Separation of molecules with different isotopic compositions by adsorption

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The isotope effect in the physical molecular adsorption rate is considered. For the lightest molecules, the direct isotope effect leads to large separation factors per adsorption event. For heavy molecules, the adsorption separation factor can, in principle, be considerably increased by selective vibrational excitation of the molecules. The separation efficiency depends on the probability for vibrational relaxation in the field of the adsorption forces. The choice of the adsorbent-adsorbate system is very important.

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1. INTRODUCTION

As is well known, the problem of laser separation of molecules having different isotopic compositions reduces to a considerable extent to the problem of separating selectively excited molecules of the required type from unexcited ones. A selective heterogeneous method of separating vibrationally excited molecules in selective adsorption processes has recently been proposed.[1] An experimental test[2] using laser excitation of BCl_3 molecules showed that differences in the adsorption rates for molecules excited to different vibrational levels lead to isotopic enrichment. The strong vibrational-temperature dependence of the condensation rate of gaseous CO_2, which was recently observed and used for isotope separation,[3] also indicates that the previously proposed[1] selective heterogeneous method of isotope separation using a laser is realizable in principle. This method is of great interest, first because it requires only the excitation of the first vibrational level of the molecule. This, in turn, leads in principle to high enrichment efficiency. Moreover, it is still unclear, even for the simplest case of physical sorption, how the separation efficiency depends on the experimental conditions and the choice of the adsorbent-adsorbate system.

Below we present the results of a theoretical study of the efficiency of the elementary adsorption act for separating molecules that differ in isotopic composition. The purpose of the study was to obtain qualitative and semiquantitative estimates. Unfortunately, it is practically impossible to give a detailed description of the objects under investigation because of their complexity.

In the case of a binary molecular mixture, the separation efficiency of the elementary adsorption act is characterized by the separation factor γ per impact of a molecule with the adsorbent surface. The separation factor is the ratio of the reflection coefficients of the molecules of the two kinds to be separated:

$$\gamma = R_1/R_2, \quad R_1 > R_2. \tag{1}$$

The reflection coefficient R is equal to $1-S$, where S is the sticking coefficient, defined as the ratio of the number of molecules that stick to the adsorbent surface to the total number of molecules that strike the surface, both referred to unit surface area and unit time:

$$S = \int P_s(v_z) v_z \exp\left\{-\frac{mv^2}{2kT}\right\} d\mathbf{v} \Big/ \int v_z \exp\left\{-\frac{mv^2}{2kT}\right\} d\mathbf{v} = \frac{1}{kT}\int_0^\infty P_s(E_z)\exp\left\{-\frac{E_z}{kT}\right\} dE_z, \tag{2}$$

where T is the gas temperature, m and $\mathbf{v}$ are the mass and velocity vector of the molecule, v_z is the normal component of $\mathbf{v}$, $E_z = mv_z^2/2$, and $P_s(v_z)$ is the sticking probability—the probability that a molecule that strikes the adsorbent surface will stick to it. The sticking probability depends mainly on v_z since the adsorption potential varies little along the surface, i.e., in the xy plane.

The sticking probability $P_s(E_z)$ is essentially the probability that the energy E_z of the molecule will be dissipated in the adsorbent lattice during the motion of the molecule through the field of the adsorption forces. In classical mechanics, P_s is a step function and, as shown by numerical calculations,[4–6]

$$P_s(E_z) = \begin{cases} 1, & E_z < E_c \\ 0, & E_z > E_c \end{cases}, \tag{3}$$

in which E_c is the critical sticking energy, i.e., the greatest possible energy exchange between the molecule and the lattice. In this case the sticking and reflection coefficients have the form

$$S = 1 - \exp(-E_c/kT), \quad R = \exp(-E_c/kT), \tag{4}$$

from which we obtain the following formula for the separation factor:

$$\gamma = \exp\{(E_{c2} - E_{c1})/kT\}. \tag{5}$$

The critical energy E_c depends on the ratio m/M of the molecular mass m to the mass M of an adsorbent lattice atom, on the adsorption interaction energy, and so on.[4–10] In a rough approximation in which the collision of a molecule with a surface atom is treated as an elastic collision of free particles,[7] the energy exchange can be estimated by the formula

$$\Delta E\approx\varkappa(E_z+D),\quad \varkappa=4mM/(m+M)^2, \tag{6}$$

in which D is the depth of the adsorption potential (the heat of adsorption). Then E_c is determined by Eq. (6) with ΔE and E_z replaced by E_c. The result is

$$E_c\approx\frac{\varkappa}{1-\varkappa}D\approx4\frac{m}{M}D \text{ if } \frac{m}{M}\ll1. \tag{7}$$

Thus, the critical sticking energy is directly determined by the mass of the molecule (the direct isotope effect). The direct isotope effect is fairly large for the lightest molecules H_2, HD, and D_2.

Now in performing an adsorption-separation experiment it must be borne in mind that the reflection coefficient for the lighter molecule should differ appreciably from zero, since otherwise all the molecules will be adsorbed. This imposes the condition $kT\approx E_{c1}$ on the gas temperature, and then

$$\gamma\approx\frac{1}{2.7}\exp\left\{\frac{E_{c2}}{E_{c1}}\right\}\approx\frac{1}{2.7}\exp\left\{\frac{m_2}{m_1}\right\}. \tag{8}$$

While γ is fairly large for the lightest molecules, for heavier molecules (N_2, O_2, CO, NCl, etc.) the relative change in the molecular mass due to isotopic substitution is small and the separation factor resulting from the direct isotope effect differs little from unity:

$$\gamma\approx1+(m_2-m_1)/m_1=1+\Delta m/m. \tag{9}$$

A possible way to increase the separation factor is to make use of selective excitation of vibrations in molecules of a specific isotopic composition.[1,2] In its motion through the field of the adsorption forces, an excited molecule may lose vibrational energy with a corresponding increase in its translational kinetic energy. In turn, this will reduce the sticking probability, which in this case can be expressed in the form

$$\begin{aligned}P_s^*(E_z)&=P_s(E_z)[1-p(E_z)]+P_s(E_z+\hbar\omega)p(E_z)\\&=P_s(E_z)-p(E_z)[P_s(E_z)-P_s(E_z+\hbar\omega)],\end{aligned} \tag{10}$$

where $p(E_z)$ is the probability that the molecule will lose a quantum of vibrational energy during its passage through the adsorption-force field and $\hbar\omega$ is the quantum energy of the molecular vibrations. It is evident from (3) that $P_s(E_z)-P_s(E_z+\hbar\omega)$ changes sharply in the region $E_z\approx E_c$.

Passing now from the sticking probability $P_s^*(E_z)$ to the reflection coefficient and taking advantage of the fact that $p(E_z)$ is a relatively smooth function, we obtain

$$R^*=R\{1+p(E_c)(\exp[\min(E_c,\ \hbar\omega)/kT]-1)\}. \tag{11}$$

Then the separation factor will be given by

$$\gamma=R^*/R=1+p(E_c)(\exp[\min(E_c,\ \hbar\omega)/kT]-1). \tag{12}$$

In principle, γ may differ strongly from unity and the concentration of the molecules whose resonance vibrations have previously been excited will increase in the gaseous phase. It is obvious, however, that in setting up an actual experiment one must be interested not only in γ, but also in the mass yield of the method. Without considering this point just now, we make use of the requirement that the reflection coefficient R not be small. Then in accordance with (4) we have $kT\approx E_c$ and

$$\gamma\approx1+p(E_c)(\exp[\min(E_c,\ \hbar\omega)/E_c]-1). \tag{13}$$

Thus, to estimate the efficiency of the elementary adsorption act in separating molecules bearing vibrational energy, one need only determine the vibrational relaxation probability and the critical adsorption energy.

In the following exposition we shall analyze in more detail the adsorption of the lightest molecules in their vibrational ground states, take into account the part played by relativistic corrections to the energy dependence of the sticking probability, and consider the adsorption of heavy molecules in excited vibrational states.

2. ADSORPTION OF H_2, HD, AND D_2 MOLECULES

Since the intramolecular forces are much stronger than the intermolecular forces, in determining the energy exchange in collisions of light adsorbate molecules with the adsorbent lattice one can neglect the excitation of intramolecular vibrations of the adsorbate, while taking into account mainly the excitation of vibrations of the adsorbent atoms (or molecules). Then the struck surface atom is regarded as part of some unexcited harmonic oscillator whose proper frequency is equal to the Debye frequency ω_D and account is taken of the coupling of this oscillator to the other adsorbent atoms and the resulting rapid dissipation of the vibrational excitation energy into the lattice. The critical sticking energy can then be determined under these assumptions as the maximum energy that the oscillator can acquire under the action of the exciting force of the incident molecule during a single collision time.[11] The exciting force is $-\partial U(z(t))/\partial z$, where $U(z)$ is the adsorption potential. We may approximate $U(z)$ by the Morse potential

$$U(z)=D\{\exp[-2(z-b)/\lambda]-2\exp[-(z-b)/\lambda]\}, \tag{14}$$

in which λ is the width of the potential curve near the dissociation limit ($\lambda\approx10^{-8}$ cm), b is the position of the minimum of the function $U(z)$, z is the normal distance from the surface, and $z(t)$ is the trajectory of the molecule in the adsorption-force field.

Using the so-called approximation of equal cutoff distances,[4,5] in which it is assumed that the constant λ for the adsorption potential and the interaction potential for the lattice atoms are approximately equal, the approximations discussed above, and the condition $m/M\ll1$, one can derive[9,10,12] the following expression for the critical sticking energy:

$$E_c\approx4\pi^2(m/M)^2Q\exp\{-2(mQ/MD)^{1/2}\}, \tag{15}$$

in which Q is the heat of sublimation of the adsorbent. Estimates of E_c obtained from formula (15) agree well

TABLE I. Critical sticking energies E_c (in K) for hydrogen molecules.

Adsorbate	Adsorbent (Q, K)				
	Ar (900)	Xe (1750)	CO_2* (3000)	N_2 (750)	H_2O * (6000)
H_2	50	11.5	103	74	475
HD	100	17	200	145	710
D_2	154	40	310	226	910

* $D \approx 800$ K [14].

with the results of numerical calculations[4,5] and experimental studies of the adsorption of atoms.[12]

There are few data on the heat of adsorption of hydrogen on solidified gases. The heat of adsorption can be estimated as the average of the heats of sublimation of hydrogen and the adsorbent.[13] Then we can complete the estimation of the critical sticking energy of molecular hydrogen with different isotopic compositions on various adsorbents. The results of such estimations are given in Table I.

It is evident from the tabulated data that the critical sticking energy is much smaller than the sublimation energy Q of the adsorbent for all the adsorbents considered; the harmonic-oscillator model for the surface atom is therefore fully applicable. It will also be seen that the critical sticking energy for H_2 and HD molecules, and also those for HD and D_2 molecules, differ from one another by factors of 2–1.5, in virtual agreement with the predictions of the very simple estimate (7). Then in accordance with (8) we obtain the following values for the separation factors at $kT \approx E_c$: $\gamma(H_2 \to HD) \approx 1.65$, and $\gamma(H_2 \to D_2) \approx 7.4$; thus, the separation factors are fairly large even for a single impact with the surface. For N impacts, the separation factor is γ^N. It is obvious, however, that N cannot be made very large, for in that case virtually all the molecules would be adsorbed and the mass yield would be small. The separation of hydrogen isotopes is of great interest; hence further analysis of the adsorption method of separating these isotopes is desirable.

3. STICKING PROBABILITY AT NEAR-CRITICAL ENERGIES

In classical mechanics the sticking probability is a step function of the form of (3). In analyzing the motion of such relatively heavy particles as molecules, the quantum corrections to (3) should, generally speaking, not be large and can be important only in the vicinity of the discontinuity of the classical probability, i.e., at $E_z \approx E_c$. Moreover, this is just the energy region in which we are most interested, for the condition $E_z < E_c < E_z + \hbar\omega$ must be satisfied in order for there to be any considerable difference between the reflection coefficients for vibrationally excited and unexcited molecules.

The following formula has been derived[12] in the semiclassical approximation, using a model in which the surface atom is represented as an unexcited harmonic oscillator of frequency ω_D:

$$\frac{dP_s(E)}{dE} = -(2\pi E_c \hbar\omega_D)^{-1/2} \exp\left\{-\frac{(E-E_c)^2}{2E_c\hbar\omega_D}\right\}. \tag{16}$$

In the limit $\hbar \to 0$, the right-hand side of (16) reduces to $-\delta(E-E_c)$; this corresponds to the step function (3) for the purely classical limiting case. Thus, as a result of the quantum corrections the sticking probability $P_s(E)$ changes continuously from values of the order of unity to values close to zero over an energy range of width $2(2E_c\hbar\omega_D)^{1/2}$ centered at E_c. When E_c is large, the spread of the $P_s(E)$ curve may exceed the quantum energy of the molecular vibrations and thus reduce the separation efficiency. Hence when using a monoenergetic molecular beam it is desirable that, with the initial value $E_z = E_c - (2E_c\hbar\omega_D)^{1/2}$ for the translational kinetic energy E_z, the increase in E_z for the molecules of the selected type due to vibrational relaxation in the field of the adsorption forces be equal to $2(2E_c\hbar\omega_D)^{1/2}$. The use of a molecular beam with a Maxwell velocity distribution smooths out the effect of the quantum corrections. For $kT \approx E_c$, the width of the molecular velocity distribution is such that the quantum corrections are not important. It is just this case that is of greatest interest (see formula (13)).

4. ADSORPTION OF HEAVY MOLECULES

A theoretical description of the physical adsorption of heavy molecules encounters a number of substantial difficulties. First, estimates of the critical sticking energy using the harmonic oscillator approximation for the surface atom lead to values of E_c somewhat higher than the binding energy of the surface atoms. Hence this approximation cannot be used. At large energy transfers the dissipation of the excitation energy of the surface atoms into the adsorbent lattice may become a bottleneck. In such cases the adsorbent-lattice defects become more important since, reducing the energy dissipation rate, they greatly reduce the sticking probability.[15] It is difficult to make quantitative allowance for the effect of the lattice defects. Instead, one can extract the critical sticking energy from experimental cryopumping data.[16]

The direct isotope effect is small for heavy molecules, so one may treat E_c as a constant empirical parameter. Then to estimate the separation factor for vibrationally excited and unexcited molecules one must know the probability for vibrational relaxation in the field of the adsorption forces. It is natural to suppose that this probability will correspond to some extent to the probability for V–T relaxation of the molecules under consideration in a gas of adsorbent molecules (or atoms).[17] We note that V–T relaxation has been well studied for many molecular gases,[18,19] and the corresponding experimental data may prove to be useful in estimating the relaxation probability in the adsorption-force field incident to collisions with an adsorbent surface.

If the electronic state of a molecule (projectile) does not change during its collision with some other particle (target), then to evaluate the vibrational relaxation probability we can use a model in which the projectile is treated as a harmonic oscillator. It is convenient to use a Morse potential to represent the interaction between the target particle and the atom of the incident molecule that strikes the target. Then, using the quasi-classical asymptotic formulas derived by Lennard-Jones *et al*,[20] it can be shown [9,10] that the probability for vibrational relaxation of a molecule colliding with a wall or with an infinitely massive particle is given by

$$p_{1,2}(E_z) \cong 2\pi^2 m \frac{m_{2,1}}{m_{1,2}} \frac{\omega\lambda^2}{\hbar} \exp\left\{-2\frac{\omega}{\omega_0}\left(\frac{D}{E_z}\right)^{1/2} \arcsin\left(\frac{E_z}{D+E_z}\right)^{1/2}\right\}, \quad (17)$$

in which the subscripts 1 and 2 specify the orientation of the molecule during the collision (atom 1 or atom 2 toward the adsorbent), m_1 and m_2 are the masses of the corresponding atoms in the molecule, $m = m_1 + m_2$, ω is the frequency of the molecular vibrations, and $\omega_0 = \lambda^{-1}(2D/m)^{1/2}$.

In the case of the collinear collision of a molecule with a particle of mass M the relaxation probability is calculated in a similar way:

$$\tilde{p}_{1,2}(E_z) \cong 2\pi^2 m \left(\frac{M}{m+M}\right)^2 \frac{m_{2,1}}{m_{1,2}} \frac{\omega\lambda^2}{\hbar} \exp\left\{-2\frac{\omega}{\tilde{\omega}_0}\left(\frac{\tilde{D}}{E_z}\right)^{1/2} \arcsin\left(\frac{E_z}{\tilde{D}+E_z}\right)^{1/2}\right\}, \quad (18)$$

where $\tilde{\omega}_0 = \lambda^{-1}(2\tilde{D}(m+M)/mM)^{1/2}$, E_z is the energy of the relative motion, and $\tilde{D}$ is the depth of the interaction potential. The parameters D and $\tilde{D}$ are orientation dependent, but in most cases this dependence is not known. When $E_z \gg \tilde{D}$ the potential well is unimportant and (18) reduces to the Landau–Teller formula.[18,21]

When $E_z \gg \tilde{D}$, D, the ratio $p/\tilde{p}$ depends only on M and is practically unity if $M \gg m$. The values of D and $\tilde{D}$ are related and, as estimates show,[22] the heat of adsorption D may exceed the two-body interaction energy by a factor of 5–7. Hence if $E_z \ll \tilde{D}$ and $M \gg m$, p may exceed $\tilde{p}$ by a factor of $\exp((D/\tilde{D})^{1/2}) \approx 10$. If $M \ll m$, $\tilde{\omega}_0$ may be considerably larger than ω_0, and $\tilde{p}$ may exceed p.

The vibrational relaxation probability in the gaseous phase can be estimated from measurements of the vibrational relaxation rate constant.

The results of the analysis presented above and the experimental data on $\tilde{p}$ lead to the conclusion that for physical adsorption, as a rule, p does not differ much from $\tilde{p}$ and is small. However, for some systems, e.g., for hydrogen halides relaxing on noble gas atoms, $\tilde{p} = 0.1-0.01$[19] and the probability for relaxing on impact with the surface may reach values in the range 1–0.1. Assuming further that the critical sticking energy for these systems is of the order of the lattice sublimation energy (~0.1 eV), we find in accordance with formula (13) that γ may have values in the range 1.2–3 for the HI–HF series. If halogen molecules are used in place of the hydrogen halides with the same adsorbents, however, the separation factors per impact will be negligibly small. This shows that the adsorbent–adsorbate system must be carefully chosen.

In concluding this section we note that increasing the vibrational excitation of the molecule tends to increase the separation factor in adsorption.

The results of the analysis presented above together with experimental data on $V-T$ relaxation can be used to estimate the efficiency of the laser adsorption method for separating polyatomic molecules.

5. CONCLUSION

The rate of physical adsorption depends on the mass of the incident molecule. For the lightest molecules (H_2, HD, D_2), $\Delta m/m \approx 1$ and the direct isotope effect leads to fairly large separation factors per adsorption event. For heavy molecules, $\Delta m/m \ll 1$ and the separation factor per adsorption is small. Reducing the gas temperature increases the separation factor, but at very low temperatures, although the yield mixture is highly enriched in molecules of one type, the absolute yield is small.

In principle, vibrational excitation of the molecules of the required isotopic composition substantially increases the adsorption separation factor, and this is especially important for heavy molecules. The separation efficiency depends on the probability for vibrational relaxation in the field of the adsorption forces, so the proper choice of the adsorbate–adsorbent pair is very important. Increasing the affinity of the adsorbent atoms for the adsorbate molecules increases the relaxation probability. A possible way to increase the adsorption separation factor is to increase the vibrational excitation of the molecules. Reducing the width of the molecular velocity distribution also tends to improve the separation efficiency.

Thus, the selective heterogeneous laser method of isotope separation can be realized in a fairly efficient manner by suitably choosing the adsorption system. It would seem useful to make a more careful theoretical analysis of the adsorption of vibrationally excited polyatomic molecules having a fairly rich spectrum of normal vibrations, and also to investigate and compare various schemes for realizing the method under discussion.

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Theorems of the Hellman–Feynman type for stationary nonadiabatic systems

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Three theorems are proved for many-particle nonadiabatic systems, establishing the qualitative features of the dependence of the binding energy on the parameter which appears in the kinetic energy operator of the Hamiltonian. The first theorem establishes a relationship between the first and second derivatives of the binding energy with respect to this parameter. The second theorem imposes a restriction on the size of the first derivative. The third theorem determines upper and lower bounds of the system's binding energy for a given value of the parameter according to values of the binding energy associated with other values of the parameter. The theorems allow us to derive rigorous estimates of the binding energy and dissociation energy of nonadiabatic systems on the basis of data which exists for comparable systems. As an example, a lower bound is estimated for the dissociation energy of the muonium molecule.

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1. The Hellman–Feynman theorem,[1,2] establishing the dependence of the eigenvalue of a quantum mechanical system on a parameter in the Hamiltonian, has been widely used in calculations for molecular systems in the case when the Born–Oppenheimer adiabatic approximation is valid, and the parameter (usually the distance between nuclei) appears in the expression for the potential energy.[3–5] However, numerous cases exist when the parameter, for example, the ratio of the particle masses, appears in the kinetic energy operator and may be regarded as the parameter of nonadiabaticity. In this connection the conditions for applicability of the adiabatic approximation cannot be satisfied with regard to the selected subsystem. Cases also exist when one is not able to single out an adiabatic subsystem. Below we shall call both types of systems stationary nonadiabatic systems. In particular, examples of the indicated systems are given by: 1) electron-positron ions and molecules of the type $e^-e^+e^\pm$[6]; 2) systems of the type, atom (ion or molecule) + positron[7]; 3) muonic molecules of the type $p\mu^-p$[8,9]; 4) systems of the type, atom (ion or molecule) + muonium, for example, $C_2H_4(\mu^+e^-)$, or "muonium" water $H(\mu^+e^-)O$[9]; the broad class of systems formed out of quasiparticles (electrons and holes).[10]

Three general theorems of the Hellman–Feynman type are proved below for many-particle nonadiabatic systems. The following basic assumptions are utilized: 1) the particles interact according to a law of the type $|r_{ij}|^{-n}$ and 2) the kinetic energy operator linearly depends on the parameter α. The theorems determine the qualitative features of the dependence of a nonadiabatic system's binding energy B_0 on the parameter α. The first theorem establishes a relationship between the first and second derivatives of B_0 with respect to α. The second theorem imposes a limitation on the size of $\partial B_0(\alpha)/\partial\alpha$. The third theorem determines rigorous upper and lower bounds for $B_0(\alpha)$ with respect to the values $B_0(\alpha_1)$ and $B_0(\alpha_2)$, where $\alpha_1 < \alpha < \alpha_2$. The obtained results are qualitative in nature and, in analogy to other qualitative results in quantum mechanics,[11] they allow one to make relatively simple estimates.

2. Let the Schrödinger equation for an N-particle system have the form

$$H\Psi_k = -B_k\Psi_k, \tag{1}$$

where k denotes the totality of quantum numbers, $k=0$ corresponds to the nondegenerate ground state of the system, and

$$\begin{gathered} H = T_1(r) + \alpha T_2(r) + V(r), \\ r = (r_1, r_2, \dots, r_N), \quad r_i = (x_i^1, x_i^2, x_i^3), \\ T_{1,2} = \sum_{ij,\,\mu\nu} b^{(1,2)}_{ij,\mu\nu} \frac{\partial^2}{\partial x_i^\mu\, \partial x_j^\nu}, \\ \bar{T}_{1,2}(\alpha) \doteq \langle 0|T_{1,2}|0\rangle, \quad \bar{T}_{1,2}(\alpha) > 0; \\ \tau(\alpha) = \bar{T}_1(\alpha)/\bar{T}_2(\alpha), \end{gathered} \tag{2}$$