Lawrence Berkeley National Laboratory

Recent Work

Title

THEORY OF POLYATOMIC PHOTODISSOCIATION: ADIABATIC DESCRIPTION OF THE DISSOCIATIVE STATE AND THE TRANSLATION-VIBRATION INTERACTION

Permalink

<https://escholarship.org/uc/item/0q66x72t>

Author

Lester, W.A.

Publication Date

1982-04-01

NRCC

NATIONAL
RESOURCE
FOR COMPUTATION
IN CHEMISTRY

RECEIVED

LAWRENCE
BERKELEY LABORATORY

MAY 28 1982

LIBRARY AND
DOCUMENTS SECTION

Submitted to the Journal of Physical Chemistry

THEORY OF POLYATOMIC PHOTODISSOCIATION: ADIABATIC
DESCRIPTION OF THE DISSOCIATIVE STATE AND THE
TRANSLATION-VIBRATION INTERACTION

Vladimir Z. Kresin and William A. Lester, Jr.

April 1982

TWO-WEEK LOAN COPY

*This is a Library Circulating Copy
which may be borrowed for two weeks.
For a personal retention copy, call
Tech. Info. Division, Ext. 6782.*

**LAWRENCE BERKELEY LABORATORY
UNIVERSITY OF CALIFORNIA**

LBL-12861

DISCLAIMER

This document was prepared as an account of work sponsored by the United States Government. While this document is believed to contain correct information, neither the United States Government nor any agency thereof, nor the Regents of the University of California, nor any of their employees, makes any warranty, express or implied, or assumes any legal responsibility for the accuracy, completeness, or usefulness of any information, apparatus, product, or process disclosed, or represents that its use would not infringe privately owned rights. Reference herein to any specific commercial product, process, or service by its trade name, trademark, manufacturer, or otherwise, does not necessarily constitute or imply its endorsement, recommendation, or favoring by the United States Government or any agency thereof, or the Regents of the University of California. The views and opinions of authors expressed herein do not necessarily state or reflect those of the United States Government or any agency thereof or the Regents of the University of California.

THEORY OF POLYATOMIC PHOTODISSOCIATION:
ADIABATIC DESCRIPTION OF THE
DISSOCIATIVE STATE AND THE TRANSLATION-VIBRATION INTERACTION

Vladimir Z. Kresin and William A. Lester, Jr.

National Resource for Computation in Chemistry
Lawrence Berkeley Laboratory
University of California
Berkeley, California 94720

Abstract

We develop an adiabatic method for the evaluation of the nuclear wavefunction describing the final dissociative state. The vibrational frequencies of the fragments are found to depend on the interfragment distance. We discuss the role of the translation-vibration interaction in polyatomic photodissociation.

This work was supported by the Director, Office of Energy Research, Office of Basic Energy Sciences, Chemical Sciences Division of the U.S. Department of Energy under Contract DE-AC03-76SF00098, and by the National Science Foundation under Grant No. CHE-7721305.

This manuscript was printed from originals provided by the authors.

I. Introduction

The photodissociation of a polyatomic molecule is a radiation induced transition from a ground or a quasidiscrete state to a dissociative (D) state. Both the former case (direct photodissociation) and the latter case (indirect photodissociation) are characterized by a final D state that contains discrete and continuous parts. To describe the dynamics of polyatomic dissociation including photo-fragment energy distributions requires an indepth understanding of the D state. In this paper we direct our consideration of polyatomic photodissociation to a detailed characterization of this state. For concreteness we limit attention to indirect photodissociation, but the present development is also applicable to direct photodissociation.

The D state is usually described by a nuclear wavefunction which is a product of two independent functions, one dependent only on the interfragment distance, and the other dependent solely on internal coordinates; see, e.g., recent reviews¹ and the discussion in Ref. 2. This separated variables approximation (SVA) is strictly valid only in the asymptotic region. Almost 50 years ago in a classic paper, Landau³ raised the problem of the description of the D state. He noted that a rigorous description of this state should contain the adiabatic coupling of the bound and continuous parts of the wavefunction. More recently in a significant paper, Band and Freed⁴ introduced the notion that the internal coordinates are adiabatically dependent on a reaction coordinate which asymptotically becomes the interfragment distance.

In this paper we develop a rigorous description of the D state following an adiabatic formulation. In Section II we describe the method of evaluation of the photodissociation rate and consider the D state explicitly in Section III. In Section IV we discuss the effect of the translation-vibration interaction and its role in determining the final D state.

II. Background

In indirect photodissociation the absorption of light leaves the molecule in an intermediate quasidiscrete (Q) state of finite lifetime. The Q state undergoes a radiationless transition to a final D state. Radiationless transitions are associated with deviations from the Born-Oppenheimer adiabatic approximation and are described by the corresponding operator, namely (see, e.g., Refs. 5 and 6)

$$\hat{H}' = - \sum_{\ell} \frac{\hbar^2}{2M_{\ell}} \frac{\partial}{\partial \vec{R}_{\ell} | \psi_{e\ell}} \frac{\partial}{\partial \vec{R}_{\ell} | \phi_{nuc}} \quad (1)$$

The notation $\partial/\partial \vec{R}_{\ell} | \psi_{e\ell}$ implies that $\partial/\partial \vec{R}_{\ell}$ operates only on the electronic wavefunction and, similarly, $\partial/\partial \vec{R}_{\ell} | \phi_{nuc}$ operates only on the nuclear wavefunction. The summation is over nuclei ℓ .

As a transition into the continuous spectrum, the $Q \rightarrow D$ transition probability is given by (see, e.g., Ref. 7)

$$dW_{DQ} = \frac{2\pi}{\hbar} |H'_{DQ}|^2 \delta(E' - E) \rho_E dE \quad (2)$$

where H_{DQ}^i , the coupling matrix element, is

$$H_{DQ}^i = \int \psi_D^*(\vec{r}, \vec{R}) \hat{H}^i \psi_Q(\vec{r}, \vec{R}) d\vec{r} d\vec{R} \quad (3)$$

and ρ_E is the density of states.

Introducing the Condon approximation permits the following simplification (see also Ref. 8)

$$H_{DQ}^i = \sum_i L_i N_i \quad (4)$$

where

$$N_i = \int \phi^{D*}(\vec{R}) \frac{\partial}{\partial Q_i} \phi^Q(\vec{R}) d\vec{R} \quad (5)$$

Here ϕ^D and ϕ^Q are the nuclear wavefunctions of the D and Q states, $\{Q_i\}$ are the normal coordinates of the Q state, and L_i are the electronic factors given by

$$L_i = \int \psi_{el}^{*D}(\vec{r}, \vec{R}) \frac{\partial}{\partial Q_i} \psi_{el}^Q(\vec{r}, \vec{R}) d\vec{r} \Big|_{\vec{R}=\vec{R}_0} \quad (6)$$

where $\psi_e^{D;Q}(\vec{r}, \vec{R})$ are the electronic wavefunctions and $\vec{R}_0$ denotes the equilibrium configuration of the Q state. The correctness of the approximation $L_i(\vec{R}) \approx L_i(\vec{R}_0)$ is connected with the Franck-Condon approximation and the existence of a small parameter $\delta \equiv A/L$. Here A is the vibrational amplitude and L is the bond length. It is, of

course, necessary to take into account the degeneracy of the Q and D states.⁹ Note also, that because a polyatomic system has several nuclear degrees of freedom, the Q → D transition can occur even when both states belong to the same potential energy surface.

The D state is characterized by the vibrational and rotational distribution of the molecular fragments. Both distributions are governed by the state of the nuclear subsystem. For this reason we shall focus on the nuclear part of the matrix element (5). To evaluate this factor one must, of course, first specify the nuclear wavefunctions ϕ^Q and ϕ^D .

The wavefunction for the Q state usually can be described by the harmonic approximation:

$$\phi^Q = \prod_i \phi_{v_i}(Q_i) \quad (7)$$

and

$$\epsilon_{nv} = \sum_i (v_i + 1/2) \hbar \omega_i$$

where Q_i are the normal coordinates, and $\phi_{v_i}(Q_i)$ is a harmonic oscillator wavefunction with normal frequency ω_i .

The applicability of the harmonic approximation can be tested by consideration of the experimental data. If the absorption spectrum is a set of equidistant bands, the harmonic approximation should be applicable (see, e.g., the investigation of Miller et al.¹⁰ of the

photodissociation of C_2N_2). If there is variable spacing between absorption bands, then it is necessary to include anharmonicity corrections. The function ϕ^Q also contains any rotational dependence.

The evaluation of the function ϕ^D presents a more difficult problem. We now turn to this problem.

III. The Dissociative State

A. Nuclear Hamiltonian. Statement of the Problem

The nuclear wavefunction ϕ^D is a solution of the nuclear Schrodinger equation

$$\hat{H}^N \phi^D = E \phi^D \quad (8)$$

where the Hamiltonian $\hat{H}^N$ is given by

$$\hat{H}^N = \hat{T}_A + \hat{T}_B + U(\vec{R}) \quad (9)$$

Here $\hat{T}_A$ and $\hat{T}_B$ are the kinetic energy operators of fragments A and B and $U(\vec{R}) \equiv E_n(\vec{R})$ is the potential energy of nuclear motion. The function $E_n(\vec{R})$ is the potential energy surface for the n-th electronic state.

It is convenient to write the Hamiltonian $\hat{H}^N$ in the form

$$\hat{H}^N = \hat{T}_{int} + \hat{T}_p + U(\rho, q_i^A, q_i^B) \quad (10)$$

where

$$\hat{T}_{\text{int}} = - \sum_{i,k}^A \frac{\partial^2}{\partial q_i \partial q_k} + \sum_{l,m}^B \frac{\partial^2}{\partial q_l \partial q_m} \quad (11)$$

$$\hat{T}_{\vec{\rho}} = - \frac{\hbar^2}{2\mu} \frac{\partial^2}{\partial \rho^2} \quad (12)$$

where q_i^A and q_l^B are the internal coordinates of fragments A and B, $\vec{\rho} = \vec{R}_B - \vec{R}_A$ ($\vec{R}_A$ and $\vec{R}_B$ correspond to the centers of mass of the separate fragments), and $\mu = M^A M^B / (M^A + M^B)$ is the reduced mass of the total system. The potential energy is conveniently expressed in terms of ρ , q_i^A and q_l^B . If, for instance, we consider the simplest polyatomic system, a triatomic molecule abc which can dissociate into atom a and diatomic fragment bc, we obtain

$$\hat{H}^N = - \frac{\hbar^2}{2\mu} \frac{\partial^2}{\partial \rho^2} - \frac{\hbar^2}{2\mu_F} \frac{\partial^2}{\partial \vec{q}^2} + U(\rho, \vec{q}) \quad (13)$$

where $\vec{\rho} = \rho \vec{n}$ ($\vec{n}$ is a unit vector directed from atom a to the center of mass of the fragment bc), $\mu_F = m_b m_c / (m_b + m_c)$ is the reduced mass of the fragment, $\vec{q} = q \vec{s}$ (q is the distance between atoms b and c, $\vec{s}$ is a unit vector directed from atom b to atom c).

Unlike the Q state, the potential energy for the D state can not be expanded in a series of the deviations of all variables from equilibrium, because ρ corresponds to translational motion. Hence, variables are not separable and the function $\phi^D(\rho, q_i^A, q_l^B)$ generally can not be well approximated as a product $\phi_1^D(\rho) \phi_2^D(q_i^A, q_l^B)$. In the

asymptotic region this separable product form is valid because the potential energy no longer depends on ρ . Because of the Franck-Condon principle, the main contribution to the coupling matrix element H_{DQ}^i (see Eq. (5)) is not connected with the asymptotic region, but comes from a region $\rho \sim \rho_0$, where ρ_0 corresponds to the equilibrium configuration of the precursor molecule. Hence, it is necessary to take into account the interfragment interaction, that is, the dependence of the potential energy on ρ . This interaction is not small, in general, and hence the deviation from the SVA is not governed by a small parameter. For this reason, the contribution of higher-order terms might be large and then, correspondingly, the SVA zeroth-order approximation would be unacceptable. Hence a general expression for ϕ^D (see below) can differ noticeably from the zeroth-order SVA.

We present here a new approach to the determination of ϕ^D . Note that because it is often a good approximation to separate rotational from translational and vibrational motion, we do so here and consider first the latter motions of the fragments.

B. Slow Translational Motion ($\Delta E^{\text{rec}} \ll \Delta E^{\text{vib}}$)

When the recoil (relative) motion is slower than the vibrational motion, we can use an adiabatic approach to evaluate $\phi^D(R)$. The Hamiltonian $\hat{H}^N$ can be written in the form:

$$\hat{H}^N = \hat{H}_{\text{tr}} + \hat{H}^A + \hat{H}^B \quad (14)$$

where

$$\hat{H}_{tr} = -\frac{1}{2\mu} \frac{\partial^2}{\partial \rho^2} + U(\rho, q_{i0}^A(\rho), q_{l0}^B(\rho)) \quad (15)$$

$$\hat{H}^Z = -\sum_{i,j}^Z \frac{\partial^2}{\partial q_i \partial q_l} + \frac{1}{2} K_{ij}^Z(\rho) \tau_i^Z \tau_j^Z \quad Z = \{A, B\} \quad (16)$$

$$\text{and} \quad \tau_i^Z = q_i^Z - q_{i0}^Z(\rho)$$

are the deviations of the internal coordinates q_i^Z from equilibrium.

The force constants $K_{ij}^Z(\rho)$ and the coordinates $q_{i0}^Z(\rho)$ can be determined from the conditions

$$\left(\partial U / \partial q_i^Z \right)_{q_i=q_{i0}(\rho)} = 0 \quad ; \quad K_{ij}^Z(\rho) = \left(\partial^2 U / \partial q_i^Z \partial q_j^Z \right) \Big|_{\substack{q_i=q_{i0}(\rho) \\ q_j=q_{j0}(\rho)}}$$

The interfragment distance ρ does not appear as an explicit expansion variable. The term H^Z can be reduced to the form

$$\hat{H}^Z = -\sum_i^Z \left(\frac{\partial^2}{\partial \theta_{iZ}^2} - \frac{1}{2} K_i^Z(\rho) \theta_{iZ}^2 \right) \quad (17)$$

where $\{\theta_{iZ}\}$ are the normal coordinates (dependent on ρ) of the Z -th fragment.

For photodissociation of a triatomic molecule, we obtain (see Eq. (13)):

$$\hat{H}^N = -\frac{\hbar^2}{2\mu} \frac{\partial^2}{\partial \rho^2} - \frac{\hbar^2}{2\mu_F} \frac{\partial^2}{\partial q^2} + U(\rho, q_0(\rho)) + \frac{1}{2} K(\rho) \tau^2 \quad (18)$$

where

$$K(\rho) = (\partial^2 U(\rho, q) / \partial q^2)_{q=q_0(\rho)} ;$$

$$(\partial U / \partial q)_{q=q_0(\rho)} = 0 ;$$

$$\tau = q - q_0(\rho) \quad (19)$$

For simplicity, we do not consider the bending motion, that is, we neglect the dependence of the potential energy $U(\rho, q)$ on the angle between $\vec{n}$ and $\vec{s}$; at the same time, we neglect the rotational motion of the fragment and treat the system as a one-dimensional oscillator. Note that the bending contribution has been discussed in Refs. 2 and 11. The rotational motion also can be considered separately (see, e.g., Ref. 12).

We shall describe our approach using the Hamiltonian of Eq. (18), but we emphasize that there is nothing in our development that limits our theory to triatomic systems (for the extension to larger systems, see Ref. 11). The solution of Eq. (8) using (18) can be written in the form¹¹

$$\phi^D(q, \vec{\rho}) = \phi_{pv}^{tr}(\vec{\rho}) \phi_v^{vib}(\rho, q) \quad (20)$$

where ϕ_v^{vib} is a harmonic oscillator wavefunction whose frequency is dependent on ρ , i.e.,

$$\phi_v^{\text{vib}}(\rho, q) = \left(\frac{\mu_F \omega(\rho)}{\pi \hbar} \right)^{1/4} \frac{1}{\sqrt{2^v v!}} e^{-\frac{\mu_F \omega(\rho)}{2\hbar} \tau^2} H_v \left(\tau \sqrt{\frac{\mu_F \omega(\rho)}{\hbar}} \right) \quad (21)$$

Here

$$\tau = q - q_0(\rho), \quad \omega(\rho) = [\mu_F^{-1} K(\rho)]^{1/2} \quad ; \quad (22)$$

$K(\rho)$ and $q_0(\rho)$ are defined by Eq. (19). The function $\phi_{pv}^{\text{tr}}(\rho)$ is a solution of

$$\left[-\frac{1}{2\mu} \frac{\partial^2}{\partial \rho^2} + U^{\text{eff}}(\rho) \right] \phi_{pv}^{\text{tr}}(\vec{\rho}) = E \phi_{pr}^{\text{tr}}(\vec{\rho}) \quad (23)$$

where

$$U^{\text{eff}}(\rho) = U(\rho, q_0(\rho)) + E^{\text{vib}}(\rho)$$

$$E^{\text{vib}}(\rho) = \left(v + \frac{1}{2} \right) \hbar \omega(\rho) \quad . \quad (24)$$

Equations (20)-(24) can be obtained¹¹ by analogy with the development of the Born-Oppenheimer approximation. Instead of a system of electrons and nuclei, we consider here only nuclear motion of a polyatomic system with several degrees of freedom, one of which is "fast" relative to the others.

The interfragment interaction is taken into account in the zeroth-order approximation (Eq. (20)) in two ways. First, the vibrational

frequency (see Eqs. (21) and (22)) depends on the distance between the fragments. Second, the effective potential energy that describes the relative motion (see Eq. (24)), contains the vibrational energy $E^{\text{vib}}(\rho)$.

Equation (23) has the form of a Schrödinger equation for a centrally symmetric field. The angular part of the wavefunction $\phi_{lm}^{\text{ang}}(\Omega_i)$ can be separated in the usual way. This function describes the angular dependence of $\phi^D(q, \vec{r})$. Moreover, we can use the semi-classical approximation (see, e.g., Ref. 7) to solve Eq. (23). Hence, the radial part of $\phi_{pv}^{\text{tr}}(\vec{r})$ is given by (in the region far from the classical turning point a_t)

$$\phi_{pv}^{\text{tr}}(\rho) = \rho^{-1} \cos[\sigma(\rho) + \delta] \quad (25)$$

where

$$\sigma(\rho) = \hbar^{-1} \int_{a_t}^{\rho} p(\rho) d\rho$$

and

$$p(\rho) = \left\{ 2\mu [E - U(\rho, q_0(\rho)) - (v + \frac{1}{2}) \hbar \omega(\rho)] \right\}^{1/2} \quad (26)$$

Because the main contribution to the matrix element (Eqs. (4) and (5)) arises from the region $\rho \sim \rho_0$ we need to know the value $\omega \equiv \omega(\rho_0)$. We emphasize that $\omega(\rho_0)$ and ω_F (the frequency of the isolated fragment) are, in general, significantly different. The frequency ω can be obtained from the force constants of the Q state. Indeed, the quantity $K(\rho_0)$ (see Eqs. (19) and (22)) is equal¹¹ to $(\partial^2 U(\rho, q) / \partial q^2)_{q=q_0(\rho_0)} \equiv K_{qq}$, where K_{qq} is the corresponding force constant of the Q state.

C. Slow Internal Motion ($\Delta E^{\text{rec}} \gg \Delta E^{\text{vib}}$)

When the recoil energy is considerably larger than the vibrational energy, we can again follow the adiabatic approach by neglecting in this case the kinetic energy of internal motion. This approach yields

$$\phi_{pv}^D = \phi_p^{\text{tr}}(\vec{\rho}, q) \phi_{pv}^{\text{vib}}(q) \quad (27)$$

The function $\phi_p^{\text{tr}}(\vec{\rho}, q)$ satisfies the equation

$$\left[-\frac{\hbar^2}{2\mu} \frac{\partial^2}{\partial \vec{\rho}^2} + U(\rho, q) \right] \phi_p^{\text{tr}}(\vec{\rho}, q) = \mathcal{E}(q) \phi_p^{\text{tr}}(\vec{\rho}, q) \quad (28)$$

Using the semiclassical approximation, we obtain the following expression for the radial part of ϕ_p^{tr} :

$$\phi_p^{tr}(\rho, q) = \rho^{-1} \cos[\sigma(\rho, q) + \delta] \quad (29)$$

where

$$\sigma = \hbar^{-1} \int_{a_t}^{\rho} p(\rho, q) d\rho \quad (30)$$

$$p^2(\rho, q) = 2\mu[\mathcal{E}(q) - U(\rho, q)] \quad (31)$$

The function $\phi_{pv}^{vib}(q)$ satisfies the following equation,

$$\left[-\frac{\hbar^2}{2\mu_F} \frac{\partial^2}{\partial q^2} + \mathcal{E}(q) \right] \phi_{pv}^{vib}(q) = E \phi_{pv}^{vib}(q) \quad (32)$$

We can see from (32) that $\phi_{pv}^{vib}(q)$ in the harmonic approximation is the harmonic oscillator wavefunction

$$\phi^{vib}(q) = \left(\frac{\mu_F \omega_c}{\pi \hbar} \right)^{1/4} \frac{1}{\sqrt{2^v v!}} e^{-\frac{\mu_F \omega_c}{2\hbar} \tau^2} H_v \left(\tau \sqrt{\frac{\mu_F \omega_c}{\hbar}} \right) \quad (33)$$

of frequency $\omega \equiv \omega_c$ where

$$\omega_c = \left[\mu_F^{-1} (\partial^2 \mathcal{E}(q) / \partial q^2)_{q=q_{oc}} \right]^{1/2} ; \quad (34)$$

$$\tau = q - q_{oc} .$$

The equilibrium position and the vibrational spectrum are defined by the following equations

$$(\partial \mathcal{E}(q)/\partial q)_{q=q_{oc}} = 0$$

$$E^{vib} = E - \mathcal{E}(q_0) = \left(v + \frac{1}{2}\right) \hbar \omega_c \quad ; \quad q_0 \equiv q_{oc} \quad (35)$$

D. "Clamped" Translational Function Approximation

When the vibrational energy is significantly smaller than the translational energy, we can take the adiabatic theory one step further. The function $\phi_p(\vec{\rho}, q)$ (see Eq. (27)) can be replaced by its value at $q = q_0$ (see Eq. (35)) so that one obtains the product function

$$\phi_{pv}^D = \phi_p^{tr}(\vec{\rho}, q_0) \phi_{pv}^{vib}(q) \quad (36)$$

This approach is analogous to the "crude" adiabatic approximation used in the theory of radiationless transitions (see, e.g., Refs. 13-15).

Note that in the harmonic approximation ϕ_{pv}^{vib} can be chosen as a solution of (32) (see Ref. 13). The function $\phi_p^{tr}(\rho, q_0)$ is a solution of

$$\left[-\frac{\hbar^2}{2\mu} \frac{\partial^2}{\partial \rho^2} + U(\rho, q_0) \right] \phi_p(\vec{\rho}, q_0) = \mathcal{E}(q_0) \phi_p(\vec{\rho}, q_0) \quad (37)$$

The angular dependence can be separated in the usual way. Using the semiclassical approximation, we arrive at the following expression for the radial part of the wavefunction

$$\phi_p(\rho, q_0) = \rho^{-1} \cos [\sigma(\rho, q_0) + \delta] \quad (38)$$

Here

$$\sigma(\rho, q_0) = \hbar^{-1} \int_{a_t}^{\rho} p(\rho, q_0) d\rho$$

where

$$p = \left\{ 2\mu [E(q_0) - U(\rho, q_0)] \right\}^{1/2} \quad (39)$$

or (see Eq. (35))

$$p = \left\{ 2\mu \left[E - U(\rho, q_0) - \left(v + \frac{1}{2} \right) \hbar \omega_c \right] \right\}^{1/2} \quad (40)$$

Note that ϕ_{pv}^D of Eq. (36) has the form of the zeroth-order separated variables approximation (SVA). It is a product of two functions. One depends only on $\vec{p}$ and the other only on q . Hence, we conclude that the SVA is valid, if internal motion is slower than relative motion.

One should note that the vibrational part of the SVA wavefunction and the function $\phi_{pv}^{vib}(q)$ of Eq. (36) differ in the value of the frequency. The SVA frequency is given by

$$\omega_{SVA} \equiv \omega_F = \left[\mu_F^{-1} (\partial^2 U^{As}(q) / \partial q^2)_{q=q_F} \right]^{1/2} \quad (41)$$

where $U^{As}(q) = U(\vec{p}, q)|_{p \rightarrow \infty}$. Here ω_F and q_0^F are values for the isolated fragment, while the frequency ω_c is given by Eq. (34). Using Eq. (31), it is possible to obtain the approximate relation between ω_c and ω_{SVA} . Indeed, we can write

$$\mathcal{E}(q) = \frac{p_0^2(q)}{2\mu} + U^{As}(q) \quad ; \quad p_0(q) = p(p, q)|_{p \rightarrow \infty} \quad (42)$$

Using Eqs. (31) and (34), we obtain

$$\omega_c^2 = \omega_F^2 [1 + \lambda] \quad (43)$$

where

$$\lambda = (\mu_F \mu \omega_F^2)^{-1} \partial^2(p_0^2(q))/\partial q^2|_{q=q_0}$$

Let us estimate the value of λ ,

$$\lambda \sim (\mu_F \mu \omega_F^2)^{-1} p_0^2/q_0^2 \quad (q_0 \equiv L \text{ is the bond length})$$

Hence, one can write

$$\lambda \sim (p_0^2/\mu \hbar \omega_F)(\hbar/\mu_F \omega_F A^2)(A^2/L^2)$$

where A is the vibrational amplitude. Because $\mu_F \omega_F A^2 \sim \hbar$ we obtain

$$\lambda \sim \alpha \delta^2 \quad ; \quad \alpha \equiv (\Delta E^{\text{rec}} / \Delta E^{\text{vib}}) \quad (44)$$

Note that the "clamped" translational function approximation dictates that δ is a small parameter (see also discussion following Eq. (6)), and consequently that λ is also small. Thus a large value of α is usually compensated by a small value of δ with the result that

$$\omega_c \approx \omega_F.$$

E. Intermediate Case and Further Discussion

We have been considering two limiting cases: $\alpha \ll 1$ (Sec. III-B and $\alpha \gg 1$ (Secs. III-C and III-D). For the intermediate case $\alpha \sim 1$, it is possible to write the appropriate solution as a linear combination of the functions (20) and (27)¹¹ with coefficients that are functions of α .

The "clamped" translational function approximation (CTFA) (previous section) enables one to obtain another form of the general solution. The construction of this solution is facilitated by carrying out a direct comparison of the "clamped" limiting case $\alpha \gg 1$ with the case $\alpha \ll 1$, Sec. III-B. In both cases the wavefunction ϕ^D is written as a product of two functions (see Eqs. (20) and (36)). Moreover, the structure of the corresponding function for each case is very similar (cf, (21) and (33); (25) and (38); (26) and (40)). One notes that, the limiting cases differ only in the explicit form of the vibrational frequency and the equilibrium position. If $\alpha \ll 1$

the frequency and the equilibrium position are functions of ρ (see Eqs. (19) and (22)), while the opposite case is characterized by constant values ω_c and q_{oc} (see Eqs. (34) and (35)). The latter quantities are expressed in terms of the function $\mathcal{E}(q)$ (see Eq. (28)), which can be obtained by averaging the potential energy over fast relative motion. Hence, we reach the conclusion that the gradual transition from the case $\alpha \ll 1$ to the opposite one is accompanied by a change in the dependence of $\omega(\rho)$ and $q_0(\rho)$ from that given by Eqs. (19) and (22) to that given by Eqs. (34) and (35). This change can be described by the interpolation function

$$\Omega(\rho) = \omega^\beta(\rho) \omega_c^{1-\beta} \quad ; \quad \beta = (\alpha^2 + 1)^{-1}$$

or

$$\Omega(\rho) = \omega_c \left(\frac{\omega(\rho)}{\omega_c} \right)^\beta \quad (45)$$

and correspondingly,

$$q_\beta(\rho) = q_{oc} (q_0(\rho)/q_{oc})^\beta \quad (46)$$

Indeed, if $\alpha \ll 1$, $\Omega(\rho) = \omega(\rho)$, while if $\alpha \gg 1$, $\Omega(\rho) = \omega_c$. The function $\Omega(\rho)$ asymptotically becomes ω_F ; see discussion following Eq. (44).

Therefore, for arbitrary α the D state can be described by the wavefunction

$$\phi^D(q, \vec{p}) = \phi^{tr}(\vec{p}) \phi^{vib}(\rho, q) \quad (47)$$

The radial part of the function ϕ^{tr} is given by Eq. (25), where

$$p(\rho) = \left\{ 2\mu [E - U(\rho, q_B(\rho)) - (v + \frac{1}{2}) \Omega(\rho)] \right\}^{1/2} \quad (48)$$

and

$$\phi^{vib}(\rho, q) = \left(\frac{\mu_F \Omega(\rho)}{\pi \hbar} \right)^{1/4} \frac{1}{\sqrt{2^v v!}} e^{-\frac{\mu_F \Omega(\rho)}{2\hbar} \tau^2} H_v \left(\tau \sqrt{\frac{\mu_F \Omega(\rho)}{\hbar}} \right) \quad (49)$$

$$\tau = q - q_B(\rho)$$

Since the main contribution to the coupling matrix element (Eqs. (4) and (5)) arises from regions of overlap of the wavefunctions (see Sec. II), we need only to know the value $\tilde{\Omega} \equiv \Omega(\rho_0) = \omega_c (\tilde{\omega}/\omega_c)^\beta$.

IV. Translation-Vibration Interaction

Let us consider for concreteness the case of internal motion of the fragments accompanied by slow relative motion, i.e., $\alpha \ll 1$. The wavefunction ϕ^D in the zeroth-order approximation is described by Eq. (20). The two factors in Eq. (20) correspond to relative (translational) and vibrational motion. The higher-order corrections to Eq. (20) describe the translational-vibrational interaction (TVI), which can be considered an additional mechanism for transitions between the states of the fragments.

These terms are connected with the problem of the final state interaction (see Ref. 8). This situation is analogous to corrections to the Born-Oppenheimer approximation. As is well-known, Born-Oppenheimer corrections describe the electron-vibration interaction in molecules (or electron-phonon interaction in the solids) and lead to the appearance of radiationless transitions (see Eqs. (1)-(3)).

Note that the TVI is different from the interfragment interaction, just as the electron-vibration interaction differs from the electron-nucleus interaction. The interfragment interaction can not be expanded in terms of a small parameter (except in the asymptotic region) and can not be considered a perturbation. However, the adiabatic approach allows one to include its main contribution in the zeroth-order approximation (Eq. (20)). In other words, the effect of the interfragment interaction is accounted for in the definition of the internal and relative motions.

For the case $\alpha \ll 1$, the smallness of the TVI is connected with the operator $\hat{T}_p$, and one can obtain¹¹ the following expression for $\hat{H}_1^{\text{tr-v}} \equiv \hat{H}^{\text{tr-v}}|_{\alpha \ll 1}$ which describes the TVI (cf. (1))

$$\hat{H}_1^{\text{tr-v}} = - \frac{\hbar^2}{2\mu_F} \frac{\partial}{\partial \rho} \text{tr} \frac{\partial}{\partial \rho} \text{vib} \quad (\alpha \ll 1) \quad (50)$$

This notation means

$$\hat{H}_1^{\text{tr-v}} \phi^D = - \frac{\hbar^2}{2\mu_F} \frac{\partial}{\partial \rho} \phi^{\text{tr}}(\rho) \frac{\partial}{\partial \rho} \phi^{\text{vib}}(\rho, q) \quad (51)$$

Let us estimate the magnitude of the TVI. Note that the semiclassical approximation implies the validity of the relation $(\mu\hbar/p^3)(\partial U^{\text{eff}}/\partial\rho) \ll 1$ (see, e.g., Ref. 7). Using this inequality and Eq. (24), we can introduce the parameter

$$\gamma \equiv (\mu\hbar^2/p^3)(\partial\omega/\partial\rho) \ll 1 \quad (52)$$

Using Eqs. (20) and (25), we obtain

$$\begin{aligned} H_1^{\text{tr-v}} \phi^D &= -\frac{\hbar}{\mu_F} p \phi^{\text{tr}} \frac{\partial \phi^{\text{vib}}}{\partial \omega} \frac{\partial \omega}{\partial \rho} \\ &\sim \frac{\hbar}{\mu} p \frac{\phi^{\text{vib}}}{\omega} \frac{\partial \omega}{\partial \rho} \phi^{\text{tr}} = \left(\frac{p^2}{\mu\hbar\omega} \right)^2 \gamma \hbar\omega \phi^{\text{vib}} \phi^{\text{tr}} \\ &\sim \alpha^2 \gamma \hat{H}^0 \phi^D \ll \hat{H}^0 \phi^D \end{aligned} \quad (53)$$

Here $\hat{H}^0$ is the unperturbed operator which has the zeroth-order function (Eq. (20)) as an eigenfunction. We see that the magnitude of the TVI is proportional to the small parameter $\alpha^2 \gamma$.

Treating the case $\alpha \gg 1$ in a similar way, we obtain

$$\hat{H}_2^{\text{tr-v}} = -\frac{\hbar^2}{2\mu_F} \frac{\partial}{\partial q} \phi^{\text{tr}} \frac{\partial}{\partial q} \phi^{\text{vib}} \quad (\alpha \gg 1) \quad (54)$$

Using Eq. (27), one can estimate the magnitude of the TVI

$$\begin{aligned}
 H_2^{\text{tr-v}} \phi^D &= -\frac{\hbar^2}{2\mu_F} \frac{\partial}{\partial q} \phi^{\text{tr}}(\rho, q) \frac{\partial}{\partial q} \phi^{\text{vib}}(q) \\
 &\sim -(\hbar^2/\mu_F)(\phi^{\text{tr}}/L)(\phi^{\text{vib}}/A) \sim \alpha^{-1}(A/L) \epsilon^{\text{tr}} \phi^{\text{tr}} \phi^{\text{vib}} \\
 &\sim \alpha^{-1} \delta \hat{H}^{\text{tr}} \phi^{\text{tr}} \phi^{\text{vib}}
 \end{aligned} \tag{55}$$

Hence, for $\alpha \gg 1$, the TVI is also of the order of a small parameter $\alpha^{-1} \delta$.

From the development above, the operator $\hat{H}^{\text{tr-v}}$ for the general case can be written in the form

$$H^{\text{tr-v}} = H_1^{\text{tr-v}} + H_2^{\text{tr-v}} \tag{56}$$

where $H_1^{\text{tr-v}}$ and $H_2^{\text{tr-v}}$ are defined by Eqs. (50) and (54). Note that $H_1^{\text{tr-v}} \phi^D_{\alpha \gg 1} = 0$ and $H_2^{\text{tr-v}} \phi^D_{\alpha \ll 1} = 0$.

If the translational energy exceeds the internal energy, it is possible to use the "clamped" translational function approximation, as discussed in Section III-D. The change of the zeroth-order wavefunction ϕ^D and the use of Eq. (36) instead of Eq. (27) changes the operator $\hat{H}_2^{\text{tr-v}}$ so that it takes the form (see Refs. 8 and 13)

$$\hat{H}_{\text{cl}}^{\text{tr-v}} = U(\rho, q) - U(\rho, q_0) = \left. \frac{\partial U(\rho, q)}{\partial q} \right|_0 \tau \tag{57}$$

Using Eqs. (47)-(49) enables us to write $\hat{H}^{\text{tr-v}}$ in the form

$$\hat{H}^{\text{tr-v}} = C_1 \hat{H}_1^{\text{tr-v}} + C_2 \hat{H}_{c2}^{\text{tr-v}} \quad (58)$$

where $\hat{H}_1^{\text{tr-v}}$ and $\hat{H}_{c2}^{\text{tr-v}}$ are defined by Eqs. (50) and (57), and $C_1 = \beta$, $C_2 = 1 - \beta$; see Eq. (45).

V. Conclusion

In this paper we have described a new adiabatic approach to polyatomic photodissociation. Attention has been focused on a proper description of the dissociative (D) state. This state contains a semiclassical part which characterizes translational motion and a quantum part associated with internal motion. Moreover, it is found necessary to take into account the interfragment interaction. Our adiabatic approach allows one to evaluate the wavefunction that describes the D state (see Eq. (47)). The adiabatic method has been used here to separate "fast" and "slow" parts of the nuclear motion in contrast to its familiar application to the separation of fast electronic motion from slow nuclear motion (Born-Oppenheimer approximation).

If vibrational motion is slower than translational motion, it is possible to use the "clamped" translational function approximation (see Eq. (36)) and to establish the correspondence between the separated variables approximation (SVA) and our approach.

The deviation from the adiabatic picture describes the translation-vibration interaction (see Section IV). We show that the corresponding term of the Hamiltonian is proportional to a small parameter. Therefore our choice of zeroth-order approximation describes the dominant contribution to the wavefunction of the system.

Based on Eqs. (2)-(5), (7) and (47) it is possible to evaluate the translational and internal energy distributions of the fragment. Analysis of the coupling matrix element (Eqs. (4) and (5)) shows that vibrational distributions can be obtained that differ significantly from a simple statistical description. Furthermore, such analysis establishes that features of H_{DQ}^i can result in an inverse vibrational distribution of photofragments,¹¹ in accord with recent experimental data.^{16,17}

Acknowledgments

The authors are grateful to Professor K. Freed for interesting discussions.

This work was supported by the Director, Office of Energy Research, Office of Basic Energy Sciences, Chemical Sciences Division of the U. S. Department of Energy under Contract DE-AC03-76SF00098, and by the National Science Foundation under Grant No. CHE-7721305.

References

1. (a) S. Rice, in "Excited States," vol. 2, ed. E. Lim, Academic Press, New York (1975), p. 111.
(b) W. Hase, "Dynamics of Molecular Collisions," P. B., p. 121, Plenum Press (1976).
(c) K. Freed and Y. Band, "Excited States," ed. E. Lim, Academic Press, New York (1977), p. 110.
(d) W. Gelbart, Ann. Rev. Phys. Chem. 28, 323 (1977).
(e) J. Simons, in Gas Kinetics and Energy Transfer (P. B. Ashmore and R. J. Donovan, Senior reporters), vol. 2, p. 58, Burlington House, London (1977).
(f) M. Okabe, Photochemistry of Small Molecules, Wiley and Sons (1978).
(g) S. Leone, "Advances in Chemical Physics" (in press).
2. J. Beswick and W. Gelbart, J. Phys. Chem. 84, 3148 (1980).
3. L. Landau, Phys. Zs. Sow. 1, 88 (1932).
4. Y. Band and K. Freed, J. Chem. Phys. 68, 1292 (1978).
5. R. Kubo, Phys. Rev. 86, 929 (1952).
6. J. Ziman, Proc. Cambr. Phil. Soc. 51, 707 (1955).
7. L. Landau and E. Lifshitz, Quantum Mechanics, Pergamon Press (1976).
8. Y. Band and K. Freed, J. Chem. Phys. 63, 3382 (1975).
9. C. Caplan and M. Child, Mol. Phys. 23, 249 (1972).
10. G. Miller, W. Jackson and J. Halpern, J. Chem. Phys. 71, 4625 (1979).

11. V. Kresin and W. A. Lester, Jr., "A New Adiabatic Approach to the Photodissociation of Polyatomic Molecules," to appear in Intern. J. Quantum Chem. Quantum Symp. 15 (1981).
12. M. Morse and K. Freed, J. Chem. Phys. 74, 4395 (1981).
13. B. Geilikman, Sov. Phys.-JETP 2, 509 (1956); J. of Low Temp. Phys. 4, 189 (1971).
14. K. Freed and W. Gelbart, Chem. Phys. Lett. 10, 187 (1971).
15. H. Longuet-Higgins, Advan. Spectr. 2, 429 (1961).
16. S. Yang, A. Freedman, M. Kawasaki and R. Bersohn, J. Chem. Phys. 72, 4058 (1980).
17. H. Zacharias, M. Geilhaupt, K. Meier and K. Welge, J. Chem. Phys. 74, 218 (1981).

This report was done with support from the Department of Energy. Any conclusions or opinions expressed in this report represent solely those of the author(s) and not necessarily those of The Regents of the University of California, the Lawrence Berkeley Laboratory or the Department of Energy.

Reference to a company or product name does not imply approval or recommendation of the product by the University of California or the U.S. Department of Energy to the exclusion of others that may be suitable.

TECHNICAL INFORMATION DEPARTMENT
LAWRENCE BERKELEY LABORATORY
UNIVERSITY OF CALIFORNIA
BERKELEY, CALIFORNIA 94720