Decay Dynamics of the Long-Range H $^1G_g^+$ State of D_2 and H_2: Experiment and Theory.

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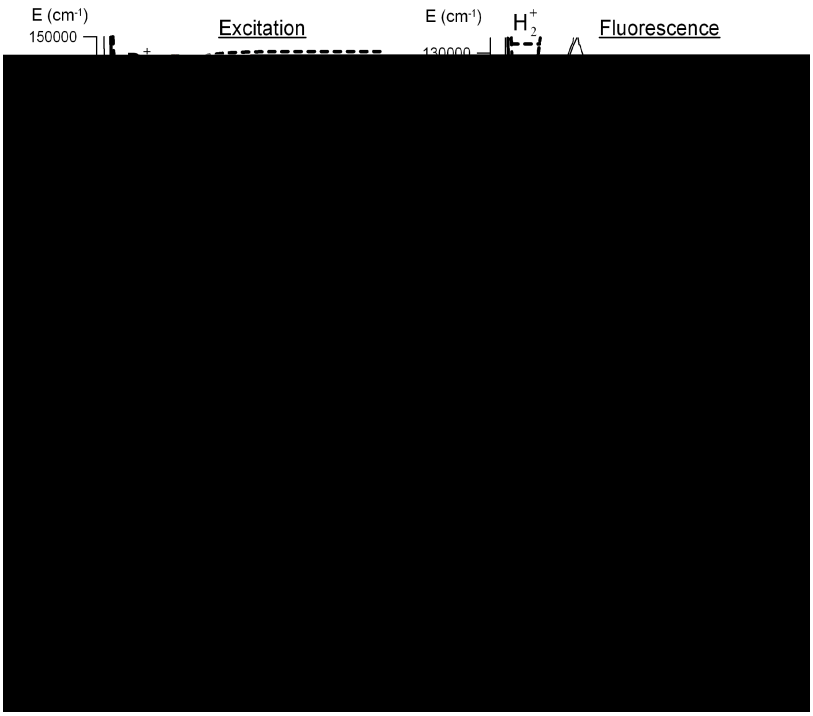

Figure 1

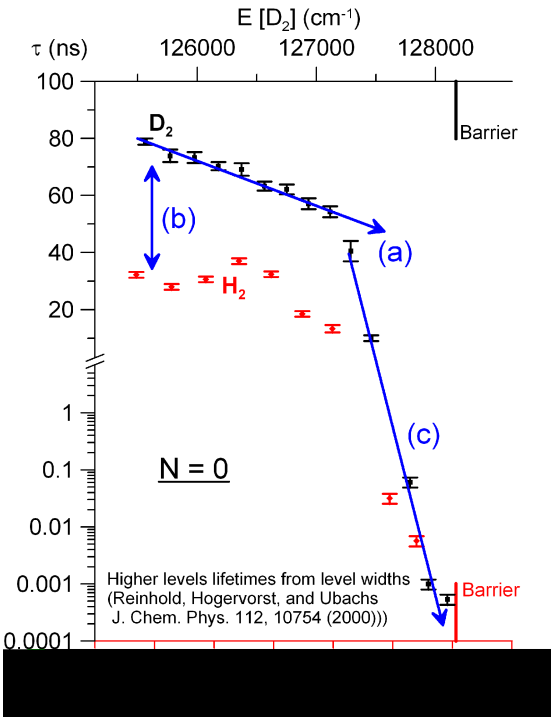

Figure 2

In 1997 Reinhold *et al.* first observed the long-range H state of H_2,[1] later measuring the lifetimes of various rovibrational levels of this state.[2] At TUS the lifetimes have been examined for more levels and more accurately. As shown in Fig 1(a) the excitation of these levels involves a VUV photon which populates an individual level in the $B\ ^1\Sigma_u^+$ state and a visible photon which then excites an individual rovibrational level of the H state. The time decay of emission to lower lying ungerade states, as shown in Fig. 1(b), was measured to obtain the level lifetimes. The combined lifetime results for $N = 0$ from Ref. 2 and the present work are shown in Fig. 2. Three features of Fig. 2 require explanation:

(a) The linear decrease in lifetimes for the lower lying D_2 levels,
(b) The approximately 2:1 ratio of D_2:H_2 lifetimes, and
(c) The dramatic drop in lifetimes by 4 orders of magnitude.

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[1] E. Reinhold, W. Hogervorst, and W. Ubachs, Phys. Rev. Lett. **78**, 2543 (1997).

[2] E. Reinhold, W. Hogervorst, and W. Ubachs, J. Chem. Phys. **112,** 10754 (2000).

Level lifetimes are the combined result of all decay pathways. The levels of the $H\!\!\!/$ state can decay in a plethora of ways including:

Emission: In Fig 1(b) we see the possibility of direct emission but also the possibility of vibrational tunnelling to the inner *H* well and then emission of a photon.

Autoionisation: In Fig. 1(b) we also see that tunnelling to the inner *H* well embeds the $H\!\!\!/$ levels in the H_2^+ ionisation continuum to which these levels can couple and decay in a process known as vibrational autoionisation.

Predissociation: In Fig. 3 we see that the $H\!\!\!/$ levels are embedded in the dissociative continua of lower lying $^1G_g^+$ states. Nonadiabatic interactions between these states leads to the $H\!\!\!/$ levels coupling to the vibrational continua of the lower states - either in the region of the outer well, or after tunnelling to the inner well.

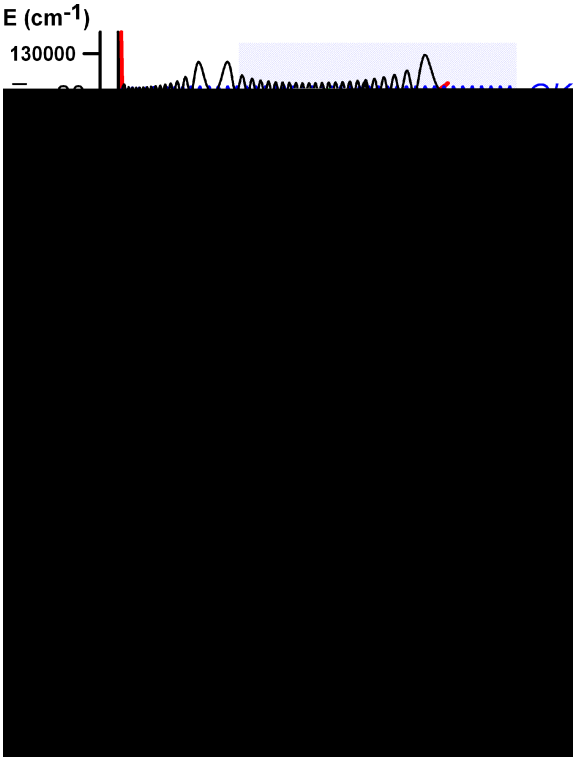

Figure 3

Within the time constraints of this talk we present the results of *ab initio* calculations of these processes, and the resulting explanations for each of the features (a)-(c) seen in Fig. 2. Fig. 4 presents a comparison of the calculated lifetimes with experiment for $N = 0$. Similar results were obtained for each of the observed values of *N* observed. The trends of the calculated level lifetimes can be seen to reproduce the experimental features reasonably well, including the features (a)-(c).

Time will not permit a discussion of our investigation of the possibility of enhanced tunnelling, nor an introduction to the non Born-Oppenheimer effects at play in some of the processes at work here.

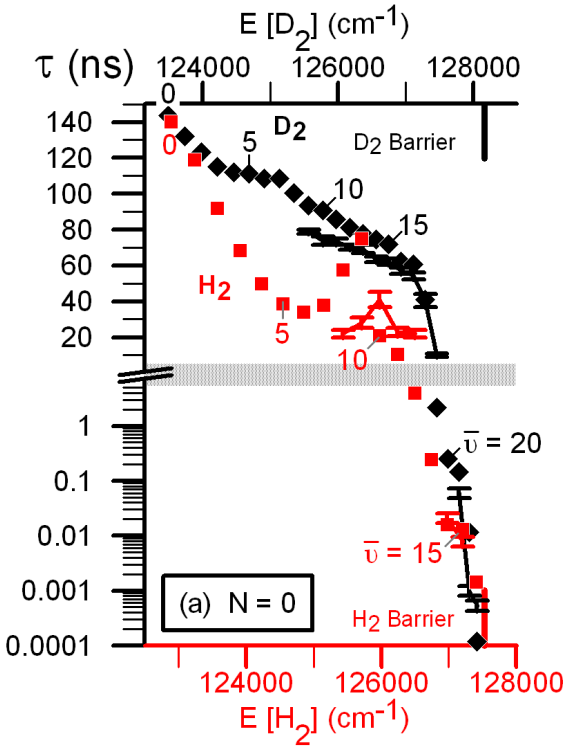

Figure 4