Ro-torsional energy correlation in the case of HSOH: between the high barrier and free-internal-rotor limits

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ABSTRACT: To obtain a conceptual explanation of the peculiar variation of the torsional tunneling splitting with rotational quantum number, *K*, observed in HSOH, we have determined the energy correlation diagram between two limiting cases. These are the free-rotor (zero-barrier) limit and the high-barrier limit. To do this we used the reduced-dimension Generalized Semi-Rigid Bender (GSRB) approach. In this context we also present the symmetries and appropriate quantum numbers for the states in the two limiting cases.

Introduction

The ro-torsional spectra of HSOH exhibit exotic behavior due to strong coupling of torsion and rotation. The observed torsional tunneling splitting changes its magnitude cyclically with the rotational quantum number, *K*, with a period depending on the ratio of the end moieties. In our previous paper [1] we reported that in the low-J region (J<10) the observed spectra can be reproduced by a reduced-dimension model based on the GSRB approach. We also compared our results with those obtained by other approaches: an algebraic model [2], based on the high-barrier matrix formalism [3], and a full-dimensional TROVE model [4]. Here we present a conceptual explanation of this cyclic variation of the torsional splitting for HSOH. We do this by inspecting the energy-level correlation between states at the free-rotor (zero-barrier) limit and at the more physical high-barrier limit [5]. In this context we also present the symmetries and appropriate quantum numbers for the states in these two limits.

Limiting cases: high-barrier limit and zero-barrier limit

At the high-barrier limit, the torsional energy levels of HSOH resemble those of a harmonic oscillator but with each level doubled by the tunneling effect. The ro-torsional quantum states of HSOH in the ground vibrational state can be represented by the product of a torsional wavefunction and a Wang-type rotational wavefunction, $|v_t^{\pm}\rangle|J,K\rangle_\gamma$. v_t=0 for the ground state and the components of the tunneling doublet are distinguished by symmetry $\pm$ ($+$ for symmetric and $-$ for anti-symmetric with respect to the symmetry operation E^*). The Wang basis is expressed for K>0 as $|J,K\rangle_\gamma = (|J,K\rangle + (-1)^\gamma |J,-K\rangle)\sqrt{2}$, which is of *e*/*f*-symmetry for $K+\gamma$ =even/odd, respectively.

At the zero-barrier limit, ro-torsional energy term values are given in the reduced-dimension model (torsion and rotation) as, approximately,

$$E(N_{OH},N_{SH};J,K) = A_{OH}N_{OH}^2 + A_{SH}N_{SH}^2 + B[J(J+1)-K^2]. \quad (1)$$

Here A_{OH} and A_{SH} are the rotational constants around the axis of internal rotation of OH and SH moiety, respectively, and B is the rotational constant in the diatomic molecule approximation. N_{OH} and N_{SH} are the quantum numbers representing the rotation of the OH and SH moieties around the internal rotation axis: $N_{OH} = |n_{OH}|$, $N_{SH} = |n_{SH}|$, and $K=|k|=|n_{OH}+n_{SH}|$. The corresponding eigenfunction is given as,

$$|n_{OH},n_{SH};J,k\rangle = N\,|n_{OH},n_{SH};k\rangle\, S_{J,k}(\theta,\phi) = N'\exp[in_{OH}\chi_{OH}]\exp[in_{SH}\chi_{SH}]\, S_{J,k}(\theta,\phi), \quad (2)$$

where the angle variables χ_{OH} and χ_{SH} are as shown in Fig. 1 and N and N' are normalization factors. The torsion-z-rotation part of the wavefunction $|n_{OH},n_{SH};k\rangle$ is symmetrized by taking the Wang-type linear combinations, $|N_{OH},N_{SH};K\rangle_\Gamma = (|N_{OH},N_{SH};K\rangle + (-1)^\Gamma\,|-N_{OH},-N_{SH};-K\rangle)/\sqrt{2}$, which are of e/f-symmetry for $K+\Gamma$ =even/odd, respectively.

Correlation Diagram

The qualitative energy-level-correlation diagram can be readily obtained by connecting levels of the same K and same symmetry between these two limits, step-by-step from the lowest energy level. We obtained a more quantitative correlation by calculating the ro-torsional energies using the GSRB Hamiltonian, with the *cis*- and *trans*-potential barriers to the internal rotation being proportional to those reported in our previous paper [1] but multiplied by a scaling factor f_{scale}. f_{scale} =0 corresponds to the zero-barrier limit, and f_{scale} =1 to the best-fit potential energy function [1]. This later forms a reasonable approximation for the high-barrier limit. A portion of the lowest energy part of this diagram for J=6 is reproduced here as Fig. 2. The magnitude of the torsional splitting changes with K=3n, 3n+1, and 3n+2. Examination of this correlation diagram leads to a conceptual understanding of the staggering of energy level splitting with K. Indeed, the diagram clearly shows that the cyclic variation of the magnitude of the torsional splitting originates in the energy level structure in the zero-barrier limit.

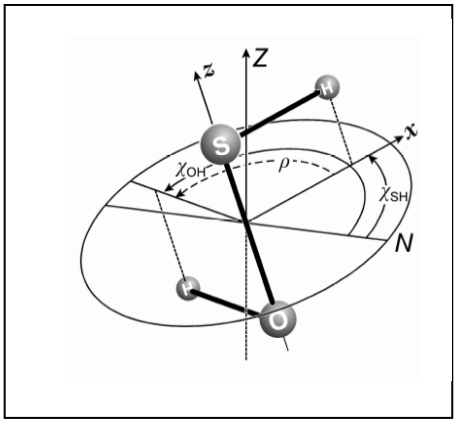

Fig. 1

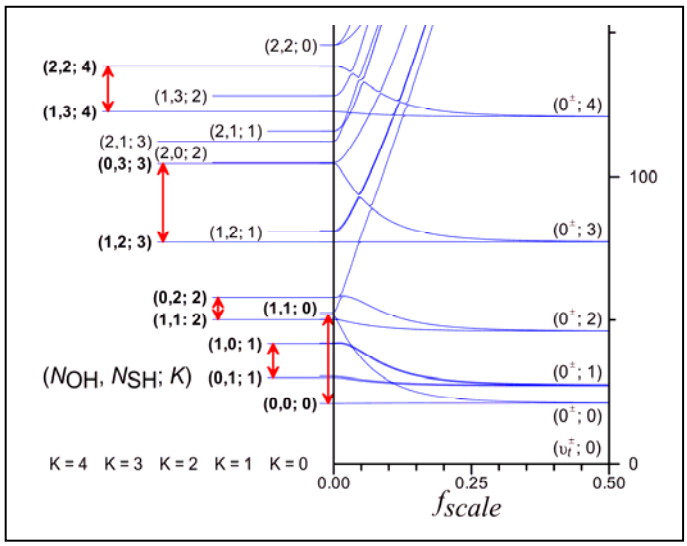

Fig. 2

[1] S.C. Ross, K.M.T. Yamada, and F. Ito, *PCCP*, **12**, 11133--11150 (2010).

[2] K.M.T. Yamada, G. Winnewisser, and P. Jensen, *J. Mol. Struct.* **695-696**, 323-337 (2004); K.M.T. Yamada, P. Jensen, S.C. Ross, O. Baum, T.F. Giesen, and S. Schlemmer, *J. Mol. Struct.* **927**, 96-100 (2009).

[3] J.T. Hougen, *Can. J. Phys.* **62**, 1392-1402 (1984); J.T. Hougen and B.M. DeKoven, *J. Mol. Spectrosc.* **98**, 375-391 (1983).

[4] R.I. Ovsyannikov, V.V. Melnikov, W. Thiel, P. Jensen, O. Baum,T.F. Giesen, and S.N. Yurchenko, *J. Chem. Phys.* **129**, 154314--1--9 (2008).

[5] K.M.T. Yamada and S.C. Ross, *J. Mol. Spectrosc.* in press (2011), doi:10.1016.