On the possibility of vibrational inhibition in a bimolecular exchange reaction

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It has been generally found that vibrational excitation of reagents causes enhancement of reaction cross sections, and, depending upon various factors like endothermicity, position of the saddle point, "sudden" nature of the potential-energy surface, etc., the magnitude of vibrational enhancement depends on the system and the reagent conditions.[1] To the best of our knowledge, there is no recorded evidence of vibrational excitation causing inhibition in a bimolecular exchange reaction. In connection with the ongoing experiments on $Li_2(v_i, J_i) + M$ collisions elsewhere,[2] we undertook a phase space theoretical study[3] for different M. For the case of M = H, we found that vibrational excitation can cause vibrational inhibition.

We realize that doing a phase space (PS) calculation (on a borrowed computer code!) is no big deal, but the findings for the particular reaction

$$H + Li_2(v_i, J_i) \rightarrow HLi + H \qquad (R1)$$

have tempted us to communicate this paper. The parameters used in the PS calculations are given in Table I and the computed reaction cross sections (σ^R) over a range of vibrational states (v_i) for two different relative translational energies (E_{trans}) for the ground rotational state ($J_i = 0$) of Li_2 are shown in Fig. 1. Also included in Fig. 1 are the results for different J_i (= 0–20) for $v_i = 0$ and 20 at $E_{trans} = 2$ kcal mol^{-1}. It is clear that translational as well as vibrational excitation of the reactants causes a decrease in σ^R. An examination of the masses of the constituent atoms in the reactant Li_2 and the product LiH makes us realize that what we have found is a consequence of the mass combination of the participating atoms in this reaction. The reactant Li_2 has very closely spaced vibrotational levels, while the product LiH, because of the mass asymmetry, has widely spaced vibrotational levels. Therefore, any increase in the total energy of the system causes an increase in the number of available states for the reactants much more than for the products.

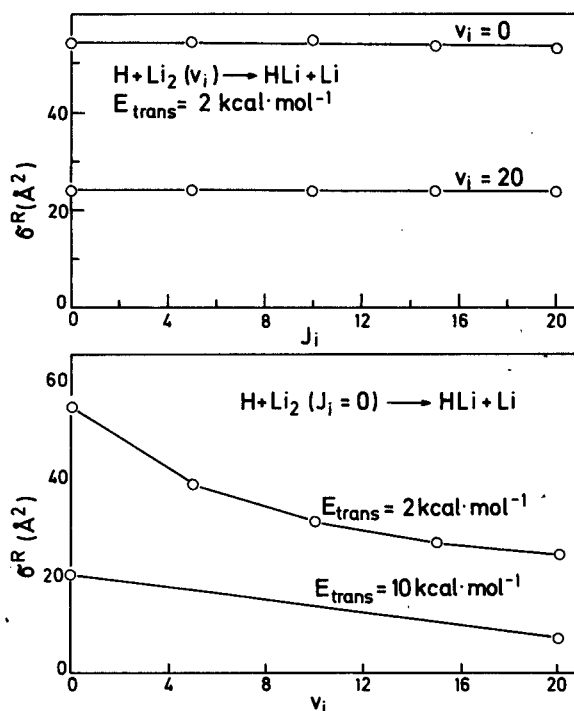We realize that our results are valid only under condi-

FIG. 1. Reaction cross section as a function of v_i and J_i for the stated E_{trans}.

tions under which the phase space theory is valid. *Ab initio* calculations[4] indicate that there is a substantial potential well for reaction (R1). Whether its depth is enough to cause complex formation remains to be investigated. Nevertheless, it would be interesting to determine experimentally whether the predicted vibrational inhibition is observable. If it is, it would suggest that the reaction proceeds statistically. If, on the other hand, vibrational enhancement is observed, overriding dynamical effects will become evident.

TABLE I. Parameters for the phase space calculation.

	Li	H	Li$_2$	LiH
Dipole moment (D)	...	...	...	5.802
Polarizability (Å^3)	22.2	0.667	44.4	13.828

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