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MOLECULAR EIGENSTATE SPECTROSCOPY: APPLICATION TO THE INTRAMOLECULAR DYNAMICS OF SOME POLYATOMIC MOLECULES IN THE 3000 TO 7000 cm^{-1} REGION

Progress Report

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ABSTRACT

This project uses high resolution infrared spectroscopy to probe the mechanism of intramolecular vibrational redistribution (IVR) in ultracold isolated polyatomic molecules. Single resonance spectra of 1-butyne and ethanol show that qualitatively different coupling mechanisms dominate in each case - anharmonic and Coriolis coupling respectively. A random matrix method for simulation of these spectra has been implemented which allows estimation of the strength of the various mechanisms at each stage of the coupling process. A new infrared double resonance (IRDR) technique employing two high resolution F-center lasers has been developed. IRDR spectra of propyne in the $2\nu_1$ region explicitly reveal a two stage coupling mechanism involving anharmonic and z-type Coriolis interactions. The data span the range between traditional high resolution spectroscopy where all line positions can be fit precisely by an explicit Hamiltonian and the domain of statistical spectroscopy.

Molecular Eigenstate Spectroscopy: Application to the Intramolecular Dynamics of Some Polyatomic Molecules in the 3000 to 7000 cm^{-1} Region

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I. Introduction

Intramolecular vibrational redistribution (IVR) appears to be a universal property of polyatomic molecules in energy regions where the vibrational density of states is greater than about 5 to 30 states per cm^{-1}. Interest in IVR stems from its central importance to the spectroscopy, photochemistry, and reaction kinetics of these molecules.

A bright state, φ_s, which in our case may be a C-H stretching vibration, carries the oscillator strength from the ground state. This bright state may mix with bath rotational-vibrational levels to form a clump of molecular eigenstates, each of which carries a portion of the oscillator strength from the ground state. In our work we explicitly resolve transitions to each of these molecular eigenstates. Detailed information about the nature of IVR is contained in the frequencies and intensities of the observed discrete transitions.

The primary goal of this research is to probe the coupling mechanisms by which IVR takes place. The most fundamental distinction to be made is between anharmonic coupling which is independent of molecular rotation and rotationally-mediated coupling. Of the rotationally-mediated mechanisms, Coriolis coupling is generally assumed to be stronger than centrifugal coupling. Coriolis interactions may be further classified as x, y, or z according to the axis about which the coupling rotation occurs. Each of these mechanisms obeys different symmetry restrictions and therefore each leaves its characteristic signature on fully resolved molecular spectra.

We are also interested in the rate at which IVR takes place. Our measurements are strictly in the frequency domain but information is obtained about the decay of the zero order state, φ_s, which could be prepared in a hypothetical experiment as a coherent excitation of the clump of molecular eigenstates. As the coherent superposition dephases, the energy would flow from the initially prepared mode into nearby overtones and combinations of lower frequency vibrational modes. The decay of the initially prepared mode is related to a pure sequence infrared absorption spectrum by a Fourier transform.[1,2,3]

The specific methods used to address these goals and the results obtained are described in the sections below.

II. Direct Infrared Absorption in a Free Jet

The sample gases were cooled to about 5 K in a pulsed slit-jet expansion. The high resolution absorption spectrum of the jet was recorded by monitoring the transmitted intensity of an F-center laser beam. To enhance the absorption signal, a multipass cell[4] is employed to pass the laser beam 25 times through the jet. Baseline subtraction is used to suppress the laser intensity noise.

Spectra of the asymmetric methyl C-H stretch bands of 1-butyne[5] and ethanol[6] were recorded at about 0.001 cm^{-1} resolution. Both of these molecules exhibited intermediate case IVR with each zero-order line being fragmented into a clump of transition to molecular eigenstates. For many of the observed spectral features, the rotational quantum numbers could be assigned rigorously by ground state combination differences. Where rigorous assignments were not possible, the most reasonable assignments were made based on our knowledge of the spectrum. In both molecules, torsional tunneling of the methyl group (3 equivalent positions) results in the splitting of the 'ground' vibrational state into A and E nuclear spin species. The ground state tunneling splitting is so small that the nuclear spin species could not be assigned by ground state combination differences. Accordingly, the most reasonable A/E assignments were based on the available symmetry constraints.

Even though the spectra excited the same chromophore in each molecule, the spectra were startlingly different for the two molecules. For 1-butyne, the measures of IVR (*see section V below*) were independent of J and show only a slight dependence on K_a. Therefore the coupling mechanism is dominantly anharmonic with some contribution from z-axis Coriolis interactions. For ethanol, there is evidence for anharmonic coupling at J=0, but the number of coupled levels increase rapidly with both J and K_a which indicates the presence of x/y and z-type Coriolis couplings respectively. It can be seen then that in both molecules more than one coupling mechanism is present although the relative strengths are qualitatively different. In Section V below, we describe the methodology that we have developed for estimating the relative strength of each mechanism when multiple coupling mechanisms are present.

The lifetimes for the decay of C-H stretching vibrations in 1-butyne and ethanol are shown in Fig. 1 and 2 respectively. Fig. 1 shows that the IVR rate in 1-butyne in independent of whether the methyl C-H or the acetylenic C-H is excited. When the methyl C-H of ethanol is excited (Fig.2), the decay is much faster and increases rapidly with K_a. In these cases, we see that the IVR rate depends not on the identity of the chromophore but on the identity of the molecule and that fast IVR is associated with a Coriolis coupling mechanism.

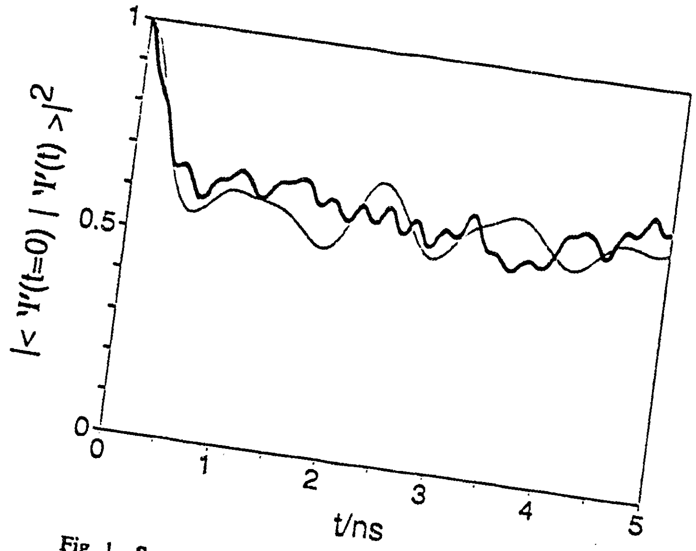

Fig. 1. Survival probability of the asymmetric methyl C-H stretch (thick line) and for the acetylenic C-H stretch (thin line) in 1-butyne. The decay times are 276 and 269 ps, respectively. The curves are calculated from experimental data and are averaged over the nuclear spin species and the largest common set of rotational levels.

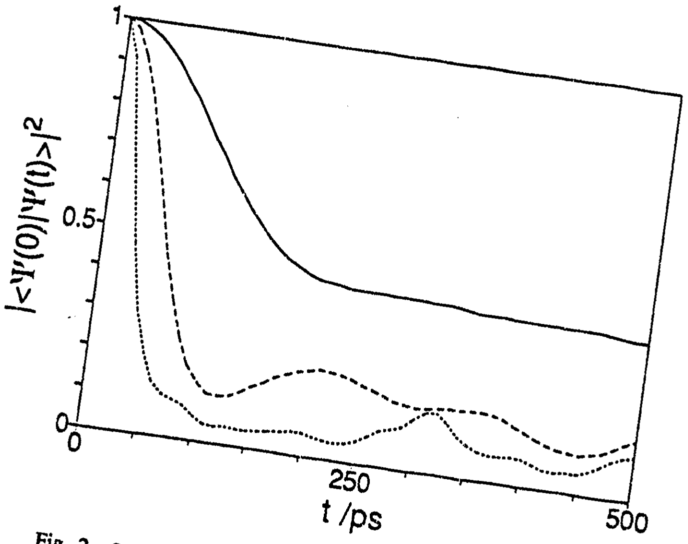

Fig. 2. Survival probability of the asymmetric methyl C-H stretch in ethanol. The decay times for $K_a=0$ (solid line), 1 (dashed), and 2 (dotted) are 116, 58, and 32 ps respectively. Note that the time scale is expanded 10-fold relative to Fig. 1.

III. Infrared Double Resonance

One of the major objectives of this grant was to develop an infrared double resonance (IRDR) technique capable of recording molecular eigenstate spectra as a probe of IVR in polyatomic molecules. This goal has been accomplished and a copy of the communication[7] describing the technique and the results obtained is appended as part of this report. The IRDR technique has the following properties:

(i) All good quantum numbers can be assigned through the use of two high resolution laser beams. The assignment ambiguities which are unavoidable in single resonance experiments are removed. In fact by the nature of the experiment, most features are fully assigned at the moment they are recorded which relieves the necessity of tedious assignments by ground state combination differences and opens the door to the study of much more complex spectra.

(ii) The equipment can be operated in a saturation mode (Fig. 3) in which the pump and probe frequencies are the same, or in two double resonance modes (Fig. 4).

(iii) Through the use of two photons, vibrations can be accessed which are completely dark to single resonance spectroscopy, *e.g.* , the $\nu_1+\nu_6$ band of propyne (Fig.4).

(iv) The molecules are cooled in a free jet.

(v) The resolution is in the range 5 to 25 MHz.

(vi) High signal-to-noise (600:1) has been obtained in the propyne $2\nu_1$ region. (See Fig. 3 of the attached reprint.[7])

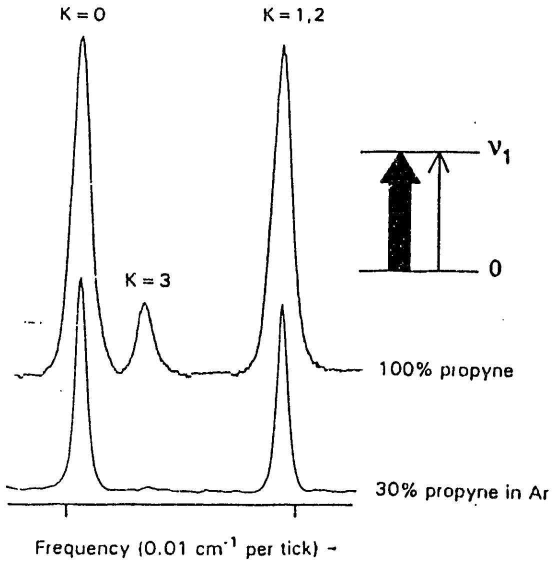

Fig. 3. Saturation spectrum of the R3 region of the propyne v_1 band.

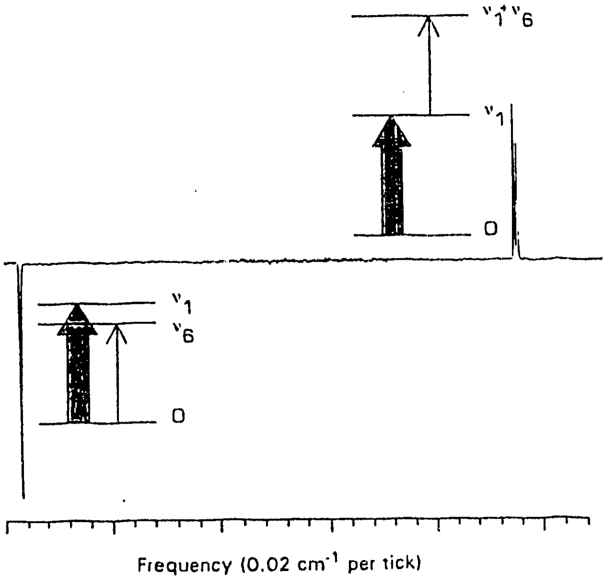

Fig. 4. Propyne spectrum illustrating two double resonance modes. The pump frequency (thick arrow) is held fixed while the probe frequency (thin arrow) is scanned.

Our results[7,8] on the v_6 , v_1+v_6 , and $2v_1$ bands of propyne, together with previous propyne spectra by other workers,[9,10] span the range of energy where IVR is turning on. As the density of states increases, it is no longer possible to fit the position of every line precisely with an explicit Hamiltonian, but we pass into the domain of statistical spectroscopy. The $2v_1$ spectra[7,10] reveal explicitly the two-stage IVR coupling mechanism, first anharmonic coupling to a relatively sparse tier of dark states which are in turn coupled to a denser tier by a z-axis Coriolis effect.

IV. Microwave-Infrared Double Resonance

Microwave-infrared double resonance spectra have been recorded for several rotational levels in the O-H stretch band of ethanol. The experiments were done at the National Institute for Standards and Technology in collaboration with Brooks Pate and Jerry Fraser. This experiment was supported by this grant only through the stipend of the student, Gerg Bethardy, who was involved in the experiment. The experiment used optothermal detection with electrostatic focusing. Although the spectra remain to be analyzed and the relative intensities are not accurate, it is clear that the IVR rate is extremely rapid - faster than for the methyl C-H stretch in the same molecule.

V. Random Matrix Simulation of Molecular Eigenstate Spectra

As the density of states increases with energy or with molecular size and flexibility, a single bright state is fragmented into an increasing number of closely spaced eigenstates. It quickly becomes impossible to identify the zero-order character of each dark state which is perturbing the bright state. The difficulty comes, in part, from our inability to calculate the energies of the zero-order dark states with sufficient precision, and, more fundamentally, from the fact that *the zero-order dark states are likely to be extensively mixed among themselves*. We are compelled, therefore, to devise a statistical treatment of the high resolution spectra in order to deal with our ignorance of the vibrational character of each interacting bath state.

We have developed a methodology[11,12] based on a class of random matrix ensembles called the Gaussian-Poisson Ensembles. Our approach builds on an extensive history of random matrix studies in the nuclear physics literature and more recently in the domain of molecular spectroscopy. We assume that there is sufficient mixing *among the bath states* to validate a statistical treatment. Our methodology is capable of simulating infrared spectra exhibiting intermediate case and also those in the sparse limit where only one or two perturbing levels are observed. By varying the parameters defining the ensemble to fit the observed spectra, we are able to extract useful mechanistic information from the experimental data.

Since a statistical method cannot be expected to reproduce the individual line positions and intensities of an experimental spectrum, certain statistical measures of IVR are selected to serve as the interface for the comparison of experiment and theory. The measures which are selected are ones which provide physical insight in their own right. They are

(i) the dilution factor, which is the inverse of the effective number of coupled levels,

(ii) the interaction width, which is a measure of the rate at which energy leaves the bright state, and

(iii) the density of coupled levels, which provides a measure of the domain of phase space which is explored by the IVR.

We have used random matrix calculations to test the accuracy with which each measure can be evaluated from real or simulated spectra and the dependence of each on the signal-to-noise ratio.

The first step in simulating a spectrum is to select the model parameters which will define an ensemble of random matrices. We have used the RMS anharmonic coupling and Coriolis couplings (each of x, y, and z types). Separate parameters are used for the bright-bath interaction and for the bath-bath interaction. The second step is to select a matrix from the ensemble by choosing individual matrix elements from the appropriate distributions. This matrix is diagonalized to create a synthetic spectrum. Many matrices (64 to 512) are selected from the same ensemble and diagonalized to obtain a representative sampling of the ensemble. Ensemble average values of the measures of IVR, their distributions, and their dependence on the rotational quantum numbers are then compared to the experimental values.

The model parameters are then varied until the agreement with experiment is satisfactory. In this way, we were able to obtain RMS anharmonic, Coriolis z-type, and Coriolis x/y-type matrix elements for the bright-bath coupling in 1-butyne and in ethanol. By matching the experimental density of states some information is also available about the Coriolis bath-bath coupling matrix elements.

VI. Time and Effort

During the academic year, September 1992 to May 1993, the principal investigator is spending 25% effort on this project. During the summer period, June to August 1993 about 66% of the principal investigator's effort will be spent on this project.

VII. Statement of Unobilgated Balance

It is estimated that, by the end of the grant period, there will no funds remaining in this grant.

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