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Author

Orel, A.E.

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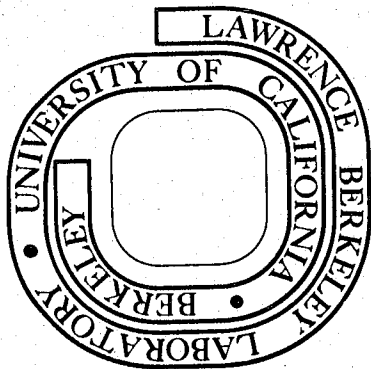
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INFRARED LASER INDUCED CHEMICAL REACTIONS:
CALCULATIONS FOR $X + H_2 \rightarrow HX + H$

A. E. Orel and W. H. Miller*

Department of Chemistry, and Materials and Molecular
Research Division, Lawrence Berkeley Laboratory,
University of California, Berkeley, CA 94720

I. INTRODUCTION

It is well-known that the rate of chemical reactions can be enhanced by vibrationally exciting the reactants with an infrared laser.¹ This has been seen experimentally and also in classical trajectory calculations, and it requires that one of the reactants have an absorption at the frequency of the laser.

We have recently pointed out,² however, that an infrared laser will in general enhance the rate of chemical reactions whether or not the reactants absorb the infrared radiation, in fact even if the reactants are infrared inactive. This collision induced absorption can be understood qualitatively by considering the simple prototype reaction $H + H_2 \rightarrow H_2 + H$, for which the reactants are indeed infrared inactive. Although the reactants have no dipole moment and thus do not absorb radiation, it is easy to see that in the transition state region of the potential energy surface the three hydrogen atoms will have a non-zero dipole moment. Furthermore, this dipole moment varies with the asymmetric stretch motion, $\vec{H} \cdots \vec{H} \cdots \vec{H}$, so that this motion can absorb energy from the radiation field, while the symmetric stretch motion, $\vec{H} \cdots H \cdots \vec{H}$, does not develop a dipole and is thus infrared inactive. The asymmetric stretch, moreover, corresponds to motion along the reaction coordinate, so the system will absorb energy from the field preferentially in the degree of freedom most effective in promoting the reaction.

One can see this somewhat more quantitatively by reference to Figures 1-3. Figure 1 sketches a reactive trajectory on the H_3 potential surface, and Figure 2 shows the qualitative time-

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dependence of the dipole moment of the 3-atom system along this trajectory. The absorption spectrum is proportional to the square modulus of the Fourier Transform of the time-dependent dipole and will have the general appearance as in Figure 3. If, for example, $\mu(t)$ has a functional form

$$\mu(t) \propto t \exp(-\frac{1}{2} t^2/t_0^2) ,$$

one finds

$$|\bar{\mu}(\omega)|^2 \equiv \left| \int_{-\infty}^{\infty} dt e^{i\omega t} \mu(t) \right|^2$$
$$\propto \omega^2 \exp(-\omega^2 t_0^2) .$$

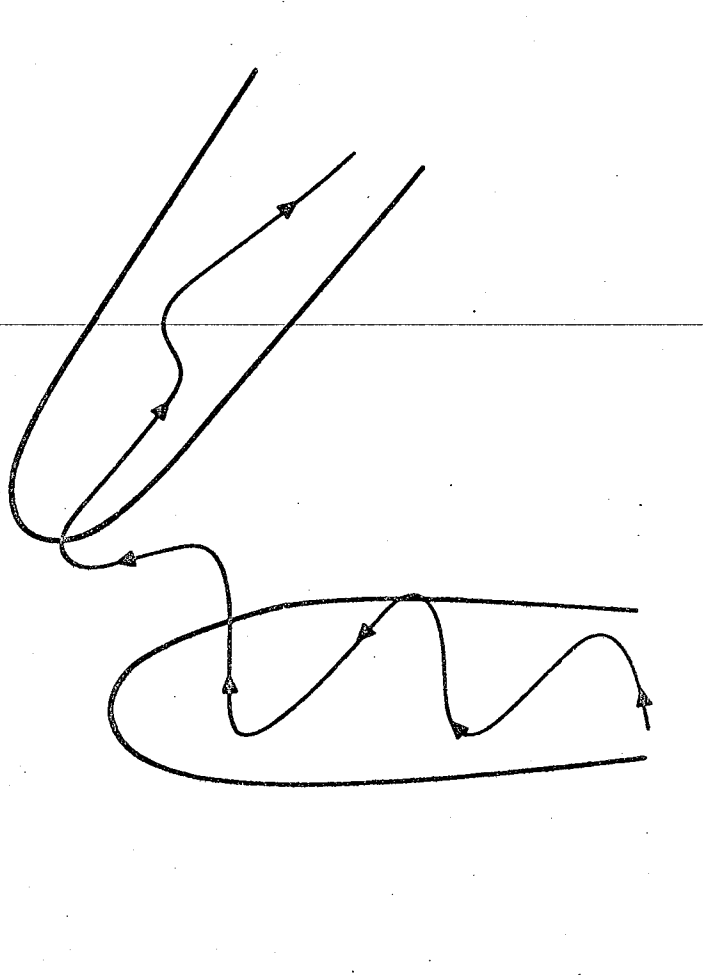


Fig. 1. Sketch of the potential energy surface for the collinear $H + H_2 \rightarrow H_2 + H$ reaction, showing a typical reactive trajectory.

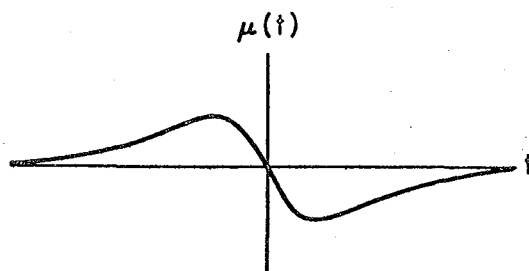


Fig. 2. Sketch of the time dependence of the dipole moment of the H-H-H system along the trajectory in Fig. 1.

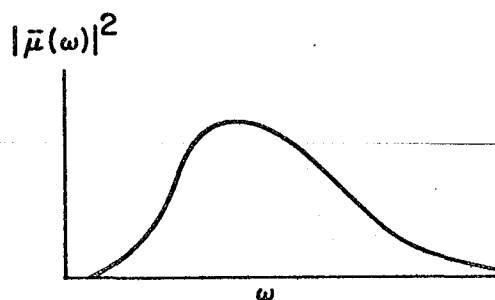


Fig. 3. Sketch of the square modulus of the Fourier transform of the time-dependent dipole of Fig. 2, as a function of frequency ω .

This reactive collision induced absorption is a completely general phenomenon since displacement of a transition state along the reaction coordinate must always be an asymmetric displacement³ and thus infrared active. It is also clear, however, that it is a weak effect--and thus requires a laser--because the system is in the transition state region of the potential energy surface for only a short period of time, i.e., the "concentration of transition states" is small.

In addition to the possibility of accelerating chemical reactions by this collision induced absorption, the effect is also of interest because it is a way of probing the reacting system directly in the interaction region. This is the closest

that one can come to having an infrared spectroscopy of the transition state.

Finally, it should be noted that collision induced absorption is a well known and much studied phenomenon in itself, e.g. in mixed rare gases.⁴ In the present paper our interest is not so much in the absorption spectrum but rather in how the absorption affects the collision dynamics, e.g., by changing non-reactive trajectories into reactive ones.

II. THEORETICAL SUMMARY

In order to carry out quantitative calculations to illustrate and characterize this reactive collision induced absorption we have developed a classical model that treats both molecular and radiative degrees of freedom by classical mechanics.⁵ For a collinear $A + BC \rightarrow AB + C$ reaction in a single mode laser cavity the classical Hamiltonian for the system is

$$H(p_r, r, p_R, R, p_X, X) = \frac{p_R^2}{2\mu} + \frac{p_r^2}{2m} + \frac{p_X^2}{2} + V(r, R) + \frac{1}{2} \omega^2 X^2 - \sqrt{\frac{4\pi\omega^2}{V}} \mu(r, R) X \quad , \quad (2.1)$$

where (r, p_r) , (R, p_R) , and (X, p_X) are the coordinates and momenta for the relative vibration of B-C, translation of A relative to the center of mass of BC, and the radiation field, respectively. m and μ are the corresponding reduced masses, ω is the frequency of the laser, V is the volume of the radiation cavity, $\mu(r, R)$ is the dipole moment of the A-B-C system of a function of its configuration, and $V(r, R)$ is the field-free potential energy surface for the A-B-C system.

One sees that within this classical framework the radiation field enters simply as an additional vibrational degree of freedom, so it is a simple matter to carry out classical trajectory calculations including all the degrees of freedom on the same (classical) footing. In doing so it is useful to replace the cartesian variables of the field, (p_X, X) , by the action-angle variables (N, Q) , so that the Hamiltonian takes the form

$$H(p_r, r, p_R, R, N, Q) = \frac{p_R^2}{2\mu} + \frac{p_r^2}{2m} + V(r, R) + \hbar\omega(N + \frac{1}{2}) - \sqrt{\frac{8\pi\hbar\omega N}{V}} \mu(r, R) \sin Q \quad . \quad (2.2)$$

N is the "quantum number" of the radiation field, i.e., the number of photons, and Q is its phase. Initial conditions for the classical trajectories, and the calculation of the trajectory, are as in the conventional "quasi-classical" approach.

The advantage of this model is that it allows one to carry out non-perturbative calculations, an important feature when dealing with lasers. It is interesting to point out, however, that this classical model is an accurate description of the interaction of radiation and matter also in the perturbative limit. It has been shown,⁴ in fact, that the model contains absorption and induced emission of radiation in the usual way, and even describes spontaneous emission correctly.

III. RESULTS

a. $H + H_2 \rightarrow H_2 + H$

This first example is not of great physical significance but is useful to illustrate the effect. For a laser frequency ω and Rabi frequency (i.e., laser power) ω_R ,

$$\hbar\omega = 945 \text{ cm}^{-1}$$

$$\hbar\omega_R = 0.1 \text{ eV} \quad ,$$

Figure 4 shows how the reaction probability as a function of initial translational energy is affected by the laser: the solid line is the field-free result and the broken line the result with the laser. The important feature is that the activation energy has been lowered by the radiation field; i.e., at energies below the field-free threshold some of the non-reactive trajectories are changed into reactive ones by absorbing energy from the field.

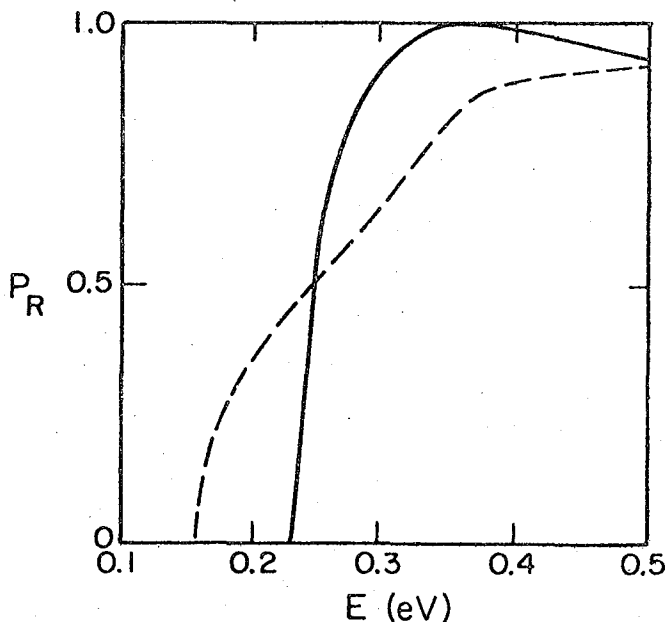


Fig. 4. Reaction probability for the collinear $H + H_2 \rightarrow H_2 + H$ reaction as a function of initial translational energy, without the radiation field (—) and with it (---).

b. $\text{Cl} + \text{H}_2 \rightarrow \text{HCl} + \text{H}$

Figure 5 shows the result of a similar calculation for the reaction of $\text{Cl} + \text{H}_2$. Here

$$\hbar\omega = 100 \text{ cm}^{-1},$$

and the results are shown for two different Rabi frequencies. The effect is qualitatively similar, and one sees the necessity of high power in the radiation field.

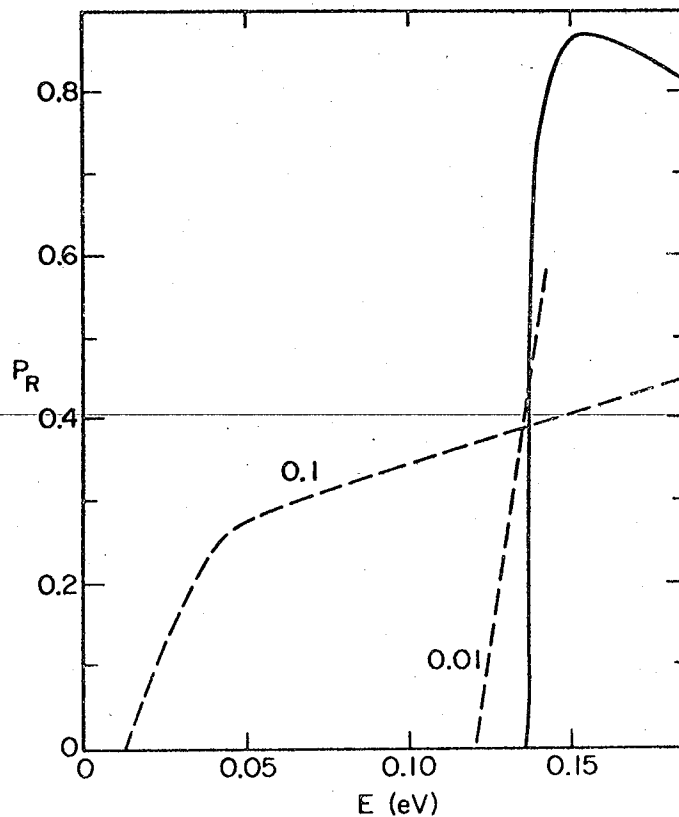


Fig. 5. Same as Fig. 4, but for the reaction $\text{Cl} + \text{H}_2 \rightarrow \text{HCl} + \text{H}$. The numbers refer to the Rabi frequency, $\hbar\omega_R$ (eV), used in the calculation.

c. $\text{F} + \text{H}_2 \rightarrow \text{HF} + \text{H}$

Figure 6 shows similar results for the $\text{F} + \text{H}_2$ reaction, here with

$$\hbar\omega = 100 \text{ cm}^{-1}$$

$$\hbar\omega_R = 0.1 \text{ eV}$$

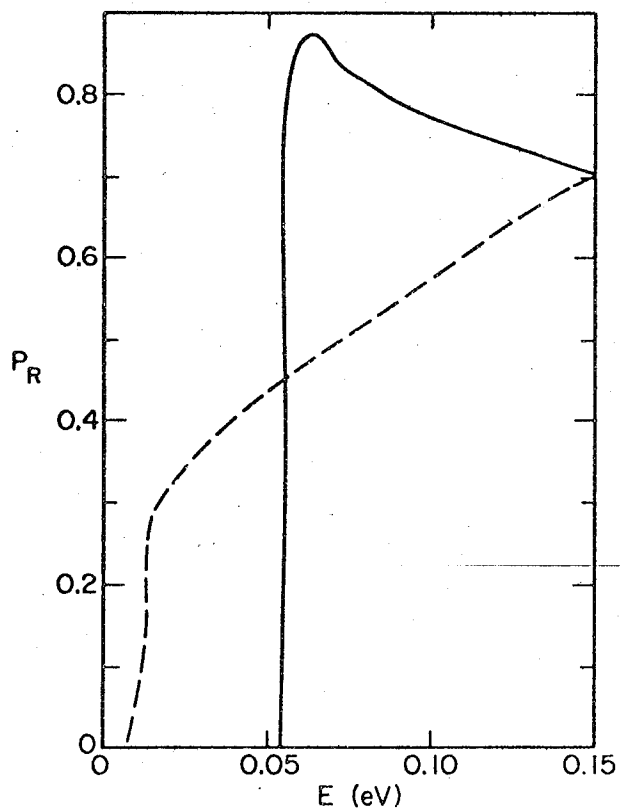


Fig. 6. Same as Fig. 4, but for the reaction $F + H_2 \rightarrow HF + H$.

IV. CONCLUDING REMARKS

We have shown that reactive systems exhibit a collision induced absorption which enhances the rate of reaction by effectively lowering the activation energy. The classical model that has been developed describes the phenomenon correctly and can be used to investigate its various aspects theoretically. Experimental studies of this process should be quite interesting.

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