

INTERPLAY OF THEORY AND EXPERIMENT IN ROTATIONAL SPECTROSCOPY

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It will be demonstrated how quantum-chemical calculations can be used to assist experimental investigations in the field of rotational spectroscopy. Examples will be given for the detection of new molecules based on high-accuracy predictions of the corresponding spectroscopic parameters, the determination of molecular geometries using rotational spectroscopy, the analysis of the hyperfine pattern in experimental spectra, and the determination of absolute NMR scales based on experimentally determined nuclear spin-rotation constants.

INVESTIGATION OF ROTATIONAL SPECTRA OF ISOTOPIC SPECIES OF TRANS-FORMIC ACID: A TEST CASE FOR THE INTERPLAY BETWEEN EXPERIMENT AND THEORY.

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Trans-formic acid is the simplest organic acid and the first that has been identified in the interstellar medium. Its astrophysical relevance has motivated this spectroscopic study. To provide highly accurate rest frequencies as well as to improve the accuracy of the spectroscopic and hyperfine parameters available in the literature, the rotational spectra of various isotopic species, namely, HCOOH, DCOOH, HCOOD, DCOOD, have been investigated. The Lamb-dip technique has been exploited to record the rotational spectra at sub-Doppler resolution in the millimeter- and submillimeter-wave frequency ranges and, when possible, to resolve the hyperfine structure due to the hydrogen and/or deuterium nuclei. Doppler-limited THz measurements (1.0-1.6 THz; with an accuracy of about 50-70 kHz) have also been carried out in order to extend the predictive capabilities of our spectroscopic parameters to higher frequencies.

The experimental investigation of the hyperfine structure has been supported by high-level quantum-chemical calculations of the parameters involved. The calculations have been carried out at the CCSD(T) level together with basis sets of quadruple- up to sextuple-zeta quality. Vibrational corrections have also been included as obtained by means of vibrational second-order perturbation theory.

Presentation mode: lecture

Time required: 15 min

ISOTOPIC EFFECTS IN PHOTOASSOCIATIVE FORMATION OF ULTRACOLD YTTERBIUM MOLECULES IN EXCITED TRIPLET STATE

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The properties of photoassociation spectra near the $^1S_0\text{-}^3P_1$ intercombination line of bosonic ytterbium¹ were studied theoretically. A mass scaled model of the excited state interaction potential that well describes bound state energies obtained in a previous photoassociation experiment² was constructed. This model was used to calculate theoretical photoassociation spectra in a range of ultracold temperatures using semianalytical theory developed by Bohn and Julienne³.

Photoassociation spectra not only give us the energies of excited bound states, but also provide information about the behavior of the ground state wavefunction. In fact, it can be shown that within the so-called *reflection approximation*^{4,5} the line intensity is proportional to the ground state wavefunction at the transition's Condon point. We show that in the case of ytterbium, the rotational structure of the photoassociation spectra depends heavily on the behaviour of the ground-state wavefunction. The change of the scattering length from one isotope to another and the resulting occurrence of shape resonances in higher partial waves determines the appearance and disappearance of rotational components, especially in the deeper lying states, whose respective Condon points lie near the ground state centrifugal barrier. Thus, photoassociation spectra differ qualitatively between isotopes. Consequently, the efficiency of molecular production in given rovibrational states depends heavily on the particular isotopic combination.

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2. S. Tojo, M. Kitagawa, K. Enomoto, Y. Kato, Y. Takasu, M. Kumakura, and Y. Takahashi, *Phys. Rev. Lett.* **96**, 153201 (2006).
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4. P. S. Julienne, *J. Res. Natl. Inst. Stand. Technol.* **101**, 487 (1996).
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Presentation mode: lecture

Time required: 15 min

Comment: *Cold molecules*

RADIATIVE MODEL FOR EMISSION SPECTROSCOPY FROM OPTICALLY THICK LABORATORY ACETYLENE SAMPLES AT HIGH TEMPERATURE

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Recently, a high temperature source has been used to produce high temperature emission spectra of acetylene in the 3 μm spectral range, under Doppler limited resolution, and the complete spectral assignment has been performed using a global rovibrational Hamiltonian^a. The present investigation focuses on the relative emission line intensities which are observed to be affected. The strongest lines intensity may be considerably reduced for high column density acetylene samples, hence affecting the 3:1 ortho:para intensity ratio. A radiative model is developed to take into account the effects generated by the strong opacity of the acetylene samples including self-absorption and absorption of the radiation emitted by the hot environment. The model is used to extract the absolute concentration of the high temperature acetylene samples from the observed relative spectral intensities. The relevance of the procedure for infrared remote sensing in high temperature astrophysical environments, such as circumstellar envelopes of cool carbon rich evolved stars, is discussed.

^aAmyay B, Robert S, Herman M, Fayt A, Raghavendra B, Moudens A, Thievin J, Rowe B, Georges R. Vibration-rotation pattern in acetylene (II): Introduction to Coriolis coupling in the global model and analysis of emission spectra of hot acetylene around 3 μm . *J. Chem. Phys.* 2009;131:114301