

Spectroscopic databases for the VAMDC and dat@osu portals

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Dijon spectroscopic databases include calculated line lists, in positions and intensities, that are obtained from experimental spectroscopic analyses. They contain 6 molecules: CH₄, C₂H₄, CF₄, SF₆, GeH₄ and RuO₄ and are all compatible with the XSAMS (XML Schema for Atoms, Molecules, and Solids) format adopted with the Virtual Atomic and Molecular Data Centre (VAMDC) Project (<http://www.vamdc.org>). VAMDC, a worldwide consortium which federates atomic and molecular databases through an e-science infrastructure, aims to provide a unique access point for scientists seeking the best atomic and molecular data for their studies. So far, development of new tools allows to easily download and compare data issued from different databases in a single XML document or into the HITRAN2004 format. Making the comparison that easy will help data users in the choice of data that best match their needs. It will also help data producers by checking the consistency of their data.

All these databases can be accessed either directly or through the VAMDC portal (<http://portal.vamdc.org>) and are also referenced through the dat@osu portal which aims to reference all research databases in the Bourgogne Franche-Comté region (<https://dataosu.obs-besancon.fr>).

Computing spectra of open-shell diatomic molecules with duo

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Duo [1] is a program designed to solve a coupled Schrödinger equation for the motion of nuclei of a given diatomic molecule characterized by an arbitrary set of electronic states. Duo is capable of both refining potential energy curves (by fitting data to experimental energies or transition frequencies) and producing line lists. Our most recent results of applying Duo to produce hot line lists for open-shell diatomic molecules include NO [2], SiH [3], PO and PS [4], C₂ [5], SN and SH [6] and AlH [7]. The line lists for TiO, MgO and YO are in progress. The published version of Duo only considers truly bound states. We are now working on extending Duo to treating quasi-bound or resonance states, or indeed the continuum itself, using the stabilization method. As an illustration, we present simulations of spectra of the quasi-bound A ¹Π - X ¹Σ⁺ system of AlH and of the continuum system A ¹Π - X ¹Σ⁺ and B ¹Σ⁺ - X ¹Σ⁺ system of NaCl.

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Accurate CO₂ Raman spectral simulation: an algebraic alternative based on anharmonic ladder operators

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The origin of this algebraic spectral analysis approach comes from the vibron model, which was devised to describe phenomenologically the nuclear motion of diatomic and polyatomic molecules [1–3]. The vibron model consists in proposing a unitary group as a dynamical group to model the vibrational (or rovibrational) Hamiltonian as an expansion in terms of its generators taking into account anharmonicities from the outset. A major problem of the model was that a link between Hamiltonian parameters and force constants did not exist and the resolution was far from the experimental accuracy. Since then, the algebraic approaches have evolved and nowadays a clear connection between the spectroscopic parameters and the force constants has been established (see e.g. [4]), providing predictions with spectroscopic accuracy (see e.g. [5–8]). This progress has permitted to simulate the CO₂ Raman spectrum [9], which has allowed us to identify new experimental vibrational bands [10].

In this presentation we show the recent results of a polyad–preserving algebraic approach to molecular structure applied to carbon dioxide in its ground electronic state. This approach has allowed us to reproduce 178 experimental data set of vibrational energies up to 26550 cm^{–1} making use of the three most common polyad schemes for this molecular species [11]. The results are comparable to those obtained with variational procedures, where a polyad number is not preserved, based on phase–space Hamiltonians [12]. In addition, we present the spectral analysis of the experimental Raman spectrum [13] based on this algebraic approach. This has permitted to assess the quality of the wave functions with respect to the previous study [10].

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Chiral rotational spectroscopy

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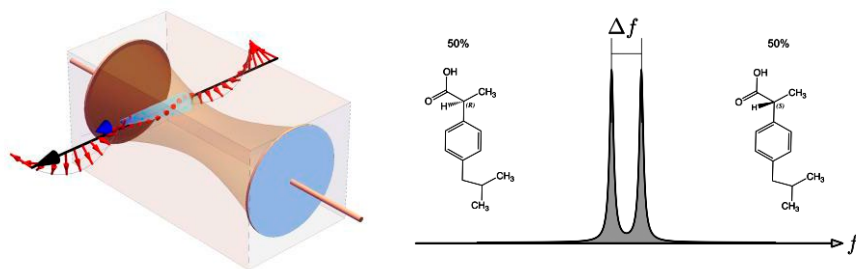
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We present the theoretical foundations of chiral rotational spectroscopy, a technique that enables the determination of the orientated optical activity pseudotensor components B_{xx} , B_{yy} and B_{zz} of chiral molecules, in a manner that reveals the enantiomeric constitution of a sample and provides an incisive signal even for a racemate. The basic property of a chiral molecule that is probed in typical optical rotation experiments using fluid samples is the isotropic sum of the electric-dipole / magnetic-dipole polarisability. The ability to determine orientated rather than isotropically averaged chiroptical information, in particular the individual optical activity polarisability components is highly attractive, as these offer a wealth of information about molecular chirality which is only partially embodied by the isotropic sum.

Our technique is based on illuminating molecules with circular polarised light (see Fig. 1) inducing oscillations in the charge and current distributions of the molecule, biasing the rotation of the molecule while shifting its energy in an orientationally and chirally sensitive manner. Such shifts constitute our orientated chiroptical response

Chiral rotational spectroscopy could find particular use in the analysis of molecules that are chiral solely by virtue of their isotopic constitution and molecules with multiple chiral centers. Our proposed technique offers the more familiar polarizability components α_{xx} , α_{yy} , and α_{zz} as by-products, which could see it find use even for achiral molecules.



Proton transfer tunneling splittings and the imaginary mode Hamiltonian: the beginning of a beautiful friendship

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Theoretical methods can be very useful in the interpretation of experimental observables, as for instance tunneling splittings. Here, we concentrate on semiclassical or quantum methods that can deal with tunneling splittings emerging from proton transfer reactions in symmetric systems. To perform this type of theoretical studies we propose the use of the imaginary-mode Hamiltonian (iMDH)[1], which is formulated in terms of the (mass-weighted) normal mode coordinates of the transition state for reaction.

iMDH is multidimensional (as is the nature of the quantum mechanical tunneling), and assumes that the normal modes perpendicular to the reaction coordinate (taken as the mode of imaginary frequency at the transition state) can be separated into enhancing (or symmetric modes), suppressing (or antisymmetric modes) and non-contributing (or undisplaced) modes. The reaction coordinate is a symmetric double well potential, whereas the rest of the normal modes are represented by harmonic oscillators linearly coupled to the reaction coordinate.

In some cases the iMDH was directly implemented in the semiclassical approximated instanton method, whereas in other cases we preferred to carry out a direct diagonalization. The iMDH allowed us to successfully calculate ground-state, as well as vibrationally excited tunneling splittings in several molecules with single or multiple proton transfer. Examples are: malonaldehyde, formic acid dimer, porphycene and the vinyl radical.

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