

THE PROTON REARRANGEMENT DYNAMICS
AND SPECTRUM OF CH_5^+

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Based on *ab initio* results the $J = 0$ and 1 proton rearrangement energy levels, and the structure of the $J = 1 \leftarrow 0$ millimeterwave spectrum, of the CH_5^+ molecular ion are calculated. The molecule should be considered as an H_2 molecule bound by a three-center two-electron bond at the apex of a pyramidal CH_3^+ ion with the H_2 axis approximately perpendicular to the C_3 axis of the CH_3^+ unit. The binding energy is about 15000 cm^{-1} . The internal rotation of the H_2 about the C_3 axis has a barrier height of 30 cm^{-1} . There is also an internal motion through a C_{2v} structure, with a barrier of 300 cm^{-1} , that involves the exchange of a CH_3^+ and an H_2 proton. As a result all 120 symmetrically equivalent minima on the potential surface are accessible, and all proton permutations are feasible. The complete nuclear permutation inversion group of 240 elements can be usefully used for the symmetry classification of the energy levels. Fortunately symmetry obliges the majority of the levels to be missing so that the spectrum is much simpler than would otherwise be the case.

Low-Barrier Rotation-Pseudorotation Hamiltonian and Application to the \tilde{B} State of Na_3

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A formalism has been developed for treating the rotation-pseudorotation problem in Na_3 , which has many analogies with the principal axis formalism for methyl-top internal rotor molecules. The pseudorotation angle χ_p and D_{3h} group theory from our previous high-barrier formalism¹ lead to a molecular Hamiltonian containing the following terms up to second order:

$$H = FP^2 + (1/2)V_3(1 - \cos 3\chi_p) + \tilde{B}J^2 + (C - \tilde{B})J_z^2 + QPJ_z + f_+J_+^2 + f_-J_-^2$$

where P is the momentum conjugate to χ_p . The F and V_3 terms represent the three-identical-well, particle-on-a-ring, pseudorotation problem. The \tilde{B} and C terms represent an oblate symmetric top rotational Hamiltonian (z axis perpendicular to the Na_3 plane). The Q term represents Coriolis interaction between the pseudo-rotational and overall-rotational angular momentum. Up to this point the Hamiltonian can be mapped onto that for methyl-group internal rotation in an oblate symmetric top. The final two terms are peculiar to the present problem. They contain products of the total angular momentum ladder operators $J_{\pm} = J_x \pm iJ_y$ and coefficients f_{\pm} , which (unlike the other coefficients F, V_3, \tilde{B}, C, Q) cannot be constants, but must be expressed as a Fourier series in the pseudorotation functions $\exp(\pm im\chi_p)$, where $m = +1 \pmod{3}$. These final two terms allow for rotation of the inertial A, B, C axes when pseudorotation causes each of the Na atoms in turn to occupy the apex position in the distorted-triangle equilibrium structure, and they are responsible for a number of unusual features in the rotational energy level pattern, which will be discussed along with a relatively successful fit of published² and unpublished measurements from earlier $\tilde{B}-\tilde{X}$ pump-probe experiments.

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THEORY OF ODD TORSIONAL TRANSITIONS IN THE $V - N$
RESONANCE RAMAN SPECTRUM OF ETHYLENEJ. K. G. WATSON^a, W. SIEBRAND^a, M. Z. ZGIERSKI^a, AND M. PAWLIKOWSKI^b^a*Steele Institute for Molecular Sciences, National Research Council of Canada,
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The $V - N$ resonance Raman spectrum of ethylene¹ shows a long progression in even quanta of the ground-state torsional mode $\nu_4''(a_u)$. Bands approximately midway between the even quanta have been assigned² to transitions to odd quanta of ν_4'' . Such transitions are forbidden according to the usual $g \leftrightarrow u$ selection rule of Raman spectroscopy. Here we consider the theory of the intensity of such transitions allowing for the fact that the excited state is twisted by 90° at equilibrium, using Hougén's double group theory³. From approximate one-dimensional torsional potentials of the V and N electronic states, it is shown that good qualitative agreement between observed and calculated intensities is obtained. The electronic transition moment is assumed to be proportional to $\cos \theta$, where θ is the torsional angle, but the calculated relative intensities are not sensitive to the precise torsional dependence. More detailed theory will require consideration of the avoided crossing affecting the V state⁴.

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ACETIC ANHYDRIDE: A TWO-TOP MOLECULE WITH A TWIST

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It has proved possible to observe the rotation-torsion spectra of acetic anhydride, d_6 -acetic anhydride and all the singly substituted ^{13}C - d_6 -acetic anhydride isotopic species using a pulsed nozzle Fourier transform microwave spectrometer.

In surprising contrast to the results from previous spectroscopic studies on the structure and dynamics of the anhydrides, $\text{R}_1\text{-CO-O-CO-R}_2$ with $\text{R}_1=\text{R}_2=\text{H}^1$ and $\text{R}_1=\text{H}$, $\text{R}_2=\text{CH}_3$,² acetic anhydride ($\text{R}_1=\text{R}_2=\text{CH}_3$) was found to have a non-planar arrangement of the heavy nuclei with both acetyl groups being twisted out of the C-O-C plane.

Unlike the few other two-top molecules which have been previously investigated and have inequivalent methyl groups (e.g. methyl acetate³ and *trans* N-methylethylidenimine⁴) the observed conformation of acetic anhydride does not have a plane of symmetry, and hence it proved necessary to modify existing software for this case to ensure that the basis functions for the internal rotation part of the Hamiltonian had the appropriate symmetry properties.

The low J , K_a b-type and c-type transitions of acetic anhydride observed in our jet spectrometer show some fine structure, and it is most likely that a concerted large-amplitude conformational inversion motion of the heavy nuclei frame of acetic anhydride takes place. The potential energy surface of acetic anhydride has been determined *ab initio* at the MP2/6-31G** level of theory⁵ and the conformation of the global minimum is in general agreement with the experimentally determined structure.

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⁵ T. K. HA, *private communication*

A DIPOLE MOMENT SURFACE FOR THE WATER MOLECULE DETERMINED FROM HIGH-J EXPERIMENTAL ROVIBRATIONAL LINE STRENGTHS IN A VARIATIONAL APPROACHS.A.Tashkun¹, VI.G.Tyuterev² and P.Jensen³.¹*Institute of Atmospheric Optics SO RAN, Tomsk 634055, Russia*²*Laboratoire de Spectrométrie Moléculaire et Atmosphérique,
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A simultaneous fitting of vibration-rotation line strengths of fundamental, overtone, combination and hot bands of the water molecule has been performed in order to determine the dipole moment surface directly from observed infrared and microwave data.

In order to calculate vibration-rotation wave function and rovibrational transition moments the recent refined potential energy function [1] for the electronic ground state of water molecule has been used which was determined from an extended set of experimental energies and transition frequencies for various isotopic species (120 vibration-rotation bands of 10 isotopomers). The calculations are carried out with the Hamiltonian written in the MORBID form and the dipole moment function is represented by an expansion in bond length displacements for stretching coordinates and in cosine of the bending angle[2].

In this paper we focus on high rotational quantum number transitions. Refined values of 9 dipole moment parameters (i.e., expansion coefficients of terms up to second order in the vibrational coordinate displacements) have been obtained from a simultaneous fitting of approximately 6750 spectral line intensities from 18 vibrational bands including hot bands of H₂O and HDO. The transitions involved in the fitting had $|\sum (V-V')| \leq 2$ and $J \leq 10$. The overall weighted relative standard deviation of the fit with only 9 adjustable parameters was 1.8, which is close to the experimental accuracy.

The results of the present work constitute a considerable improvement over "global" calculations from available ab initio dipole moment surfaces.

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TORSION-ROTATION-VIBRATION EFFECTS IN THE DEGENERATE
VIBRATIONAL FUNDAMENTAL ($\nu_{12} = 1 \leftarrow 0$) OF CH_3CD_3

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Torsion-rotation-vibration effects in the lowest-lying degenerate fundamental ($\nu_{12} = 1 \leftarrow 0$) of CH_3CD_3 have been studied. Spectra between 640 and 740 cm^{-1} have been obtained at a resolution of 0.002 cm^{-1} using a Fourier transform spectrometer. The temperature and pressure of the sample were 130 K and 0.4 Torr, respectively. A total of 1936 transitions have been identified. Torsional splittings for most (K, σ) series have been observed, where $\sigma = 0, -1, +1$ labels the different torsional sublevels. These torsional splittings are caused by the Coriolis interactions between the torsional state ($\nu_{12} = 1, \nu_6 = 0$) and the torsional stack of the ground vibrational state. Because of the near degeneracy of the levels ($\nu_{12} = 0, \nu_6 = 3$) and ($\nu_{12} = 1, \nu_6 = 0$), four (K, σ) series exhibit resonant perturbations. For three of these series, perturbation-allowed ($\nu_6 = 3 \leftarrow 0$) torsional transitions have been assigned. The measurements from the present experiment and frequencies from previously reported studies in the ground vibrational state were fitted to within experimental uncertainty using an effective Hamiltonian discussed earlier in connection with CH_3SiH_3 [Moazzen-Ahmadi *et al.* 170, 516 (1995)].