

NONLINEAR OPTICAL SPECTROSCOPY OF “POTENTIALLY FRUSTRATED” PROTON-TRANSFER DYNAMICS

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Reactions involving the transfer of protons between distinct chemical moieties, as often guided by the action of attendant hydrogen bonds, are among the most prevalent of transformations in chemistry and biology. This talk will describe nonlinear spectroscopic investigations of classically hindered hydron migration taking place in the ground [\tilde{X}^1A_1] and the lowest-lying singlet [$\tilde{A}^1B_2(\pi^*\pi)$] excited states of tropolone and kindred species, where an intramolecular hydrogen bond adjoins hydroxylic (proton-donating) and ketonic (proton-accepting) oxygen centers. Aside from elucidating the substantial effects incurred by $\pi^* \leftarrow \pi$ electron promotion, these studies have explored the vibrational specificity of ground-state dynamics by implementing a fully coherent variant of the venerable stimulated emission pumping technique within the coherent framework of two-color resonant four-wave mixing (TC-RFWM) spectroscopy. By combining the state-selectivity inherent to double-resonance excitation with the spectral simplification afforded by polarization-resolved detection, the TC-RFWM scheme can discriminate and dissect features that are inaccessible to more traditional spectroscopic probes. A variety of vibrational bands spanning the $0 \leq E_{\text{vib}} \leq 1800\text{cm}^{-1}$ portion of the ground-state potential energy hypersurface have been interrogated, with extracted values of tunneling-induced bifurcation reflecting the pronounced and specific dependence of hydron-migration rates on nuclear degrees of freedom. Such vibrationally mediated behavior will be discussed in terms of modulated donor-acceptor displacements and intrinsic permutation-inversion symmetries, with choreographed motion of the reaction site found to exert the most substantial influence on the efficacy of proton transfer.

EMPIRICAL LOWER STATE ASSIGNMENTS FROM TEMPERATURE DEPENDENT SPECTRA: ROTATIONAL ASSIGNMENTS OF METHANE TRANSITIONS NEAR $1.38\mu\text{m}$

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Overtone spectroscopy accessing high vibrational states in polyatomic molecules is both exciting and challenging. The challenges arise mostly from the multiple vibration-vibration and vibration-rotation couplings that cause the observed spectra to be heavily perturbed. Traditional approaches for line-by-line assignments of such spectra often fail even for small molecules for excitations in the near infrared and visible spectral regions, because no regular rovibrational progressions can be identified in the spectra that would guide the initial assignments. Additional experimental information that guides the rovibrational assignments of these heavily perturbed spectra is highly desirable.

In this contribution we present an experimental approach for determination of empirical lower state rotational quantum numbers based on the temperature dependence of the absorption line strengths. Methane overtone spectrum in the icosad region near 7200cm^{-1} is used to demonstrate the technique. This spectrum is at present mostly unassigned due to the high complexity of its rovibrational structure. We demonstrate how spectra obtained at room temperature, liquid nitrogen temperature and in supersonic jet expansion can be combined to provide reliable estimates of the lower state rotational quantum numbers for a range of rotational states including the $J=0$ states that identify the positions of vibrational band origins.

Presentation mode: lecture

Time required: 15 min

COMPLETE EXPERIMENTAL ROVIBRATIONAL EIGENENERGIES OF THE [H,C,N] MOLECULAR SYSTEM UP TO 9000 CM⁻¹ ABOVE THE GROUND STATE

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The [H,C,N] molecular system is the ideal candidate to test new models aimed to calculate the manifold of the rotational, vibrational and electronic states of a molecule with more than two atoms. The isomerization reaction $\text{HCN} \rightleftharpoons \text{HNC}$ is one of the most important model systems for the study of unimolecular reactions. This work reports the experimental characterization of all rovibrational eigenenergies up to 9000 cm⁻¹ above the ground state of the molecular system in the HCN^a and HNC^b part of the potential surface. This complete list of eigenenergies is the final result from the analysis of several very dense high temperature hot gas emission spectra measured and analyzed over the last years. Another important result of the analysis of the emission spectra covering the complete infrared region from 300 cm⁻¹ up to 10000 cm⁻¹ is a large set of precise spectroscopic constants. For all combined excitations of the ν_1 and ν_3 stretching modes with $v_1 = 1 \dots 4$ and $v_3 = 1 \dots 4$ in combination with bending modes $v_2 = 4 \dots 12$ accurate spectroscopic constants have been determined^c. Probably due to these measurements, the [H,C,N] molecular system has the largest number of experimentally measured rovibrational states among all molecules with more than two atoms. For both isomers new “complete” anharmonic fits of the vibrational dependence of the vibrational term values and rotational constants have been determined and will be discussed.

^aG. CH. MELLAU, Complete experimental rovibrational eigenenergies of HNC up to 9000 cm⁻¹ above the ground state, *in preparation*, (2010).

^bG. CH. MELLAU, Complete experimental rovibrational eigenenergies of HNC up to 3743 cm⁻¹ above the ground state, *submitted to J. Chem. Phys.*, (2010).

^cG. CH. MELLAU, The ν_1 Band System of HNC, *submitted to J. Mol. Spectrosc.*, (2010).

Presentation mode: lecture

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HIGH RESOLUTION INFRARED SPECTROSCOPY OF [1.1.1]PROPPELLANE: THE REGION OF THE ν_9 (e') Band

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The region of the infrared-active ν_9 CH₂ bending band of [1.1.1]propellane has been recorded at a resolution (0.0025 cm^{-1}) sufficient to distinguish individual rovibrational lines. This region includes the partially overlapping bands $\nu_9(e') = 1459\text{ cm}^{-1}$, $2\nu_{18}(l = 2, E') = 1430\text{ cm}^{-1}$, $\nu_6 + \nu_{12}(E') = 1489\text{ cm}^{-1}$, and $\nu_4 + \nu_{15}(A_2'') = 1518\text{ cm}^{-1}$. In addition, the difference band $\nu_4 - \nu_{15}(A_2'')$ was observed in the far infrared near 295 cm^{-1} and analyzed to give good constants for the upper ν_4 state. The close proximities of the four bands in the ν_9 region suggest that rotational and Fermi resonance couplings could be significant, and theoretical band parameters obtained from Gaussian *ab initio* calculations were helpful in guiding the band analyses. The analyses of all four bands were accomplished, based on our earlier report of ground state constants determined from combination differences involving more than 4000 pairs of transitions from five fundamental and four combination bands¹. This paper presents the analyses and determination of the upper state constants of all four bands in the region of the ν_9 band. Complications were most evident in the $2\nu_{18}(l = 2, E')$ band, which showed significant perturbations due to mixing with the nearby $2\nu_{18}(l = 0, A_1')$ and $\nu_6 + \nu_{12}(E')$ levels which are either infrared inactive as transitions from the ground state, or, in the latter case, too weak to observe. These complications are discussed and a comparison of all molecular constants with those available from *ab initio* calculations at the anharmonic level is presented.

1. R. Kirkpatrick, T. Masiello, N. Jariyasopit, A. Weber, J. W. Nibler, A. Maki, T. A. Blake, and T. Hubler, *J. Molec. Spectrosc.* 248 (2008) 153-160.

Presentation mode: lecture

Time required: 15 min

Comment: *Session on infrared spectra*