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

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

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

Abstract

The matrix element describing the transition from a bound to an unbound state in photodissociation of a linear triatomic molecule is found to yield an inverse vibrational distribution when the recoil energy of the photofragment is less than or comparable to the internal energy.

I. Introduction

Photofragment dynamics is a present focus of significant interest because of the availability of synchrotron sources and a variety of new lasers for preparing initial states, and because of improved detection techniques including laser induced fluorescence and time-of-flight mass spectrometry for probing final states. In a recent experimental investigation of the photodissociation of CS_2, Yang, et al. [1] obtained energy distributions of the CS fragments differing in a striking way from a statistical distribution. To the "surprise" of these authors,

linear surprisal plots, describable by a single parameter, were obtained for the CS fragments. Such plots correspond to a negative temperature or equivalently, to an exponential increase with vibrational state v of the matrix elements to the final state v.

A subsequent study of the photodissociation of NO_2 by Zacharias et al. [2] also resulted in an inverse vibrational distribution of the product diatomic (NO) fragment. The probability of a transition to a final dissociative state depends on the density of states of the fragments and on the matrix element that connects the initial state to the final state. We shall show below that under certain conditions an inverse distribution is a direct consequence of features of the coupling matrix element.

II. Theory

The Photodissociation Rate. For simplicity we restrict consideration to a linear symmetric triatomic system (Fig. 1). The generalization to a nonlinear system is straightforward. For concreteness we consider in-direct photodissociation which is characterized by the existence of an intermediate quasidiscrete state. The quasidiscrete state undergoes a radiationless transition to the final dissociative state.

The probability dw of a transition in the continuous spectrum (in units of $\hbar = 1$) is given by (see, e.g., ref. [3])

$$dw = 2\pi \; |H'_{DQ}|^2 \delta(E-E') \; \rho_E dE \qquad (1)$$

ρ_E is the density of states, and (see, e.g., [4,5])

$$H'_{DQ} = \sum_i L_i \int \phi^{D^*}(\rho,\tau) \frac{\partial}{\partial Q_i} \phi^Q(Q_1,Q_2) d\vec{R} \qquad (2)$$

where

$$L_i = \int \psi^{el}(\vec{r},\vec{R}) \frac{\partial}{\partial Q_i} \psi^{el}(\vec{r},\vec{R}) d\vec{r} \Big|_{\vec{R}=\vec{R}_o} \qquad (3)$$

Here Q_i denotes the coordinates of the i-th normal mode of the quasidiscrete state Q, ϕ^D and ϕ^Q are the nuclear wavefunctions of the dissociative and quasidiscrete states, ρ is the distance between the centers-of-mass of the two fragments and τ denotes the collection of internal coordinates of the fragments; see Fig. 1. In addition, ψ^{el} is the electronic wavefunction and R_o denotes the equilibrium configuration of the quasidiscrete state.

The wavefunction for the quasidiscrete state $\phi^Q(Q_i)$ usually can be described by the harmonic approximation, (see, for example, ref. [3]). In accord with this approximation, we write

$$\phi^Q = \prod_i \phi_{n_i}(Q_i) \qquad (4)$$

where ϕ_{n_i} is a harmonic oscillator wavefunction.

The function ϕ^D describes the relative and internal motions of the fragments. A careful examination of the Schrödinger equation for the final dissociative state reveals that it is impossible rigorously to separate variables because of the mutual influence of the recoil

(translational) and internal (vibrational and rotational) motion of the fragments. This problem is considered in detail by the authors in ref. [5]. The function ϕ^D can be written in the form [5]

$$\phi^D = \phi_v^{vib} \; (\tau,\rho) \; \phi_{p v}^{tr} \; (\rho) \tag{5}$$

where ϕ_v^{vib} describes the vibrational motion of the diatomic fragment AB, and is given by

$$\phi_v^{vib} \; (\tau,\rho) = \frac{1}{(2^v \; v!)^{1/2}} \; \left(\frac{\mu_F \Omega(\rho)}{\pi}\right)^{1/4} \; \exp\left(-\frac{\mu_F \Omega(\rho)}{2} \; \tau^2\right) \times H_v\left(\tau\sqrt{\mu_F \Omega(\rho)}\right) \tag{6}$$

Here we have chosen the internal coordinate τ, see Eq. (2), to have the form $\tau = \ell - \ell_0(\rho)$, and $\mu_F = m_A m_B/(m_A + m_B)$.

The function $\phi_{pv}^{tr}(\rho)$ describes the relative motion and its radial part (except for the region near the classical turning points) is given by

$$\phi_{pv}^{tr} = \rho^{-1} \cos [\sigma(\rho) + \delta] \tag{8}$$

where $\sigma = \int_{a_t}^{\rho} p(\rho) d\rho$ (a_t is the inner classical turning point) and the momentum p is given by

$$p = \left\{2\mu \; [E - U^{eff}(\rho)]\right\}^{1/2} \tag{9}$$

Here

$$U^{eff} = U(\rho, \ell_0(\rho)) + E^{vib}(\rho) + E^{rot}, \quad \mu = \frac{m_A(m_A + m_B)}{2m_A + m_B}$$

$$E^{vib}(\rho) = \left(v + \frac{1}{2}\right) \Omega(\rho)$$

(10)

The frequency $\Omega(\rho)$ depends on the ratio $\alpha \equiv \Delta\epsilon^{rec}/\Delta\epsilon^{vib}$ [5]. If, for instance, $\alpha \ll 1$, i.e., the vibrational motion is accompanied by slow relative motion, $\Omega(\rho)$ and $\ell_0(\rho)$ are defined by the relations

$$\Omega \equiv \omega(\rho) \quad ; \quad \omega(\rho) = \left[\mu_F^{-1} \left(\frac{\partial^2 U(\rho, \ell)}{\partial \ell^2} \right)_{\ell = \ell_0(\rho)} \right]^{1/2}$$

(11)

and

$$(\partial U(\rho, \ell)/\partial \ell)_{\ell = \ell_0(\rho)} = 0$$

If $\alpha \gg 1$, $\Omega = \omega_F$ where ω_F is the frequency of the isolated fragment. The explicit expression, valid in the general case, is derived in ref. [5].

We restrict consideration here to the case $\alpha \lesssim 1$; see, for example, recent studies of Zacharias et al. [2] and Bersohn et al. [6]. According to ref. [2], the photodissociation of NO_2 is characterized by partitioning of energy into 70 percent internal and 30 percent recoil energy of the NO fragment. We comment on the case $\alpha \gg 1$ later in this section.

The wavefunctions ϕ^D and ϕ^Q also contain any rotational dependence. We shall not explicitly indicate this dependence. Moreover, the linear molecule is characterized by bending vibrations. Since for a linear system in the harmonic approximation they are uncoupled from longitudinal displacements [7], they also need not be explicitly indicated for present purposes. Rotational dependence and bending vibrations do not change the present development and will be considered in detail elsewhere. Note that bending vibrations as well as rotations are generally slower than longitudinal vibrations, so that their inclusion could be considered as a next step in a systematic adiabatic approach.

Vibrational Distributions. In the evaluation of the matrix element needed to describe the energy distribution of the fragments, it has been found essential to take proper account of the ρ-dependence of Ω, and more specifically, because of the Franck-Condon character of the matrix element, to introduce $\tilde{\Omega} \equiv \Omega(\rho_0)$ and $\tilde{\tau} \equiv \tau(\rho_0) = \ell - \ell_0(\rho)$ in ϕ^D in evaluating (2). Here ρ_0 corresponds to the equilibrium value of ρ in the quasi-discrete state and can be expressed in terms of the force constants of the precursor molecule. Note that $\Omega(\rho_0) \neq \omega_f$.

The quasidiscrete state is characterized by the excitation of a definite vibrational level. Hence, the function ϕ^Q can be written in the form (the linear triatomic system ignoring bending motion for the present has two normal modes; see Fig. 1).

$$\phi^Q = \phi_n(Q_1)\, \phi_0(Q_2) \tag{12}$$

Using Eqs. (2), (5), (6), and (8) and the relation

$$\frac{1}{\sqrt{\omega_k}} \frac{\partial}{\partial Q_k} \phi_{n_k}(Q_k) = -\left(\frac{n_k + 1}{2}\right)^{1/2} \phi_{n_k+1}(Q_k) + \left(\frac{n_k}{2}\right)^{1/2} \phi_{n_k-1}(Q_k) \qquad (13)$$

we obtain for the matrix element (2)

$$H_{DQ}^{\cdot} = \int \exp\left\{-\frac{\mu_F \tilde{\Omega}}{2} \tilde{\tau}^2 - \frac{\omega_1}{2} Q_1^2 - \frac{\omega_2}{2} Q_2^2\right\} \cos\left[\sigma(\rho) + \delta\right]$$

$$(14)$$

$$\times F(\tilde{\tau}, Q_1, Q_2) \, d\vec{R}$$

where

$$F = \frac{1}{\sqrt{2^{n+\nu} \nu! n!}} \left(\mu_F \tilde{m} m_A \tilde{\Omega} \omega_1^3 \omega_2 / \pi^3\right)^{1/4} L_1^2 \rho^{-1}$$

$$\times \left[n H_{n-1}(Q_1 \sqrt{\omega_1}) - \frac{1}{2} H_{n+1}(Q_1 \sqrt{\omega_1})\right. \qquad (15)$$

$$\left. - \left(\frac{\omega_2}{\omega_1}\right)^{1/2} \frac{L_2}{2L_1} H_n(Q_1 \sqrt{\omega_1}) H_1(Q_2 \sqrt{\omega_2})\right]$$

where $\tilde{m} = m_A (2m_A + m_B)/m_B)$, and H_n denotes a Hermite polynomial of order n. Here we have purposely separated the exponential parts of the vibrational wavefunctions.

The triatomic system is characterized by the following normal modes (see, e.g, ref. [7]):

$$Q_a = \tilde{m}^{1/2}(\Delta x_1 + \Delta x_3), \quad Q_s = m_A^{1/2}(\Delta x_1 - \Delta x_3) \tag{16}$$

where Δx_1, Δx_2, Δx_3 are the longitudinal displacements. Setting $Q_1 \equiv Q_a$, $Q_2 \equiv Q_s$, making the transformation x_1, x_2, $x_3 \to \ell$, ρ, R_C, using Eq. (16), and imposing the condition that the center of mass is at rest, i.e., $R_C = 0$, we obtain after simple manipulations,

$$Q_a = \tilde{m}^{1/2}\left[(1-\alpha)\tilde{\tau} - \left(\frac{1-\alpha}{1+\alpha}\right)\rho'\right]$$

$$\tag{17}$$

$$Q_s = m_A^{1/2}\left[(1-\alpha)\tilde{\tau} + \rho'\right]$$

where $\alpha = m_A/(m_A + m_B)$ and $\rho' = \rho - \rho_0$. Using Eqs. (14) and (17), we obtain

$$H'_{DQ} = \int d\rho' d\tilde{\tau} e^{-f}\cos(\tilde{p}\rho' + \delta')\tilde{F}(\tilde{\tau},\rho') \tag{18}$$

where

$$f = A\tilde{\tau}^2 - B\tilde{\tau}\rho' + C\rho'^2 \tag{19}$$

$$A = \mu_F \, \tilde{\Omega} + \tilde{m} \, \omega_a (1-\alpha)^2 + m_A \omega_s (1-\alpha)^2$$

$$B = \tilde{2} \, m \, \omega_a \, \frac{(1-\alpha)^2}{1+\alpha} - 2 \, m_A \omega_s (1-\alpha)$$

$$C = \tilde{m} \, \omega_a \left(\frac{1-\alpha^2}{1+\alpha} \right) + m_A \omega_s \tag{20}$$

$\delta' = \sigma(\rho_0) + \delta$; $\tilde{p} \equiv p(\rho_0)$; $\tilde{\Omega} = \Omega(\rho_0)$. Here $\tilde{F}(\tilde{\tau}, \rho') = I \, F(\tilde{\tau}, \, Q_1, \, Q_2)$ and I is the Jacobian of the transformation from cartesian to internal coordinates. We emphasize that F is a polynomial, contains no exponential dependence, and can be written in the form

$$F = \sum_{t,s} a_{ts} \rho'^{t} \tilde{\tau}^{s} \tag{21}$$

Using the relation [8]

$$\int_{\infty}^{\infty} x^n \, e^{-(ax^2+bx+c)} \cos (px + q) \, dx =$$

$$\left(\frac{-1}{2a} \right)^n \left(\frac{\pi}{a} \right)^{1/2} \exp \left(\frac{b^2 - p^2}{4a} + c \right) \sum_{k=0}^{E\left(\frac{n}{2}\right)} \frac{n!}{(N-2k)! \; k!}$$

$$\times \, a^k \sum_{j=0}^{n-2k} \binom{n-2k}{j} b^{n-2k-j} p^j \cos \left(\frac{pb}{a} - q - \frac{\pi}{2} j \right)$$

we obtain

$$H'_{D \ll Q} = K \exp\left(-\frac{\tilde{p}^2}{C}\right) \qquad \qquad (22)$$

where K is a slowly varying function and contains no exponential dependence. According to (21), increase of the momentum p leads to a decrease of H'_{DQ}. This behavior of H'_{DQ} is qualitatively connected with the increase in the number of oscillations of the semi-classical wavefunction $\phi^{tr}_{pv}(\rho)$ with increase of ρ. Using Eqs. (9), (10), and (22), we obtain

$$H'_{DQ} = \tilde{K} e^{\alpha v} \qquad \qquad (23)$$

where $\alpha \sim 1$, $\tilde{K} = K \exp\left(-\chi(\rho_0)\right)$, and

$$\chi(\rho) = \frac{2\mu}{C} \left[E - U(\rho, \ell_0(\rho)) - \frac{1}{2} \Omega - E^{rot}\right]$$

The expression for α may be obtained using Eqs. (9) and (18)-(20). Note that K contains no exponential dependence on vibrational quantum number v. For some systems, of course, one can encounter forbidden transitions for which $K = 0$.

We see that the matrix element H'_{DQ} increases exponentially with v. Since the vibrational distribution of the fragment is described by (1), then

$$W \sim \exp(2\alpha v) \qquad . \qquad \qquad (24)$$

This expression corresponds to a negative temperature dependence. This inverse distribution is a direct result of the functional dependence of the coupling matrix element.

Although consideration here has focused on a linear triatomic system, there is nothing in our development that limits our results to such systems. It is a direct result of the exponential dependence of vibrational wavefunctions and the semiclassical nature of heavy-particle relative motion.

The energy distribution of the fragments can be also affected by final state interactions. The interaction between fragments is strong, particularly at short distances. However, and this is the advantage of our approach, this strong interaction is included in the zeroth-order approximation (5) by the ρ dependence of ϕ_v^{vib} and because $E^{vib}(\rho)$ is a part of U^{eff}; see Eq. (10). In other words, the effect of the interfragment interaction is accounted for in the definition of the internal and relative motion. For this reason, the contribution of the final state interaction will be small (for a detailed analysis, see ref. [5]).

The case $\alpha \gg 1$. We have been considering the case $\alpha \lesssim 1$, i.e., the situation when the recoil energy E^{rec} is less than or comparable to the internal energy E^{int}. It is possible, of course, to observe experimentally the case $E^{rec} \gg E^{int}$ (see. e.g. [6,9]).

An increase of E^{rec} leads to an increase of the number of oscillations n of the integrand of Eq. (14). If n becomes very large, the major contribution to the integrand may come from the region near the classical turning point. In this case Eq. (8) is not applicable and it is necessary to use an approach which properly treats the turning point region. We note that the case $\alpha \gg 1$ was considered in refs. [4] and [10] for direct photodissociation and explicit models of the repulsive surface. Those studies resulted in a peak in the fragment vibrational distribution, indicating inversion in the lowest levels only. We shall treat the case of arbitrary α in a later paper.
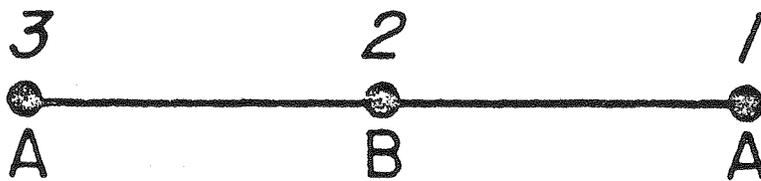
III. Concluding Remarks

In this paper we have shown that a detailed consideration of the matrix element (2) results in vibrational distributions that differ significantly from a simple statistical description. It is found that features of the matrix element (2) can result in an inverse vibrational distribution of fragments when $\Delta\epsilon^{rec} \lesssim \Delta\epsilon^{int}$. Qualitatively, this result is connected with the translational factor (8) of the dissociative state wavefunction which occurs in (2). At a fixed available energy a decrease of vibrational energy results in an increase of $\Delta\epsilon^{rec}$ and, correspondingly, an increase in the number of oscillations of the translational factor. This results in a relative decrease in the matrix element (2) and an inverse distribution. The present approach also can be applied to nonlinear systems and again leads to inverse distributions under certain conditions. This generalization is straightforward and will be presented in a later paper. Thus we see that the observation of inverse vibrational distributions [1,2] is readily understood from a consistent theoretical description.
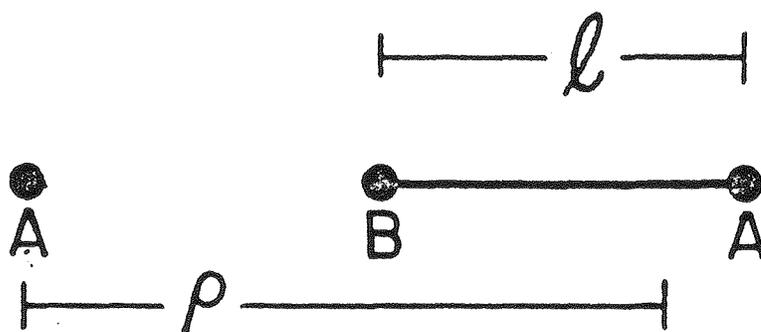
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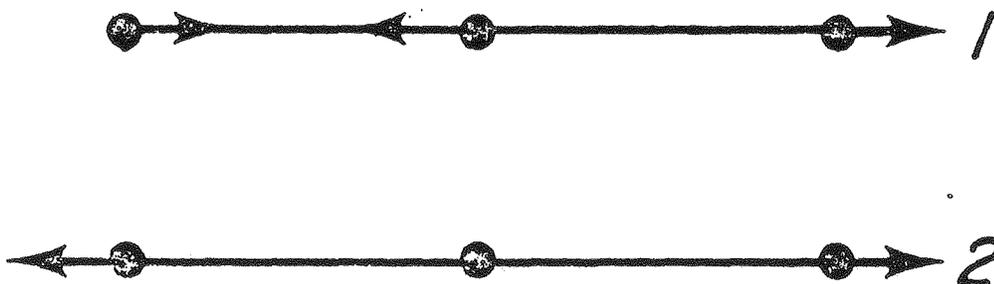
Figure Captions

Figure 1: Linear symmetric triatomic system (a) molecular arrangement and coordinates: ρ – distance from fragment atom A to center of mass of diatomic fragment BA, ℓ – internuclear distance of BA; (b) 1 – asymmetric vibration; 2 – symmetric vibration.

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