STATISTICAL THEORY OF VIBRONIC SPECTRA. DETERMINING THE SHAPES OF MOLECULAR ELECTRONIC BANDS.

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A method aimed at determining the envelopes of bands in molecular spectra, corresponding to the transitions between two Born-Oppenheimer states is presented. First, expessions for moments of the transition energy distribution are derived. Then the moments corresponding to the pertinent quantum chemical model are evaluated. Finally, a smooth function for which the appropriate moments are equal to the 'exact' ones is constructed. The feasibility and the accuracy of this approach is illustrated by considering several exactly solvable one-dimensional models and the numerically exact potential of the hydrogen molecule. The envelopes of the spectra in the case of the model potentials have been calculated using 2- and 3- moment Gram-Charlier representations of the transition energy distributions and compared with the exact intensity distributions. It is demonstrated that while the Gram-Charlier and Edgeworth type expansions give a correct description of the molecular bands in the case of the harmonic oscillator-like potentials, they are inappriopriate if departure from harmonicity is considerable. Therefore in these cases the new trial function is proposed. In the case of the hydrogen molecule the dependence of the transition energy distribution on the temperature is also presented.

APPLICATION OF A cw $AgGaS_2$ DIFFERENCE FREQUENCY SPECTROMETER WITH TWO DIODE LASERS AS PUMP SOURCES FOR HIGH RESOLUTION MEASUREMENTS OF CO AND OCS NEAR 4.75 μm

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Experiments with a tunable cw difference frequency spectrometer applying the non-linear crystal $AgGaS_2$ and two diode lasers as pump sources are presented.

In contrast to the majority of known applications of the difference frequency mixing with solid state or gas lasers we apply two single mode diode lasers with emission wavelengths of 690 nm and 805 nm, respectively. By fixing the emission wavelength of one diode laser and tuning the wavelength of the second laser by changing temperature or excitation current we can cover typically 0.87 cm^{-1} (FWHM) in good agreement with recently published data and theory. With an input power of 20 mW and 5.5 mW we achieved an IR output power in the nW-range.

To demonstrate the capabilities of the spectrometer we scanned CO and OCS absorption lines near 2107 cm^{-1}. From these experiments we deduce an overall signal-to-noise ratio of 1000:1 and a spectral resolution of better 30 MHz. With these parameters a trace gas detection of CO under immission conditions will be possible.

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MOGADOC - A POWERFUL DATABASE FOR SPECTROSCOPISTS AND RADIOASTRONOMERS

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For many years the MOGADOC (MOlecular GAsphase DOCumentation) database has been a powerful tool for scientists all over the world to retrieve information about gas phase investigations. Covering literature on laboratory as well as atmospheric or astronomical work it provides the user with fast and easy access to literature of each field, making it possible to keep track of current subjects of interest and molecules under study.

One of the unique features of this database is that the sources used for compiling the information not only include „standard" journals, but also publications that are difficult to access or „grey" literature like workshops, conferences and symposia. Currently the customer's version of this database contains over 22,500 bibliographic entries for over 6,000 compounds. The coverage of publications is virtually complete for studies using rotational spectroscopy. Recently extensive efforts are being made to include numeric structural data which, up to now, allows the user to search and display numeric entries for over 3,300 molecular data sets that include interatomic distances, bond angles and dihedral angles. The bibliographic information includes keywords forming a controlled hierarchical thesaurus characterising the contents of the article which makes it possible to select the publications of interest very conveniently.

The database is available as an inhouse version for IBM compatible PCs under Windows™. Graphical input interfaces and user-friendly search forms provide easy access to the data without requiring knowledge of a certain command syntax. For retrieval experts a Messenger-like command language is available. More information and a demo version is available via **http://www.uni-ulm.de/strudo/mogadoc/** in the WWW.

New Fast Line-by-Line Package. Basic Principals.

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It is well known that the line-by-line method of calculation of the absorption characteristics of a gas medium is standard and is applied for verification of approximate models of transmittance and for direct modeling of the radiative transfer in molecular absorbing media. In this connection, development and creation of new highly efficient algorithms are urgent problems of indubitable interest for specialists [1].

In this work, we describe a new algorithm for calculating of the transmittance that includes recent advances in the line-by-line calculation method. The high speed of operation is provided due to preliminary selection of absorption lines [2], frequency grid optimization [3], and new method of reduction of nonhomogeneous path to equivalent homogeneous one. This algorithm is now one of the fastest known algorithms.

References:

1. Report on the ITRA, International Radiation Commission Working Group on Remote Sensing / Edited by A.Chedin, H.Fisher, K.Kunzi, D.Spaukuch, N.A.Scott, University of Maryland, (1988).
2. A.A. Mitsel and K.M. Firsov, A fast Line-by-Line Method, JQSRT, v.54, n.3, pp. 549-557, (1995).
3. B.A. Fomin, Effective line-by-line technique for calculating radiation absorption in gases, Preprint IAE-5658/1, Russian Research Center "Kurchatov Institute", Moscow (1993), 13p.

High Resolution Diode-Laser-IR-Spectra of CdH

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The R-branch of the $v = 2 \leftarrow 1$ transition of the isotopomeres ^{114}CdH and ^{112}CdH have been observed for the first time. The CdH have been synthesized in a specially designed hollow-cathode, multi-pass, reaction cell and the high resolution IR-spectra have been recorded with a diode laser, the resolution being about 0.001 cm^{-1}.

The general setup of the reaction cell and the reaction parameters of the formation of CdH will be shown.

To extract the structural parameters from experimental data, the recorded lines were fitted with earlier data [1,2] to the usual Dunham expression.

The Dunham-coefficients derived and molecular constants will be presented and discussed.

[1] R.-D. Urban, U. Magg, H. Birk, H. Jones, J. Chem. Phys. **92**, 14 (1990)

[2] H. Birk, R.-D. Urban, P. Polomsky, H. Jones, J. Chem. Phys. **94**, 5435 (1991)

WEAKLY BOUND MOLECULAR COMPLEXES OBSERVED BY FREE- JET ABSORPTION MICROWAVE SPECTROSCOPY

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A free jet absorption microwave spectrometer operating in the frequency range 60-78 GHz has been equipped with a pulsed nozzle obtained from a slightly modified fuel injector. The concentration modulation produced by the pulsed gas source (5 Hz) together with the stark modulation (33 kHz) allows phase locked detection and identification of the rotational transitions.

To test the capabilities of the spectrometer we have observed the rotational spectrum of the Pyridine - Argon complex and obtained the complete determination of quartic and four sextic centrifugal distortion constants.

We proceeded assigning the rotational spectrum of the Pyrimidine- Ar complex and of some five- ring atom molecules such as 2,5- dihydrofuran, 2,3- dihydrofuran and tetrahydrofuran.

In the case of the unsaturated molecules the rare gas atom is located above the ring plane on a line that goes trough the centre of mass of the molecule but is not perpendicular to the molecule's plane, while in the case of tetrahydrofuran the rare gas atom seems to be bound to the oxygen atom..

The ground state rotational constants have been accounted for utilising two equivalent models: one considers the Ar atom undergoing two harmonic van der Walls' bending motions and the other one sees the rare gas atom freely rotating above the ring plane. The calculations were performed with a two dimensional flexible model and easily reproduced the observed moments of inertia.

Simulation of Laser Atmospheric Gas Sounding by Differential Absorption Method - Computer Codes LPM and SAGDAM.

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Two computer dialogue codes LPM and SAGDAM are intended for simulation of the atmospheric gases remote sensing laser systems. They are of interest specialists in the field of the atmosphere laser sounding, designers of optical systems, post-graduates and students of ecological departments of Universities.

The dialog program LPM (Long-Path Method) is intended for imitative modeling of the concentration gas analysis (H2O, CO2, O3, NH3, C2H4) with the path double-wave gas analyzer, equipped with two tunable CO2-lasers. Modeling is designed for four laser systems using the isotopes of CO2. In addition the program determines optimal pairs of wavelengths and the gas concentration reconstruction error, including the measuring error and the systematic error.

The dialog package SAGDAM (Sounding of Atmospheric Gases by Differential Absorption Method) is intended for simulation of the potentialities of the DAS method for sounding water vapor and ozone on the vertical and slant directions with ground-based, airborne and spaceborne lidars. Moreover, the package enables one to model the ground-based, airborne and spaceborne systems for sounding the integral gas content by a long-path differential absorption method. The spectral range is near UV, visible, and infrared spectral ranges.

The program calculates: 1) vertical profiles of the absorption coefficients and transmittance of the gas under study and the foreign gases, as well as the transmittance of aerosol and Rayleigh atmosphere; 2) spatially resolute lidar returns; 3) signals reflected from a topo-target or a mirror reflector; 4) sounding relative error including random error and systematic error.

The program enables one to determine the optimal pairs of wavelengths for sounding a gas in the specified altitude range and minimum-detectable concentration of the gas under study (for the long-path method).