

Orbifold representation of
effective HamiltoniansBORIS ZHILINSKII*Université du Littoral, Dunkerque, 59279, France*

Theory of invariants is applied to represent and to analyse systematically the effective Hamiltonians under the presence of the invariance symmetry group. The method consists in constructing first the Integrity Basis which enables one to use polynomial or rational function expansion of effective Hamiltonians in terms of a finite number of basic polynomials. The description of the ring of invariant functions and the Integrity Basis is based on the technique of the Molien (generating) functions. Molien function shows in symbolic form the structure of the module of invariant functions: the number and the degree of basic and auxiliary invariant polynomials. The second step consists in using the invariant polynomials as variables for the parametrization of the phase space of the dynamic problem governed by the effective Hamiltonian under study. This gives the geometrical representation of the phase space - *orbifold*.

Any effective Hamiltonian can be represented as a function defined over the orbifold. Any fixed energy corresponds to the energy surface which cut the orbifold. The important qualitative characteristics is the topological structure of the individual energy surface. If the topological structure of the energy section changes under the smooth variation of the energy the corresponding energy is related to the stationary manifold of the effective Hamiltonian. Thus the geometrical form of the orbifold is useful for the description of stationary orbits, i.e. for the qualitative analysis of the Hamiltonian.¹

The application of the general approach will be demonstrated on several different examples: effective Hamiltonians for rotational problem for individual vibrational state, effective Hamiltonians for vibrational polyads, and effective Hamiltonians for Rydberg states of hydrogen atom under the presence of electric and magnetic fields.

¹ D. SADOVSKII AND B. ZHILINSKII, *Phys. Rev. A* **47**, 2653-2671 (1993); **48**, 1035-1044 (1993); S. BRODERSEN AND B. ZHILINSKII, *J. Mol. Spectrosc.* **163**, 326-338 (1994); **169**, 1-17 (1995); **172**, 303-318 (1995); D. SADOVSKII, B. ZHILINSKII, AND L. MICHEL, *Phys. Rev. A* (1996), *in press*.

ROTATIONALLY RESOLVED
MAGNETIC VIBRATIONAL CIRCULAR DICHROISMP. Bouř,^a C. N. Tam^b and T. A. Keiderling^b^a *Institute of Organic Chemistry and Biochemistry, Academy of Sciences of the Czech Republic, Flemingovo nám 2, 16610, Praha 6, Czech Republic*^b *Department of Chemistry, University of Illinois at Chicago, M/C 111, 845 West Taylor Street, Chicago, Illinois 60607-7061, USA*

The vibrational circular dichroism (VCD) is a differential absorption of the left and right circularly polarized infrared light. Here, we report observations and analyses of spectra of diamagnetic molecules in a strong magnetic field. Although the resolution achieved is rather small (0.1 cm^{-1}) in comparison with standards in the absorption spectroscopy, spectra corresponding to vibrational transitions are rotationally resolved (RR MVCD) and can be analysed on the basis of exact rotational wavefunctions. Thus the RR MVCD spectroscopy provides an information about vibrational and rotational magnetic moments of molecules, as an alternative to classical Zeeman studies.

The absorption index for the left/right circularly polarized light for the transition $g \rightarrow e$ is proportional to the electric dipole integral $|\langle g | \mu_{\pm} | e \rangle|^2$, where $\mu_{\pm} = \mu_X \pm \mu_Y$. X and Y are the laboratory axes, axis Z is parallel to the light propagation and to the intensity of the magnetic field. Using the symmetric top wavefunction basis and the Wigner-Eckart theorem, an analytic expression for RR MVCD spectral intensities can be found.¹

On the basis of the analysis of RR MVCD of acetylene, we estimated its rotational magnetic moments in the ground and vibrationally excited states² as well as the purely vibrational magnetic moment in the ν_3 state.³⁻⁴

[1] Bouř, P.; Tam, C.N.; Wang, B. and Keiderling, T.A. *Molecular Physics* **1996**, *87*(2), 299-318.

[2] Tam, C.N.; Bouř, P.; and Keiderling, T.A. *J Chem. Phys.* **1996**, *104*, 1813.

[3] Bouř, P.; Tam, C.N.; Keiderling, T.A. *J. Phys. Chem.* **1996**, *100*, 2062-2065.

[4] Bouř, P.; Tam, C.N.; Keiderling, T.A. *J. Phys. Chem.* **1995**, *99*, 17810-17813.

SPECTROSCOPIC DEVELOPMENT FOR THE ANALYSIS OF MEASUREMENTS FROM THE GLOBAL OZONE MONITORING EXPERIMENT

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This talk presents details of several of the developments in quantitative molecular spectroscopy that support the analysis of data from the European Space Agency's Global Ozone Monitoring Experiment (GOME). GOME was launched on the European Remote Sensing 2 satellite on April 20, 1995. It has currently operated for more than one year, obtaining nadir atmospheric spectra from 240-790 nm. The spectral resolution is 0.2 nm in the ultraviolet and 0.4 nm in the visible. The objectives of the GOME project include enhanced mapping of ozone, with emphasis on the global distribution of tropospheric ozone.

The major spectroscopic feature that permits tropospheric O_3 to be distinguished from stratospheric O_3 in nadir viewing is the nonlinear, structured temperature dependence of absorption in the ultraviolet Huggins bands. Details of the Huggins band absorption as they affect retrieval of height-resolved O_3 determinations are presented. Accurate analysis of GOME spectra to retrieve concentrations of O_3 and other atmospheric species must account for the inelastic scattering of light from the Fraunhofer irradiance spectrum, including corrections for atmospheric absorptions (the "Ring effect"). An improved characterization and parameterization of the microscopic molecular physics for Ring effect scattering due to the rotational Raman effect is presented. GOME uses the visible $O_2 A$ band for cloud correction in the O_3 retrieval process. The determination of an improved molecular spectroscopic database for $O_2 A$ band absorption is presented and correction for pressure- and temperature-dependent formation of the O_2-O_2 collisional complex is discussed.

CAVITY RING DOWN SPECTROSCOPY (CRDS)

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An overview of this high sensitivity linear absorption method will be given, including a brief outline of recent spectroscopic applications. The various features of CRDS will be discussed, which are the following: High sensitivity, due to the long equivalent absorption path length (up to about 100 km); Measurement of absolute absorption coefficients, which can be obtained directly if some precautions are taken; Spectral resolution, limited until now by the pulsed laser employed; Spectral coverage, which includes all the visible, the near infrared, and the near UV with reduced sensitivity. Future perspectives will also be discussed, in particular the promise to obtain a much improved spectral resolution.

A NEW "MULTI-MOLECULE" RITZ PROGRAM

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The "Ritz" program, first used for the analysis of the FT absorption spectra of methanol isotopomers, has been extended to enable the treatment of other molecules. The new version of the program first reads an ASCII file with information specific to the molecule (quantum numbers used for labeling the levels, selection rules, available approximate wavenumbers for the vibrational modes . . .), then loads the databases containing the already assigned lines and levels for the molecule, if available, and enters an interactive mode. As the older "Ritz" program, the new "multi-molecule" Ritz program evaluates the energy levels involved in the assigned transitions by the Rydberg-Ritz combination principle, then extrapolates the energies of new levels by parabolic (or more complex) extrapolations. A new feature of this program is that the levels of a new sequence, for which an extrapolation is not possible, can be searched for by an "expert system" technique. This new method, still in progress, has been checked by searching for new excited torsional or vibrational level sequences of CD_3OH and $^{13}\text{CH}_3\text{OH}$. The program has also been tested with preliminary analyses of the small-amplitude vibrational ground state of hydrazine and of the ground inversion state of cyanamide. Full investigations of the IR-FIR hydrazine spectrum (in collaboration with Li-Hong Xu, University of New Brunswick), and of the cyanamide spectrum (in collaboration with Brenda and Manfred Winnewisser, Justus-Liebig University of Giessen) have been initiated.

AN ANALYTIC EXPRESSION FOR THE MOLECULAR EMISSION
SIGNAL OBSERVED IN COAXIAL-NOZZLE
FOURIER-TRANSFORM MICROWAVE SPECTROSCOPY

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Transient microwave spectroscopy was introduced by Dicke and Romer^{1 2} approximately 40 years ago. In the early eighties, Balle, Flygare, and coauthors developed a time-domain microwave spectrometer based on a pulsed supersonic gas expansion perpendicular to the axis of a Fabry-Perot resonator³, and provided theoretical expressions for the shape of the observed transient molecular signal^{4 5}.

Since the velocity equilibration of the molecules during the gas expansion minimizes Doppler and pressure broadening, the achievable linewidth in such an experiment should be very small. Unfortunately, the short transit time of the polarized gas through the small active region of the cavity limits the resolution. Both sensitivity and resolution of the spectrometer can be greatly improved by a coaxial arrangement of the microwave resonator and the gas expansion source⁶. Due to the propagation of the molecular beam along the symmetry axis of the mirrors, both the transit time through the active region of the cavity and the volume of the gas ensemble interacting with the active region of the resonator are maximized. With this arrangement, the lines of the molecular emission signal appear in the frequency domain as completely resolved doublets with individual linewidths of approximately 1kHz (HWHM). The experimental results are explained using the density matrix formalism to yield expressions analogous to the optical Bloch equations. An analytical function for the shape of the free induction decay (FID) of the molecular signal is derived by calculating the transient electrical field using Maxwell's equations.

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³ T. J. BALLE AND W. H. FLYGARE, *Rev. Sci. Instrum.* **52**, 33 (1981).

⁴ E. J. CAMPBELL, L. W. BUXTON, T. J. BALLE, AND W. H. FLYGARE, *J. Chem. Phys.* **74**, 813 (1981).

⁵ E. J. CAMPBELL, L. W. BUXTON, T. J. BALLE, M. R. KEENAN, AND W. H. FLYGARE, *J. Chem. Phys.* **74**, 829 (1981).

⁶ J.-U. GRABOW AND W. STAHL, *Z. Naturforsch.* **45a**, 1043 (1990).