Metastable rovibrational *f*-symmetry levels of theI ^1Đ_g state of H_2, HD, and D_2: experiment and theory

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The I $^1\Pi_g$ state of H_2 can decay by the two mechanisms shown in Figure 1. These mechanisms are:

(a) emission to lower states of ungerade symmetry,

and

(b) pre-dissociation following tunnelling through the potential energy barrier.

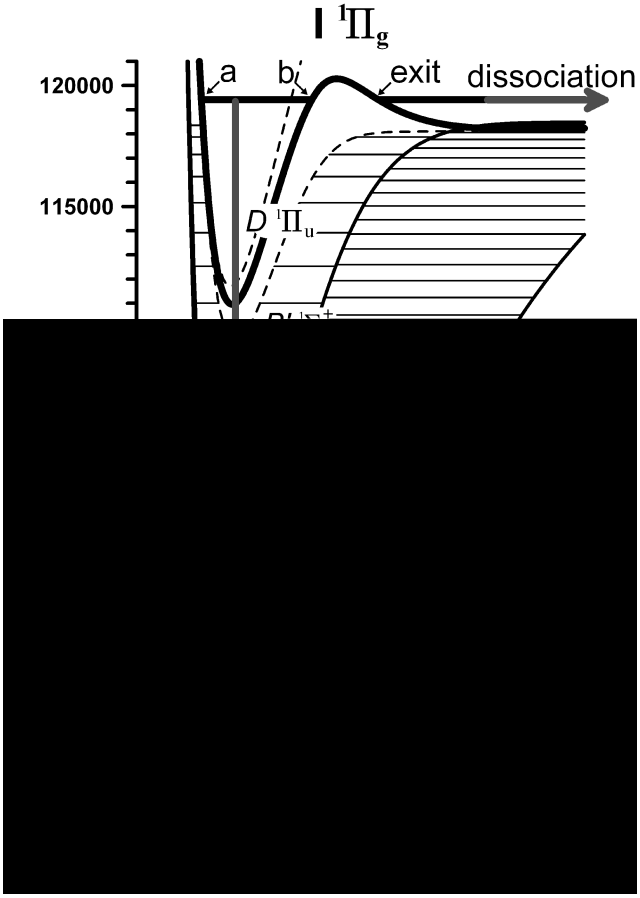

Figure 1

The possibility of decay means that the ro-vibrational levels of the I sate are metastable and therefore have finite lifetimes. These lifetimes have been measured by direct observation of the time-dependence of the decay of the fluorescence. Here we present accurate experimental measurements of the lifetimes and term values of the metastable rovibrational *f*-symmetry levels of the I $^1\Pi_g$ state of HD.

We also present *ab initio* results for both of these decay processes for H_2, HD, and D_2. The theoretical calculations provide an explanation of the rotational dependence of the observed lifetimes for HD, the lack of rotational dependence for D_2, and the approximately equal lifetimes for $N = 1$ for HD and D_2. The calculated lifetimes for the metastable levels of H_2 explain why no experimental data is yet available for the parent isotopomer. However, the use of recently updated Hönl-London factors with published *ab initio* electronic transition moments reveals a larger than expected discrepancy with experiment for levels of HD and D_2 for which emission is the dominant decay mechanism.