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Isotope effects for molecules in a cavity

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A model problem of the motion of a particle in an impenetrable cavity is considered in order to establish how the energy levels and transition energies between them depend on the linear size, R, of the cavity and on the particle mass. In the case of one-particle problem with a uniform potential inside the cavity there exists a simple qualitative solution that describes the effect of the cavity size and shows that a decrease in R can cause the isotopic frequency shift to increase as compared to the free system. The estimates obtained were used to interpret the results of numerical calculations of low-lying energy states of hydrogen molecule and its isotopomers confined within impenetrable spherical cavity. The effect of the cavity radius on the structure of the low-lying part of the energy spectra of H_2, D_2, and HD molecules and on the reliability of adiabatic separation of nuclear variables are considered. The approach provides a qualitatively correct description of the changes in the energy level positions but the behavior of the isotopic frequency ratio is too smooth compared with results of more accurate calculations.

Key words: hydrogen molecule, molecule in cavity, isotopic frequency shift, rovibrational energy levels, separation of variables.

Analysis of the influence of isotopic substitution on the spectral characteristics of molecules is an important and efficient tool of investigation of the structure of molecular systems. In the framework of a simple harmonic model the frequency ratio of two isotopomers can be estimated as the square root of the inverse ratio of their masses. However, experiments also give abnormally large isotopic shifts. For instance, considerations of vibrational motions of entire hydrogen molecule confined in an octahedral cavity between fullerene molecules in solid C_{60} shows that H—D-substitution leads to a frequency ratio of about $\sqrt{2.3}$,[1] which means that the model mentioned above is inapplicable in this case.

When studying motions of molecular systems in cavities of solids or cage structures (*e.g.*, a fullerene or zeolite) or in a crystal or matrix defect, one must take into account a variety of different-type factors among which constraints on the region of free motion of particles deserves particular attention. The model of a system placed in a cavity with impenetrable walls is often used in studies of complex physicochemical systems (see, *e.g.*, Refs 2—12 and references cited therein). In this work we considered the influence of the cavity size on the magnitude of isotopic frequency shift. First, we performed a qualitative study of a model problem of the motion of a particle in a uniform potential; some of the results obtained were found to be valid for any potential. The estimates obtained make it possible to interpret the results of numerical calculations of the lowest part of rovibrational spectra of hydrogen molecule isotopomers in a spherical cavity, which corresponds to the motions of the system as a whole.

The model system

Consider a model problem of the motion of a particle of mass m within a domain $\Omega(R)$ of linear size R (*e.g.*, a sphere of radius R) and impenetrable walls. This is an example of the problem with Dirichlet boundary conditions $\varphi|_{r\in\partial\Omega} = 0$ ($\partial\Omega$ denotes the domain boundary) for the wave function of the system whose Hamiltonian (from this point on analytical expressions are written in the system of atomic units) has the form

$$H(m,R) = -\frac{1}{2m}\Delta + V(r). \qquad (1)$$

The dependence, though in implicit form, of the Hamiltonian on the parameter R is very important because formal expression (1) written with different boundary conditions can define different self-conjugate operators (see, *e.g.*, Ref. 13). Consider a stationary state with the wave function $\psi_j(r)$ and energy $E_j(m,R)$. At $m = 1$, we will use

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simplified notations of the energy and other quantities, *e.g.*, $E_j(1,R) = E_j(R)$. The energy of a free system, which corresponds to the infinite space problem, is given by

$$E_j(m) = E_j(m,\infty) = \lim_{R\to\infty} E_j(m,R). \qquad (2)$$

Denote the free-system energy at $m = 1$ as E_j. Relationship (2) expresses an important property of the Dirichlet problem, namely, an increase in R causes the energy, $E_j(m,R)$, of the system to monotonically decrease and go in the limit into the free-system energy.[14–16] Therefore, the energy of the system can be written as the sum

$$E_j(m,R) = E_j(m) + \mu_j(m,R),$$

where $\mu_j(m,R)$ is a monotonically decreasing function which tends to zero at $R \to \infty$. The behavior of the function $\mu_j(m,R)$ at large R is closely related to the behavior of the electron density $\rho_j(\boldsymbol{r})$ of a given stationary state at $|\boldsymbol{r}| \approx R$ (see Refs 15, 16). In the text below we will also often use a physically apparent statement that the wave functions of the system and, hence, the functions $\mu_j(m,R)$ decrease more rapidly when an increase in $|\boldsymbol{r}|$ is accompanied by both an increase in the mass and a decrease in the state number j (see Refs 15, 16).

From the Hellmann—Feynman theorem and positive definiteness of the kinetic energy operator it follows that the energy decreases as the particle mass increases. However, the minimax approach[14] with a non-negative potential V gives with ease that by virtue of relationship

$$H(m,R) = \frac{1}{m}[H(1,R) + (m-1)V] \qquad (3)$$

the bound-state energies obey the following inequality at $m > 1$:

$$E_j(m,R) > m^{-1}E_j(1,R). \qquad (4)$$

Problem of uniform potential

Let the potential $V(r)$ be a homogeneous function of order n, *i.e.*, $V(\alpha r) = \alpha^n V(r)$. This type of potentials arises in, *e.g.*, studies of vibrational motions of a nucleus of a one-electron atom in impenetrable spherical cavity[8] at $n \approx 2$; at large n, the r^n-type potentials can also be used to simulate the potential of the spherical cavity itself. Note that at $R = \infty$ the discrete spectrum of the free-motion problem with uniform potential exists only at nonzero energies. At $-2 < n < 0$ (smaller n values give rise to specific problems concerned with definition of the self-conjugate operator using the formal operator (1)[13,14]), the bound states are characterized by $E_j < 0$ and both the wave functions of the free-motion problem and the function $\mu_j(m,R)$ exponentially decrease with an increase in R. If $n > 0$, the E_j values are positive and the function $\mu_j(m,R)$ even faster decreases with an increase in R.[10] A specific case is $n = 0$ (free-motion problem has no discrete spectrum) and one must formally set $E_j = 0$ in all general relationships.

Replacement of variables $r \to \alpha r$ shows that the function $\psi_j(\alpha r)$ is an eigenfunction of the following Hamiltonian

$$-\frac{1}{2m\alpha^2}\Delta + \alpha^n V(r) = \alpha^n\left[-\frac{1}{2m\alpha^{n+2}}\Delta + V(r)\right] \qquad (5)$$

and obeys the Dirichlet boundary condition for the problem in the domain $\Omega(R/\alpha)$. Therefore,

$$E_j(m,R) = \alpha^n E_j(m\alpha^{n+2}, R/\alpha). \qquad (6)$$

By setting $\alpha = m^{-1/(n+2)}$ we found that consideration of the dependence of the energy on m is reduced to analysis of the dependence of the energy levels of the problem with $m = 1$ on the cavity size:

$$E_j(m,R) = m^{-\frac{n}{n+2}} E_j(Rm^{\frac{1}{n+2}}) = m^{-\frac{n}{n+2}}[E_j + \mu_j(Rm^{\frac{1}{n+2}})]. \qquad (7)$$

It should be emphasized that this ratio is independent of both the shape of the domain Ω and the dimension of the space on which the operator Δ acts. For the free-motion system ($R = \infty$, $\mu_j(\infty) = 0$) the ratio (7) means that a change in the particle mass causes the energy of the stationary state to change by a factor of $m^{-n/(n+2)}$, which is obvious in the case of harmonic oscillator ($n = 2$) or hydrogen-like atom ($n = -1$). Here, it is important that we can also specify the character of the changes in energy with an increase in R. Relationship (7) is also valid for $n = 0$.

Energy level positions

According to Eqn. (7), in the case of uniform potentials there is a better estimate compared to inequality (4), namely:

$$\frac{E_j(1,R)}{E_j(m,R)} = m^{(1-\frac{2}{n+2})}\left[1 + \frac{\mu_j(R) - \mu_j(Rm^{\frac{1}{n+2}})}{E_j + \mu_j(Rm^{\frac{1}{n+2}})}\right]. \qquad (8)$$

At $-2 < n < 0$, the energies $E_j(m,R)$ can change their signs at certain R, so the ratio (8) can take any value. If $n > 0$, the energies are positive and monotonicity of the function μ_j means that the energy ratio, which decreases with an increase in R, tends (probably, nonmonotonically if R is not too large) to the limiting value $m^{[1-2/(n+2)]}$ corresponding to free system.

This statement is valid not only for uniform potentials, because an increase in the mass causes the wave functions and corresponding densities to be localized in the vicinity of the minimum of the potential and to rapidly decrease in the classically forbidden region (compared to the case $m = 1$). Therefore, with an increase in R the $E_j(m,R)$ value changes much slower than $E_j(1,R)$ and both the $E_j(1,R)/E_j(m,R)$ ratio and $E_j(1,R)$ decrease. Thus the energy ratio for the system with constraints must be larger than for free systems, being at the same time not too large by virtue of inequality (4).

Transition Energies

Consider changes in the transition energies $\Delta E_{ij}(m,R) = E_i(m,R) - E_j(m,R)$ using simplified notations similar to those introduced for energy in the Section "The model system":

$$\Delta E_{ij}(1,R) = \Delta E_{ij}(R), \qquad \Delta E_{ij}(m) = \Delta E_{ij}(m,\infty),$$
$$\Delta E_{ij} = \Delta E_{ij}(1,\infty). \tag{9}$$

If $i > j$ and R values are small, the transition energies of the states of different symmetry types can behave in very complicated manner (example is provided by the hydrogen atom confined in a spherical cavity).[17—19] At large R, one can expect that higher-lying levels change to a greater extent, *i.e.*, the $\Delta E_{ij}(m,R)$ values decrease with an increase in R (this is a typical situation of matrix shift toward higher frequencies; a decrease in frequency implies taking into account the interaction between the molecule and the environment and can not be described using the model considered). Like in the previous Section, by virtue of smallness of the wave functions of the system with a large mass one can expect that the $\Delta E_{ij}(m,R)$ value changes only slightly compared to $\Delta E_{ij}(1,R)$ far from the minimum of the potential, so the "isotopic ratio"

$$\gamma_{ij}(m,R) = \Delta E_{ij}(1,R)/\Delta E_{ij}(m,R) \tag{10}$$

must *decrease* with an increase in R and tend to $\gamma_{ij}(m) = \Delta E_{ij}/\Delta E_{ij}(m)$ for free system.

For the free system with uniform potential one has $\gamma_{ij}(m) = m^{[1-2/(n+2)]}$, so in accordance with Eqn. (7) one gets

$$\gamma_{ij}(m,R) - \gamma_{ij}(m) = \frac{\Delta E_{ij}(R)}{\Delta E_{ij}(m,R)} - \frac{\Delta E_{ij}}{\Delta E_{ij}(m)} =$$
$$= m^{(1-\frac{2}{n+2})}\frac{[\mu_i(R) - \mu_i(Rm^{\frac{1}{n+2}})] - [\mu_j(R) - \mu_j(Rm^{\frac{1}{n+2}})]}{\Delta E_{ij} + \mu_i(Rm^{\frac{1}{n+2}}) - \mu_j(Rm^{\frac{1}{n+2}})}. \tag{11}$$

The differences $\delta_i = \mu_i(R) - \mu_i(Rm^{1/(n+2)})$ are positive in advance because μ_i monotonically decreases with an increase in R and $m > 1$. The sign of expression (11) is determined by the sign of the difference $\delta_i - \delta_j$. By estimating $\delta_i - \delta_j$ using the Lagrange formula we get

$$\delta_i - \delta_j = [\partial\mu_i(R\theta) - \partial\mu_j(R\theta)]R(1 - m^{\frac{1}{n+2}}) =$$
$$= R(m^{\frac{1}{n+2}} - 1)[\partial\mu_j(R\theta) - \partial\mu_i(R\theta)], \tag{12}$$

where ∂ denotes the derivative with respect to R and θ is a point from the segment $[1, m^{1/(n+2)}]$. Since the energy of the higher-lying level i decreases to a greater extent compared to the energy of the level j with an increase in R, we get $0 > \partial\mu_j > \partial\mu_i$, *i.e.*, $\delta_i > \delta_j$. Thus,

$$\gamma_{ij}(m,R) \geq \gamma_{ij}(m,\infty) = m^{(1-\frac{2}{n+2})}. \tag{13}$$

If $n > 2$ and the potential is more flattened than the quadratic potential in the vicinity of the origin, the isotopic ratio *a priori* exceeds $m^{1/2}$; however, this is also possible at $n \leq 2$ owing to the effect of the cavity walls. A one-dimensional rectangular potential well ($n = 0$) is characterized by $\gamma_{ij}(m,R) = m$ at any R. Therefore, at very small R, when any potential under study vanishes compared to the kinetic energy, it is also possible to find the $\gamma_{ij}(m,R)$ values that approach the value m.

Transition energies do not obey relations of the type (4) and there is no upper bound of the isotopic ratio $\gamma_{ij}(m,R)$. For instance, in the case of a two-well potential the tunneling splitting of energy levels exponentially decreases with an increase in the barrier height and particle mass, *i.e.*, isotopic substitution can lead to very large γ_{ij} values.

The appearance of transitions $i \to j$ characterized by $\gamma_{ij}(m,R) > m$ implies that the following inequality holds

$$E_i(R) - mE_i(m,R) > E_j(R) - mE_j(m,R). \tag{14}$$

If this is valid for any $m > 1$ (because at $m = 1$ we get an equality), a similar inequality must hold for the derivatives with respect to m (they are denoted as ∂_m in the text below) at least at $m = 1$. Direct calculations using the Hellmann—Feynman theorem give

$$\partial_m[E_i(R) - mE_i(m,R)]|_{m=1} =$$
$$= -E_i(m,R) - m\partial_m E_i(m,R)|_{m=1} =$$
$$= T_i(R) - E_i(R) = -V_i(R), \tag{15}$$

where T_i and V_i are the average kinetic and potential energy of the state i, respectively. In other words, if inequality (14) is valid for any $m > 1$, then

$$\int_{\Omega} V(\psi_i^2 - \psi_j^2)\mathrm{d}r \leq 0. \tag{16}$$

Apparently, in the case of the problem with a nonnegative potential this inequality can hold only if the potential is localized in the region where $|\psi_i| < |\psi_j|$ at $i > j$.

If potentials are small, the known functions of the problem of a particle in a box can be used as ψ_k. For instance, in the case of one-dimensional problem the $|\psi_k|^2$ values near the walls are proportional to k^2 with the same coefficient, so the potential localized in a narrow region near the wall of the potential box does not obey inequality (16). However, for those potentials that are less localized near the walls there can also appear transitions for which inequality (16) holds and the isotopic ratios exceed the value m. Examples can be provided with ease even for simple combinations of rectangular potentials. In the text below we will see the validity of the remarks made.

H_2 and D_2 molecules in a spherical cavity. Computational methods

Consider a hydrogen molecule in a spherical cavity of radius R. Let us estimate the energies of rovibrational states for a simple electronic energy model, namely, the potential is given by the same Morse function as in the case of free molecule (parameters can be found using the spectroscopic constants of the H_2 molecule).[20] Nuclear motions in the cavity were studied by two methods denoted as method A and method B.

Method A. Numerical solution to the three-dimensional problem for the states with zero total angular momentum with respect to the center of the cavity. The Schrödinger equation was solved in the coordinates r_1, r_2, $z = \cos\theta$, where r_j is the distance from the center of the cavity to the jth nucleus ($r_j \le R$) and θ is the angle between the radius-vectors of the nuclei. The dependence of the wave functions on the angle θ was specified by a combination of Legendre polynomials with the maximum power N_p; the fourth-order finite element scheme with N_r elements was employed for each radial coordinate.[21] The problem thus discretized was solved by the inverse iteration method.[22—24] These calculations are stable only for low-lying states. The parameters of the computational scheme and the basis set dimension N_{total}, which provide the accuracy of calculations with an error of at most 0.02 cm^{-1} are listed in Table 1.

Table 1. Parameters for calculations of H_2 and D_2 molecules

R/a.u.	N_r	N_{total}
2.0	14	64288
3.0	16	83968
4.0	18	106272
5.0	20	131200
6.0	22	158752

R is the cavity radius, N_r is the number of finite elements with respect to radial coordinates, and N_{total} is the total dimension of the basis set. In all cases, $N_p = 40$.

Method B. Complete adiabatic separation of nuclear variables. In this case the problem of nuclear motions in a spherical cavity is reduced to solving a sequence of one-dimensional Schrödinger equations. After discretization the system of these equations permits estimation of the energies of stationary states by dichotomy (for more details, see Ref. 12). In this approximation it is convenient to use spherical coordinates for the Jacoby variables, which allows the problem of the molecule in a cavity to be related to the free-molecule problem. The finite difference scheme of solving the Schrödinger equation included 10,000 nodes per 1 a.u. for the radial variables and 10,000 nodes for the angular variables. A tenfold decrease in these values causes the energy estimates to be changed by about 0.01 cm^{-1}.

When using method B, the state of the molecule in the cavity can be characterized by the approximate quantum numbers that describe vibrational motions of nuclei relative to each other (v), angular momentum of the molecule with respect to the center of mass (L), and radial vibrations of the center of mass of the molecule relative to the center of the cavity (v_c). In the states with zero total momentum specification of L also defines the angular momentum N of the center of mass with respect to the center of the cavity (by virtue of the momentum composition rule one has N = L). Low-lying states corresponding to the motion of the entire molecule are characterized by zero vibrational quantum number v and can be described by two quantum numbers (L, v_c) (or, which is the same, (N, v_c)).

The results of calculations of four low-lying states are listed in Table 2 (listed are positions of the energy levels with respect to the ground state (0,0)). The values obtained by the method B were used for the assignment of the (L,v_c) states. The energies listed correspond to three lowest-lying excited states. At any R, these states were assigned to the types (0,1), (0,2), and (1,0), except for the case R = 2 a.u. where the third states of the H_2 and D_2 molecules belong to the (2,0) type and the case R = 6 a.u. for HD molecule (here, the third excited state belongs to the (0,3) type).

States of hydrogen molecule in the cavity

Agreement between the energy estimates obtained in different approximations is more qualitative than quantitative. At large cavity radii, the estimates obtained by different methods differ only slightly; however, at small R they become significant (~50 cm^{-1}), much exceeding the accuracy of each computational method. This is due to the fact that nearly exact calculations by the method A provide (by virtue of the variational principle) the upper bounds of the energy estimates, whereas

Table 2. Energies (in cm^{-1}) of low-lying states ($\mathrm{L,v_c}$) with zero total momentum calculated for hydrogen molecule isotopomers in a spherical cavity of radius R with respect to the ground state

R /a.u.	Method	H_2			D_2			HD		
		(0,1)	(0,2)	(1,0)	(0,1)	(0,2)	(1,0)	(0,1)	(0,2)	(1,0)
2.0	*A*	388.2	760.9*	324.4	192.6	376.1*	159.9	190.4	503.2	323.4
	B	348.3	776.3	300.7	172.3	384.3	148.1	210.9	540.8	238.9
3.0	*A*	145.2	366.9	181.9	72.1	182.9	90.9	90.7	227.0	142.4
	B	132.4	344.9	177.8	65.6	171.4	88.7	86.4	220.0	135.4
4.0	*A*	73.8	194.1	149.2	37.0	97.3	74.8	49.7	129.7	108.5
	B	68.9	181.8	147.8	34.2	90.4	74.0	45.9	119.3	111.0
5.0	*A*	45.2	119.4	136.6	24.8	63.8	68.2	31.5	80.9	102.2
	B	42.1	111.6	136.1	20.9	55.6	68.3	28.2	74.2	102.0
6.0	*A*	33.9	86.7	129.7	22.3	53.9	65.3	25.6	63.8	96.5**
	B	28.3	75.4	130.4	14.1	37.5	65.5	19.0	50.3	93.4

* The values correspond to the (2,0) level. Adiabatic estimates of the energy of the (0,2) state are 867.4 and 431.9 cm^{-1} for H_2 and D_2, respectively.

** The value corresponds to the (0,3) level. In the adiabatic approximation the energy of the state (1,0) is 97.7 cm^{-1}.

method *B* systematically underestimates the values obtained not only for the ground but also excited states owing to specific features of the Morse type potentials (see Ref. 25). It is noteworthy that in all cases rotational states of the center of mass (states of the (1,0) type) were estimated more correctly than the pure vibrational states (0,1) and (0,2). Generally, the dependences of energy on R obey a common pattern for both computational methods.

The states in question are characterized by $\mathrm{v} = 0$, *i.e.*, nuclei execute no vibrational motions relative to each other. Using a point model of a particle in a box, the energy of the molecule in the states ($0,\mathrm{v_c}$) corresponding to radial vibrations of the center of mass with respect to the center of the cavity can be estimated at $[\pi^2(\mathrm{v_c} + 1)^2]/(2mR^2)$. However, this simple estimate appreciably underestimates the energies compared to those listed in Table 2 because the center of mass of an extended molecule executes free oscillations only outside of the boundary layer. The thickness of this layer is of the same order of magnitude as the equilibrium internuclear distance, R_e, in the molecule, *i.e.*, the center of mass moves in the effective cavity of a smaller size.[12] Nevertheless, the energy ratios for transitions from the ground state to the (0,1) and (0,2) states, calculated by both methods using the model of free motion of a particle in a box are very similar to 8/3. As R increases, the energies of the ($0,\mathrm{v_c}$) states tend to zero at any $\mathrm{v_c}$. For instance, at $R = 6$ a.u. the (0,3) state of the HD molecule is the third excited state, whereas it was the sixth excited state at $R = 2$ a.u.

The dependence of energy on R for the (L,0) states that describe rotational motion can be estimated taking into account the facts that N = L and that the total energy of the molecule in the cavity is estimated at large R as the sum of the energies of two independent rotations:

$$E_{(\mathrm{L},0)} - E_{(0,0)} = \mathrm{B_cN(N + 1) + B_0L(L + 1)} = = \mathrm{(B_c + B_0)L(L + 1)}, \qquad (17)$$

where $\mathrm{B_0}$ is the rotational constant of the molecule and $\mathrm{B_c}$ is the rotational constant of the center of mass, which decreases in proportion to R^{-2} as R increases. At small R, the energy levels of the particle in the spherical cavity are ordered as follows: 1s, 1p, 1d, 2s, 1f,...,[26] *i.e.*, the states with N = 1 correspond to the lowest excited state. In the case of the H_2 and D_2 molecules this holds already at $R = 2$ a.u., though estimates of the type (17) are much underestimated even at $R = 6$ a.u. With an increase in R the energies of the (L,0) states tend to $\mathrm{B_0L(L+1)}$.

Thus, an increase in the cavity radius unavoidably leads to degeneration of the (L,0) and ($0,\mathrm{v_c}$) states. For H_2 molecule the (1,0) state is degenerated with the (0,1) state at $R \approx 2.7$, while the (1,0) and (0,2) states become degenerate at $R \approx 4.6$ a.u. This is also observed for the D_2 molecule at similar R values, while for the HD molecule degeneration of the (1,0) and (0,1) states occurs at $R < 2$, the (1,0) and (0,2) states become degenerate at $R \approx 4.2$, and the (1,0) and (0,3) states become degenerate at $R \approx 5.7$ a.u.

It should be emphasized that here we deal with crossing rather than pseudocrossing of the "potential curves" $E_j(R)$. Rotational states of the H_2 molecule with L = 0 are *para*-states (with zero nuclear spin), those with L = 1 being *ortho*-states (with nuclear spin 1). Therefore, the zero-spin nuclear wave functions studied in this work have different symmetry with respect to permutation of proton coordinates. Namely, for even L the wave functions are even with respect to this permutation and for odd L they are also odd.

Note that degeneration of different spin states underlies the usually discussed mechanisms of *ortho—para*-transitions (see, *e.g.*, a review on the problem in a monograph[27](see Section 13)). Therefore, degeneration of the (1,0) and (0,v_c) states at certain *R* is quite important. Indeed, even a minor perturbation responsible for the interaction between different spin states can lead to formation of states composed of strongly mixed *ortho*- and *para*-states. It should be emphasized that the interaction between the *ortho*- and *para*-states is very weak so that real *ortho—para*-transitions can occur only in the presence of additional perturbation sources (*e.g.*, corresponding particles in the material surrounding the cavity). We believe that the degeneration itself is of interest, because it points that encapsulation of molecules in a cavity can cause the appearance of new reaction channels. For many other important effects, such as complexity of the shape of real cavities, and estimation of separation of *ortho*-hydrogen and *para*-hydrogen in zeolites see, *e.g.*, Ref. 28 and references cited therein.

Isotopic ratios

Consider the influence of isotopic substitution on the transition energy ratio for transitions from the ground state. In the simplest approximation (hydrogen molecule executes no vibrational motions, v = 0), the energy of the low-lying states characterized by the quantum numbers (L, v_c) are inversely proportional to the total or reduced mass of the molecule (see above). For instance, the parameter B_c in ratio (17) is inversely proportional to the total mass of the molecule and the parameter B_0 is inversely proportional to its reduced mass. The total and reduced masses of the H_2 and D_2 molecules differ by a factor of two; therefore, for these molecules the ratio of the same transition energies must approach a value of 2 in the lowest part of the spectrum and a conventional (for vibrational spectra) value of $\sqrt{2}$ in the case of states with v = 1. The isotopic ratios γ_{ij} for the low-lying states are listed in Table 3. In the case of H_2/D_2 molecules these ratios vary only slightly but they decrease with an increase in *R* in a quite regular manner. This decrease is more pronounced if calculations are carried out by the method *A*; both computational methods, *A* and *B*, give consistent results (significant differences at *R* = 6 are due to low transition frequencies). Qualitative estimates (see the end of Section "Transition Energies") showed that the isotopic ratio must not exceed a value of 2 at large *R*. The fact that this is invalid in the adiabatic approximation is a consequence of (i) smallness of the quantities in question and (ii) significance of the errors characteristic of this approximation.

Table 3. Isotopic ratios γ_{ij} for low-lying states of hydrogen molecule isotopomers as functions of the cavity radius *R*

R /a.u.	Meth-od	H_2/D_2			H_2/HD		
		(0,1)	(0,2)	(1,0)	(0,1)	(0,2)	(1,0)
2.0	*A*	2.03	2.02*	2.02	1.70	1.51	1.20
	B	2.02	2.02	2.03	1.65	1.60	1.26
3.0	*A*	2.01	2.01	2.00	1.60	1.62	1.28
	B	2.02	2.01	2.00	1.53	1.57	1.31
4.0	*A*	2.00	1.99	1.99	1.48	1.50	1.37
	B	2.01	2.01	2.00	1.50	1.52	1.33
5.0	*A*	1.82	1.87	2.00	1.43	1.48	1.34
	B	2.01	2.01	1.99	1.49	1.50	1.33
6.0	*A*	1.52	1.61	1.99	1.33	1.36	—**
	B	2.01	2.01	1.99	1.49	1.50	1.34

* For the (2,0) state, see note to Table 2; in the adiabatic approximation the estimate for the (0,2) state is 2.01.

** No estimate is given for the (0,3) state of H_2 by the method *A* (see note to Table 2). The adiabatic estimate refers to the (1,0) state.

Consider the HD and H_2 molecules. As should be expected, their transitions to the (0,v_c) states (see Table 3) are characterized by an isotopic ratio of nearly 3/2 (mass ratio of the molecules), while for rotational motions ((1,0) state) at large *R* the most significant is the reduced mass ratio (4/3) determined by the smallness of B_c compared to B_0. A complex dependence of these parameters on *R* (for instance, the effective rotational constant of the molecule increases at small *R* [12]) leads to a local increase in the isotopic ratio.

For the states corresponding to pronounced vibrations of nuclei relative to each other (for instance, at v = 1), the frequency shifts upon change in *R* estimated by the method *B* are very small for *R* > 3 a.u. Therefore, the isotopic ratio for the corresponding transitions remain almost unchanged compared to those found for free H_2 and D_2 molecules (the changes are of the order of about 0.01). In the case of HD and H_2 molecules the decrease in the isotopic ratios with an increase in *R* is more pronounced. At *R* = 2 a.u. and v = 1, the isotopic shift of the (0,2) state is overestimated by nearly 0.06 compared to free molecule (for the remaining states of the same types as in the case v = 0 (see Table 3), the changes are at most 0.02).

* * *

The estimates presented above suggest that for the molecule within a cavity with impenetrable walls one can expect an increase in the isotopomer frequency ratio compared to free molecule. This is more a trend than statement (example with the HD/H_2 molecules shows that the frequency ratio sometimes decreases in the case of transitions to the (1,0) state). A more rigorous statement seems to be unsubstantiated because collisions of the molecule executing vibrational and rotational motions with the cavity walls can cause significant energy redistribution compared to the model of structureless material point (see Section "Problem of uniform potential").

If the potential energy of the molecule in the cavity excludes localization of nuclear density near the walls (when the confinement effects of relatively free motion of the molecule are insignificant), the isotopic effects can be described in the same way as in the case of free molecules. However, if the cavity is relatively small (its size equals a few equilibrium internuclear distances), constraints can play a very important role. Even at $R = 6$ a.u. the motion of the hydrogen molecule in the cavity can hardly be considered free (the γ_{ij} values for transitions to the $(0,\mathrm{v_c})$ states are similar to the harmonic estimate $\sqrt{2}$) (see Tables 2 and 3). This is observed even when the effect of boundaries on the electronic subsystem (similar effects were described in Refs 8—11) is ignored.

Adiabatic separation of nuclear variables provides a qualitatively correct description of changes in the energies of low-lying states compared to the more accurate method of numerical integration of multidimensional problems. At large R, the method B seems to be quite reliable. However, it is difficult to make substantiated predictions of such specific characteristics as the isotopic ratio based on simple estimates. Taken altogether, the estimates made show that adiabatic separation "masks" fine energy effects, especially at relatively small R, though it can be used for qualitative analysis of the system of rovibrational states of molecules in a cavity.

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