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A Theoretical Study on Vibrational Predissociation Rates of Ne-I_2

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A new theoretical method, named the SCF-DWB-IOS approximation, is suggested to investigate the vibrational predissociation of triatomic van der Waals complexes. The meta stable vibrational excited states are described with SCF (self-consistent-field) approximation and the fragmented diatomic continuum states are determined by using IOS (infinite order sudden) approximation. The dissociation process itself is studied by using DWB (distorted wave Born) approximation. As a test case, the predissociation rates, rotational state distributions of products, and the lifetimes of vibrationally excited states of Ne-I_2 are all computed which are in reasonable agreements with other theoretical and/or experimental results. The suggested SCF-DWB-IOS approximation scheme is found to be a very simple but efficient theoretical tool to investigate the vibrational predissociation dynamics of small van der Waals complexes.

Introduction

The predissociation dynamics of van der Waals complexes has attracted a lot of attention both experimentally and theoretically.[1-30] In weakly bound molecules, vibrational motions deviate from harmonic behavior a lot even in the vibrational ground state. It is thus important to obtain the vibrational energy level structure of the complexes from potential energy functions and to theoretically investigate vibrational predissociation process of van der Waals complexes. The need for theoretical methods arises from a rapid progress in experimental van der Waals complex spectroscopy.

For triatomic van der Waals complexes, many theoretical and experimental studies have been made to understand the dissociation dynamics.[23,24] The vibrational predissociation process, in which excess vibrational energy flows into a weak van der Waals bond to break it up, is particulary well studied. From a theoretical point of view, triatomic van der Waals complexes provide ideal model systems for the predissociation study. Because the electronic states involved are well studied, and the potential energy surfaces are known, and the relevant quantities like transition dipole moments are well characterized.

We propose a new approximate quantum mechanical method which can describe the vibrational predissociation dynamics of triatomic van der Waals complexes, *e.g.*, particulary diatom-rare gas atom complexes. This new method is designed to calculate dissociation rates, lifetimes of metastable vibrational excited states and rotational state distribution of dissociated diatomic fragments.

To determine vibrational excited states of triatom complexes (bound state), we utilize a self-consistent-field (SCF) approximation. The SCF approximation and the configuration interaction (CI) method are used to calculate the vibrational energy levels of triatomic van der Waals complex. The SCF and CI method are widely used in electronic structure calculations, but the vibrational structure calculations using SCF and CI are not frequently reported.[27,31] In SCF method,[1,5,20,21,22] the each vibrational mode is described as moving in an effective field, being the average of the full potential over the motions of all the other modes, and consists of wavefunctions called modal wavefunctions corresponding to orbitals in electronic structure theory. The validity and accuracy of the SCF approximation which omits the correlation between modes depend on the choice of coordinates, because each modal wavefunction is represented with each variable composing the coordinates chosen. The correlation part missing in SCF approximation is incorporated in CI method. In CI, the true vibrational wavefunctions are expressed in linear combination of configurations which are a product of modal wavefunctions. And the CI matrix is set up and diagonalized to have more exact vibrational energies and wavefunctions. In the previous report,[27] the comparison of SCF with CI is made to find that the simple SCF is a very reasonable method when Jacobi coordinates are utilized. In the present work, we consider the SCF approximation to characterize the vibrational structure of Ne-I_2 complex.

After dissociation, the translational motion of diatom and atom (continuum state) and the rotational motion of diatom are determined by using the infinite order sudden (IOS) approximation. IOS assumes that the dissociation of the complex, Ne-I_2, occurs much faster than one period of rotation of diatom, I_2. The interaction which causes the dissociation of van der Waals complex is treated by using the distorted wave Born (DWB) approximation. Through the couplings between vibrational modes, vibrational energy of diatom flows to a weak van der Waals bond which eventually breaks up. This is a vibrational to translational energy transfer and the rate of energy flow is assumed to be the first order coupling between the bound state and the continuum state. This distorted wave Born approximation is, in spirit, identical with the well known Fermi's Golden Rule. We call the whole scheme the SCF-DWB-IOS approximation.

In the present work, this new scheme is applied to the vibrational predissociation process of Ne-I_2 van der Waals complex. This new method has once been applied to collinear Ne-I_2 and He-I_2.[22] But in this work we consider full 3-dimensional Ne-I_2 complex. The vibrational predissociation phenomenon of Ne-I_2 has been investigated theoretically and experimentally before.[32,33] Also a reliable potential energy function is known.[3] It is the main reason why we choose Ne-I_2 complex to test the new theoretical method.

In the next section a brief summary of our new method SCF-DWB-IOS approximations is provided. The calculational details, *e.g.*, the potential energy functions used and numerical aspects of computations, follow. Also, calculational results, discussions, and conclusions are provided in the last section.

Method

We utilize the Jacobi coordinates for triatomic van der Waals complexes. The Hamiltonian H for AB-C system is then written as,

$$H(r,R,\theta)=-\frac{1}{2\mu_1 r^2}\frac{\partial}{\partial r}(r^2\frac{\partial}{\partial r})-\frac{1}{2\mu_2 R^2}\frac{\partial}{\partial R}(R^2\frac{\partial}{\partial R})+\frac{j^2}{2\mu_1 r^2}+\frac{l^2}{2\mu_2 R^2}+V(r,R,\theta) \quad (1)$$

where r is the distance between atoms A and B, R is the distance between the center of mass of diatom AB and atom C. μ_1 is the reduced mass of atom A and B, and μ_2 is the reduced mass of diatom AB and atom C. j and l are angular momenta associated with r and R, respectively. V(r, R, θ) is the potential energy function.

When $J=j+l=0$,

$$j^2=l^2=\frac{-1}{\sin\theta}\frac{\partial}{\partial\theta}(\sin\theta\frac{\partial}{\partial\theta}). \quad (2)$$

The Schrödinger equation is H(r, R, θ) Φ(r, R, θ)=EΦ(r, R, θ). If we substitute Φ(r, R, θ) with Ψ(r, R, θ)/rR, the reduced equation is

$$H(r,R,\theta)\Psi(r,R,\theta)=E\,\Psi(r,R,\theta) \quad (3)$$

where

$$H(r,R,\theta)=-\frac{1}{2\mu_1}\frac{\partial^2}{\partial r^2}-\frac{1}{2\mu_2}\frac{\partial^2}{\partial R^2}+\frac{j^2}{2\mu_1 r^2}+\frac{l^2}{2\mu_2 R^2}+V_1(r)+V_2(r,R,\theta). \quad (4)$$

Here $V_1(r)$ is a potential energy function for diatom AB and $V_2(r, R, \theta)$ is the rest part of whole potential, *i.e.*, $V(r, R, \theta)=V_1(r)+V_2(r, R, \theta)$.

Eq. (3) is solved for a bound state by using SCF approximation and for a dissociation state by using IOS approximation. When the bound state solution is designated as $\Psi^{i}_{\nu_1\nu_2\nu_3}(r,R,\theta)$ and the dissociating state solution as $\Psi^{f}_{\nu_1'j}(r,R,\theta)$, the Golden rule expression of the dissociation rate R is

$$R(\nu_1\nu_2\nu_3\rightarrow\nu_1'j)=\frac{2\pi}{\hbar}\rho(E)|<\Psi^{f}_{\nu_1'j}(r,R,\theta)|V_c|\Psi^{i}_{\nu_1\nu_2\nu_3}(r,R,\theta)>|^2. \quad (5)$$

under DWBA. The V_c and ρ(E) will be defined later.

The outline of SCF procedure is as follows. We assume that the bound state wavefunction can be approximated as

$$\Psi^{i}_{\nu_1\nu_2\nu_3}(r,R,\theta)\approx\Psi^{SCF}_{\nu_1\nu_2\nu_3}(r,R,\theta)=\phi^{(1)}_{\nu_1}(r)\,\phi^{(2)}_{\nu_2}(R)\phi^{(3)}_{\nu_3}(\theta) \quad (6)$$

and

$$H^{SCF}(r,R,\theta)\,\Psi^{SCF}_{\nu_1\nu_2\nu_3}(r,R,\theta)=E^{SCF}_{\nu_1\nu_2\nu_3}\,\Psi^{SCF}_{\nu_1\nu_2\nu_3}(r,R,\theta). \quad (7)$$

Then the modal wavefunctions ϕ should satisfy
$H^{SCF}(r, R, \theta)=h^{(1)}(r)+h^{(2)}(R)+h^{(3)}(\theta)$,
$h^{(1)}(r)\phi^{(1)}_{\nu_1}(r)=\varepsilon^{(1)}_{\nu_1}\phi^{(1)}_{\nu_1}(r)$, $h^{(2)}(R)\phi^{(2)}_{\nu_2}(R)=\varepsilon^{(2)}_{\nu_2}\phi^{(2)}_{\nu_2}(R)$,
and $h^{(3)}(\theta)\phi^{(3)}_{\nu_3}(\theta)=\varepsilon^{(3)}_{\nu_3}\phi^{(3)}_{\nu_3}(\theta)$ where $\varepsilon^{(1)}$, $\varepsilon^{(2)}$, and $\varepsilon^{(3)}$ are modal eigenvalues, ν_1, ν_2, and ν_3 are vibrational quantum numbers associated with coordinates r, R, and θ, respectively, and

$$h^{(1)}(r)=-\frac{1}{2\mu_1}\frac{\partial^2}{\partial r^2}+\frac{1}{2\mu_1 r^2}<j^2>_\theta+V_1(r)+<V_2(r,R,\theta)>_{R,\theta} \quad (8)$$

$$h^{(2)}(R)=-\frac{1}{2\mu_2}\frac{\partial^2}{\partial R^2}+\frac{1}{2\mu_2 R^2}<l^2>_\theta+<V_2(r,R,\theta)>_{r,\theta} \quad (9)$$

$$h^{(3)}(\theta)=\frac{1}{2\mu_1 r^2}<j^2>_r+\frac{1}{2\mu_2 R^2}<l^2>_R+<V_2(r,R,\theta)>_{r,R}. \quad (10)$$

The subscripts after bracket < > indicate that quantities are integrals over the modal functions which the subscripts designate. The total SCF energy for the (ν_1, ν_2, ν_3) state is $E^{i}_{\nu_1\nu_2\nu_3}\approx E^{SCF}_{\nu_1\nu_2\nu_3}=\varepsilon^{(1)}_{\nu_1}+\varepsilon^{(2)}_{\nu_2}+\varepsilon^{(3)}_{\nu_3}+E_{cor}$ where the correction energy is,

$$E_{cor}=-<\frac{1}{2\mu_1 r^2}>_r<j^2>_\theta-<\frac{1}{2\mu_2 R^2}>_R<l^2>_\theta-2<V_2(r,R,\theta)>_{r,R,\theta}. \quad (11)$$

The SCF equations are iteratively solved to obtain converged modal eigenfunctions and eigenenergies for a prechosen reference (ν_1, ν_2, ν_3) bound state.

Now we turn to determination of a final state wavefunction, $\Psi^{f}_{\nu_1'j}(r,R,\theta)$ where ν_1' and j indicate vibrational and rotational quantum numbers of free diatom AB, respectively. Here we use a vibrationally diabatic approximation, which is $\Psi^{f}_{\nu_1'j}(r,R,\theta)\approx\phi^{d}_{\nu_1'}(r)\psi^{E}_{j}(R,\theta)$ where $\phi^{d}_{\nu_1'}(r)$ is a vibrational wavefunction of the state ν_1' of diatom AB, which is a solution of the vibrational Schrödinger equation of diatom AB, *i.e.*, $[-\frac{1}{2\mu_1}\frac{\partial^2}{\partial R^2}+V_1(r)]\phi^d_{\nu_1'}(r)=E^d_{\nu_1}\phi^d_{\nu_1'}(r)$. The Schrödinger equation for the continuum wavefunction $\psi^E_j(R,\theta)$ is

$$[-\frac{1}{2\mu_1}\frac{\partial^2}{\partial R^2}+\frac{1}{2\mu_2 R^2}l^2+<phi^d_{\nu_1'}(r)\,|\,\frac{1}{2\mu_1 r^2}\,|\,\phi^d_{\nu_1'}(r)>j^2$$
$$+<\phi^d_{\nu_1'}(r)\,|\,V_2(r,R,\theta)\,|\,\phi^d_{\nu_1'}(r)>-(E^i_{\nu_1\nu_2\nu_3}-E^d_{\nu_1'})]\psi^E_j(R,\theta)=0. \tag{12}$$

When the rotational motion is much slower than the translational motion, we could reasonably use the infinite order sudden approximation. Under IOS, we set $j^2=\bar{j}(\bar{j}+1)=l^2$ because total angular momentum is fixed as zero, then the scattering equation we obtain is one-dimensional, *i.e.*,

$$[-\frac{1}{2\mu_1}\frac{\partial^2}{\partial R^2}+\frac{1}{2\mu_2 R^2}\bar{j}(\bar{j}+1)+B\bar{j}(\bar{j}+1)$$
$$+\bar{V}_2(R;\theta)-E]\psi^E_j(R;\theta)=0 \tag{13}$$

where B is a rotational constant of diatom at vibrational state ν_1', $\bar{V}_2$ is the averaged V_2 integral over $\phi^d_{\nu_1'}(r)$, E is the energy which is $E^i_{\nu_1\nu_2\nu_3}-E^d_{\nu_1'}$. $\psi^E_j(R;\theta)$ parametrically depends on angle θ. And $\psi^E_j(R,\theta)$ can be approximated as

$$\psi^E_j(R,\theta)=\sqrt{(2j+1)/2}\,\phi^E_j(R;\theta)P_j(\theta) \tag{14}$$

where $P_j(\theta)$ is a Legendre function. In the present study we chose $\bar{j}=j$ which is a final rotational quantum number. The real wavefunction we calculate has an asymptotic form of

$$\phi^E_{j,real}(R;\theta)\rightarrow k^{-1}[A(\theta)\sin(kR-\frac{\bar{j}}{2}\pi)+B(\theta)\cos(kR-\frac{\bar{j}}{2}\pi)] \tag{15}$$

where $A(\theta)$ and $B(\theta)$ can be determined at asymptotic limit of R. The final state wavefunction $\Psi^f_{\nu_1'j}(r,R,\theta)$ is therefore,

$$\Psi^f_{\nu_1'j}(r,R,\theta)=\phi^d_{\nu_1'}(r)2[B(\theta)+iA(\theta)]^{-1}$$
$$\phi^E_{j,real}(R;\theta)\sqrt{(2j+1)/2}\,P_j(\theta). \tag{16}$$

Here we want to compute the lifetime of vibrationally excited triatomic van der Waals complex which eventually leads to dissociate into diatom and atom fragments. The dissociation process is assumed to be due to mode-mode coupling which causes energy transfer (and predissociation) from vibrational motion of triatom to kinetic motion of atom C. The coupling, V_c is generally so weak that a perturbative approach could be suitable and, consequently, V_c could be regarded as V_c=H-H^{SCF} in DWBA approximation. The density of final state at energy E, $\rho(E)$, is $\rho(E)=\mu_2 p/(2\pi\hbar)^3$ where p is a momentum. Then the DWBA form of predissociation rate R from the (ν_1, ν_2, ν_3) initial triatomic state to the (ν_1', j) final diatomic state given in Eq. (5) can be rewritten as,

$$R(\nu_1\nu_2\nu_3\rightarrow\nu_1'j)=\frac{2j+1}{2\pi^2\hbar^2 v}\,|\sum_{\theta_\alpha}\omega\theta_\alpha[B(\theta_\alpha)+iA(\theta_\alpha)]^{-1}$$
$$P_j(\theta)\phi^3_{\nu_3}(\theta_\alpha)\sum_{R_\alpha}\omega_{R\alpha}\,\phi^E_{j,real}(R_\alpha;\theta_\alpha)\,\phi^2_{\nu_2}(R_\alpha)$$
$$\sum_{r_\alpha}\omega_{r\alpha}\,\phi^d_{\nu_1'}(r_\alpha)\,\phi^1_{\nu_1}(r_\alpha)\,V_c(r_\alpha,R_\alpha,\theta_\alpha)\,|^2. \tag{17}$$

where v is a relative velocity.
The half-width, Γ is $\Gamma(\nu_1\nu_2\nu_3\rightarrow\nu_1'j)=\hbar\,R\,(\nu_1\nu_2\nu_3\rightarrow\nu_1'\,j)/2$,

$$\Gamma(\nu_1\nu_2\nu_3\rightarrow\nu_1')=\sum_j\Gamma(\nu_1\nu_2\nu_3\rightarrow\nu_1'j),\text{ and}$$
$$\Gamma(\nu_1\nu_2\nu_3)=\sum_{\nu_1'}\Gamma(\nu_1\nu_2\nu_3\rightarrow\nu_1').$$

And a predissociation lifetime of the (ν_1, ν_2, ν_3) state, τ is $\tau(\nu_1\nu_2\nu_3)=\hbar/2\Gamma(\nu_1\nu_2\nu_3)$. The detailed methodology will be published elsewhere.[31]

Computations

The SCF equations (Eqs. (7)-(10)) are iteratively solved to obtain converged modal eigenfunctions and eigenenergies for a prechosen (ν_1, ν_2, ν_3) bound state. And for each bound state, separate SCF calculations are performed. We have used the numerical grid representations, instead of using basis function representations, to solve the equations. As we see in Eqs. (8) and (9), the differential equations involving r and R coordinates can be easily solved. But the θ coordinate (Eq. (10)) imposes a small problem in numerical grid representations. So we adopt the discrete variable representation (DVR) by Light and Bacic.[4,18,19] Light and coworkers have defined a general discrete variable representation for quantum mechanical problems which is a dual space of normal truncated variational basis representations, *i.e.*, it is related by orthogonal (or unitary) transformations. The DVR is established in order to simplify the approximate evaluation and manipulation of the Hamiltonian operator. In particular, the kinetic energy operator, easily evaluated in the variational basis representation, is transformed to the DVR, whereas the remaining potential operators, which are difficult to evaluate in the basis representation, are approximated directly in DVR. The finite difference method is used to solve the SCF differential equations numerically.

The IOS equation (Eq. (13)) is solved at various angles, θ, using a fifth order Adams-Moulton algorithm with numerical grid representations of the wavefunctions. The number of angles chosen is equal to a number of grids used in solving Eq. (10), which is equal to the number of Legendre functions used in DVR.

We have utilized atom-atom pairwise Morse type potential energy functions, where the whole potential is assumed to be a sum of diatomic potentials. For Ne-I_2, the Gray's potential parameters are used.[3] The relevant Morse parameters, D_e (dissociation energy), β (exponential factor), and r_e (equilibrium distance) are 4600.19 cm^{-1}, 0.9583 au^{-1}, and 5.6966 au for I-I, and 42.5 cm^{-1}, 0.81 au^{-1}, and 7.5589 au for Ne-I atom pair, respectively. The electronic state of Ne-I_2 is the excited B state in which the I_2 has a symmetry of $^3\Pi_0^+$. The atomic masses of Ne and I are 63746 and 231332 au, respectively.

In numerical integrations of SCF equations, the starting point, the end point, and grid size are repeatedly tested so that optimum number of grid points are determined. For the internuclear distance of I_2, *i.e.*, r axis, integraion is performed from 4.8 to 8.0 au with a grid of 0.001 au, for R axis the range is from 5.0 to 20.0 au with a grid of 0.05 au for Ne-I_2 complex. For angle part, Legendre functions of l=0 to 40 are used for θ axis basis functions. It corresponds to 41 grid points in DVR scheme.

What we have investigated are the vibrational energy levels (ν_1, ν_2, ν_3) of the bound Ne-I_2 complex, the predissociation rates from Ne-I_2 (ν_1, ν_2, ν_3) to I_2 ($\nu_1'=\nu_1-1$, j)+Ne, the rotational state distribution of I_2 (ν_1', j), and consequently, lifetimes of Ne-I_2 (ν_1, ν_2, ν_3). The calculations were performed for several initial states of Ne-I_2 ranging from ν_1=19 to 23. Therefore the vibrational states whose predissociation dynamics studied are ν_1=19-23 vibrational states of Ne-I_2. We applied our method to rather highly excited states because experimental results are available for the states.

Results and Discussion

The SCF method has been known to be a good approximation for determining vibrational structure of floppy molecules, *e.g.*, van der Waals complexes.[20,21,27] Using SCF, we have calculated many vibrational state energies of Ne-I_2 complex but only relevant vibrational levels are presented in Table 1. $E_{\nu_1}(I_2)$ are the vibrational energy levels of diatom I_2 which are exactly solved under a given potential energy function. $E^{SCF}_{\nu_1,\nu_2,\nu_3}$ are the vibrational energy levels of Ne-I_2 complex calculated with SCF approximation. Though we do not present CI values in the present paper, these SCF values are almost identical with CI values (within 5 significant digits), which supports the SCF approximation.

$E^{SCF}_{\nu_1,\nu_2,\nu_3}-E_{\nu_1}$ in the third column of Table 1 are van der Waals bond energy levels between Ne and I_2. As shown in the Table, the van der Waals bond energies depend on vibrational levels of ν_1 even when ν_2 and ν_3 are 0. Of course the dependency is not large, but it indicates that there is a vibrational mode coupling which cannot be neglected. In another words, the vibrational motion of I-I bond in Ne-I_2 is different from that in free I_2 because the van der Waals bond between Ne and I_2 affects the nature of I-I bond. Our calculated van der Waals bond energies, D_0 are ~66 cm^{-1}. The van der Waals bond well depth is 85 cm^{-1} derived from the potential function (see the previous section) so that the zero point energy of van der Waals bond is ~19 cm^{-1}. For example, for ν_1=23 state, the zero point energy is 18.6 (=85-66.3724) cm^{-1}.

The predissociation process of interest is Ne-I_2 (ν_1, ν_2, ν_3) → I_2 ($\nu_1'=\nu_1-1$, j)+Ne. It occurs through the relaxation of stretching motion of Ne against I_2 by one quantum (ν_1 to ν_1-1) and the energy released flows into the van der Waals bond to break it up. The total energy released is given in Table 1 under the heading of $E^{SCF}_{\nu_1-1,\nu_2,\nu_3}-E^{SCF}_{\nu_1,\nu_2,\nu_3}$. Of course these break up energies depend on the vibrational state of interest, but over all they are in the order of 90 cm^{-1} which is certainly larger than D_0 (~66 cm^{-1}) to break the van der Waals bond. These break-up energies are very similar to experimental values measured by Levy *et al.*[34]

Table 1. Vibrational energy levels (cm^{-1}) of Ne-I_2 and I_2

(ν_1,ν_2,ν_3)	$E_{\nu_1}(I_2)^a$	$E^{SCF}_{\nu_1,\nu_2,\nu_3}$ ^{b}	$E^{SCF}_{\nu_1,\nu_2,\nu_3}-E_{\nu_1}$ ^{c}	$E^{SCF}_{\nu_1-1,\nu_2,\nu_3}-E^{SCF}_{\nu_1,\nu_2,\nu_3}$ ^{d}
(0,0,0)	−4537.1086	−4604.4614	−67.3528	
(19,0,0)	−2462.5788	−2529.1787	−66.5999	93.50
(20,0,0)	−2370.8207	−2437.3668	−66.5461	91.88
(21,0,0)	−2280.8051	−2347.2953	−66.4902	90.07
(22,0,0)	−2192.5318	−2258.9642	−66.4324	88.33
(23,0,0)	−2106.0009	2172.3733	−66.3724	86.59

[a] This is the vibrational state energy of I_2 with respect to I+I separate atom limit. [b] SCF value for Ne-I_2. This is the vibrational state energy with respect to Ne+I+I separate atom limit. [c] The van der Waals bond energy between Ne and I_2 diatom. [d] It is the energy which breaks up the van der Waals bond.

Figures 1, 2, and 3 display the calculated rotational state distributions of the I_2 diatom fragment from ν_1=19 → ν_1'=18, ν_1=20 → ν_1'=19, and ν_1=23 → ν_1'=22 predissociation, respectively. In Figure 1, our distribution has a longer tail in high j, compared to Garcia-Vela *et al.*'s results which were calculated with a different potential function.[33] For Ne-I_2(19,0,0) → Ne+I_2(18, j) dissociation, the rotational distribution of I_2 is weakly bimodal. For Ne-I_2(20,0,0) → Ne+I_2(19, j) dissociation, our results are in good agreement with extensive but more time consuming calculations by Gray in which same potential energy function is used as ours.[3] It supports the validity of our new method suggested in this paper. This distribution also exhibits a bimodal feature where there are two maxima in distribution curve. It is different from

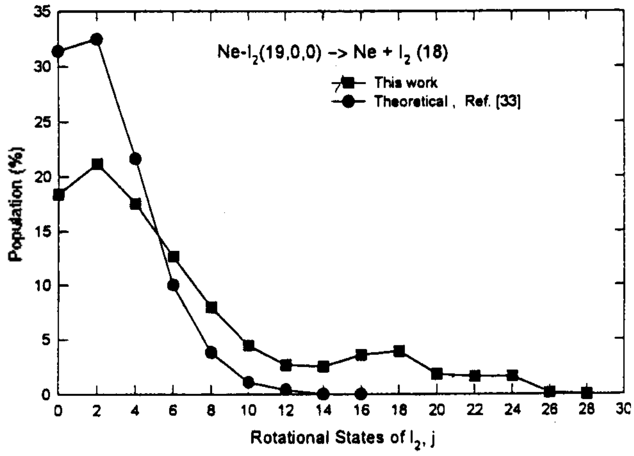

Figure 1. The rotational state distribution of I_2(18, j) fragment from predissociation of Ne-I_2(19,0,0).

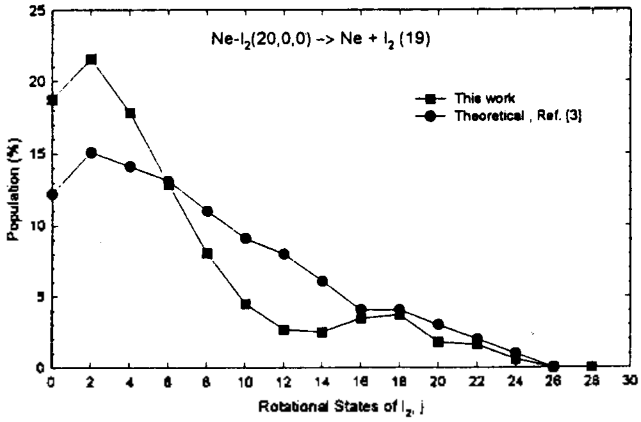

Figure 2. The rotational state distribution of I_2(19, j) fragment from predissociation of Ne-I_2(20,0,0).

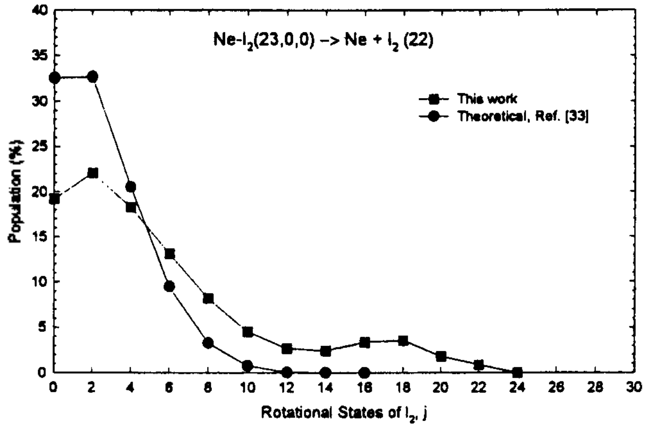

Figure 3. The rotational state distribution of $I_2(22, j)$ fragment from predissociation of Ne-I_2(23,0,0).

Table 2. Lifetimes (*ps*) of Ne-I_2 (ν_1,0,0) which vibrationally predissociate into Ne+I_2 (ν_1-1)

ν_1	This work	Exptl[a]	Theoretical[b]
19	83	87.4	100.0
20	74	78.4	84.5
21	61	69.6	71.5
22	59	58.3	60.5
23	53	53.3	51.5

[a] Ref. 32. [b] Ref. 33.

that found in He-I_2.[31] For Ne-I_2(23, 0, 0) → Ne+I_2(22, *j*) dissociation, our distribution again shows bimodal but Garcia-Vela *et al.*'s do not. Overall our distributions are spread over more rotational states than Garcia-Vela *et al.*'s. To our knowledge, experimental distributions have not been measured yet. Therefore the discrepancy between the two theoretical calculations could be due to the different potential energy function employed in each calculation. Garcia-Vela's potential has a deeper van der Waals bond well than ours. Though we do not present them all, we have calculated many other distributions for predissociation processes leading to different vibrational states.

The lifetimes of vibrational excited states, ν_1=19-23 of Ne-I_2 complex are listed in Table 2. The lifetimes are time intervals during which Ne-I_2 exists before it vibrationally dissociates into fragments of Ne and I_2. As seen in the Table, our calculated values are in quantitative agreement with experimental values or other theoretical values calculated using more complicated method. In fact, when we calculate lifetimes, we considered all possibilities of relaxation precesses, *i.e.*, two, three, four, etc. quantum transitions in addition to one quantum transition. What we found is that one quantum process is fastest. And all the other processes are so slow that they can be completely neglected. This result indicates that the important factor governing the vibrational predissociation rates is the vibrational relaxation time, not the break-up energy released by relaxation.

We learn that overall the new method works reasonably. The excited states of Ne-I_2 are correctly described and lifetimes of the excited states are very accurately determined. The rotational distributions of I_2 fragment are also accurately produced within a given accuracy of potential energy function used.

Conclusions

The excited vibrational motion of I_2 in triatomic Ne-I_2 van der Waals complex is relaxed to give off energy to break the weak Ne-I_2 van der Waals bond. The dynamics of this vibrational predissociation process is theoretically investigated. A new and simple theoretical tool for investigating the process is suggested. The initial unstable bound state of complex is calculated using the self-consistent-field approximation. The modal coupling which causes dissociation is approximated with distorted wave Born approximation, *i.e.*, the coupling between the bound state of complex and continuum state of fragments is considered to be the first order interaction in a perturbative sense. The dissociated continuum state is determined using the infinite order sudden approximation.

The three simple approximations which have been known for a long time are combined to produce a new method for studying vibrational predissociation process of van der Waals complexes. With an example of Ne-I_2, each approximation is thoroughly tested. It has been found that the new SCF-DWB-IOS approximation scheme is, at least for the system tested, useful and efficient. The more applications of the method to many systems and extension of the method, *e.g.*, inclusion of rotational motions, are under way.

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A Monte Carlo Simulation Incorporated with Genetic Algorithm for the Transition Deposition of LB Film of Fatty Acid

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A Monte Carlo simulation incorporated with the genetic algorithm is presented to describe the defect known as "transition from Y-to X-type deposition" of the cadmium arachidate Langmuir-Blodgett multilayer film. Simulation is performed based on the detachment models of XY-type deposition. The transition is simulated by introducing a probability of surface molecule detachment considering interaction between neighboring molecules. The genetic algorithm is incorporated into Monte Carlo simulation to get the optimum value of the probability factors. The distribution of layers having different thickness predicted by the simulation correlates well with the measured distribution of thickness using the small-angle X-ray reflectivity. The effect of chain length and subphase temperature on the detachment probability are investigated using the simulation. Simulation results show that an increase (or a decrease) of two hydrocarbon chain is roughly equivalent to the detachment probability to a temperature decrease (or increase) of 15 K.

Introduction

Up to date, the Langmuir-Blodgett (LB) film technique has been applied to the fabrication of nanoscale molecular thin films with optically, electronically, or biologically useful functional properties. Since the ordered structure of LB films exhibits the optical and electrical characteristics in the molecular level, LB film technique has been applied to the molecular electronic devices.[1-6] However, due to the defects during the deposition, it is difficult to obtain the desired films, which prevents the practical application of LB film technique. For long-chain fatty acids that have a long hydrophobic hydrocarbon alkyl chain ("tail") and hydrophilic carboxyl group ("head"), LB film deposition is comparatively easy by their strong head-head and tail-tail interaction.

Long-chain fatty acids form a monolayer at the air-water interface when they are spread. This floating monolayer is transferred onto a substrate by passing the substrate during the upward or downward passage through the air-water interface. The transfer ratio is defined as the ratio of the film-coated area of the substrate to the consumed area of the floating monolayer. In the Y-type deposition, the transfer ratio is the same on both upstrokes and downstrokes. Y-type film has a centrosymmetric or bilayer structure because of tail-to-tail and head-to-head deposition. On the contrary, if the monolayer is transferred only on downstrokes, this type of film is called as X type. It could be expected that X-type film have a non-centrosymmetric structure owing to head-to-