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Author

Orel, A.E.

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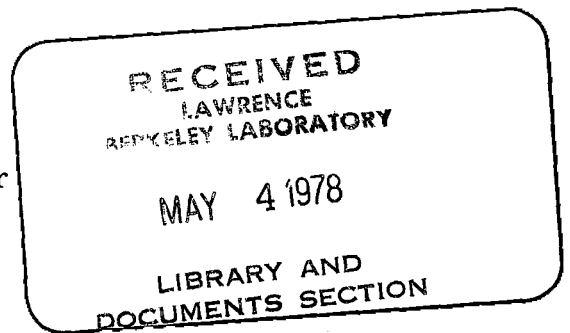
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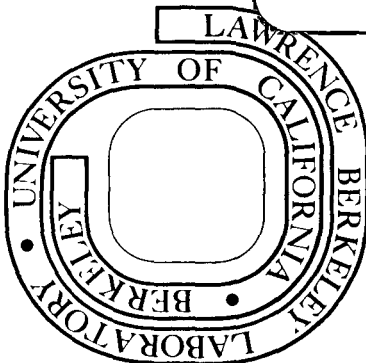
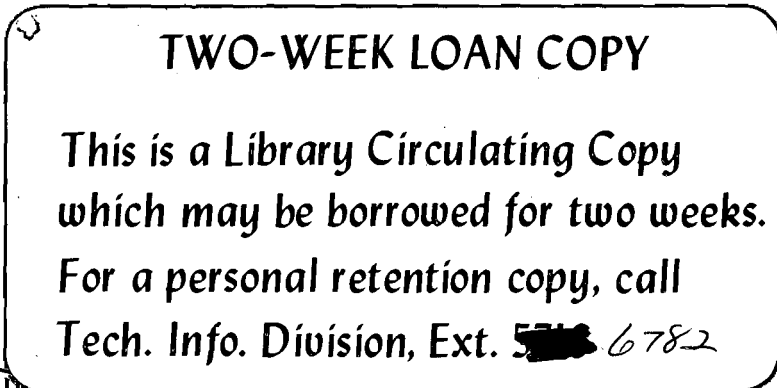
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A. E. Ore1 and W. H. Miller

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INFRARED LASER INDUCED CHEMICAL REACTIONS

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

It is well-known that an infrared laser can accelerate chemical reactions by vibrationally exciting one of the reactant species; e.g., $\text{HCl}(v) + \text{K} \rightarrow \text{KCl} + \text{H}$ proceeds much faster for $v = 1$ than for $v = 0$.¹ For the laser to be effective in promoting the reaction this way it is thus necessary for its frequency to be in the region that excites HCl from the $v = 0$ to the $v = 1$ vibrational state.

This Communication points out that infrared lasers can enhance chemical reactions even if they are far from any regions where the reactants absorb, or even if the reactants are infrared inactive. As prototype for a reaction with an activation barrier consider the $\text{H} + \text{H}_2 \rightarrow \text{H}_2 + \text{H}$ reaction, for which the reactants are clearly infrared inactive. In the transition state region of the potential energy surface, however, it is clear that motion along the reaction coordinate--the asymmetric stretch, $\overset{\uparrow}{\text{H}} \cdots \overset{\rightarrow}{\text{H}} \cdots \overset{\uparrow}{\text{H}}$ --is infrared active, i.e., the dipole moment of the three-atom system varies with this coordinate. The symmetric stretch, $\overset{\uparrow}{\text{H}} \cdots \text{H} \cdots \overset{\uparrow}{\text{H}}$, on the other hand, is infrared inactive since the dipole moment does not vary with this displacement. An infrared laser can thus excite the system when it is in the transition state region, and the energy is put specifically into motion along the reaction coordinate, the degree of freedom most effective in promoting the reaction.

The most interesting consequence of this type of "collision-induced adsorption" is that the activation energy for the reaction is lowered by the presence of a high power infrared laser. This effect is easily understood since without a field there are no trajectories that react at energies below the classical threshold, while in the presence of the field some of these non-reactive trajectories gain sufficient energy from the

field to become reactive.

The effect can be seen explicitly by carrying out the appropriate calculation for a one-dimensional example. If the zero of energy is chosen as the top of the potential barrier, then the classical reaction probability without a laser field is a step function: $P_R(E) = 1$ for $E > 0$, and 0 for $E < 0$, as seen in Figure 1. In the presence of the field a simple perturbation theory calculations gives $P_R(E) \approx \frac{1}{2} + \frac{1}{\pi} \sin^{-1}(E/E_0)$, where $E_0/\hbar \sim \omega_R$, the Rabi frequency associated with the transition; this is also shown in Figure 1. High laser power is thus required; e.g., for a reasonably strong dipole transition, a laser power of 10^6 watts/cm² corresponds to only $\hbar\omega_R \sim 1$ cm⁻¹, a small shift, but a power of 10^{12} watts/cm² would give $\hbar\omega_R \approx 1000$ cm⁻¹ and thus a large effect.

More realistic (and non-perturbative) calculations have been carried out for the prototype $H + H_2$ reaction. The theoretical approach² being used treats both the molecular degrees of freedom and the radiation field classically; one carries out a classical trajectory calculation for the complete system, the molecular system plus the field oscillator. Figure 2 shows results for the collinear version of the reaction, and one sees that the qualitative behavior is similar to that of the one-dimensional model discussed above. These results are for $\hbar\omega_R = 0.1$ eV and an empirical (but qualitatively correct) dipole moment function for the H_3 system. The laser frequency corresponds to the CO_2 laser $\hbar\omega = 948$ cm⁻¹, although other frequencies have been investigated. Though not highly sensitive to laser frequency, there is nevertheless an optimum intermediate region: The dashed curve in Figure 1 is only slightly different for $\hbar\omega \sim 500$ cm⁻¹, but the threshold-lowering is significantly less for much higher (~ 2000 cm⁻¹) or lower (~ 100 cm⁻¹) frequencies.

In concluding we note that this type of laser induced reaction is expected to be quite general since the reaction coordinate is the "least symmetric"³ degree of freedom of the transition state and will thus always be infrared active. Other examples of more physical interest are being explored.

References

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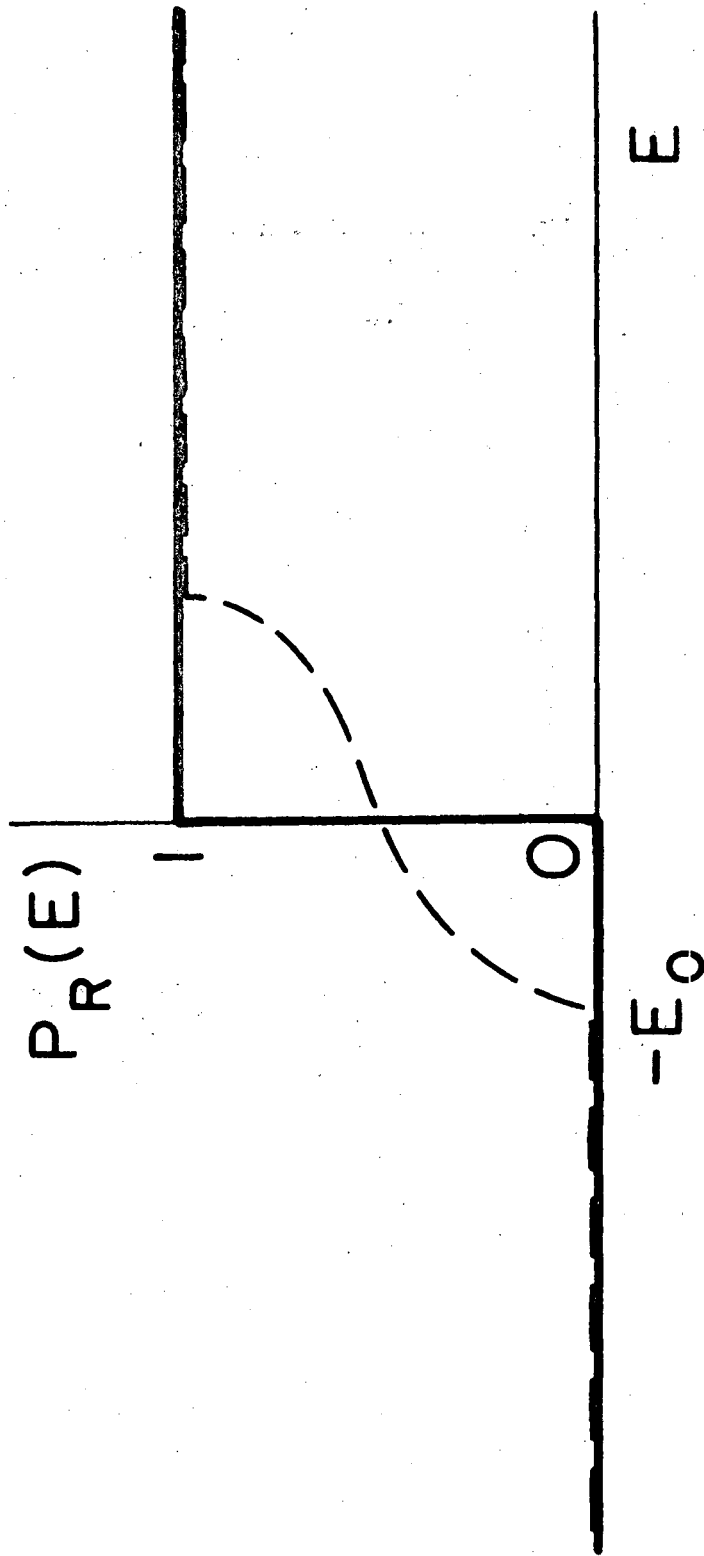
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Figure Captions

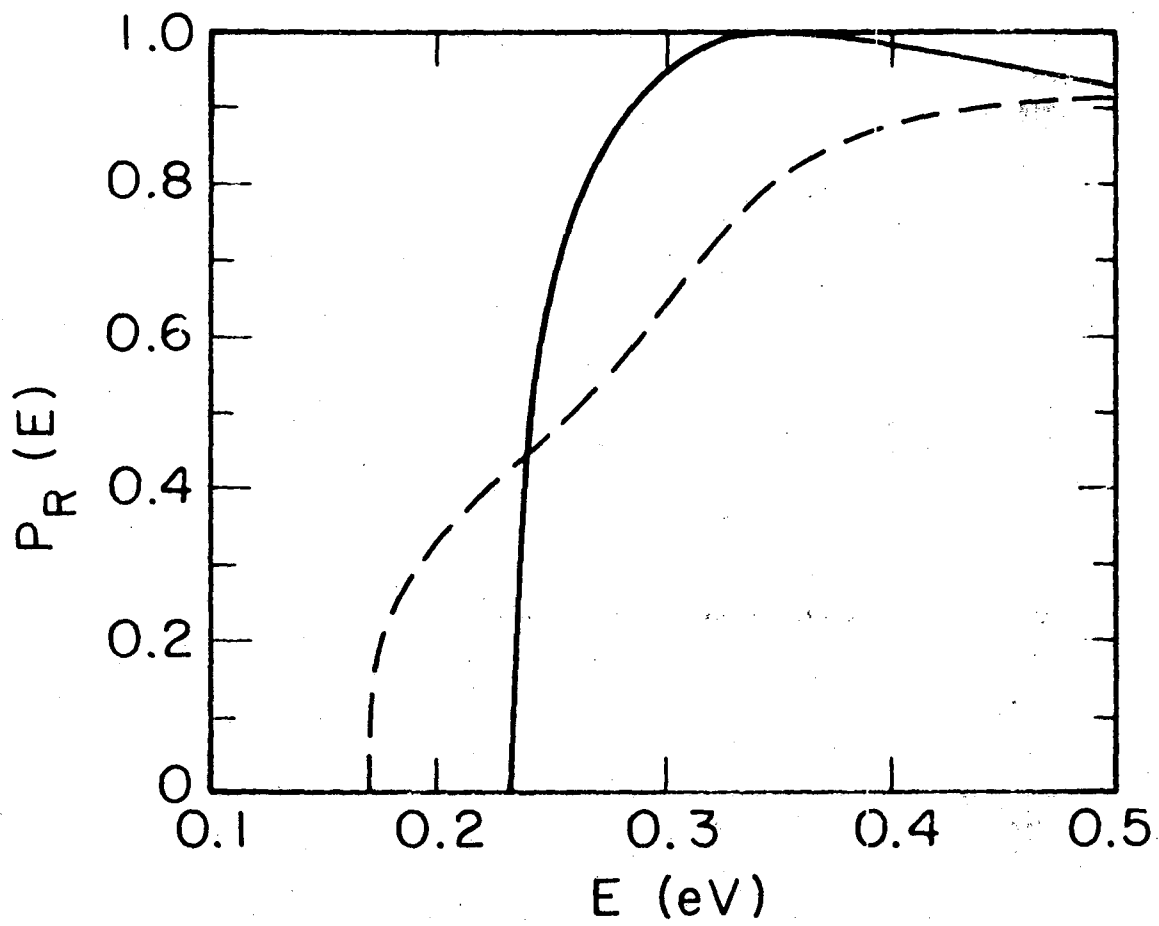
1. Classical "reaction probability" for a particle incident on a one-dimensional potential barrier, as a function of the energy E relative to the top of the barrier. The solid line is for the field-free case, and the dashed line the result in the presence of a laser field.

2. Classical reaction probability for the collinear $\text{H} + \text{H}_2 (v=0) \rightarrow \text{H}_2 + \text{H}$ reaction on the Porter-Karplus potential surface, as a function of the initial translational energy E . The solid curve is the ordinary field free result, and the dashed curve the result in the presence of a laser of frequency $\hbar\omega = 948 \text{ cm}^{-1}$ and of an intensity such that $\hbar\omega_R = 0.1 \text{ eV}$.



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Figure 1



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Figure 2

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LAWRENCE BERKELEY LABORATORY
UNIVERSITY OF CALIFORNIA
BERKELEY, CALIFORNIA 94720