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REACTION HAMILTONIAN AND STATE-TO-STATE DESCRIPTION OF CHEMICAL REACTIONS*

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Abstract

A chemical reaction is treated as a quantum transition from reactants to products. A specific reaction Hamiltonian (in second quantization formalism) is introduced. The approach leads to Franck-Condon-like factor, and adiabatic method in the framework of the nuclear motion problem.

The influence of reagent vibrational state on the product energy distribution has been studied following the reaction Hamiltonian method. Two different cases (fixed available energy and fixed translational energy) are distinguished. Results for several bimolecular reactions are presented.

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I. Introduction

For bimolecular chemical reactions there are powerful methods for the investigation of collision dynamics [1-3]. The prediction of state-to-state energy distributions, however, remains a formidable problem. Interest here focuses on the evaluation of product vibrational energy distributions for reactions that occur on a single potential energy surface.

Two of us have described a method, based on a specific Reaction Hamiltonian in second quantization formalism, to predict state-to-state energy distributions. The approach, similar in structure to Bardeen's theory to tunneling, [ ] leads to the evaluation of a Franck-Condon-type (FC) matrix element [4-5]. The FC approaches have appeared for the determination of product energy distributions of chemical reactions and of photodissociation [6,8-13]. These methods have been developed from scattering theory, [7] and from assumptions on the applicability of the Golden Rule in a dressed-oscillator model for both reaction and photodissociation. In the latter case, the operator causing the transition was not obtained [14].

In this paper we summarize the RH method and apply it to selected A + BC reactions. Further, we treat the role of reagent vibrational energy on the product energy distribution.

The structure of the paper is as follows. The approach which leads to the description of a chemical reaction as a quantum transition and to the introduction of the reaction Hamiltonian (in second quantization

representation) is presented in the next section. The evaluation of the FC factor is then addressed in Sec. III. The effect of the initial excitation of the reactants on the vibrational distribution of the products is considered in Sec. IV and several applications of the theory are presented in Sec. V. Discussion follows in Sec. VI and a summary concludes the paper.

II. Reaction as a Quantum Transition. Reaction Hamiltonian

Consider a chemical reaction in which the reactants and products belong to the same potential energy surface $\epsilon_n(\vec{R})$; here $\{\vec{R}\}$ denotes nuclear coordinates. The Schroedinger equation can be written in the form

$$(\hat{H}_e + \hat{T}_{\vec{R}})\ \Psi(\vec{r},\vec{R}) = E\Psi(\vec{r},\vec{R}) \tag{1}$$

where $\{\vec{r}\}$ denotes electronic coordinates, $\hat{T}_{\vec{R}}$ is the nuclear kinetic energy operator, and $\hat{H}_e$ is the electronic Hamiltonian,

$$\hat{H}_e = \hat{T}_{\vec{r}} + V(\vec{r},\vec{R}) \tag{2}$$

Here $\hat{T}_{\vec{r}}$ is the kinetic energy operator of the electrons, and $V(\vec{r},\vec{R})$ is the total potential energy. In accord with the Born-Oppenheimer (BO) approximation, the electronic term is defined by the equation:

$$\hat{H}_e\psi_n(\vec{r},\vec{R}) = \epsilon_n(\vec{R})\ \psi_n(\vec{r},\vec{R}) \tag{3}$$

where $\psi_n(\vec{r},\vec{R})$ is the electronic wave function. Now, consider Eqs. (1)-(3) with a new potential $\tilde{V}(\vec{r},\vec{R})$. The effect of the substitution $V \rightarrow \tilde{V}$ is a change of the electronic terms from ε_n, $\varepsilon_n + 1$ to $\tilde{\varepsilon}_R$, $\tilde{\varepsilon}_P$ so that

$$[\hat{T}_{\vec{r}} + \tilde{V}(\vec{r},\vec{R})]\ \tilde{\psi}_R(\vec{r},\vec{R}) = \tilde{\varepsilon}_R(\vec{R})\ \tilde{\psi}_R(\vec{r},\vec{R}) \tag{4}$$

$$[\hat{T}_{\vec{r}} + \tilde{V}(\vec{r},\vec{R})]\ \tilde{\psi}_P(\vec{r},\vec{R}) = \tilde{\varepsilon}_P(\vec{R})\ \tilde{\psi}_P(\vec{r},\vec{R}) \tag{5}$$

We choose the potential $\tilde{V}(\vec{r},\vec{R})$ such that the term $\tilde{\varepsilon}_R(\vec{R})$ is given by $\varepsilon_n(\vec{R})_{|i}$ (the index "i" identifies the reactant channel). In an analogous way, we introduce a term $\tilde{\varepsilon}_P(\vec{R})$ which behaves as $\varepsilon_n(\vec{R})_{|f}$ (the product channel).

The terms $\tilde{\varepsilon}_R(\vec{R})$ and $\tilde{\varepsilon}_P(\vec{R})$ are similar to diabatic surfaces (see the next section). The corresponding nuclear wave functions are solutions of

$$[\hat{T}_{\vec{R}} + \tilde{\varepsilon}_R(\vec{R})]\ \tilde{\phi}_{R\upsilon}(\vec{R}) = E\ \tilde{\phi}_{R\upsilon}(\vec{R}) \tag{6}$$

$$[\hat{T}_{\vec{R}} + \tilde{\varepsilon}_P(\vec{R})]\ \tilde{\phi}_{P\upsilon'}(\vec{R}) = E\ \tilde{\phi}_{P\upsilon'}(\vec{R}) \tag{7}$$

Hence, one can introduce the states $\tilde{\Psi}_R(\vec{r},\vec{R}) = \tilde{\psi}_R(\vec{r},\vec{R})\ \tilde{\phi}_R(\vec{R})$ and $\tilde{\Psi}_P(\vec{r},\vec{R}) = \tilde{\psi}_P(\vec{r},\vec{R})\ \tilde{\phi}_P(\vec{R})$, which are eigenstates of the Hamiltonian

$$\tilde{H} = \hat{T}_{\vec{r}} + \hat{T}_{\vec{R}} + \tilde{V}(\vec{r},\vec{R}) \tag{8}$$

and describe the states of the reactants (R) and the products (P), respectively. Indeed, the function $\tilde{\phi}_R(\vec{R})$ (and, hence, $\tilde{\Psi}_R(\vec{r},\vec{R})$) is

exponentially small in the product channel (see Eq. (6)), and $\tilde{\phi}_P(\vec{R})$ is exponentially small in the reactant channel.

A chemical reaction can be treated as a quantum transition from reactants to products. From the above considerations, the Schroedinger equation (1) can be rewritten in the form

$$(\tilde{H} + \Delta H)\, \Psi(\vec{r},\vec{R}) = E\, \Psi(\vec{r},\vec{R}) \tag{9}$$

where $\tilde{H}$ is defined by Eq. (8), and

$$\Delta H = V(\vec{r},\vec{R}) - \tilde{V}(\vec{r},\vec{R}) \tag{10}$$

The term ΔH can be considered as the part of the Hamiltonian that governs transitions between eigenstates of the Hamiltonian $\tilde{H}$. We can use the usual theory of quantum transitions (see, e.g., Ref. 16) based on the time-dependent Schroedinger equation with Hamiltonian $\hat{H} = \tilde{H} + \Delta H$ to determine the probability of reaction. Further, we are concerned here with reactions occurring on a single adiabatic potential energy surface, which we treat in a quasiadiabatic (nondiagonal) representation. Thus in accordance with the BO approximation, one can neglect the coupling of electronic and nuclear motions owing to $\hat{T}_{\vec{R}}$; see also ref. 11. This coupling is important, for example, in electronic predissociation accompanied by a change of adiabatic potential energy surface. The term ΔH, which does not depend on time, can cause transitions between states of the same energy (see, e.g., ref. 16). (This property is relevant because energy is conserved in the elementary step). Thus, we arrive at the expression for the probability of the transition per unit of time:

$$dw_{f\leftarrow i} = \frac{2\pi}{\hbar}\left|a_{fi}\right|^2 \delta(E_f - E_i)\,d\nu_f \tag{11}$$

where $d\nu_f = \rho_f dE_f$, ρ_f is the density of states, and the amplitude a_{fi} is given by

$$a_{fi} = \int \tilde{\Psi}_f^{*}(\vec{r},\vec{R})\ \Delta H \tilde{\Psi}_i(\vec{r},\vec{R})\ d\vec{r}d\vec{R} \tag{12}$$

Here $i \equiv R$ denotes the state of the reactants and $f \equiv P$ denotes the state of the products.

Equation (11) is the result of first-order time-dependent perturbation theory and involves the approximation of neglect of all virtual transitions; cf, ref. 11. If higher-order corrections are important, the probability is given by an expression of the same form as (11) with, however, the matrix element a_{fi} replaced by the T-matrix element[17] connecting states i and f. See the paragraph following Eq. (21) for further discussion.

Based on Eqs. (2) and (10), we obtain (cf., Ref. 15)

$$a_{fi} = \int \tilde{\psi}_f^{*}(\vec{r},\vec{R})\ \tilde{\phi}_f^{*}(\vec{R})\ [\hat{H}_e - \tilde{\varepsilon}_i(\vec{R})]\ \tilde{\psi}_i(\vec{r},\vec{R})\ \tilde{\phi}_i(\vec{R})\ d\vec{r}d\vec{R} \tag{13}$$

Equation (13) can be rewritten in the form

$$a_{fi} = \int \tilde{\phi}_f^{*}(\vec{R})\ \tilde{\phi}_i(\vec{R})\ L(\vec{R})\ d\vec{R} \tag{14}$$

where

$$L(\vec{R}) = \int \tilde{\psi}_f^{*}(\vec{r},\vec{R})\ [\hat{H}_e - \tilde{\varepsilon}_i(\vec{R})]\ \tilde{\psi}_i(\vec{r},\vec{R})\ d\vec{r} \tag{15}$$

The orthogonality of $\tilde{\psi}_i$ and $\tilde{\psi}_f$ enables Eq. (15) to be expressed in the form $L(\vec{R}) = \int \tilde{\psi}_f^{*}(\vec{r},\vec{R})\, \hat{H}_e\, \tilde{\psi}_i(\vec{r},\vec{R}) d\vec{r}$. One sees that the function $L(\vec{R})$ contains the electronic wave functions describing the diabatic states (see below) and the electronic Hamiltonian (2).

The function $L(\vec{R})$ contains relatively smooth functions, and one can write

$$a_{fi} = L(\vec{R}_0)F \tag{16}$$

where

$$F = \int \tilde{\phi}_f^{*}(\vec{R})\, \tilde{\phi}_i(\vec{R})\, d\vec{R} \tag{17}$$

is a FC-type factor and $L(\vec{R}_0)$ is a constant ($\vec{R}_0$ denotes the geometry of the transition state, i.e., the crossing point of the diabatic states). Hence, the determination of product energy distributions reduces to the analysis of the nuclear dynamics and to the evaluation of a FC-type factor (see Sec. III).

The transformation $V \rightarrow \tilde{V}$ introduced above is most conveniently pictured in terms of quasiadiabatic states as introduced by O'Malley [18]. The electronically adiabatic potential energy surface results from the interaction of two quasiadiabatic surfaces which cross. One of the two adiabatic surfaces corresponds to the reactant state, the other one corresponds to the product state. In this sense they give a localized picture of the potential energy surface. The crossing of the two quasiadiabatic surfaces occurs at the saddle point of the adiabatic

surface. In the FC approximation, the quantum transition occurs near the crossing point of the quasiadiabatic surfaces.

We have introduced in Eqs. (11)-(17), the matrix element for chemical reaction. As a next step, one can introduce the reaction Hamiltonian (in second quantization representation). In this representation the total Hamiltonian can be written in the form:

$$\hat{H} = \hat{H}_0 + \hat{H}_{P \leftarrow R} \tag{18}$$

where $\hat{H}_0 = \hat{H}_P + \hat{H}_R$ describes the state of reactant and product subsystems and $H_{P \leftarrow R}$ governs reaction per se. The latter term can be written in the form:

$$\hat{H}_{P \leftarrow R} = \sum_{f,i} a_{fi}\, b_f^{+}\, b_i \tag{19}$$

Here $i \equiv \{n,\nu\}$ denotes reactant states, n is a set of electronic states, ν corresponds collectively to vibrational, translational, and rotational motions; {f} denotes product states, and b_i and b_f^+ are the operators of annihilation and creation. This Hamiltonian is analogous to the tunneling Hamiltonian [19].

The amplitude of a $R \rightarrow P$ transition is (for a Bose system)

$$A_{P \leftarrow R} = \langle \tilde{\psi}_P \hat{H}_{P \leftarrow R} \tilde{\psi}_R \rangle = \sum_{f,i} a_{fi} (n_f+1)^{1/2} n_i^{1/2} \tag{20}$$

For Fermions one replaces (n_f+1) by $(-1)^{\nu_i+\nu_f}(1-n_f)$ where $\nu_{i(f)}$ is the number of states preceding i(f) as described, for example, in ref. 19.

If one assumes initially that $n_f = 0$, then the number of transitions P_f (per unit time) to product states of the same energy is

$$P_f = \sum_i |a_{fi}|^2 n_i \delta(E_f - E_i) \rho_f(E) dE \qquad (21)$$

Equations (21) and (11) arise from first-order time-dependent perturbation theory. It is important here to recall that the validity of this approximation depends on the product of the coupling matrix element and the characteristic time of the perturbation being small [17]. Hence (21) and (11) are valid even if a_{fi} is large for sufficiently short characteristics times. Note that higher-order corrections correspond to virtual transitions. The second-order correction is non-zero only if one includes transitions to electronic states above the diabatic states discussed above. Here we assume that such electronic states are too high in energy to contribute, ref. 11. The matrix element corresponding to a virtual transition between vibronic states belonging to the same diabatic state vanishes in second order because of orthogonality.

III. Franck-Condon Factor. Distribution of Reaction Products

According to Eqs. (16) and (17), the calculation of product energy distributions is reduced to one of nuclear dynamics. In order to evaluate the FC factor (17), it is necessary to obtain expressions for the nuclear wave functions $\tilde{\phi}_R$, $\tilde{\phi}_p$. These wave functions are the solutions of the nuclear Schroedinger equation:

$$[\hat{T}_R + U_k(\vec{R})]\,\phi_k(\vec{R}) = E\,\phi_k(\vec{R}) \tag{22}$$

$$U_k(\vec{R}) \equiv \epsilon_k(\vec{R});\ k = \{R,P\}$$

The main difficulty in solving Eq. (22) for R and P states arises from nonseparability of variables. Indeed, if we consider, for example, the state of reactants, the potential energy $V_R(\vec{R})$ can be expressed in terms of q_R and ρ_R, where q_R denotes the internal coordinates of the reactants, and ρ describes the intermolecular separation of the reactants. The potential energy $V_R(\vec{R})$ cannot be expanded in a series of deviations of all variables from equilibrium, because ρ_R corresponds to translational motion. To address this problem, we employ our adiabatic method [20] in which the nuclear wave function $\phi_R(\vec{R})$ is written as the product

$$\phi_R(\vec{R}) = \phi^{vib}(q_R,\rho_R)\,\phi^{tr}(\rho_R)\,\phi^{rot} \tag{23}$$

The interaction between reactants results in a dependence of the vibrational frequencies on the distance ρ_R and, moreover, the effective potential energy describing the relative translational motion contains the vibrational energy $E^{vib}(\rho_R)$ as an additional term. Based on this method, we have evaluated the FC factor and product energy distributions for several systems.

Consider the evaluation of the FC factor (see Eq. (17)) for a atom-diatom system. According to Eqs. (16), (17), and (23), we obtain

$$a_{fi} = L_o F \tag{24}$$

Here L_o is defined by Eqs. (13)-(16); the subscript o denotes the region of overlap, and

$$F = \int \phi_f^{tr}(\rho_2)\, \phi_f^{vib}(\tau_2,\rho \quad \phi_i^{tr}(\rho_1)\, \phi_i^{vib}(\tau_1,\rho_1)\, d\tau d\rho \tag{25}$$

$$(\tau_1 = q_1 - q_{1o};\ \tau_2 = q_2 - q_{2o})$$

Both τ_1 and ρ_1 can be written as a linear combination of ρ_2 and τ_2. Hence, the integrand of Eq. (25) can be expressed solely in terms of ρ_2 and τ_2. For present purposes, rotational degrees of freedom are ignored which reduces angular integrations to a constant multiplicative factor. The integrand is nonseparable and so cannot be written, in general, as a product of independent functions of ρ_2 and τ_2.

In this paper, we limit consideration to the case AB + C → BC + A (cf., ref. 21) where

$$M_B >> M_A,\ M_C \tag{26}$$

Other cases will be considered elsewhere. The condition (26) means that the reaction is an exchange of the lighter mass atoms A and C. An example of such a reaction is

$$HO + D \rightarrow H + OD \tag{27}$$

which has been studied by Margitan, et al. [22a].

Condition (26) is approximately satisfied for the reactions

$$ClI+D \rightarrow Cl+ID \; . \tag{28}$$

$$Li + HF \rightarrow LiF + H \tag{29}$$

A molecular-beam and study of reaction (28), see ref. [22b], included the measurement of the product translational energy distribution. This distribution is characterized by a peak at small relative translational energy E^{tr}. It is of interest to understand the origin of this peak and to determine the distribution. Reaction (29) has been studied by Becker et al. [37].

If condition (26) is satisfied, then the center of mass is found on atom B, and $q_2 = q_2$ and $\rho_2 = q_1$. The main contribution to the integral (25) comes from the region of overlap of $\tilde{\phi}_f$ and $\tilde{\phi}_i$, and one can write

$$a_{if} = B \int \phi_f^{tr}(q_1)\, \phi_f^{vib}(\tilde{\tau}_2)\, \phi_i^{tr}(\varsigma_2)\, \phi_i^{vib}(\tilde{\tau}_1)\, dq_1 dq_2 \; . \tag{30}$$

Here

$$\phi_f^{vib}(\tilde{\tau}_2) \equiv \phi_f^{vib}(\tilde{\tau}_2, q_{1o}),\ \phi_i^{vib}(\tilde{\tau}_1) \equiv \phi_i^{vib}(\tau_1, q_{2o}),$$

$$\tau_2 = q_2 - q_{2o}(\rho_{2o}),\ \tau_1 = q_1 - q_{1o}(\rho_{1o}),\ B = (q_{1o}q_{2o})^{-2} \int d\Omega F(\Omega) \tag{31}$$

Expression (30) can be written in the form:

$$a_{if} = BI_1I_2 \tag{32}$$

where

$$I_1 = \int \phi_f^{tr}(q_1)\, \phi_i^{vib}(\tilde{\tau}_1)\, dq_1 \tag{33a}$$

$$I_2 = \int \phi_i^{tr}(q_2)\, \phi_f^{vib}(\tilde{\tau}_2)\, dq_2 \tag{33b}$$

Thus, the integration in (30) can be separated into two independent parts. The integrals (33a) and (33b) have clear physical meaning. The $R \rightarrow P$ transition results in the transformation of the initial vibrational degree of freedom into a final translational degree of freedom and vice versa. The integral (33a), describing the probability of the $R \rightarrow P$ transition, contains the overlap of ϕ_f^{tr} and ϕ_i^{vib}; the reverse relationship holds for term I_2. We assume that the reactant AB is in the ground vibrational state. (The effect of reagent vibrational excitation will be considered in the next section.)

Note also that the function ϕ^{tr} describing the translational motion of the reactants (products) can be determined in the semiclassical approximation. The result of the evaluation of the FC factor for reaction (28) is presented in ref. 4. We note that the translational distribution has a peak in the region $E^{tr}/E^{tot} \approx 20\%$, in accord with experimental data. Correspondingly, the vibrational distribution is inverted up to $v = 4$. The origin of this inversion is the same as that previously described for polyatomic photodissociation [20]. A decrease of v and a corresponding increase of E^{tr} results in an increase of the number of oscillations of the semiclassical wave function. (Here it is

assumed that the momentum p_f is large: $p_f A_i \gg 1$, A_i is the reagent vibrational amplitude. The increase of the number of oscillations leads to a decrease of F and, hence, to an inverted vibrational distribution.

For reaction (28) we have used the approximation $\Omega_i \approx \Omega_{i,\,AS} = 384.3\ cm^{-1}$ and $\Omega_f \approx \Omega_{f,AS} = 1639.64\ cm^{-1}$ [23a], where the subscript AS denotes the free molecule or "asymptotic" frequency. Based on this approximation, we have obtained a qualitative description of this reaction and good agreement with experimental data [26b]. In order to carry out a detailed comparision of theory and experiment, one should calculate the ρ-dependent frequencies, (not approximate them by free molecule asymptotic values, see above), evaluate the equilibrium distances, and take into account the exact relation between the masses M_A, M_B, and M_C. Note that calculations of Eades and Dunning [24] establish the appropriateness of the use of asymptotic frequencies for reaction (29).

We emphasize that the present analysis is not restricted to the collinear approximation. We are interested in the relative vibrational distribution of products. (According to adiabatic theory, slow rotational and bending motions can be considered as a next step.) For the light plus heavy-light system, one has the relations, $\rho_1 = q_2$, $\rho_2 = q_1$ (see above) and the integrand of the FC factor depends only on two variables.

For reaction (27), we have found [4,5] that the translational distribution of the products drops off much more rapidly with increasing E^{tr} than it does for reaction (28). The measurements of the product

energy distribution for reaction (27) have not been carried out. It would be interesting to perform such measurements to test the theoretical predictions.

IV. Effect of Reagent Vibrational Excitation on the Product Vibrational Distribution

The influence of reagent vibrational state on the product vibrational energy distribution has been studied by various methods. Polanyi and coworkers measured and analyzed the vibrational state dependence of reaction rates for a number of systems using arrested-relaxation infrared chemiluminescence experiments complemented by classical trajectory studies [25,26]. The reactions of K with HCl and Sr, Ca, and Ba with HF provide excellent examples of large increases in reactivity that can be obtained by vibrational excitation [27]. The reactions of H_2 with $O(^3P)$ and $O(^1D)$ have been studied experimentally [28] and theoretically [29], the latter using ab initio potential energy surfaces and a number of collision approaches. Comparisons of quantum with classical calculations for the Li + FX (X = H,D) system have also appeared [30].

A FC approach has been used to study the reaction D + HI → DI + H at low energy [10]. By reducing the reactive transition matrix to products of 1-D integrals of distorted wave basis functions on diabatic surfaces, it was found that change of the initial vibrational quantum number did not noticeably affect the DI vibrational distribution. A similar approach was used with the distorted wave Born approximation to describe exchange

reactions of X + Cl_2 and X + F_2 (X = H,D) with "half-collision" diabatic surfaces [8]. The reactant vibrational state did not affect the product distribution for these reactions. Other FC-type models have appeared that give qualitative agreement for certain reactions [14,31,32].

A mixed stochastic/FC approach has been developed [33] and applied to reactions which are assumed to proceed through the formation of an intermediate complex and applied to H + Cl_2 → HCl + Cl. The authors neglected the influence of the relative translational motion of the reactants (products). Baer [34] has also investigated this reaction using a quantum mechanical close-coupling method. For vibrationally excited reactants, the product energy distribution was found to broaden and to contain more structure.

Exothermic triatomic exchange reactions have been treated in a collinear reaction model leading to an analytic expression for the population of product vibrational states for a number of mass combinations [35]. Some earlier treatments focused on the bobsled effect, but they were unable to account for multiquantum transitions [32-36]. We want to emphasize the important role of translational motion in governing these distributions.

Evaluation of the FC factor provides a prediction of the relative vibrational distribution of products for a given initial state of reactants. Having determined this distribution for reagents in the ground state, our goal here is to study the change of the distribution (if any) caused by vibrationally excited reagents.

It is useful to distinguish between two different cases. One corresponds to reaction at fixed total energy and the other to reaction at fixed initial translational energy. Both cases can be studied experimentally.

We use a semiclassical approximation to describe the relative translational motion of the reactants (products) in the region where $\rho_i A_f \gg 1$; ρ_i is the relative linear momentum of reactants and A_f is the vibrational amplitude of the production diatomic. The harmonic approximation was employed to describe the vibrational motion but is not essential. In refs. 4 and 5 it was established that the vibrational frequencies are rigorously those for the FC overlap region. Here, however, we assume that they do not differ significantly from their asymptotic values. Strongly speaking, this corresponds to the neglect of final-state interactions.

V. Applications

We have applied the reaction Hamiltonian method to the atom-diatom reactions:

$$Li + FH \rightarrow LiF + H \tag{34a}$$

$$H + BrCl \rightarrow HBr + Cl \tag{34b}$$

There are several reasons for this choice. First, both reactions involve the exchange of the lighter mass atoms A and C, i.e., $M_B \gg M_A, M_C$. As shown in Sec. III, FC factor for such a system can be

evaluated analytically, and it allows one to make a qualitative analysis of the main factors governing product vibrational distributions. In addition, these reactions represent two limiting cases. Reaction (34a) is usually characterized by a noticeable relative change of the initial translational energy when reactants are excited to their first excited state for fixed total energy (see Sec. VI), whereas reaction (34b) involves only a small change of E^{tr}. This difference is shown below to be an important factor in determining the magnitude of the change of the product distribution as a function of reagent vibrational state v_i. Furthermore, these reactions have been studied experimentally for $v_i = 0$ [37,38].

Reactions (34a) and (34b) are characterized by different values of the ratio $\Gamma = \omega_i/\omega_f$ where ω_i and ω_f are the reactant and product diatomic vibrational frequencies. The frequencies used here are [23]: $\omega(LiF) = 910.39\ cm^{-1}$ and $\omega(FH) = 3958.4\ cm^{-1}$, so that $\Gamma = 4.3$. For reaction (6b), $\omega(BrCl) = 444.3\ cm^{-1}$, and $\omega(HBr) = 2559.3\ cm^{-1}$ leading to $\Gamma = 0.17$.

(a) Li + FH.

Figure 1 shows the product translational energy distribution for ground state reactants at $E^{tr} = 3$ kcal/mol. The present theoretical prediction is found to be in good agreement with the measurement of Lee and coworkers [37].

Figures 2 and 3 show how the distribution may be affected by changing the initial state of the reactants. Figures 2a, 2b, and 2c are for the case of constant total energy while Fig. 3 illustrates the effect of fixed translational energy.

All distributions have different peak positions in addition to varying shapes. For excited reactants the peak (maximum) is shifted to smaller final vibrational quantum number. Figures 2 and 3 also indicate that one effect of vibrationally excited reactants is bimodality in the product vibrational distribution. This is consistent with Child's finding [39] concerning interference structure in reaction probabilities. He reports that product distributions of direct reactions should have the same number of maxima or minima as the reagent wavefunction. For the maximum energetically allowed final quantum vibrational state (e.g., $v_{max} = 6$), this newly seen lower frequency peak becomes increasingly important as the initial available energy is decreased (compare Figs. 2a and 2b). In addition to a direct pathway, reaction (34a) can also proceed through the formation of a long-lived intermediate. The good agreement between the direct channel analysis presented here and experimental data shows that the direct channel is dominates in determining the product energy distribution for the energy range for which comparison with experiment has been made. This conclusion regarding reaction mode (direct or complex) is possible in principle for this system as discussed by Becker, et al. [37a]. A detailed analysis will be presented elsewhere.

(b) H + BrCl.

Figure 4 illustrates the good agreement obtained between the present calculations and the Polanyi and Skrlac [38] experimental results for $BrCl(V_i = 0)$. Figure 5, however, shows no affect on the product energy distribution for $BrCl(V_i = 1)$.

VI. Discussion

The effect of reagent vibrational state on the product energy distribution depends on several factors. In the reaction Hamiltonian approach, the analysis of these dependencies is reduced to the analysis of a FC-type factor [4,5].

Consider a reaction at fixed initial translational energy for ground state ($v_i = 0$) reactants characterized by a peak (maximum) in the product distribution at $v = v_p$. If $\Gamma \gg 1$ and $E^{tr} \sim \hbar\omega_i$, then the total energies for $v_i = 0$ and $v_i = 1$ are considerably different. For the case of the same product state $v = v_p$, there is more product translational energy for $v_i = 1$ than for $v_i = 0$. This increase of product translational energy results in an increase of the number of oscillations in the translational wavefunction (see Eq. (23) and ref. 20b), and hence a decrease of the FC factor (see Eq. (17)). Therefore, one can expect to find the peak of the product distribution when $v_i = 1$ at larger v than that for $v = 0$. This situation is exemplified by reaction (34a) in Fig. 3. On the contrary, if $\Gamma < 1$, and $E^{tr} \gg \hbar\omega_i$ then the difference in total energy between $v_i = 0$ and $v_i = 1$ at fixed translational energy is not large enough to cause change of v_p.

In a similar way, one can analyze the appearance of the shift for fixed total energy. For example, since the initial translational energy is much smaller for $v_i = 1$ than for $v_i = 0$, then the FC factor will be larger for $v_i = 1$ (due to the decrease in oscillations of the translational function) leading to a larger probability at a smaller final vibrational state than that for $v_i = 0$. (See Fig. 2)

This effect is easily seen by analyzing the reaction probability. Upon integration of the FC-type term, the probability (as a function of product vibrational quantum number) is given by

$$W \sim \frac{1}{2^v v!} \quad H_v^2(s) \tag{35}$$

where H_v is the vth Hermite polynomial and

$$s = (2m_i E^{tr}/m_f \hbar\omega_f)^{1/2}$$

m_f = reduced mass of product diatom, and $E^{tr} = E^{tot} - (v_i + 1/2)\hbar\omega_i$. Therefore, for reactions (34a) and (34b),

$$s(v_i = 0) \sim (2E_g/\hbar\omega_f)^{1/2};$$

$$s(v_i = 1) = [2(E_g - \hbar\omega_i)/\hbar\omega_f]^{1/2} \sim [s(v_i = 0) - \Gamma]^{1/2};$$

so that

$$\Delta s \equiv s(v_i = 0) - s(v_i = 1)$$

$$= \left(\frac{2}{\hbar\omega_f}\right)^{1/2} \left\{\left(E_g\right)^{1/2} - \left(E_g - \hbar\omega_i\right)^{1/2}\right\}$$

where

$$E_g = E^{tr} \text{ for } v_i = 0$$

The function Δs shows the dependence of the reaction probability on the relative change in initial translational energy for vibrationally excited reactants. When $E_g >> \hbar\omega_i$, there is no substantial change in s and the FC integral is similar for ground-state and first-excited-state reactants. Thus, the two product energy distributions for reaction (6b) are similar in structure. However, when E_g and $\hbar\omega_i$ are similar in magnitude, the percentage change in s is very large. In fact, $\Delta \equiv \Delta s/s(v_i = 0) = 1$ for $E^{tr} = \hbar\omega_i$.

When s for the excited reagent is very different from that of the ground-state reagent, the nuclear wavefunction may change significantly leading to a change in the product distribution.

This qualitative analysis enables one to understand the mechanism of the shift of the vibrational peak of the product energy distribution. Note that the important parameters in this analysis are E^{tr} and $\hbar\omega_i$. We emphasize the importance of the behavior of the translational wavefunction. The form chosen to describe the translational wavefunction, i.e., delta function, Airy function, or step function is also important.

Lagana [30f] has discussed the affect of reagent translational energy on total reactive probabilities in terms of oscillating structure in the

distribution. Here we also stress its importance on the product vibrational distribution and on the most favored product vibrational state.

The present approach can be extended to provide rigorous comparisons for systems with arbitrary mass ratios. Note that Polanyi, et al. [40] observed a shift in the product energy distribution for the reaction F + HCl → HF + Cl for $v_i = 0,1$. This measurement was for fixed initial translational energy (cf., Fig. 2a), and the increase in total available energy from reactant vibrational energy produced a shift in v_p.

The reaction D + HI → H + DI has been studied [10] using Airy functions to describe the translational motion in the low temperature region. In this study the excitation of reactants from $v_i = 0$ to $v_i = 1$ was not accompanied by significant shift in the product distribution. Note that these cases do not result in a large change in $s(\Delta \sim 0.2)$. Hence, the previous finding is consistent with the present qualitative analysis. A detailed analysis based on a more accurate treatment of the translational wavefunction will be given elsewhere. Note that the semiclassical approximation is not valid if the translational energy is small.

VII. Summary

The reaction Hamiltonian method provides a quantum state-to-state description of a bimolecular chemical reaction. The main results can be summarized as follows:

(1) Chemical reaction and polyatomic photodissociation can be treated as nonstationary phenomena. An analysis based on the theory of quantum transitions can be used to evaluate the energy distribution of the products (fragments).

A second-quantization formalism facilitates the introduction of a specific reaction Hamiltonian.

(2) The evaluation of the energy distribution is reduced to the calculation of a FC factor. The nuclear wave function can be obtained following our previously published theory of polyatomic photodissociation.

(3) The FC factor has been evaluated for triatomic systems of experimental interest (CH + D → Cl + ID and OH + D → OD + H). A peak in the translational distribution of the products has been obtained. The appearance of the peak is due to semiclassical features of the wave function describing the translational motion of the products.

(4) The energy distribution of the products depends strongly on the reagent vibrational state. If the reagent is prepared in an excited state, it can result in a noticeable shift of the peak of the product vibrational distribution, as well as in the appearance of new structure, for example, bimodality for $v_i = 1$. The occurrence of a shift in the maximum of the distribution is connected with characteristics of the translational and vibrational wave functions.

(5) The magnitude of the change of the vibrational distribution for a atom-diatom reaction depends strongly on the relative magnitude of the initial translational energy to the vibrational spacing as well as on

$\Gamma \equiv \omega_i/\omega_f$, where ω_i and ω_f are the vibrational frequencies of the diatom reactant and product, respectively. Moreover, it is important to distinguish between cases: 1) fixed total energy and 2) fixed translational energy.

The reactions Li + FH → LiF + H and H + BrCl → HBr + Cl have been studied.

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Figure Captions

Fig. 1 Product translational energy distribution for Li + HF(v_i = 0) → LiF + H. Hatched area indicates limits of fit to experimental data.

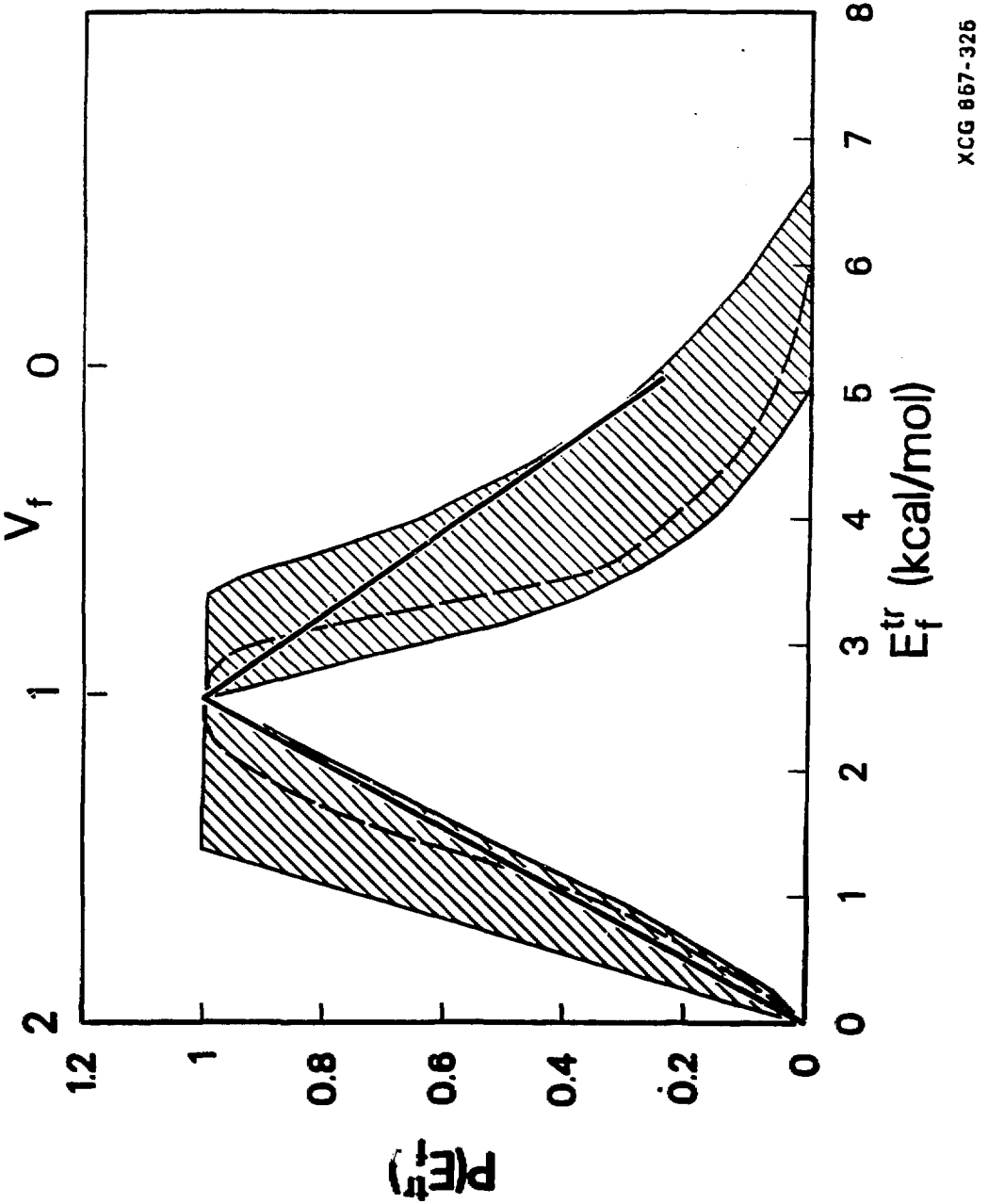
Fig. 2 Product energy distributions for Li + HF → LiF + H. —— denotes HF(v_i = 0); - - - denotes HF(v_i = 1) (a) E^{tot} = 16.5 kcal/mol; (b) E^{tot} = 15.6 kcal/mol; (c) E^{tot} = 20.8 kcal/mol.

Fig. 3 Product energy distributions for Li + HF → LiF + H. —— denotes HF(v_i = 0); - - - denotes HF(v_i = 1). Initial relative translational energy E^{tr} = 3.4 kcal/mol.

Fig. 4 Product translational energy distribution for H + BrCl(v_i = 0) → HBr + Cl; solid line is the theoretical curve; - - - experimental curve (ref. 18).

Fig. 5. Product energy distribution for H + BrCl → HBr + Cl. —— denotes BrCl(v_i = 0); - - - denotes BrCl(v_i = 1); E^{tot} = 43.89 kcal/mol.

Fig. 1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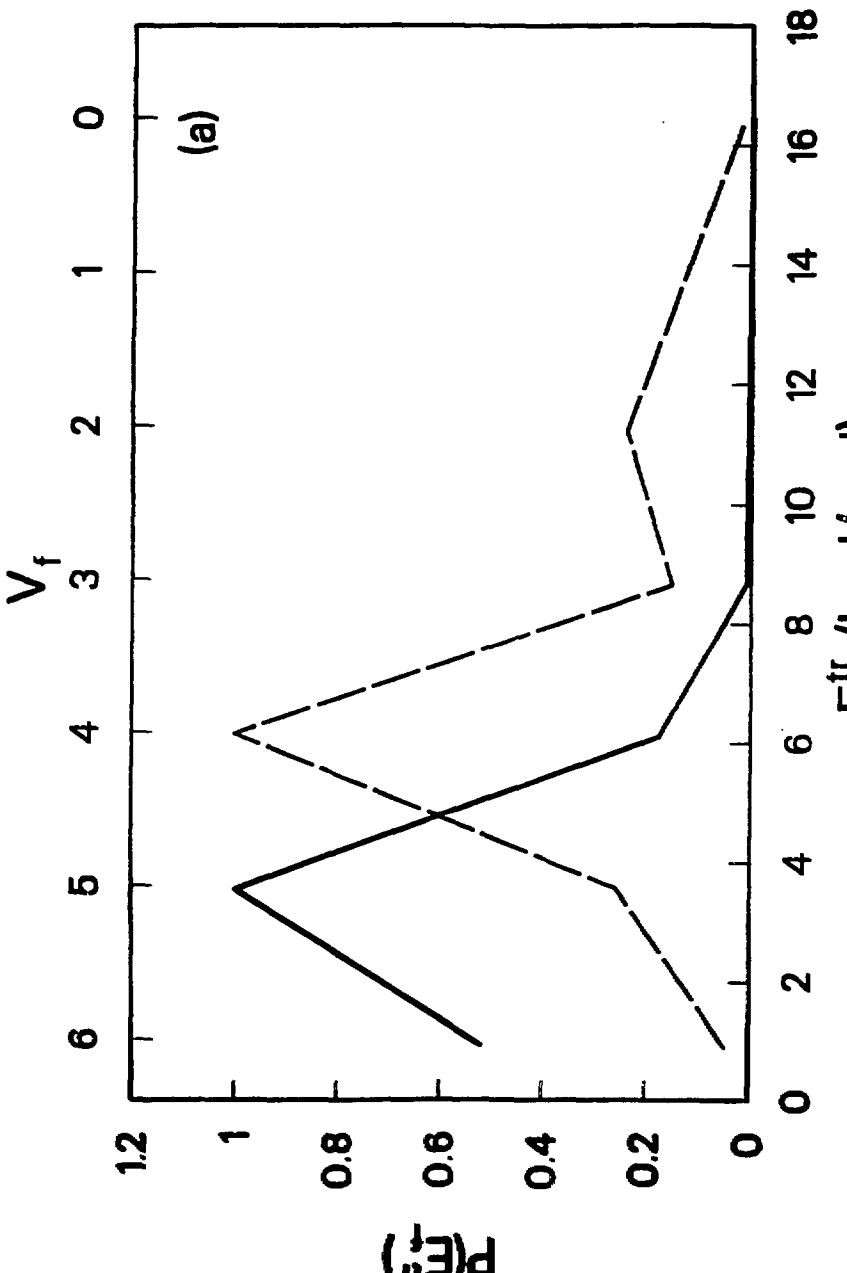
2
3
4
5
6
7
8
E_f^{tr} (kcal/mol)
XCG 867-326

Fig. 2a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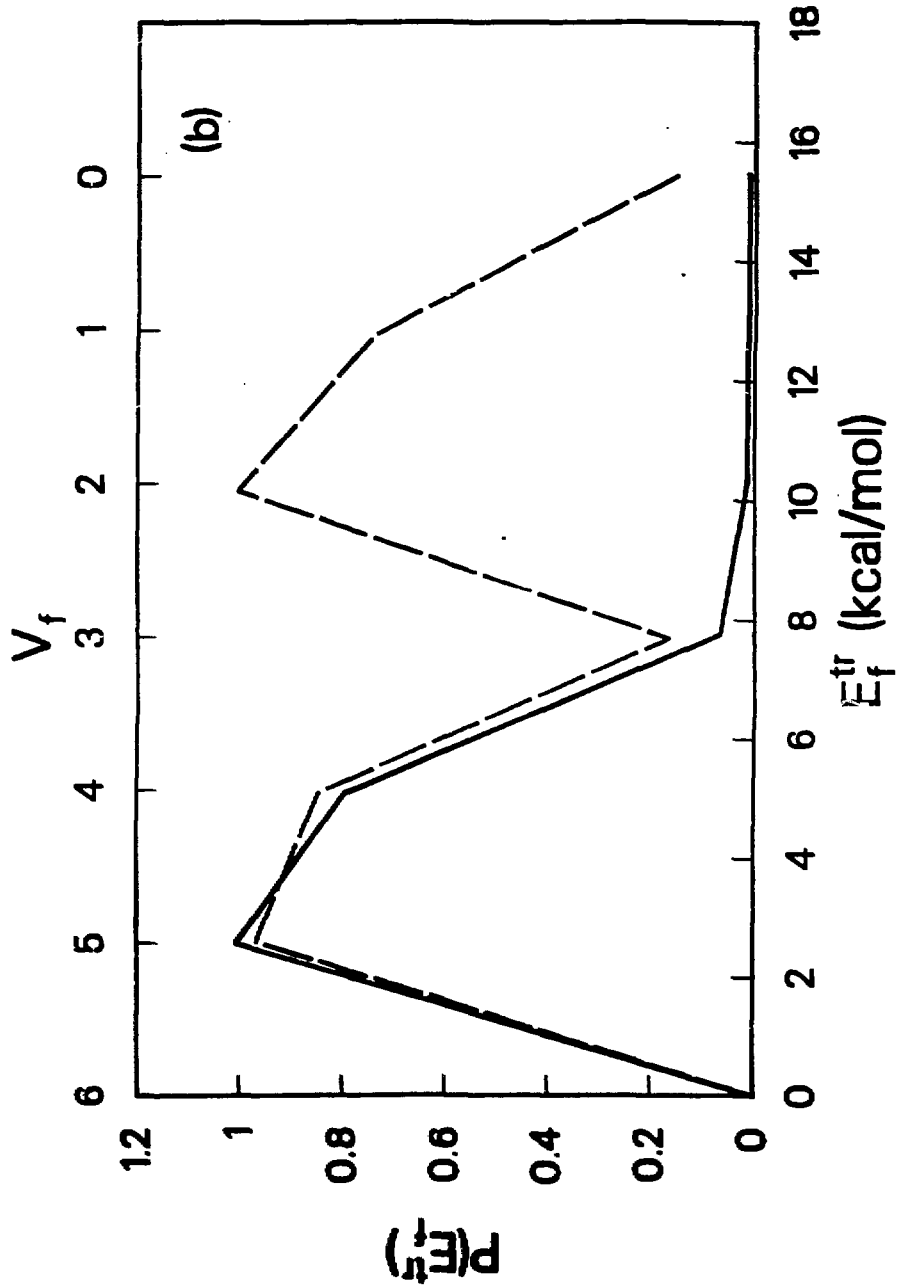
8
10
12
14
16
18

Fig. 2b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E_f^{tr} (kcal/mol)
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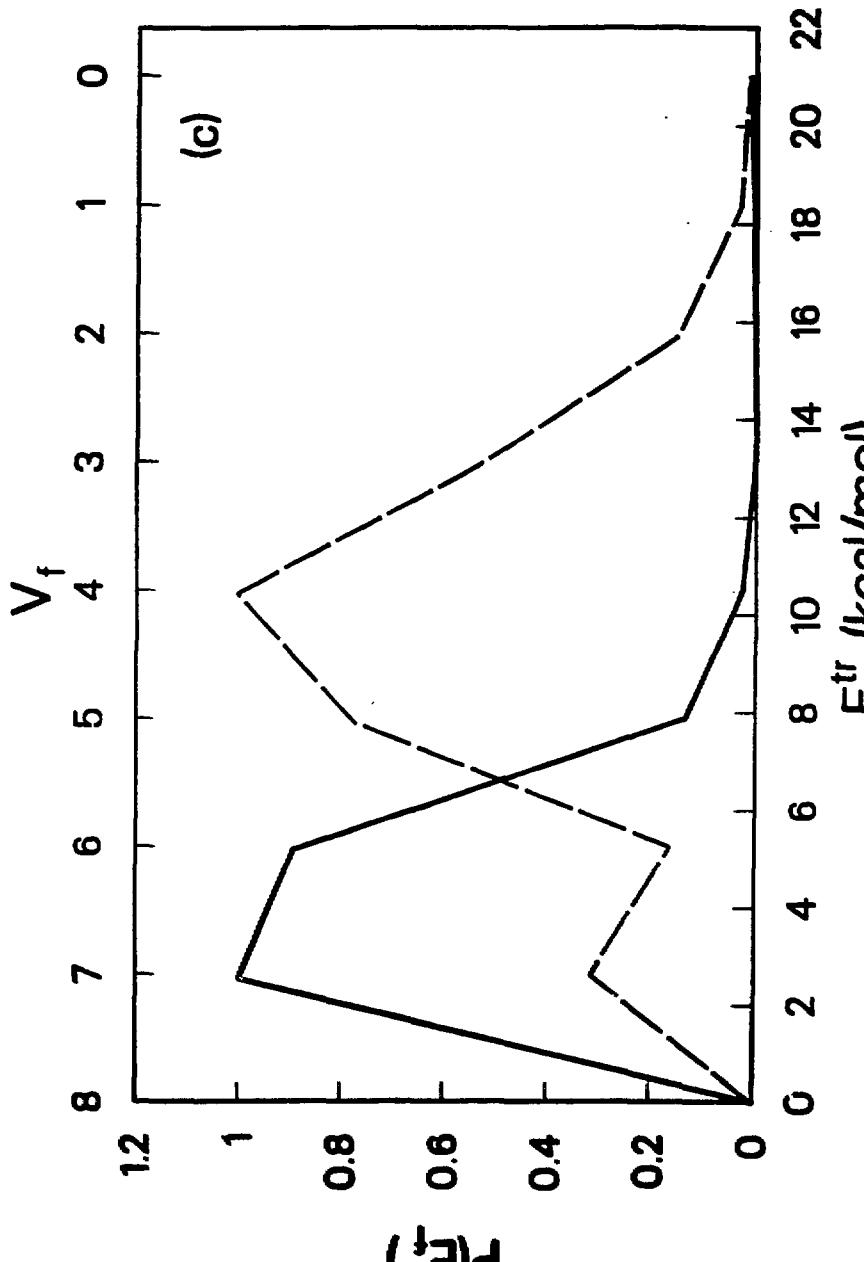
Fig. 2c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E_f^{tr} (kcal/mol)
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XCG 857-328

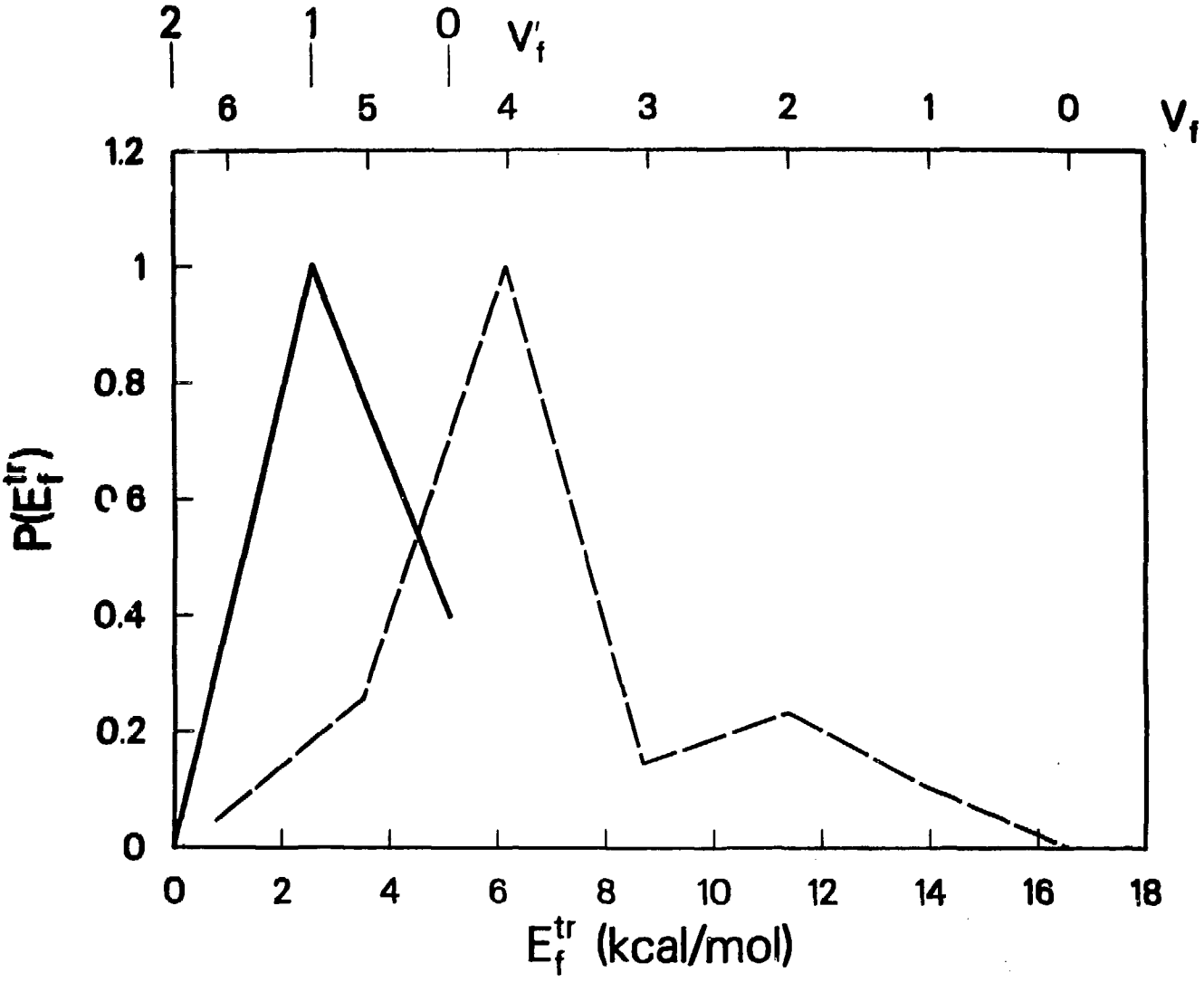

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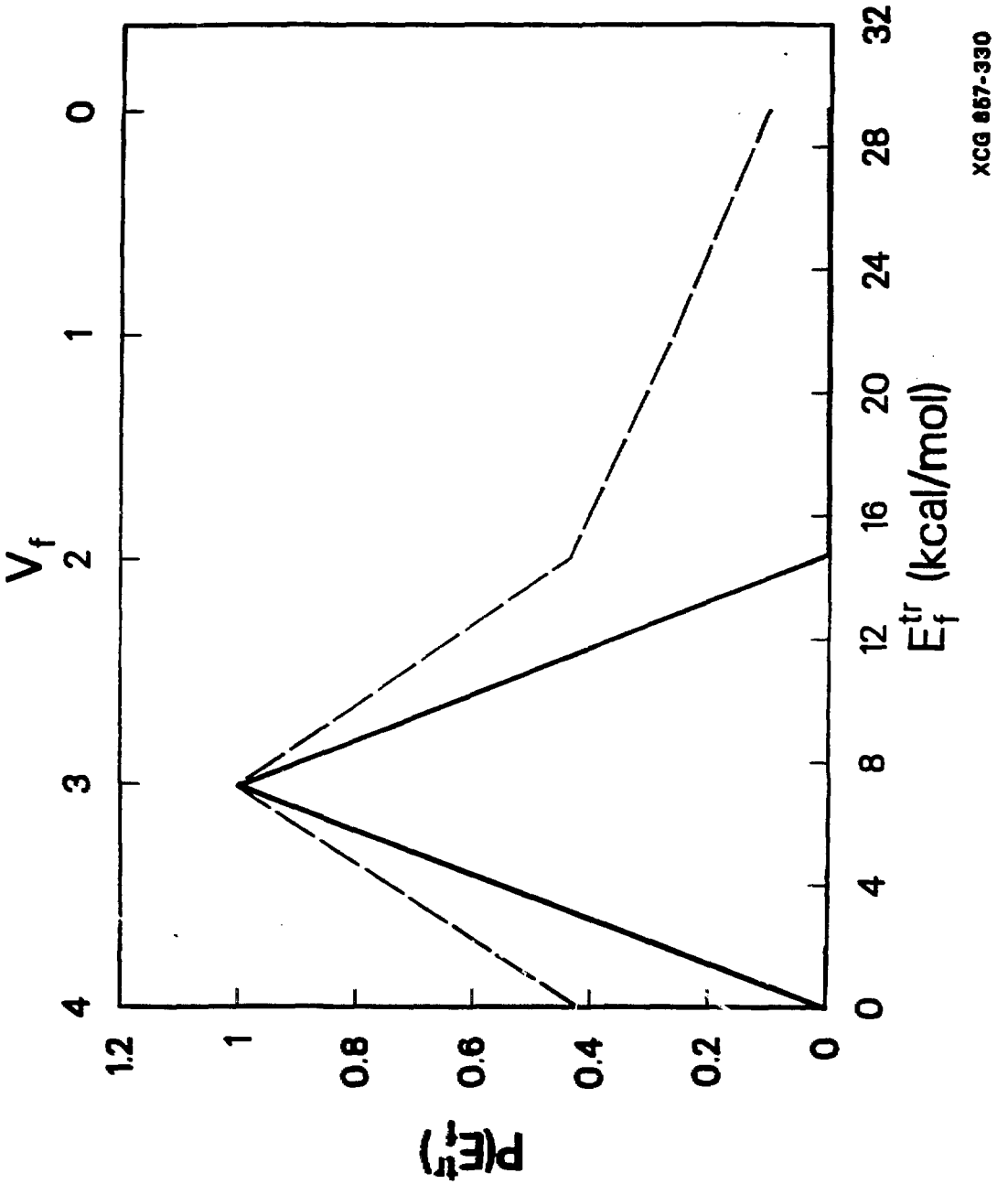
Fig. 3

Fig. 4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8
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16
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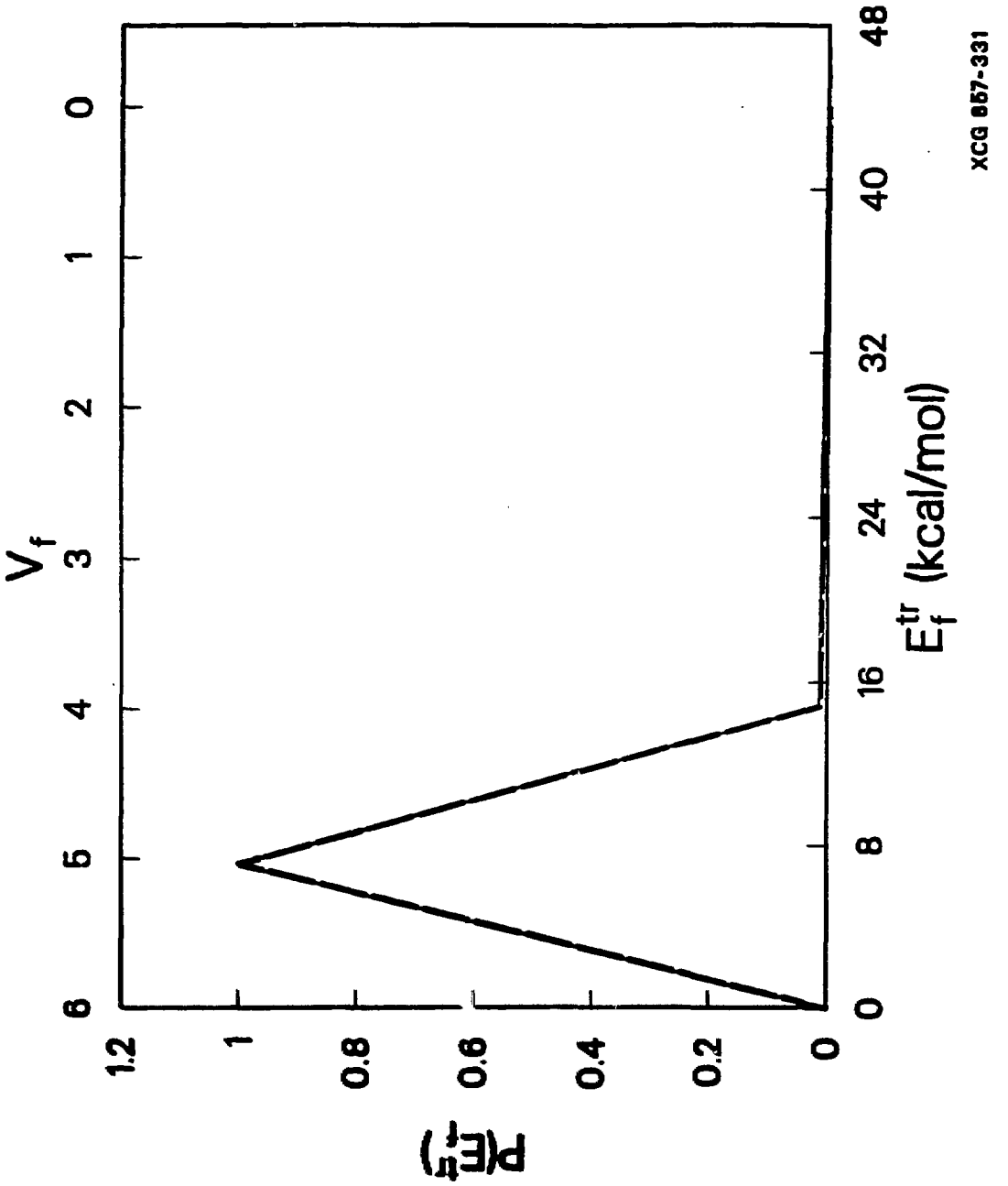
24
28
32
E_f^{tr} (kcal/mol)
XCG 857-330

Fig. 5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E_f^{tr} (kcal/mol)
6
5
4
3
2
1
0
V_f
XCG 857-331