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VIBRATIONAL ENHANCEMENT OF THE REACTION RATE AND STERIC REQUIREMENTS IN THE $H + D_2(v)$ AND $D + H_2(v)$ REACTIONS

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The cone of acceptance for $H+H_2$ reactive collisions is shown to open up upon stretching of the H_2 bond. At a given translational energy, the steric factor is thus much larger for vibrationally excited reagents as demonstrated by classical trajectory computations for $H+D_2(v)$ and $D+H_2(v)$. At a given total energy, the efficacy of reagent vibrational excitation is conveniently represented by a surprisal plot. The surprisal parameter is essentially isotopically invariant.

1. Introduction

There is considerable current interest in the role of reagent vibrational excitation in the $H + H_2$ exchange reaction and its isotopic variants [1–10]. This is due not only to direct experiments [1–4] and dynamical computations [5–10] but also to indirect experiments [11] using very hot H_2 molecules.

Detailed balance can be invoked to show [12] that this question is also directly related to the recently observed [13,14] vibrational energy disposal in the $H + D_2 \rightarrow D + HD(v)$ reaction [13–15].

For reactions with an early or late energy release [16] one can relate the energy requirements to the location of the barrier in the entrance or exit valleys [16]. How can one however interpret the relative role of reagent translation versus vibration in these and other [17,18] nearly thermoneutral reactions with their barrier being roughly midway [9] enroute from reagents to products?

2. The angle dependent barrier

Fig. 1 is a polar plot of the $H + H_2$ realistic [20] potential energy surface. The top panel is for H_2 constrained to its equilibrium separation. The bottom panel is for H_2 stretched to 1.9 au. Rather than an angle-dependent barrier [21] (which gives rise to the steric factor [22–24]) there is clearly a well, favoring nearly collinear approach. The origin of the well is obvious on inspection of the traditional contour map representation of the potential for a fixed angle of approach. Take first the map for a collinear configuration of the three atoms. Consider the line corresponding to a fixed but stretched reagent bond, fig. 2. As we move along this line closer in, the potential drops due to the bending of the reaction path. The well in fig. 1b is a reflection of the lower frequency for the symmetric stretch of H_3 as compared to the stretch in H_2 [25]. Next consider the contour map, fig. 2b, for a bent configuration of H_3. Due to the higher barrier along the reaction path, there is no longer a drop in the potential as one moves in at a fixed H_2 distance.

The well shown in fig. 1b is thus the same well first discussed in ref. [25] and shown there to give rise to the resonances in the reaction dynamics.

3. The steric factor — trajectory computations

For ground-state reagents, the angle-dependent barrier to reaction determines the cone of acceptance. Reaction takes place essentially over that range of initial orientations where there is enough translational energy (along the line-of-centers) to surmount the barrier [26]. The considerations of section 2 suggest that for stretched reactants the barrier will be lower. Hence,

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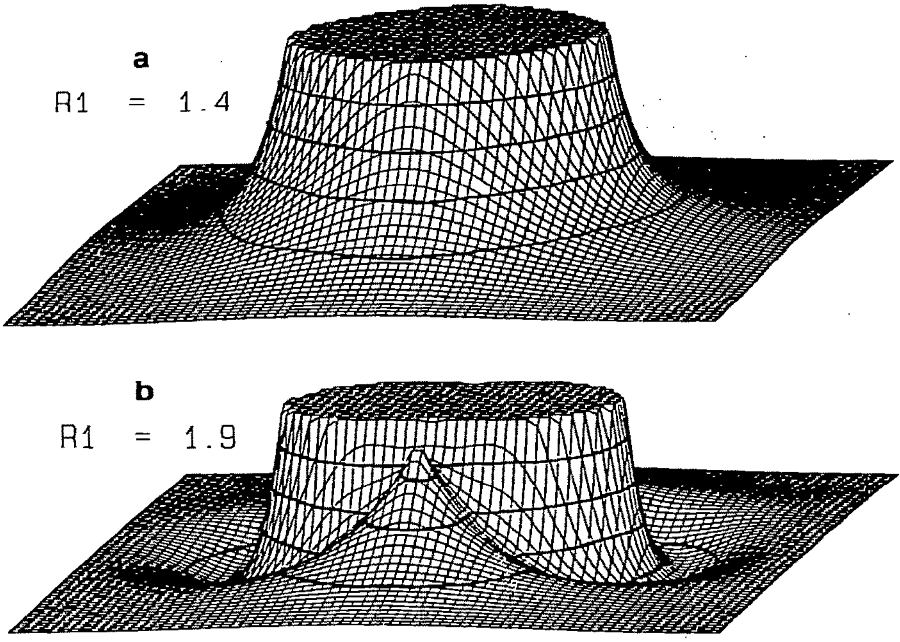

Fig. 1. A stereoscopic projection of the LSTH potential [20] for H + H_2 for a fixed H_2 internuclear separation. In this polar plot the coordinates are the distance of the incident H atom to the center of mass of H_2 and the angle of orientation θ of this distance with respect to the H_2 axis. (a) The H_2 separation is at its equilibrium value. (b) H_2 separation is 1.9 au, roughly corresponding to the outer turning point of the $v = 1$ vibrational state. Shown in both plots are potential energy contours at intervals of 0.02 hartree. The maximum potential value plotted is 0.1 hartree.

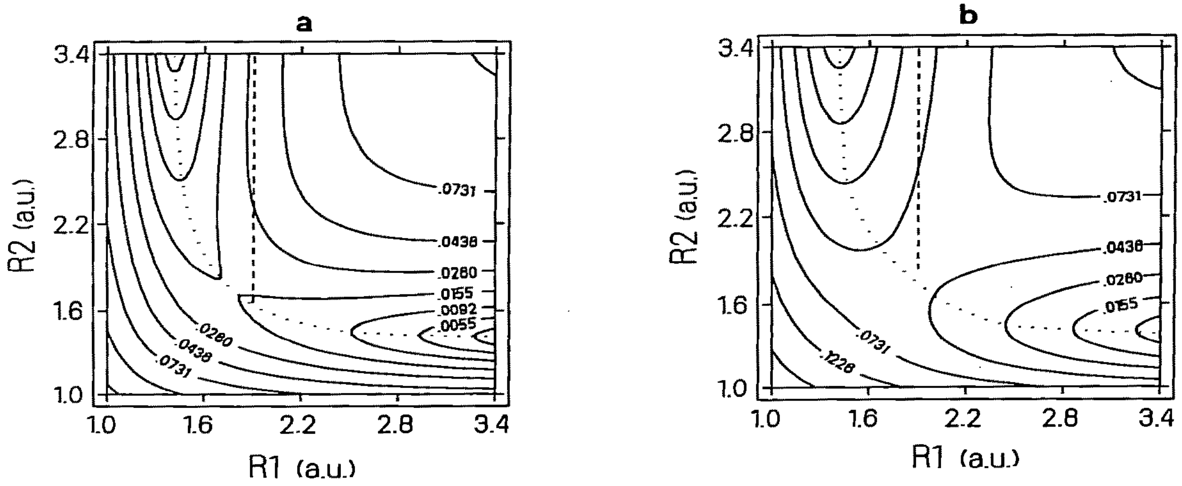

Fig. 2. A contour plot of the LSTH potential [20] for (a) a collinear configuration and (b) a fixed, 90°, angle of H with respect to H_2. The broken line, parallel to the abscissa is drawn at an H_2 separation of 1.9 au, corresponding to fig. 1b. The marked contour levels are in hartree.

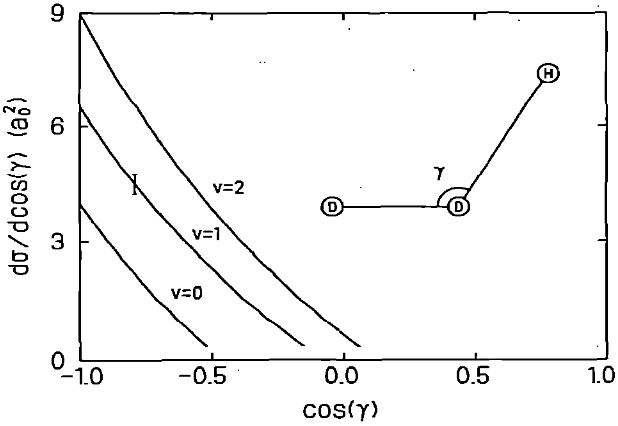

Fig. 3. The reaction cross section (in a_0^2) for oriented reagents in the H + $D_2(v)$ reaction versus cos γ. The area under each curve is the reaction cross section for randomly oriented reagents. Trajectory computations on the LSTH potential [20] at an initial translational energy of 0.55 eV. The measure of the statistical uncertainty in the Monte Carlo trajectory computations is indicated by the bar.

at a given reagent translation, vibrational excitation * will lead to reaction over a wider range of initial orientations. Trajectory computations were carried out for a number of initial translational energies for the H + $D_2(v)$ and also D + $H_2(v)$ reactions. For a given initial translational energy, the orientation dependence of the reaction cross section was determined for several initial vibrational states. Fig. 3 is typical of the results so obtained. The increasing steric factor upon vibrational excitation is quite evident.

As can be seen in fig. 3, increasing reagent vibrational excitation not only opens up the cone of acceptance but also leads to increased reactivity at any given initial orientation. In the simplistic line-of-centers model, the differential cross section for a given orientation is directly determined by the barrier height for that orientation [24,26]. It follows that the angle-dependent barrier is indeed lowered upon vibrational excitation. The lowered barrier implies that the range of impact parameters that can contribute to reaction, at a given orientation, extends to higher values [24].

Upon vibrational excitation the cone of acceptance opens up both to allow reaction over a wider range of initial orientations and to accept a wider range of initial impact parameters.

The line-of-centers criterion suggests and trajectory computations [26] show that increasing the initial translational energy will also increase the range of initial orientations that lead to reaction. Another question is, therefore, whether a given energy increment is more effective as translational or as vibrational excitation. To examine this point trajectory computations were performed at a given total energy, but for different partitions of the given total between vibration and translation. The comparatively high vibration frequency of the hydrides means that such computations are possible only at higher total energies where the cross section is already large. In that range, both forms of excitation were found to be, very roughly, equally effective. Since the difference is only quantitative but not qualitative, we need a more precise measure.

4. Surprisal analysis

On prior grounds, at a given total energy E all initial states of the reagents should react at the same rate [27]. The computed reaction cross sections were therefore multiplied by the initial (sharp) relative velocity to obtain the reaction rate. Since the prior distribution is uniform, a surprisal analysis consists of plotting a set of rates (all computed at the same total energy) versus the fraction, E_v/E, of reagent energy present as vibration. A linear surprisal plot means that the reaction rate $k(v \rightarrow; E)$ for H + $D_2(v)$ (or for D + $H_2(v)$) can be represented as

$$-\ln k(v \rightarrow; E) = \lambda_0 + \lambda_v(E_v/R) , \quad (1)$$

where λ_0 is a constant (that is, dependent on λ_v and possibly on E only). λ_v is thus a differential measure of the change of reaction rate, at a given total energy, with E_v,

$$\lambda_v = -\partial \ln k(v \rightarrow; E)/\partial(E_v/E) . \quad (2)$$

A positive value of λ_v means that at a given value of the total energy, the reaction rate diminishes when energy is put into vibration (at the expense of translation). Vice versa for negative values of λ_v.

Our observation is that λ_v is nowhere large. As long as the cross section rises with reagent translation, λ_v

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* For the anharmonic H_2 potential, the molecule is to be preferentially found in extended configurations.

is somewhat positive. Translation is then more efficient than vibration in inducing the reaction. Once the cross section levels and then decreases, vibrational excitation is somewhat more effective. The mechanism is probably that at higher translational energies some trajectories that did cross the barrier to reaction do not proceed to form products but recross back to the reactants region. Hence excess reagent translational excitation is not beneficial to reaction.

The near invariance of the surprisal parameter for isotopic substitution has been noted for many other reactions and can also be derived from dynamical considerations [28]. We have also performed a surprisal analysis of the role of reagent vibrational excitation in the $D + H_2(v)$ reaction. At, say, $E = 0.059$ au (above $v = 0$), the value of λ_v is $\lambda_v = -0.54 \pm 0.06$ as compared to $\lambda_v = -0.46 \pm 0.08$ for $H + D_2(v)$.

As in other reactions, and as clearly indicated by the theoretical considerations, the isotopic invariance of λ_v applies when the vibrational energy (rather than the vibrational state) is used as the basis for comparison.

5. Concluding remarks

Reagent vibrational excitation in the $H + H_2$ exchange reaction and its isotopic variants lowers the angle-dependent barrier to reaction. The cone of acceptance is then both wider and, for a given initial orientation, accepts a wider range of impact parameters. At a given initial translational energy, the steric factor will therefore markedly increase upon reagent vibrational excitation.

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