Contributed Lectures   I

Lecture Hall AI

August 31, Wednesday, 14:30 − 16:30

An ab initio study of SbH_2 and BiH_2: The Renner Effect, Spin-Orbit Coupling, Local Mode Vibrations and Rovibronic Energy Level Clustering in SbH_2

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We present the results of ab initio calculations for the lower electronic states of the Group 15 (pnictogen) dihydrides, SbH_2 and BiH_2. For each of these molecules the two lowest electronic states become degenerate at linearity and are therefore subject to the Renner effect. Spin-orbit coupling is also strong in these two heavy-element containing molecules. For the lowest two electronic states of the SbH_2 molecule we construct the three-dimensional potential energy surfaces and corresponding dipole moment and transition moment surfaces by multi-reference configuration interaction techniques. Including both the Renner effect and spin-orbit coupling, we calculate term values and simulate the rovibrational and rovibronic spectra of SbH_2. Excellent agreement is obtained with the results of matrix isolation infrared spectroscopic studies and with gas phase electronic spectroscopic studies in absorption. For the heavier dihydride BiH_2 we calculate bending potential curves and the spin-orbit coupling constant for comparison. For SbH_2 we further study the local mode vibrational behaviour and the formation of rovibronic energy level clusters in high angular momentum states.

^{13}C-substituted C_{60}^{+}: Predictions of the rotational spectra

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1. Introduction

On the basis of laboratory spectra using mass-selected He-tagging spectroscopy, Maier and coworkers recently [1] reported that two diffuse interstellar bands can be assigned to the C_{60}^{+} ion. Stimulated by their work we consider the possibility of high resolution spectroscopy of C_{60}^{+}. The C_{60}^{+} ion is spherical and rotational transitions are therefore not expected. However, if one carbon atom is substituted by ^{13}C the centre of mass will no longer coincide with the centre of charge and we expect a sizable dipole moment and thus the possibility of rotational spectroscopy in the MW region. We denote singly substituted species as $13^{1}C_{60}$. Because C_{60} is composed of 60 carbon atoms the number density of $13^{1}C_{60}$ in natural abundance is comparable with that of the normal species. It is therefore worth predicting the rotational spectrum of $13^{1}C_{60}^{+}$. The predicted MW spectra will be presented at the meeting.

2. The rotational constants and the dipole-moment of $13^{1}C_{60}^{+}$: I_h Model

Due to the very large number of electrons in this system it is reasonable to assume that the structure of the C_{60}^{+} ion (Fig.1) is not very different from that of neutral C_{60} of I_h symmetry. Because the positions of each carbon atom are equivalent in this assumption, the $13^{1}C_{60}^{+}$ ion is a prolate symmetric-top. The predicted rotational constants are A=82.98 MHz and B=82.81 MHz. From the shift of the center-of-mass due to the isotope substitution the dipole moment can easily be calculated to be 0.006 D.

3. The rotational constants and the dipole-moment of $13^{1}C_{60}^{+}$: D_{5d} Model

In 1990 Ceulemans and Fowler [2] pointed out that the structure of the C_{60}^{+} ion may be distorted by the Jahn-Teller effect. In fact the matrix isolation spectra of C_{60}^{+} by Kern *et al.* [3] indicate that in its ground electronic state the ion is of D_{5d} symmetry. By calculating the structure using Density Function Theory (DFT) with the B3LYP functional we found that the locations of the 60 carbon atoms can be classified into four categories by their distance, R, from the center of mass. The singly substituted ions, $13^{1}C_{60}^{+}$, can therefore be classified into four categories depending on which atom is substituted. Furthermore, depending at which site the substituted atom is located, $13^{1}C_{60}^{+}$ is either an asymmetric-top without symmetry, *i.e.* of C_1-symmetry (chiral), or one with C_s-symmetry where the symmetry plane passes through the substituted carbon atom.

References

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Effective hyperfine-structure functions of ammonia

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The hyperfine structure of the rotation-inversion ($v_2 = 0^+, 0^-, 1^+, 1^-$) states of the $^{14}NH_3$ and $^{15}NH_3$ ammonia isotopomers is rationalized in terms of effective hyperfine-structure functions, which are determined by fitting to available experimental data within the framework of the non-rigid inverter theory. Using only a moderate number of fitting parameters in the vibrational-inversion-rotation and effective Hamiltonian, the global fit provides immediate functions for the majority of fitted data. The predicted characteristics provide values of parameters in the effective Hamiltonian for a large number of lines in the ammonia rotation-inversion spectrum. In future experiments this may help derive spectroscopic constants of the observed inversion and rotation-inversion transitions deperturbed from the hyperfine effects. The significance of the deperturbed band centers of ammonia comes to the forefront in the study of fundamental physics as probes of a variable proton-to-electron mass ratio, since they are more adequate than their counterparts obtained at the usual `rotational' resolution.

Recent advances in the theory of the ozone molecule: ab initio calculations, band intensities and highly excited ro-vibrational states

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An accurate description of the complicated shape of the potential energy surface [1], of dipole moment surfaces and that of the highly excited vibration states [2] is of crucial importance for various unsolved issues in the spectroscopy and dynamics of ozone and remains a challenge for the theory. We shall present new ab initio dipole moments surfaces of the ozone molecule as well as the results of first-principles variational calculations for lines intensities in the far infrared range. The comparisons of predicted spectra with experimental ones [3], with data included in S&MPO information system [4] and in HITRAN-2012 database [5] will be presented. The remaining issues will be discussed both for cold and hot band transitions. This work permitted to obtain for the first time a good agreement of ab initio ozone band intensities with observations in a wide range of overtone and combination bands. The second part of the study will summarize recent results [6] of global variational calculations of high-energy states of ozone near the dissociation threshold taking into account the coupling and possible transitions among three ozone potential wells in the D_{3h} symmetry. Detailed descriptions of metastable ozone states above the dissociation threshold, their lifetimes and corresponding wave functions with an impact on the dynamics will be presented in [6]. We acknowledge the support from LEFE CHAT CNRS program and from Mendeleev funding TSU grant.
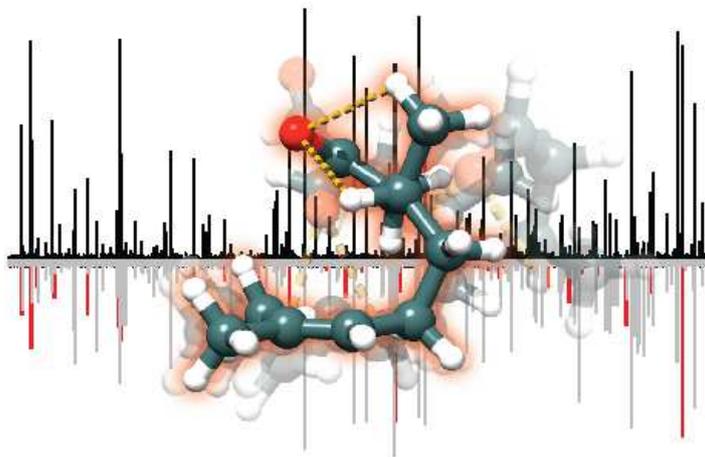
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Conformational flexibility of acyclic monoterpenes revealed by broadband rotational spectroscopy

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Understanding the interplay between the three-dimensional structure of a biomolecule and its functionality is critical for rationalising ligand–receptor interactions. Using broadband rotational spectroscopy we reveal the complex conformational space of the extremely flexible acyclic monoterpene citronellal. We identify an unprecedented number of conformations for a chiral molecule of this size in the experimental conditions of our supersonic expansion. Studies of relative stability using different carrier gases reveal conformational relaxation pathways that strongly favour ground-state structures with globular conformations. Our observations allow us to derive structural aspects of this biosynthetic precursor that are insightful on the relation between its structure and functionality.[1]

Fig. 1: High resolution rotational spectroscopy is used to map the conformational landscape and derive conformational relaxation pathways of citronellal.

References

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Detections of Long Carbon Chains CH₃CCCCH, C₆H, l-C₆H₂ and C₇H in the Low-Mass Star Forming Region L1527

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Long carbon chains CH₃CCCCH, C₆H, l-C₆H₂, and C₇H were detected in the low-mass star forming region L1527 having a warm carbon chain chemistry (WCCC) by using Green Bank 100 m telescope. The $K = 0$, 1, and 2 lines of the $J = 11$–10 rotational transition of CH₃CCCCH were detected, and the column density and excitation temperature were determined to be 5.6×10^{12} cm^{-2} and 20 K, respectively. The $^2\Pi_{1/2}$ state of C₆H, locating 15.04 cm^{-1} higher than the $^2\Pi_{3/2}$ state, was detected for the first time in both of dark cloud and WCCC region. The column densities of the $^2\Pi_{1/2}$ and $^2\Pi_{3/2}$ states of C₆H in L1527 were derived to be 1.6×10^{11} and 1.1×10^{12} cm^{-2}, respectively, leading the temperature of 11 K between the two states. Detection of l-C₆H₂ was limited for the $K_a = 1$ lines of ortho species so far, except for circumstellar envelop. In the present observations, however, the $K_a = 0$ line of para species was detected. The column densities of the ortho and para species of l-C₆H₂ were independently obtained to be 1.3×10^{11} and 0.6×10^{11} cm^{-2}, respectively. C₇H was detected for the first time except for circumstellar envelop. The column density of C₇H was estimated to be 6.2×10^{10} cm^{-2} from the $J = 24.5$–23.5 and 25.5–24.5 lines. These results of detections would suggest that long carbon chains are rich in L1527 as well as the starless dark cloud TMC-1.
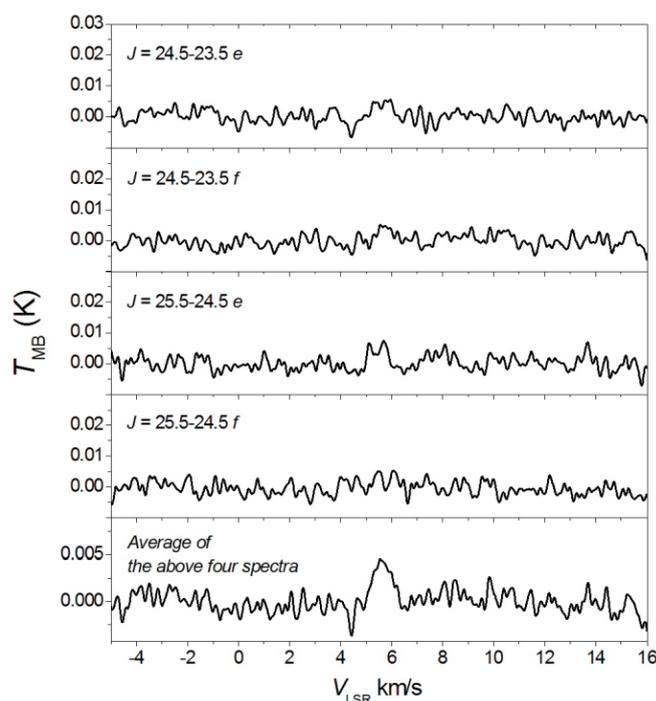
Fig. 1: The J = 24.5–23.5 and 25.5–24.5 transitions of C₇H observed by Green Bank 100 m telescope. The average of the four spectra is described in the bottom trace.