

Empirical potential energy surface and bending angle probability densities for the electronic ground state of HCO^+

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In molecular spectroscopy parlance, a linear molecule is defined as one whose potential energy minimum is at a linear geometry. The nature of the *average* structure of a linear triatomic molecule – linear or bent? – has given rise to much discussion recently. We contend that the average structure of a linear triatomic molecule is bent. The purpose of the present work is to underpin this argument with results from Coulomb Explosion Imaging (CEI) experiments for the linear DCO^+ ion [R. Wester et al., *J. Chem. Phys.*, 2002, 116, 7000]; these experiments allow a direct experimental measurement of the bending angle probability density. We aim at simulating theoretically the CEI experiments for DCO^+ . The possibility of obtaining a detailed simulation is hampered by the fact that the DCO^+ ions investigated in the CEI experiment populate very highly excited vibrational states. This creates numerical problems for the theoretical calculations. We can conclude, however, that the results of the CEI experiment are in support of the average structure of a linear molecule being bent.

Torsion rotation program for nitromethane CH₃NO₂

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Nitromethane, CH₃NO₂, is the simplest representative of molecules with a C_{3v} symmetric top rotating relative to a C_{2v} frame. A very low six-fold barrier to internal rotation makes the torsional label *m* an almost good quantum number. The rotational quantum number *K_a* is much worse as a label because nitromethane is an asymmetric top closer to the oblate limit ($\kappa=0.25$). The PI symmetry group, G₁₂, is isomorphic to C_{6v} point group which possesses 6 irreducible symmetry species. However, a permutation of two oxygen atom ¹⁶O of nuclear spin equal to 0 allows only for a half of the species, namely A₁, A₂ and E₂. In the ground vibrational state the torsion-rotation functions must fulfill a strict condition $m+K_a = \text{even}$. If nitromethane is in a vibrational state of B₁, B₂ or E₁ the required condition is $m+K_a = \text{odd}$. Each torsion-rotation state is additionally labeled with *J* quantum number and a symmetry species in C_{6v} group.

The presented program allows for a determination of the condition "even or odd" for $m+K_a$. Furthermore, the torsion-rotation basis functions are derived using a full symmetry of G₁₂ group which results in relatively easy assignment of *m* and *K_a* as approximate labels to torsion-rotation energy levels. The Hamiltonian is similar to that used by Ilyushin [1] – it introduces the ρ constant which minimizes the torsion – rotation coupling and all interaction terms with $\cos 6\alpha$, $\sin 6\alpha$, $\cos 3\alpha$, $\sin 3\alpha$ functions. The detailed expressions will be shown.

This approach is closer to the Sørensen's program [2] than to the Ilyushin's approach [1] where *K_a* is no longer a label for the torsion-rotation states. On the other hand Sørensen did not use a full expansion on *m* but included limited interactions with neighboring torsional states in a range [*m*-6 to *m*+6]. The new program allows for calculation of transitions between different torsional states and facilitates determination of combination states where torsional transitions overlap a vibrational excitation.

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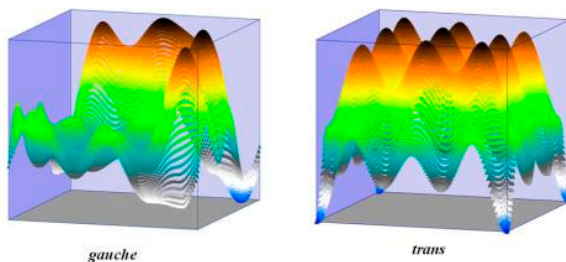
Weak intramolecular interaction effects on the structure and torsional spectra of ethylene glycol isotopologues, an astrophysical species

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A variational procedure of reduced dimensionality based on CCSD(T)-F12 calculations is applied to understand the far infrared spectrum of various isotopologues of Ethylene-Glycol [1] a detected molecule in gas phase [2]. This molecule can be classified in the double molecular symmetry group G_8 and displays nine stable conformers, *gauche* and *trans*. In the *gauche* region, the effect of the potential energy surface anisotropy due to the formation of intramolecular hydrogen bonds is relevant. For the primary conformer, the ground vibrational state rotational constants of the main isotopologue are computed at 6.3 MHz, 7.2 MHz and 3.5 MHz from the experimental parameters [3].

Ethylene glycol displays very low torsional energy levels whose classification is not straightforward. Given the anisotropy, tunneling splittings are significant and unpredictable. The ground vibrational state splits into 16 sublevels separated ~ 142 cm^{-1} . Transitions corresponding to the three internal rotation modes allow assign previous observed Q branches. Band patterns, calculated between 362.3 cm^{-1} and 375.2 cm^{-1} , between 504 cm^{-1} and 517 cm^{-1} and between 223.3 cm^{-1} and 224.1 cm^{-1} , that correspond to the tunnelling components of the ν_{21} fundamental (ν_{21} = OH-torsional mode), are assigned to the prominent experimental Q branches [1]. Isotopic displacements of the bands can help assignments.



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Modelling temperature dependent anharmonic spectra of pyrene (C₁₆H₁₀): comparison of computational approaches

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A2.4.

Polycyclic Aromatic Hydrocarbons (PAHs) are believed to be responsible for the Aromatic Infrared Bands (AIBs) observed in many astronomical objects [1]. The excitation mechanism involves the absorption of an UV photon via an electronic transition and a sequence of radiationless transitions converting most of the absorbed energy into vibrational excitation in the electronic ground state [2].

The hot molecule then relaxes by emitting IR photons, the resulting spectrum being dominated by many hot bands, all slightly shifted with respect to the corresponding 1→0 fundamentals due to anharmonicity. IR spectra of PAHs are usually computed at OK either by scaled harmonic or by 2nd order perturbation theory but none of them describes the thermal behavior of the bands.

We used the new AnharmoniCaOs code [3] to compute the temperature dependent IR spectra of pyrene (C₁₆H₁₀). After identifying resonance terms, we iteratively construct the polyad and solve the effective Hamiltonian. Monte Carlo sampling of the vibrational states up to 12000 cm⁻¹ is used to obtain the temperature dependent spectra up to 600K. Our code works efficiently at low and moderately high temperature but due to high computational cost it is very expensive to extend it to higher temperature, relevant for astrophysics. This calls for methods based on classical molecular dynamics (MD) simulations, albeit at the cost of losing all information on the detailed structure of hot bands. We calculated the potential energy surface using the Density Functional based tight binding (DFTB) method [4] as available in the deMonNano code [5]. Finite temperature IR spectra are then derived from MD trajectories, computing the Fourier transform of the autocorrelation function of the dipole moment [6].

We report here more specifically on different characteristics of the temperature-dependent IR spectrum including band position and width with temperature. We compare the results from both computational methods and with experimental data [7, 8]. Considerations on the weak and strong points of each method are provided.

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Non-adiabatic coupling in the ozone molecule

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The question whether a Berry phase should be included in the calculation of rovibronic states of the ozone molecule in its electronic ground state has been addressed in the present work [1]. Since several conical intersections connect the three lowest singlet states, a phase of π generated by a symmetry-demanded conical intersection between states 2 and 3 might be present, or it might be compensated by further conical intersections. Hyperspherical coordinates were employed here as they provide a natural choice for the cyclic coordinate that is needed to investigate the presence or absence of such a topological phase. On a hyperspherical grid, we have computed the electronic energies of the three lowest singlet states using a multi-reference configuration interaction (MRCI) procedure. Non-adiabatic coupling terms along the cyclic variable were evaluated numerically. Investigation of the behaviour of the adiabatic-to-diabatic transformation angles, using the quantization criterion of the non-adiabatic coupling terms (Baer and Alijah, *Chem. Phys. Lett.* 319, 489 (2000)), shows that a geometrical phase is retained. This phase has no practical effect on the well-established energy values of the rovibrational states located deeply in the three equivalent C_{2v} potential wells, but will come into action as highly excited states reach the dissociation region.

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The long-range behavior of *ab initio* transition dipole moments and spin-orbit coupling matrix elements between the low-lying electronic states of alkali heterodimers

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Often times the most efficient laser cooling pathways require the use of weakly bound states close to the dissociation limits as intermediate steps. The exact singlet/triplet composition of these states as well as their exact energies and radiative properties must therefore be known in advance with high precision and accuracy. Unfortunately, these states are heavily influenced both by the exact shape of the potential energy curve (PEC) and by the asymptotic behavior of the spin allowed transition dipole moments (TDMs) and spin-orbit coupling (SOC) matrix elements. Thus, having correct long range TDM and SOC functions, together with the relevant PECs [1,2], could be applied to the comprehensive coupled-channel (CC) treatment of the competitive radiative and predissociative dynamics of the mutually perturbed rovibronic states located in the vicinity of dissociation thresholds

The asymptotic behavior of spin allowed TDMs and SOC matrix elements between electronic states converging to the lowest three dissociation limits were investigated for the lightest heteronuclear alkali diatomics XY ($X, Y = \{Li, Na, K, Rb\}$). The TDM and SOC functions are evaluated in the basis of the spin-averaged wavefunctions corresponding to pure Hund's coupling case (a) by means of effective core pseudopotentials. The electronic correlation is accounted for by applying the multi-reference configuration interaction method to only two valence electrons for all considered molecules and core-polarization potentials are used to take the core-valence effect into account.

In this work, the leading asymptotic behavior of the TDM and SOC functions has been found to be R^{-3} and R^{-6} . Additionally, in the case of the TDM functions, our *ab initio* results [3] have been found to coincide with their analytical counterparts obtained within the framework of the long-range perturbation theory by Chu and Dalgarno [4].

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