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ROVIBRATIONAL EXCITATION WITHIN THE INFINITE CONICAL WELL: DESORPTION OF DIATOMIC MOLECULES

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ABSTRACT

An analytic model for the hindered rotational states of a diatomic molecule adsorbed upright on a solid surface is discussed. Various model dynamics situations, within the sudden approximation, designed to simulate desorption are presented and rotational state distributions are calculated including both rotational and translational degrees of freedom. Criteria are established for observing rotationally cool desorbed molecules.

INTRODUCTION

Stimulated by several recent experimental studies in which the rotational state distributions of diatomic molecules scattered or desorbed from metallic surfaces have been measured (refs. 1), we have constructed a simple, analytic model for a quantum mechanical hindered rotor, (ref. 2) designed to simulate the rotational states of a diatomic molecule hindered by a solid state or surface environment. Consideration of both the energy levels and dynamics associated with this model should lead to insights useful for the understanding of the reported experiments. The single most striking feature of the model study was the recognition of the role played by the zero-point kinetic energy resulting from the spatial localization of the rotor. If the hindered rotor is subjected to a dynamical situation in which the hindering potential is switched off, such as occurs in desorption, the ultimate disposal or redistribution of the zero-point energy can strongly influence the characteristics of observed rotational state distributions, as will be shown.

In this paper, various aspects and extensions of our previous work are described. The model is presented in the next section followed by some illustrative numerical consequences. Next, a simple classical analysis of the partitioning of available energy between rotational and translational degrees of freedom in desorbed molecules is given. Finally, drawing upon analogies with gas phase photodissociation of polyatomic molecules, some preliminary results for

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electron and photon stimulated desorption are presented.

MODEL

In order to describe the quantum mechanics of a hindered rotor in a reasonably tractable manner we have adopted a philosophy inspired by papers on two topics, one being nodal hydrogenic surface impurity wavefunctions (refs. 3) and the other the quantum mechanics of gears (ref. 4). In both of these works, simple and elegant results have been obtained for the quantum mechanical properties of familiar systems in which not-so-familiar boundary conditions are imposed, in the first case a plane surface on the spherical Coulomb problem and in the second, the constraints of mutually compatible rotational states (dictated by wheel radii, gear teeth ratio, chatter, etc.) of two free rotators.

The related characteristics of the present model are displayed in the inset of Fig. 1. Free rotations of a rigid dumbell (diatomic molecule) are allowed about some point on the molecular axis (Left: about center of mass; Right: about one end) provided the polar angle lies within the domain $0<\theta<\beta$. In other words, the angle-dependent hindering potential is an infinite-conical well, the spherical coordinate analog of a Cartesian coordinate infinite-square well. The special features of this potential stem from the fact that the angular part of the Schrodinger equation is identical with that of the free rotor, the distinction lying solely in the boundary conditions. The polar eigenvalue equation is just Legendre's equation (with $x = \cos\theta$)

$$(1-x^2)\frac{d^2P}{dx^2} - 2x\frac{dP}{dx} + \left(\nu(\nu+1) - \frac{m^2}{1-x^2}\right)P = 0 \qquad (1)$$

subject to the unusual boundary condition $P(x=\cos\beta) = 0$, that is the wavefunction must vanish at the infinitely repulsive cone wall. The resulting rotational eigenfunctions are

$$\psi_\nu^{rot}(\theta,\phi) = \begin{cases} A_{\nu m}(2\pi)^{-1/2} P_\nu^{|m|}(\cos\theta)\exp(im\phi) & ,\ 0\le\theta<\beta \\ 0 & ,\ \beta\le\theta<\pi \end{cases} \qquad (2)$$

and the energy eigenvalues

$$\epsilon = B\nu(\nu+1) \qquad (3)$$

with $B = \hbar^2/2I$, I the moment of inertia, and $A_{\nu m}$ a normalization constant. If $\beta=\pi$, then $\psi_{\nu m}^{rot}$ are just the familiar $Y_{\ell m}$'s and ν takes on integer values only. If $\beta=\pi/2$, the eigenfunctions are still the $Y_{\ell m}$'s but now only those states satisfying $\ell+m$ = odd are allowed as this condition picks out those states with nodes on the boundary (refs. 3). For $\beta<\pi/2$, although the quantum numbers ν are generally non-integers, $P_\nu^{|m|}$ remains an associated Legendre function (of arbitrary order) (ref. 5).

The lowest four quantum numbers numerically obtained from Eq. 1 are shown in Fig. 1 as a function of the cone angle. These intuitively appealing results show that as β decreases, not only does the zero-point kinetic energy associated with the increased localization increase dramatically, but also so do the excitation energies. For instance, with $\beta \simeq 10°$ (an upright adsorbed diatomic) the zero point energy $\simeq$ 180 B and the lowest lying excitation energy is $\sim$ 160 times that of the equivalent free rotor.

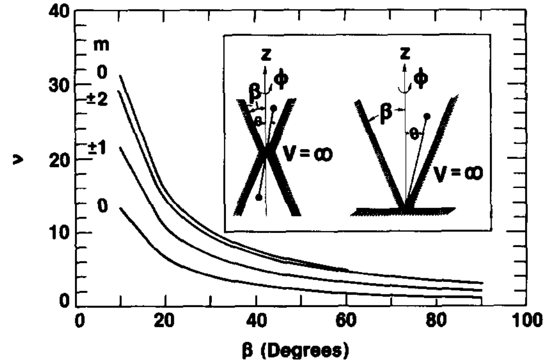

Fig. 1. The four lowest rotational quantum numbers as a function of the cone angle. The azimuthal quantum numbers are labeled on the left. Inset: Infinite conical well model treated here.

SUDDEN UNHINDRANCE: ROTATIONAL HEATING

A model dynamics problem can be envisioned in which the hindering potential is suddenly switched off, as might occur when a molecule is ejected from the solid state environment responsible for the hindrance. Under these circumstances, the zero-point kinetic energy of the hindered rotor must influence the dynamics and/or final state energy distributions. In fact for hindered rotations about the center of the mass (left side in Fig. 1 inset), sudden release of the hindering potential will result in purely hindered to free rotational transitions (no center of mass translational energy), producing a final free rotational state distribution which appears "hot" due to conversion of zero point to free rotational energy. Within the sudden limit (refs. 6), the rotational state distribution is given by a sum of rotational Franck-Condon factors between $Y_{\ell m'}^{free}$ and $\psi_{\nu,m}^{rot}$, weighted by appropriate thermal factors, that is

$$P(\ell) = \frac{1}{Z_{hin}} \sum_{\nu>1,m,m'} \exp[-B\nu(\nu+1)/k_bT]\ |\langle Y_{\ell m'}^{free}\ |\psi_{\nu m}^{rot}\rangle|^2 \qquad (4)$$

where T is the ambient temperature and Z_{hin} the hindered-rotor partition function. The Franck-Condon factors have been calculated analytically for the infinite conical well and these results will be reported separately (refs. 2,7). We note that if $B\nu_g(\nu_g+1)/k_bT >> 1$ (ν_g is the ground state quantum number), the expected heating effect will be due to conversion of zero-point energy, not thermal excitation. Consequently, the more narrow the cone, the "hotter" the real-temperature-independent free rotor distribution. State distributions obtained from Eq. 4, for a "typical" value of $B/k_bT = 0.05$ ($\theta_{rot} = B/k_b = 5$ K, $T \simeq 100$ K say) are shown in Fig. 2. As expected, the smaller the hindrance angle, the greater the population of high ℓ states

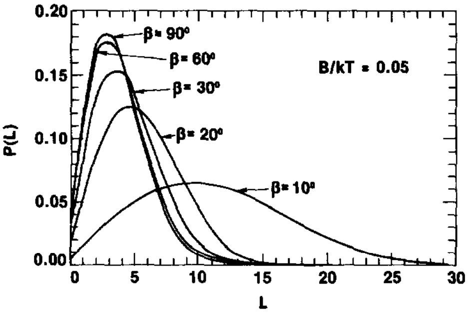

Fig. 2. Rotational-state distribution for the suddenly unhindered rotor on the left in Fig. 1, as a function of the free-rotor rotational quantum number.

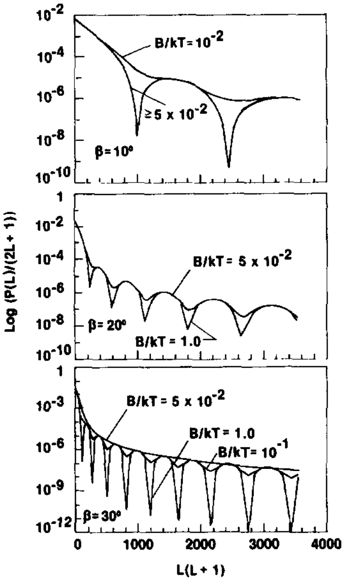

Fig. 3. Rotational-state distributions for the suddenly unhindered (left) rotor, plotted in the form $\log[P(\ell)/(2\ell+1)]$ vs. $\ell(\ell+1)$.

It is also enlightening to plot the distributions in the form $\log[P(\ell)/(2\ell+1)]$ vs. $\ell(\ell+1)$, as has been done in Fig. 3. Two distinctly different regimes appear. For $\ell \lesssim 20$-30, a linear behavior is seen in which T_r, an effective "rotational temperature", can be identified by equating the slope of the curves to $-B/k_bT_r$. For the rather narrow cones characterized by large quantum numbers, T_r is fairly independent of T, the actual ambient temperature. Furthermore as β decreases, the inverse slope or apparent rotational temperature increases. Both of these characteristics support our conjecture that conversion of zero-point rather than thermal kinetic energy into free rotational energy is the mechanism responsible for population of the free-rotor excited states within our model problem. We will not comment here on the high ℓ behavior other than to note that the periodicity in ℓ, varying as $180°/\beta$, is related to the commensurability between free and hindered rotations (ref. 2).

CLASSICAL ROTATIONAL COOLING

As appealing as the ideas of the last section are, they deal with only half of the relevant physics pertaining to desorption of a hindered diatomic molecule, for not only is the hindering potential switched off but also the bond which "clamps" one end of the molecule to the surface is broken. Thus in addition to free rotation, free center-of-mass translation is also permitted in the final state. For the example already discussed (left model in Fig. 1), the only possibility is hindered-to-free rotational energy flow since the center-of-mass is always at rest. For desorption (right model in Fig. 1), the hindered rotational energy divides between rotational and translational due to the addition of the extra degree of freedom in the final state. This is not easy to work with within a clean quantum mechanical model due to algebraic complications arising from a space-fixed vs. body-fixed axis description of the hindered and free rotor (refs. 8).

Nonetheless a simple classical model, again in the sudden limit, demonstrates the essential features. Consider the 3 steps in "desorption" shown in Fig. 4.

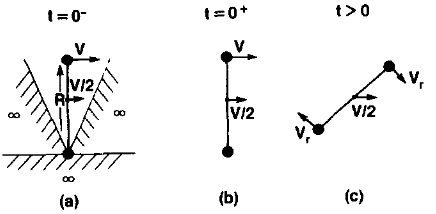

Fig. 4. Classical model for sudden unhindrance and release of right rotor in Fig. 1. Time sequences are: a) Just before release, b) Just after release, c) Finite time after release.

Originally at time $t=0^-$, the loose end of the rotor is moving in the cone with a velocity v due to the zero point energy as shown in Fig. 4a. For a homonuclear molecule, the center-of-mass is also moving with velocity v/2. Thus the initial energy is

$$\varepsilon_{rot}^{hin} = \frac{1}{2} mv^2 = \frac{1}{Z_{hin}} \sum_{\nu,m} B\nu(\nu+1)\exp(-B\nu(\nu+1)/k_bT) \simeq B\nu_g(\nu_g+1). \qquad (5)$$

At time t=0, the potential is switched off <u>and</u> the bound atom released, as in Fig. 4b. Sometime later (t>0), the situation is as shown in Fig. 4c, where not only is the center-of-mass translating, but also the molecule is rotating about the center-of-mass. The total energy is

$$\varepsilon_{free} = \varepsilon_{cm} + \varepsilon_{rot}^{free} = \frac{1}{2}(m_1+m_2)\frac{v^2}{4} + \frac{1}{2}(m_1+m_2)\, v_r^2$$

with $m_1 = m_2$ and $\varepsilon_{hin} = \varepsilon_{free}$ (a consequence of the sudden approximation), yielding $v_r = v/2$ or $\varepsilon_{rot}^{free} = \varepsilon_{rot}^{hin}/2$. Consequently, if

$$B\nu_g(\beta)\ (\nu_g(\beta) + 1) < 2\ k_bT, \tag{6}$$

the molecules will emerge rotationally cooler than if they were in equilibrium with the substrate. For example, if $\beta \simeq 10°$, then with $B/k_b \simeq 3$ K (approximately N_2 or NO), $B\nu_g(\nu_g + 1)/k_b \simeq 500$ K, which is much less than $2T \sim 1000$ K, as in the Cavanagh-King thermal desorption experiment.[1] Under these conditions, Eq. 6 is well satisfied, so we would anticipate the rotationally cool desorbed molecules observed experimentally (ref. 1).

PHOTODISSOCIATION/STIMULATED DESORPTION

The final topic focuses on the formal similarities which exist between the photodissociation of a triatomic molecule, due to electronic excitation (ref. 9), and photo (or electron) stimulated desorption (ref. 10) in the limit in which the fragment "atom" is taken to be infinitely massive (the substrate). In either case, emphasis is placed on total system Franck-Condon factors associated with the switch from an initial to final state potential surface dictated by the implicit electronic transition. The Franck-Condon factors order the importance of various allowed final channels via the partitioning of available energy between vibrational, rotational, and translational (VTR) degrees of freedom. Within Golden Rule perturbation theory, the transition rate induced by radiation of energy ω to some final state is

$$\begin{aligned} P_\omega(fin) &= \frac{2\pi}{\hbar}\left|\int \psi_{fin}^{VTR}(Q)\ V_\omega(Q)\ \psi_{in}^{VTR}(Q)dQ\right|^2 \delta(\varepsilon_f - \varepsilon_i - \hbar\omega) \\ &\simeq \frac{2\pi}{\hbar}\left|\tilde{V}_\omega \int \psi_{fin}^{VTR}(\underset{\sim}{Q})\ \psi_{in}^{VTR}(\underset{\sim}{Q})\ d\underset{\sim}{Q}\right|^2 \delta(\varepsilon_f - \varepsilon_i - \hbar\omega) \end{aligned} \tag{7}$$

with

$$V_\omega(\underset{\sim}{Q}) = \langle \phi_f(\underset{\sim}{x};\underset{\sim}{Q}) | V_\omega(\underset{\sim}{x}) |\ \phi_i(\underset{\sim}{x};\underset{\sim}{Q}) \rangle_{\underset{\sim}{x}} \simeq \bar{V}.$$

In Eq. 7, ψ^{VTR} describes nuclear motion states in terms of abstract coordinates $\underset{\sim}{Q}, \phi(\underset{\sim}{x};\underset{\sim}{Q})$ are Born-Oppenheimer electronic states, $V_\omega(\underset{\sim}{x})$ is the interaction due to the radiation, and $\bar{V}$ is assumed constant with $\underset{\sim}{Q}$ over the range spanned by the integrand.

To apply Eq. 7 to desorption, consider the limit in which both the diatomic as well as chemical bond are taken to be rigid (no explicit vibrational motion) so that the initial and final state wavefunctions may be written as

$$\psi_{in}^{TR}(Q) \rightarrow |\nu,m;\beta> \; = N_i \; \psi_m^{rot} \; (\theta,\phi) \; \delta(R_{cm} - R/2) \; \delta(\hat{R}_{cm} - \hat{r}) \qquad (8a,b)$$

and

$$\psi_{fin}^{TR}(Q) \rightarrow |k,\ell,m'> = \; N_f \; e^{ik \cdot R_{cm}} \; Y_{\ell m'} \; (\theta,\phi)$$

where N_i and N_f are normalization constants, $\underset{\sim}{k}$ is the wave vector of the center of mass translation in the final state, $\underset{\sim}{R}_{cm}$ is the position vector of the center-of-mass, and $\psi_{\nu m}^{rot}$ are given by Eq. 2. If we define $\hbar\omega_c$ as the threshold radiation to produce an $\ell = \underset{\sim}{k} = 0$ desorbed molecule from the hindered rotor ground state and $\Delta = \hbar(\omega-\omega_c)$ as the excess radiation energy above threshold, then the probability for desorption into a free rotational state ℓ with center-of-mass wavevector $\underset{\sim}{k}$, thermally averaged over initial states, is given by

$$P_\omega(\ell,\underset{\sim}{k}) = \frac{2\pi}{\hbar}|\bar{V}|^2 \sum_{\nu,m,m'} \frac{\exp(-B_{hin}\nu(\nu+1)/k_bT)}{Z_{hin}} \; |<\underset{\sim}{k},\ell,m'|\nu,m;\beta>|^2 \qquad (9)$$

$$\times\delta[B_{hin}(\nu(\nu+1)-\nu_g(\nu_g+1)) + \Delta - B_{free}\ell(\ell+1) - \hbar^2k^2/2M]$$

and the probability for final state ℓ, regardless of direction or translational energy by

$$P_\Delta(\ell) = N\int P_\omega(\ell,\underset{\sim}{k}) \; d^3\underset{\sim}{k}. \qquad (10)$$

Explicit calculation of the Franck-Condon factors is a formidable job which has been detailed elsewhere (refs. 7,11). Using these reported results, some examples for $P_\Delta(\ell)$ are shown in Fig. 5, plotted in the normalized form $\log[P_\Delta(\ell)/((2\ell+1) P_\Delta(0)]$ vs. $\ell(\ell+1)$ for a value of $B_{free}/k_bT = 0.9$ (for example H_2 and T = 100 K), hindrance angles β = 30°, 60°, and 90°, and several values of Δ/k_bT. Although the results in Fig. 5 exhibit an overall non-Boltzmann behavior, if we venture straight line fits to judiciously chosen regions, we could identify increasing rotational temperatures for higher incident excitation (large Δ), which are not necessarily higher than the temperature of the substrate. Furthermore, for fixed (large) ℓ and Δ, smaller β (more zero point energy) yields distributions somewhat more populated at large ℓ than does the larger β initial state. Two simple generalizations can be made from these observations. First, the greater the excitation energy, the hotter the rotational temperature and secondly, the larger is the initial zero point energy, the hotter is the final state. Work is in progress to extend these preliminary studies to the point where more useful intuitive guidelines can be uncovered.

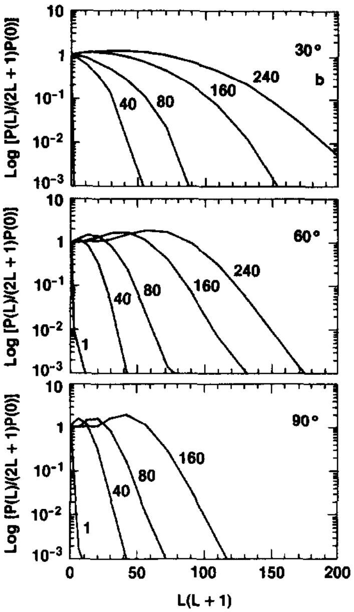

Fig. 5. Plots of $\log[P_{\Delta}(\ell)/(2\ell+1)P_{\Delta}(0)]$ vs. $\ell(\ell+1)$ for stimulated desorption of the hindered rotor, with center-of-mass motion included, for hindrance angles β = 30°, 60°, and 90°, treating Δ, the energy above the excitation threshold parametrically.

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