Tunnelling splitting of HOOD observed in FIR spectra

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Abstract

The torsion-rotation spectra of HOOD were recorded in high resolution by an FTIR spectrometer at the SOLEIL synchrotron radiation facility. Because the *cis*-tunnelling effect is negligibly small compared with the *trans*-tunnelling effect, the observed tunnelling splitting for HOOD does not exhibit the cyclic variation with the rotational quantum number *K* that is seen in HSOH. The nature of the torsional tunnelling in HOOD will be discussed, as will the GSRB model calculation based on the torsional potential energy function predicted by *ab initio* calculations.

Introduction

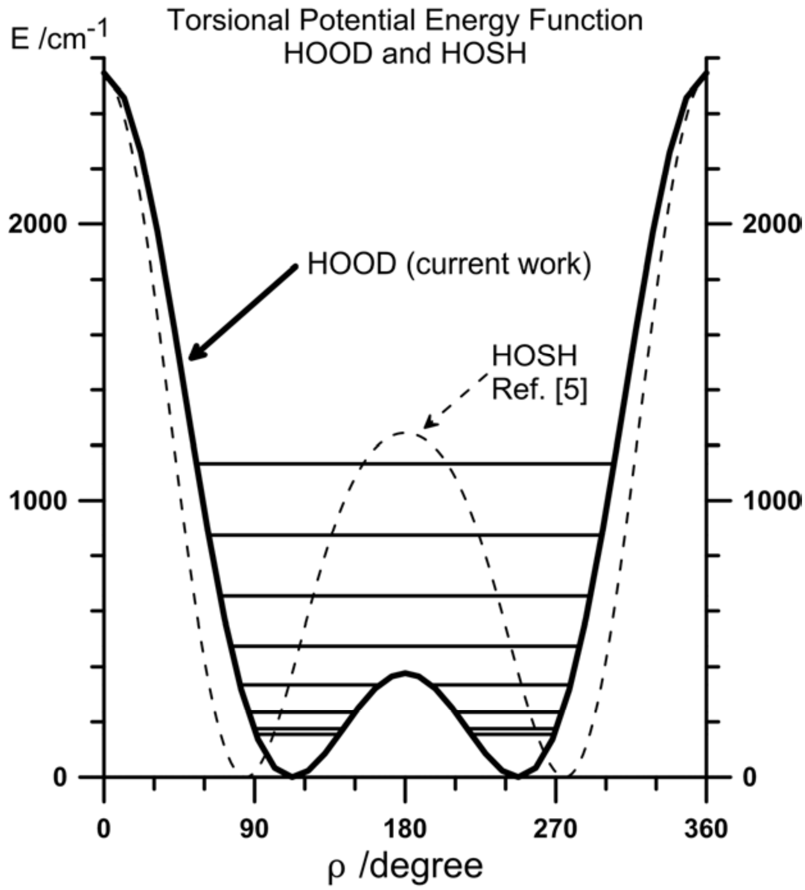
Last year in Hiroshima we reported a conceptual explanation of the torsional tunnelling splitting of HSOH [1]. Those splittings have a peculiar variation with the rotational quantum number *K*. The peculiarity originates from the accidental almost 2:1 ratio of the moments-of-inertia of the two internally rotating moieties, *i.e.* SH and OH. We expected a similar effect in mono-deuterated hydrogen peroxide, HOOD, for which the ratio of the moments-of-inertia is also close to 2:1. Although torsion-rotation interactions in hydrogen peroxide have been studied intensively for the symmetrical species, HOOH and DOOD [2,3], almost no investigation has been reported for HOOD. Currently the spectroscopy group in Köln is reporting the FIR spectra of HOOD measured with the Bruker IFS 125 spectrometer installed on the AILES beam line of the SOLEIL synchrotron radiation facility [4].

Observed spectra

The recorded spectra cover the range from 15 to 600 cm^{-1} with a resolution of 0.0011 cm^{-1}. In the lowest wavenumber region, from 15 to 110 cm^{-1}, we have assigned more than 1000 *c*- and *b*-type transitions. The *c*-type transitions belong to a ro-torsional band involving transitions between the tunnelling doublet components while the *b*-type transitions are purely rotational. The observed intensities of those lines are consistent with the permanent dipole moments estimated by an *ab initio* calculation: μ_a = 0.0458 D, μ_b = 0.5593 D, and μ_c = 1.7252 D.

The spectral assignments were easily made for $K''>2$. From the combination differences of the observed *b*- and *c*-type transitions, the tunnelling energy splitting $\Delta_{\rm split}$ was determined directly from experiment. This splitting increases with increasing *J*, and decreases with increasing *K*. The *J*,*K*-dependence of the splitting can be reproduced by a simple polynomial, and, in marked contrast to HSOH, does not show any cyclic variation with the quantum number *K*. The magnitude of Δ_{split} is observed to be largest for HOOH and smallest for DOOD, *i.e.* Δ_{split}(HOOH) > Δ_{split}(HOOD) > Δ_{split}(DOOD). We have also observed that the decreasing tendency of Δ_{split} with the increase of *K* quantum number is in proportion to the magnitude of Δ_{split}.

Barrier to torsional motion



The simple *K*-dependence of the torsional splittings suggests that the *cis*-tunnelling effect should be negligibly small in HOOD compared to the more complicated case of HSOH. This corresponds well with the *ab initio* potential energy barrier heights at the *trans*-configuration (ρ=180º) where the barrier in HOOD is very low compared to that in HSOH, thereby allowing relatively free tunneling between the equivalent minima.

References

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