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CHEMICAL REACTION AS A QUANTUM TRANSITION*

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Abstract

In this theory a chemical reaction is treated as a quantum transition from reactants to products. It leads to a Franck-Condon-like factor for the evaluation of product energy distributions. Second quantization representation is used to enable a Hamiltonian for reaction to be defined. A specific adiabatic method is used to describe the dynamics of nuclear motion. The theory is applied to the reactions: $\text{HO} + \text{D} \rightarrow \text{OD} + \text{H}$ and $\text{ClI} + \text{D} \rightarrow \text{Cl} + \text{ID}$. Polyatomic photodissociation can also be treated by a similar formalism.

I. Introduction

The present paper is concerned with evaluation of the energy distribution of products of a bimolecular chemical reaction, and of the fragments of a polyatomic photodissociation for which, in both cases, the event occurs on a single potential energy hypersurface. The latter (see, e.g., [1,2]), indirect photodissociation via predissociation of type II, has not been studied in detail.

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For bimolecular reactions there are powerful methods for the investigation of the dynamics of chemical reactions; see, for example, refs. 3-5. As is well documented, however, the prediction of state-to-state energy distributions remains a formidable problem.

Franck-Condon-type approaches have appeared for the determination of energy distributions of reaction products and of photofragments [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 [14]. In the latter case, the operator causing the transition was not obtained.

In this paper, a method is proposed, leading to a Franck-Condon-like factor, that is characterized by the following features: (1) It is a unified approach that treats both chemical reaction and indirect photodissociation as quantum transitions. The method is similar in structure to Bardeen's theory of tunneling [15]. The matrix element describing the transition can be obtained in explicit form. Then the problem of the evaluation of the energy distribution of the products (fragments) is reduced to the evaluation of a Franck-Condon factor. (2) A specific reaction Hamiltonian is introduced in second quantization representation. (3) The quantum transition occurs between quasiadiabatic states, as defined by O'Malley [16], which provide a "localized" description of the electronically adiabatic potential energy surface. (4) The Franck-Condon factor arises from steps similar to those introduced in our theory of indirect polyatomic

photodissociation of type I in which interfragment interaction is described. The concept of a bound-continuous state developed in ref. 17 is used here to facilitate the description of the nuclear dynamics of reactants and products.

The structure of the paper is as follows. The method 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 Sec. II. Also contained in this section is the description of the diabatic states essential for the development of the Franck-Condon expression. Section III addresses the problem of the evaluation of the Franck-Condon factor and presents several applications of the theory.

II. Reactant $\rightarrow$ Product Transition: Reaction Hamiltonian

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

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

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

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

Here $\hat{T}_r$ 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:

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

where $\psi_n(\vec{r}, \vec{R})$ is the electronic wave function. Now, consider Eqs. (1) and (2) 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 , $\epsilon_n + 1$ to ϵ_R , ϵ_P so that

$$[\hat{T}_r + \tilde{V}(\vec{r}, \vec{R})] \tilde{\psi}_R(\vec{r}, \vec{R}) = \tilde{\epsilon}_R(\vec{R}) \tilde{\psi}_R(\vec{r}, \vec{R}) \quad (4)$$

$$[\hat{T}_r + \tilde{V}(\vec{r}, \vec{R})] \tilde{\psi}_P(\vec{r}, \vec{R}) = \tilde{\epsilon}_P(\vec{R}) \tilde{\psi}_P(\vec{r}, \vec{R}) \quad (5)$$

We choose the potential $\tilde{V}(\vec{r}, \vec{R})$ such that the term $\tilde{\epsilon}_R(\vec{R})$ is given by $\epsilon_n(\vec{R})|_i$ (the index "i" identifies the reactant channel). In an analogous way, we introduce a term $\tilde{\epsilon}_P(\vec{R})$ which behaves as $\epsilon_n(\vec{R})|_f$ (the product channel, or the photofragmentation channel in the case of indirect photodissociation).

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

$$[\hat{T}_R + \tilde{\epsilon}_R(\vec{R})] \tilde{\phi}_{Rv}(\vec{R}) = E \tilde{\phi}_{Rv}(\vec{R}) \quad (6)$$

$$[\hat{T}_R + \tilde{\epsilon}_P(\vec{R})] \tilde{\phi}_{Pv}(\vec{R}) = E \tilde{\phi}_{Pv}(\vec{R}) \quad (7)$$

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

$$\tilde{H} = \hat{T}_r + \hat{T}_R + \tilde{V}(\vec{r}, \vec{R}) \quad (8)$$

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.

For indirect photodissociation, one can similarly introduce states $\tilde{\Psi}_Q(\vec{r}, \vec{R}) = \tilde{\psi}_Q(\vec{r}, \vec{R}) \tilde{\phi}_Q(\vec{R})$ and $\tilde{\Psi}_D(\vec{r}, \vec{R}) = \tilde{\psi}_D(\vec{r}, \vec{R}) \tilde{\phi}_D(\vec{R})$ describing the predissociative quasi-discrete state Q and the dissociative state of the fragments D.

A chemical reaction can be treated as a quantum transition from reactants to products. Similarly, indirect photodissociation is a $Q \rightarrow D$ (quasidiscrete to dissociative state) quantum transition. Indeed, the Schroedinger equation [1] can be rewritten in the form

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

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

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

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. 18) based on the time-dependent Schroedinger equation with Hamiltonian $H = \tilde{H} + \Delta H$ 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, and with predissociation by vibration. Thus in accordance with the Born-Oppenheimer approximation, one can neglect the coupling of electronic and nuclear motions due to $\hat{T}_R$; see also ref. 11. This coupling is important 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. 18). (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:

$$dw_{f \leftarrow i} = \frac{2\pi}{\hbar} |a_{fi}|^2 \delta(E_f - E_i) dv_f \quad (11)$$

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

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

Here $i \equiv R(Q)$ denotes the state of the reactants, or the predissociative quasidiscrete state, and $f \equiv P(D)$ denotes the state of the products, or the dissociative state.

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 element¹⁹ 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)

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

Equation (13) can be rewritten in the form

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

where

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

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

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

where

$$F = \int \tilde{\phi}_f(\vec{R}) \tilde{\phi}_i(\vec{R}) d\vec{R} \quad (17)$$

is a Franck-Condon 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 (photo-fragment) energy distributions reduces to the analysis of the nuclear dynamics and to the evaluation of a Franck-Condon factor (see below, Sec. III).

Quasiadiabatic Representation

The transformation $V \rightarrow \tilde{V}$ introduced in Sec. II is most conveniently pictured in terms of quasiadiabatic states as introduced by O'Malley [16]. 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 Franck-Condon approximation, the quantum transition occurs near the crossing point of the quasiadiabatic surfaces.

Second Quantization Reaction Hamiltonian

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:

$$\hat{H} = \hat{H}_0 + \hat{H}_{P \leftarrow R} \quad (18)$$

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

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

Here $\{i\} \equiv \{n, v\}$ denotes reactant states, n is a set of electronic states, v corresponds collectively to vibrational, translational, and rotational motions; $\{f\}$ denotes products states, and b_i and b_f^+ are the operators of annihilation and creation. In a similar way, one can introduce the Hamiltonian $\hat{H}_{D \leftarrow Q}$, describing the transition from a quasidiscrete state $\rightarrow$ photofragments. These Hamiltonians are analogous to the tunneling Hamiltonian [20].

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

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

For Fermions one replaces (n_f+1) by $(-1)^{v_i+v_f}(1-n_f)$ where $v_i(f)$ 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

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

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.¹⁹ Hence (21) and (11) are valid even if a_{fi} is large for sufficiently short characteristic 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, cf, 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. Evaluation of the Franck-Condon Factor

According to Eqs. (16) and (17), the calculation of product (photo-fragment) energy distributions is reduced to one of nuclear dynamics. In order to evaluate the Franck-Condon factor (17), it is necessary to obtain expressions for the nuclear wave functions $\tilde{\phi}_Q$, $\tilde{\phi}_D$ (photo-dissociation) or $\tilde{\phi}_R$, $\tilde{\phi}_P$ (bimolecular reaction). These wave functions are the solutions of the nuclear Schroedinger equation:

$$[\hat{T}_{\vec{R}} + U_k(\vec{R})] \tilde{\phi}_k(\vec{R}) = E \tilde{\phi}_k(\vec{R}) \quad (22)$$

$$U_k(\vec{R}) \equiv \tilde{\epsilon}_k(\vec{R}); k = \{Q, D: R, P\}$$

The quasidiscrete Q state can be described (in the harmonic approximation) by the function $\tilde{\phi}_Q$ which is a product of functions corresponding to different normal modes of the Q state. The main difficulty in solving Eq. (22) for the dissociative state, as well as

for R and P states, arises from nonseparability of variables. Indeed, if we consider, for example, the dissociative state, the potential energy $V_D(\vec{R})$ can be expressed in terms of q_D and ρ_D , where q_D denotes the internal coordinates of the fragments, and ρ_D describes the intermolecular separation of the fragments. The potential energy $V_D(\vec{R})$ cannot be expanded in a series of deviations of all variables from equilibrium, because ρ_D corresponds to translational motion.

To address this problem, we employ our adiabatic method [17] in which the nuclear wave function $\tilde{\phi}_D(\vec{R})$ is written as the product

$$\tilde{\phi}_D(\vec{R}) = \phi^{\text{vib}}(q_D, \rho_D) \phi^{\text{tr}}(\rho_D) \phi^{\text{rot}} \quad (23)$$

The interfragment interaction results in a dependence of the vibrational frequencies on the distance ρ_D and, moreover, the effective potential energy describing the relative translational motion contains the vibrational energy $E^{\text{vib}}(\rho_D)$ as an additional term. Based on this method, we have evaluated the Franck-Condon factor and product (photofragment) energy distributions for several systems.

Photodissociation of $C_2N_2(\tilde{C}^1\Pi_u)$

The method described above has been applied to the study of indirect photodissociation (type II predissociation) of $C_2N_2(\tilde{C}^1\Pi_u)$.

Electronic structure studies of cyanogen show that the $\tilde{C}^1\Pi_u$ state is best described as a $n \rightarrow \pi^*$ excitation where "n" represents a nitrogen atom lone pair electron and " π^* " is the lowest-lying unoccupied

orbital. It correlates adiabatically to a ground state $\text{CN}(X^2\Sigma^+)$ fragment and an electronically excited $\text{CN}(A^2\Pi)$ fragment [20]. The $\text{CN}(X^2\Sigma^+)$ radical has an unpaired electron located on the carbon atom. The $\text{CN}(A^2\Pi)$ radical results from the excitation of a π electron into the half-filled orbital on the carbon atom. The collinear interaction of $\text{CN}(X^2\Sigma^+)$ and $\text{CN}(A^2\Pi)$ is repulsive. In terms of molecular orbital theory, $\text{C}_2\text{N}_2(\tilde{C}^1\Pi_u)$ has an $n^3\pi^8\pi^*1$ configuration, and the $\text{CN}(X^1\Sigma^+) + \text{CN}(A^2\Pi)$ supermolecule has an $n^4\pi^7\sigma^*1$ configuration. The predissociative character of the adiabatic potential energy surface is due to the avoided curve crossing of these two diabatic states. Using standard quantum mechanical programs, it is straightforward to generate the potential energy surface for the quasibound state and for the dissociative state independently.

At the crossing point of these two diabatic surfaces the nuclear wave functions, approximated by harmonic oscillators for all bound vibrational modes, were calculated. The energy second derivatives with respect to the nuclear coordinates were obtained from numerical differences of analytically calculated first derivatives.

Present findings are that the vibrational distribution of the photo-fragments depend on the vibrational mode initially excited. Preliminary measurements [21] at 164 nm show that the ratio $n(v=1)/n(v=0) \approx 0.65$. Our calculations are in a qualitative agreement with this data. A detailed analysis will be presented elsewhere.

Distribution of reaction products. The state of reactants (products) is analogous to a dissociative state. Indeed, polyatomic photodissociation is a transition from a bound state to a bound-continuous state of fragments, whereas a chemical reaction is a transition from the bound-continuous state of the reactants to the bound-continuous state of the products.

We consider the evaluation of the Franck-Condon factor for a triatomic system. One obtains

$$F = \int \tilde{\phi}_f^{\text{tr}}(\rho_2) \tilde{\phi}_f^{\text{vib}}(\tau_2, \rho_2) \tilde{\phi}_i^{\text{tr}}(\rho_1) \tilde{\phi}_i^{\text{vib}}(\tau_1, \rho_1) d\tau_i d\rho_j \quad (24)$$

The integrand can be expressed solely in terms of ρ_2 and τ_2 . For present purposes, the rotational degrees of freedom are ignored which reduces the angular integration to a constant factor. Moreover, we limit consideration to the case $AB + C \rightarrow AC + B$ where

$$M_B \gg M_A, M_C \quad (25)$$

that is, the reaction is an exchange of the lighter mass atoms A and C. An example of such a reaction is

which has been studied by Margitan, et al. [22] Condition (25) is approximately satisfied for the reaction

A molecular beam study of this reaction [23] included the measurement of the product translational energy distribution. A peak of small $\Delta\epsilon^{tr}$ has been observed, and it is of interest to understand the origin of this peak.

We assume that the reactant AB is in the ground vibrational state. Note also that the function $\tilde{\phi}^{tr}$ describing the translational motion of the reactants (products) can be determined in the semiclassical approximation. The result of the evaluation of the Franck-Condon factor for reaction (27) is presented in Fig. 1. We note that the translational distribution has a peak in the region $\Delta\epsilon^{tr}/\Delta\epsilon^{av} \approx 20\%$, in accord with the 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 (see Ref. 17). A decrease of v and a corresponding increase of $\Delta\epsilon^{tr}$ 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 amplitude of the vibration of the reactant.) The increase of the number of oscillations leads to a decrease of F and, hence, to an inverted vibrational distribution.

For reaction (27) we have used the approximation $\Omega_i = \Omega_{i,AS} = 384.3 \text{ cm}^{-1}$ and $\Omega_f = \Omega_{f,AS} = 1639.64 \text{ cm}^{-1}$ [24], 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 the experimental data [23].

In order to carry out a detailed comparison of theory and experiment, one should calculate the necessary 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 .

For reaction (26), we have found [25] that the translational distribution of the products drops off much more rapidly with increasing ϵ_f^{tr} than it does for reaction (27). The measurements of the product energy distribution for reaction (26) has not been carried out. It would be interesting to perform such measurements to test the theoretical predictions.

Summary

We have shown that the reaction Hamiltonian method provides a quantum state-to-state description of a polyatomic photodissociation and bimolecular chemical reaction.

The main results can be summarized as follows:

1. Chemical reaction and polyatomic photodissociation can be treated as non-stationary phenomena. An analysis based on the theory of quantum transitions can be used to evaluate the energy distribution of the products (fragments).
2. A second quantization formalism facilitates the introduction of a specific reaction Hamiltonian.
3. A method of introducing diabatic states is described.

4. The problem of the evaluation of the energy distribution is reduced to the calculation of a Franck-Condon factor. The nuclear wavefunction can be obtained following our previously published theory of polyatomic photodissociation.
5. Preliminary results of the application of the theory to photodissociation of C_2N_2 , and the reactions $ClI + D \rightarrow Cl + ID$ and $OH + D \rightarrow OD + H$ are indicated.

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References

1. G. Herzberg, The Spectra and Structures of Simple Free Radicals, (Cornell University Press, Ithaca, New York, and London, 1971).
2. C. Caplan and M. Child, *Molec. Phys.* 23, 249 (1972).
3. J. Light, in Atom-Molecule Collision Theory, edited by R. B. Bernstein (Plenum Press, New York, 1979) p. 467.
4. R. Wyatt, in Atom-Molecule Collision Theory, edited by R. B. Bernstein (Plenum Press, New York, 1979) p. 477.
5. A. Kuppermann, in *Theoretical Chemistry*, 6, pt. A, edited by D. Henderson (Academic Press, New York, 1981) p. 80.
6. R. Walker and J. Light, *Ann. Rev. Phys. Chem.*, 31, 401 (1980).
7. R. Wyatt, in Atom-Molecule Collision Theory, edited by R. B. Bernstein (Plenum Press, New York, 1979) p. 567.
8. V. Halavee and M. Shapiro, *J. Chem. Phys.*, 64, 2836 (1979).
9. G. Schatz and J. Ross, *J. Chem. Phys.*, 66, 1021 (1977); 66, 1037 (1977); 66, 2943 (1977).
10. K. Fung and K. Freed, *Chem. Phys.*, 30, 249 (1978).
11. C. Vila, J. Kinsey, J. Ross, and G. Schatz, *J. Chem. Phys.*, 70, 2414 (1979).
12. C. Vila, d. Zvijac, and J. Ross, *J. Chem. Phys.*, 70, 5362 (1979).
13. J. Wong and P. Brumer, *Chem. Phys. Lett.*, 68, 517 (1979).
14. M. Berry, *Chem. Phys. Lett.*, 27, 73 (1974); *J. Chem. Phys.* 61, 3114 (1974).
15. J. Bardeen, *Phys. Rev. Lett.*, 6, 57 (1961).
16. T. O'Malley, *Phys. Rev.*, 162, 98 (1967).

17. V. Z. Kresin and W. A. Lester, Jr., Int. J. Quan. Chem., Symp. 15, 703 (1981); Chem. Phys. Lett., 87, 392 (1982); J. Phys. Chem., 86, 2182 (1982).
18. L. Landau and E. Lifshitz, Quantum Mechanics, Pergamon Press, Oxford, 1976.
19. See, for example, A. Davydov, Quantum Mechanics, Pergamon Press, Oxford (1976).
20. M. Cohen, L. Falicov, and J. Philips, Phys. Rev. Lett., 8, 316 (1962).
21. C. E. Dateo, M. Dupuis, and W. A. Lester, Jr., submitted to J. Chem. Phys.
22. W. M. Jackson, private communications.
23. J. Margitan, F. Kaufman, and J. Anderson, Chem. Phys. Lett., 34, 485 (1975).
24. J. McDonald, P. LeBreten, Y. Lee, and D. Herschbach, J. Chem. Phys., 56, 769 (1972).
26. K. Huber and G. Herzberg, Molecular Spectra and Molecular Structure. IV. Constant of Diatomic Molecules, (Van Nostrand Reinhold, New York).
27. V. Z. Kresin and W. A. Lester, Jr., to be submitted.

Figure Caption

Figure 1 Energy distribution of the products for the reaction
 $\text{C}\ell\text{I} + \text{D} \rightarrow \text{C}\ell + \text{ID}.$

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