

Absorption spectrum for the transition state H_3^\ddagger —A quantum mechanical model study

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Abstract. The absorption spectrum for the transition state in the collinear reaction $H + H_2 \rightarrow H_3^\ddagger \rightarrow H_2 + H$ is predicted, using the time-independent Schrödinger equation for a model consisting of a one-dimensional rectangular potential barrier and a well.

Keywords. Absorption spectrum; transition state; quantum mechanical study.

1. Introduction

In recent years, the possibility of a direct spectroscopic observation of transient species which are intermediate between reactants and products, usually referred to as the transition state (TS) or reaction complex, has triggered off a lot of research (Polanyi 1979; Foth *et al* 1982). Arrowsmith *et al* (1980, 1983) reported the emission spectrum of the TS for the reaction,



by monitoring the wings to the sodium D-line emission. Polanyi and Wolf (1981) and Carrington *et al* (1982) interpreted the wings as arising from the emission from Na^* while the separating NaF is still in the vicinity. Brooks and coworkers (Hering *et al* 1980; Brooks *et al* 1982; Maguire *et al* 1983) have reported evidence for absorption from the TS in reactions:



and



Interest in the TS spectroscopy stems from the fact that it may provide some glimpse of the reactive potential-energy surface (PES) in the region crucial to the determination of the outcome of a molecular collision, complementary to the results from state-to-state chemistry (Brooks and Hayes 1977) which focusses attention on reactants and products, thus yielding only indirect information about the structure of the reaction complex.

It is thus of fundamental interest to interpret the wings to the Lyman- α absorption line in $H + H_2$ collisions. Polanyi and coworkers (Mayne *et al* 1984a) computed the absorption spectrum for the TS of the collinear reaction



Dedicated to Professor Sadhan Basu on the occasion of his 65th birth anniversary.

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by determining the probability density distribution for the TS on the chemically accurate Siegbahn-Liu-Truhlar-Horowitz (SLTH) (Liu 1973; Siegbahn and Liu 1978; Truhlar and Horowitz 1978, 1979) *ab initio* PES using the quasi-classical trajectory (QCT) technique. They assumed vertical transitions from the ground state to one of the low-lying excited states that correlates with $\text{H}^*(2p) + \text{H}_2$. They found that as the collision energy increased, the intensity of the spectrum diminished and there was a considerable red shift for the wings to the Lyman- α line. Subsequently they extended (Mayne 1984b) their study to collisions in three dimensions using a diatomics-in-molecules (DIM) surface for the upper state, and concluded that the qualitative features of the spectrum remained invariant while going from collinear geometry to three dimensions.

Engel *et al* (1985) have carried out time-independent quantum mechanical (QM) calculations and predicted the absorption spectrum for the collinear reaction (R4), for two different vibrational states ($v = 0$ and $v = 1$) of the hydrogen molecule and at collision energies below the reaction threshold, using the same PES as Polanyi and coworkers did. The QM and QCT results were compatible as far as the basic trends were concerned.

Recently Agrawal *et al* (1985) have reported results of a time-dependent wave mechanical treatment of the collinear reaction (R4) for $v = 0$ and $v = 1$ at two different collision energies that are well above the reaction threshold, thus complementary to the results of Engel *et al* (1985).

Here we report the results from a time-independent QM calculation of the absorption spectrum for the same reaction, using a simple model mimicking the relevant PES. Calculations have been carried out for collision energies both above and below the reaction threshold.

2. Details of the model

The correlation diagram for the first few electronic states of H_3 is given elsewhere (Mayne *et al* 1984a). We reproduce schematically the potential-energy profile along the reaction coordinate for the collinear (H, H_2) collision, for the ground state and one of the excited states that correlates with $\text{H}^*(2p) + \text{H}_2$, in figure 1. We have constructed a model in terms of a rectangular barrier and a well with the height and the depth taken from Mayne *et al* (1984a) as shown by dashed lines in figure 1. We imagine the collision event to be as follows: a plane wave with a specified energy E approaches the barrier and is scattered, thus in part reflected, and in part transmitted. Further, one argues that being scattered, part of it leaks into the upper PES (the square well) and gets caught in one of its bound states. We assume vertical transitions from the ground state to the excited bound state and calculate the spectrum for different values of collision energies. An advantage of this model rests with the fact that the collision energies are highly resolvable.

The exercise has been executed in three parts: (1) the rectangular well problem, (2) the rectangular barrier problem, and (3) the intensity calculation.

Eigenvalues and eigenfunctions for the bound states of the potential well were obtained via the graphical technique, as described by Schiff (1968), for example. The wavefunction for the scattering off the barrier was determined by the standard procedure (Schiff 1968), corresponding to three energies: (i) energy below the barrier, $E = V_0/2$, where $V_0 = 0.4$ eV, (ii) energy above the barrier, $E = (4/3)V_0 = 0.533$ eV and (iii) energy corresponding to unit transmission coefficient, $E = 0.4177$ eV.

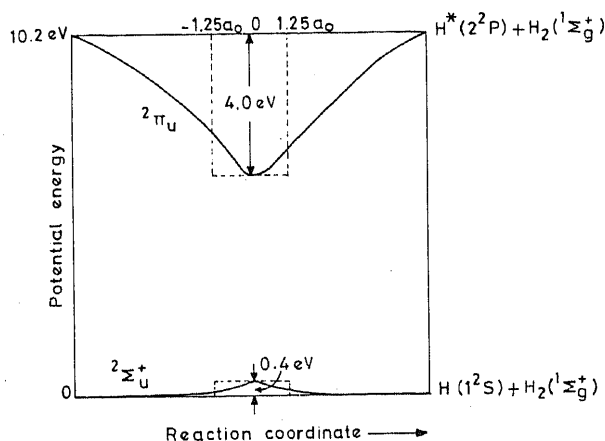


Figure 1. Representation of the potential-energy profile along the reaction path for the collinear collision of $H(H^*) + H_2$. The dashed lines indicate the truncated model used in this study.

For absorption from the ground state (barrier) to the excited state (well),

$$\text{intensity of spectral lines} \propto |\langle \psi_e | \mu | \psi_g \rangle|^2 \quad (1)$$

where μ is the electronic transition moment. In the absence of any available information on μ , the above matrix element can still be estimated roughly by noting that

$$|\langle \psi_e | \mu | \psi_g \rangle|^2 \propto \frac{|\langle \psi_e | \psi_g \rangle|^2}{\Delta E}, \quad (2)$$

where ΔE is the energy difference $E_e - E_g$. Earlier workers (Mayne *et al* 1984a; Engel *et al* 1985; Agrawal *et al* 1985) had also used the same approach. Since the algebra of evaluating the above matrix elements is straightforward, we only give the final results of the intensity calculation.

3. Results and discussion

Absorption spectra of the TS obtained at three different E values are given in figures 2–4 which clearly demonstrate the presence of wings to the Lyman- α line in each case. These wings terminate at frequencies corresponding to transition from the ground state to the highest bound excited state (at the high frequency end of the spectrum) and corresponding to transition from the ground state to the lowest bound state (at the low frequency end of the spectrum). The frequency range over which the spectra extend compares well with its classical counterpart shown in figure 4 of Mayne *et al* (1984a). Our model also leads to the same conclusion as the other detailed studies (Mayne *et al* 1984a; Engel *et al* 1985; Agrawal *et al* 1985) that the red-shifted wing becomes more intense with increase in E .

An important aspect of the results reported by Mayne *et al* (1984a) was the red shift of the peaks in the wings with increase in the collision energy. It was attributed to a large build-up of probability density at the translational turning point which moves towards

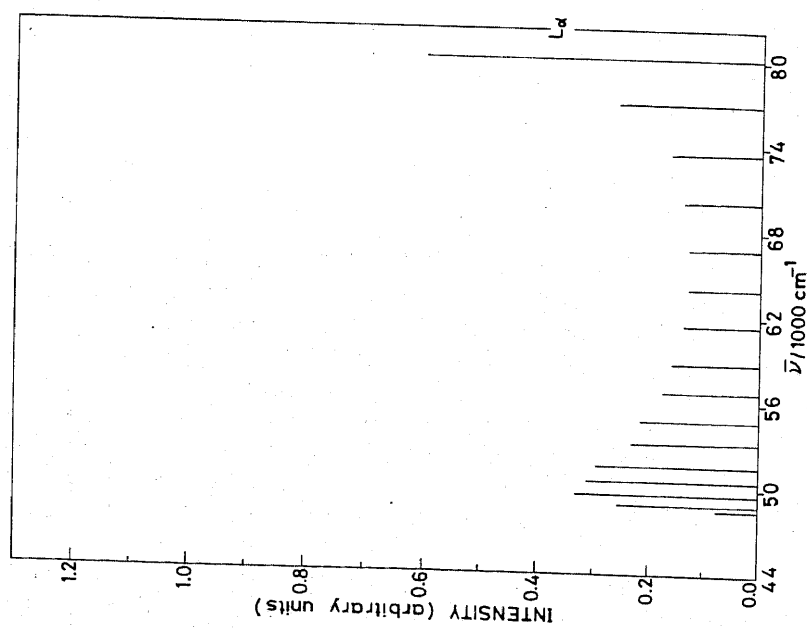


Figure 2. Predicted absorption spectrum for $E = V_0/2 = 0.2$ eV. L_α indicates the Lyman- α line.

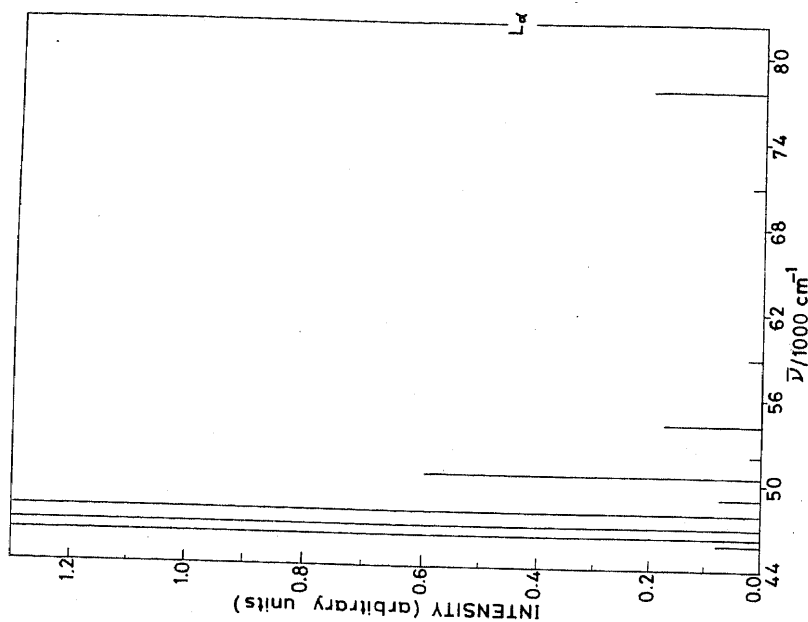


Figure 3. Same as figure 2 for $E = (4/3)V_0 = 0.5333$ eV.

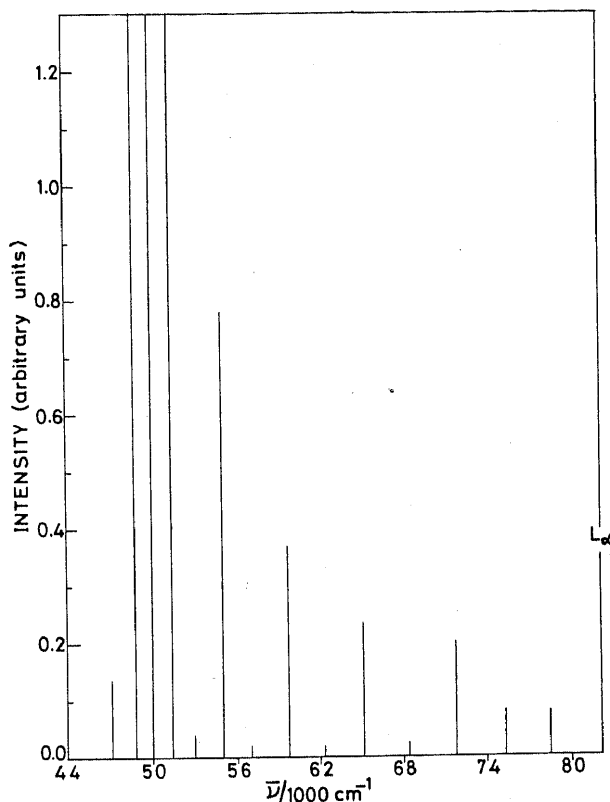


Figure 4. Same as figure 2 for $E = 0.4177$ eV with unit transmission coefficient.

smaller values of the transition frequencies as collision energy is increased. The same basic trend is clearly present in the results of our model calculations in figures 2–4.

Quantitatively, however, there is a basic difference between our results and those of Engel *et al* (1985). Adjacent bound states get farther from each other with increase in E for the rectangular potential well used by us while the spacing between them decreases with increase in energy for an anharmonic (Morse) oscillator used by the other workers (Engel *et al* 1985).

We have tried to rationalize our spectra by studying the $|\psi|^2$ plots of the wave functions in the upper bound states and the ground state. It is clear from the plots in figure 5 that the build-up of probability density for the collision energy below the barrier height is mostly around the classical turning point. Thus the spectral lines corresponding to transitions to the higher bound states of the excited state have greater intensity, because those states have an appreciable value of $|\psi|^2$ around that region of x -space. For collision energies greater than the barrier the transmission coefficient is close to one (and equal to one for $E = 0.4177$ eV). It follows thus that the distribution of $|\psi|^2$ is almost uniform in the whole of the x -space. Consequently, the intensity of spectral lines is dominated by E in the denominator in (2). Thus, with an increase in collision energy, the intensity of the lines away from the L_α line increases in qualitative accord with the results obtained by other more elaborate studies (Mayne *et al* 1984a; Engel *et al* 1985; Agrawal *et al* 1985).

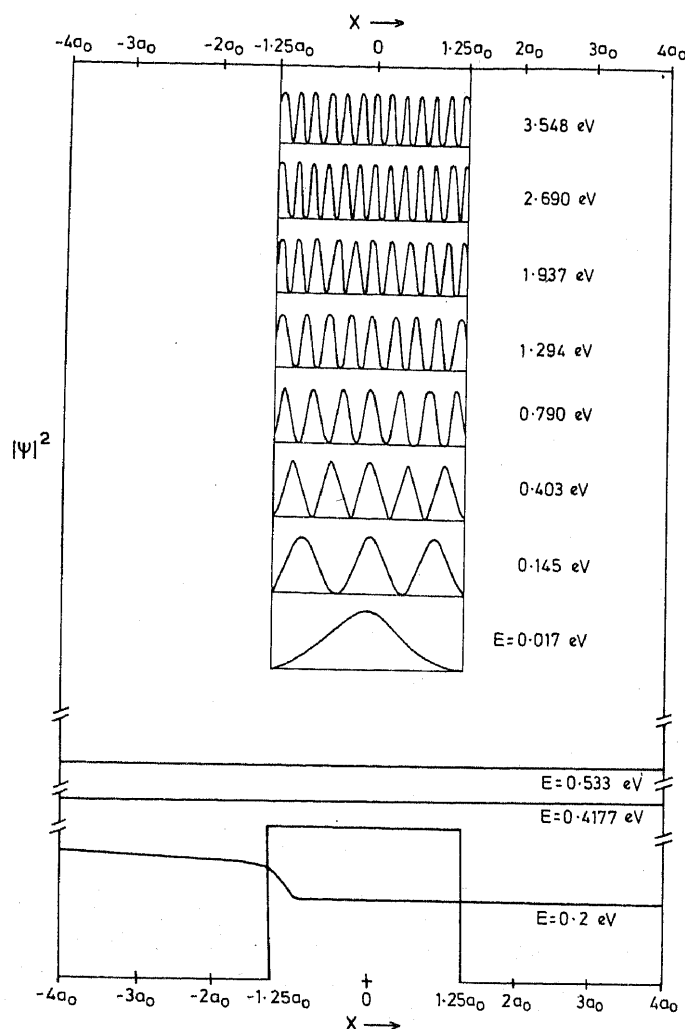


Figure 5. Plots of $|\psi|^2$ for the ground state for different energies and for different bound states of the excited state. For the latter, $|\psi|^2$ is given only for alternate energy states, to avoid crowding.

4. Summary

A model system of a rectangular barrier and a well with parameters appropriate for H_3 , has been worked out to yield the absorption spectra for the transition state at three different collision energies. It is gratifying to note that results from our simple model correlate well with those obtained from the more realistic models by other workers using QCT and time independent as well as time dependent QM calculations.

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