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The goal of this work has been the theoretical analysis of dynamics from highly excited vibrational spectra of polyatomic molecules, especially, of molecules with classically chaotic dynamics.

The high excitation ranges of these spectra of highly excited molecules present fundamental new problems of spectral analysis which must first be overcome.

We have sought to lay the foundation for a comprehensive new framework for analyzing spectra in which the dynamics are complicated by strongly interacting degrees of freedom. Ideally, this framework will allow for high energy "unassignable" spectra the kind of detailed level-by-level analysis customary at lower energy. To be really successful, we believe this scheme must be founded in a systematic understanding of the complex underlying classical dynamics of the molecule.

Progress has been made toward a procedure for classifying and extracting the dynamical information contained in experimental highly excited spectra.

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"CHAOTIC SPECTRA OF SMALL MOLECULES"

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1. Michael E. Kellman and E.D. Lynch, "Reply to Comment on 'Semiclassical Phase Space Evolution of Fermi Resonance Spectra'", J. Chem. Phys. 89, 3396 (1988).

2. L. Xiao and M.E. Kellman, "Unified Semiclassical Dynamics for Molecular Resonance Spectra", J. Chem. Phys. 90, 6086 (1989)

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4. Z. Li, L. Xiao, and M.E. Kellman, "Phase Space Bifurcation Structure and the Generalized Local-to-Normal Transition in Resonantly Coupled Vibrations", J. Chem. Phys. 92, 2251 (1990).

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8. M.E. Kellman, "Approximate Constants of Motion for Vibrational Spectra of Many-Oscillator Systems with Multiple Anharmonic Resonances", J. Chem. Phys. 93, 6630 (1990).

9. M.E. Kellman and L. Xiao, "New Assignment of Fermi Resonance Spectra", J. Chem. Phys. 93, 5821 (1990).

10. J.M. Standard and M.E. Kellman, in press, J. Chem. Phys.

TECHNICAL REPORT

1. INTRODUCTION.

The goal of this work [1] has been the theoretical analysis of dynamics from highly excited vibrational spectra of polyatomic molecules, especially, of molecules with classically chaotic dynamics. The impetus is the growth in recent years of detailed experimental spectra, at unprecedented levels of excitation. In this contract period, we have focused largely, though not exclusively, on spectra of O_3 and C_2H_2, which have received intense experimental scrutiny from the groups of J.L. Kinsey and R.W. Field at MIT, and elsewhere. These highly excited spectra give direct evidence for previously unknown or unobservable dynamical effects in molecules.

These new phenomena present novel challenges for the interpretation of spectra, as well as opportunities for obtaining previously inaccessible information. e.g., reliable potential energy surfaces at high energy. But the high excitation ranges of these spectra present fundamental new problems of spectral analysis which must first be overcome.

In this contract period, we have sought to lay the foundation for a comprehensive new framework for analyzing spectra in which the dynamics are complicated by strongly interacting degrees of freedom. Ideally, this framework will allow for high energy "unassignable" spectra the kind of detailed level-by-level analysis customary at lower energy. To be really successful, we believe this scheme must be founded in a systematic understanding of the complex underlying classical dynamics of the molecule. A systematic procedure for classification of the dynamics would make possible a dynamically based assignment of high energy spectra. At the same time, this framework should be designed to easily extract the dynamical information encoded in the newly rationalized spectra, including knowledge of molecular potential surfaces, energy transfer processes, and eventually, molecular rearrangements and bimolecular reactivity.

Progress has been made under the contract toward this procedure for classifying and extracting the dynamical information contained in experimental highly excited spectra. The work has developed in three main directions, outlined below.

2. DYNAMICS OF STRONGLY COUPLED VIBRATIONS FROM EXPERIMENTAL SPECTRA.

A. Polyad Phase Sphere Dynamics From Fits of Resonance Spectra.

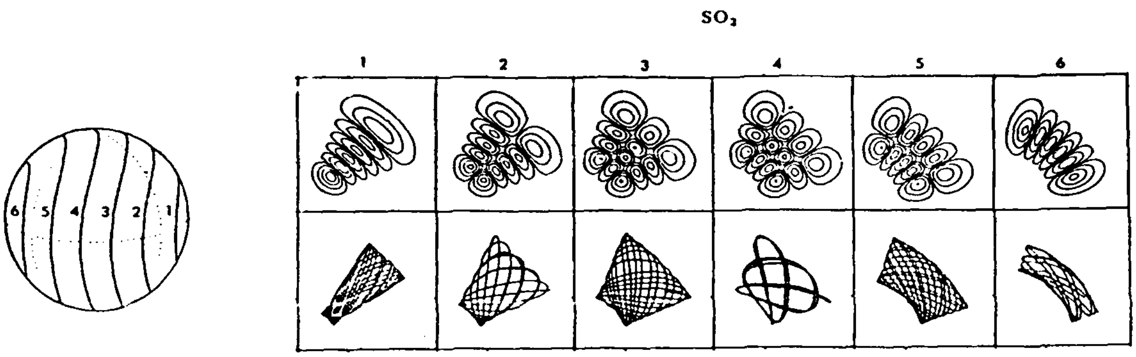
An early goal of this research has been a systematic method to visualize the dynamics of coupled molecular vibrations of an experimental spectrum, for example, a fit with a Darling-Dennison resonance Hamiltonian for the stretches of a symmetric triatomic like H_2O, or a Fermi resonance Hamiltonian for coupled bend and stretch in a molecule like CO_2. There are now prospects on the horizon for spectra of radicals [11] of sufficient detail to allow this kind of analysis. We have devised a method [2] to extract semiclassical dynamics from fits of overtone and combination spectra. Each energy level in the spectrum corresponds to a trajectory which is plotted on the "polyad phase sphere", giving a convenient graphical representation of the dynamics. For example, the phase sphere can be used to classify and assign spectra of ABA triatomics which display the transition from normal to local modes. The phase sphere trajectories can be transformed into easily visualized trajectories in coordinate space. These coordinate space trajectories have distinctive patterns which are reflected in the quantum wave functions and quantum number assignments.

This phase sphere analysis has been applied [2] to experimental spectra of H_2O, O_3, and SO_2. This analysis shows that H_2O is a molecule which displays the normal to local modes transition, while SO_2 is a pure normal modes molecule. Perhaps surprisingly, ozone also displays the normal-local transition. The phase sphere and coordinate trajectories for a representative experimental polyad of each of these molecules is shown in Figure 1.

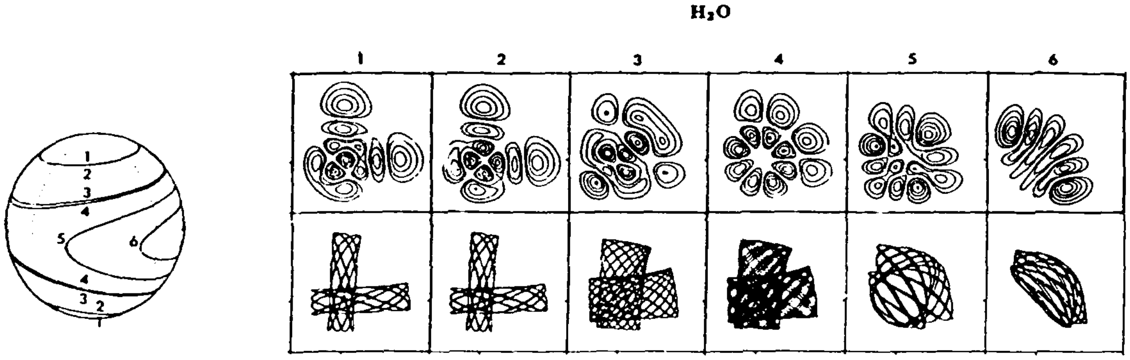
B. Bifurcation Theory and Catastrophe Map Classification of Strongly Coupled Dynamics.

The phase sphere approach gives a very convenient representation of molecular dynamics extracted from the information "encoded" in the experimental spectrum, in particular, the normal-local transition in ABA triatomics. The next step [4,7] has been to devise a systematic classification of the dynamical information in the phase spheres of spectra of general coupled molecular vibrations, e.g., Fermi resonance spectra. Essentially, what is desired is a **generalization of the language of the normal-local transition**, to describe the dynamics of arbitrary coupled systems.

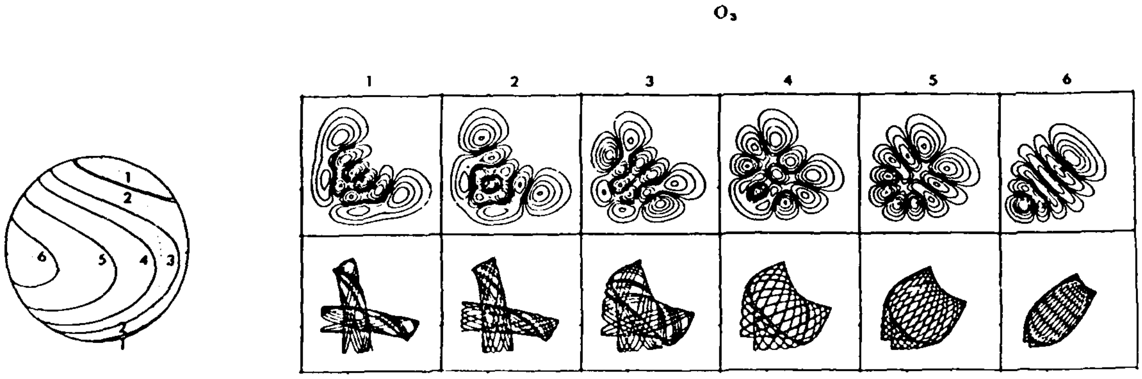
The idea of the transition from normal to local modes [12-17] has been a landmark in thinking about dynamics of coupled molecular vibrations. It has stimulated new interpretations of spectra [18], new formulations of the quantum mechanical description of vibrations [19], investigations of intramolecular energy transfer and reaction dynamics [20-24], and theoretical investigations of the transition's dynamical origin [25,26]. The phase sphere dynamics of ABA triatomics depicted in Fig. 1 above are described in a completely satisfactory way in the language of the normal-local transition. However, the normal-local taxonomy is inadequate when discuss-


SO$_2$

Probability density for eigenfunctions and corresponding coordinate space trajectories of polyad 5 for SO$_2$.


H$_2$O

Probability density for eigenfunctions and corresponding coordinate space trajectories of polyad 5 for H$_2$O.


O$_3$

Probability density for eigenfunctions and corresponding coordinate space trajectories of polyad 5 for O$_3$.

Figure 1. Polyad phase spheres, coordinate trajectories, and wavefunctions for $P = 5$ polyads of SO_2, H_2O, and O_3, from the Darling-Dennison fit of stretching levels of experimental spectra. Each trajectory corresponds to the semiclassical motion of one of the six overtone and combination levels of the polyad with $P = (n_1 + n_2) = 5$ quanta. SO_2 clearly has an undivided phase space in which all trajectories have normal mode character. H_2O has a phase space with a separatrix dividing normal and local mode regions. Surprisingly, ozone is also a molecule with a normal-local modes transition. Transformed into coordinate space, the trajectories clearly display their local or normal character. The wavefunctions correspond closely to the semiclassical trajectories.

ing general resonances such as Fermi resonance with 2:1 frequency ratio. To get beyond the limitations of the language of the normal-local transition, we have used bifurcation theory [4] to obtain the **phase space bifurcation structure** of resonant systems. This bifurcation analysis becomes especially transparent and readily usable with the help of some ideas and methods from catastrophe theory [7]. To see what this engenders, Figure 2 shows the catastrophe map analysis of the stretching dynamics of SO_2 and H_2O, based on the Darling-Dennison fit of these molecules' experimental spectra. Figure 3 shows the catastrophe map analysis of the 2:1 Fermi resonance dynamics of CO_2 and the coupled C-H bend-stretch motion in a series of substituted methane molecules. It is evident that the catastrophe map classifications for the two kinds of resonance, 1:1 Darling- Dennison and 2:1 Fermi resonance, are very much different. The 1:1 system has two zones: a zone of pure normal modes behavior, for a molecule like SO_2, and a zone of mixed behavior with the normal-local transition, for a molecule like H_2O. In contrast, the catastrophe map for 2:1 Fermi resonance has a very different structure, with four zones instead of two. (Technically, in bifurcation language, the 1:1 resonance shows the unfolding of a pitchfork, and the 2:1 resonance the unfolding of a transcritical bifurcation.) The use of this catastrophe map analysis in a new procedure for assigning spectra is outlined next.

C. New Assignments of Highly Excited Spectra of Strongly Coupled Vibrations.

The information on the polyad phase sphere and the catastrophe map is the basis for a new method to assign spectra, rooted in a systematic understanding of the underlying semiclassical dynamics. We contend that the traditional assignment of normal mode quantum numbers makes little sense, for example, in a molecule with the normal-local transition where some levels have normal mode dynamics, but others have local mode dynamics. Instead, it makes far more sense to make a **mixed assignment** of normal mode quantum numbers to levels with normal mode dynamics, and local mode quantum numbers to levels with local mode dynamics. An example of this new assignment procedure [3] for the normal-local transition of H_2O is given in Figure 4. For systems with 2:1 Fermi resonance, this approach has been combined with the catastrophe theory analysis to give a new assignment of spectra of CO_2 and substituted methanes. An example is given in Figure 5.

3. APPROXIMATE CONSTANTS OF MOTION AND QUANTUM NUMBER ASSIGNMENTS OF POLYATOMICS WITH REDUCED DIMENSION DYNAMICS.

We believe that the catastrophe map is the key to classifying dynamics and assigning spectra of strongly coupled degrees of freedom in a molecule. So far, we have dealt with two strongly coupled degrees of freedom. A necessary future step will be to use the bifurcation and catastrophe analysis for three or more coupled degrees of freedom. However, when all the strongly coupled degrees of freedom have been dealt with, there still remain the degrees of freedom which remain undisturbed by the interactions between the strongly coupled modes. This is trivial if there is only a single pair of coupled modes. However, with multiple resonances between many degrees of freedom, there can be highly nontrivial constants of motion and good quantum numbers. In general, these are associated with a complex partitioning of molecular phase space between coupled and uncoupled degrees of freedom. This sectioning of phase space has a highly nonintuitive relation to the zero-order normal modes, as will be seen.

In a recent paper [8], we presented a theory of these approximate dynamical constants. This theory, related to a method used in a van Vleck perturbation theory study [27], focused on Hamiltonians of the kind spectroscopists use to fit highly excited spectra of polyatomics with multiple Fermi resonances. The formalism reduces to simple methods of vector algebra, so is very easy to apply. An example analyzed in our paper, Ref. 8, is a multiple resonance fit of the FTIR spectrum of acetylene up to 10,000 cm^{-1}. of Winn and Smith [28].

The determination of approximate dynamical constants of a many degree-of-freedom system seems not to have received much attention. But they could have important ramifications for the analysis of highly excited spectra and energy transport in molecules. Approximate dynamical constants would be extremely useful as quantum numbers which could be assigned to spectra of highly excited states. Furthermore, a system with one or more approximate constants would have motion in a subset of phase space of reduced dimension, equivalent to "bottlenecks" to vibrational energy flow. The elucidation of the dynamical quantum numbers from fits of experimental spectra therefore gives empirical information about these bottlenecks.

Our theory of dynamical constants in [8] was developed in terms of the fit of an experimental spectrum, in order to establish immediate contact with experimental systems, but it actually applies to far more general situations than spectroscopic fitting Hamiltonians, as will be discussed below. In particular, the idea of dynamical constants is expected to be extremely useful in making tractable the quantum mechanical calculation of rovibrational states. Dynamical constants are also expected to lead to predictions of important observations in classical dynamics simulations.

4. BOOTSTRAP FITTING OF EXPERIMENTAL SPECTRA AND POTENTIAL ENERGY SURFACES OF HIGHLY EXCITED POLYATOMICS.

Figure 2. Catastrophe map classification of spectra of 1:1 resonant systems. Located on the map are polyads 1-6 of SO_2 in Zone I and H_2O in Zone II. The coordinates of the catastrophe map are the molecular control parameters μ for strength of the mode coupling, and β for the asymmetry (which is zero for stretches of an ABA molecule). The phase spheres and corresponding trajectories and probability density for wavefunctions in coordinate space of polyad 5 for SO_2 (A) and H_2O (B) are shown above the catastrophe map.

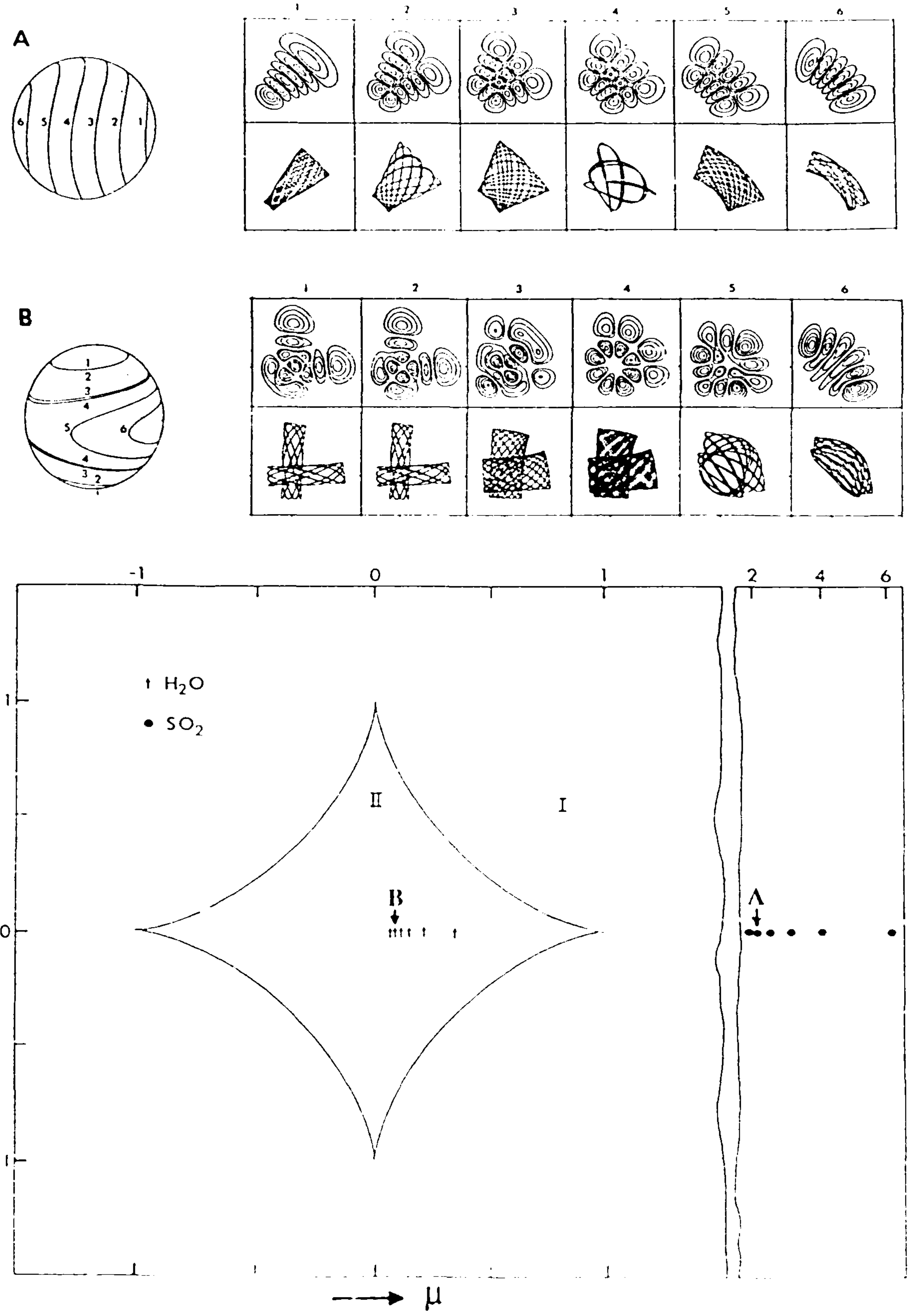
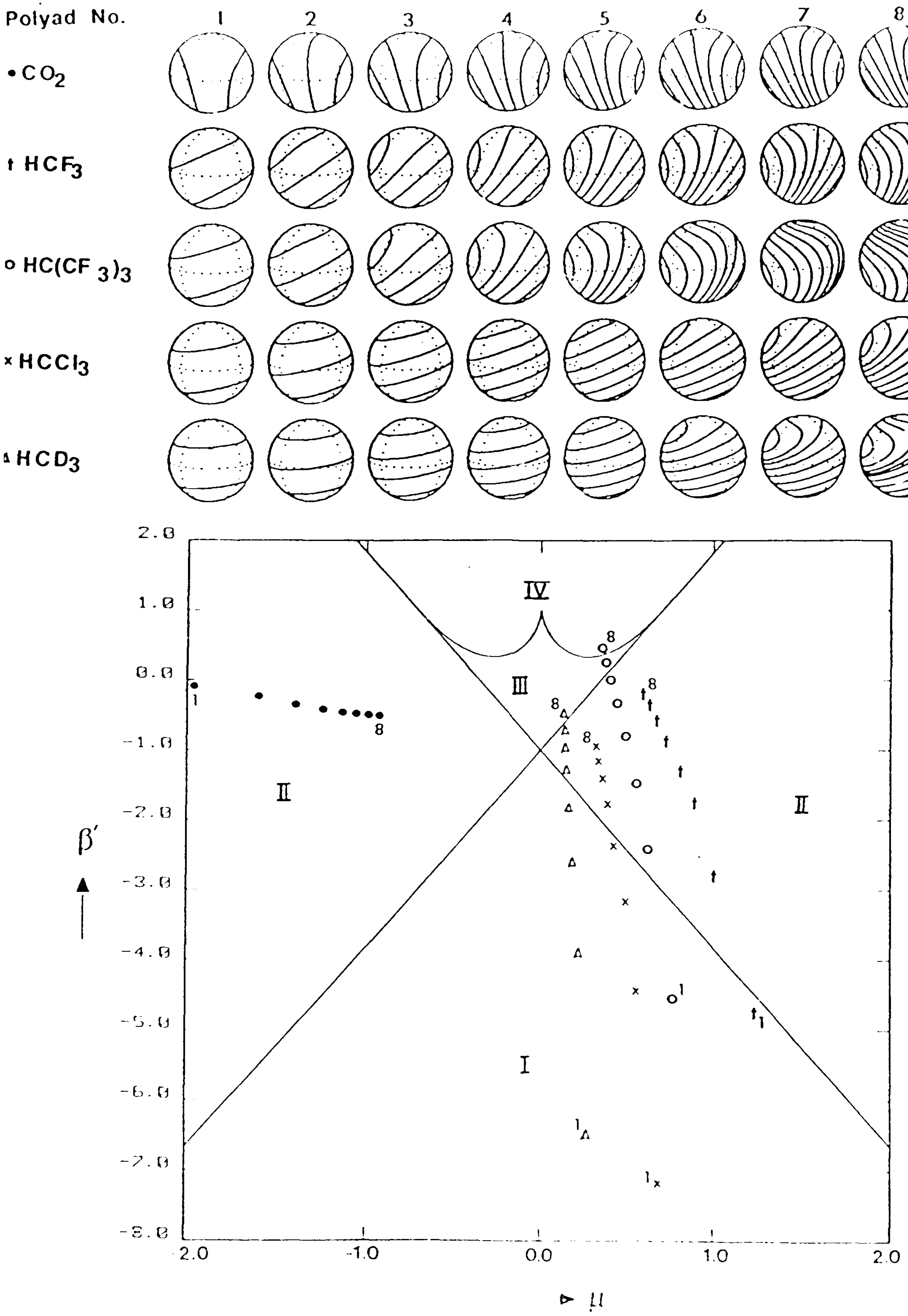

A
6
5
4
3
2
1
1
2
3
4
5
6
B
1
2
3
4
5
6
4
3
2
1
1
2
3
4
5
6
-1
0
1
2
4
6
1
0
-1
H$_2$O
SO$_2$
II
I
B
A
μ

Figure 3. Catastrophe map classification of spectra of 2:1 resonant systems. The following page shows the classification of polyads 1-8 of spectra of CO_2, CHF_3, $CH(CF_3)_3$, $CHCl_3$, and CHD_3. The next page after is a "master diagram" of the bifurcation and catastrophe analysis of the 2:1 system, showing (a) the catastrophe manifold; (b) the projection of the catastrophe manifold onto the molecular control space; (c) the catastrophe map; and (d) some bifurcation diagrams obtained by taking various sections of the catastrophe manifold.



Polyad No.
1
2
3
4
5
6
7
8
• CO2
t HCF3
o HC(CF 3)3
× HCCl3
Δ HCD3
2.0
1.0
0.0
-1.0
-2.0
-3.0
-4.0
-5.0
-6.0
-7.0
-8.0
IV
III
II
I
β′
2.0
-1.0
0.0
1.0
2.0
μ

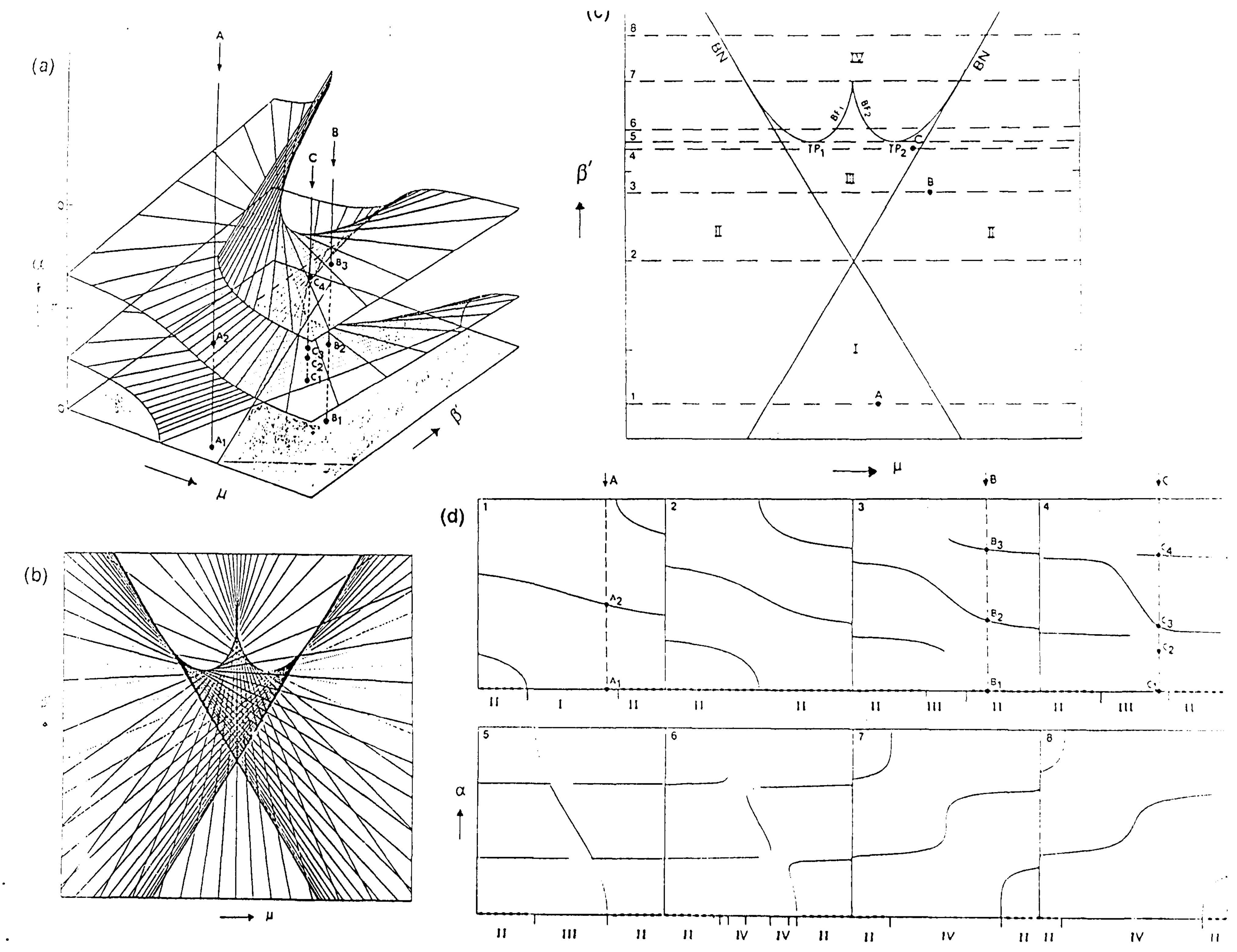
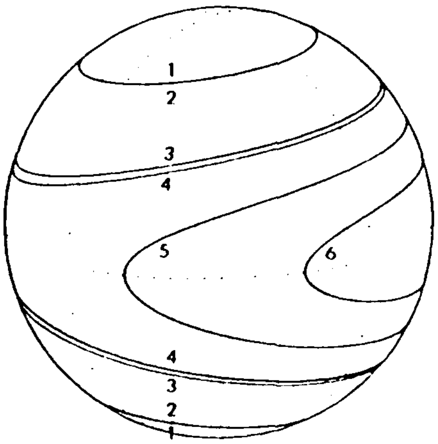

(a)
A
B
C
A_1
A_2
B_1
B_2
B_3
C_1
C_2
C_3
C_4
α
μ
β′
(b)
μ
(c)
β′
μ
BN
BN
I
II
II
III
IV
TP_1
TP_2
Bf_1
Bf_2
A
B
C
1
2
3
4
5
6
7
8
(d)
α
A
B
C
A_1
A_2
B_1
B_2
B_3
C_1
C_2
C_3
C_4
1
2
3
4
5
6
7
8
II I II II II II III II II III II
II III II II IV IV II II IV II II IV II

Figure 4. The new "mixed" normal-local assignment of H_2O. In the figure, polyad 5 is shown. The trajectories are numbered in order of increasing energy. Levels corresponding to trajectories in the local mode region are labeled with local mode quantum numbers n_1, n_2 as $(n_1\ n_2)^+$ or $(n_1\ n_2)^-$, depending on symmetry with respect to the C_2 axis. Levels corresponding to trajectories in the normal mode region are labeled with normal mode quantum numbers n_s, n_a as $[n_s\ n_a]$.

The table gives the assignment of the stretching spectrum of H_2O for polyads 1-5. The levels are grouped into polyads P. The second column gives the experimental levels; the third column, the levels from the fit with the Darling-Dennison Hamiltonian. The right column gives the new mixed normal-local assignment.

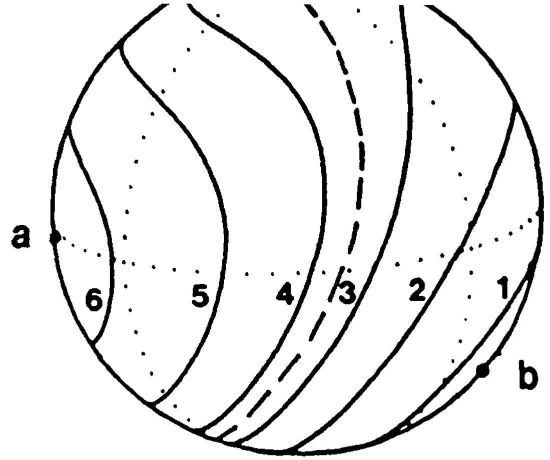
	EXPERIMENT	FIT	ASSIGNMENT
P = 1	3657.05	3654.13	$(10)^+$
	3755.93	3754.92	$(10)^-$
P = 2	7201.54	7199.69	$(20)^+$
	7249.82	7249.67	$(20)^-$
	7445.05	7443.13	[02]
P = 3	10599.66	10601.62	$(30)^+$
	10613.41	10615.73	$(30)^-$
	10868.86	10866.40	[12]
	11032.40	11031.91	[03]
P = 4	13828.30	13832.41	$(40)^+$
	13830.92	13834.72	$(40)^-$
	14221.14	14219.34	$(31)^+$
	14318.80	14319.34	[13]
	14536.87	14537.50	[04]
P = 5	16898.40	16895.46	$(50)^+$
	16898.83	16895.73	$(50)^-$
	17458.20	17458.95	$(41)^+$
	17495.52	17495.61	$(41)^-$
	17748.07	17748.57	[14]
		17948.12	[05]



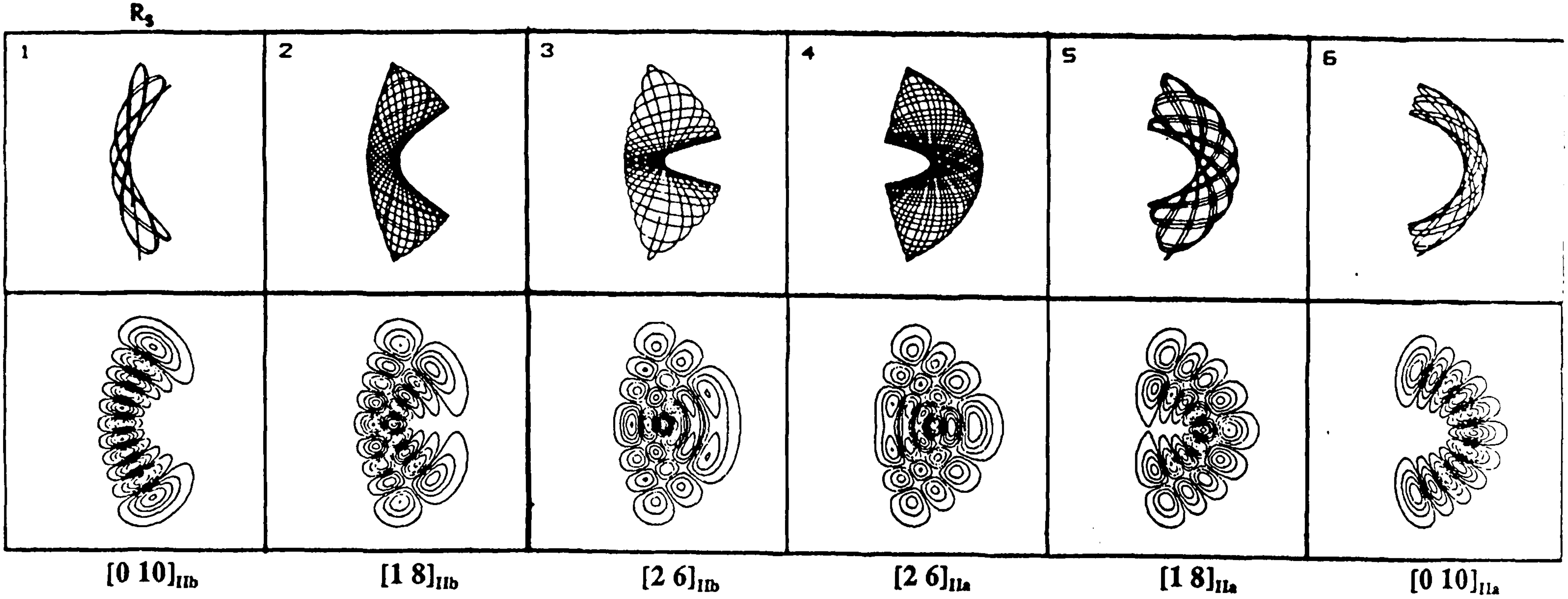
P = 5

LEVEL	ASSIGNMENT
1	$(50)^+$
2	$(50)^-$
3	$(41)^+$
4	$(41)^-$
5	[14]
6	[05]

Figure 5. New quantum number assignment for the P = 5 of $CH(CF_3)_3$ polyad from Zone II of the catastrophe map for the 2:1 system in Fig. 3. This polyad has strong coupling, with "resonant collective modes" in regions a and b on the sphere. The resonant collective modes are strong mixtures of the zero-order bend and stretch modes, as can be seen in the coordinate space trajectories and wave functions for the six levels. In each region a or b, there are two modes 1 and 2, as can be seen from the nodal patterns and shapes of the trajectories. The levels are assigned as $(n_1\ n_2)_{IIa}$ or $(n_1\ n_2)_{IIb}$, indicating the number of quanta in collective mode 1 and 2 of region a or b, for a polyad in Zone II of the catastrophe map.



P = 5



The preceding work on bifurcations and dynamical constants aims at understanding and exploiting the structure that considerable structure can exist in the phase space of highly excited, strongly coupled molecular vibrations. This structure is totally destroyed with the transition to completely chaotic dynamics. The work described next is concerned with analyzing spectra apart from any structure at all that might exist in the strongly coupled phase space. In particular, we are concerned with obtaining **molecular potential surfaces** from analysis of spectra, even when there is global chaos. However, the methods described are expected to be no less useful in obtaining greatly improved surfaces when the chaos is less than global, with assignable quantum numbers remaining for some degrees of freedom.

The resonance Raman experiments of Imre *et al.* [29] for ozone obtained the overtone and combination spectrum almost up to dissociation, so they probe the highly anharmonic region of the potential. We have therefore used [10] the ozone spectrum as an ideal test case to investigate the status of current potential energy surfaces and the use of the bootstrap method to obtain potential surface information from fitting of very highly excited spectra. The vibrational spectrum on the ground electronic state of ozone is a system where one might expect existing potential surfaces to fail badly in accounting for highly excited data. Usual methods of obtaining empirical surfaces [30] essentially rely on a low-energy expansion of the surface around the equilibrium configuration. *Ab initio* potential calculations give a more "global" view of the potential surface than empirical surfaces, but as recent work on ozone by Schaeffer *et al.* [31] shows, a very large basis set and a very large degree of correlation are needed just to get the correct ordering for the symmetric and antisymmetric stretch fundamentals! We have performed accurate quantum mechanical calculations of the ozone vibrational spectrum to test two of the best [32,33] current surfaces. The resulting comparison of one of these surfaces with the experimental data, displayed in Figure 6, shows gross qualitative disagreement between the calculated and experimental spectrum, pointing up the inadequacy of current empirical methods for surfaces for truly highly excited states. Our general expectation is that fitting of highly excited spectra will be extremely valuable for potential surfaces and dynamics precisely in the high energy, anharmonic region where current methods are most likely to fail. Figure 6 shows the test of the potential surface we obtained for ozone using the high-energy data of [29], using the bootstrap method. Figure 6 shows that the vibrational spectrum calculated on this surface is in good qualitative agreement with the data, and in particular, is far better than the spectra we calculated from current surfaces. We believe this surface for the stretching modes of ozone is the best in existence, and shows the promise of the bootstrap approach for obtaining molecular potentials from analysis of high energy spectra. We are now extending this approach to the full three vibrational degrees of freedom of triatomics, using the detailed CS_2 spectra of L.D. Ziegler at Northeastern University as a first test case.

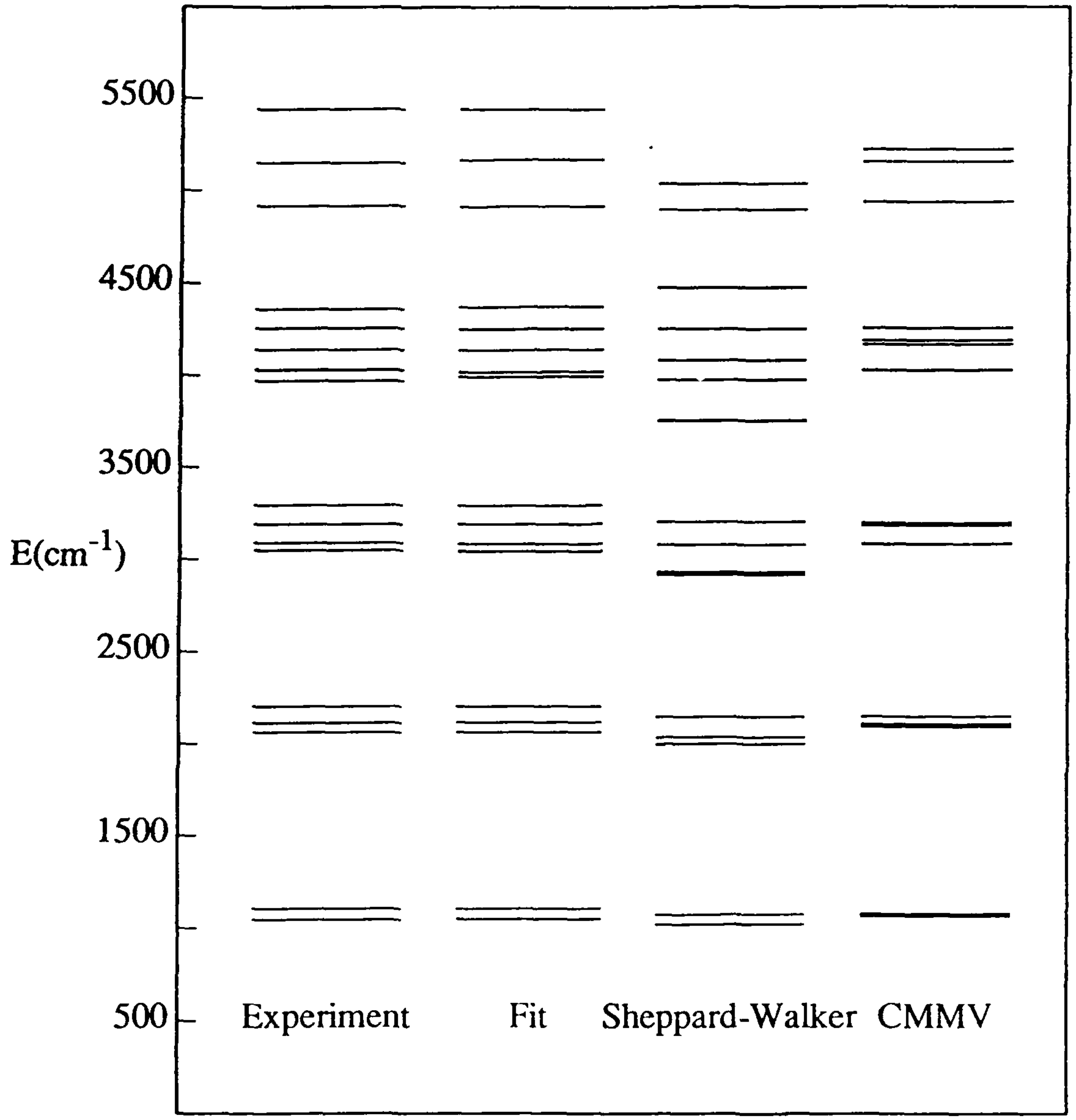


Figure 6. Comparison of experimental ozone stretch vibration levels from data of Imre *et al.* with levels calculated on the new surface (FIT) obtained with the bootstrap fit of the experimental spectrum, and with current empirical surfaces (Shepard-Walker and CMMV).

REFERENCES.

1. Relevant recent work of the principal investigator is found in Refs. 2-10.

2. L. Xiao and M.E. Kellman, "Unified Semiclassical Dynamics for Molecular Resonance Spectra", J. Chem. Phys. 90, 6086 (1989); M.E. Kellman, Chem. Phys. Lett. 113, 489 (1985); J. Chem. Phys. 83, 3843 (1985); M.E. Kellman and E.D. Lynch, J. Chem. Phys. 85, 7216 (1986).

3. M.E. Kellman and L. Xiao, "New Assignment of Vibrational Spectra of Molecules with the Normal-to-Local Modes Transition", Chem. Phys. Lett. 162, 486 (1989).

4. Z. Li, L. Xiao, and M.E. Kellman, "Phase Space Bifurcation Structure and the Generalized Local-to-Normal Transition in Resonantly Coupled Vibrations", J. Chem. Phys. 92, 2251 (1990).

5. J.M. Standard, E.D. Lynch, and M.E. Kellman, "Bootstrap Approach to Fitting Spectra of Molecules with Classically Chaotic Dynamics", J. Chem. Phys. 93, 159 (1990).

7. L. Xiao and M.E. Kellman, "Catastrophe Map Classification of the Generalized Normal-Local Transition in Fermi Resonance Spectra", J. Chem. Phys. 93, 5805 (1990).

8. M.E. Kellman, "Approximate Constants of Motion for Vibrational Spectra of Many-Oscillator Systems with Multiple Anharmonic Resonances", J. Chem. Phys. 93, 6630 (1990).

9. M.E. Kellman and L. Xiao, "New Assignment of Fermi Resonance Spectra", J. Chem. Phys. 93, 5821 (1990).

10. J.M. Standard and M.E. Kellman, in press, J. Chem. Phys.

11. W. Xie, C. Harkin, H.-L. Dai, W.H. Green, and C.B. Moore, J. Mol. Spectr. 138, 596 (1990).

12. W. Siebrand and D.F. Williams, J. Chem. Phys. 49, 1860 (1968).

13. B.R. Henry, Acc. Chem. Res. 10, 207 (1977).

14. M.E. Long, R.L. Swofford, and A.C. Albrecht, Science 191, 183 (1976).

15. M.S. Burberry and A.C. Albrecht, J. Chem. Phys. 71, 4631 (1979).

16. R. Wallace, Chem. Phys. 11, 189 (1975).

17. R. Wallace and A.A. Wu, Chem. Phys. 39, 221 (1979).

18. R.T. Lawton and M.S. Child, Mol. Phys. 40, 773 (1980).

19. M.L. Sage, Chem. Phys. 83, 1455 (1979).

20. D.W. Chandler, W.E. Farneth, and R.N. Zare, J. Chem. Phys. 77, 4447 (1982).

21. J.M. Jazinski, J.K. Frisoli, and C.B. Moore, J. Chem. Phys. 79, 1312 (1983).

22. B.G. Sumpter and D.L. Thompson, J. Chem. Phys. 82, 4557 (1985).

23. L.J. Butler, T.M. Ticich, M.D. Likar, and F.F. Crim, J. Chem. Phys. 85, 2331 (1986)

24. N.F. Scherer, F.E. Donny, A.H. Zewail, and J.W. Perry, J. Chem. Phys. 84, 1932 (1986).

25. C. Jaffe and P. Brumer, J. Chem. Phys. 73, 5646 (1980).

26. E.L. Sibert III, J.T. Hynes, and W.P. Reinhardt, J. Chem. Phys. 77, 3583 (1982).

27. L.E. Fried and G.S. Ezra, J. Chem. Phys. 86, 6270 (1987).

28. B.C. Smith and J.S. Winn, J. Chem. Phys. 89, 4638 (1988).

29. D.G. Imre, J.L. Kinsey, R.W. Field, and D.H. Katayama, J. Phys. Chem. 86, 2564 (1982).

30. J.N. Murrell, S. Carter, S.C. Farantos, P. Huxley, and A.J.C. Varandas, Molecular Potential Energy Functions (John Wiley, Chicester, 1984).

31. G.E. Scuseria, T.J. Lee, A.C. Scheiner, and H.F. Schaeffer III, J. Chem. Phys. 90, 5635 (89).

32. M.G. Sheppard and R.B. Walker, J. Chem. Phys. 78, 7191 (1983).

33. S. Carter, I.M. Mills, J.N. Murrell, and A.J.C. Varandas, Mol. Phys. 45, 1053 (1982).