

**ULTRA-SENSITIVE AMMONIA PROBES OF A VARIABLE PROTON-TO-ELECTRON MASS RATIO**

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The mass sensitivity of the vibration-rotation-inversion energy levels of ammonia is probed using the nonrigid inverter theory. It is shown that the sensitivity exhibits non-negligible centrifugal distortion dependence, which is currently disregarded. The centrifugal distortion effects are especially important in the case of the  $\Delta k = +/-3$  "forbidden" transitions involving accidentally coinciding ro-inversional states  $|a, J, k\rangle$  and  $|s, J, k\rangle$  of the  $\nu_2$  vibrational state of  $^{14}\text{NH}_3$ .

The energy differences of these states exhibit record-breaking mass sensitivities (see [1,2]), thus appearing as new ultra-sensitive probes of the cosmological variability of the proton-to-electron mass ratio.

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**DYNAMICS OF ETHYL RADICAL**Marek Kręglewski, Iwona Gulaczyk

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The calculation of potential surfaces becomes a common practice. When the potential surface is calculated for all vibrational degrees of freedom, the energies for different molecular configurations from electronic Schrödinger equation are directly used in the rovibrational part. The problem is not so straightforward if the dimensionality of the rovibrational part is reduced to selected vibrations. It is often the case when large amplitude vibration is analyzed. In such cases the electronic potential surface must be corrected for zero-point vibrational energies of these vibrations, which are not explicitly calculated. The zero-point correction is often calculated in harmonic approximation. It would be interesting to analyze differences between harmonic and anharmonic contributions to the zero-point energies.

The two dimensional potential energy surfaces for inversion of the methylene group and torsion of the methyl group in the ethyl radical has been calculated using B3LYP method and the aug-cc-pVQZ basis set. The potential was corrected for harmonic zero-point vibrational energies of remaining 13 motions calculated with the Gaussian03 program, and fitted to the mixed Fourier expansion. In a separated calculation the anharmonic corrections were added. The rotation-inversion-torsion energies were calculated using a semi rigid model allowing relaxation of the molecular structure. The ab initio PES was modified to reproduce spectroscopic data. We show how the vibrational corrections modify the potential surface and how it compares to the effective experimental potential. The effective barrier to internal rotation is  $2.2 \text{ cm}^{-1}$  comparing to the ab initio values of  $18.9 \text{ cm}^{-1}$  and  $40.2 \text{ cm}^{-1}$  in harmonic and anharmonic approximations, respectively.

**THE SPECTRUM OF HOT METHANE IN ASTRONOMICAL  
OBJECTS USING A COMPREHENSIVE COMPUTED LINE LIST**

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Hot methane spectra are important in environments ranging from flames to the atmospheres of cool stars and exoplanets. A new spectroscopic line list, 10to10, for <sup>12</sup>CH<sub>4</sub> containing almost 10 billion transitions was recently reported [1]. Here present two astrophysical applications of 10to10, where we model a spectrum of the bright T4.5 dwarf 2MASS 0559-14 and simulate the atmospheric transmission of two exoplanets, the warm Neptune GJ 436b and hot Jupiter HD 189733b [2]. Use of 10to10 in models of T4.5 leads to significantly better agreement with observations and in studies of the hot exoplanets leads to up to a twentyfold increase in methane abundance. It is demonstrated that proper inclusion of the huge increase in hot transitions which are important at elevated temperatures is crucial for accurate characterizations of atmospheres of brown dwarfs and exoplanets, especially when observed in the near-infrared. We believe that this line list will have a large effect on the field of exoplanets and cool stars.

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**N-MODE REPRESENTATION OF THE ROTATIONAL-VIBRATIONAL  
HAMILTONIAN USING CURVILINEAR COORDINATES AND AN ECKART  
AXES SYSTEM**

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We present a new practical method to construct an  $N$ -mode expansion [1] of the rotational-vibrational Hamiltonian employing curvilinear coordinates and a molecule-fixed frame defined by the Eckart conditions [2]. The main attempt has been done towards efficient black-box-type variational calculations for a general medium size molecule of an arbitrary structure. We introduce new methodologies for computing expansion coefficients of the kinetic and potential energy operators at high accuracy that is only limited by the machine epsilon. The method has been incorporated into the variational program code TROVE [3] and applied to compute the rotational-vibrational energies and spectra of  $C_2H_4$  molecule. Extensive tests of our approach applied to other molecules will be also presented.

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**NEW INSIGHT ON THE OZONE TRANSITION STATE NEAR THE  
DISSOCIATION THRESHOLD FROM *AB INITIO* CALCULATIONS AND  
HIGHLY SENSITIVE SPECTROSCOPIC EXPERIMENTS**

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An accurate description of the complicated shape of the potential energy surface (PES) and that of the highly excited vibration states is of crucial importance for various unsolved issues in the spectroscopy and dynamics of ozone and remains a challenge for the theory. Most of previous *ab initio* calculations predicted an activation barrier at the entrance of the dissociation channel followed by a shallow van der Waals (vdW) minimum along the dissociation reaction coordinate. Various calculations at high level of the electronic structure calculations have suggested that the minimum energy path (MEP) shape has a “reef”-like structure [1] with a submerged barrier below the dissociation limit. The important impact of the barrier height and the depth of the vdW minimum on the dynamics of the formation and fragmentation of the excited ozone molecule have been discussed in several studies ( see Schinke et al [1], Dawes et al [2] and references therein). These studies suggested that rate coefficient of the O + O<sub>2</sub> exchange reaction should be very sensitive to the shape of the PES in the transition state (TS) region and one of the major obstacles in our understanding of the ozone kinetics is the lack of a quantitatively accurate PES. In this work we compare our vibrational predictions using two versions of the full dimensional ozone PES obtained from recent very accurate *ab initio* calculations [3] (one keeping the “reef structure” on the TS and another without the “reef barrier”) and new experimental ozone band centers. The latter ones have been derived from analyses [4-6], not yet fully published, of new spectra recorded with extremely sensitive laser CRDS technique [6] in the range approaching the dissociation energy. The impact of the shape of the PES near the TS (existence or not of the “reef structure”) on vibration energy levels was studied here for the first time. We conclude that the *ab initio* PES without the reef structure provides vibrational prediction with an average error of 1 cm<sup>-1</sup> which is much better than all available calculations that involve the activation barrier on the TS. Our result can be considered as the first spectroscopically supported argument that the “reef structure” would be an artefact of previous *ab initio* calculations.

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## STUDY OF IR SPECTRA OF THE ISOTOPIC SPECIES OF NITROSYL HALIDES USING THE U(4) ALGEBRAIC MODEL

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In the study of IR spectra of polyatomic molecules, the U(2) and U(4) algebraic models[1-2] have been attracting a wider scientific community of the globe in recent years. The models already have been applied in the study of IR spectra of linear triatomic, linear tetratomic and some other small, medium and large-sized molecules[3-5]. In many aspects, the U(4) and U(2) algebraic models are in advantageous positions with respect to their traditional counterparts. However, it is to be noted that the U(2) algebraic model is one-dimensional in nature and it does not take into account rotational motions of a molecule. Simply to provide a global vibrational picture of a certain molecule, the rotational degrees of freedom are completely disregarded in the U(2) algebraic model. Such a drawback is overcome with the introduction of the U(4) algebraic model. The full treatment of molecular rovibrational degrees of freedom can be achieved in the three-dimensional framework of the U(4) algebraic model. The three dimensional framework of the U(4) algebraic model leads us to a more complex and realistic picture of a molecular system as well as producing a more exacting algebraic treatment. The three-dimensional algebraic model is definitely much more difficult to manipulate than the one-dimensional one, purely for algebraic aspects. Due to this reason, the U(4) algebraic model could proceed till today only up to the approximation of linear tetratomic molecules[4]. So far the cases of bent polyatomic molecules are concerned, successful applications[6] of the U(4) algebraic model could be reported so far only for a few bent triatomic molecules. Thus, for the U(4) algebraic model, more or less, the entire kingdom of the bent polyatomic molecules is left unattended till today. In this study, we report a successful application of the U(4) algebraic model in the IR spectral analysis of the isotopic species of nitrosyl halides. With a detail spectral analysis, it has been shown in this study that all the isotopic species of NOF, NOCl, NOBr and NOI can be approximated very well using the U(4) algebraic model.

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## THE FIRST LOW-LYING ELECTRONIC STATES OF STRONTIUM MONOXIDE

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The first 13 lowest-lying electronic states including the ground state  $X^1S^+$  of SrO molecules have been investigated. The energy calculations, using ab initio methods have been performed at the ScF and the CASSCF/MRCI levels with the geometry  $C_{2v}$ , in an interval of internuclear distances around the equilibrium of the ground state.

Almost all available experimental spectroscopic data have been reported based on the analysis of the high resolution transition bands in the IR, the orange and the visible regions, identifying 7 electronic states,  $X^1S^+$ ,  $a^3P$ ,  $A^1P$ ,  $b^3S^+$ ,  $A'^1S^+$ ,  $C^2S^+$  and  $(2)^1P$  [1-4]. Within the 13 calculated electronic state sin this work, 6 electronic states ( $((4)^1S^+$ ,  $(1)^1D$ ,  $(2,3)^3S^+$ ,  $(1,2)^3D$ , and  $(2)^3P$ ) yet unobserved have been predicted. The spectroscopic constants  $w_e$ ,  $w_e x_e$ ,  $B_e$ ,  $a_e$ , the internuclear distances  $R_e$  and the energies  $T_e$  referred to the ground state have been determined. The potential energy curves (PECs) have been plotted for these singlet and triplet states and the transition dipolar moments have been calculated. These studies have improved the rotational spectroscopic constants of the observed perturbed states  $A^1P$  and  $A'^1S^+$  at different vibrational levels due to the spin orbit interaction with  $b^3S^+$ .

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