**Annotated Bibliography of Research Carried Out from 1993 to 1999
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**Spectroscopic Investigation of the Vibrational Quasi-Continuum
Arising from Internal Rotation of a Methyl Group**

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This report covers work carried out during a six year period under a DoE interagency grant. Because all results have been published as full papers in appropriate refereed journals that are openly available in most scientific libraries, the report takes the form of an annotated bibliography. In the interests of scientific continuity and bibliographic usefulness, however, work carried out on this same project from 1990-1992 under an earlier DoE award, as well as related work currently (2000-2002) in progress, will also be discussed. It should be stressed, however, that only work directly connected to the grantee is cited explicitly in this final grant report. The many important papers by other workers in the field during the last decade must be obtained from reference citations in the 21 publications mentioned below.

Scientific Introduction

Virtually all attempts to generate energy via exothermic chemical reactions involve intramolecular vibrational storage and transfer mechanisms. Similarly, attempts to laser-enhance chemical syntheses, isotope separations, and other chemical reactions are complicated by vibrational energy storage and conversion problems.

One set of important questions in such processes concerns the way in which energy stored in a discrete (and often well-characterized) vibrational state is "degraded" by leakage into an underlying (and often poorly understood) vibrational quasi-continuum. These questions are currently being studied in numerous laboratories, experimentally in both the time and the frequency domain, and theoretically from a number of different points of view. In spite of the large amount of work devoted to studying the quasi-continuum, however, we still have no reliable predictive theory to treat its effects quantitatively.

The present project focussed on contributions which high-resolution molecular spectroscopy and its theoretical underpinnings could make to our understanding of this difficult set of essentially dynamical problems. In particular, its goal was to investigate in

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detail by using spectroscopic techniques phenomena involving the vibrational quasi-continuum in two simple prototype systems. Acetaldehyde (CH_3CHO) and methanol (CH_3OH) were chosen for the study because: (i) methyl groups are known to be efficient promoters of intramolecular vibrational redistribution (IVR), (ii) the internal rotation of a methyl group is an easily describable large-amplitude motion, which should retain its simple character even at high levels of excitation, and (iii) internal rotation is the only very low frequency mode in acetaldehyde and methanol, and as such can be considered to be the "cause" of the high vibrational state densities in the quasi-continuum at moderate energies.

The project is divided conceptually into two parts: (I) understanding the isolated one-dimensional large-amplitude internal rotation motion below, at, and above the top of the torsional barrier, and (II) understanding interactions of fundamental and overtone states of small-amplitude bond stretching and bending motions with bath states arising from multi-quantum excitation of the internal rotation motion (torsional quasi-continuum precursor states).

Part I: Understanding the Internal Rotation Motion by Itself

The Internal Rotation Manifold below the Barrier

Energy levels in this low-energy region, where the internal rotation is in reality better thought of as a small-amplitude torsional motion, do not often participate in IVR and such levels have been extensively studied spectroscopically in the past. The principal contribution of this project in this energy region was to introduce an improved computer program, based on a rho axis method theoretical treatment already available in the literature, and then to show that several thousand measured spectral transitions in the microwave and infrared regions could be theoretically fitted to nearly experimental measurement precision using 50 molecular constants or so, and to further show that this computer program and these molecular constants permitted prediction of interpolated levels, and to some extent extrapolated levels also, to experimental measurement precision.

In some sense, studies in this energy region were primarily a confidence building exercise to demonstrate that modern theory and experiment could be brought into agreement to within their expected capabilities. The first tests were carried out on acetaldehyde, CH_3CHO , (mostly before the grant period covered in this report) and are described in the following three papers:

1. **The Ground Torsional State of Acetaldehyde.** I. Kleiner, J. T. Hougen, R. D. Suenram, F. J. Lovas and M. Godefroid, *J. Mol. Spectrosc.* 148, 38-49 (1991).

2. The Ground and First Torsional States of Acetaldehyde. I. Kleiner, J. T. Hougen, R. D. Suenram, F. J. Lovas and M. Godefroid, *J. Mol. Spectrosc.* **153**, 578-586 (1992).

3. The Laboratory Spectrum of Acetaldehyde at 1 mm. W. L. Barclay, Jr., M. A. Anderson, L. M. Ziurys, I. Kleiner and J. T. Hougen, *Astrophys. J. Suppl.* **89**, 221-226 (1993).

Acetaldehyde was attacked first, because it is theoretically a very clean system, with internal rotation as its only large-amplitude motion. The success with acetaldehyde prompted us to attempt a similar treatment for methanol, CH_3OH , which has the possible complication of a second large-amplitude vibrational motion involving the OH bending motion. Nevertheless, for this molecule also, good results were obtained, as described in:

4. Global Fit of Rotational Transitions in the Ground Torsional State of Methanol. Li-Hong Xu and J. T. Hougen, *J. Mol. Spectrosc.* **169**, 396-409 (1995).

The above work permitted refinement of some intensity calculations for methanol of astrophysical interest, as described in:

5. Line Strengths of Torsion-Rotation Transitions of methanol for $J \leq 22$, $K \leq 14$ and $v_t \leq 2$ from Hamiltonian based Calculations. M. A. Mekhtiev, P. D. Godfrey, and J. T. Hougen, *J. Mol. Spectrosc.* **194**, 171-178 (1999).

The Internal Rotation Manifold just below the Barrier

As the energy content of the internal rotation motion increases, the small-amplitude torsional *vibration* gradually turns into a large-amplitude internal *rotation*. These are qualitatively different motions, requiring qualitatively different zeroth-order theoretical treatments (as illustrated, for example, by the well-known difference in their semi-classical quantization conditions). Attempts to fit energy levels just below the top of the barrier, where the internal rotation motion has a character intermediate between a vibration and a rotation thus led to a number of theoretical questions, which were attacked separately from our spectral fitting activities.

A comprehensive investigation of symmetry questions (the different molecular symmetry groups, different energy level labels, different selection rules, etc.) which arise in internal rotation problems when passing from below to above the barrier was carried out and discussed in:

6. Selection Rules and Intensity Calculations for a C_s Asymmetric Top Molecule Containing a Methyl Group Internal Rotor. J. T. Hougen, I. Kleiner and M. Godefroid, J. Mol. Spectrosc. 163, 559-586 (1994).

In particular, a detailed discussion is presented in the above paper of the relationships between four different molecular symmetry groups, i.e., D₂, C_s, C_{3v} and C_{3v}^(m), which are commonly used to discuss energy level symmetry species and electric-dipole selection rules for internal rotor problems in molecules with a symmetric-rotor top and a frame with a plane of symmetry. Particular attention is given to confusion arising from the fact that the smaller groups are not always subgroups of the larger ones, and that the groups are applied to different parts of the whole problem, (i.e., D₂ to pure rotation, C_s to vibration-rotation, and C_{3v} and C_{3v}^(m) to torsion-rotation). The meaning in this context of the traditional K_a, K_c labels for rotational energy levels in molecules with internal rotation is examined in detail. A discussion is also given of the relationship between three different schemes for defining a molecule-fixed axis system in internal rotation problems, i.e., the principal axis method (PAM), the internal axis method (IAM), and a hybrid between the two, the "rho axis method" (RAM), paying particular attention to the meaning of *a*-type, *b*-type and *c*-type transitions when using each of these axis systems.

A theoretical treatment of torsion-rotation energy levels using the techniques of semiclassical quantization of classical trajectories on rotational energy surfaces, which is based on methods already described in the literature and which permits good qualitative understanding of some of the peculiarities of the torsion-rotation energy level behavior near the top of the barrier, is given in:

7. Rotational Energy Surfaces of Molecules Exhibiting Internal Rotation. J. Ortigoso and J. T. Hougen, J. Chem. Phys. 101, 2710-2719 (1994).

The above study is limited to torsional states at or below the top of the barrier to internal rotation, where the extra (torsional) degree of freedom can be eliminated by expanding eigenvalues of the torsion-K-rotation Hamiltonian as a Fourier series in the rotational degree of freedom. For acetaldehyde, this corresponds to considering $\nu_t = 0, 1$ and 2 torsional levels. The rotational energy surfaces are characterized by locating their stationary points (maxima, minima, and saddles) and their separatrices. Rather complicated catastrophe histories describing the creation and annihilation of pairs of stationary points as a function of J are found at moderate J for given torsional quantum ν_t and symmetry species (A,E). Trajectories on the rotational energy surface which quantize the action are examined, and changes from rotational to vibrational trajectories caused by changes in the separatrix structure are found as a function of J for $\nu_t = 2$. The concept of a "best" quantization axis for the molecule-fixed component of the total angular

momentum is examined from a classical point of view, and it is shown that labeling ambiguities encountered in the literature for torsion-rotation energy levels calculated numerically in the rho axis system can be eliminated by reprojecting basis-set K values onto an axis passing through an appropriate stationary point on the rotational energy surface.

A more advanced theoretical discussion of these same energy levels, using the concepts of coherent quantum states (also taken from the literature) to explain some of the otherwise apparently erratic behavior, is given in:

8. The K-rotational labeling problem for eigenvectors from internal rotor calculations: Application to energy levels of acetaldehyde below the barrier. J. Ortigoso, I. Kleiner, and J. T. Hougen, *J. Chem. Phys.* **110**, 11688-11699 (1999).

In the above work projections of rotational eigenvectors over angular momentum coherent states are used to show that classical trajectories on the appropriate rotational energy surface give faithful representations of the quantum wave functions. Irregularities in the rotational energy level structure within a given torsional state can then be understood in terms of extra separatrices in the classical phase space and unusual wave function densities in the coherent state projections.

The above theoretical works were carried out in conjunction with global fits of levels near the top of the barrier for both acetaldehyde and methanol, using the previously mentioned computer program. In the acetaldehyde work we fit to within experimental accuracy a data set obtained by combining 1014 $\nu_t = 0$, 840 $\nu_t = 1$, and 430 $\nu_t = 2$ microwave lines with 420 $\nu_t = 1 \leftarrow 0$ and 404 $\nu_t = 2 \leftarrow 1$ far-infrared lines. The final fit, which includes essentially all available infrared and microwave transitions involving torsional levels below the top of the barrier, requires 48 parameters to achieve an overall unitless weighted standard deviation of 1.06, and is described in detail in:

9. The Second Torsional State of Acetaldehyde. S. P. Belov, M. Yu. Tretyakov, I. Kleiner and J. T. Hougen, *J. Mol. Spectrosc.* **160**, 61-72 (1993).

In the methanol work, data for $\nu_t = 0$ (below the barrier) and $\nu_t = 1$ (straddling the barrier) were treated. Altogether 909 microwave lines and 197 tunable far-infrared lines were globally fit to give a unitless weighted standard deviation of 1.033, using 56 adjustable and 8 fixed parameters. Some difficulties remained in fitting high K and Jb -type tunable far-infrared lines, but these were later found to arise from measurement error. The satisfactory fit leads to the conclusion that up through the first excited torsional level, a traditional one-dimensional internal rotation model is capable of accurately describing methanol energy levels, without consideration of other large-amplitude motion effects,

such as might arise, for example, from the OH bending vibration. This fit is described in detail in:

10. Global Fit of Torsional-Rotational Transitions in the Ground and First Excited Torsional States of Methanol. Li-Hong Xu and J. T. Hougen, *J. Mol. Spectrosc.* **173**, 540-551 (1995).

The two global fits above were able to reach nearly experimental measurement precision, but they required use of a number of molecular constants "forbidden" by the concepts of reduced Hamiltonians (which are obtained by contact transformation methods and described in the literature). This prompted a reexamination of whether or not such contact transformation procedures (which involve a number of mathematical assumptions concerning the ordering of perturbation terms according to a smallness parameter) can be applied to the combined torsion and rotation problem. Our conclusions that the reduced Hamiltonian procedure is not always applicable, and the computational experiments on which the conclusions are based, are described in theoretical paper:

11. Contact Transformations and Determinable Parameters in Spectroscopic Fitting Hamiltonians. M. A. Mekhtiev and J. T. Hougen, *J. Mol. Spectrosc.* **199**, 284-301 (2000).

In this paper, numerical fitting experiments were carried out on the three-dimensional (three-Eulerian-angle) asymmetric rotor problem, using $J \leq 20$ unitless energy levels generated artificially from a full orthorhombic Hamiltonian with quadratic through octic operators in the angular momentum components. Results were analyzed using the condition number κ of the least squares matrix, which is a measure of its invertibility in the presence of round-off and other errors. Transferring the numerical and algebraic understanding obtained from the simpler three-dimensional pure rotational problem to the more complicated four-dimensional methyl-top internal rotor problem supports the empirical observation that presently existing data sets for methanol and acetaldehyde are most efficiently fit using partially reduced Hamiltonians and further suggests that expanding the methanol data set to transitions involving levels of higher J , K and ν_t would favor even more strongly the use of partially reduced (rather than completely reduced) fourth-order Hamiltonians.

While not directly related to the energy transfer questions associated with this DoE report, it turns out that the experience gained with global fits near the top of the barrier could easily be transferred to spectral measurements for molecules with very low torsional barriers (which are traditionally quite difficult to treat theoretically). These recent quite successful fits (presently of interest primarily for interstellar molecular

spectroscopy, though with further development also of potential interest for biomimetic molecular spectroscopy) are described in the two papers:

12. The Ground and First Excited Torsional States of Acetic Acid. V. V. Ilyushin, E. A. Alekseev, S. F. Dyubko, S. V. Podnos, I. Kleiner, L. Margules, G. Wlodarczak, J. Demaison, J. Cosléou, B. Maté, E. N. Karyakin, G. Golubiatnikov, G. T. Fraser, R. D. Suenram, and J. T. Hougen, *J. Mol. Spectrosc.* **205**, 286-303 (2001).

13. Reinvestigation of the Microwave Spectrum of Acetamide. R. D. Suenram, G. Golubiatnikov, I. I. Leonov, J. T. Hougen, J. Ortigoso, I. Kleiner, and G. T. Fraser, *J. Mol. Spectrosc.* **208**, 188-193 (2001).

The Internal Rotation Manifold above the Barrier

Numerous unsolved theoretical problems also exist for the energy region above the top of the barrier. One theoretical investigation in this project led to the proposal of an alternative torsional quantum number for levels above the barrier in internal rotor molecules. Roughly speaking, we now believe that the traditional torsional quantum number ν_t , which groups together in one (ν_t, J) -manifold $2J+1$ K -levels of approximately the same energy, is most appropriate for quasi-harmonic-oscillator levels, as found below the barrier, while the alternative quantum number ν_T , which groups together in one (ν_T, J) -manifold $2J+1$ K -levels lying approximately on a parabola defined by $E \approx (K - K_{min})^2$, is most appropriate for incipient free-rotor levels, as found above the barrier. This work is described in detail in:

14. Some Properties and Uses of Torsional Overlap Integrals. M. A. Mekhtiev and J. T. Hougen, *J. Mol. Spectrosc.* **187**, 49-60 (1998).

A discussion of classical trajectories on rotational energy surfaces and of coherent-state quantum projections for an asymmetric-top molecule containing a freely rotating internal symmetry top whose symmetry axis is not coincident with a principal axis of the molecule was carried out to gain further qualitative understanding of energy torsion-rotation energy levels well above the barrier, i.e., for levels in the free-rotor limit. We found in particular that stationary points on the rotational energy surface increase in number from two to four to six as J/n increases from zero to infinity (where J is the total and n is the free-internal-rotor angular momentum). For some J/n values trajectories can arise that sample a large fraction of the K values (where K is the z -axis projection of J), corresponding in quantum wave functions to extensive K mixing in the symmetric-top basis set $|J, K\rangle$. When such mixing cannot be made small for any choice of z axis

direction, we call it *K* scrambling. This work is described in more detail in:

15. K-scrambling in a near symmetric top molecule containing an excited noncoaxial internal rotor. J. Ortigoso and J. T. Hougen, J. Chem. Phys. **112**, 10212-10220 (2000).

A partially successful global fit of nearly 3000 torsion-rotation transitions involving levels below, at, and above the barrier was carried out for acetaldehyde, as described in:

16. The Third and Fourth Torsional States of Acetaldehyde. I. Kleiner, J. T. Hougen, J.-U. Grabow, S. P. Belov, M. Yu. Tretyakov, and J. Cosleou, J. Mol. Spectrosc. **179**, 41-60 (1996).

The quality and extent of the fit of levels above the barrier was limited by our lack of knowledge of the perturbations in the internal rotation levels caused by interaction with the lowest small-amplitude vibration, which lies near $\nu_t = 4$ in the internal rotation manifold. Attempts to deal with these perturbations, which from another point of view are the interactions responsible for torsionally enhanced IVR, lead naturally into the second part of the project.

Part II: Understanding Interactions of Small-Amplitude Vibrations with Bath States Arising from Multiquantum Excitation of the Internal Rotation Motion

Theoretical studies for torsionally mediated interactions in the vibrational manifold

The studies of low-lying small-amplitude vibrational bands reported in the literature for acetaldehyde and methanol all lead to the same conclusion, namely: it is not possible using existing theory to understand the upper state energy levels in any detail. Most published vibrational band analyses for these two molecules thus present extensive quantum number assignments but no quantitative fits. These wide-spread modeling difficulties suggest that interactions between vibrational fundamentals and the quasi-continuum precursor states in acetaldehyde and methanol are quite large, even at very low vibrational energies, i.e., suggest that the torsionally mediated interactions thought to be responsible for the creation of intra-molecular vibrational energy redistribution (IVR) doorway states higher up in the vibrational continuum are already well developed in a region where relatively complete high-resolution spectroscopic understanding is possible.

The second part of this project thus involved several theoretical studies, beginning with a paper which formulated an effective Hamiltonian for the vibration-torsion-rotation

problem in methyl top containing molecules by singling out the large-amplitude torsional motion for special parametric treatment in the small-amplitude vibrational and overall rotational problems. This rather formal algebraic work is described in:

17. Coordinates, Hamiltonian, and Symmetry Operations for the Small-Amplitude Vibrational Problem in Methyl-Top Internal-Rotor Molecules like CH_3CHO . J. T. Hougen, J. Mol. Spectrosc. 181, 287-296 (1997).

To use the vibration-torsion-rotation formalism above, which contains a large number of unknown torsionally dependent parameters, significant input from quantum chemistry calculations is necessary. Before using such input, however, it seemed prudent to try to validate quantum chemistry results at the level of detail required for application to the vibration-torsion-rotation problem. Validation efforts were carried out using Gaussian 94 to obtain quantum chemistry results at the top and bottom of the internal rotation barrier (corresponding to two stationary points of the potential surface). Results at these two points were used to determine two coefficients in the Fourier expansion $C_0 + C_3(1-\cos 3\gamma)$ of various parameters used in the spectroscopic fitting Hamiltonian. This work is extremely encouraging for methanol, because the Gaussian 94 results for four pairs of C_0 , C_3 coefficients are in very good agreement with the corresponding torsion-rotation fitting parameters. Unfortunately, the analogous results for acetaldehyde, with its one additional nucleus and six additional electrons, are rather disappointing, forcing one to consider at least three possibilities: (i) the experimental fitting parameters for the more asymmetric-top molecule acetaldehyde are contaminated by Hamiltonian reduction effects (an arcane problem for high-resolution spectroscopists), (ii) acetaldehyde falls just beyond the present practical limit for extreme high precision Gaussian calculations (basis set size, convergence criteria, etc.), or (iii) the good agreement between *ab initio* calculations and experiment for the four C_3 Fourier expansion coefficients in methanol was just fortuitous. This work is described in more detail in:

18. On the physical interpretation of torsion-rotation parameters in methanol and acetaldehyde: Comparison of global fit and *ab initio* results. Li-Hong Xu, R. M. Lees, and J. T. Hougen, J. Chem. Phys. 110, 3835-3841 (1999).

A follow-up to this theoretical work, begun after the DoE grant expired, concerns itself primarily with three questions: (i) What is the range of commonly used definitions for the internal rotation angle, and how do variations within this range affect intercomparisons among results from various laboratories? (ii) Do projected force constant variations with internal rotation angle delivered by present commercial *ab initio* packages have sufficient precision to allow meaningful extraction of higher order torsion-

rotation-vibration interaction terms? (iii) What fraction of the extensive chemical reaction dynamics literature can be easily adapted for use in high-resolution spectroscopic studies of small-amplitude vibrations in methyl top internal rotor molecules? Answers to these questions are discussed both from an algebraic and from a numerical computation point of view in:

19. Torsional Angle Definitions and Linear and Quadratic Force Field Variations along the Torsional Coordinate for CH₃OH and CH₃CHO. Li-Hong Xu, J. T. Hougen, R. M. Lees, and M. A. Mekhtiev.

Further information on the results presented in this preliminary manuscript can be obtained by contacting any of its authors.

A group-theoretical treatment of inverted torsional splittings, which have been reported in the literature for certain excited vibrational states of methanol, was also carried out after the grant period expired. In this work, group-theoretical methods were used to show that inverted torsional splittings in fundamental levels of small-amplitude vibrations of methanol-like molecules can be parameterized and understood in terms of the energy level patterns induced when a pair of high-barrier torsionally split components of given ν_t and ${}^1A + {}^1E$ symmetry species in the molecular symmetry group G_6 is allowed to interact with small-amplitude vibrational modes of symmetry vE . Such doubly degenerate vE vibrational modes arise rather naturally in G_6 (isomorphic with the point-group C_{3v}) for those methyl-group vibrations in C_s -point-group asymmetric tops like CH₃CHO that are analogs of the degenerate methyl-group stretch, bend, and rocking vibrations in C_{3v} -point-group symmetric tops like CH₃-C $\equiv$ C-H. This group-theoretical treatment is somewhat different than, but (as a comparison of model parameters shows) still fundamentally similar to, the recent local mode explanation of inverted torsional splittings in the C-H stretching fundamental region in methanol. This work is presented in:

20. Torsional Splittings in Small-Amplitude Vibrational Fundamental States of Methanol-Type Molecules. J. T. Hougen, *J. Mol. Spectrosc.* **207**, 60-65 (2001).

Experimental studies of vibrational states embedded in the torsional manifold

A particularly favorable case for studying the creation of doorway states opening into the internal rotation bath is given by the lowest vibrational fundamental band ν_{10} of acetaldehyde at 509 cm⁻¹, which lies at approximately $\nu_t = 4$ in the torsional bath manifold. Analyses of portions of an older far-infrared spectrum and of a new spectrum over a wider frequency range in the torsional hot-band region have yielded a large number

of quantum number assignments but no satisfactory least-squares fits. Since the ν_{10} fundamental is the lowest small-amplitude vibration in the molecule and is also rather well isolated from higher lying vibrations, the large perturbations observed for this fundamental can only arise from direct interactions with the internal rotation bath states, which makes the study of ν_{10} a key component in any high resolution investigation of torsionally mediated IVR. This work, which has proved to be far more difficult than anticipated because of complications arising from congestion at the band center, is still in progress, but a preliminary manuscript on the work, which includes experiment and theory from five laboratories, has been prepared:

21. Assignments, Theoretical Discussion, and Semi-Quantitative Fit of the ν_{10} Band of Acetaldehyde near 509 cm^{-1} . I. Kleiner, N. Moazzen-Ahmadi, A. R. W. McKellar, T. A. Blake, R. L. Sams, S. W. Sharpe, G. Moruzzi, and J. T. Hougen.

It might be argued that the problem of small-amplitude vibrations interacting with the torsional bath precontinuum should be easier to treat in CH_3OH than in CH_3CHO because the infrared spectrum of methanol is much better resolved, and therefore much more completely assigned, than that of the heavier species acetaldehyde. As a counter argument, however, the problem in methanol is significantly more difficult because there are at least four strongly interacting "lowest" small-amplitude fundamentals lying in the 1000 cm^{-1} region, whose interactions with each other and with the torsional precontinuum must all be treated simultaneously. In any case, even though the 509 cm^{-1} region in acetaldehyde seems at the moment to be more favorable for initial detailed IVR-related spectroscopic studies than is the 1000 cm^{-1} region in methanol, a parallel spectroscopic attack on methanol will be continued (in part because of the greater reliability of *ab initio* calculations for methanol). The continuation of the earlier work on methanol in this project is being carried out primarily by R. M. Lees and Li-Hong Xu at the University of New Brunswick in Canada, but further information can also be obtained by contacting the author of this report.

Summary and Conclusions

A coherent body of theoretical and experimental high-resolution spectroscopic work has been produced, which, as described above, has considerably advanced our quantitative knowledge of energy levels in the internal rotation bath for molecules with one methyl rotor. Although the DoE grant period expired before a full attack on the problem of interaction between an isolated small-amplitude vibrational state and the torsional bath (i.e., on possible mechanisms for torsionally enhanced IVR) could be organized at NIST, the main thrust of the work inspired by this grant is nonetheless being

continued by many of the original members of the DoE funded team in their own laboratories. Readers of this report with interest in subsequent developments of this work, should thus contact the author of this report or any of the coauthors of the papers cited above. For closely related published work not covered in this report, the following e-mail addresses (which are neither all-inclusive nor mutually exclusive) may be useful.

1. For vibration-rotation band analyses in acetaldehyde, or for other applications of the internal rotation fitting program: isabelle.kleiner@ppm.u-psud.fr
2. For vibration-rotation band analyses in methanol, or for other applications of the methanol data: xuli@unb.ca or lees@unb.ca
3. For a suite of semiautomatic assignment programs for vibration-rotation bands of internal-rotor or other large-amplitude-motion molecules: giovanni@moruzzi1.df.unipi.it
4. For other aspects of the mathematical analysis of the semi-classical and quantum properties of the energy level structure in internal rotor molecules: imto430@iem.cfmac.csic.es (Juan Ortigoso)
5. For a similar extensive body of high-resolution spectroscopic measurements and theory on symmetric-top molecules with a methyl rotor (e.g., CH_3CH_3 or CH_3SiH_3): ahmadi@phas.ualgary.ca or iozier@physics.ubc.ca