

Infrared Diode Laser Spectroscopy of Short-Lived Molecules

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"Static" diode laser spectroscopy in a low-pressure hollow-cathode discharge has been successfully applied for different short-lived molecules and ions. Very high sensitivities were achieved due to the large effective pathlength of the White-cell (200 m), which contains the discharge. The infrared spectroscopy of BrCN^+ in its $^2\Pi$ ground electronic state is shown as an example.

First test results with a modified apparatus are also shown. The changes on the spectrometer enable the simultaneous detection of the mass spectrum of neutral and ionic constituents of the discharge plasma and the high resolution infrared spectra. This modification will make the search for new absorptions of neutral molecules and ions in discharges much easier.

A new method was developed for performing "kinetic spectroscopy" in discharges. This method opens a wide range of possibilities for the study of discharge kinetics as well as for time resolved diode laser spectroscopy. These studies were carried out in a hollow cathode discharge, where short lived neutrals and ions can be produced under favourable conditions. Due to the high temperatures in such a discharge, molecules are produced in highly excited vibrational, or in some cases excited electronic states. The production of CN in different rovibrational states (up to $v=8$) is shown as an example.

An *Ab Initio* Calculation of the Rotation-Vibration Energies
and the Transition Moments in the Electronic Ground State of C_3

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The C_3 molecule is of major importance in combustion processes, and it plays a role in astrochemistry. It has a very anharmonic bending mode with a bending fundamental energy observed experimentally¹ at 63 cm^{-1} , and a rather irregular vibrational energy level pattern caused by substantial interactions between the bending and stretching motions². We have carried out an *ab initio* calculation of the CASCF potential energy surface and the corresponding dipole moment surfaces for C_3 employing a very large basis set and have used the *ab initio* results for a further calculation of the rotation-vibration energies in the lower part of the energy spectrum using the MORBID approach³. The *ab initio* calculation reproduces qualitatively the observed² variation of the bending energy pattern with stretching excitation.

We conclude from the *ab initio* results obtained in the present work, and from a fitting to experimental data carried out with the MORBID computer program, that the equilibrium structure of C_3 is linear.

Using the MORBID rotation-vibration wavefunctions and the *ab initio* dipole moment, we have calculated the vibrational transition moments for selected vibrational transitions. We determine transition moments of 0.44 and 0.35 Debye, respectively, for the ν_2 and ν_3 bands. The *ab initio* dipole moment values have further been used to calculate the line strengths, integrated absorption coefficients, and peak absorption coefficients of the low- J transitions in the ν_2 and ν_3 bands of $^{12}C_3$; these results are in keeping with recent experimental observations¹.

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²F. J. Northrup, T. J. Sears, and E. A. Rohlfling, *J. Mol. Spectrosc.* **145**, 74 (1991) and references therein.

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Analysis and Prediction of Spherical Top Molecules Spectra

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NEW HOT BANDS and COLD BANDS IN THE SPECTRA OF PROPYNE

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Our studies on the lowest energy levels of propyne $\text{CH}_3\text{C}\equiv\text{CH}$ have been pursued in three spectral regions (9-11 μm , 16 μm and 30 μm), using FT and TDL spectra. We shall show that in many cases, the hot bands are a much easier way to reach excited states than the direct study of the cold bands. For instance, we could find only a handful of lines belonging to $2\nu_{10}^{\pm 2}$ and not much more to $2\nu_{10}^0$ as contrasted to several thousands⁽³⁾⁽⁴⁾ for $2\nu_{10}^{\pm 2}-\nu_{10}$ and $2\nu_{10}^0-\nu_{10}$. In the same way, we have well analyzed the 'superhot' band $3\nu_{10}^{\pm 3}-2\nu_{10}^{\pm 2}$ whereas $3\nu_{10}^{\pm 3}$ is invisible.

Particularly interesting is the $\nu_9 = \nu_{10} = 1$ system around 1000 cm^{-1} . For the A_1+A_2 component ($\ell_9 = -\ell_{10} = \pm 1$), we have almost completely assigned the hot band at 16 μm , $(\nu_9+\nu_{10})^0-\nu_{10}$ and the PAPE type cold band at 10 μm , and to a smaller extent the hot band at 30 μm , $(\nu_9+\nu_{10})^0-\nu_9$. For the E component ($\ell_9 = \ell_{10} = \pm 1$), we have almost completely assigned the hot band at 16 μm , $(\nu_9+\nu_{10})^2-\nu_{10}$ and to a smaller extent the hot band at 30 μm , $(\nu_9+\nu_{10})^2-\nu_9$ and the perpendicular type cold band at 10 μm .

In all these hot bands, we have found nice examples of A_1, A_2 splittings, giving in most cases two 'families' of P, Q and R branches in the same K subband.

With 11 hot bands now more or less completely assigned (all with an E type lower level), propyne holds the record among symmetric top molecules.

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THE HIGH RESOLUTION ROTATIONAL-TORSIONAL SPECTRUM OF
METHANOL IN THE LABORATORY AND IN SPACE

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Methanol is a well-known interstellar molecule, occurring both in quiescent and star-forming regions of dense interstellar clouds. Detection of interstellar gaseous methanol occurs through line emission in the millimeter-wave and submillimeter-wave portions of the electromagnetic spectrum ($\nu < 1$ THz) generated by transitions between rotational-torsional energy levels. Methanol is even seen in at least several masing transitions. Its high abundance in star-forming regions makes an understanding of its dense spectrum, made complex by internal rotation, essential to ever hope to identify spectral features of other molecules.

We have recently extended previous work in our laboratory on the high resolution rotational-torsional spectrum of methanol and its isotopomers to assign high angular momentum transitions through $J = 24$ for both normal methanol and $^{13}\text{CH}_3\text{OH}$.¹ The data have been analyzed to experimental accuracy via an extended internal axis Hamiltonian. The resulting spectroscopic constants have been used to predict accurately the frequencies of a large number of transitions below 1 THz and excitation energies below 1000 cm^{-1} not measured in the laboratory. A reasonably complete set of transition frequencies for both isotopomers now exists for radioastronomers. Current work in our laboratory on both CH_3OD and CH_2DOH , both of which have been identified in interstellar space, is also progressing.

In addition to methanol, the internal rotor methyl formate is another interstellar molecule with high abundances in star forming regions. We have recently begun an experimental study of the rotation-torsion spectra of the symmetric deuterated species - DCOOCH_3 .

The support of NASA for our program in laboratory astrophysics is gratefully acknowledged. Spectral analyses have been undertaken on the CRAY YMP/8 Supercomputer of the Ohio Supercomputer Center, and we acknowledge the time received for use on this machine.

¹ T. Anderson, E. Herbst, and F. C. De Lucia, *Astrophys. J. Suppl.*, in press.