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LASER-INDUCED NON-ADIABATIC COLLISION PROCESSES

A.E. Orel

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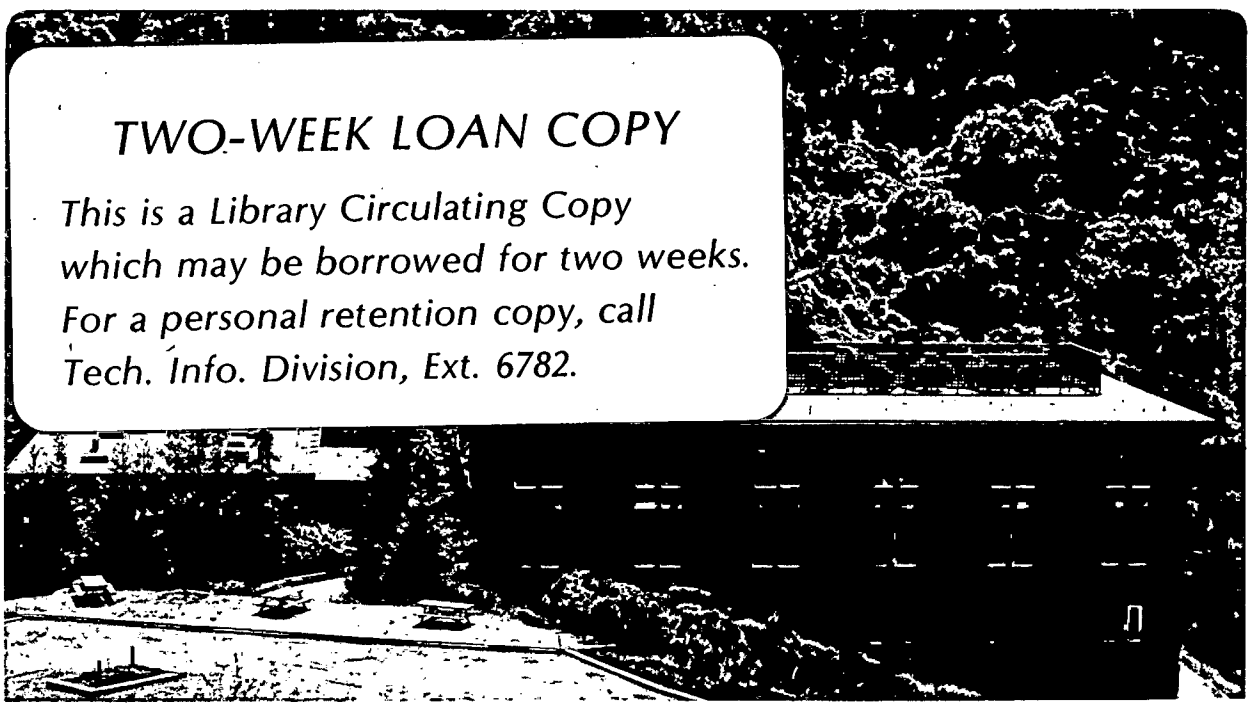

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LASER-INDUCED NON-ADIABATIC COLLISION PROCESSES

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I. INTRODUCTION

The subject of laser interactions with molecular processes has generated great interest both experimentally and theoretically. This interest has been enhanced by the possibilities for laser-catalyzed chemical reactions, isotopic selectivity and perhaps even the determination of the transition state structure. The degree of success in this area has been limited by the extreme difficulties of the experiments involved and also the lack of simple and qualitatively accurate theoretical models that can be applied to a wide range of systems.[1-18]

In this paper we present a classical model which describes the interaction of a visible/UV laser with a two-state system. In this model all degrees of freedom--translation, vibration, rotation, electronic, and the laser field itself are described by classical mechanics and therefore in a dynamically consistent fashion. This model has several advantages. First, since all degrees of freedom are treated equally, it is possible to observe resonance phenomena that cannot be seen if certain degrees of freedom are treated with different approximations. Second, since the method basically involves the addition of two degrees of freedom, that is, four equations of motion to the standard classical trajectory calculation, it is possible to handle cases where quantum mechanical treatments are presently impossible (e.g., three-dimensional two-state collision systems).

The classical model is briefly outlined in Section II, including the additional complications involved in a full three-dimensional calculation,

and applied to both collinear and three-dimensional LiF + H → Li + FH for a variety of field strengths and laser frequencies. It is found that at certain collision energies (which depend on the laser frequency) below the classical threshold the reaction probability is greatly enhanced due to a Franck-Condon like effect. The same argument is able to predict structure in the reaction probability for a quantum mechanical calculation even when the reaction probability is too small to be seen classically.

Finally in the last two sections we present preliminary calculations on two other interesting phenomena. The possibility of laser inhibition of a chemical reaction is studied using a collinear model with parameters similar to $H + H_2$. This inhibition is a very large effect which can be seen at quite small laser field strengths, and which can sometimes destroy the effect of increased reaction probability on the lower state. The last section deals with the isotopic effects on reaction probability induced by the substitution of deuterium for hydrogen in the collinear reaction LiF + H.

II. THE CLASSICAL MODEL: APPLICATION TO LiF + H

Since the theory for the classical description of a two-state system in a laser field has been described previously, only a brief presentation is given here.[12] The classical Hamiltonian for this system has the form

$$H = H_{MOL} + H_{RAD} + H_{INT} \quad , \tag{2.1}$$

where,

$$H_{MOL}(\underset{\sim}{p},\underset{\sim}{x},n,q) = \frac{\underset{\sim}{p}^2}{2m} + (1-n)\, H_{00}(\underset{\sim}{x}) + n\, H_{11}(\underset{\sim}{x}) + 2\sqrt{n(1-n)}\, H_{01}(\underset{\sim}{x}) \cos q \tag{2.2}$$

$$H_{RAD} = \hbar\omega N \tag{2.3}$$

$$H_{INT} = -\sqrt{\frac{8\pi\hbar\omega}{V}}\sqrt{N}\;\; \mu(\underset{\sim}{x},n,q) \cos Q \tag{2.4}$$

where $(\underset{\sim}{x},\underset{\sim}{p})$ are the nuclear coordinates and momentum, (n,q) are the classical action-angle variables describing the electronic degree of freedom, (N,Q) are the classical action-angle variables for the laser field, $H_{nn'}(\underset{\sim}{x})$ $n = 0,1$ is the diabatic potential energy surface, ω is the laser frequency, V is the volume of the radiation field, and $\mu(\underset{\sim}{x},n,q)$ is the component of the molecular dipole moment along the polarization vector of the laser. The dipole moment μ can be expressed in terms of the action-angle variables for the electronic degree of freedom (n,q) as

$$\mu(\underset{\sim}{x},n,q) = (1-n)\, \mu_{00}(\underset{\sim}{x}) + n\, \mu_{11}(\underset{\sim}{x}) + 2\sqrt{n(1-n)}\, \mu_{01}(\underset{\sim}{x}) \cos q \tag{2.5}$$

where $\mu_{nn'}(x)$ $n = 0,1$, is the matrix of the dipole moment operator in the electronic basis.[19-22] Therefore the complete Hamiltonian for this system becomes

$$H(\underset{\sim}{p},\underset{\sim}{x},n,q,N,Q) = p^2/2m + (1-n)\, H_{00}(\underset{\sim}{x}) + n\, H_{11}(\underset{\sim}{x}) + 2\sqrt{n(1-n)}\, H_{01}(\underset{\sim}{x}) \cos q + \hbar\omega N - \sqrt{\frac{8\pi\hbar\omega}{V}}\, \sqrt{N} \cos Q[(1-n)\mu_{00}(\underset{\sim}{x}) + n\mu_{11}(\underset{\sim}{x}) + 2\sqrt{n(1-n)}\, \mu_{01}(\underset{\sim}{x}) \cos q] \quad .$$

Though this is the complete classical description of the system, for the cases studied here several simplifying approximations are valid.

1) $H_{01} = 0$: This corresponds to neglecting any electronically adiabatic effects in the absence of the field.[19-22]

2) $\mu_{00}(\underset{\sim}{x}) = \mu_{01}(\underset{\sim}{x}) = 0$: This approximation neglects the interaction of nuclear motion with the laser field within an electronic state.[9-11] This is valid because the laser frequency used in this application is visible/UV not infrared. The Hamiltonian then simplifies to

$$H(\underset{\sim}{p},\underset{\sim}{x},n,q,N,Q) = \frac{\underset{\sim}{p}^2}{2m} + (1-n)\, H_{00}(\underset{\sim}{x}) + n\, H_{11}(\underset{\sim}{x}) + \hbar\omega N - \sqrt{\frac{8\pi\hbar\omega}{V}}\, 2\sqrt{N}\sqrt{n(1-n)}\, \mu_{01}(\underset{\sim}{x}) \cos Q \cos q \quad . \tag{2.7}$$

(The usual Langer modification $n(1-n) \rightarrow (n+\frac{1}{2})(\frac{3}{2}-n)$ is also made to equation (2.7); N is so large that changing $N \rightarrow N + \frac{1}{2}$ has no effect.)

The first system studied was collinear LiF + H → Li + HF. This system has been studied quantum mechanically by Light, et al.[7] and more

recently by Kulander.[18] The parameters for the two LEPS potential surfaces used in the calculation are listed in Table II of reference 7. The Hamiltonian is that of Eq. (2.7) and standard quasi-classical trajectories were run on the system with the four additional equations of motion due to the laser field and electronic degree of freedom. Further details can be found in reference 12.

The reaction probability for two different laser frequencies and the same laser field strength are shown in Figure 1. These curves have several important features that are typical of the process both classically and quantum mechanically.

The threshold for reactive scattering is lowered. This effect increases as the field strength increases and also is largest when the laser frequency is equal to the asymptotic splitting between the two potential energy surfaces. This is caused by transitions to the excited state surface where the reaction probability is much higher.

A much more interesting phenomenon occurs at much lower translational energies, where peaks occur in both the quantum and classical reactive probabilities. These peaks are due to a Franck-Condon like effect between the nuclear motion, the field and the two potential energy surfaces. If the laser frequency is fixed, this determines a set of intersection points between the excited state surface and the dressed ground state surface (the ground state + $\hbar\omega$). At certain translational energies, the classical turning points (both vibrational and translational) occur at this intersection. Since the system spends most of its time in the vicinity of the classical turning point, there is an enhancement in the probability of transition to the upper potential energy surface and hence a peak in the reactive probability. Classically two peaks are predicted, one at

the inner turning point and the other at the outer vibrational turning point. Of course quantum mechanically the ground vibrational state wave function is not peaked at the classical turning points but has only one maximum. It is interesting to note that in quantum calculations only one peak was observed at the "small r", the so-called "outer" turning point of the collinear system.[18] This effect is quite general and seen in all the systems studied.

In the three-dimensional calculations the equations of motion become slightly more complicated. As in the collinear case $\mu_{01}(\underset{\sim}{x})$ is taken as a constant. However

$$\mu_{01}(\underset{\sim}{x}) = \vec{\mu}_{01}\cdot\hat{\varepsilon} = \mu_{01}(\hat{\mu}\cdot\hat{\varepsilon}) \tag{2.8}$$

where $\vec{\mu}_{01}$ is a vector of constant magnitude μ_{01} in a direction $\hat{\mu}$ which is perpendicular to the plane of the three atom system. Therefore $\frac{\partial\mu_{01}(\underset{\sim}{x})}{\partial\underset{\sim}{x}}$, where $\underset{\sim}{x}$ is the vector of coordinates of the particles, is no longer zero as in the collinear case but a function of the relative positions of the atoms.

Besides this additional complication the calculation is carried out using standard quasi-classical trajectory methods[23] (which have been described elsewhere) with the inclusion of the four equations of motion describing the laser field and electronic degree of freedom.

It was found that the cross-sections for three-dimensional LiF + H on the ground state surface without the field were extremely small. The cross-section at one laser intensity and several laser frequencies is compared to that without the field in Figure 2. The threshold for reaction was lowered in all cases. There was no significant variation found with

the polarization of the laser field. At most frequencies there were no low translational energy peaks and those that occurred were significantly reduced. This is due in part to the three-dimensional nature of the problem since the simple vibrational/translational turning point structure is washed out by the rotation of the system. Also, the motion on the ground state is primarily repulsive for many of the approach parameters so the system cannot enter into a favorable region for excitation to the upper potential energy surface.

III. LASER INHIBITION OF CHEMICAL REACTION

The model used in this calculation is very similar to that described by Light, et al.[7] The ground state surface was taken to be the Karplus-Porter potential surface for $H + H_2$. The excited state was taken to be a LEPS surface for $H + H_2$ shifted upward by 0.5 eV but with the Sato parameter δ as 0.20. The effect of this change is to lower the barrier to reaction and shift the reaction path slightly. As described in the previous section and in reference 12 it is possible to predict for a given laser frequency the resonant translational energies, that is the translational energies where transitions to the excited potential energy come into resonance causing a peak in the reactive probability. Figure 3 shows the difference between the two potential energy surfaces at the vibrational/translational turning points for the system as a function of translational energy. To obtain the translational energies where the Franck-Condon like factors are favorable for transition to the upper surface, a horizontal line is drawn across the graph at the laser frequency.

A quasi-classical calculation was carried out for this system as described in the previous section. In Figure 4 the probability of transition to the excited potential energy surface as a function of translational energy is plotted for one laser field strength and a series of laser frequencies. Peaks occur at the predicted translational energies.

So far only the effect of the laser on the reactive probability on the lower surface has been considered. It is also possible to study the effect of the laser on the reaction probability on the excited surface. At the laser frequencies and field strengths studied for LiF + H the

effect was small, due to the large differences in the potential energy surfaces. However in this model the two potential energy surfaces are very similar so the region of favorable interaction overlaps considerably. In Figure 5 the reaction probability in the presence of the field at several laser frequencies is compared to that of the field-free case. There is significant inhibition of reaction on the upper state potential energy surface. In Figure 6 this effect is illustrated as a function of field strengths. For even quite low field strengths ($\mu \cdot E = 0.001$ eV) the effect is still pronounced. It is important to note that the largest probability for transition to the upper state potential energy surface from the lower surface occurs where a large inhibition of the reaction probability on the upper surface occurs. These two effects tend to cancel, resulting in the reaction probability on the lower surface shown in Figure 7. Quantum mechanically a similar effect occurs, however a residual peak is still seen at the positions marked in Figure 3.[18] It is interesting to note that these again occur at the "small r" (outer) turning point.

IV. EFFECT OF ISOTOPIC SUBSTITUTION

In this section preliminary results on the effect of isotopic substitution on the enhancement of chemical reactions via a collision induced absorption is discussed. The system studied is the same as that used in Section II but with the hydrogen replaced with deuterium. All other parameters remained the same. In Figure 8 the results for LiF + D are compared to those of LiF + H for one laser frequency and field strength. As can be seen, the peak is shifted and narrowed. This suggests the interesting possibility that isotopic-specific enhancement may occur during a chemical reaction, though much further work is necessary before any definitive statement can be made.

V. CONCLUSION

The purpose of this paper was to illustrate the use of a completely classical model to study the laser enhancement of chemical reactions via a collision induced absorption. It is found that the model is easy to apply to a wide range of collinear and three-dimensional examples. It is interesting to note that the quantum mechanical calculation is in qualitative agreement with the classical calculation in the collinear A + BC examples and that a very simple calculation (c.f. Figure 3) can predict the Franck-Condon structure in the quantum-mechanical reaction. A further study of three-dimensional systems is necessary to see if the low energy structure in the reaction probability is always weak or whether this is an artifact of the particular model. Other preliminary calculations have illustrated the laser inhibition of chemical reactions with very small field strengths as well as isotopic effects in these systems. Further work is necessary to explore these interesting possibilities.

Finally there is one aspect of these processes which has not yet been explored, the absorption spectra itself. That is, changes in the laser field (the absorption and emission of photons) due to the collision. This could be an interesting probe of the two potential energy surfaces involved in the reaction.

Acknowledgments

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Figure Captions

1. Total reaction probability for collinear H + LiF → HF + Li as a function of the initial translational energy E_{tr}, from a quasi-classical trajectory calculation. LiF is initially in its ground vibrational state. The dotted curve is the laser-free result. The other two curves are for a laser power such that $\mu_{01}E_0 = 0.01$ eV and a frequency $\hbar\omega = 6.2$ eV (solid curve) and 6.4 eV (dashed curve). (Reprinted with permission of The Journal of Chemical Physics.)

2. Total cross-section (a_0^2) for three-dimensional H + LiF → HF + Li as a function of the initial translational energy E_{tr}, from a quasi-classical trajectory calculation. LiF is initially in its ground vibrational-rotational state. The dotted curve is the laser-free result. The other two curves are for a laser power such that $\mu_{01}E_0 = 0.01$ eV and a frequency $\hbar\omega = 6.5$ eV (solid curve) and 6.2 eV (dashed curve).

3. Shown are the Franck-Condon frequencies $\Delta V \equiv V_1(R_k,r_k) - V_0(R_k,r_k)$ where (R_k,r_k), k = 1,2 are the two simultaneous translation-vibration turning points on the ground state potential surface, as a function of the initial translational energy, E_{tr}, for the model system with $H + H_2$ parameters. The position of peaks in the quantum mechanical probability for $\mu_{01}E_0 = 0.01$ are marked by crosses.

4. The probability for transition to the upper state potential surface for the model $H + H_2$ system as a function of the initial translational energy E_{tr}, from a quasi-classical trajectory calculation. H_2 is initially in its ground vibrational state. The curves are for a laser power such that $\mu_{01}E_0 = 0.01$ eV and a frequency $\hbar\omega = 0.017\ a_0$

(solid curve), 0.0165 a_0 (dashed curve) and 0.016 a_0 (dash-dot curve).

5. Total reaction probability on the upper state surface for the model $H + H_2$ system as a function of initial translational energy, E_{tr}, from a quasi-classical calculation. H_2 is initially in its ground vibrational state. The dotted curve is the laser-free result. The curves are for a laser power such that $\mu_{01}E_0 = 0.01$ eV and frequency $\hbar\omega = 0.017\ a_0$ (solid curve), 0.0165 a_0 (dashed curve) and 0.016 a_0 (dot-dash curve).

6. Total reaction probability as in Figure 5. The dotted curve is the laser-free result as in Figure 5. The laser frequency is $\hbar\omega = 0.017\ a_0$ and the laser field strength is such that $\mu_{01}E_0 = 0.01$ eV (solid curve), 0.005 eV (dashed curve) and 0.001 eV (dash-dot curve).

7. Total reaction probability on the state surface for the model $H + H_2$ system as a function of initial translational energy, E_{tr}, from a quasi-classical calculation. H_2 is initially in its ground vibrational state. The dotted curve is the laser-free result. The curves are for a laser power such that $\mu_{01}E_0 = 0.01$ eV and frequency $\hbar\omega = 0.017\ a_0$ (solid curve), 0.0165 a_0 (dashed curve) and 0.016 a_0 (dash-dot curve).

8. Total reaction probability for collinear $LiF + H \rightarrow HF + Li$ (solid curve) and collinear $LiF + D \rightarrow DF + Li$ (dashed curve) as a function of initial translational energy, E_{tr}, from a quasi-classical calculation. LiF is initially in its ground vibrational state. The curves are for a laser power such that $\mu_{01}E_0 = 0.01$ eV and a laser frequency $\hbar\omega = 6.2$ eV.

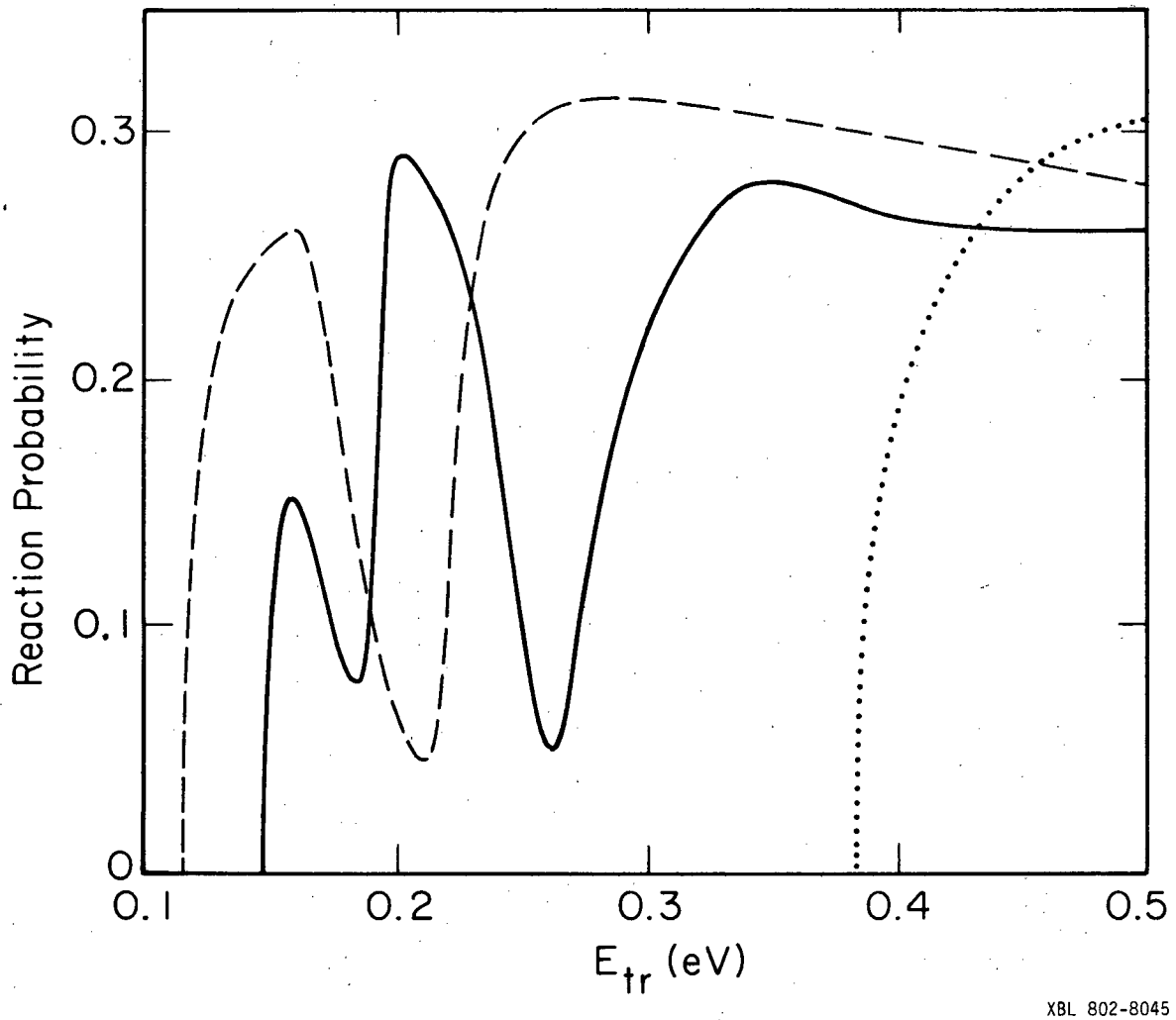

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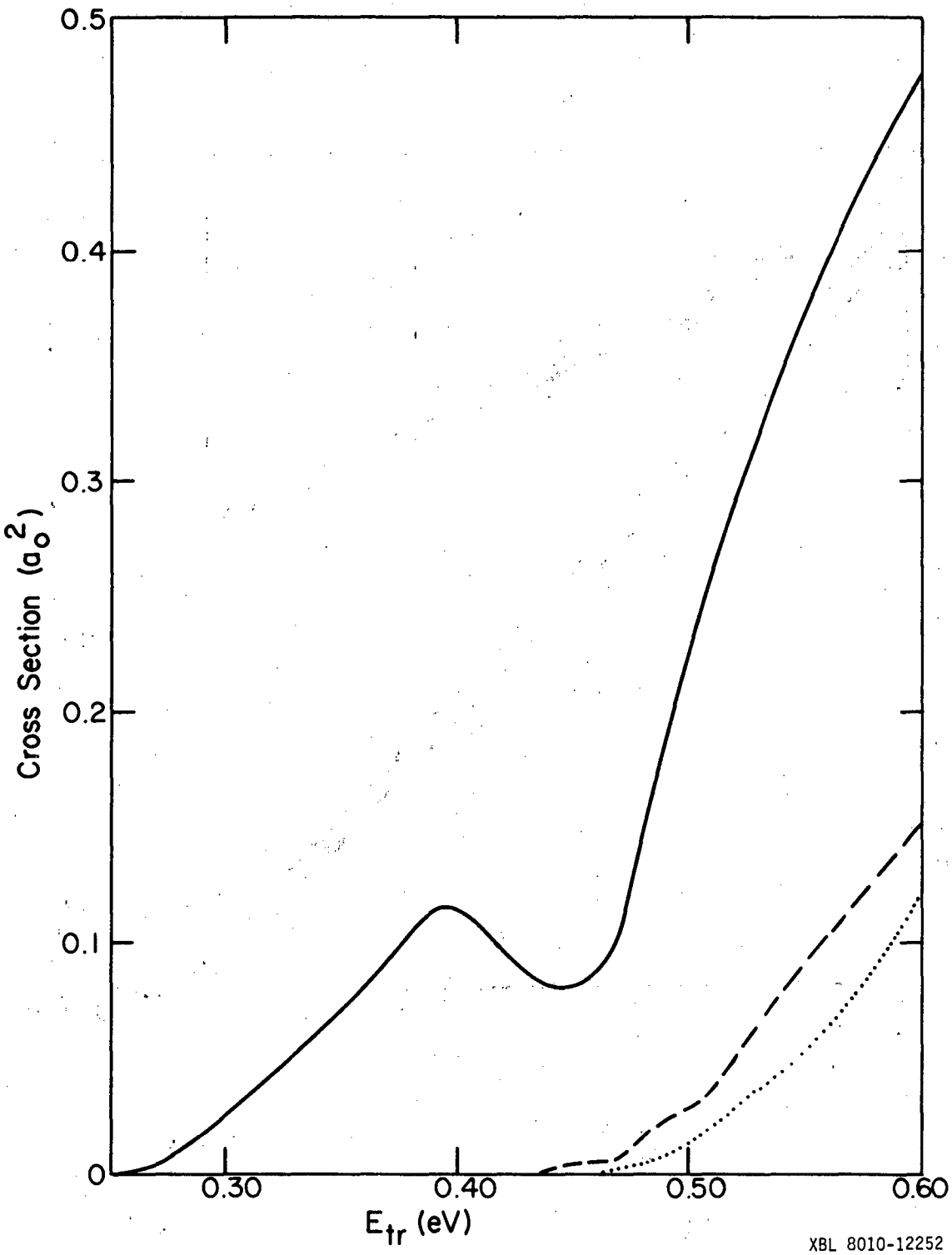
Figure 1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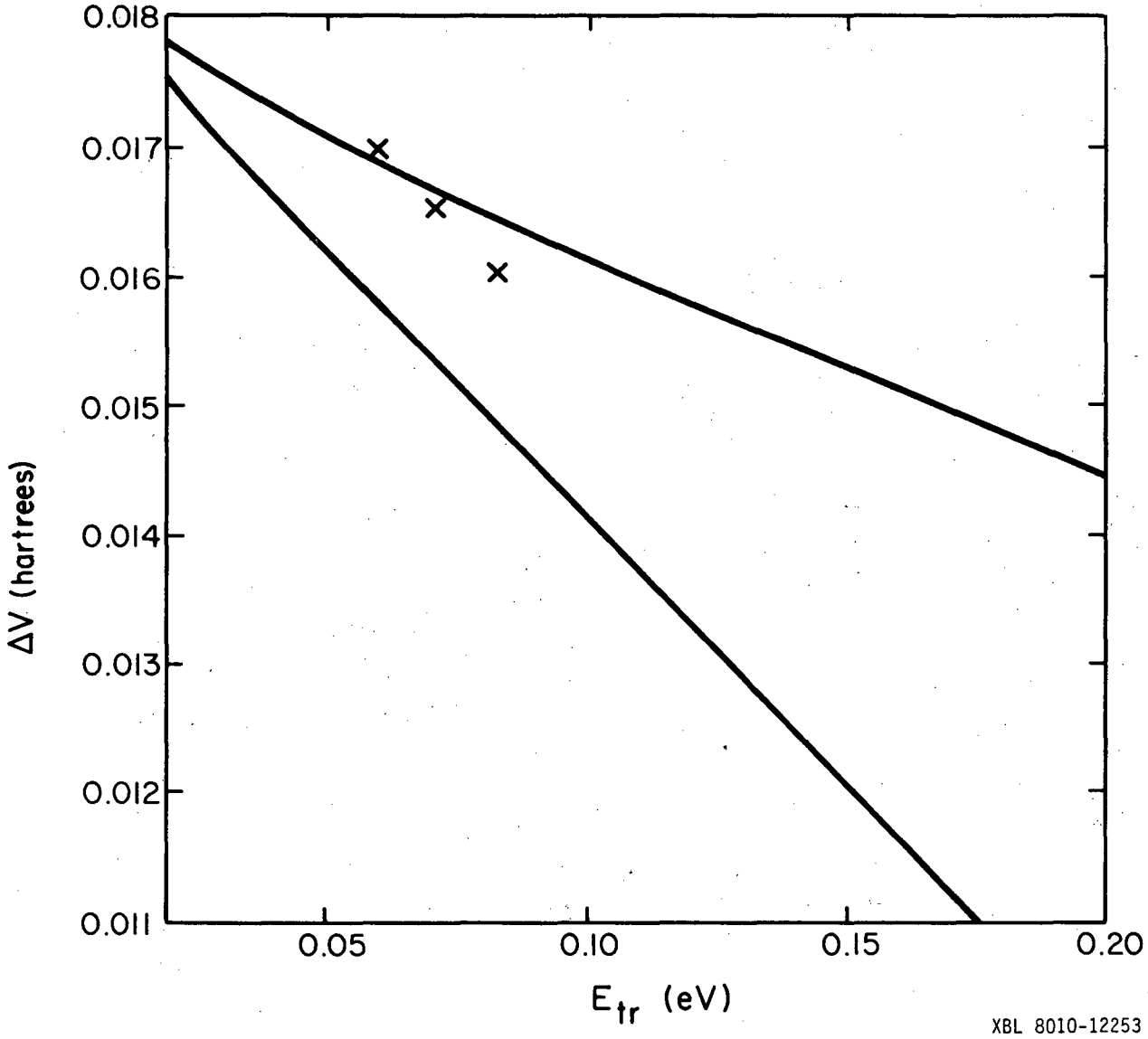
E_{tr} (eV)
XBL 8010-12252

Figure 2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0.017
0.016
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ΔV (hartrees)
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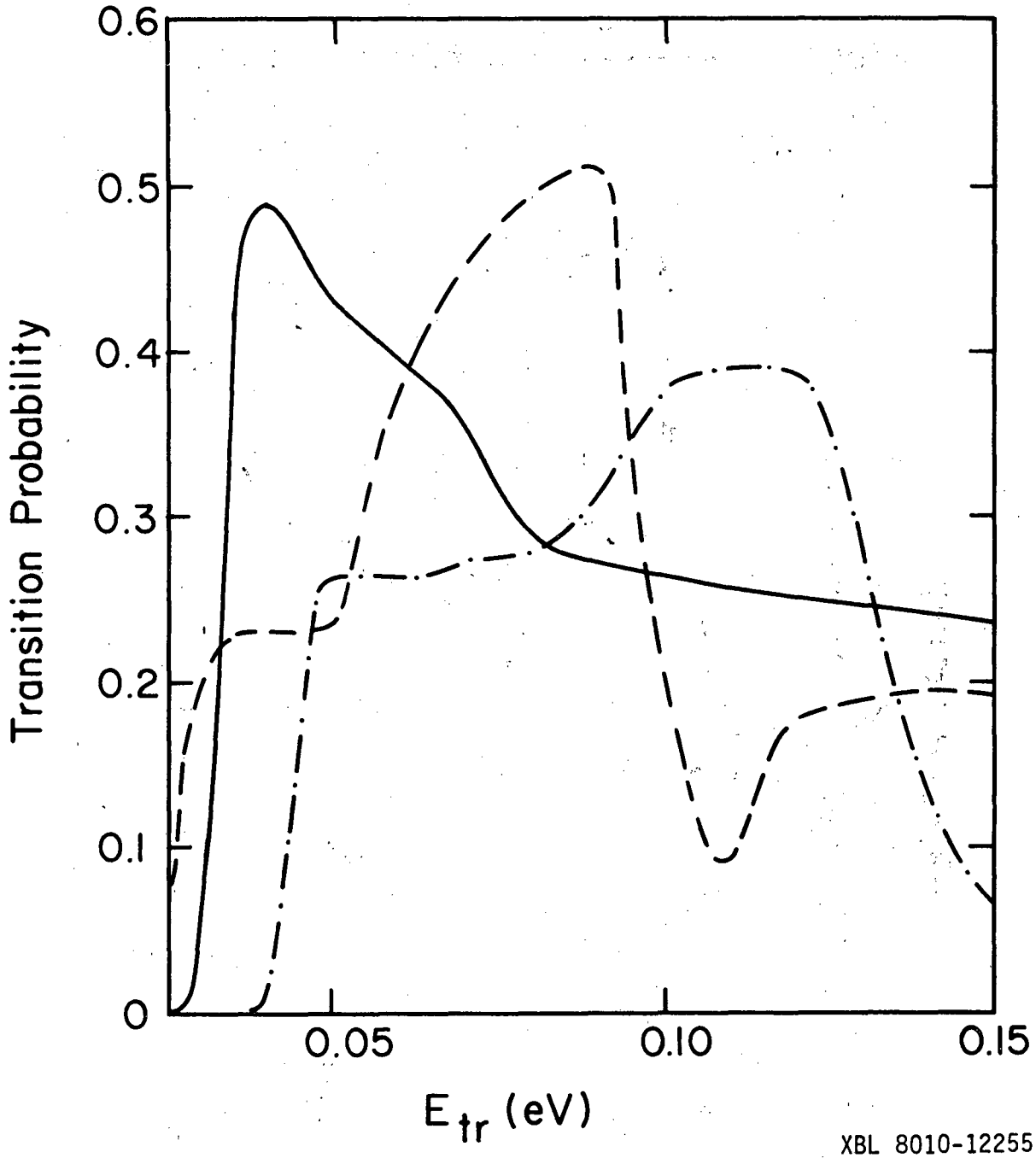
0.15
0.20
E_tr (eV)
XBL 8010-12253

Figure 3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0.4
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0.1
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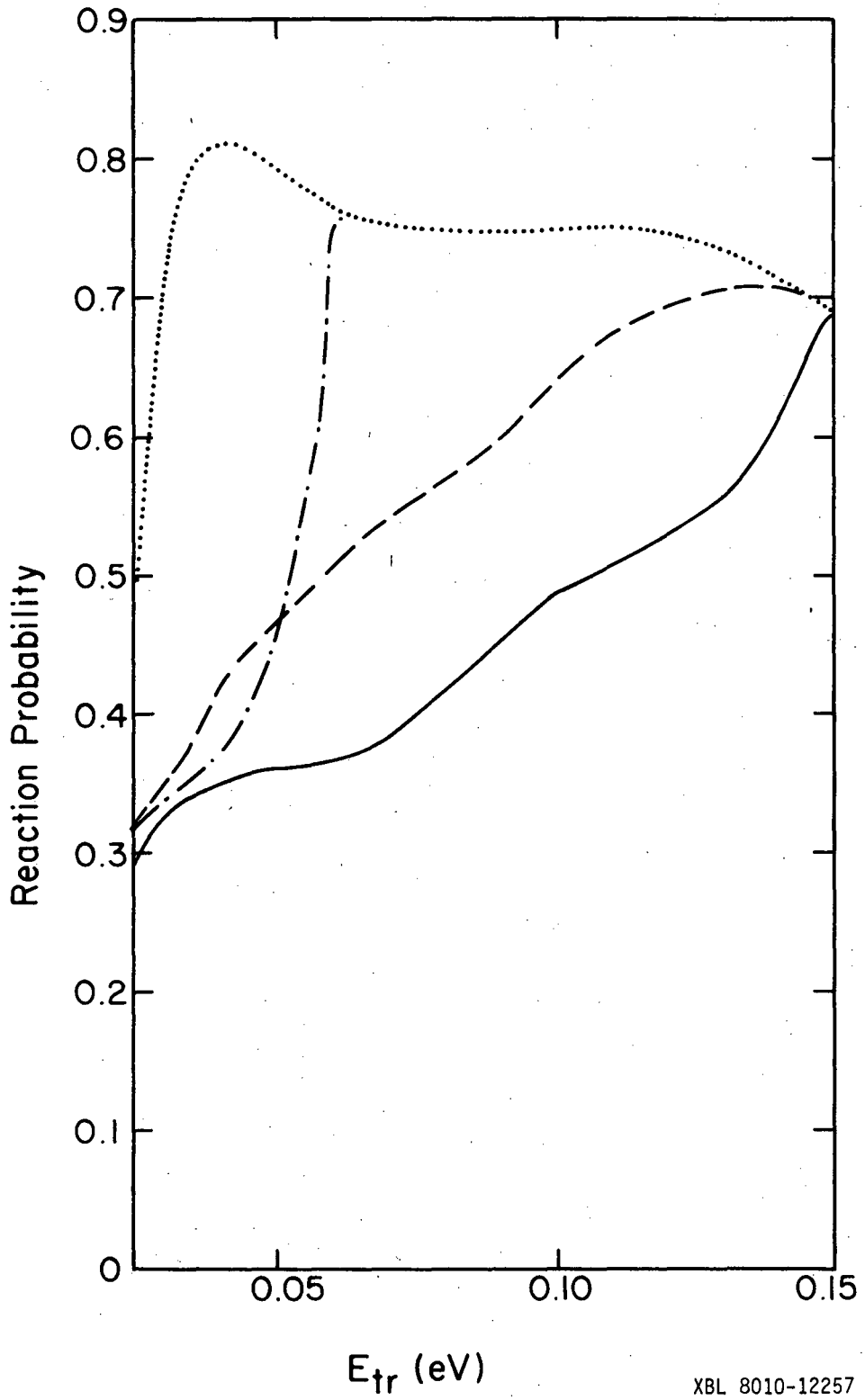
0.15
E tr (eV)
XBL 8010-12255

Figure 4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0.8
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0.4
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Reaction Probability
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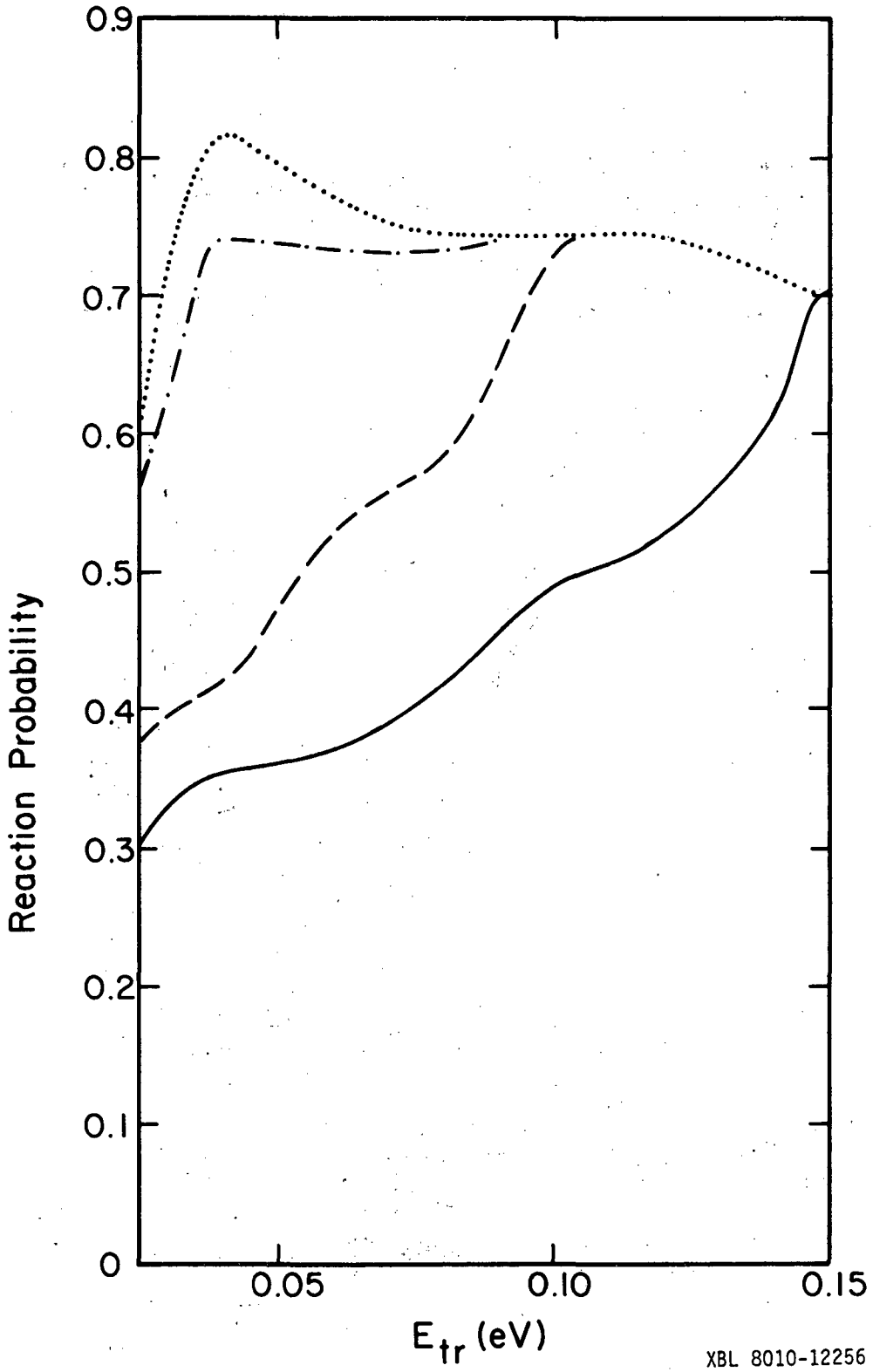
E_{tr} (eV)
XBL 8010-12257

Figure 5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Reaction Probability
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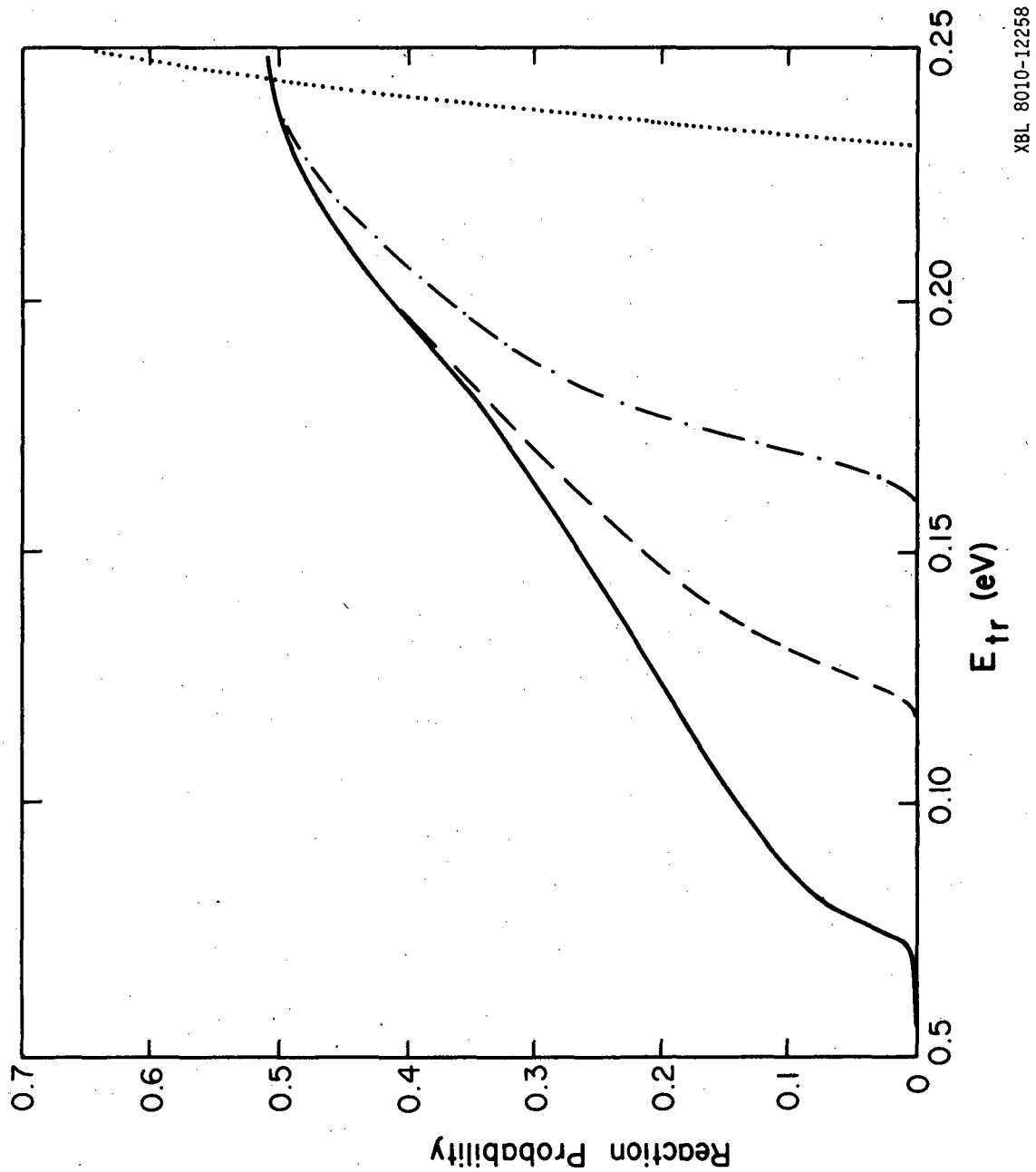
E_{tr} (eV)
XBL 8010-12256

Figure 6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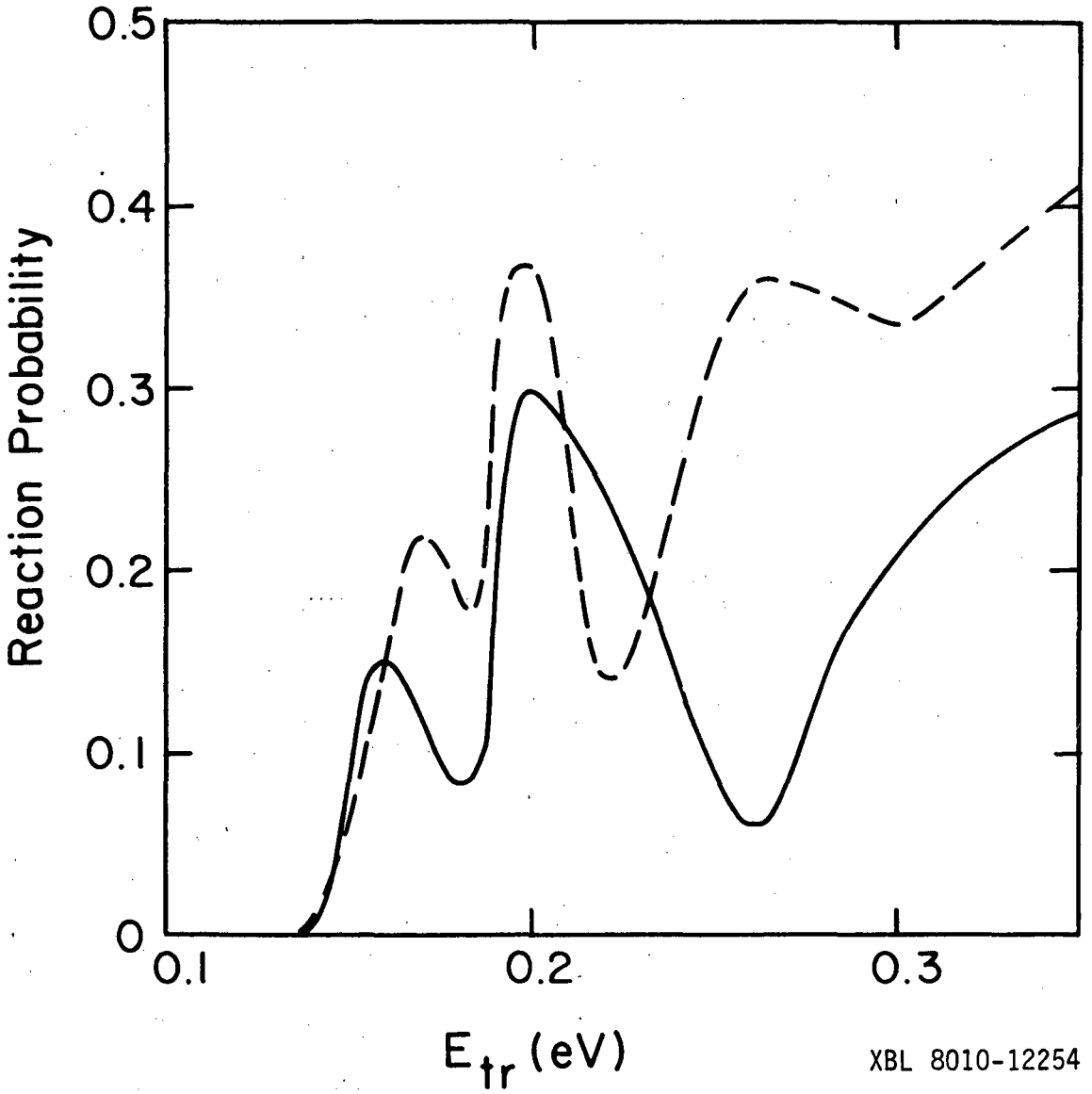
E_{tr} (eV)
XBL 8010-12258

Figure 7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Reaction Probability
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E_{tr} (eV)
XBL 8010-12254

Figure 8

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