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Evidence of Vibrational Mode-Coupling in 2-Fluoroethanol *via* High Resolution Infrared Spectroscopy in a Molecular Beam

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Abstract

The rotationally resolved high resolution spectrum of 2-fluoroethanol in a molecular beam has been measured in an effort to determine the extent of mode-selective vibrational coupling. The high resolution spectrum of an asymmetric CH stretch clearly demonstrates that mode-coupling is present in 2-fluoroethanol. The extent of mode-coupling is significantly less than would be predicted based on previous work on molecules of a similar size and density of states. The small amount of mode-coupling in the CH stretch is consistent with the slow photoisomerization rate of 2-fluoroethanol upon excitation of the CH stretch, and is evidence that supports mode-selective vibrational coupling in the isomerization reaction of 2-fluoroethanol.

Evidence of Vibrational Mode-Coupling in 2-Fluoroethanol via High Resolution Infrared Spectroscopy in a Molecular Beam

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The rotationally resolved spectrum of 2-fluoroethanol (2FE) has been measured to determine the extent of mode-selective vibrational coupling. The photo-isomerization of 2FE in low temperature matrices has been studied extensively.[1-10] By exciting the OH or CH stretch in matrix isolated 2FE it is possible to induce isomerization from the more stable Gg' to the Tt conformer. Controversial evidence from some experiments suggests that mode-selective vibrational coupling occurs between hydrogen stretching modes and modes that participate in the Gg'-to-Tt isomerization of 2FE.[1-4] The relative quantum efficiencies for isomerization in an Ar matrix show that excitation of the OH stretch is 7 times more efficient in inducing isomerization than excitation of a CH stretch.[4] Thus far, studies have failed to determine conclusively whether the discrepancy in isomerization efficiencies are caused by mode-selective coupling of the hydrogen stretches to the isomerization coordinate[1-4], or by matrix effects involving the surrounding media[8-10]. By examining 2FE in a molecular beam we remove the ambiguity of the environmental effects and the role of mode-selective coupling can be definitively and quantitatively evaluated.

High resolution infrared spectroscopy in molecular beams measures the degree of vibrational coupling by identifying the molecular eigenstates directly. The molecular eigenstates in larger molecules are often superposition states of the zeroeth order vibrational states. The number and intensities of the transitions present in a rotationally resolved spectrum provides a direct measurement of the extent of mixing between different vibrational modes. de Souza, Kaun and Perry first used high resolution infrared spectroscopy to determine the molecular eigenstates in 1-butyne[11,12], and this study was later extended by McIlroy and Nesbitt[13,14]. The spectra of McIlroy and Nesbitt clearly resolve transitions to many molecular eigenstates within the acetylenic stretch of 1-butyne. From analysis of the spectra it was determined that extensive coupling occurs between vibrational modes. Since 2FE is of a similar size and has a similar density of states, mode coupling should be spectrally apparent in 2FE as well. The extent of the coupling would be expected to correlate with the rate of the isomerization, if mode-selective coupling does in fact determine the rate of isomerization.

The rotationally resolved spectrum of the asymmetric CH stretch of the fluorinated carbon[3] was measured covering the spectral region from 2978-2989 cm^{-1}

with a spectral resolution of 12 MHz. The experimental apparatus will be described in detail elsewhere[15], but briefly consisted of a color-center laser pumped by a dye laser, which in turn was pumped by an argon ion laser. The laser was crossed with a skimmed molecular beam. The method of optothermal detection was used after the design of Miller and coworkers.[16] Helium carrier gas at a pressure of 6 psi was passed over the liquid sample of 2FE and expanded through a nozzle of 50 μ diameter.

To analyze the data, our experimental spectrum was compared to a calculated spectrum using a rigid rotor model and exact diagonalization of the rotational Hamiltonian.[17] The details of the data analysis, as well as a complete discussion of the results of this analysis will be presented elsewhere.[15] When the fit is optimized, there are more peaks in the experimental data than are calculated using the rigid rotor model. The additional peaks are characteristic of vibrational mode-coupling. Many, although not all, of the individual peaks in the calculated spectrum correspond to a small cluster of peaks in the experimental data. A cluster of peaks result when the intensity of a single peak from one vibrational mode is distributed over a number of vibrational modes. Thus, the presence of clusters of peaks is indicative of the presence of vibrational mode-coupling between the asymmetric CH stretch and other vibrational modes in 2FE.

The extent of mode-coupling was determined from the intensities and the spacing of peaks within a cluster of peaks. The number of peaks in the cluster depends on the density of states, as well as the degree of mixing between the optically active light state and the manifold of dark states. From the location and intensities of the individual transitions in a cluster of peaks, we can evaluate the magnitude of the matrix element which couples the light state to specific individual dark states. Note that the average separation between the peaks in these clusters is 0.004 cm^{-1}. Therefore, the magnitude of the matrix element need not be very large in order to have a significant effect in mixing states.

To verify that a cluster of peaks is, in fact, caused by mixing of states, one can compare two sets of transitions to the same excited state. The same pattern of peak spacing and intensities should appear for two different transitions to the same excited rotational state. Shown in Figure 1 are several spectral regions consisting of pairs of transitions to the same excited state. The similarity of the patterns is apparent, and we conclude that mode-coupling is causing these clusters of peaks.

From a simple state counting algorithm that treats the normal modes in 2FE as harmonic oscillators[18], with the exception that the C-C torsion and the O-H torsion are treated as hindered rotors[19], 2FE has 58 states/cm^{-1} at the CH stretching region.

With this density of states, virtually all modes must be coupled to the optically active mode. The fact that all modes appear to couple to the optically active mode is similar to the previous studies of terminal acetylenes.[13,14] In contrast, however, the average matrix element that couples the asymmetric CH stretch to other modes is 0.0029 ± 0.0011 cm^{-1} which is a factor of 2-3 smaller than those calculated for the terminal acetylenes[19]. The small magnitude of the matrix element in 2FE relative to butyne is particularly surprising given that the acetylinic CH stretch would be expected to couple poorly to the other modes in butyne as the author's note. The small amount of coupling in 2FE is consistent with the slow rate of isomerization observed when this CH stretch was excited in a matrix. Further experiments are necessary to fully quantify the relationship between mode-coupling and isomerization rates. In particular, the high resolution infrared spectrum of the OH stretch is essential for comparison with the current high resolution spectrum of the CH region. One might expect that the mode-coupling would be more substantial in the OH stretch to account for the faster reaction rate upon excitation of this mode in matricies. Such experiments are currently underway in our laboratory. The results presented here demonstrate the power of high resolution spectroscopy to resolve the controversy surrounding the role of mode-selective chemistry in the isomerization reaction of 2FE.

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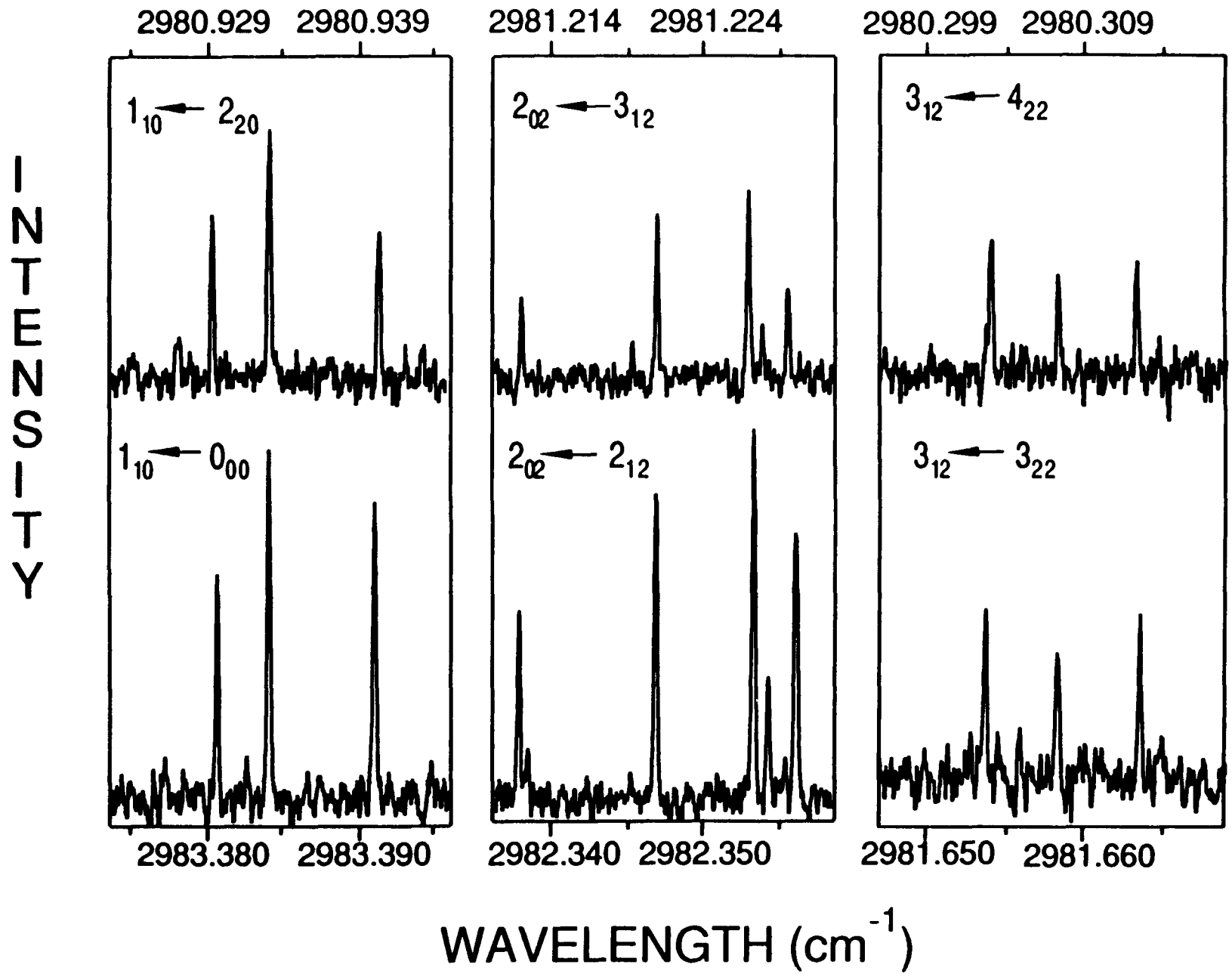
Figure Caption:

Figure 1: Each panel in the figure shows two sets of transitions to the same excited state. The transitions are labeled with the J and K_a and K_c quantum numbers as J_{K_a,K_c} corresponding to the labels of the zeroeth order uncoupled states. The left panel shows two sets of transitions to the 1_{10} excited state. The middle and right panels are to the 2_{02} and 3_{12} excited states respectively. In each case the similarity of the patterns of peaks positions and intensities are apparent, demonstrating the presence of vibrational mode-coupling.


2980.929
2980.939
2981.214
2981.224
2980.299
2980.309
$1_{10} \leftarrow 2_{20}$
$2_{02} \leftarrow 3_{12}$
$3_{12} \leftarrow 4_{22}$
$1_{10} \leftarrow 0_{00}$
$2_{02} \leftarrow 2_{12}$
$3_{12} \leftarrow 3_{22}$
2983.380
2983.390
2982.340
2982.350
2981.650
2981.660
INTENSITY
WAVELENGTH (cm^{-1})