Contribution of restricted rotors to quantum sieving of hydrogen isotopes

B. C. Hathorn,[1] B. G. Sumpter,[2] and D. W. Noid[2]

[1]*Computer Science and Mathematics Division, Oak Ridge National Laboratory, Oak Ridge, Tennessee 37831*
[2]*Chemical and Analytical Sciences Division, Oak Ridge National Laboratory, Oak Ridge, Tennessee 37831*

The rotational eigenvalues of isotopically substituted hydrogen molecules adsorbed into single-walled carbon nanotubes are calculated using a semiclassical method and using a model potential. The resulting eigenvalues are used to calculate the separation factors due to rotational confinement between different isotopic species as a function of temperature and nanotube size. The results show that even for small shifts in the eigenvalues, significant fractionations should occur, suggesting possible application as an isotope-separation technique.

I. INTRODUCTION

The adsorption of hydrogen molecules on graphite and carbon nanostructures has been of great interest in the last several years as carbon nanotubes have come to the forefront as a possible storage medium for hydrogen for fuel-cell devices. A number of promising advances have been shown where nanotubes can absorb large amounts of hydrogen [1–7] however the results are far from free of controversy, due to possible contamination of the samples [8]. Other researchers have found that graphitic nanofibers show small preference to graphitic carbon in the adsorption of hydrogen [9]. Essentially, the experimental results depend on the possibility of the carbon substrate to act as a kind of molecular sieve in absorbing the hydrogen molecules.

Molecular sieves have been used to separate mixtures of molecules based on the size and shape of the molecules. The separation of isotopes based on size or shape selectivity, however, cannot be accomplished by classical means, because isotopic species have the same shape and size, and differ only in the mass [10]. The usual methods of isotopic separation [11], such as chemical exchange, diffusion, and laser isotope separation are difficult, energy intensive, and expensive, and new methods of efficient isotope separation, which are cheap and efficient would be a major advance.

There are a number of differences that are manifested in molecules upon isotopic substitution. Experimentalists frequently employ vibrational shifts in the isotopic species to investigate molecular structures, the investigation of mass-dependent kinetic isotope effects dates to the pioneering work of Washburn and Urey [12], and the subsequent treatment of isotopic kinetics of Bigeleisen and Meyer [13]. The systematic treatment of isotope effects in thermodynamics properties, such as equilibrium constants, which we employ herein, dates to Urey's pioneering 1947 work [14].

Recently, it has been proposed that the introduction of quantum zero-point energy in the translational coordinates of molecules enclosed in carbon nanostructures could be employed in separation of isotopes [10,15]. The source of this effect is the effective shift of the equilibrium constant for the absorbed and unabsorbed molecules. The shift in the equilibrium constant was shown to be smaller for particles that contained larger masses. The separation factor, effectively given by the ratio of equilibrium constants, is then seen to depend strongly on the masses of the molecules. It was suggested in path-integral calculations that nanostructures of a diameter larger than approximately 7 Å showed only weak selectivity [10], while smaller carbon nanotubes exhibited very large selectivity. An important advance was made in this study by the extension of the results away from the regime of dilute absorption to that involving higher pressures using a grand canonical Monte Carlo treatment [10]. The study neglected, however, small effects that arise from the asymmetry of the molecule. In the previous study the molecules were assumed to be rigid spherelike particles [16] with isotropic rotations when exposed to the confining environment, whereas real molecules have definitive shapes, leading to anisotropic rotational potentials. Such anisotropy leads to the restriction of the rotational motion.

The hindering potential of hydrogen adsorbed onto single-walled nanotubes has been measured recently by inelastic neutron diffraction, and showed small rotational barriers. The samples used were as-produced single-walled nanotubes, and were approximately 1.7 nm in diameter, based on the spacing of the hexagonal close-packed lattice [17]. A model for the shift rotational eigenvalues for hydrogen molecules bound to a flat surface was utilized nearly four decades ago in an effort to interpret both the isotopic enrichment and the statistical distribution of ortho- and para-hydrogen bound to a surface [18,19]. In the present case we extend the treatment to the case where the molecule is enclosed inside a cylindrical structure.

In the present work, we extend the theoretical treatment of the quantum sieve past the previously employed one and two-dimensional models to incorporate the quantization of the restricted rotational motion. We find that inclusion of the rotational restriction allows for enhanced selectivity over the recently employed models that consider translational confinement alone.

In analogy to the translational motion recently treated by Wang *et al.* [10], the rotation of a diatomic molecule, has a rotational energy given by $E = BJ(J+1)$ where J is the total angular momentum. Since the value of J may be zero, there is no zero-point energy. It is well known, however, that introduction of a potential shifts the energies of the rigid rotor, and introduces a component of zero-point energy [18–20].

In the present paper, we consider the quantization of the rotational motion of a diatomic molecule in a carbon nanostructure. We calculate the rotational eigenvalues as a function of the size of the structure. The eigenvalues obtained are then employed to calculate partition functions, which, in turn, yield the effective isotopic fractionations. In addition, we do not employ the approximation that the temperature is sufficiently low so as to require that all molecules are in their ground state, however, in the present case that approximation corresponds to the low-temperature limit.

In Sec. II we recall the basic equations leading to the separation factor in the one and two-dimensional systems previously employed. We then extend the model to incorporate rotational effects. The details of the method employed to obtain the eigenvalues is discussed. In Sec. III we present the results of our calculations, both of the eigenvalues and of the isotopic selectivity. In Sec. IV we discuss the results.

II. THEORY

We consider herein the balance of equilibrium between and adsorbed species and a free species in the gas phase. The ratio of concentrations of absorbed and free molecules can be given in terms of the equilibrium constant for the reaction

$$K = \frac{Q_{ads}}{Q_{free}}, \tag{1}$$

where Q_{ads} is the partition function of the adsorbed species and Q_{free} is the partition function of the free molecule in the gas phase [10,15]. If we consider a mixture of noninteracting molecules, the ratio of concentrations of adsorbed molecules to those in the gas phase is then given by the ratio of equilibrium constants. We term this ratio here to be the separation factor S:

$$S = \frac{K_1}{K_2} = \left(\frac{Q_{ads,1}}{Q_{ads,2}}\right)\left(\frac{Q_{free,2}}{Q_{free,1}}\right), \tag{2}$$

where K_i is the equilibrium constant for the absorption of species i. We note that we have assumed in writing 2 that the species are noninteracting on the substrate and in the gas phase, which is the typical dilute gas approximation. In the approximation of noninteracting degrees of freedom, the partition function can be written as a product of independent partition functions over the different degrees of freedom,

$$Q = Q_{trans}Q_{rot}. \tag{3}$$

For the present case, we have omitted any vibrational or electronic partition functions, as the temperatures for the present investigation will be sufficiently low to ensure that the molecules reside in the lowest vibrational state, and the latter electronic partition function will be identical for different isotopes. The separation factor may now be construed as a product of a translational and rotational component, $S = S_{trans}S_{rot}$, where each of the separation factors are individually calculated from Eq. (2). Such a separation has been utilized elsewhere [18] and attempted corrections to such an approximation have been estimated for a limited number of cases in the case of a molecule absorbed on a planar surface [19].

The ratio of translational partition functions, S_{trans} has been discussed previously in some detail [10,15], and we will not describe it herein, focusing our attention to the purely rotational aspects of the quantum confinement. We note, however, that the approximation that the rotational and translational motions can be separated will not be exact inside the carbon nanostructure, for instance, when the translational motion takes the molecule in close proximity to the wall, the rotational potential will become much larger, and will not exhibit true cylindrical symmetry. In the present case, we approximate the rotational potential as being that of the molecule in the center of the nanotube, which corresponds to its average translational position. At this point the molecule is at the maximum possible distance from the walls, and we expect the perturbation of the rotational eigenvalues would be as small as it could be in the given nanotube. We expect that calculations done at this value would be a lower bound for the true separation (the true separation factor could be written as $S = S_{trans}S_{rot}S_{trans\text{-}rot}$ with $S_{trans\text{-}rot} > 1$).

The calculation of the partition functions of the hindered rotational motion requires the eigenvalues of the restricted rotor. In the present case we consider a linear rigid rotor. The classical mechanical Hamiltonian for the rotor is [21]

$$H = B\left(p_\theta^2 + \frac{p_\phi^2}{\sin^2\theta}\right) + V(\theta,\phi). \tag{4}$$

The first term corresponds to the rotational kinetic energy, expressed in polar coordinates, the second term represents the potential interaction between the molecule and the environment, and is explicitly dependent on the molecular orientation. The constant, $B = \hbar/2\mu d^2$ is the rotational constant of the diatomic molecule, with bond length d and a reduced mass μ. Frequently, the partition function can be obtained from the classical approximation [21],

$$Q = \int \exp[-\beta H(\mathbf{q},\mathbf{p})]d\mathbf{q}d\mathbf{p}, \tag{5}$$

where the integral is over all allowable coordinates and momenta $(\mathbf{q},\mathbf{p})$, and $\beta = 1/k_BT$. In the present case, however, where the interest is in low-temperature phenomena, the classical partition function must be corrected by accounting for wide spacings of the energy levels with respect to k_BT, and when a potential is present, the zero-point energy. The correct quantum partition function is given by [21]

$$Q = \sum_i \exp(-\beta E_i), \tag{6}$$

where now i indexes the quantum levels of the system, each of which has energy E_i. For the partition function of ''free'' rotational states, we have employed the quantum-rotational partition function [21],

$$Q_{rot,free} = \sum_J g(J)(2J+1)\exp[-\beta B(J)(J+1)]. \quad (7)$$

The function $g(J)$ is the weighting due to the nuclear spin statistics, which give rise to the traditional ortho- and para-spin states. For heteronuclear diatomics, $g(J)=1$ for all values of J. In the present calculation we have assumed that the adsorbed molecules maintain a statistical distribution of ortho- and para-states, as activated carbon has been observed to catalyze the interconversion of the two species. For homonuclear diatomics with half-integral spin (corresponding to H_2 and T_2 in the present case, each of which have nuclear spins of $I=1/2$ [22]) we have

$$Q_{rot,free} = \sum_{J\,even}(2J+1)\exp[-\beta B(J)(J+1)] + 3\sum_{J\,odd}(2J$$
$$+1)\exp[-\beta B(J)(J+1)]. \quad (8)$$

For the D_2 isotopomer (with nuclear spin of $I=1$ [22]), the relevant nuclear spin statistics give rise to

$$Q_{rot,free} = 6\sum_{J\,even}(2J+1)\exp[-\beta B(J)(J+1)]$$
$$+3\sum_{J\,odd}(2J+1)\exp[-\beta B(J)(J+1)]. \quad (9)$$

In most statistical mechanical applications at moderate temperatures, the nuclear spin statistics can be accounted for by replacing the nuclear spin weightings with their average in the form of a symmetry number in Eq. (7). Such an approximation is typically valid in the range $kT>5B$ which in the case of hydrogen molecules corresponds to temperatures larger than approximately 200 K [21]. In the present case it is not possible to do so since we are interested in the low-temperature limit, and there may be significant corrections to the rotational partition function arising from coupling of the nuclear spin states, as such, we have chosen to treat the nuclear spin weightings exactly.

In order to calculate the quantum levels of the restricted rotor in the present case, we make use of a semiclassical treatment. The semiclassical treatment allows the extraction of approximate eigenvalues for the system from the classical mechanical Hamiltonian in the spirit of the WKB approximation [23], albeit in multiple dimensions [24]. In the present case, careful selection of the coordinates reduces the necessary calculation to a one-dimensional one, and the carryover from WKB is direct. The usual one-dimensional WKB quantization condition is given by quantization of the action [23],

$$\oint p\,dq = 2\pi\hbar\left(n+\frac{1}{2}\right), \quad (10)$$

where the integral is carried out over a complete cycle of the classical motion. The quantum number n must be integral, and for a given randomly selected classical trajectory may not be so. However, the energy varies monotonically with the

action integral, and consequently the eigenenergies can be found from an interpolation of the function of $E(n)$ to integer values of n.

For a free rotor, the correct quantization condition would be

$$\oint p\,dq = 2\pi\hbar J(J+1) \quad (11)$$

arising from the different boundary conditions, from the continuity of the wave function, and giving rise to a set of quantum levels where there is no zero-point of energy. Calculations of the free rotor quantum levels with the quantization condition (11) lead to the exact quantum levels of the rigid rotor. We have applied Eq. (10) for the quantum states in the present case, as the $m^2/\sin^2\theta$ term in the effective potential serves to restrict the trajectory from the points $\theta=0$ and $\theta=\pi$.

In the case of $m=0$, we have considered the quantization condition to be that of the free rotor Eq. (11) if there is no barrier presented by the potential $V(\theta,\phi)$ that restricts the range of motion. In a case where there is a barrier to free rotation through the whole range of the azimithul coordinate, $0\le\theta\le\pi$, the eigenvalues are found with the standard quantization for a bound system, Eq. (10). In the case where there are two separate quantization conditions for a single system (e.g., where there is free rotation above the barrier and the system is bound below the barrier) the two sets of quantum numbers are tabulated separately, and the corresponding interpolations are done independently.

In the present case we define the azumithal angle, θ in Eq. (4) to be the rotation away from the principal axis of the nanotube cylinder, which is treated as having a cylindrically symmetric potential, $V(\theta,\phi)$ being independent of ϕ. In this case, p_ϕ^2 is quantized by m^2, and the effective one-dimensional Hamiltonian becomes

$$H = \frac{1}{2\mu R^2}\left(p_\theta^2 + \frac{m^2}{\sin^2\theta}\right) + V(\theta,\phi). \quad (12)$$

Numerical integration of trajectories using Eq. (12) using Hamilton's equations of motion [25],

$$\dot{q} = \frac{\partial H}{\partial p}, \quad (13)$$

$$\dot{p} = -\frac{\partial H}{\partial q}, \quad (14)$$

is now straightforward, and can be rapidly accomplished until the requisite condition for a complete cycle in the left-hand side of Eq. (10) is accomplished.

In addition to the direct calculation of the energy eigenvalues, care must be taken to obtain the correct degeneracy of a given eigenstate. In the present calculation, we use the simplification of calculating energy states for integers $m\ge0$. For states with $m>0$, the degeneracy of the state is 2, owing to two possible orientations of the rotation with respect to the fixed axis, which would normally be accounted

for by the m and $-m$ quantum numbers, which are degenerate. In addition, for states with $E(n) < V(\pi/2, \phi)$, the molecule will not be able to surmount the barrier to rotation in the tube, and there will be a degeneracy, resulting from the two possible orientations of the molecule within the carbon nanotube. In principle, such states will interact to lift the degeneracy, however the semiclassical eigenvalue method does not yield such splittings, which are expected to be small. In our calculation, such states are treated as doubly degenerate.

The nuclear spin degeneracy is handled in a procedure analogous to that which was accomplished by White and Lassettre [18]. The states are correlated to the free rotor states by taking $(n+m) \to J$. The nuclear spin statistics of a rotation with quantum number J and are then applied.

For the purposes of the present calculation, we have employed a modified Lennard-Jones type potential [26] for the interaction of the molecule with the nanotube. In order to preserve the cylindrical symmetry of the system, which allows the reduction of the dimension of the problem, we have assumed the cylinder is uniform, with an attraction to the molecule given by

$$V(\theta, \phi) = -2\epsilon \left(\frac{r^*}{r_{LJ}}\right)^6 + \epsilon \left(\frac{r^*}{r_{LJ}}\right)^{12} \qquad (15)$$

with the Lennard Jones interaction distance between the end of the molecule and the wall of the nanotube being given by

$$r_{LJ} = R - \left(\frac{d}{2}\right)\sin \theta. \qquad (16)$$

In these expressions, R is the radius of the nanotube and d is the bond length of the molecule in the tube.

The crude estimation of Lennard Jones parameters ϵ and r^* has been accomplished by adjusting the interaction parameters between hydrogen molecules and methane [26], but shifting the distances of interaction from the center of the hydrogen molecule to the ends, reducing r^* for the hydrogen-methane interaction by half the bond length of the hydrogen molecule ($d = 0.74$ Å). The parameter ϵ, which controls the depth of the attractive well, is doubled in the present case, resulting from the symmetry of the system, where each end of the molecule is equidistant from the surface of the nanotube, and contributes equally. The final approximate parameters we have used in the present calculation are $\epsilon = 148$ K and $r^* = 3.412$ Å [27].

III. RESULTS

A. Potential surface

The potential surface we have used for the present calculation is shown in Fig. 1. At small cylinder radii, the repulsive part of the potential forces alignment of the molecule with the principal axis of the cylinder ($\theta = 0$ or π). At longer radii, the most attractive potential is for the molecule orthogonal to the principal axis ($\theta = \pi/2$).
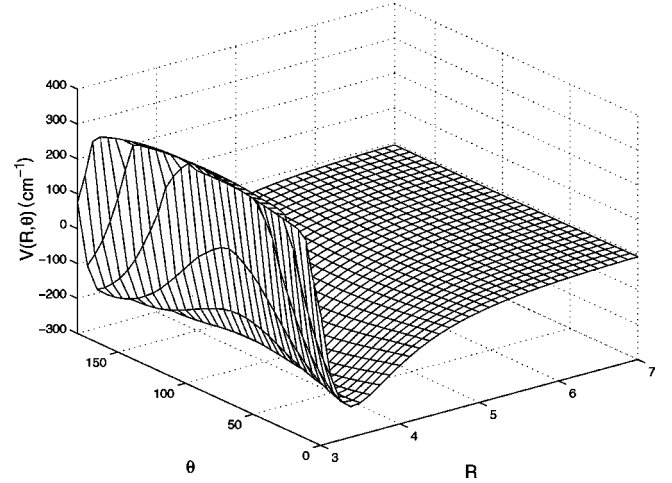

FIG. 1. Potential surface for the rotational interaction between a diatomic hydrogen molecule and the carbon nanotube, as a function of the nanotube radius.

B. Dependence of eigenvalues on cylinder size

The eigenvalues obtained from the semiclassical quantization show a continuous variation as the size of the cylinder is varied. The eigenvalues for H_2 for the $m = 0$ states are illustrated in Fig. 2. In the large radius limit, the states approach those of a free rotor (represented by the point at $R = 8.0$ Å). The apparent discontinuity in the lowest eigenvalue at approximately $R = 5.3$ Å arises from the lowest eigenvalue crossing over the separatrix from a rotor like state to a bound harmonic oscillatorlike state. The extent of the discontinuity is largest for the H_2 molecule of all of the isotopic combinations, and is less than approximately 5 cm^{-1}. A second discontinuity is present at approximately $R = 3.5$ Å where the lowest energy configuration transitions from aligned with the tube to orthogonal to it, and there is a resulting separatrix. The quantum states for $|m| > 0$ states (not shown) are similarly continuous and asymptotically approach the free rotor limit.
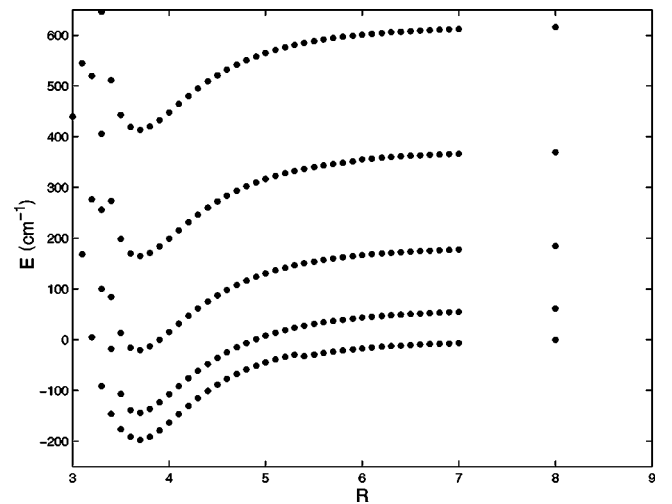

FIG. 2. Variation of eigenvalues as a function of cylinder radius for H_2 molecule. The points at $R = 8$ Å represent the asymptotic free rotor limit $E(J) = BJ(J+1)$, and are not calculated from the semiclassical quantization method.
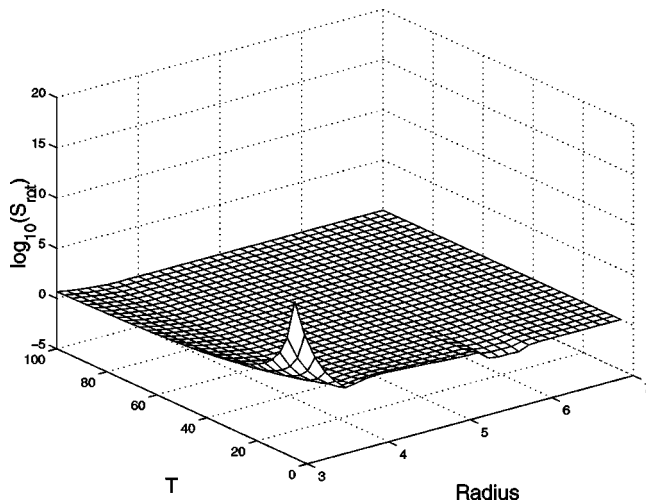
FIG. 3. Contribution to isotopic selectivity due to rotational restriction as a function of cylinder size and temperature, for D_2 molecules. The feature in the vicinity of $R = 5.5$ Å is a result of the presence of the transition between rotational and vibrational character of the eigenvalues, resulting in the discontinuity of the lowest eigenvalue in Fig. 2.

C. Rotational separation factors

The extent of the isotopic separation due to the quantization of the rotational motion, as calculated from Eq. (2) using rotational partition functions has been calculated as a function of temperature and nanotube size for all possible hydrogen isotopomers, D_2, T_2, HD, HT, and DT relative to the H_2 standard, and is illustrated in Figs. 3–7, over temperatures between 5 and 100 K. The separation factors at low temperature are very large, up to fifteen orders of magnitude, and as a result the separation factors have been expressed on a logarithmic scale. The feature at approximately $R = 5.5$ Å at low temperatures is an artifact of the small discontinuity that separates the rotational eigenstates from the vibrational eigenstates as the barrier to rotation grows.

An example of a single cut through the surface for T_2 at a temperature of 20 K is represented in Fig. 8. The feature due
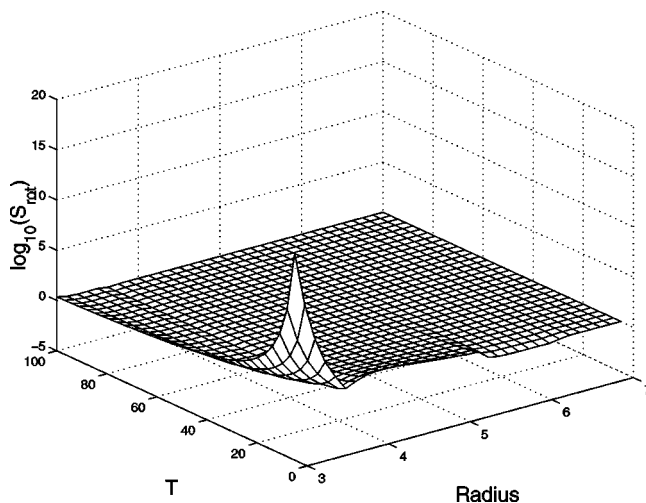

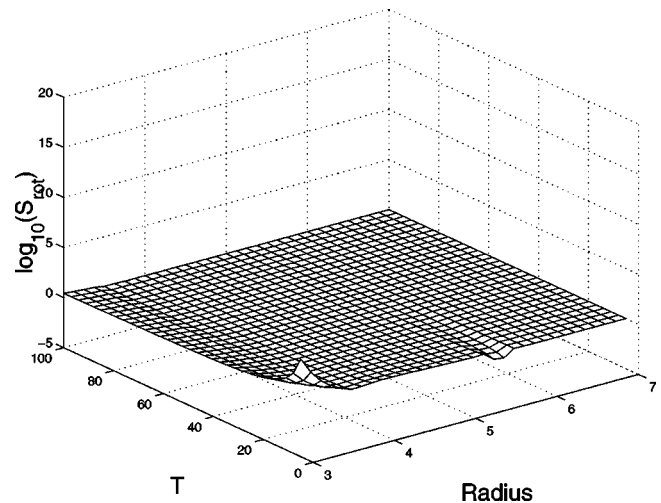FIG. 5. Same as Fig. 3, but for HD molecules.

FIG. 6. Same as Fig. 3, but for HT molecules.
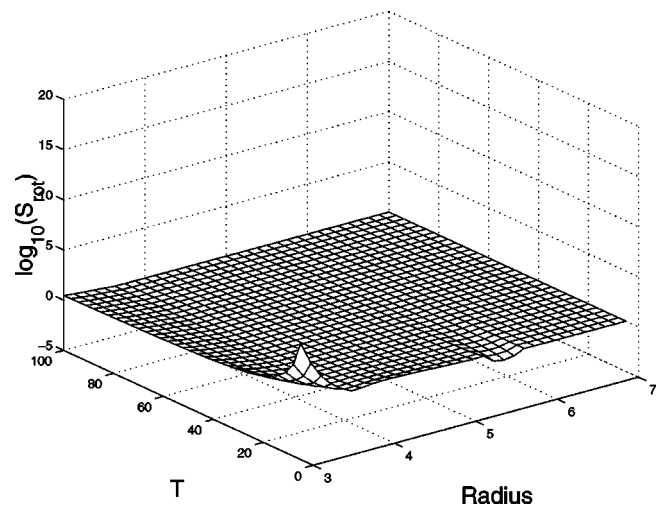

FIG. 4. Same as Fig. 3, but for T_2 molecules.

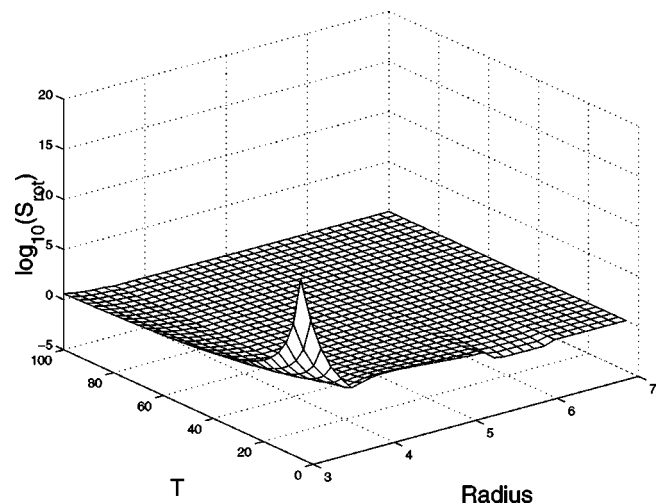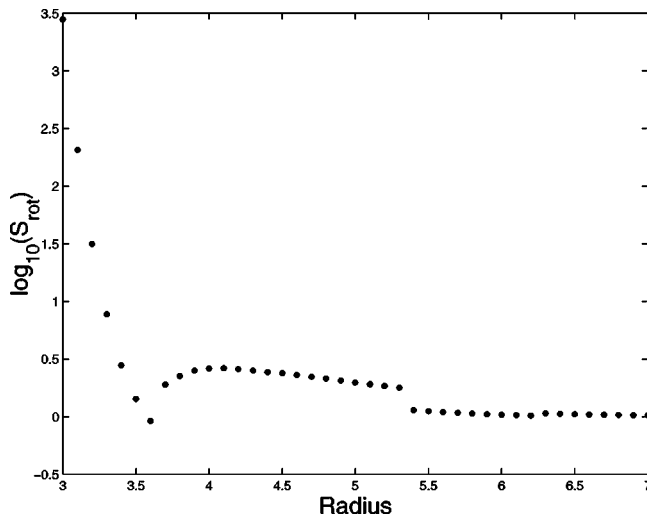FIG. 7. Same as Fig. 3, but for DT molecules.

FIG. 8. Rotational separation factors for T_2 relative to H_2 as a function of cylinder size at $T = 20$ K.

to the discontinuity is evident at approximately $R = 5.5$ as is a second discontinuity at the position of a second separatrix at approximately $R = 3.5$, where the barrier to rotation now exceeds the barrier for crossing through the principal axis of the cylinder, or the transition from the lowest energy configuration being aligned in the direction of the wall of the tube or aligned with it.

IV. DISCUSSION

We first remark on some limitations of the method that has been employed here to evaluate the eigenvalues. As was described in Sec. II, we have assumed a *de facto* separation of the coordinates between rotation and translation for the molecule in the nanotube. Such a separation was made to retain the cylindrical symmetry of the potential for rotation, independent of the position of the molecule within the cylinder. Naturally, such a separation is very approximate, but in the present context, where we see that as the separation becomes more dramatic as the motion develops more vibrational character as the molecules are closer to the wall, the separation obtained in this approximation that treats the molecules as having the largest distance from the cylinder walls, we find a lower bound for what we would expect the true separation to be. One could, in fact, solve the full rotation-translation coupled problem, but the present case reduces the dimensionality of the problem to a single dimension, where the full rotation-translation problem is a four-dimensional problem, and substantially more difficult [24]. We intend to return to this question in a future study.

Another question that arises in the present calculation is the question of splittings in the bound states. For a number of cylinder sizes, there is a barrier to rotation that gives a symmetric double-well problem in the θ coordinate. Such a system will have one eigenvalue corresponding to each of the wells when the energy of the system is below the barrier between the wells. The quantum states will, however, interact, producing a splitting between the two formerly degenerate energies. In the present case, we have neglected the splitting, calculating the energies and giving the resultant

eigenstates a twofold degeneracy. The expected splittings, on the other hand, are expected to be small, and for all except the lowest temperatures in the present study, they are expected to be much smaller than $k_B T$.

We return now to the results of the present study. We observe that the separation factors obtained from the present model are very large at low temperatures and for small nanotubes, and are clearly dependent on the mass of the molecules. The largest nanotube in the present study is approximately 1.5 nm, and is comparable to the size of the hexagonally close-packed lattice of nanotubes in some experimental systems [17]. Even for the larger tubes and higher temperatures, calculated separations that may be large enough to be experimentally observed (a factor of approximately 2 for 5 Å (radius) nanotubes at 20 K, with much larger effects for smaller tubes), are obtained, despite the fact that in our calculations and in the experimental observations [17] the gross amount of perturbation to the rigid rotor eigenvalues is small. We note that in the present study, very large selectivity is observed in the range of 6–8 Å for the cylinder diameter, in previous studies that focused on translational confinement [10], comparable selectivity was observed in this range, suggesting that both the translational and rotational confinement lead to significant selectivity.

In addition, we note that the present results for the separation are above and beyond those that are obtained from consideration of the quantization of the translational motion alone [10], and thus the combination of the two separation factors should produce larger effects than either one by itself. Essentially, the separation factor arises from the introduction of zero-point energy into modes, which in the free state have no zero-point energy. The result is an effective "chemical potential" (equivalent to the zero-point of energy) for adsorption onto the substrate, which is purely dependent on the mass of the molecule and its moments of inertia. Naturally, since this effect arises from small differences in the ground states of the partition-function ratios, it is largest at the lowest temperatures observed. The case of translational confinement introduces zero-point energy for two translational modes, and in the present calculation we have introduced zero-point energy for two additional rotational modes.

In the present study, we observe that, in addition to the consideration translational confinement of a molecule in a nanotube, there are significant quantum effects that arise from the restriction of the rotational motion. The addition of the zero-point energy, which arises from the confinement of these degrees of freedom (two, in the case of a linear rotor), obtained from a crude potential, significantly enhances the isotopic separation factor over that for a model that includes only the confinement of the translational motion.

[1] A.C. Dillon, K.M. Jones, T.A. Bekkedahl, C.H. Kiang, D.S. Bethune, and M.J. Heben, Nature (London) **386**, 377 (1997).

[2] C. Liu, Y.Y. Fan, M. Liu, H.Y. Cong, H.M. Cheng, and M.S. Dresselhaus, Science **286**, 1127 (1999).

[3] P. Chen, X. Wu, J. Lin, and K.L. Tan, Science **285**, 91 (1999).

[4] A. Chambers, C. Park, R.T.K. Baker, and N.M. Rodriguez, J. Phys. Chem. B **102**, 4254 (1998).

[5] C. Park, P.E. Anderson, A. Chambers, C.D. Tan, R. Hidalgo, and N.M. Rodriguez, J. Phys. Chem. B **103**, (1999).

[6] Y.Y. Fan, B. Liao, M. Liu, Y.L. Wei, M.Q. Lu, and H.M. Cheng, Carbon **37**, 1649 (1999).

[7] Y. Ye, C.C. Ahn, C. Witham, B. Fultz, J. Liu, A.G. Rinzler, D. Colbert, K.A. Smith, and R.E. Smalley, Appl. Phys. Lett. **74**, 2307 (1999).

[8] R.T. Yang, Carbon **38**, 623 (2000).

[9] C.C. Ahn, Y. Ye, B.V. Ratnakumar, C. Witham, R.C. Bowman, and B. Fultz, Appl. Phys. Lett. **73**, 378 (1998).

[10] Q. Wang, S.R. Challa, D.S. Sholl, and J.K. Johnson, Phys. Rev. Lett. **82**, 956 (1999).

[11] See, for instance, O. Atabek, M. Chrysos, and R. Lefebvre, Phys. Rev. A **49**, R8 (1994); *Separation of Isotopes*, edited by H. London (George Newnes, London, 1961).

[12] E.R. Washburn and H.C. Urey, Proc. Natl. Acad. Sci. U.S.A. **18**, 496 (1932).

[13] J. Bigeleisen and M. Meyer, J. Chem. Phys. **15**, 261 (1947).

[14] H.C. Urey, J. Chem. Soc. **1947**, 561 (1947).

[15] J.J.M Beenakker, V.D. Borman, and S.Yu. Krylov, Chem. Phys. Lett. **232**, 379 (1995).

[16] Q. Wang and J.K. Johnson, J. Chem. Phys. **110**, 577 (1999).

[17] C.M. Brown, T. Yildirim, D.A. Neumann, M.J. Heben, T. Gennett, A.C. Dillon, J.L. Alleman, and J.E. Fischer, Chem. Phys. Lett. **329**, 311 (2000).

[18] D. White and E.N. Lassettre, J. Chem. Phys. **32**, 72 (1960).

[19] A. Katorski and D. White, J. Chem. Phys. **40**, 3138 (1964).

[20] K. S. Pitzer, *Quantum Chemistry* (Prentice-Hall, New York, 1953), and references cited therein.

[21] D. A. McQuarrie, *Statistical Mechanics* (Harper & Row, New York, 1976), and references cited therein.

[22] *CRC Handbook of Chemistry and Physics*, 81st ed., edited by David R. Lide (CRC Press, Boca Raton, 2000).

[23] See, for example, L.I. Schiff, *Quantum Mechanics*, 2nd ed. (McGraw-Hill, New York, 1955).

[24] See, for example, I. Percival, Adv. Chem. Phys. **36**, 1 (1977); D.W. Noid, M.L. Koszykowski, and R.A. Marcus, Annu. Rev. Phys. Chem. **21**, 267 (1981); S.K. Knudson and D.W. Noid, J. Chem. Educ. **66**, 133 (1989); D. W. Noid, S. K. Knudson, and B. G. Sumpter, Comput. Phys. Commun. **51**, 11 (1988).

[25] H. Goldstein, *Classical Mechanics* (Addison-Wesley, Reading, 1980).

[26] T. L. Hill, *An Introduction to Statistical Thermodynamics* (Dover, New York, 1986), and references cited therein.

[27] The interaction parameters between hydrogen and methane can be approximated by the relationships $\epsilon_{A,B} = \sqrt{\epsilon_{A,A}\epsilon_{B,B}}$ and $r^*_{A,B} = (r^*_{A,A} + r^*_{B,B})/2$, where A and B represent different molecular species. In the present case, the parameters for hydrogen molecules are $\epsilon_{H_2,H_2} = 37.0$ K and $r^*_{H_2,H_2} = 3.278$ Å. The corresponding parameters for methane are $\epsilon_{CH_4,CH_4} = 148.2$ K and $r^*_{CH_4,CH_4} = 4.285$ Å. From these relationships, we obtain approximate Lennard Jones interaction parameters of $\epsilon_{H_2,CH_4} = 74.0$ K and $r^*_{H_2,CH_4} = 3.782$ Å.