

Universal behaviour of diatomic halo states and mass sensitivities of their properties

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A simple one-parameter scaling of the interaction potentials allows for a fairly close fitting of the wavefunctions of the corresponding diatomic halo states, reflecting thus the universality in the low-energy scattering of atoms. This universality means that all the parameters characterizing the diatomic halo states can be determined with high precision if one of these characteristics is accurately known. It can be applied to determine not only the scattering properties, but also their accurate mass sensitivities which appear eminently promising for probing the constancy of the proton-to-electron mass ratio.

High energy states of polyatomic molecules: application to hot spectra

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Knowledge of accurate line positions and line intensities of various molecules and their isotopic species in wide spectral and temperature ranges is essential for the modelling of optical properties of planetary atmospheres, brown dwarfs and for other astrophysical applications. This implies reliable calculations of highly excited molecular energy states in large range of vibrational and rotational quantum numbers. The final aim is understanding of highly excited molecular states important for dynamics and construction of comprehensive lists of transitions based on accurate and extensive *ab initio* variational calculations for a large variety molecular species as for exemple CH₄ [1–4] PH₃ [5] C₂H₄ [6] SiH₄, CH₃F [7] GeH₄ [8] including all isotopologues and accounting for their symmetry properties. In case of elevated temperatures, quantum–mechanical calculations of ro–vibrational energy levels are very demanding and require a special attention, both in terms Hamiltonian/basis–set reduction [9,10] and data compression [11] to make calculations more feasible and final line lists lighter. The TheoReTS database and information system [11] (<http://theorets.univ-reims.fr>, <http://theorets.tsu.ru>) developed by Reims and Tomsk groups for planetary and astrophysical spectroscopy applications will be briefly summarized, including examples on hot methane [12] and hot ethylene [13] data.

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Absolute vibrational assignment from fragmentary spectroscopic data in two isotopologues

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In this contribution we discuss application of the isotope effect to establish the absolute vibrational numbering in electronic states of diatomic molecules. This is illustrated by examples of single electronic states with various shapes of the potential curves (both regular and irregular) and states coupled by perturbations. The minimum number of spectroscopic data (either term values or spectral line positions) necessary to provide a unique numbering is considered. We show that at favourable conditions just four term energies (or spectral lines) in one isotopologue and one term energy in the other suffice.

Atmospheric oxygen mm-absorption: models review and uncertainties evaluation

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Molecular oxygen is one of the main atmospheric absorbers of millimeter-wave radiation. Oxygen molecule has a band around 60 GHz and a single spectral line at 118.75 GHz formed by fine structure magnetic dipole transitions within pure rotational triplets. "Zero-frequency" lines corresponding to the transitions without quantum number change are also allowed for magnetic dipole molecules. Millimeter-wave oxygen spectrum is influenced by the collisional coupling redistributing the absorption in comparison to the sum of the uncoupled line profiles [1].

Information on the O₂ microwave spectrum is of importance for applications. In particular, the band is used for retrieving vertical pressure and/or temperature profiles from remote sensing data. These applications require knowledge of the line parameters with high accuracy and models of the molecular oxygen spectrum in atmosphere, accounting for the coupling effect.

There is noticeable reciprocal influence between considered groups of the lines through the collisional process. Adjusting model parameters for the band shape changes calculated absorption in the wings of the band far from resonant lines. Current study considers "perturbative" approach [2] providing analytical band profile description used in MPM (Millimeter-wave Propagation Model) and one based on the semi-empirical collisional cross-sections calculations [3] within ECS (Energy Corrected Sudden) formalism.

Earlier models [4,5] has shown inconsistency of the calculated absorption at the band wings. This led to the review of the resonator spectrometer recordings from the year of 2009 models were based on. The data were refined for oxygen concentration value reassignment for each recording. With the refined data, aforementioned models of the millimeter-wave oxygen spectrum in atmosphere were updated. Up-to-date broadening coefficients and their temperature dependences [6] were also included in the models. Updated models provide better residuals for the data they are based on, as well as better representation of the later independent measurements data (not used for models optimization) and better agreement between the models.

Line intensities, central frequencies and broadening coefficients included into models are known up to finite uncertainty, which leads to the uncertainty of the calculated absorption value. Parameters accounting for collisional coupling derived from measurements also have uncertainties because of measurements noise as well as individual line parameters uncertainties.

Model spectroscopic parameters are partially correlated, i.e. joint variation of the parameters values might not change the calculated absorption. Correlation of the parameters for both aforementioned models was estimated together with the calculated absorption uncertainty influenced by this correlation. This uncertainty can also be propagated to the brightness temperature calculation uncertainty.

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Anharmonic IR spectra of chemical warfare agents from ab initio molecular dynamics simulations

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Chemical warfare agents (CWAs) are one of the most dangerous chemical compounds used against humans, mostly at war conditions but also in terrorist attacks. The most popular CWAs, for example sulfur mustard (HD), adamsite (DM) or Clark I (DA), are relatively small molecules with a limited number of degrees of freedom. Since these chemical compounds are extremely dangerous their research is restricted to the selected certified laboratories and therefore the knowledge about their spectroscopic properties, in particular FT-IR spectra, is limited.

The small size of CWA molecules make them an ideal target for the theoretical studies utilizing state-of-the-art methods, including ab initio molecular dynamics (AIMD). The advantage of in silico research is the precise description of physicochemical properties of CWAs without the risk of the direct exposure.

We investigate the structural properties of the selected CWA molecules in the gas phase by Car-Parrinello molecular dynamics simulations. We perform thorough conformation analysis of different configurations using density functional theory to analyze the behavior of the system at finite temperature. For each local minimum structure the harmonic IR spectrum is obtained during the vibrational analysis procedure. As the last step, the anharmonic dynamical finite temperature IR spectrum from the Fourier Transform of the dipole moment autocorrelation function is obtained to mimic the experimental IR spectrum.