

High-resolution spectroscopy of molecules with large amplitude vibrations - progress and challenges

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The interpretation of the spectra of molecules with one or more large-amplitude vibrations (LAV) is a fascinating but difficult task. The presence of multiple equivalent minima in the molecular potential energy surface due to torsional or inversion motions can lead to substantial and seemingly erratic tunnelling splittings in the spectrum and the existence of several distinct molecular symmetry species that can have quite widely differing statistical weights and intensities. Since the LAV is intrinsically of low frequency, a ladder of LAV states will be populated at most temperatures adding further complexity and density to the spectrum. When coupled with the higher frequency small-amplitude vibrational (SAV) modes, the LAV motions greatly increase the state density in the energy manifold, creating numerous channels for interactions among the modes and modifying the usual structure of the SAV absorption bands.

These features make LAV species particularly important in the areas of molecular astrophysics and IVR dynamics. In molecular astronomy, the richness of the spectra of such species as methanol and ethyl cyanide have led to their classification as "Interstellar weeds" whose spectra must be well understood in the laboratory to permit full exploitation of the observational data coming in from new instruments such as HIFI on the Herschel Space Observatory and the ALMA array in Chile. In studies of intramolecular vibrational redistribution (IVR), the role of the LAV motions in mediating and enhancing internal energy transfer among the modes is of great interest and importance in connection with efforts at coherent control of chemical reactions.

In recent years, developments in submillimetre-wave sources and synchrotron-based FIR spectrometers have added powerful capabilities for LAV study, while improved computational power has enabled detailed modelling of the spectra as well as large-scale quantum chemical calculations of the torsional dependence of molecular structures and vibrational manifolds. In this talk, we will discuss some of our recent progress in spectral assignment and mapping of torsion-rotation energy manifolds, the compilation of extensive laboratory databases, global modelling of the spectra, and the ab initio calculation of torsion-dependent molecular properties. With high-resolution synchrotron spectra in the FIR region, we are extending assignments to high torsional states to reach the energy regime of both free internal rotation and SAV states.

This progress also brings new challenges. As we climb the torsional ladder from the hindered torsion regime below the barrier to free rotation high above the barrier, we shift the nature of our torsional functions. Evidence of strong torsion-mediated interactions among the SAV states points to the need for multistate treatments, a major challenge for the future.

Presentation mode: lecture

Time required: MINUTES REQUIRED min

Comment: *INVITED LECTURE*

TORSION AND OVERALL ROTATION INTERACTION^a IN CH₂DOH

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Due to the asymmetry of the CH₂D group, the internal rotation problem in the partially deuterated species of methanol CH₂DOH is a complicated one as, unlike in the normal species CH₃OH, the inertia tensor depends on the angle of internal rotation.^b The CH₂DOH species also displays a dense far infrared torsional spectrum difficult to assign. Recently 38 torsional subbands of CH₂DOH have been identified,^c but for most of them there is neither an assignment nor an analysis of their rotational structure.

In this paper an analysis of the rotation-torsion spectrum of CH₂DOH will be presented. The rotational structure of 23 torsional subbands have been assigned. These subbands are $\Delta v_t \geq 1$ perpendicular subbands with a value of v_t' up to 10^c and values of K' and K'' ranging from 0 to 9. For all subbands, the Q -branch was assigned, for a few subbands, the R - and P -branches could also be identified. The results of the rotational analysis with an expansion in $J(J+1)$ of the new subbands and of already observed ones^d will be presented. When available, microwave lines within the lower torsional level, recorded in this work or already measured,^e were added to the data set.

Subband centers were analyzed with a torsional Hamiltonian based on the exact rotation-torsion Hamiltonian of the molecule. 62 experimental wavenumbers were reproduced with an RMS value of 0.12 cm⁻¹. The spectroscopic parameters corresponding to the hindering potential and to the inertia tensor were retrieved.

A theoretical approach aimed at calculating the rotation-torsion energy levels has also been developed. It is also based on the exact rotation-torsion Hamiltonian and accounts for the dependence of the inertia tensor on the angle of internal rotation. Distortion effects are taken into account with an expansion in terms of rotation-torsion operators with C_s symmetry. This approach will be used to carry out preliminary global analyses of the available data.

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^bQuade and Lin, *J. Chem. Phys.* **38** (1963) 54.

^cLauvergnat, Coudert, Klee, and Smirnov, *J. Mol. Spec.* **256** (2009) 204.

^dQuade, Liu, Mukhopadhyay, and Su, *J. Mol. Spec.* **192** (1998) 378; and Mukhopadhyay, *J. Mol. Struct.* **695-696** (2004) 357.

^eLiu and Quade, *J. Mol. Spec.* **146** (1991) 252; and Mukhopadhyay *et al.*, *J. Chem. Phys.* **116** (2002) 3710.

Presentation mode: lecture

Time required: 15 min

Comment: 15 Minute Lecture

A VARIATIONALLY COMPUTED HOT (UP TO $T=1500$ K) LINE LIST FOR NH_3 .

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We present a “hot” line list for the ground electronic state of NH_3 computed variationally with the program suite TROVE. The line list is a catalogue of transitions where, for each transition, we give the Einstein coefficient and frequency/wavenumber together with the term values involved and their assigned quantum numbers. The computed list should fully characterize the absorption/emission processes of NH_3 at temperatures up to 1500 K. This work is a response to the growing astrophysical demands for information on the absorption properties of ammonia at high temperatures. The hot line list contains more than a billion transitions in the wavenumber range 0–12000 cm^{-1} ; these transitions involve 1.2 million energy levels below 18000 cm^{-1} and with J -values up to 35. It is so far the most comprehensive and accurate line list for NH_3 . It derives its quality from a new ‘spectroscopic’ potential energy surface of NH_3 generated in a least-squares fit to the NH_3 experimental energy levels available in the literature. Even before it was fully completed, the hot line list was included in astrophysical studies, a discovery of a very cool brown dwarf (UGPS 0722-05) and an analysis of the atmosphere of a transiting hot Neptune (GJ436b). In this contribution we will report our approach to the technical challenges of large scale intensity calculations. The accuracy of the new line list will be evaluated through a comparison with the experimental information available in the literature.

Presentation mode: lecture

Time required: 15 min

HIGH RESOLUTION SPECTROSCOPY OF $^{14}\text{NH}_3$ AROUND 1000 cm^{-1} DEDICATED TO THE DETERMINATION OF THE BOLTZMANN CONSTANT

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We report on the last results obtained at Laboratoire de Physique des Lasers on the linear absorption line shape study of ammonia at low-pressure. Both experimental and theoretical aspects of this spectroscopic work are dedicated to the determination of the Boltzmann constant k_B . For that purpose the Doppler broadening and the temperature of the gas have to be measured simultaneously at a few ppm. The absorption cell is placed inside a large thermostat filled with an ice-water mixture. The stability and the homogeneity of the molecular gas temperature around 273.15 K is better than $550\text{ }\mu\text{K}$ (2 ppm). The high accuracy spectrometer developed in our group for decades is used in a specific optical set-up to record an isolated absorption line of $^{14}\text{NH}_3$.

The spectrometer is based on a CO_2 laser and operates between 800 and 1300 cm^{-1} . We chose to focus on the ν_2 (inversion mode) saQ(6,3) rovibrational line of $^{14}\text{NH}_3$ at 965.79 cm^{-1} . The CO_2 laser emits on its R(6) line at 966.25 cm^{-1} and is frequency stabilized on the R(23) $A_1^1(-)$ saturated absorption line of OsO_4 , resulting in a spectral line width smaller than 10 Hz ($3 \times 10^{-10}\text{ cm}^{-1}$). The ammonia absorption line is recorded using a side-band generated by an electro-optic modulator. The gas fills an absorption cell which can be used either in single or multiple pass configuration (resp. 37 cm and 3.5 m , pressure ranging from 0.1 to 10 Pa). The linear absorption spectra (100 MHz FWHM) are recorded over 250 MHz ($8.3 \times 10^{-3}\text{ cm}^{-1}$) for various pressures. A recent improvement of the experimental setup also enables to record the hyperfine structure of the line over 1.5 MHz by saturated absorption. We observe $\Delta F = 0$ main components, $\Delta F = \pm 1$ transitions and Doppler-generated level crossings, in very good agreement with theoretical predictions.

The detailed study of linear absorption line shape includes many physical effects, some of them being negligible in our experiment¹. An analysis which takes into account pressure broadening, hyperfine structure, saturation of the molecular transition, transit time broadening, Lamb-Dicke-Mossbauer (LMD) narrowing, etc, leads to a determination of the Doppler broadening, proportional to $\sqrt{k_B T}$, and thus to k_B .

After several years of improvement^{1,2}, we are now able to measure the Doppler width of the saQ(6,3) rovibrational line of $^{14}\text{NH}_3$ at 273.15 K with a statistical uncertainty of 4.5 ppm . This results from 70 h of acquisition corresponding to 7000 spectra with pressures ranging from 0.1 to 2.5 Pa , that we fitted with a Galatry profile. It is very appealing for the metrological application of this work, since this measurement is the first direct determination of the Boltzmann constant by laser spectroscopy which will take part in the current discussion on fixing the value of the Boltzmann constant in order to redefine the temperature scale.

1. C. J. Bordé, C. R. Physique, 10, 866-882 (2009).
2. C. Daussy et al., Phys. Rev. Lett, 98, 250801 (2007).
3. K. Djerroud et al., C. R. Physique, 10, 883-893 (2009).

Presentation mode: lecture

Time required: 15 min