filled
with a densely distributed network of resonance zones, called the Arnold web [2, 22–24]. In
the nonintegrable case, this network of resonances has associated with it a stochastic layer
[2, 22–24]. It is believed that, unlike two degree of freedom systems, the chaotic zones of
phase space in many dimensional systems are dense and connected, forming a single region.
An initially chaotic trajectory can move along the Arnold web and come arbitrarily close to
any point in the phase space. The process of Arnold diffusion [2, 22–24] may however be
extremely slow [24, 40].

The present paper addresses the problem of long–time correlations and energy relaxation
in many degree of freedom molecular systems. We describe the dynamics and phase space
structure of the three degree of freedom Hamiltonian for planar carbonyl sulfide (OCS)
previously studied by Carter and Brumer [7] and Wagner and Davis [9]. The study of
nonlinear systems with three or more degrees of freedom is considerably more difficult than
investigations of two mode systems. Simple and familiar methods, such as the construction
of Poincare surfaces of section, are difficult to apply. For progress to be made, new and
more general methods of analysis are required.

Our approach to the problem of understanding many–dimensional systems is based on a
powerful Fourier transform–based method for characterizing dynamics in many degrees of
freedom, which we call local frequency analysis (LFA). As we shall show below, local fre-
quency analysis is an especially appropriate framework for analyzing transport in multimode
systems, as attention is directly focused on the important phase space structures leading to
both enhanced transport and long-time correlations. A brief account of this method and the results obtained for planar OCS have been given previously [15]. Subsequent to our previous account, variants of LFA have been applied to several molecular problems [41–43].

The organization of this paper is as follows: in Sec. II, the Hamiltonian for OCS is given, and the numerical aspects of generating trajectory timeseries are outlined. In Sec. III, the method of local frequency analysis is described, and the assumptions underlying its application are discussed. In Sec. IV, a test of the method on the well-studied collinear version of OCS is presented, illustrating the information obtainable by this approach. In addition, a statistical calculation of intramolecular flux is described, based on the definition of regions according to the ratio of the evolving frequencies. Sec. V is concerned with the application of the local frequency method to an investigation of the dynamics and phase space structure of planar OCS. Based on the results obtained, a schematic picture of transport and trapping is presented. Sec. VI contains a discussion of outstanding problems and possible directions to follow in further investigations of this important problem. In addition, some results on the application of LFA to the standard map and a coupled set of two standard maps are given. This treatment of a simple and tractable system provides a first step in the direction of verifying the details of the picture of many dimensional chaotic dynamics that emerges from our study of planar OCS. Further discussion and conclusions are given in Sec. VII.
II. MODEL OF OCS

The system treated in this paper is a model of OCS restricted to vibrate in a fixed plane. This system was first treated by Carter and Brumer [7], and subsequently by Davis and Wagner [9] and Davis [10]. The potential energy surface used is of the Sorbie–Murrell type [44], which has been fit to the OCS normal mode expansion of Foord, Smith, and Whiffen [45]. The potential is of the form:

\[ V(R_1, R_2, R_3) = \sum_{i=1}^{3} V_i(R_i) + V_{\text{INT}}(R_1, R_2, R_3) \]  

(2.1)

where

\[ V_i(R_i) = D_i \left\{ 1 - \exp \left[ -\beta_i(R_i - R_i^0) \right] \right\}^2 \]  

(2.2)

\[ V_{\text{INT}}(R) = A P(\Delta R_1, \Delta R_2, \Delta R_3) \prod_{i=1}^{3} \left[ 1 - \tanh \left( \frac{\gamma_i \Delta R_i}{2} \right) \right] \]  

(2.3)

\[ \Delta R_i = R_i - R_i^0. \]  

(2.4)

The internal coordinates are defined as follows: \( R_1 \) is the CS separation, \( R_2 \) is the CO separation, while \( R_3 \) is the OS distance. \( P(\Delta R_1, \Delta R_2, \Delta R_3) \) is a quartic polynomial in its arguments, and \( A, D_i, R_i^0, \beta_i, \gamma_i \) \((i = 1, 2, 3)\) are constants. The values for the potential parameters are given in Ref. 7, along with the form of the kinetic energy in these coordinates. This potential is considered to be a comparatively realistic one, even at the high energies studied here.

To generate timeseries for subsequent analysis, trajectories were integrated for 45 ps. Planar cartesian coordinates were used for the trajectory integrations, which were run at an energy of 20,000 \( \text{cm}^{-1} \). A Burlirsch–Stoer variable stepsize integrator [46] was initially employed to calculate the timeseries for 400 initial conditions, belonging to 8 ensembles of 50 trajectories each (although the ensembles differed in their attributes, this feature is not important for the work described here). The trajectories were initially [9, 10] generated and stored with points spaced too far in time for satisfactory Fourier analysis. The timeseries were therefore filled in with a 6th order Adams–Moulton predictor–corrector integrator [46] before subsequent spectral analysis. All initial conditions were chosen to have (conserved) total angular momentum \( J = 0 \).
III. METHOD OF LOCAL FREQUENCY ANALYSIS

In this Section, we describe the method of local frequency analysis [15]. The basic idea is to determine “time-dependent fundamental frequencies” for the (possibly chaotic) motion. In a strict sense, this is impossible, as precise knowledge of both frequency and time violates the time/frequency uncertainty principle. The complementarity between knowledge of frequency and time is reflected in the inverse relation between signal length and frequency resolution in conventional FFT analysis [47]. However, by considering short segments of a timeseries which are nonetheless long enough to provide sufficient frequency resolution, it is possible to find approximate frequencies associated with finite time intervals using FFT methods (cf. the concept of evolutionary power spectra, discussed in Ref. 48).

We note that use of the FFT algorithm is not essential to the LFA method. Recently developed approaches such as the Linear Prediction [49] or MUSIC [50] methods are suitable for spectral analysis of very short timeseries. In these methods, choice of an appropriate model, e.g., a quasiperiodic timeseries plus noise, enables local fundamental frequencies to be extracted from timeseries only a few vibrational periods long. Both Linear Prediction and MUSIC have been applied very recently to LFA of molecular systems [42, 43, 51].

In the work reported here, LFA of chaotic motion is accomplished by fast Fourier transformation of short sequential trajectory segments. The regions of phase space occupied by the trajectory are characterized by the local frequencies, or, more precisely, by ratios or linear combinations thereof. The evolution of the system can then be followed by monitoring the changes of local frequencies with time. As we shall see below, important phase space structures, i.e., those leading to both enhanced transport and long-time correlations, appear to be naturally defined by relations between the frequencies of motion, and the local frequency representation thus focuses attention directly on the essential features of the dynamics.

Briefly, the procedure used in our analysis of OCS is as follows:

1. Hamilton’s equations for the three degree of freedom planar OCS system are integrated for 45 ps, as discussed in Sec. II.

2. The trajectory timeseries are divided into 128 overlapping segments, each of approximately 1.4 ps in length. The midpoint of each region is approximately 0.35 ps from the next, giving a 75 percent overlap of adjacent segments. Overlapping segments are
used to improve the time resolution, as frequency values were obtained every 0.35 ps.

3. Fast Fourier transforms of the segments are computed [47]. Each segment is multiplied by the -74 dB Blackman–Harris window function before the FFT analysis. (See Refs. 52 and 53 for a discussion of this window function.) The frequency resolution is then determined by the 1.4 ps length of the Fourier transform window.

4. Frequencies are numerically determined by a nonlinear least squares fit of spectral features to a 3–point Gaussian lineshape function [53]. The maximum peaks in the cartesian coordinates approximating the CO stretch, CS stretch, and bend are determined. In practice, frequencies falling into a certain empirically determined range are taken, to avoid occasional spurious results due to interferences from strong overtones of other modes.

5. Segments are characterized by an ambiguity index, defined as the ratio of the amplitudes of the second largest and largest peaks appearing in the spectra of a single coordinate. The ambiguity index is used to identify segments where the spectra become sufficiently complex to make the assignment of a single frequency difficult. We shall discuss this point in more detail below.

The results of this calculation are local fundamental frequencies, associated with the midpoint in time of each overlapping segment. These frequencies, denoted $\omega_{CO}$, $\omega_{CS}$, and $\omega_{bend}$, are those for the largest peaks in the spectra of the CO stretch, CS stretch, and bend motion, respectively. To compare with the frequency data, normal mode energies corresponding approximately to the CO stretch, CS stretch, and bend, are also determined. These are averaged over overlapping segments in the same manner as in the frequency calculations.

For the LFA approach to be useful, interesting dynamics should occur on a timescale that is comparable to or longer than the duration of the window defining the trajectory segments. The trajectories in this case may then possess definite frequencies over one or more segments, and it is then possible to define local frequencies as a function of time (i.e., segment) in the restricted sense described above.
IV. ILLUSTRATION OF THE METHOD: TWO DEGREE OF FREEDOM COLLINEAR OCS

In this Section we demonstrate the LFA method by treating the collinear OCS system studied in detail by Davis [10]. In this case, the picture of the dynamics provided by LFA can easily be compared with independent indicators, such as configuration space trajectories and surfaces of section.

When computed for the full 45 ps duration of the orbit, the Fourier transforms of the CO and CS coordinates of the collinear OCS trajectory shown in Fig. 2 have, as is typical for chaotic dynamics, a “grassy” appearance [54], reflecting the fact that the timeseries is not quasiperiodic and thus is not characterized by two definite frequencies (cf. however [55]).

Fig. 4 shows the configuration space orbit, \((Q_{CS}, P_{CS})\) surface of section, and the two cartesian coordinate spectra for a 1.4 ps segment of this trajectory. The midpoint in time of the segment occurs 19.318 ps after the start of integration, as indicated in the upper left corner of the Figure. This segment of the trajectory is trapped in the vicinity of a 3:1 resonance zone.

Fig. 4a shows this segment in configuration space. The characteristic “S–shape” of a 3:1 resonance is visible, with the trajectory undergoing 3 CO oscillations during each CS period. Fig. 4b shows the \((Q_{CS}, P_{CS})\) surface of section for this segment. The trajectory is trapped near the three quasiperiodic islands resulting from the 3:1 resonance. Figs 4c,d show the CO and CS coordinate Fourier spectra. The spectra are relatively simple, a result of the trapping of the trajectory near a quasiperiodic region of the phase space. In contrast to the full 45 ps spectra, well–defined local frequencies clearly exist for the segment. The two arrows indicate the fundamental peaks chosen for analysis of this segment. (Due to the distortion of the trajectory resulting from nonseparability in the coordinates used for Fourier transforms, the second harmonic of the CS motion is actually larger than the fundamental peak in the CO spectrum; a lower cut–off in CO frequency avoids an incorrect peak selection in this case.)

The values of the local frequencies for this segment are \(\omega_{CO} = 60.278 \text{ ps}^{-1}\) and \(\omega_{CS} = 20.087 \text{ ps}^{-1}\), which are in the ratio \((\omega_{CO}/\omega_{CS}) = 3.0008\). LFA via FFT clearly detects the 3:1 resonant condition between the two modes which occurs during this segment. (Units for \(\omega\) are cycles per picosecond throughout.)
In Fig. 5 the configuration space orbit, surface of section, and coordinate spectra are given for a different segment of the same trajectory. As indicated by the time value in the upper left corner of the Figure, this segment occurs about 7.6 ps after the one shown in Fig. 4. The trajectory is again localized, but in a different region of phase space, near the 5:2 resonance zone. The distinctive configuration space signature of the 5:2 resonance is visible in Fig. 5a. This trajectory segment undergoes 5 cycles of the CO motion for every 2 oscillations of the CS bond.

The 5:2 resonance is also plainly visible on the CS surface of section. The trajectory is localized very near the quasiperiodic region inside of the 5:2 resonance, and the chain of 5 islands appears clearly.

Figs. 5c and 5d show the CO and CS coordinate spectra of this segment. The Fourier spectra are again simple, due to the highly localized motion. Clear qualitative differences in peak location and amplitude between these plots and the spectra shown in Fig. 4 should be noted. The numerical values of the local frequencies are $\omega_{CO} = 57.252 \text{ ps}^{-1}$ and $\omega_{CS} = 22.896 \text{ ps}^{-1}$, with the ratio $(\omega_{CO}/\omega_{CS}) = 2.5005$. Again, this frequency ratio clearly and unambiguously identifies the dynamical character of the segment.

We also observe trapping of collinear OCS trajectories in the 8:3 resonance zone (not shown). Note that the rational 3/8 is the Farey sum of the rationals 2/5 and 1/3 [17].

We now consider a transition of this chaotic trajectory across the $2 + \gamma$ cantorus. Fig. 6 shows the configuration space orbits for six sequential segments. The elapsed times in ps, evaluated at the midpoints of each segment, are given at the top of each plot. A qualitative change in the motion evidently occurs between the third and fourth segments. Note in particular the rapid increase in the CS stretch amplitude, with a “tendril” abruptly protruding beyond the confines of earlier segments around $T = 38.980 \text{ ps}$. This feature is marked by a small arrow in the fourth plot.

Fig. 7 shows the same six segments, except now on the CS surface of section. The transitions are clearly visible in this representation: the first segment is trapped near the 5:2 islands. During the second and third segments, the motion has moved into the chaotic layer outside the broken 5:2 separatrix. Between the third and fourth segments, the trajectory has abruptly crossed the $2 + \gamma$ cantorus, and a rapid increase in the CS energy (a rough measure of which is the distance from the origin on the CS surface of section) occurs. The last three segments wander in the chaotic region outside of the 3:1 resonance zone. An arrow
indicates points of the fourth segment that have crossed the noble bottleneck.

Fig. 8 displays the coordinate spectra of four segments shown in the previous two Figures, along with the midpoint times. A pronounced change in the spectra occurs as the cantorus is crossed: the spectra have a more “noisy” appearance for segments in the irregular region around the 3:1 islands than they do for segments in the localized region around the 5:2 resonance zone. As the trajectory passes from the segment centered around \( T = 38.636 \) ps to the segment at \( T = 39.325 \) ps, the CO/CS frequency ratio changes from 2.4804 to 2.8575, crossing \( 2 + \gamma \approx 2.6180 \). Monitoring the local frequencies enables this transition to be detected directly.

As illustrated above, it is possible to use local frequency data to define regions in phase space, based on the ratio of the CO and CS frequencies. By varying the frequency ratio defining the boundary between two regions and calculating the flux of an ensemble of trajectories across the boundary, the ratio leading to minimum transport can be found. To calculate the flux it is simply necessary to count the number of times the local frequency ratio passes through the prescribed value per unit time. Note that the phase space dividing surface itself need not be constructed. We have performed this calculation on an ensemble of 50 collinear trajectories at \( E = 20,000 \) cm\(^{-1}\). Fig. 9 shows the total number of crossings of a boundary defined by the ratio of the CO and CS frequencies as a function of that ratio. The flux goes to zero around \( (\omega_{CO}/\omega_{CS}) = 2.45 \), which is the edge of the dynamically allowed range for this system. A maximum is seen at 2.5, corresponding to the 5:2 resonance zone. This peak occurs because the local frequency ratios of trajectories trapped in this resonance “jitter” around 2.5, leading to an enhanced value for the flux. The minimum falls at about 2.57, which is near the noble number \( 2 + \gamma = 2.618 \), as expected.

In summary, results for collinear OCS obtained by LFA correlate very well with the view of chaotic motion provided by configuration space plots and surfaces of section. These results provide confidence that the method will yield meaningful results for multidimensional systems.
V. EXTENSION TO MANY DIMENSIONAL SYSTEMS: PLANAR OCS

We now describe the application of LFA to the study of chaotic dynamics in the three degree of freedom model of planar OCS described above. Except for the addition of another degree of freedom, the technical aspects of applying LFA to planar OCS are identical to those in the collinear case.

Planar OCS exhibits qualitatively similar behavior to that observed in collinear OCS. Long-time correlations are seen, and ensembles of trajectories show slow, nonexponential intramolecular energy relaxation \[7, 9\]. At 20,000 cm\(^{-1}\), planar OCS is in fact less chaotic than collinear OCS at the same energy, and its relaxation times are typically longer than those of the corresponding two degree of freedom system. This can be understood by noting that the same amount of energy is distributed over more degrees of freedom in planar OCS, resulting in less energy per mode on the average, and thus weaker couplings and less chaotic behavior.

Examination of CO coordinate spectra belonging to segments of single planar OCS trajectories shows that the spectra change with time, and that, as for the collinear problem, local frequencies to be meaningfully defined using the FFT method of spectral analysis. Following the evolution of chaotic trajectories in the space of local frequencies provides a useful framework for understanding the details of chaotic dynamics and phase space structure. As discussed above, the phase space of a many-dimensional nonintegrable system is densely filled with resonance zones and their accompanying stochastic layers. (The Arnold web \[2, 22–24\]). For an integrable Hamiltonian \(H^0(I)\) the resonance zones are defined by conditions on the frequencies:

\[
\mathbf{k} \cdot \mathbf{\omega} = \sum_{i=1}^{N} k_i \omega_i = 0, \tag{5.1}
\]

for all integers \((k_1, \ldots, k_N)\), where \((\omega_1, \ldots, \omega_N)\) are the frequencies of motion \(\omega = \partial H^0/\partial I\). Chaotic trajectories of the full Hamiltonian can move along the network of resonance zones, and determination of the local frequencies enables the evolution of a trajectory segment in relation to this web to be followed.

We have seen that barriers to rapid relaxation in two degree of freedom systems are characterized by irrationality conditions between the frequencies of motion. These phase space structures consist of noble cantori \[4, 10\], and transitions across them are accompanied by...
characteristic spectral changes as the frequency ratios pass through noble numbers. Partial
separatrices around nonlinear resonances also form bottlenecks to rapid transport [6, 11–
14, 20]; in this case, distinctive locking of frequency ratios at rational values occurs within
the resonance zones. Although the mechanisms leading to long–time correlations in $N \geq 3$
dimensional systems may fundamentally differ from those in the two degree of freedom case,
it is plausible that important higher dimensional phase space objects might also be defined
by relations between the frequencies of motion. We shall supply evidence for this viewpoint
below.

These considerations make it desirable to have a pictorial view of the dynamics in fre-
quency space. For 3 mode systems, a particularly convenient representation of the spectral
evolution is provided by the frequency ratio plane. Since it is not the absolute magnitudes of
the frequencies, but instead relations between them, that are of central importance in non-
linear dynamics [2], the essential structure of the Arnold web for a three degree of freedom
system can be represented on a two dimensional plot (“tune space”, cf. [56]).

Fig. 10 shows the frequency ratio plane in the range relevant for planar OCS. Frequencies
satisfying resonance conditions:

$$k_1 \omega_{\text{bend}} + k_2 \omega_{\text{CS}} + k_3 \omega_{\text{CO}} = 0 \quad (5.2)$$

appear as lines on this plot. A number of important resonance lines have been drawn and
labeled by their values of $(k_1, k_2, k_3)$; the plane is of course densely covered with high order
resonance lines. Also included on the plot are dashed lines representing pairwise irrational
relations between the frequencies. For instance, the horizontal dashed line labeled $(5 - \gamma)$
corresponds to those points on the plane where $(\omega_{\text{CO}}/\omega_{\text{bend}}) = 5 - \gamma$. Vertical dashed
lines result from CS/bend irrational ratios, while the sloped dashed lines correspond to
irrational CO/CS frequency pairs. These pairwise irrational lines have been included for
later reference; unlike the resonance conditions, their dynamical significance remains to be
demonstrated.

A. Results and Examples

We now illustrate several common types of trajectory behavior observed in planar OCS.
In analyzing the dynamics, we considered 8 ensembles of 50 trajectories each (400 total).
Each trajectory was 45 ps in duration, and was broken into 128 overlapping segments, as described in Sec. III. Careful scrutiny of 400 individual trajectories was performed, and it was found that a number of distinct patterns of behavior appeared repeatedly in the data, indicating that a few important mechanisms for intramolecular energy redistribution are playing a role. We shall now illustrate these by describing several typical trajectories in detail.

1. Transport along CS/Bend 3:2 resonance

Fig. 11 shows the time–dependent local frequency ratios and averaged mode energies for a chaotic planar OCS trajectory. The top frame gives the CS/bend local frequency ratios, the second frame shows the same for CO/CS, while the third frame gives the CO/bend values. The frequency data are plotted as solid symbols, one (or more, see below) for each of the 128 segments. Also included are horizontal lines, indicating pairwise resonant conditions (dotted) and noble ratios of the form $L \pm \gamma$, where $L$ is an integer and $\gamma = 0.6180\ldots$ is the golden mean (dashed). The bottom three frames show locally averaged normal mode energies for CO, CS, and bend, respectively. Energy averages were performed over the same intervals used to determine the local frequencies.

It should be noted that, for certain segments, more than one value for the local frequency ratio has been plotted. These result from ambiguous segments having spectra with at least two peaks of comparable intensity. A segment is considered ambiguous if the second largest peak is greater than 80 percent of the maximum peak amplitude. Restricting the calculation to the largest peak in each spectrum for unambiguous spectra, or to the two largest peaks for spectra that are ambiguous, the resulting frequency ratio combinations were determined and plotted. The bend spectra were found never to be ambiguous, so 4 possible combinations result in the worst case of both CO and CS ambiguity.

The frequency ratios change with time as the trajectory evolves. The changes are sometimes smooth and continuous, and other times sharp and abrupt. The evolution of frequency ratios roughly parallels the normal mode energy exchange, and can be qualitatively understood by noting that CO and CS frequencies decrease with increased excitation in the corresponding mode, while the bend frequency increases when energy is transferred into bending motion.
A notable feature of the particular trajectory of Fig. 11 is the occurrence of several groups of successive segments where the CS/bend frequency ratio is fairly constant around the value \((\omega_{CS}/\omega_{bend}) = 1.5\). While \((\omega_{CS}/\omega_{bend})\) executes small fluctuations around this value, the other frequency ratios and the normal mode energies show substantial and erratic changes.

Fig. 12 shows the configuration space projections for 8 contiguous segments that were chosen to include several time intervals with a CS/bend frequency ratio of approximately 3/2. Vertically down from the top are plots with axes \((Q_{CO}, Q_{CS})\), \((Q_{CO}, Q_{bend})\), and \((Q_{bend}, Q_{CS})\), respectively. Time increases from left to right horizontally. The initial and final segments of this group are marked by arrows labeled (A) and (B) on Fig. 11. Although these projections onto coordinate planes are in general less informative than the configuration space plots shown above for collinear OCS, some features stand out clearly nonetheless. In this case, one can clearly see the trajectory enter a region of phase space characterized by a 3:2 resonance between the CS and bend modes.

The configuration space regions occupied by each projection of the trajectory vary substantially, indicating exchange of energy between the modes. This can be seen by examining Fig. 11: between segments (A) and (B), extensive energy transfer involving all three modes occurs. *Throughout these changes, the CS and bend modes remain locked in the 3:2 resonance condition.*

The picture that emerges from an analysis of these and other examples found in the full trajectory ensemble is of the dominant role played by the CS/bend 3:2 resonance zone as a pathway for facile energy relaxation. Note that motion *along* a resonance zone of the type discussed here is characteristic of \(N \geq 3\) mode systems [22–24].

2. Long-time correlations near junctions of resonance lines

We now consider another typical behavior seen in planar OCS. Fig. 13 shows a trajectory which exhibits much less activity than the previous example. The motion is strongly localized for about 20 ps before any significant energy exchange occurs.

LFA indicates that the CO/CS frequency ratio is locked around \((\omega_{CO}/\omega_{CS}) = 7/3\) for the initial two thirds of the trajectory. The CS/bend and CO/bend ratios are also nearly constant, although more variation is observed here. The CS/bend ratio falls on or near the 2:1 resonant line. As the trajectory evolves, small but abrupt changes in the CS/bend and
CO/bend frequency ratios are seen. Of particular interest is the transition of the CO/bend frequency ratio across the dashed line in the third frame, occurring around 8 ps. This dashed line falls at 4.382, and corresponds to the pairwise noble ratio \( \frac{\omega_{CO}}{\omega_{bend}} = 5 - \gamma \).

Fig. 14 shows the configuration space projections of the segment (A)–(B) indicated on Fig. 13. Segment (A) falls in the CS/bend 2:1 resonance zone. Passing from the second to third segment, a subtle change in the configuration space CS/bend projection is visible. Here, the trajectory is leaving the 2:1 resonance zone. Fig. 15 displays the (C)–(D) segments, during which the trajectory returns to the original region of phase space. The final 2:1 CS/bend resonance is particularly clear in configuration space. Throughout these transitions, the ratio \( \frac{\omega_{CO}}{\omega_{CS}} \) remains near the value 7/3, suggesting that the trajectory is moving along the (0,7,-3) resonance zone.

Further examination of the frequency data reveals that the trajectory of Fig. 13 undergoes transitions between intersections, or junctions, of resonance lines. Near its beginning, the trajectory is near the intersection of the (2,-1,0) and (0,7,-3) resonance zones. The sudden jump in frequency ratios that occurs between (A) and (B) takes the trajectory along the (0,7,-3) CO/CS resonance line to a junction with another resonance. [In doing so, the CO/bend local frequency ratio crosses the noble number \( \frac{\omega_{CO}}{\omega_{bend}} = 5 - \gamma \).] After this large jump, the trajectory wanders among several nearby resonance junctions before hopping back along (0,7,-3) to the vicinity of (2,-1,0), the CS/bend 2:1 resonance.

Long-time trapping can also occur for trajectories that sample areas of phase space that are more strongly chaotic than the regions visited by the trajectory shown in Figs. 13–15. Fig. 16 shows a trajectory starting off in a fairly chaotic region, then becoming localized for many hundreds of vibrational periods, before finally returning to an area of pronounced chaos. During the time interval between 12 ps and 25 ps, the trajectory wanders among the junctions of a large number of resonance zones, including \((4, -7, 2), (2, 6, -3), (6, -1, -1), (8, -5, 4), (7, -4, 0), (3, 3, -2), (5, -3, 0), \) and \((5, 2, -2)\).

3. Pairwise barriers to chaotic transport

After about 25 ps, the trajectory shown in Fig. 16 escapes from its localized region and begins a period of pronounced energy exchange. This abrupt transition in behavior correlates with a sudden jump of the CO/CS and CS/bend frequency ratios across the noble numbers
2 + γ and 1 + γ, respectively. The CS/bend local frequency ratio rapidly moves from 5/3 to 3/2 (the ambiguous transition segment actually shows both of these possibilities, reflecting the intermediate step of an intensity exchange between two peaks, a commonly observed spectral signature of transition). Just at the point of crossing, the CO/bend frequency has moved on the dotted line in the third frame, indicating a 13:3 CO/bend resonance condition.

Figs. 17 and 18 show the frequency ratio/energy and configuration space plots of another trajectory exhibiting the same qualitative behavior of sudden changes in localization. For the first 20 ps of the trajectory, the frequency ratios show a hopping between piecewise constant values. This pattern of frequencies corresponds to infrequent transitions between the junctions of intersecting resonance lines.

Between segments (A) and (B), a pronounced exchange of CO and CS energy occurs, accompanied by a crossing of \( \omega_{CO}/\omega_{CS} = 2 + \gamma \), as in the previous example. Again, this crossing occurs when a resonance condition exists between the CO and bend modes. This time, however, it is the (4,0,-1) resonance line that is coincident with the energy exchange.

The configuration space plots given in Fig. 18 show the CO to CS energy flow very clearly: the top frames containing the \((Q_{CO}, Q_{CS})\) projections indicate a sudden change in the shape of the trajectory boundary between the fourth and fifth segments shown. During the fourth segment, the trajectory apparently crosses a phase space barrier and then rapidly fills out an area that is elongated in the vertical CS direction, with concomitant restriction of the horizontal CO bond excursion. The initial “tendril” of the relaxation is marked with an arrow in the fourth frame of Fig. 18.

Several other clear examples of the relaxation mechanism just described were observed in the full ensemble, and evidence for resonance transport across pairwise irrationals in other regions of phase space was also found.

B. Phase Space Structure of Planar OCS

We now summarize our observations on the dynamics of planar OCS, and formulate a picture of phase space consistent with the observed transport. The following types of behavior emerge from the examples described above, and from many other trajectories not shown here:

- Long-time trapping near the intersections of resonance lines.
• Relatively slow diffusion along the Arnold web, occurring via infrequent transitions between resonance junctions along high order or weakly driven resonances.

• Rapid transport *along* important low order resonance zones.

• Apparent inhibition of chaotic transport by phase space dividing surfaces associated with pairwise local frequency ratios given by noble numbers.

• Passage through noble bottlenecks along transverse low order resonance lines.

The slow wandering of trajectories along the network of intersecting resonance lines is typical of the Arnold diffusion mechanism for phase space transport [22–24]. LFA reveals an additional feature of this slow transport process: long time trapping at the *intersection* of resonance zones, in the neighborhood of periodic orbits characterized by the simultaneous satisfaction of two resonance conditions. This observation suggests that the transport observed here is not actually “diffusive”, in that the rate of transport is not determined by a random drift along the resonance zones, but rather by the rate of transport into and out of the resonance junctions themselves. Enhanced transport of chaotic trajectories along low–order, strongly driven resonances, such as the 3:2 CS/bend resonance, is also in accord with the previously discussed mechanism of resonance streaming [2, 22, 23, 57, 58].

The mechanism leading to long–time trapping of trajectories at resonance intersections has previously received little attention (cf. however the recent paper by Kook and Meiss [27](b)). For two degree of freedom systems, correlations result from the passage of trajectories into resonance zones through the surrounding broken separatrices. In three degrees of freedom, it is plausible to assume that a similar mechanism exists: passage in and out of resonance zones may be slowed due to barriers formed by the multidimensional analogues of broken separatrices [32, 33, 35]. Motion may still occur relatively freely along resonance layers. If two linearly independent resonance lines intersect, motion along one resonance may be blocked by the broken separatrix of the other. Near the periodic orbit at the crossing, an encircling partial barrier that is in some sense the union of the separatrices is evidently present, and passage of a trajectory into or out of the resonance junction region may be inhibited as a result. This conjecture seems to be in accord with the results observed for planar OCS.
Another interesting result is the observation that pairwise frequency ratios related to noble numbers, which are of such importance in the theory of transport in two degrees of freedom, appear to play a role in the inhibition of rapid relaxation in this three degree of freedom system. While one would perhaps expect this by analogy with what is known about collinear OCS, there is an important and fundamental difference between the two cases that should be noted: in two degrees of freedom, specifying the ratio of the two frequencies of motion at fixed energy may be thought of as defining a partial barrier of codimension one. In collinear OCS, for instance, the condition \((\omega_{CO}/\omega_{CS}) = 2 + \gamma\) specifies the noble cantorus that acts as a minimum flux intramolecular bottleneck. In \(N\) degrees of freedom, specifying one relation between the frequencies provides a single constraint in addition to the conservation of total energy, and thus also results in a codimension one surface. If \(N = 3\), the surface is 4-dimensional, and cannot be the multidimensional analogue of a single irrational cantorus, which would require two conditions on the frequencies and be \(N = 3\) dimensional. A codimension one surface defined by a single frequency condition has the correct dimensionality to divide the energy shell and act as a barrier to transport, but must be a fundamentally different object than the remnant of an invariant torus which forms the corresponding dividing surface in two degrees of freedom \([32, 33, 35]\).

A rigorous justification for the role of pairwise bottlenecks in the phase space of planar OCS is lacking at present. For an arbitrary three degree of freedom system, there is no reason to expect simple pairwise frequency relations to play a distinguished dynamical role. In the case of planar OCS, though, we are treating coordinates for which the motion is, very roughly speaking, separable (as illustrated by the approximate alignment of the configuration space orbit “boxes” along the coordinate axes). This approximate separability adds credence to the notion that collinear structure, such as the CO/CS noble frequency ratios, and also pairwise relations involving the bend mode, should play a role in the dynamics of planar OCS: out of the many possible types of phase space condition that could affect the dynamics of a generic system, the Hamiltonian of OCS is evidently strongly influenced by pairwise ones. In addition, we expect the collinear phase space structure to emerge in the limit of zero bend energy, and thus it may not be surprising to find the CO/CS pairwise noble frequency ratios playing a role in regions of phase space close to the linear configuration.

The 4-dimensional barriers to relaxation are, of necessity, very different phase space objects than the cantori dividing surfaces of two degree of freedom systems. In particular,
they are intersected everywhere by transverse resonance lines, which provide conduits for transport across them. Our data suggests that, for resonances that are of high order or not well “driven” by the Hamiltonian, the pairwise barriers are effective in impeding the crossing of trajectories. If trajectories end up in an important low order resonance, however, they may rapidly stream through the dividing surfaces.

Although this picture of the phase space dynamics of planar OCS is plausible, other formal approaches to the origins of long–time correlations and inhibition of free transport are possible, based on recent number theoretic results on mutually irrational pairs of irrational numbers [59]. We briefly discuss these alternatives below, along with some studies of multidimensional symplectic maps, whose purpose is to clarify some of the questions raised by our work on planar OCS.
VI. APPLICATION TO COUPLED STANDARD MAPS

Our detailed study of the classical Hamiltonian for planar OCS has suggested a consistent and appealing picture of chaotic dynamics in many-dimensional systems. Due to the complexity of the Hamiltonian and associated computational requirements, however, further confirmation of this picture has proven difficult. Nevertheless, the ideas developed for OCS can be tested on simpler model systems.

We now apply LFA to symplectic maps in two and four dimensions. The particular systems described below are single and coupled variants of the familiar Chirikov–Taylor standard map [3]. Symplectic (the multidimensional generalization of area–preserving) maps capture the important features of nonlinear Hamiltonian systems, while being very simple and economical from a computational standpoint.

The standard map is given by the set of difference equations [2, 3]:

\[ I_{n+1} = I_n + \frac{k}{2\pi} \sin(2\pi \theta_n) \]  
\[ \theta_{n+1} = \theta_n + I_{n+1}. \]  

These equations are iterated, given initial values of \( I \) and \( \theta \). The constant \( k \) is the stochasticity parameter, whose value determines the behavior of the map: as \( k \) is increased, the map becomes more chaotic. This system has been intensively studied, and much is known about the details of its dynamics [2–5, 20]. In particular, the invariant torus with winding number given by \( \gamma \) (and, by symmetry, the equivalent torus at \( 1 - \gamma \)) is known to break into a cantorus at the value \( k = 0.9716 \ldots \), and is the last nonresonant torus to do so as \( k \) is increased [4].

We have investigated this system using LFA. The analogue of the frequency ratio for two degree of freedom continuous systems is the winding number of the map, which is given by the average of the angle \( \theta \) over a number of iterations. For the standard map, this is equivalent to averaging the action. LFA for this system is straightforward and unambiguous, and accomplished by simply averaging the variable \( I \) over relatively short, overlapping segments of a long sequence of iterations.

Fig. 19 compares the evolution of the unaveraged variable \( I \) with the local winding number, averaged over overlapping segments of 100 iterations, with a 75 percent overlap of adjacent sections. The value of \( k = 1.1 \) was chosen, which is slightly above the critical value...
for the breakup of the last bottleneck to global chaotic transport \[4\]. The averaging smooths out the large fluctuations of \(I\). Trapping in resonance zones and transitions across the intervening bottlenecks are evident in the Figure as flat regions and rapid, sudden changes, respectively.

It is possible to use the local frequencies to define regions in the phase space of the standard map, as done above for collinear OCS. Figs. 20 and 21 show the result of determining the total flux across dividing surfaces defined in terms of winding number, as a function of the winding number. Fig. 20 was calculated at \(k = 1.0\), just above the critical value \(k = 0.9716\ldots\). An interesting and apparently self–similar structure results. The global minima of the flux fall very near the noble cantori at \(<I> = \gamma\) and \(<I> = 1 - \gamma\). Fig. 21 shows a similar calculation performed at \(k = 1.2\), significantly above criticality. The flux through the noble cantori has greatly increased, as expected. We note that these plots are qualitatively similar to the flux vs. frequency ratio result obtained for collinear OCS, shown in Fig. 9, although here, due to the simplicity of the system, better statistics are obtained.

We have also investigated a system of two coupled standard maps, given by the difference equations for \((I, J, \theta, \psi)\):

\[
\begin{align*}
I_{n+1} &= I_n + \frac{k_1}{2\pi} \sin(2\pi \theta_n) + \frac{b}{2\pi} \sin[2\pi(\theta_n + \psi_n)] \tag{6.3a} \\
\theta_{n+1} &= \theta_n + I_{n+1} \tag{6.3b} \\
J_{n+1} &= J_n + \frac{k_2}{2\pi} \sin(2\pi \psi_n) + \frac{b}{2\pi} \sin[2\pi(\theta_n + \psi_n)] \tag{6.3c} \\
\psi_{n+1} &= \psi_n + J_{n+1}. \tag{6.3d}
\end{align*}
\]

Here, \(k_1, k_2,\) and \(b\) are constants. This system provides a model for the return map of the four–dimensional surface of section obtained for a continuous three degree of freedom system [2]; the two independent winding numbers are directly analogous to the two frequency ratios used to construct Fig. 10. This system has been recently considered in Refs. 25–27.

Fig. 22 shows the evolution of the local winding number \(<I>\) for the coupled standard map. The averaging is again over segments of 100 iterations. The behavior seen here is qualitatively similar to the results observed for the single standard map, with trapping near resonance zones and sudden transitions between localized regions.

Figs. 23 and 24 show the resulting dynamics in winding number space, constructed by plotting \(<I>\) vs. \(<J>\) for many segments of a long iteration. These Figures provide a direct
picture of the Arnold web for the system of eq. (6.3). The resonance network is clearly visible as the grid of darkened lines on the plots.

Fig. 23 was generated with $k_1 = k_2 = 0.8$ and $b = 0.02$, below the critical value $k_i = 0.9716\ldots$ for the uncoupled maps. If the maps were uncoupled, the trajectory could not enter the region with either of the winding numbers greater than 0.382 or less than 0.618. Here the trajectory does (slowly) find its way into this region by moving along the Arnold web. If we had iterated long enough, the trajectory would have presumably explored the entire square.

Fig. 24 shows the dynamics for $k_1 = k_2 = 1.2$ and $b = 0.02$. Transport throughout the square is now much more rapid. Dark spots of high point density occur at the intersection of resonance lines, indicating trapping of the trajectory at resonance junctions.

These results for the coupled maps show the same qualitative features found in our study of planar OCS. Further detailed study of the coupled standard map system will help elucidate more fully the chaotic dynamics of many dimensional systems [35].
VII. DISCUSSION AND CONCLUSIONS

The model proposed above for the phase space structure and dynamics of planar OCS is based on qualitative observations of many trajectories. However, a rigorous basis for our conclusions is lacking at present. Transport along resonance layers is a many dimensional effect with no analogue in two degrees of freedom, and is in accordance with the usual picture of Arnold diffusion and recent work on rapid transport along resonance zones [57, 58]. On the other hand, our focus on the dynamical significance of pairwise noble frequency ratios is in essence an assumption that there exist important barriers to energy redistribution in the phase space of planar OCS consisting of continuous families of the corresponding two degree of freedom dividing surfaces. While plausible, there is at present no theoretical justification for this assumption.

We now briefly outline two other points of view concerning the structure of multidimensional phase space, which may lead to a more complete theory of bottlenecks in many mode systems. Both are based on generalizations of the number theoretic analysis, which was so successful in understanding two degree of freedom systems [2, 4], to higher dimensional dynamics. The fundamental differences between two and higher dimensions are explicitly recognized. We restrict our discussion to three degree of freedom systems.

The first approach focuses on the resonance lines. As we have discussed, facile mode-mode energy flow in planar OCS occurs along the network of the Arnold web. We thus imagine the dynamics to consist of a sequence of transitions between resonance junctions along the joining resonance zones. In this picture, phase space is decomposed into regions surrounding each periodic orbit—the resonance junctions. This is the multidimensional generalization of the results of MacKay, Meiss and Percival on the complete partitioning of the phase space of area-preserving maps into resonance zones [20]. (A similar picture has been described by Kook and Meiss [27].)

A crucial question then concerns the nature of barriers to motion along resonance lines. A natural conjecture is that the resulting bottlenecks are given by irrationality conditions involving the three frequencies of motion, subject to the single resonance condition $k_{\text{res}} \cdot \omega = 0$, where $k_{\text{res}}$ is the resonance condition connecting the initial and final junctions. The result of implementing this assumption is a pairwise relation between the frequencies which holds at the intersection of the resulting pairwise “antiresonance” line with the resonance zone,
i.e., at a single “point” along $k_{res} \cdot \omega = 0$. The pairwise condition holding at this point is in some cases a noble number, although this is not always true (non–noble numbers appear for certain resonances and junctions). Since this irrationality condition holds at a single point along a resonance line, global barriers to relaxation must correspond to continuous families of these points, each associated with an irrationality condition holding along one of the dense set of resonance lines. It is not clear whether the resulting curve in the frequency ratio representation is smooth and differentiable, or rough and fractal in character.

The second approach considers the complement of the Arnold web, and addresses the problem of determining the most robust tori in three dimensional systems. For this point of view, Kim and Ostlund [59] have considered the three dimensional generalization of the noble frequency ratios appearing in the two degree of freedom theory. They introduced an algorithm for generating simultaneously irrational pairs of irrational numbers, which they argued are the correct three dimensional generalizations of the noble numbers. The dynamical significance of these numbers is not firmly established, but it is strongly suspected that they correspond to the most robust tori in three degree of freedom systems.

Fig. 25 shows a plot of the $2^{14}$ most irrational pairs of numbers in the unit square, calculated by the method of Kim and Ostlund [59]. Only the lower left half has been calculated; the upper right can be obtained by reflection. The plot clearly has a self–similar, scaling property. The essential feature to note is that these irrational pairs avoid the resonance lines. If Fig. 25 were superimposed on the winding number plane of the coupled standard maps, for instance, the Arnold web would fall in the white areas of the plot. The set of robust invariant tori in three dimensions thus forms the complement of the Arnold web.

Fig. 26 shows the most irrational pairs of frequency ratios falling in the dynamically relevant range for planar OCS. It is observed that these points, presumably corresponding to particularly robust tori, avoid the important low order resonance lines. An alternate picture of transport and trapping suggests itself, based on a diffusion through the “maze” presented by the robust tori [60]. Regions where persistent tori are densely distributed cause long–time trapping of the wandering trajectory, while the unblocked resonance zones allow rapid flow between resonance junctions. Bottlenecks along resonance lines may result from a pinching of the resonance zone by families of robust tori.

Both of these viewpoints must be regarded as speculative at present, and are mentioned
here as a stimulus for future research.

In conclusion, we have seen that local frequency analysis [15] is a very useful tool for studying nonlinear systems. This method should find application in both fundamental investigations of the details of chaotic phase space structure and dynamics, and in more practical studies of realistic and physically interesting chemical systems.

VIII. ACKNOWLEDGEMENTS

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FIG. 1: Time dependence of normal mode energies for a planar OCS trajectory at an energy of 20,00 cm$^{-1}$. The labels CO, CS and Bend indicate the internal coordinates approximated by the normal modes. Arrows mark points of sudden energy exchange between the normal modes.
FIG. 2: \((Q_{CS}, P_{CS})\) surfaces of section for a collinear OCS trajectory. (a) First 24.6 ps of the trajectory. (b) Next 4.5 ps. Between (a) and (b), the trajectory crosses a phase space bottleneck.
FIG. 3: Phase space structure of collinear OCS. Shown are the 3:1 and 5:2 resonance zones, and the $2 + \gamma$ golden mean cantorus separating the two chaotic regions illustrated in Fig. 2.
FIG. 4: Configuration space trajectory, surface of section, and coordinate Fourier spectra for a 1:4 ps segment of the collinear OCS trajectory shown in Fig. 2. The segment is trapped near a 3:1 resonance zone. The peaks indicated in the CO and CS spectra are in the ratio $\omega_{CO}/\omega_{CS} = 3.0008$. 
FIG. 5: Configuration space trajectory, surface of section, and coordinate Fourier spectra for a later segment of the same collinear OCS trajectory shown in Fig. 4. This segment is trapped near a 5:2 resonance zone. The peaks indicated in the CO and CS spectra are in the ratio $\omega_{CO}/\omega_{CS} = 2.5005$. 

$\omega_{CO}/\omega_{CS} = 5:2$
FIG. 6: Six sequential segments of the collinear OCS trajectory of Fig. 2, shown in configuration space. During the 4th segment ($T = 38.980$), the trajectory crosses the $2 + \gamma$ cantorus. The initial crossing is indicated by an arrow.
FIG. 7: The same six sequential segments of Fig. 6, shown in the \((Q_{CS}, P_{CS})\) surface of section.
FIG. 8: Coordinate power spectra of four of the six trajectory segments shown in Figs 6 and 7. During the time spanned by these segments, the ratios of the frequencies of the largest CO and CS peaks passes through the value $\omega_{CO}/\omega_{CS} = 2 + \gamma$, corresponding to a cantorus associated with this frequency ratio.
FIG. 9: Flux versus CO/CS frequency ratio. A minimum in the flux appears around $\omega_{\text{CO}}/\omega_{\text{CS}} = 2.57$. See text for discussion.
FIG. 10: Frequency ratio space for planar OCS. Resonance lines (solid) and pairwise noble conditions (dashed) are indicated.
FIG. 11: Local frequency ratios and locally averaged normal mode energies versus time for a planar OCS trajectory. From the top: CS/bend frequency ratio; CO/CS frequency ratio; CO/bend frequency ratio; locally (time) averaged CO normal mode energy; locally averaged CS normal mode energy; locally averaged bend normal mode energy. This trajectory exhibits transport along the CS/bend 3:2 resonance channel. Arrows A – B indicate several segments in the 3:2 resonance zone.
FIG. 12: Configuration space projections for eight contiguous segments A – B indicated in Fig. 11. From the top: \((x, y) = (Q_{CO}, Q_{CS}), (Q_{CO}, Q_{bend}), (Q_{bend}, Q_{CS})\) projections. Time increases from left to right. A sketch of the characteristic 3:2 resonant trajectory shape appears in the 4th segment.
FIG. 13: Local frequency ratio and locally averaged normal mode energies for a planar OCS trajectory. See caption of Fig. 11 for details. This trajectory exhibits long-time trapping and slow movement along the 7:3 CO/CS resonance channel.
FIG. 14: Configuration space projections of segments A – B for the trajectory shown in Fig. 13. See caption of Fig. 12 for details. A 2:1 CS/bend resonance is visible in the first segment as the U-shaped projection in the lowest frame.
FIG. 15: Configuration space projections of segments C – D for the trajectory shown in Fig. 13. See caption of Fig. 12 for details. A return to the 2:1 CS/bend resonance is clearly visible.
FIG. 16: Local frequency ratios and locally averaged normal mode energies for a trajectory of planar OCS. See captions of Fig. 11 for details. This trajectory exhibits both long-time localization and segments of pronounced chaos.
FIG. 17: Local frequency ratios and locally averaged normal mode energies for a trajectory of planar OCS. See caption of Fig. 11 for details. This trajectory illustrates the possible role of pairwise noble frequency ratios as barriers to relaxation, and transverse resonance lines as pathways across phase space bottlenecks.
FIG. 18: Configuration space projections of segments A – B shown in Fig. 17.
FIG. 19: A comparison of the unaveraged action (upper) and locally averaged action (lower) for the standard map, $k = 1.1$. The averaged action is equivalent to a local winding number (i.e., frequency ratio), as discussed in the text.
FIG. 20: Flux versus winding number for the standard map, $k = 1.0$. 
FIG. 21: Flux versus winding number for the standard map, $k = 1.2$. 
FIG. 22: Evolution of the local winding number $\langle I \rangle$ for two coupled standard maps. Averaging is over segments of 100 iterations.
FIG. 23: $\langle I \rangle$ versus $\langle J \rangle$ for two coupled standard maps, $k_1 = k_2 = 0.8$, $b = 0.02$. The Arnold web is clearly visible as the dark lines on the plot.
FIG. 24: \langle I \rangle versus \langle J \rangle for two coupled standard maps, \( k_1 = k_2 = 1.2, b = 0.02 \). The Arnold web is clearly visible as the dark lines on the plot.
FIG. 25: $2^{14}$ mutually irrational pairs of numbers, as described in the text. Each point is presumed to represent a robust torus of a dynamical system. Note that the complement of this set of points corresponds to resonance lines.
FIG. 26: Robust pairs of irrational frequency ratios in the dynamically relevant range for planar OCS.