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HINDERED ROTATION AND EXTERNAL ELECTRIC FIELD EFFECT OF ADSORBED DIATOMIC MOLECULES

Y.T. Shih[a], D.S. Chunu*[b] and W.N. Mei[c]

[a]Institute of Electro-Optical Engineering, National Chiao Tung University, Hsinchu, Taiwan, Republic of China
[b]Department of Electrophysics, National Chiao Tung University, Hsinchu, Taiwan, Republic of China
[c]Department of Physics, University of Nebraska at Omaha, Omaha, Nebraska 68162, USA

A finite conical well was proposed to model the surface hindering potential to which a horizontally adsorbed molecule is subjected. Eigenfunctions and eigenvalues for this model were presented. In addition to the hindering rotation, the external electric field effect on the rotational states of a horizontally adsorbed dipole molecule was also investigated by variational calculation. We found that, as with our previous result of the vertical configuration, the rotational energy levels of the horizontally adsorbed molecule exhibit oscillatory behavior when plotted as functions of the hindrance angle. On the other hand, our result showed that the Stark shifts of the rotational energies were suppressed by the conical well if the field strength is not comparable with the hindering potential. However, when the applied field is strong, large negative shifts were found. Furthermore, the plotted angular distributions of wave function showed that a very strong electric field will enduce a change of adsorption configuration from horizontal to vertical. Copyright © 1996 Published by Elsevier Science Ltd

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1. INTRODUCTION

Recently, the rotational motion of a molecule which interacts with a solid surface has attracted increasing interest. Many experimental studies such as surface neutron scattering [1], surface infrared spectroscopy [2], electron energy loss spectroscopy [3, 4], electron- and photon-stimulated desorption [5, 6], thermal desorption [7–9], and gas-surface inelastic scattering [10–12] had provided fruitful information about the rotational states of adsorption systems. For example, the measured rotational-state distributions of molecules scattered or desorbed from surfaces were found to exhibit a temperature-independent non-Boltzmann feature, which can be attributed to the hindered rotations of adsorbed molecules [6, 13–15].

* Author to whom all correspondence should be addressed.

On the other hand, theoretical studies on the hindered rotation of the adsorbed molecules were also reported [13–16]. Gadzuk et al. [13, 14] suggested an infinite-conical-well to model the surface hindering potential to which the adsorbed molecules are subjected. They obtained the rotational state energy spectra for both vertical and horizontal adsorption configurations. In our previous work [15], we extended the work of Gadzuk et al. to consider a finite-conical-well model. Different from the results obtained by the hard-wall conical well proposed by Gadzuk et al., it was found that for a vertically adsorbed diatomic molecule, the rotational energy levels of the soft-wall hindered molecule exhibited oscillatory behavior when plotted as functions of the hindrance angle. By using the analogy of the Kronig–Penny model, we showed that this particular behavior which did not appear in the hard-wall case is clearly the manifestation of the rotational invariance of the present model. In this

communication, we extend our previous study to the horizontal configuration.

It is well known that the rotational energies of a free molecule placed in an electric field are split due to the interaction between the molecular dipole moment and the electric field [17]. In addition to the splittings, theoretical investigations [18, 19] showed that, when the applied electric field is strong, the rotational energies have large negative shifts. On the other hand, for a horizontally adsorbed dipole molecule in an electric field applied in the perpendicular direction, due to the suppression of the hindering potential, one should expect that there are no large Stark shifts in the rotational energies if the dipole-field interaction is not comparable with the hindering potential. However, when the applied field is very strong, large Stark shifts shall take place. Furthermore, in a strong electric field, the dipole molecule shall be oriented in the field direction. Therefore, one should expect that there is an adsorption configuration change from horizontal to vertical as the field is very strong. The chemical reactions between surface and adsorbed molecules may depend on the adsorption configurations of adsorbates. An applied electric field may be used to control the rates of the surface reactions. Therefore, it is interesting to study the rotational states of an adsorbed molecule in an applied electric field.

2. HINDERED ROTATION

The Hamiltonian for the hindered molecular rotation in spherical coordinates is given by

$$H = L^2 + V^{hin}(\theta), \tag{1a}$$

$$L^2 = -\left[\frac{\partial}{\partial\theta}\sin\theta\frac{\partial}{\partial\theta}(\sin\theta) + \frac{1}{\sin^2\theta}\frac{\partial^2}{\partial\phi^2}\right], \tag{1b}$$

where $V^{hin}(\theta)$ is the hindering potential energy to which the molecule is subjected. For convenience, the energy is expressed in the unit of the rotational constant $B = \hbar^2/2I$, where I is the molecular moment of inertia.

In the horizontal configuration, the molecular axis is preferred to parallel the surface. Therefore, $V^{hin}(\theta)$ is minimum about $\theta = \pi/2$. The hindering potential used to model the constraint upon the rotational motion of a horizontally adsorbed molecule can be written as:

$$V^{hin}(\theta) = \begin{cases} 0, & \alpha \leq \theta \leq \beta, \\ V_0, & 0 \leq \theta < \alpha \text{ or } \beta < \theta \leq \pi. \end{cases} \tag{2}$$

The potential $V^{hin}(\theta)$ describes a finite conical well in the polar space, V_0 is the potential barrier height, and

α and β are opening angles of the cone. Unlike the previous study of an infinite conical well [14], we used soft wall potential here to study the adsorption behavior in the weaker molecule-surface interaction range.

Since the potential depends upon θ only, thus permitting us to factorize the hindered molecular wave function:

$$\Psi(\theta, \phi) = \frac{1}{\sqrt{2\pi}}\Theta(\theta)\exp(im\phi); \quad m = 0, \pm1, \pm2, \ldots. \tag{3}$$

This leads to the differential equation

$$(1 - \xi^2)\frac{d^2\Theta}{d\xi^2} - 2\xi\frac{d\Theta}{d\xi} + \left[\nu'(\nu' + 1) - \frac{\mu^2}{1 - \xi^2}\right]\Theta = 0, \tag{4}$$

where $\xi = \cos\theta$, and ν' is defined as

$$\nu'(\nu' + 1) = \begin{cases} \nu(N + 1), & \alpha \leq \theta \leq \beta, \\ \nu(\nu + 1) - V_0, & 0 \leq \theta < \alpha \\ & \text{or } \beta < \theta \leq \pi. \end{cases} \tag{5}$$

In equation (5), the hindered rotational energy has been expressed as

$$E = \nu(\nu + 1). \tag{6}$$

Now let

$$\Theta(\xi) = (1 - \xi^2)^{|m|/2}w(\xi), \tag{7}$$

and change the variable ξ to z:

$$z = (1 - \xi)/2, \tag{8}$$

the differential equation in equation (4) is transformed into the hypergeometric equation [20, 21]:

$$z(1 - z)\frac{d^2w}{dz^2} + (|m| + 1)(1 - 2z)\frac{dw}{dz}$$
$$- (|m| - \nu')(|m| + \nu' + 1)w = 0. \tag{9}$$

The regular solutions at $z = 0$ and 1 are

$$w_{1(0)}(\nu', m, z) = F(a, b; c; z), \tag{10a}$$

$$w_{1(1)}(\nu', m, z) = F(a, b; 1 + a + b - c; 1 - z), \tag{10b}$$

respectively, and the irregular solution at $z = 0$ is

$$w_{2(0)}(\nu', m, z) = F(a, b; c; z)\ln z$$
$$+ \sum_{n=1}^{\infty}\frac{(a)_n(b)_n}{(c)_n n!}z^n[\psi(a + n) - \psi(a) + \psi(b + n)$$
$$- \psi(b) - \psi(c + n) + \psi(c) - \psi(1 + n) + \psi(1)]$$
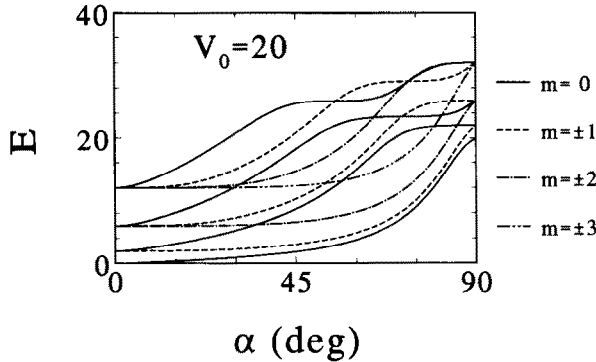$$- \sum_{n=1}^{|m|}\frac{(n - 1)!(1 - c)_n}{(1 - a)_n(1 - b)_n}z^{-n}, \tag{10c}$$

Fig. 1. Low-lying rotational energy levels of a horizontally adsorbed diatomic molecule as functions of the hindrance angle α (in degrees) with $\beta = 180° - \alpha$ for potential barrier height $V_0 = 20$.
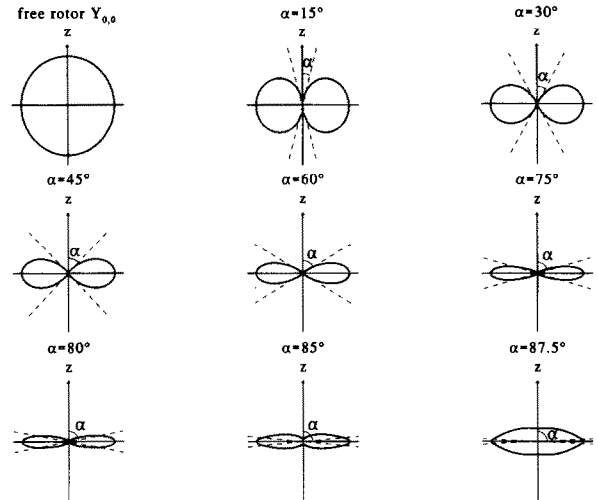

Fig. 2. Angular distributions of the ground state wave function Ψ of a horizontally adsorbed diatomic molecule for different hindrance angles α with $\beta = 180° - \alpha$ and potential barrier height $V_0 = 20$. $\Psi = Y_{0,0}$ when the confinement potential is absent.

where $F(a, b; c; z)$ is the hypergeometric function and

$$\begin{cases} a = |m| - \nu', \\ b = 1 + |m| + \nu', \\ c = 1 + |m|. \end{cases} \tag{10d}$$

Thus the solution for equation (4) in three different potential regions can be written as

$$\Theta(\xi) = \begin{cases} C_I \mathscr{P}_{(+1)}(n', m, \xi), & \cos\alpha < \xi \leq 1, \\ C_{II}\mathscr{P}_{(+1)}(\nu, m, \xi) \\ \quad + D_{II}\mathscr{Q}_{(+1)}(\nu, m, \xi), & \cos\beta \leq \xi \leq \cos\alpha, \\ C_{III}\mathscr{P}_{(-1)}(\nu', m, \xi), & -1 \leq \xi < \cos\beta, \end{cases} \tag{11}$$

where

$$\mathscr{P}_{(+1)}(\nu', m, \xi) = (1 - \xi^2)^{|m|/2} w_{1(0)}(\nu', m, z), \tag{12a}$$

$$\mathscr{P}_{(-1)}(\nu', m, \xi) = (1 - \xi^2)^{|m|/2} w_{1(1)}(\nu', m, z), \tag{12b}$$

$$\mathscr{Q}_{(+1)}(\nu', m, \xi) = (1 - \xi^2)^{|m|/2} w_{2(0)}(\nu', m, z). \tag{12c}$$

One can easily see that, for unspecified ν' and m, $\mathscr{P}_{(+1)}$ converges at $\xi = +1$ but diverges at $\xi = -1$. On the contrary, $\mathscr{P}_{(-1)}$ converges at $\xi = -1$ but diverges at $\xi = +1$. But $\mathscr{Q}_{(+1)}$ diverges at both values $\xi = +1$ and -1. In order to determine ν, one has to match the boundary conditions at $\xi_1 = \cos\alpha$ and $\xi_2 = \cos\beta$ which yield

$$[\mathscr{P}_{(+1)}(\nu, m, \xi_1)\mathscr{P}'_{(+1)}(\nu', m, \xi_1)$$

$$- \mathscr{P}_{(+1)}(\nu', m, \xi_1)\mathscr{P}'_{(+1)}(\nu, m, \xi_1)]$$

$$\times [\mathscr{P}_{(-1)}(\nu', m, \xi_2)\mathscr{Q}'_{(+1)}(\nu, m, \xi_2)$$

$$- \mathscr{Q}_{(+1)}(\nu, m, \xi_2)\mathscr{P}'_{(-1)}(\nu', m, \xi_2)]$$

$$+ [\mathscr{P}_{(+1)}(\nu', m, \xi_1)\mathscr{Q}'_{(+1)}(\nu, m, \xi_1)$$

$$- \mathscr{Q}_{(+1)}(\nu, m, \xi_1)\mathscr{P}'_{(+1)}(\nu', m, \xi_1)]$$

$$\times [\mathscr{P}_{(-1)}(\nu', m, \xi_2)\mathscr{P}'_{(+1)}(\nu, m, \xi_2)$$

$$- \mathscr{P}_{(+1)}(\nu, m, \xi_2)\mathscr{P}'_{(-1)}(\nu', m, \xi_2)] = 0, \tag{13}$$

for non-trivial coefficients C and D, where $\mathscr{P}'_{(+1)} = d\mathscr{P}_{(+1)}/d\xi$, $\mathscr{Q}'_{(+1)} = d\mathscr{Q}_{(+1)}/d\xi$. For given m, α, β, and V_0, one can determine ν by solving equation (13) numerically, thus obtaining the eigen-energies from equation (6).

Figure 1 shows the low-lying rotational energy levels of a horizontally adsorbed diatomic molecule as functions of the cone opening angle α for potential barrier height $V_0 = 20$. For convenience, in our calculation, a symmetric conical well is considered, i.e. $\beta = 180° - \alpha$. One can note that when α changes from zero to $\pi/2$, the energy which corresponds to the lth free rotational state increases from $E = l(l + 1)B$ to $E = l(l + 1) + V_0$. As in the case of vertically hindered molecules [15], the energy levels of horizontally hindered molecules also exhibit the oscillatory behavior when the level energies are plotted as functions of hindrance angle. The oscillatory behavior of rotational energies was ascribed to the phenomenon of resonance transmission. This particular behavior is the manifestation of the rotational invariance of the present model.

Figure 2 shows the angular distributions of the ground state hindered molecular wave function for different hindrance conditions. The wave function started from free state $Y_{0,0}$ and changes to the hindered states when confined by the conical well. One can note the wave function is significantly distorted

due to the compression of the potential wall. Even at suitable conditions, the ground state hindered wave function is similar to that of free molecular state $Y_{1,1}$. When α approaches $\pi/2$, the wave function returns to that of free rotor again.

3. ELECTRIC FIELD EFFECT

Now let us consider a situation that the adsorbed molecule bears a dipole moment μ and is subjected to an applied electric field $\mathscr{E}$ which is parallel to the normal direction of the surface. The Hamiltonian of the system is given by

$$H = L^2 + V^{hin}(\theta) - \omega\cos\theta, \tag{14}$$

where

$$\omega = \frac{\mu\epsilon}{B}. \tag{15}$$

There is no analytic solution for equation (14), thus an approximation method should be used. Consider that the system is symmetric about z axis and, for a strong electric field, the molecular axis orients along the direction of the field so that the molecular wave function is concentrated about $\theta = 0$, thus this physical situation can be well described if we use a variational wave function given by

$$\Psi(\theta, \phi) = \Psi^{(0)}(\theta, \phi)\exp(\lambda\cos\theta) \tag{16}$$

where λ is the variational parameter, and $\psi^{(0)}(\theta, \phi)$ the zero-field hindered molecular wave function as stated in equation (3). From equation (16) one can note that λ will reflect the effect of electric field. With a strong field, the dipole moment of the molecule almost points in the field direction, hence a large λ is expected. On the other hand, when the field is very weak, Ψ reduces to the zero-field hindered molecular wave function $\Psi^{(0)}$, therefore a vanishing λ is expected.

Using equations (14) and (16) the eigen-energies of a hindered adsorbed molecule in the presence of an electric field can be obtained by minimizing

$$E(\lambda) = \frac{\langle\Psi|H|\Psi\rangle}{\langle\Psi|\Psi\rangle}, \tag{17}$$

with respect to λ. This procedure requires two inner products which can be evaluated numerically:

$$\langle\Psi|\Psi\rangle = \int_{-1}^{+1}|\Theta^{(0)}(\xi)|^2\exp(2\lambda\xi)\mathrm{d}\xi, \tag{18}$$

and

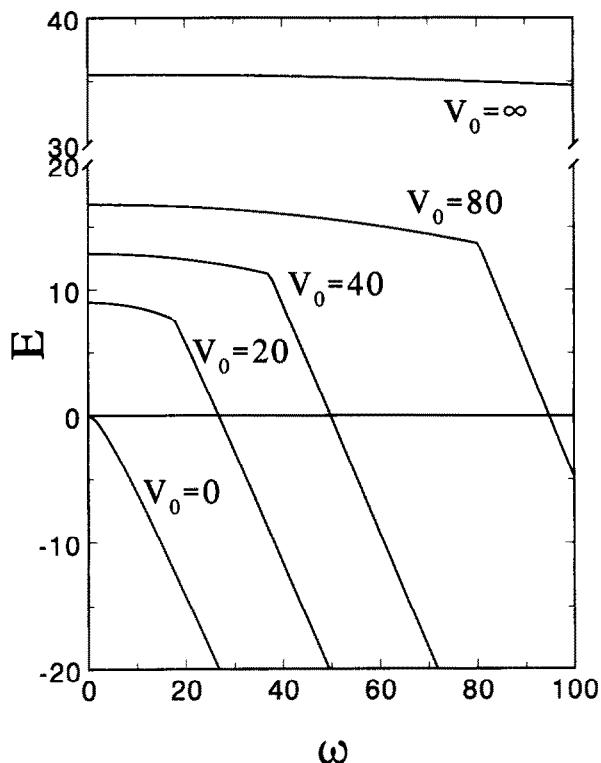$$\langle\Psi|H|\Psi\rangle = \int_{-1}^{+1}\Theta^{(0)*}(\xi)\,p(2\lambda\xi)$$

Fig. 3. Ground state energy of the horizontally adsorbed dipole molecule in an external electric field as a function of the field strength parameter ω for different potential barrier heights and $\alpha = 75°$ with $\beta = 180° - \alpha$.

$$\times\left\{[E^{(0)} - \lambda^2(1 - \xi^2) + (2\lambda - \omega)\xi]\right.$$

$$\left.\times\Theta^{(0)}(\xi) - 2\lambda(1 - \xi^2)\frac{\mathrm{d}\Theta^{(0)}(\xi)}{\mathrm{d}\xi}\right\}\mathrm{d}\xi. \tag{19}$$

In equations (18) and (19), $\Theta^{(0)}(\xi)$ is the zero-field hindered polar wave function given from equation (11) and $E^{(0)}$ the zero-field hindered rotational energy determined from equations (6) and (13).

Figure 3 shows the ground rotational state energy of the horizontally adsorbed dipole molecule in an external electric field, obtained by minimizing $E(\lambda)$ with respect to λ, as a function of the field strength parameter ω for different potential barrier heights. For the sake of comparison, the ground rotational state energy of a free dipole molecule in an external electric field is also presented. The variational wave function of a free dipole molecule in an external field is chosen as

$$\Psi(\theta, \phi) = Y_{l,m}(\theta, \phi)\exp(\lambda\cos\theta). \tag{20}$$

The inner products $\langle\Psi|\Psi\rangle$ and $\langle\Psi|H|\Psi\rangle$ for such a
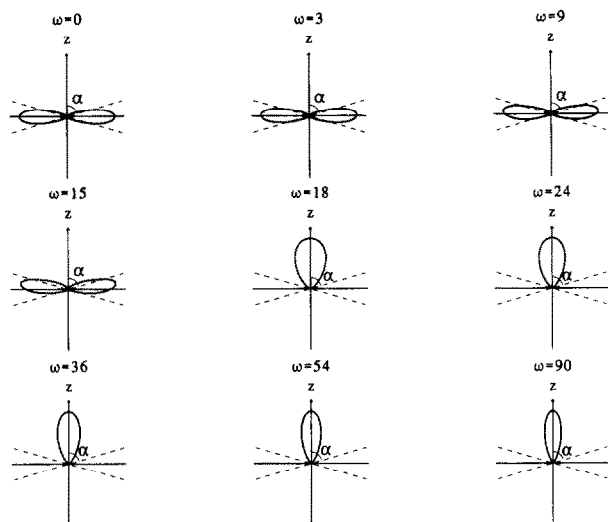
Fig. 4. Angular distributions of the ground state wave function Ψ of a horizontally adsorbed diatomic molecule in an external electric field for different field strengths. The hindering potential parameters used are $V_0 = 20$, $\alpha = 75°$, and $\beta = 180° - \alpha$.

wave function Ψ can be evaluated in analytical forms which have been presented elsewhere [19].

It is readily seen that the shifts of the rotational energies due to the electric field are very different between the free and hindered molecules. For increasing electric fields, the ground rotational state energy of the free molecule shows large negative shift, while that of hindered molecule has small negative shift for field strength ω less than V_0 and has large negative shift for $\omega > V_0$. One can note that almost no shift takes place when $V_0 = \infty$. Figure 3 shows that the Stark shift of the rotational energies of horizontally adsorbed molecules will be suppressed by the conical well potential if the field strength is weaker than the hindering potential. One can also note in Fig. 3 that the rotational energies E vary abruptly as $\omega \sim V_0$. This shows that our variational wave function may be not very suitable when the field strength is close to the hindering potential. A more precise variational wave function is necessary for this situation. However, for weaker and stronger electric fields, our variational wave function can still produce reliable results.

Figure 4 shows the angular distributions of the ground state hindered molecular wave function in an external electric field for different field strengths. One can note, for small field strength, the wave function changes slightly from the zero-field wave function and the molecule is still horizontally adsorbed. However, when the applied field strength is comparable with the hindering potential, wave function changes significantly and almost penetrates the conical well.

Furthermore, when the field strength is very large, the wave function is concentrated about the z axis. In such a case, in fact, the molecule is vertically adsorbed on the surface. Therefore, a very strong electric field is able to induce a change of adsorption configuration from horizontal to vertical.

4. CONCLUSION

We have investigated the hindered rotation and external electric field effect of horizontally adsorbed diatomic molecules. The surface hindering potential to which the adsorbed molecule is subjected was modeled as a horizontal finite conical well. Our result showed that the energy levels of the horizontally hindered molecule exhibit oscillatory behavior when plotted as functions of hindrance angle. This oscillatory behavior was ascribed to the phenomenon of resonance transmission.

When considering the external electric field effect, an dipole-field interaction was added to the hindering potential. The variational method was utilized to investigate the electric field effect on the molecular hindered rotation. Our results shows that the Stark shift of the rotational energies was suppressed by the conical well potential if the field strength is smaller than the hindering potential. On the other hand, since the wave function will concentrate about the field direction at large field strength, a very strong electric field will induce a change of adsorption configuration from horizontal to vertical.

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