DOE/ER/14161--T1

Final Performance Report for DE-AI05-90ER14161

Under the terms of the agreement, reports were submitted annually, both for the contractors' meetings and during the grant renewal process. Also, results obtained from the research were published and are available in the open literature. As an example, I include below a report from the 1994 renewal application, which summarizes work carried out under DE-AI05-90ER14161 and also gives a list of publications resulting from this work.

**Spectroscopic Investigation of the Vibrational Quasi-Continuum
Arising from Internal Rotation of a Methyl Group**

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Introduction

The goal of this project is to use spectroscopic techniques to investigate in detail phenomena involving the vibrational quasi-continuum in a simple prototype system. Acetaldehyde ($\text{CH}_3\text{-CHO}$) was chosen for the study because: (i) methyl groups are thought to be efficient promoters of intramolecular vibrational relaxation (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, (iii) internal rotation is the only very low frequency mode in acetaldehyde, and as such can be considered to be the "cause" of high vibrational state densities at moderate energies, and (iv) the aldehyde carbonyl group offers the possibility of both vibrational and electronic spectral probing.

The project is divided conceptually into three parts: (i) understanding the one-dimensional large-amplitude internal rotation motion below, at, and above the top of the torsional barrier, (ii) understanding fundamental and overtone states of the traditional small-amplitude bond stretching and bending motions, and (iii) understanding interactions involving states with multi-quantum excitations of at least one of these two kinds of motion.

The project is divided geographically in the sense that the post-doctoral fellow funded by this grant works at NIST in collaboration with the PI, but a significant effort has been made to enlist the help of other laboratories (world-wide) when their complementary skills and instrumentation are clearly useful to the project. The success of this effort is illustrated by the fact that Charles Parmenter is chairing a special session at the 1993 Columbus Symposium devoted entirely to acetaldehyde spectroscopy and generic methyl-rotor IVR questions.

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Principal Results from First 3-Year Grant Period 1990-1993

Torsion

As a result of four (DoE sponsored) papers¹⁻⁴, we now understand experimentally, and theoretically to within experimental measurement accuracy, torsion-rotation levels from all three torsional states below the top of the torsional barrier. A fifth paper⁵, primarily theoretical in nature and very nearly completed, clarifies some confusing points associated with K_a, K_c energy level quantum number labeling problems and with spectral line intensity calculations when acetaldehyde loses its plane of symmetry during the internal rotation motion. The significance of our work on the torsional levels is twofold: (i) we have produced a critically evaluated and vastly extended high-resolution infrared and microwave data set for levels below the barrier, which cleared up a number of conflicting frequency measurements in the literature, and (ii) we have shown (surprisingly) that only small extensions of the literature model were necessary to understand all levels below the top of the torsional barrier.

Ordinary Vibrations

Investigations of four ordinary vibrational states in acetaldehyde are in progress, using data from infrared Fourier transform, jet-cooled diode-laser, jet-cooled CO₂-side-band-laser double-resonance studies, etc. The significance of our work on ordinary vibrational levels varies somewhat from level to level.

920 cm⁻¹ Band: The NBS Shimanouchi tables list this band as a methyl rocking fundamental. We have recorded the band using the CO₂ side-band laser spectrometer at NIST, and have shown conclusively⁶ that the alternative assignment to a combination band $\nu_{14} + \nu_{15}$ involving one quantum of the torsion, first proposed by Hollenstein and Günthard⁷ on the basis of matrix isolation isotopic studies, is correct. It is clearly important, before plunging into the vibrational quasi-continuum, to identify with certainty the location of all vibrational fundamentals in acetaldehyde.

867 cm⁻¹ Band: Hollenstein and Günthard also suggested that the unexpectedly large intensity of the 920 cm⁻¹ combination band arises from a Fermi resonance interaction with the strong 867 cm⁻¹ fundamental. We have recorded and assigned a jet-cooled diode-laser spectrum of this band at NIST with the hope of making a simultaneous analysis of it and the 920 cm⁻¹ band to determine if the 20 cm⁻¹ Fermi interaction constant is correct. A constant of this size would mean that anharmonic interactions involving the torsion can be driven by energies approaching 15% of the torsional fundamental frequency. It is important to achieve a better understanding of this situation, because precisely such large anharmonic interactions (which will persist, or

grow even larger as one moves up the vibrational ladder) are thought to represent one possible cause of methyl-rotor enhanced IVR effects.

1734 cm^{-1} Band: This is the carbonyl stretch fundamental, whose high-resolution room-temperature Fourier transform spectrum defied all attempts at analysis five years ago. We have recorded at NIST a jet-cooled laser-diode spectrum of this band, and Anne Andrews seems to have a credible preliminary assignment of significant portions of the spectrum. Since this band has been postulated to suffer from significant methyl-rotor-enhanced IVR⁸, the following rather important questions are at stake. (i) If, as appears likely now, the jet-cooled spectrum is analyzable with little sign of bath-state-induced spectral line fragmentation, then one possible conclusion is that the methyl top does not significantly enhance IVR at the bath state density found at this excitation energy. (ii) On the other hand, one can speculate that methyl top IVR enhancement proceeds via Coriolis interactions, which will only turn on at higher J. This speculation would predict that warmer beams should exhibit fragmented spectral lines. (iii) One can speculate still further (and this argument is preferred by the PI) that methyl top IVR enhancement proceeds via gyroscopic interactions, which will only turn on when the top begins to rotate. This speculation predicts that transitions to states built on the carbonyl stretch by adding one or more quanta of the torsion will exhibit strongly fragmented spectral lines, even though the density of bath states is not significantly higher a few hundred cm^{-1} above the carbonyl stretch than it is in the vicinity of the stretch itself. It is clearly important to determine which of these speculations is correct and to quantify the relation between the amount of fragmentation and the amount of overall and/or internal rotation. (We note in passing that a spectrum of the first overtone of the carbonyl stretch has also been recorded and partially assigned at NIST.)

763 cm^{-1} Band: This is the second lowest fundamental band (after excluding the large-amplitude torsion) and it was recorded (on a Bruker Fourier transform spectrometer in Belgium) in order to gain confidence in the theoretical model, etc. in the low-energy excitation region where no significant interactions with bath states are expected. Analysis is proceeding well (in France), but fitting difficulties of the order of 0.1 cm^{-1} persist in the upper state. The fact that such difficulties are also found in the other bands described here raises the question of whether any small-amplitude vibrations in a methyl top molecule can be fully understood by conventional vibration-rotation procedures. It is tempting to speculate here that some Born-Oppenheimer-like parameterization of the whole small-amplitude vibrational problem in terms of the large-amplitude torsional angle may be necessary.

DOE SPONSORED PUBLICATIONS

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3. S. P. Belov, M. Yu. Tretyakov, I. Kleiner and J. T. Hougen, J. Mol. Spectrosc. **160**, 61-72 (1993). "The Second Torsional State of Acetaldehyde"
4. W. L. Barclay, Jr., M. A. Anderson, L. Ziurys, I. Kleiner and J. T. Hougen, Ap. J. Supplement, **89**, 221-226 (1993). "The Laboratory Spectrum of Acetaldehyde at 1 mm ($230-325\text{ cm}^{-1}$)"
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6. S. P. Belov, G. T. Fraser, J. Ortigoso, B. H. Pate and M. Yu. Tretyakov, Mol. Phys. **81**, 359-368 (1994). "Electric-Resonance Optothermal Spectrum of the 920 cm^{-1} $\nu_{14} + \nu_{15}$ Torsional Combination Band of Acetaldehyde"

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7. H. Hollenstein and Hs. H. Günthard, Spectrochim. Acta, **27A**, 2027-2060 (1971).
8. V. A. Walters, S. T. Colson, D. L. Snavely, K. B. Wiberg and B. M. Jamison, J. Phys. Chem. **89**, 3857-3861 (1985).