

**A HYBRID FITTING PROGRAM FOR METHYLAMINE-LIKE MOLECULES  
WITH TWO LARGE-AMPLITUDE MOTIONS**Jon T. Hougen<sup>1</sup>, Isabelle Kleiner<sup>2</sup><sup>1</sup>Sensor Science Division, NIST, Gaithersburg, MD 20899-8441, USA<sup>2</sup>Laboratoire Interuniversitaire des Systèmes Atmosphériques (LISA), UMR 7583 (CNRS/Univ. Paris Est & Paris Diderot), 61 avenue du Général de Gaulle, F-94010 Créteil cedex, France

Effective tunneling-rotational Hamiltonians containing all terms allowed by group theory have been successfully used to fit microwave and infrared spectra nearly to experimental error for a variety of molecules with two or more large-amplitude motions (LAMs). Such tunneling treatments, however, have well-known weak points: (i) Tunneling Hamiltonians cannot treat levels near or above the top of the barrier to the tunneling motion. (ii) Tunneling-rotational levels for different sets of vibrational quantum numbers must be treated separately. (iii) The physical meaning of the various coefficients in the effective tunneling Hamiltonian is often obscure.

In this talk we present the intuitive ideas and group theory underlying a hybrid effective Hamiltonian formalism for methylamine-like molecules, where the internal rotation motion is treated using traditional expressions for the kinetic energy operator and three-fold potential energy function, while the umbrella motion (or its analog) is still treated by a tunneling formalism. One motivation for this hybrid approach is the hope that it will allow us to treat all torsional states having a given umbrella-motion quantum number simultaneously, analogous to the global fits of methyl-top internal rotation in molecules with only that LAM. This would eliminate weak points (i) and (ii) above for the methyl internal rotation motion, although not for the inversion motion. A second motivation is the desire to fix an unresolved problem in the internal-rotation tunneling splitting parameters for the OH and OD isotopologs of 2-methylmalonaldehyde (2-MMA), which we believe is connected with weak point (iii) above.

A computer program has been written, which strongly resembles a version of BELGI written some years ago to treat two interacting small-amplitude vibrational states in acetaldehyde. The program has successfully passed a number of checking tests, and we are thus now in the process of applying it to a fit of the extensive data set for 2-MMA, containing about 2500 microwave and far-infrared transitions. This data set has already been fit to experimental measurement error in the literature, but the fit led to conflicting results for the internal-rotation barrier, i.e.,  $V_3(\text{OH}) = 401 \text{ cm}^{-1} \neq V_3(\text{OD}) = 312 \text{ cm}^{-1}$ , associated with weak point (iii) above.

## MULTICHANNEL QUANTUM DEFECT THEORY FOR POLAR MOLECULE

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We propose a general approach for non-penetrating Rydberg states of polar molecules. First, we estimate the accuracy of Born-Oppenheimer (BO) and inverse Born-Oppenheimer (IBO) approximations for these states [1]. This estimation enables us to determine the space and energy regions where BO and IBO approximations are valid. It depends on the interplay between  $l$ -coupling (due to dipole potential of the core) and  $l$ -uncoupling (due to rotation the core). Next we consider the intermediate region where both BO and IBO are not valid. For this intermediate region we propose a modification of Fano's multichannel quantum defect theory (MQDT) to match BO and IBO wavefunctions and show that it gives reliable results [2]. They are demonstrated on the example of SO molecule.

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## A NEW HOT LINE LIST FOR FORMALDEHYDE

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The ExoMol project [1] aims at providing spectroscopic data for key molecules that can be used to characterize the atmospheres of exoplanets and cool stars. Here we present a new hot line list for formaldehyde ( $\text{H}_2\text{CO}$ ). Formaldehyde has proved to be an important molecule for probing the interstellar medium as its spectral characteristics provide a useful means of examining the composition of carbon isotopes [2] as well as in densitometry for star forming regions in galaxies [3]. However, there is limited spectral data on formaldehyde at higher rotational excitations which important for higher temperatures found in exoplanetary atmospheres such as hot Jupiters.  $\text{H}_2\text{CO}$  is of growing importance for studies of various astrophysical phenomena such its recent discovery in comets [4]. This makes it vital to have a robust line list which covers a large range of transitions. The line list was computed using the variational ro-vibrational solver TROVE [5] with a refined ab initio potential energy surface [6] and dipole moment surface. We also present an accurate room-temperature spectrum of  $\text{H}_2\text{CO}$  which is compared to the experimental data from HITRAN and CDMS. A development of an effective-Hamiltonian-free approach for analysing spectra of polyatomic molecules based on our variational approach is discussed.

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**NON-EMPIRICAL CONSTRUCTION OF THE EFFECTIVE DIPOLE MOMENT OF METHANE BY CONTACT TRANSFORMATIONS**

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Effective Hamiltonians (EH) and dipole moment operators (DM) are still widely used to analyze and model the high resolution spectra. The MOL\_CT program suit developed within our team aims to build effective non-empirical spectroscopic models from ab initio calculations by considering a generalized formulation of Contact Transformations (CT) [1]. On the one hand, the CT allow to establish a link between the molecular potential energy surface and spectroscopic parameters involved in empirical models EH. Furthermore, these transformations can also be applied to the calculation of intensities [2]. In recent years the approach of CT has been successfully applied to triatomic systems. For this study we have extended this work to more complex systems and higher symmetry (methane) [1]. Effective dipole model for the intensities of methane has been built from our new dipole moment surface [3]. Preliminary results for the first polyads of methane will be presented, and a comparison with experimental data from databases. The extension of this approach to the ethylene molecule will be discussed.

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THE ROVIBRATIONAL SPECTROSCOPY OF  $\text{H}_5^+$ 

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The fourth-age quantum chemical code GENIUSH [1-3] is used for the variational determination of rotational-vibrational energy levels corresponding to reduced- and full-dimensional models of  $\text{H}_5^+$ , a molecular ion exhibiting several strongly coupled large-amplitude motions. [4] The computations are supplemented with one- and two-dimensional analytic results which help to understand the peculiar rovibrational energy-level structure computed correctly for the first time. An unusual aspect of the results is that the canonical Eckart-embedding of molecule-fixed axes, a cornerstone of the computational spectroscopy of semirigid molecules, is found to be inadequate. Furthermore, it is shown that while the 1D “active torsion” model provides proper results when compared to the full, 9D treatment, models excluding the torsion have limited physical significance. The structure of the rovibrational energy levels of  $\text{H}_5^+$  proves that this is a prototypical astructural molecule: the rotational and vibrational level spacings are of the same order of magnitude and the level structure drastically deviates from that computed via perturbed rigid-rotor and harmonic-oscillator models.

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**DEPOPULATION OF METASTABLE HELIUM BY RADIATIVE ASSOCIATION IN INTERSTELLAR ENVIRONMENT**

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Radiative association is an important process of formation of molecular ions/molecules in interstellar space. Radiation due to spontaneous radiative processes has important astrophysical implications, since metastable atomic states provide most of the light emitted from planetary nebulae. Due to the relatively large amount of helium in interstellar space, we investigated the depopulation of the metastable levels of He( $2^3S$ ), having a unusually long lifetime [1], and He( $2^1S$ ) by radiative collisions with hydrogen, helium and lithium ions [2,3,4]. Through the process of radiative association these collisions result in the formation of molecular cations HeH<sup>+</sup> and HeLi<sup>+</sup>, either in singlet or high-spin electronic state, and He<sub>2</sub><sup>+</sup> in doublet electronic states.

Energy dependent cross-sections for spontaneous and stimulated processes on a particular spin manifold are calculated using a fully quantal approach and considering the association to rotational-vibrational states of the lowest electronic states from the initial continuum states: He( $2^3S$ ) + A<sup>+</sup> → HeA<sup>+</sup> or He( $2^1S$ ) + A<sup>+</sup> → HeA<sup>+</sup>, where A = H or Li; He( $2^3S$ ) + He<sup>+</sup> → He<sub>2</sub><sup>+</sup> or He( $2^1S$ ) + He<sup>+</sup> → He<sub>2</sub><sup>+</sup>. Evaluation of the cross-sections is based on highly accurate quantum calculations taking into account all possible state-to-state transitions at thermal energies (for spontaneous association) or at higher background temperatures (stimulated association). The corresponding rate coefficients are presented as function of temperature. A noticeable effect on the radiative association by black-body background radiation is only obtained for the one state process.

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**EXPERIMENTAL AND THEORETICAL COLLISIONAL PARAMETERS OF  
CH<sub>3</sub>D-N<sub>2</sub> LINES FOR REMOTE SENSING OF PLANETARY ATMOSPHERES: J-  
AND K- DEPENDENCES AND TEMPERATURE EXPONENTS**

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A precise knowledge of collisional line shape parameters for monodeuterated methane perturbed by various gases is required for remote sensing of planetary atmospheres, in particular those of Jupiter, Saturn, Uranus, and Titan. Despite the low isotopic abundance in the methane, CH<sub>3</sub>D strongly contributes to the weak absorption in the transparency windows of CH<sub>4</sub> (namely, the windows at 1.58 μm and 1.28 μm). Because of the isotopic substitution H→D, a significant change in the vibrational frequency ν<sub>2</sub> is produced and the second harmonic 3ν<sub>2</sub> falls in the region of 6430 cm<sup>-1</sup>, i.e. in the 1.58 μm CH<sub>4</sub> transparency window. In this work we present CH<sub>3</sub>D-N<sub>2</sub> broadening coefficients calculated by a semiclassical method involving exact trajectories [1] and measured recently with the use of two Fourier transform spectrometers: the McMath-Pierce FTS located on Kitt Peak and a Bruker IFS 125 HR FTS at the Jet Propulsion Laboratory (JPL). To model the intermolecular interaction potential, we use a sum of long- and short-range interactions. For the long-range forces, we account for the main electrostatic as well as induction and dispersion contributions. The short-range terms are represented by pairwise atom-atom interactions taken as 12-6 Lennard-Jones dependences. The influence of various high-order multipoles in the broadening coefficient is studied at low, middle and high values of the rotational quantum number J. Main features of the K-dependences and temperature dependences are also analyzed. The computed values are compared to our experimental results and data available in the literature for various types of infrared bands [2-4].

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**AB INITIO MODEL OF ANOMALOUSLY BROADENED H<sub>2</sub> Q(1) LINE  
PERTURBED BY Ar**

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Essential discrepancies between thermally averaged speed-dependent collisional broadening obtained experimentally [1,2] and from *ab initio* close-coupling (CC) calculations for the H<sub>2</sub>/D<sub>2</sub>-Ar systems were reported [3-5]. For instance, at room temperature the broadening of the Q(1) line obtained experimentally was almost two times larger than the theoretical one. To explain these discrepancies we performed calculations of the H<sub>2</sub>-Ar potential energy surface (PES) by employing the RCCSD(T) method in combination with the large aug-cc-pCVQZ basis and the 332211 midbond basis set. In the calculations the stretching of the H<sub>2</sub> bond was considered. However, we found that the broadening of the H<sub>2</sub> Q(1) line determined from CC calculations with this new PES was even less consistent with the experimental value than the previous broadening determined from CC calculations with an earlier PES [6]. Next, we replaced the phenomenological line profile [5] with much more physical line shape [7] in which absorber velocity change is described by the *ab initio* billiard-ball model. It was already shown that this model provides appropriate description of the velocity-changing collisions for the H<sub>2</sub>-Ar system [8]. We found that this approach gives the H<sub>2</sub> Q(1) line broadening, for the mixture of 5% of H<sub>2</sub> and 95% of Ar, very close to experimental values, see Fig. 1. Our model not only properly handles the dynamics of optically active molecules, in particular a strong competition between velocity-changing and phase/state-changing collisions, but also constitutes a first step toward application of advanced *ab initio* line-shape models in ultra-accurate optical metrology based on molecular spectroscopy.

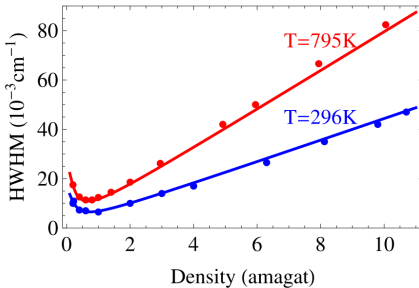


Figure 1: Half width at half maximum (HWHM) of the H<sub>2</sub> Q(1) line as a function of density for mixture of 5% H<sub>2</sub> and 95% Ar. Dots represent experimental results [2], while lines correspond to our *ab initio* calculations.

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GLOBAL MODELING OF NO<sub>2</sub> HIGH RESOLUTION SPECTRA

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The global modeling of the NO<sub>2</sub> line positions and intensities has been performed within the framework of the method of effective operators. The 195 parameters of polyad model of effective Hamiltonian have been fitted to 28016 line positions collected from the literature in the 0.006 – 7916 cm<sup>-1</sup> wavenumber range. The global root mean squares residual of the fit is 0.017 cm<sup>-1</sup>. The used effective Hamiltonian takes explicitly into account both the spin-rotation interactions within each vibrational state together with numerous vibrational rotational resonances. Indeed, because of ( $\omega_1 \approx \omega_3$ ), ( $\omega_3 \approx 2\omega_2$ ) and ( $\omega_1 \approx 2\omega_2$ ) approximate relationships between the three harmonic frequencies of NO<sub>2</sub>, resonances due to first and second order C-type Coriolis interactions, and Fermi and Darling-Dennison interactions have been taken into account for.

Using the eigenfunctions of the global effective Hamiltonian the effective dipole moment parameters for the  $\Delta P=1-4$  series of transitions have been fitted to the observed line intensities collected from the literature. Here  $P=2v_1+v_2+2v_3$  is a polyad number, where  $v_i$  ( $i=1,2,3$ ) are vibrational quantum numbers.

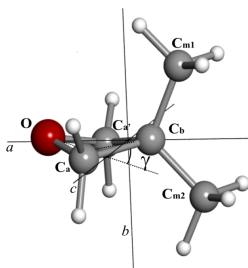
The obtained sets of the effective Hamiltonian and effective dipole moment parameters allowed us generating the high temperature line list for NO<sub>2</sub> molecule in the 560 – 3360 cm<sup>-1</sup> range with intensity cutoff 10<sup>-25</sup> cm/molecule at temperatures 296 K and 1000 K.

## THE EQUIVALENCE OF THE METHYL GROUPS IN PUCKERED 3,3-DIMETHYL OXETANE

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The spectroscopic study of molecules with large amplitude vibrations have led to reconsider the concept of molecular structure. Sometimes, the classical view of identifying definite bond lengths and angles is meaningless and to reproduce the experimental data one must have information on the large amplitude molecular vibration and the corresponding dynamical path. 3,3-dimethyloxetane [1-3](DMO) has non-planar ring equilibrium configuration ( $\gamma = 17.5^\circ$ ) and a double minimum potential function for ring-puckering with a barrier of  $47 \text{ cm}^{-1}$ [1,2]. The observation of endocyclic  $^{13}\text{C}$  and  $^{18}\text{O}$  monosubstituted isotopologues [3] allow to conclude that the ring is puckered. However an interesting feature was observed for the  $^{13}\text{C}$  substitutions at the methyl carbon atoms. While two different, axial and equatorial,  $^{13}\text{C}$ -methyl groups spectra are predicted from a rigid non-planar ring DMO model, only one spectrum was found. The observed rotational transitions appear at a frequency close to the average of the frequencies predicted for each isotopologue and the observed lines have the same intensity as that found for the  $^{13}\text{C}_a$  isotopomer and double that that found for the  $^{13}\text{C}_b$  isotopomer [3]. This behaviour evidences that the two methyl groups of DMO are equivalent as could be expected for a planar ring. In this work we show how consideration of the potential function and a reasonable path for ring puckering motion to calculate the proper kinetic energy terms, allow to reproduce the experimental results, not expected from non-dynamical considerations of the molecular structure.



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**TRAJECTORY ANALYSIS OF RO-VIBRATIONAL PROBLEM**

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Generalized Euler equations are presented to solve a purely rotational problem for an isolated vibrational state. The corresponding effective rotational Hamiltonian can be derived directly from the complete ro-vibrational Hamiltonian for a real molecule. We investigate rotational phase trajectories to understand and to explain quantum rotational multiplets structure.

For a full-dimensional ro-vibrational problem generalized Euler equations are used together with Hamilton's equations regarding vibrational dynamic variables. The complete system of dynamic equations is solved numerically. Both model and high quality *ab initio* potential functions can be used to obtain a set of classical ro-vibrational trajectories for a molecule under investigation.

Possible applications of the presented approach include:

- the dynamics of fast rotating molecules exhibiting large-amplitude internal motion;
- the dynamics of weakly bound molecular pairs including trajectories corresponding to all kinds of pair states: bound, free, and metastable.

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**INFLUENCE OF THE ISOTOPIC SUBSTITUTION ON THE EFFECTIVE DIPOLE  
MOMENT PARAMETERS OF CARBON DIOXIDE MOLECULE**

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The equations relating the  $q^0J$ ,  $qJ$ ,  $q^2J$  and  $q^3J$ -types parameters of the matrix elements of the effective dipole moment operator with the dipole moment derivatives and the force field constants have been derived by means of contact transformations in the case of carbon dioxide, including the asymmetric isotopologues of this molecule. The respective equations for the rare isotopologues in terms of molecular constants of the principal one have also been derived using the isotopic relations for the molecular constants. The numerical values of the considering effective dipole moment parameters for all stable isotopologues have been evaluated using the force field constants and dipole-moment derivatives of Wattson and Rothman [1]. The calculated values show that the isotopic substitution does not change considerably the effective dipole moment parameters describing the line intensities of the bands which are active for both symmetric and asymmetric isotopologues. But it was found that isotopic substitution of the oxygen atom leads to the strong changes of the effective dipole moment parameters describing the line intensities of the bands which are active only for asymmetric isotopologues. The comparison of the calculated values of the effective dipole moment parameters to those obtained in the literature [2-5] by fitting to the observed line intensities shows that they are in very good agreement.

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