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ADIABATIC APPROACH IN THE THEORY OF POLYATOMIC PHOTODISSOCIATION:
APPLICATION TO C$_2$N$_2$*

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Abstract

An adiabatic method for nuclear motion has been developed and applied to single-photon predissociation of C$_2$N$_2$ (C$^1$I$^{	ext{u}}$). The theoretical predictions are in good accord with recent measured product energy distributions.

Introduction

Photodissociation dynamics is a present focus of significant interest because of the availability of new lasers for preparing initial states, and because of improved detection techniques including laser-induced fluorescence for probing final states. A main goal of the present theoretical effort is to evaluate energy distributions of photofragments. In this paper we focus on the analysis of the vibrational distribution in the collinear model obtained following an adiabatic theory of photodissociation developed by two of us.

The structure of the paper is as follows. A method enabling one to treat polyatomic photodissociation on the basis of the theory of quantum transitions is described in Sec. I. Section II addresses the problem of nuclear dynamics for the dissociative state. The evaluation of the vibrational energy distribution with application to C$_2$N$_2$ is carried out in Sec. III.

I. Polyatomic Photodissociation as a Quantum Transition

There are two principal types of polyatomic photodissociation. Direct photodissociation corresponds to a transition from the ground state to the dissociative state of the fragments due to the interaction with an external field. Indirect photodissociation is a more complicated phenomenon and corresponds to a radiationless transition from an initially prepared excited state.

Both types of polyatomic photodissociation can be treated on the basis of the non-stationary theory of quantum transitions. This approach provides one means of obtaining a state-to-state description of the phenomenon. A golden-rule formalism (or $T$-matrix method in the case of strong interactions) can be used to evaluate the energy distributions of the fragments.

The applicability of the quantum theory of transitions arises from the possibility of separating the part of the total Hamiltonian which causes the transition. It is trivial for direct photodissociation, where the interaction with incident radiation represents this part of the Hamiltonian. Indirect photodissociation, which is accompanied by a change in potential energy surface (type I or electronic predissociation) can also be described by such a formalism. In this case, the non-adiabatic interaction, that is, the deviation from the Born-Oppenheimer (BO) approximation, can be treated as a perturbative part of the Hamiltonian.

Indirect photodissociation of type II or vibrational predissociation represents a more complicated case. This case represents a transition from a predissociative state to the photofragment state that occurs on a single adiabatic potential energy surface (pes). Such processes cannot occur for diatomic molecules, but they can be observed for polyatomic systems. The transition is caused by intramolecular energy transfer, that is, by internal redistribution of vibrational energy.

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Despite the fact that both states belong to the same PES, an approach has been developed that enables this type of indirect photodissociation to be described as a quantum transition. The method is analogous to Bardeen's theory of tunneling. The main aspects of the method follow. Consider the equation
\[ H_e \psi_n(\mathbf{r}, \mathbf{R}) = e_n(\mathbf{R}) \psi_n(\mathbf{r}, \mathbf{R}) \] (1)
describing, in accord with the BO approximation, the electronic term. Here
\[ H_e = T_r + V(\mathbf{r}, \mathbf{R}) \] (2)
Introduce a new potential \( \tilde{V}(\mathbf{r}, \mathbf{R}) \) in place of \( V(\mathbf{r}, \mathbf{R}) \). The effect of this substitution \( V \rightarrow \tilde{V} \) is a change of the electronic terms \( e_n, e_{n+1} \) to new electronic terms \( \tilde{e}_n, \tilde{e}_0 \), for which the notation will become clear shortly, so that
\[ [T_r + \tilde{V}(\mathbf{r}, \mathbf{R})] \tilde{\psi}_n(\mathbf{r}, \mathbf{R}) = \tilde{e}_n(\mathbf{R}) \tilde{\psi}_n(\mathbf{r}, \mathbf{R}) \] (3)
\[ [T_r + \tilde{V}(\mathbf{r}, \mathbf{R})] \tilde{\psi}_0(\mathbf{r}, \mathbf{R}) = \tilde{e}_0(\mathbf{R}) \tilde{\psi}_0(\mathbf{r}, \mathbf{R}) \] (4)
We choose the potential \( \tilde{V}(\mathbf{r}, \mathbf{R}) \) so that a term \( \tilde{e}_0(\mathbf{R}) \) corresponds to the quasidiscrete (predissociative) channel (and becomes equivalent to \( e_{n+1}(\mathbf{R}) \) in the region \( \rho \rightarrow \infty \)), and the term \( \tilde{e}_0(\mathbf{R}) \) behaves as \( e_n(\mathbf{R}) \) in the photofragmentation channel.

The terms \( \tilde{\psi}_0(\mathbf{R}) \) and \( \tilde{\psi}_0(\mathbf{R}) \) are similar to diabatic surfaces. We see here that they can be introduced on the basis of the BO approximation.

Nuclear wavefunctions, which correspond to the terms \( \tilde{\psi}_0(\mathbf{R}) \) and \( \tilde{\psi}_0(\mathbf{R}) \) are solutions of
\[ [T_r + \tilde{e}_0(\mathbf{R})] \tilde{\phi}_0(\mathbf{R}) = \tilde{e}_0(\mathbf{R}) \tilde{\phi}_0(\mathbf{R}) \] (5)
\[ [T_r + \tilde{e}_0(\mathbf{R})] \tilde{\phi}_0(\mathbf{R}) = \tilde{e}_0(\mathbf{R}) \tilde{\phi}_0(\mathbf{R}) \] (6)
Hence, one can introduce the states
\[ \tilde{\psi}_0(\mathbf{r}, \mathbf{R}) = \tilde{\psi}_0(\mathbf{r}, \mathbf{R}) \tilde{\phi}_0(\mathbf{R}) \] (7)
and
\[ \tilde{\psi}_0(\mathbf{r}, \mathbf{R}) = \tilde{\psi}_0(\mathbf{r}, \mathbf{R}) \tilde{\phi}_0(\mathbf{R}) \] (8)
which are eigenstates of the Hamiltonian
\[ \tilde{H} = \tilde{T}_r + \tilde{V}(\mathbf{r}, \mathbf{R}) \] (9)
The functions (7) and (8) describe the predissociative quasidiscrete (Q) state and the dissociative (D) state of the photofragments. Indeed, the function \( \tilde{\phi}_0(\mathbf{R}) \) (and, hence, \( \tilde{\psi}_0(\mathbf{r}, \mathbf{R}) \)) is exponentially small in the D channel, and \( \tilde{\phi}_0(\mathbf{R}) \) is exponentially small in the Q channel.

The total Schrödinger equation can be written in the form
\[ (\tilde{H} + \Delta H) \Psi(\mathbf{r}, \mathbf{R}) = E \Psi(\mathbf{r}, \mathbf{R}) \] (10)
where \( \Delta H \) is defined by Eq. (9), and
\[ \Delta H = \tilde{V}(\mathbf{r}, \mathbf{R}) - V(\mathbf{r}, \mathbf{R}) \] (11)
Indirect photodissociation of type II can be treated as a quantum transition between the Q and D states (see Eqs. (7) and (8)) which are eigenstates of the Hamiltonian \( \tilde{H} \); this transition is governed by \( \Delta H \). The term \( \Delta H \) does not depend on time and can cause transitions between states of the same energy; see, e.g., ref. 7. This property is relevant because energy is conserved in the elementary step. Following the usual theory of quantum transitions, the solution is sought in the form
\[ \Psi(t) = c_f(t) \Psi_f \exp(i E_f t) + c_i(t) \Psi_i \exp(i E_i t) \]
where \( c_f = \Psi_f \) and \( c_i = \Psi_i \) leading to the following expression for the probability of transition per unit time,
\[ dW_{f \rightarrow i} = 2 \pi \rho_f |a_{fi}|^2 \delta(E_f - E_i) \rho_f \] (12)
where \( dW_f = \rho_f dE_f, \rho_f \) is the density of states, and the amplitude \( a_{fi} \) is given by
Equation (12) is the result of first-order time-dependent perturbation theory and involves the approximation of neglect of all virtual transitions, cf., refs. 5 and 6. If higher-order corrections are important, the probability is given by an expression of the same form as (12) with, however, the matrix element \( a_{fi} \) replaced by the T-matrix element, see, e.g., ref. 8, connecting states \( i \) and \( f \) (for more detailed discussion, see ref. 1).

The amplitude for the transition from the predissociative state \( n\nu \) to the photofragment state \( n'\nu' \) can be reduced to the form

\[
a_{fi} = \int \tilde{\psi}_f^*(r,R) \Delta V \tilde{\psi}_i(r,R) \, dr \, dR
\]

Equation (13)

Consider the structure of the integrand of Eq. (14). The nuclear function \( \tilde{\phi}_i(R) \) differs significantly from zero only in a small region of internal coordinate values \( r - a \), where \( a \) is the amplitude of vibration. Similarly, the function \( \tilde{\phi}_f(R) \) differs noticeably from zero in a small region for a range of coordinate values \( r - a \). The product \( \tilde{\phi}_f(R) \phi_i(R) \) is a peaked function differing significantly from zero only at small deviations of all nuclear coordinates from equilibrium. The function \( L(R) \) contains relatively smooth functions and one can write

\[
a_{fi} = L(R_0) F
\]

where

\[
F = \int \tilde{\phi}_f^*(R) \phi_i(R) \, dR
\]

is a Franck-Condon (FC) factor and \( R_0 \) denotes equilibrium values of coordinates for the predissociative state.

If one is interested in relative fragment energy distributions, the matrix element \( L(R_0) \) can be taken as constant. Then, according to Eq. (16) the fragment energy distribution is given by \( a_{fi} = F \), where

\[
F = \int \phi_{n\nu}^*(R) \phi_{n'\nu'}(R) \, dr
\]

Hence, the determination of the energy distributions of the fragments reduces to the evaluation of a FC factor of the Q and D states. A more accurate treatment follows from the expression for the matrix element for photodissociation (14). These equations are similar to the expressions obtained from scattering theory for chemical reaction.4,5,6 By contrast the approach here is based on the theory of quantum transitions and is similar in approach to Bardeen's theory of tunneling.2 Further, in the present development, terms corresponding to higher-order transitions contain products of FC factors for different virtual transitions which results in additional orders of smallness in a perturbative sense. (This is additional justification for limiting consideration here to Eq. (12).) This is in contrast to the theory of refs. 4, 5, and 6 which leads to a single FC factor.

If we consider a system containing many molecules and fragments, it is convenient to use second quantization formalism. This approach is discussed in ref. 1.

II. Nuclear Dynamics

1. Bound and Quasibound states. It has been shown in the last section, how the problem of the evaluation of photofragment energy distributions can be reduced to the analysis of nuclear dynamics. Indeed, it is necessary to evaluate integrals containing the nuclear wavefunctions (see Eq. (17)).

According to the dressed oscillator model, the normal modes describing the dissociative state are assumed to be part of the set of normal modes for the initial bound state. However, the initial and final states (G and D for a direct photodissociation, or Q and D for indirect photodissociation) are each characterized by their own sets of normal modes that are related to each other by a linear transformation.9
The nuclear wavefunctions $\phi_G$ and $\phi_D$ are bound or quasibound states. (We drop the use of tildes from this point on.) In the harmonic approximation each can be written as a product

$$\phi_G(R) = \prod_i \phi_{v_i}(Q_i)$$

$$\phi_D(R) = \prod_i \phi_{v_i}(Q_i)$$

where $Q_i$ are the normal modes, and $\phi_{v_i}(x)$ describe the states of the harmonic oscillator with normal frequency $\omega_i(x)$. The function $\phi_G$ corresponds usually to the lowest vibrational level which can be well described by the harmonic approximation. The applicability of this approximation to the predissociative $Q$ state is not obvious and can be ascertained from the nature of the absorption spectrum. If it consists of a set of equidistant bands, the harmonic approximation should be applicable; see, e.g., ref. 10. Otherwise, it is necessary to include anharmonicity corrections, or to use an appropriate model potential such as a Morse potential.

2. Dissociative State. We now turn to the most difficult aspect of nuclear motion for photodissociation, namely, the evaluation of the nuclear wavefunction of the $Q$ state. This state is unusual because it contains both a discrete part corresponding to the internal finite motion of the individual fragment molecules and a "continuous" part describing their relative motion. There is strong interference of these two types of motion. Because of the necessity to take into account the interfragment interaction, the method for obtaining a valid expression for $\phi_D(\rho, q_A, q_B)$ is not obvious. Here $\rho = (R_B - R_A)$ is the distance between the fragment centers of mass. The potential energy can be expressed in terms of coordinates $q_A, q_B$, and $\rho$, that is, $U = U(\rho, q_A, q_B)$. In order to obtain the expression for the nuclear wavefunction $\psi(\rho, q_A, q_B)$, one solves the Schrödinger equation associated with the nuclear Hamiltonian expressed in terms of fragment Hamiltonians. Unlike the bound $Q$ state, the potential energy $U(\rho, q_A, q_B)$ cannot be expanded in a series of the deviations of all variables from equilibrium, because $\rho$ corresponds to translational motion. Hence, the variables are not separable.

Because of the nonseparability of variables, the nuclear wavefunction $\phi_D(\rho, q_A, q_B)$ generally cannot be well approximated as a product $\phi_1(\rho) \phi_2(q_A, q_B)$. In the asymptotic region the separated variables approximation (SVA) is strictly valid because the potential energy no longer depends on $\rho$. However, the main contribution to the coupling matrix element $H_D Q$ is not connected with the asymptotic region. Because of the FC principle, this main contribution comes from a region $\rho - \rho_0$, where $\rho_0$ 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 $\rho$. At short distances the interfragment interaction is not small and, generally speaking, the deviation from the SVA is not governed by a small parameter. One can develop a rigorous adiabatic approach in the framework of the nuclear problem which facilitates the evaluation of the nuclear wavefunction for the $Q$ state.\textsuperscript{11,12}

Note that the SVA implies $\phi_D(\rho, q_A, q_B) = \phi_1(\rho) \phi_2(q_A, q_B)$ and is connected with the assumption, $U(\rho, q_A, q_B) = U_1(\rho) + U_2(q_A, q_B)$, which means total decoupling of internal and relative translational motion; see, for example, ref. 13. In other words, it implies the absence of the so-called final-state interactions. That is why the use of the SVA is accompanied usually by additional analysis of this interaction. The method followed here\textsuperscript{11,12} is not connected with the use of the SVA. The mutual influence of the internal and relative motions is taken into consideration explicitly.

According to refs. 12 and 13, the $D$ state for a collinear triatomic molecule can be described by the wavefunction

$$\phi_D(q, \rho) = \phi_{\text{tr}}(\rho) \phi_{\text{vib}}(\rho, q)$$

The radial part of the function $\phi_D$ is the solution of the equation

$$\left[ -\frac{1}{2} \frac{\partial^2}{\partial \rho^2} + \frac{1}{2} \frac{\partial^2}{\partial \rho^2} + u_{\text{eff}}(\rho) \right] \phi_{\text{tr}}(\rho) = E \phi_{\text{tr}}(\rho)$$

where

$$u_{\text{eff}} = U(\rho, q_0(\rho)) + \epsilon_{\text{vib}}(\rho)$$
and \( q_0(\phi) \) can be determined by the condition
\[
\left( \frac{\partial U(\phi, q)}{\partial q} \right)_{q = q_0(\phi)} = 0
\]

In the semiclassical approximation,
\[
\phi_{\text{tr}} = \sqrt{\frac{2\hbar}{\pi p}} \cos(\sigma(\phi) + \delta)
\]

where
\[
\sigma(\phi) = \frac{1}{2} \int_0^\phi p(\phi) \, d\phi
\]

and
\[
p = \sqrt{2\mu \left[ \mathcal{E} - U_{\text{eff}}(\phi) \right]}^{1/2}
\]

More explicitly, one has
\[
p(\phi) = \sqrt{2\mu \left[ \mathcal{E} - U(\phi, q_r(\phi)) - (\nu + 1/2) \hbar \omega(\phi) \right]}^{1/2}
\]

and
\[
\phi_{\text{vib}}(\phi, q) = \frac{\mu \hbar}{\hbar^2} \left( \frac{1}{\sqrt{2\mathcal{E}}} \right) e^{-\frac{\mu \hbar \omega(\phi) \tau^2}{2\hbar^2}} H_n(\tau) \sqrt{\frac{\mu \hbar \omega(\phi)}{\hbar^2}}, \quad \tau = q - q_r(\phi)
\]

The function \( \Omega(\phi) \) is given by\(^{12} \)
\[
\Omega(\phi) = \omega_c \left( \frac{\omega(\phi)}{\omega_c} \right)^{\frac{1}{2}}
\]

and, similarly,\(^{12} \)
\[
q_r(\phi) = q_{OC} \left( \frac{q_0(\phi)}{q_{OC}} \right)^{\frac{1}{2}} \quad \text{for} \quad \alpha = e_{\text{tr}}/e_{\text{vib}}
\]

We emphasize that the interaction between fragments is taken into account in two ways. First, the vibrational frequency and the equilibrium position depend on the distance between the fragments. Second, the effective potential energy \( U_{\text{eff}} \), describing the relative motion, contains the vibrational energy (Eq. (22)).

**Franck-Condon Factor.**

The FC factor depends on the quantum numbers describing the initial state and the state of the photofragments and, hence, its evaluation enables one to obtain a state-to-state description of polyatomic photodissociation. The FC factor is, in general, a multi-dimensional integral:
\[
F = \int \phi_i(\vec{R}) \phi_n(\vec{R}) \, d\vec{R}
= \int \phi_i(\vec{R}) \phi_A(\vec{R}_A) \phi_B(\vec{R}_B) \phi_{\text{tr}}(\vec{\phi}) \, d\vec{R}
\]

where \( \phi_i(\vec{R}) \) describes the bound (or quasibound in the case of predissociation) state of the precursor molecule, \( \phi_A(B)(\vec{R}_A(B)) \) is a nuclear wavefunction of the A(B) fragment, and \( \phi_{\text{tr}} \) describes their relative motion. Note that the adiabatic approach enables one to treat the slow rotational motion separately (e.g., \( \phi_\text{i}(\vec{R}) = \phi_\text{i,vib} \cdot \phi_\text{i,rot} \)). On this basis, we now can discuss the evaluation of the vibrational distribution of the fragment and postpone the analysis of the rotational distribution without loss of generality.
In the harmonic approximation $\phi_1 = \Pi_2 \phi_1(Q_2)$, $\phi_a = \Pi_k \phi_a(Q_k)$, and $\phi_B = \Pi_n \phi_B(Q_n)$, where $Q_2$, $Q_k$, $Q_n$ are the sets of normal modes. In the dressed oscillator model the set $Q_2$ contains $Q_k$ and $Q_n$ as subsets. Generally, this is not the case, however, these coordinates are coupled to $\phi$ by a linear transformation.

Several general comments are appropriate.

1) As has been shown above, the fragment vibrational frequencies and equilibrium positions depend on interfragment distances. The main contribution to the FC factor comes from the overlap region at small internuclear distances and, hence, the frequencies and equilibrium positions correspond to this region. They differ from asymptotic values and must be calculated. Such a calculation has been carried out for C$_2$N$_2$ (see below). In the absence of such data, one can use asymptotic values which may enable one to obtain at least a qualitative description. Note also, that the translational wavefunction $\delta r$ is the solution of the Schrödinger equation (22) with an effective potential energy $U_{\text{eff}}$ that contains the vibrational energy.

2) For direct photodissociation, it is necessary to go into account that the transition from $\phi$ is associated with a change of $\Phi$ and, hence, to a shift of equilibrium position. The value of the FC factor depends strongly on this shift; an increase in the shift results in a noticeable decrease of the FC factor.

For direct photodissociation of a linear triatomic molecule, ABC + h$\nu$ $\rightarrow$ A + BC, the FC factor can be written in the form (12)

$$F = \int \delta r(\rho) e^{-\tau^2/2A^2} H(\tau/A) e^{-Q_1^2/2A_1} e^{-Q_2^2/2A_2} d\tau d\rho$$

Here $\tau = \rho - \rho_0$, $\rho_0$ and $A$ are the BC equilibrium distance and amplitude of vibration, $Q_1$ and $Q_2$ are the normal modes of ABC, $A_1$ and $A_2$ are the amplitudes of the normal vibrations: $A_1 = (\omega_1 A_1)^{-1/2}$, $A_2 = (\omega_2 A_2)^{-1/2}$, $\omega_1$ and $\omega_2$ are the normal-mode frequencies, and $\rho$ is the distance between the atom A and the center-of-mass of the diatomic BC. It is assumed that the molecule is initially in the ground vibrational state. The integrand contains several variables not all of which are independent. If one chooses $\tau$ as independent variables, then $Q_1$ and $Q_2$ can be expressed in terms of $\tau$ and $\rho$ through a linear transformation, i.e.,

$$Q_1 = a_{11} \tau' + a_{12} \rho'; Q_2 = a_{21} \tau' + a_{22} \rho'$$

where $\tau' = \tau - \tau_0$, $\tau_0$, and $A$ are the equilibrium values of $\tau$ and $A$ for the ground state, and $\delta \rho_0 = \rho - \rho_0$. Here $\tau_0$, $\rho_0$, and $A_0$ are the equilibrium values of $\tau$, $\rho$, and $A$ for the ground state, and $\delta \rho_0 = \rho_0 - \rho_0$ is the bond length change. Integrating over $\tau$, one can obtain, after some manipulations,

$$F = e^{-\bar{\phi}^2/2A^2} \int d\rho \delta r(\rho) \bar{\phi}$$

where $\bar{\phi} = \exp(-D_0 A)^2/2A^2$ is the effective vibrational wavefunction; $D_0 = \rho_0 + 400, \delta \rho_0 = \rho - \rho_0$. We emphasize that the displacement $\delta \rho_0$ results in a change of the equilibrium geometry $\rho_0 = \rho_0$, and it affects the region of overlap of $\delta r(\rho)$ and $\bar{\phi}$ in (32). Furthermore, one can prove that $\bar{\phi} > 0$, and, hence, the increase of the shift $\delta \rho_0$ results in an exponential decrease of the magnitude of the FC factor.

The function $\delta r$ describes the relative translational motion of the photofragments. This motion is describable in the semiclassical approximation (except in the turning point region) by an oscillating wavefunction for which the number of oscillations increases with an increase of the relative momentum. An increase of the number of oscillations results in a decrease of the FC factor. Hence, the semiclassical behavior of the translational wavefunction makes a transition to a state with large momentum less favorable. Because of conservation of energy, the resulting state is characterized by a small vibrational quantum number. This effect can result in an inverted vibrational distribution of the fragment.

11. Application to Photodissociation of C$_2$N$_2$

Recent experimental studies have indicated that C$_2$N$_2$ undergoes predissociation at wavelengths between 164 nm and 154 nm resulting in two CN fragments. Cyanogen shows four weak electronic transitions in the near UV corresponding to absorptions from the ground state C$_2$N$_2$(X 1$\Sigma_g^+$) to C$_2$N$_2$(a 3$\Pi_u$) at 300 nm, to C$_2$N$_2$(B 3$\Delta_g$) at 250 nm, to C$_2$N$_2$(B 1$\Sigma_u^+$) at 220 nm, and to C$_2$N$_2$(D 3$\Pi_u$) at 207 nm. There is also a stronger electronic transition to C$_2$N$_2$(C 4$\Delta_u$) beginning at 170 nm. Presumably between 164 to 154 nm, the initial excitation leads to vibrationally excited C$_2$N$_2$(C 4$\Delta_u$) which
then dissociates. Figure 1A indicates how these electronic states of $C_2N_2$ correlate to separated CN fragments. The three energetically lowest channels for dissociation and their thresholds are:

$$
C_2N_2 \rightarrow CN(X^2\Sigma^+) + CN(X^2\Sigma^+) \quad 222.2 \text{ nm} \quad \text{I}
$$

$$
CN(X^2\Sigma^+) + CN(A^2\Pi) \quad 184.7 \text{ nm} \quad \text{II}
$$

$$
CN(A^2\Pi) + CN(A^2\Pi) \quad 157.9 \text{ nm} \quad \text{III}
$$

Miller et al. report the CN($X^2\Sigma^+$) nascent vibrational populations detected by laser induced fluorescence after flash photolysis of $C_2N_2$ under collisionless conditions at 164 nm, 158 nm, and 154 nm. They report only the ratio of the CN($X^2\Sigma^+$, $v = 1$) to CN($X^2\Sigma^+$, $v = 0$) populations. In all cases, they find this ratio to be less than 1, but increasing with higher photon energy.

Taherian, et al. have measured the CN($A^2\Pi$) nascent vibrational distribution resulting from F2 laser excitation of $C_2N_2$ at 1576 Å. They reported the CN($A^2\Pi$) populations detected by CN(AXX) emission spectra and observed CN($A^2\Pi$) vibrationally excited up to the thermodynamic limit of $v = 5$, with a bimodal distribution with peaks at $v = 0$ and $v = 2$.

Electronic structure studies of $C_2N_2(C_3^1 \Pi_u)$ indicate it is best described as an $n + \sigma^*$ excitation where $n$ represents a nitrogen atom lone-pair electron and $\sigma^*$ is the lowest-lying unoccupied orbital. The CN($A^2\Pi$) radical results from the excitation of an $\sigma$ electron into a half-filled $\pi$ orbital localized on the carbon atom. From molecular orbital theory, $C_2N_2(C_3^1 \Pi_u)$ has an $n^4\sigma^*\pi^1$ configuration whereas the CN($X^2\Sigma^+$) + CN($A^2\Pi$) supermolecule has an $n^4\pi^*\sigma^1$ configuration. Using ab initio multiconfiguration Hartree-Fock techniques, diabatic potential energy surfaces for the quasibound state and the dissociative state can be constructed. The predissociative character of the adiabatic surface is due to the avoided crossing of these two diabatic states.

From ab initio MCHF calculations, molecular geometry, force constants, and harmonic frequencies were obtained for the predissociative $C \Pi_u$ state in excellent agreement with the limited experimental data available. The initially prepared state was found to remain linear. As a first approximation, collinear dissociation has been studied thus neglecting bending vibrations and rotations. The generalization of the theory including these motions is straightforward and will be presented elsewhere. The nuclear wavefunction is approximated by the product of three harmonic oscillator functions describing the normal mode stretches. The frequencies and normal coordinates of these modes were obtained from the ab initio calculations. The validity of the harmonic approximation is supported by the equidistant bands of the $C_2N_2$ absorption spectra. For systems where there is variable spacing between absorption bands, it would, of course, be necessary to include anharmonicity corrections.

For the dissociative state, the harmonic approximation is also employed to describe the internal degrees of freedom. Rigorous evaluation of the FC factor would entail knowledge of the frequencies and the force constants of the dissociative state in the region of overlap. These can be obtained by ab initio calculations. In the study these quantities were approximated by asymptotic experimental values, i.e., the frequencies of the separated CN($A^2\Pi$) and CN($X^2\Sigma^+$) fragments. This approximation is analogous to what is frequently termed the neglect of final-state interactions. The semiclassical approximation was employed to obtain the translational wavefunction. For products in higher vibrational levels and hence, low translational energy, this approximation could be unreliable and a more accurate translational wavefunction would be required.

Figure 1B illustrates the results we obtained compared to experiment at 1576 Å. There is qualitative agreement with a bimodal distribution possessing a main peak at $v = 2$ and a secondary peak at $v = 0$. However, as pointed out by Taherian, et al, at 1576 Å, Channel III (or two excited CN($A^2\Pi$) fragments) becomes energetically accessible but only for $v = 0$. On this basis, all of the CN($A^2\Pi$) $v = 1$ through $v = 5$ population comes solely from Channel II, but the $v = 0$ population is the sum of contributions from Channels II and III. In order to make a comparison with our theoretical results, which only consider Channel II, one must subtract the contribution of Channel III from the experimental distribution. One should note that the percentage of the $v = 0$ population from Channel II, labeled C, is unknown experimentally. We can however assume different values of C and obtain distributions based on this assumption for comparison with theory. Figure 1B presents the populations of the CN($A^2\Pi$) vibrational levels relative to the $v = 0$ population resulting from assumed values of C, and the theoretical ratios. We find that one must assume that at least 50% of the $v = 0$ population comes
from channel II to retain bimodal character. If one assumes that \( C < 50\% \), the
distribution is singly peaked at \( v = 2 \). Hence, by assuming that \( C > 50\% \), qualitative
agreement with experimental data is obtained.

![Figure 1A](image)

Correlation diagram for collinear dissociation of low-lying excited states of
\( \text{C}_2\text{N}_2 \) into two CH radicals. Both the \( \text{C} \, ^{1}\Pi_{u} \) (present study) and the \( \text{B} \, ^{1}\Sigma_{u} \) states
are observed to exhibit indirect photodissociation.

Figure 1B.

\( \text{CN}(A \, ^{2}\Pi) \) nascent vibrational distributions at 157.6 nm. Solid line indicates theore­
tical results of present study. Dashed lines indicate experimental results for different
values of \( C \), the assumed percentage of \( v = 0 \) population coming from the adiabatic channel
II. From the diagram we see that values of \( C > 50\% \) give good agreement of theory with
experiment.

It should be noted, however, that the calculated results depend strongly on several
factors. First, there is some ambiguity as to the amount of available energy because of
uncertainties in dissociation and excitation energies. Even small changes in the total
available energy can alter the number of energetically accessible vibrational levels,
causing dramatic changes in the behavior of the final distributions. These quantities
need to be more precisely determined. Furthermore, consideration must be given to the
possibility of additional electronic channels contributing at different energies. In
general, the distributions are mode-sensitive and will vary depending on which initial
vibrational state the precursor system is assumed to be excited.

As mentioned above, in the experimental study of the formation of the \( \text{CN}(X \, ^{2}\Sigma^{+}) \)
fragment the authors reported only the ratio of the \( v = 1 \) to \( v = 0 \) populations and found
the \( v = 1 \) population less than that for \( v = 0 \). Our approximate calculations, however,
yield a non-statistical distribution. Disagreement could possibly lie in the breakdown
of the semiclassical approximation for the translational wavefunction. At 164 nm, there
are only a few vibrational levels energetically accessible. The amount of translational
energy even for the low vibrational levels \( v = 1 \) and \( v = 2 \) is much less than that present
at 1576A. It is possible under these conditions that the semiclassical approximation is
not valid, and a more exact translational wavefunction would be appropriate.
References


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