PHYSICAL REVIEW C VOLUME 21, NUMBER 1 JANUARY 1980

Influence of vibrations of gas molecules on neutron reaction cross sections

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(Received 9 April 1979)

The change in molecular vibrational energy upon absorption of a neutron by a nucleus bound in a free molecule can influence resonance shape and other aspects of neutron reaction cross sections. A formalism is developed for centrosymmetric molecules such as UF_6 and applied to the shape of the 6.67 eV resonance in ^{238}U. The ratio of the resonance shape for $^{238}UF_6$ gas and for solid $^{238}U_3O_8$ has been measured and compared with the calculation. Reasonable agreement is obtained indicating the validity of the calculation and the necessity to include vibration effects to avoid large errors in measurements and calculations on gas-containing systems.

[NUCLEAR REACTIONS $^{238}U(n,\gamma)$ measured at 6.67 eV resonance; Effect of molecular vibrations studied experimentally and theoretically.]

I. INTRODUCTION

When a neutron strikes a nucleus bound in a free molecule, the molecule will recoil with the possibility of changing its vibrational and rotational state. The energy available to the compound nucleus is therefore not that obtained simply by conserving energy and momentum in the neutron-nuclear collision since energy conservation must include the change in the molecular excitation. The means and necessity of taking such effects into account has not been studied except for the brief consideration of the effect by Steinwedel and Jensen.[1] The similar effect for nuclear γ-ray emission or absorption has been studied recently in detail by V. S. Letokov[2] for centrosymmetric molecules such as SF_6. For such molecules the change in rotational state can be neglected to a very good approximation so that the calculation is significantly simplified. We report here a calculation of the resonance shape for the 6.67 eV resonance in $^{238}UF_6$ and compare the calculation with a measurement of the ratio of gas to solid $^{238}U_3O_8$ carried out at the NBS electron linear accelerator.

II. THEORY

The probability P_{ba} for a molecular transition from an initial state a to a final state b upon collision of a neutron with a molecule is given by the expression

$$P_{ba} = |\langle\psi_b^*(\vec{R})|e^{-i\vec{K}\cdot\vec{R}}|\psi_a(\vec{R})\rangle|^2, \tag{1}$$

where $\vec{K}$ is the wave number associated with the neutron and molecular center-of-mass motion and $\vec{R}$ is the position of the nucleus struck by the neutron. The vector $\vec{R}$ can be written $\vec{R}=\vec{R}_o+\vec{r}+\vec{u}$, where $\vec{R}_o$ is the vector from the origin to the position of the center of mass of the molecule, $\vec{r}$ is the vector from the molecular center of mass to the equilibrium position of the nucleus, and $\vec{u}$ is the vector from the equilibrium position of the nucleus to its instantaneous position. After the separation of translational and vibrational variables, the matrix element of Eq. (1) can be written

$$\langle\psi_b^*(R)|e^{-i\vec{K}\cdot\vec{R}}|\psi_a(R)\rangle$$
$$=\langle T_b^*|e^{-iK\cdot R_o}|T_a\rangle\langle\psi_b(\vec{r},\vec{u})|e^{-i\vec{K}\cdot(\vec{r}+\vec{u})}|\psi_a(\vec{r},\vec{u})\rangle, \tag{2}$$

where T_a and T_b are the wave function for the initial and final molecular translation, and $\psi(\vec{r},\vec{u})$ describes the molecular vibration and rotation.

For a centrosymmetric molecule, one nucleus is located at the center of mass which has $\vec{r}=0$ always. If the neutron strikes this nucleus, which in the case of UF_6 would be the uranium nucleus, the vector $\vec{r}$ may be neglected. Since the uranium nucleus vibrates around the center of mass even in its ground state, changes in rotational state always are possible. However, calculations of the rotational energy transfer show it to be very small compared with vibrational energy transfer. The effects of rotations therefore will be neglected. The transition probability required in this case reduces to the calculation of the matrix element

$$\langle\psi_b^*(\vec{u})|e^{-i\vec{K}\cdot\vec{u}}|\psi_a(\vec{u})\rangle .$$

The vibrations of the nucleus can be expressed as a product of the various normal modes ψ_l including all degeneracies. We assume a harmonic oscillator approximation for the vibration and write the harmonic oscillator wave functions[3] in terms of the Hermite polynomials as

$$\psi_l = N_{m_l} e^{-\alpha Q^2/2} H_{m_l}(\sqrt{\alpha_l}Q) . \tag{3}$$

In Eq. (3), the vector $\vec{u}$ has been rewritten in terms of the normal modes as $\vec{u}_l = Q_l \vec{\rho}_l$ when ρ_l is the lth normal molecular coordinate and Q_l is the associated displacement amplitude. The smallest energy quantum of the lth normal mode $\hbar\omega_l \equiv \hbar^2\alpha_l$ and m_l is the order of the lth vibrational mode. For the ground state $m=0$, and for the first excited state of the vibrational mode $m=1$, etc. The normalization constant N_{m_l} is defined as $[2^{m_l} m_l!(\pi/\alpha_l)^{1/2}]^{-1/2}$. Therefore the required matrix element becomes

$$\langle\psi_b^*(\vec{u})|e^{-i\vec{K}\cdot\vec{u}}|\psi_a(\vec{u})\rangle = \Pi_l\langle\psi_{m_l'}^*(Q_l)|e^{-i\vec{K}\cdot\vec{\rho}_l Q_l}|\psi_{m_l}(Q_l)\rangle\,, \tag{4}$$

where the product runs over all of the normal modes participating in the vibration. The problem reduces to calculating matrix elements of the type

$$S_{k_l,j_l} = \langle\psi_{k_l}^*(Q_l)|e^{-i\vec{K}\cdot\vec{\rho}_l Q_l}|\psi_{j_l}(Q_l)\rangle\,, \tag{5}$$

where j is the initial order of the l vibration and k is the final order.

Upon substituting Eq. (3) in Eq. (5), and evaluating the integral[3] it is found that the probability for a transition $P_{k,j}$ can be written

$$P_{k,j} = |S_{k_l,j_l}|^2 = \frac{j!}{k!} Z^{k-j} e^{-Z}[L_j^{k-j}(Z)]^2\,, \tag{6}$$

where $Z = (\vec{K}\cdot\vec{\rho})^2/2\alpha_l$ and the $L_j^{k-j}(Z)$ are the Laguerre polynomials. These polynomials can be written

$$L_j^{k-j}(Z) = \sum_{\nu=0}^{j} (-1)^\nu \frac{k!}{(j-\nu)!}\frac{1}{(k-j+\nu)!}\frac{Z^\nu}{\nu!}\,. \tag{7}$$

The average energy δ transferred into molecular excitation for an initial state j assuming only one normal mode is

$$\delta_j = \sum_{k=0}^{\infty} P(k,j)\hbar\omega(k-j)\,. \tag{8}$$

For the case where the molecule initially is in the ground state, $[L^k(Z)]^2 = 1$ and $P_{k,0} = Z^k e^{-Z}/k!$ which is the Poisson distribution. The average energy change from Eq. (8) then becomes in this case $\delta_0 = Z\hbar\omega$. The quantity Z depends on the energy of the neutron, the value of $\hbar\omega$ for the normal mode, the angle of incidence between the neutron and the direction of the normal mode oscillation, and on the mass and force constants of the atoms in the molecule.

Lektokhov[2] points out for the simple case of a linear triatomic XY_2 molecule that the quantity $\vec{\rho}$ reduces to $(2m_Y/m_X M)^{1/2}$ where m_X, m_Y, and M are the masses of the atom X, atom Y, and of the molecule. For a neutron incident along the direction of the vibration, the quantity Z becomes

$$Z = \frac{2E_r}{\hbar\omega_l}\frac{m_Y}{m_X}\,, \tag{9}$$

where E_r is the molecular recoil energy.

The average energy taken up by molecular vibration δ_0 is then $\delta_0 = Z\hbar\omega = 2E_r m_y/m_X$. Therefore if $2m_Y > m_X$, the energy transferred to vibration is greater than that going into recoil of the molecule. The difference between the kinetic energy available before the reaction and the total of recoil and vibrational excitation is carried into compound nucleus formation.

The influence of vibrational energy increments such as these on cross sections was first pointed out by Lamb,[4] who carried out a calculation for energy increments associated with phonon exchange. These concepts were further developed by many authors and for neutron energies less than 1 eV by Bowman and Schrack.[5] Following these papers, we find that the transfer in molecular vibration energy therefore influences the neutron cross section through two terms, the energy dependent neutron width and the resonance denominator. To a small degree it also influences the total width since Γ_n represents one component of the total width. For the resolved resonance region of heavy nuclei, the influence on the neutron width is small and will be neglected here. However, for the same nuclei and for energies below a few eV, both the effect on Γ_n and the resonance denominator must be taken into account.

The reaction cross section for the special case of a neutron incident along the oscillation direction of one of the normal modes of a linear triatomic molecule initially in its ground state is then found to be

$$\sigma = \pi\lambda\!\!\!^{-2} g \sum_{k=0}^{\infty} \frac{Z^k e^{-Z}}{k!}\left(\frac{\Gamma_n^0(E-k\hbar\omega)^{1/2}\Gamma_r}{(E-E_0-k\hbar\omega)^2+\Gamma^2/4}\right)\,, \tag{10}$$

where Z is given by Eq. (9), E is the center-of-mass energy in eV, Γ_r is the reaction width, g is the usual statistical factor, and $\lambda\!\!\!^{-}$ is the wavelength divided by 2π of the incident neutron in the c.m. system. The parameter Γ_n^0 is the neutron width normalized to a neutron energy of 1 eV by the expression $\Gamma_n^0 = \Gamma_n(1\text{ eV}/E\text{ eV})^{1/2}$.

Some useful observations are immediately apparent from Eq. (10). The second term within the sum is a suitably modified Breit-Wigner resonance term. The first term is a probability or weighting factor (from the Poisson distribution) for each value of k. For the case of a resonance with very narrow width (approximating a delta function), the cross section exhibits an envelope of terms displaced by $k\hbar\omega$ from E_0. The standard deviation in the envelope is derived from the Poisson distribution which gives

$$\Delta_{\text{mol vib}} = (Z\hbar\omega)^{1/2} = \left[2E\hbar\omega\left(\frac{m_Y}{m_X}\right)\left(\frac{m}{m_X+2m_Y}\right)\right]^{1/2}. \tag{11}$$

For a monatomic gas the standard deviation (Doppler effect) is given by

$$\Delta_{\text{mono}} = \left[2EkT\left(\frac{M}{M+m}\right)\left(\frac{m}{M+m}\right)\right]^{1/2}. \tag{12}$$

In the above expressions E is the laboratory neutron energy, m is the mass of the neutron, M is the mass of an atom of monatomic gas, and kT is the temperature of the gas in the same energy units as E. Comparing Eqs. (11) and (12) it is interesting to note that both of the expressions have the same neutron energy dependence.

Of course the molecules themselves are not at rest but are moving with a Maxwellian velocity distribution so that a resonance will exhibit spreading both from vibrational exchange and the conventional Doppler effect. Since both of these distributions are normal distributions, the total spreading effect can be obtained by adding them in quadrature to obtain

$$\Delta_{\text{mol}} \simeq \left[\frac{2EmkT}{m_X+2m_Y}\left(1+\frac{\hbar\omega m_Y}{kTm_X}\right)\right]^{1/2}. \tag{13}$$

The factor in parentheses on the right can be viewed as a correction term to be added for molecular vibration for the case of a linear triatomic molecule initially in its ground state.

The calculation of the effects for a practical case are significantly complicated by several factors. First, usually there are several normal modes present which compete with one another in the energy exchange process. Second, these normal modes also have degeneracies which must be taken into account. Third, for room temperature systems, most molecules are in some state of excitation other than ground state. Fourth, in practice, the direction of oscillation of any particular normal mode is randomly oriented to the direction of neutron motion. In the following calculation all of these factors are included for the purpose of predicting the shape of the 6.7 eV resonance in ^{238}U.

III. APPLICATION TO ^{238}UF$_6$

The molecule ^{238}UF$_6$ is a solid at standard temperature and pressure, but is in a gaseous state at room temperature for pressures below 100 Torr. The molecule has six normal modes. The two of these which involve the uranium nucleus are shown in Fig. 1. Since the other four modes do not involve an oscillation of the uranium nucleus, the collision of a neutron with the ^{238}U nucleus does not excite or deexcite these modes. It is clear in accordance with the symmetry of the molecule that each of the ν_3 and ν_4 modes can exist in all three directions so that both modes are three-fold degenerate.

With a knowledge of the degeneracies of all normal modes[6] and their associated vibrational quanta,[7] the probability for population of the ν_3 and ν_4 vibrations was calculated following the prescription of Jackson.[8] In general, several normal modes are excited simultaneously with the ν_3 and ν_4 modes. Since only the ν_3 and ν_4 modes are of interest, the probabilities for all combinations which involve the ν_3 and ν_4 have been summed and the results for ν_3 and ν_4 presented in Table I. The first and second column give the number of quanta associated with the ν_3 and ν_4 mode, the third column is the probability of that particular vibrational mode, and the fourth column shows the cumulative probability. The energy of the ν_3 vibrational quantum is 78 meV and of the ν_4 vibrational quantum is 23 meV.

Note that only 0.189 of the molecules are in the ground state. The most probable molecular excitation has no ν_3 quanta and only a single ν_4 quantum of energy. Since both normal modes are triply degenerate, this mode can exist in three ways which can be written (000; 100), (000; 010), and (000; 001) where each digit refers to the number of quanta (order) of each of the degeneracies. The next most probable mode carries two ν_4 quanta which can be distributed as (000; 200), (000; 020), (000; 002), (000; 110), (000; 011), and (000; 101). Note the small probability for the single ν_3 quantum.

Returning to Eqs. (4) and (5), the required probability for a transition from one condition of molecular vibration to another may be rewritten

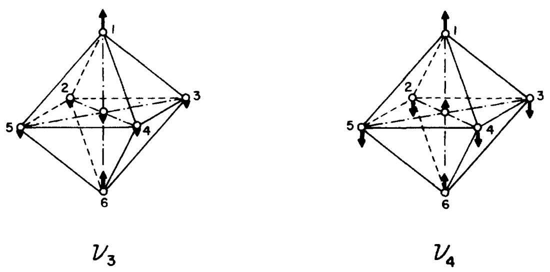

FIG. 1. The normal modes shown are the only two involving the central uranium nucleus. Note that each is three-fold degenerate.

$$P=\left|\langle\psi_b^*(\vec{u})\left|e^{-\vec{K}\cdot\vec{u}}\right|\psi_a(\vec{u})\rangle\right|^2={}_l\left|S_{k_l,j_l}\right|^2, \tag{14}$$

where the sum over l includes all normal modes and their degeneracies. For the two normal modes with their three-fold degeneracy of concern here, we denote the initial state by $(j_1j_2j_3, j_1'j_2'j_3')$ and the final state by $(k_1k_2k_3, k_1'k_2'k_3')$. The probability for a transition from an initial state to some final state, therefore, can be written from Eqs. (14) and (6) as

$$P_{k_1k_2k_3,k_1'k_2'k_3';j_1j_2j_3,j_1'j_2'j_3'}=\frac{j_1!j_2!j_3!j_1'!j_2'!j_3'!}{k_1!k_2!k_3!k_1'!k_2'!k_3'!}Z_{31}^{k_1-j_1}Z_{32}^{k_2-j_2}Z_{33}^{k_3-j_3}Z_{41}^{k_1'-j_1'}Z_{42}^{k_2'-j_2'}Z_{43}^{k_3'-j_3'}e^{-(Z_{31}+Z_{32}+Z_{33}+Z_{41}+Z_{42}+Z_{43})}$$

$$\times\left[L_{j_1}^{k_1-j_1}(Z_{31})L_{j_2}^{k_2-j_2}(Z_{32})L_{j_3}^{k_3-j_3}(Z_{33})L_{j_1}^{k_1'-j_1'}(Z_{41})L_{j_2}^{k_2'-j_2'}(Z_{42})L_{j_3}^{k_3'-j_3'}(Z_{43})\right]^2. \tag{15}$$

The indices are necessary on the Z factors owing to the dot product $\vec{K}\cdot\vec{u}$ which takes into account the angle between the incoming neutron direction and the direction of oscillation of a normal vibration. For the ν_3 vibration we may define Z_3 as the value of Z when $\vec{K}$ and $\vec{u}$ are aligned; similarly for Z_4. Using the direction cosines the Z_3 factors are related by the quantity $Z_{31}=Z_3\cos^2\beta$, $Z_{32}=Z_3\cos^2\beta'$, and $Z_{33}=Z_3\cos^2\beta''$, and similarly for Z_4. By making use of the relationship $\cos^2\beta+\cos^2\beta'+\cos^2\beta''=1$, Eq. (15) can be rewritten

$$P=\frac{j_1!j_2!j_3!j_1'!j_2'!j_3'!}{k_1!k_2!k_3!k_1'!k_2'!k_3'!}Z_3^{(k_1+k_2+k_3-j_1-j_2-j_3)}Z_4^{(k_1'+k_2'+k_3'-j_1'-j_2'-j_3')}e^{-(Z_3+Z_4)}$$

$$\times\left\{\cos\beta^{2(k_1+k_1'-j_1-j_1')}\cos\beta'^{2(k_2+k_2'-j_2-j_2')}\cos\beta''^{2(k_3+k_3'-j_3-j_3')}\right.$$

$$\left.\times\left[L_{j_1}^{k_1-j_1}(Z_3\cos^2\beta)L_{j_2}^{k_2-j_2}(Z_3\cos^2\beta')L_{j_3}^{k_3-j_3}(Z_3\cos^2\beta'')L_{j_1'}^{k_1'-j_1'}(Z_4\cos^2\beta)L_{j_2'}^{k_2'-j_2'}(Z_4\cos^2\beta')L_{j_3}^{k_3'-j_3'}(Z_4\cos^2\beta'')\right]^2\right\}. \tag{16}$$

Since neutrons are incident in all directions, Eq. (16) next must be averaged over all directions before comparison with experiment.

The direction cosines can be redefined in terms of the usual independent angular variables γ and α of a spherical coordinate system. Therefore the incoming momentum vector of length l which strikes the uranium nucleus can be written in terms of the new coordinates as

$$\begin{aligned} l\cos\beta&=l\cos\gamma\cos\alpha,\\ l\cos\beta'&=l\cos\gamma\sin\alpha,\\ l\cos\beta''&=l\sin\gamma. \end{aligned} \tag{17}$$

The function $P(\beta,\beta',\beta''\ldots)$ can be written $P(\alpha,\gamma\ldots)$ when the dots represent other variables besides angular variables. The value of $P(\alpha,\gamma\ldots)$ averaged over all directions can be obtained by evaluating the integral over one octant of the sphere

$$\bar{P}=\frac{2}{\pi}\int_0^{\pi/2}\int_0^{\pi/2}P(\alpha,\gamma)\cos\gamma\,d\gamma\,d\alpha. \tag{18}$$

The angular variables enter both in the direction cosines of Eq. (16) and in the Laguerre functions. A general solution of Eq. (18) is not known to the authors. However, a useful solution for a particular case can be obtained by making use of the definition of the Laguerre function, Eq. (7). By reference to Eqs. (16) and (17) it is clear that P can be expressed as a sum of terms involving sines and cosines of the angles α and γ. Upon substituting Eqs. (17) and (7) into Eq. (16) and performing the operation of Eq. (18) we find using integral 3.621.5 of Ref. 3 that

$$\bar{P}=\frac{1}{2\pi}\frac{j_1!j_2!j_3!j_1'!j_2'!j_3'!}{k_1!k_2!k_3!k_1'!k_2'!k_3'!}Z_3^{(k_1+k_2+k_3-j_1-j_2-j_3)}Z_4^{(k_1'+k_2'+k_3'-j_1'-j_2'-j_3')}$$

$$\times e^{-(Z_3+Z_4)}\sum_{\substack{\text{all}\\\text{indices}}}\ \underset{\substack{\text{all}\\\text{indices}}}{C}\ Z_3^{(n_1+n_2+n_3)}Z_4^{(n_1'+n_2'+n_3')}$$

$$\times\frac{\Gamma(k_1+k_1'-j_1-j_1'+n_1+n_1'+\frac{1}{2})\Gamma(k_2+k_2'-j_2-j_2'+n_2+n_2'+\frac{1}{2})\Gamma(k_3+k_3'-j_3-j_3'+n_3+n_3'+\frac{1}{2})}{\Gamma(k_1+k_2+k_3+k_1'+k_2'+k_3'-j_1-j_2-j_3-j_1'-j_2'-j_3'+n_1+n_2+n_3+n_1'+n_2'+n_3'+\frac{3}{2})}. \tag{19}$$

TABLE I. Probability for initial state population at room temperature.

ν_3 quanta	ν_4 quanta	Probability	Cumulative probability
0	0	0.189	0.189
0	1	0.2242	0.4132
0	2	0.1773	0.5905
0	3	0.1168	0.7073
0	4	0.0693	0.7766
0	5	0.0383	0.8149
0	6	0.0202	0.8351
0	7	0.0103	0.8454
1	0	0.0256	0.8710
1	1	0.0304	0.9014
1	2	0.0240	0.9254
1	3	0.0160	0.9414
1	4	0.0094	0.9503
2	0	0.0023	0.9531
2	1	0.0027	0.9558
2	2	0.0021	0.9579
2	3	0.0014	0.9593

In Eq. (19) the primed indices always refer to indices associated with Z_4 and the unprimed indices are associated with Z_3. The indices n are defined by the squares of the Laguerre functions indicated in Eq. (16). These indices represent the power to which $Z\cos^2\beta$ is raised in each term of the expansion.

$$\begin{aligned} &n_1 \rightarrow (Z_3\cos^2\beta)^{n_1}, \\ &n_2 \rightarrow (Z_3\cos^2\beta')^{n_2}, \\ &n_3 \rightarrow (Z_3\cos^2\beta'')^{n_3}, \\ &n_1' \rightarrow (Z_4\cos^2\beta)^{n_1'}, \\ &n_2' \rightarrow (Z_4\cos^2\beta')^{n_2'}, \\ &n_3' \rightarrow (Z_4\cos^2\beta'')^{n_3'}. \end{aligned} \tag{20}$$

The quantity C is the numerical coefficient of each term resulting from the product of the square of the Laguerre functions of Eq. (16).

As an example the probability $\bar{P}(2000, 000; 100, 000)$ will be calculated. All Laguerre functions are unity except

$$[L_1^{2-1}(Z_3\cos^2\beta)]^2 = 4 - 4Z_3\cos^2\beta + Z_3^2\cos^4\beta. \tag{21}$$

The sum of Eq. (19) therefore contains three terms all with $n_2 = n_3 = n_1' = n_2' = n_3' = 0$. Each term has its own value of n_1 which is $n_1 = 0$, 1, and 2, respectively for the three terms. Likewise, each also has its value of C which is 4, −4, and 1, respectively. Performing the other operations indicated in Eq. (19) yields the result

$$\bar{P}(200, 000; 100, 000)$$

$$= e^{-(Z_3+Z_4)}\left(\frac{2Z_3}{3} - \frac{6Z_3^2}{15} + \frac{1}{14}Z_3^3\right). \tag{22}$$

Similarly

$$\bar{P}(100, 100; 000, 100)$$

$$= \frac{Z_3}{3}e^{-(Z_3+Z_4)}\left(1 - \frac{6Z_4}{5} + \frac{3Z_4^2}{7}\right). \tag{23}$$

This method of solution is practical for weakly excited molecules, small changes in excitation energy, and values of $Z < 0.5$ and therefore is suitable for the problem at hand. The calculation was carried through by weighting the various initial states with the initial thermal probabilities, calculating the transition probabilities to states of lower, higher, or the same state of excitation, and summing together all transitions representing the same energy change. The results are summarized in Table II.

Some approximations were necessary to make the calculation manageable. Only the initial states of Table I: 0, 0, 0, 1, 0; 2, and 1; 0 representing a total of 60% of the possible initial states were calculated in detail. For initial states of higher excitation it was found from an array of sample calculations that the *changes* in excitation were approximately the same as the result calculated in detail for the 60% of lower initial excitation energy. The apportionment of energy exchange of Table II for the different processes are those calculated only for the 60%. The displacement en-

TABLE II. Probabilities and energy changes for neutron induced transitions.

Transition[a]	No change	$\nu_4\uparrow$	$\nu_4\downarrow$	$\nu_3\uparrow$	$\nu_3\downarrow$	$\nu_4\downarrow$ $\nu_3\uparrow$
Probability	0.683	0.205	0.068	0.033	0.0	0.010
ΔE (eV)	0	0.023	−0.023	0.078	−0.078	0.055

[a] The upward directed arrow implies excitation of the molecule to a higher lying state and the consequent absorption of energy by the molecule. The downward directed arrow implies deexcitation and energy release from the molecule. For the last column two normal modes change simultaneously.

ergies ΔE of Table II represent the amount that the neutron energy must be increased (decreased) to compensate for energy absorbed (emitted) in an induced change in excitation.

The results of Table II now must be converted into a form easily compared with experiment. The experimental resonance shape would be the sum of resonance shapes weighted by the transition probabilities and displaced in energy by the appropriate value for ΔE. Before this can be done, however, the appropriate form for the resonance shape must be selected.

If the target molecule were rigid and at rest, the resonance shape would be the unbroadened Breit-Wigner shape shifted upward by the amount of recoil energy given by $m_n E/(m_u + 6m_f + m_n)$ for UF_6. However, the molecules are in thermal motion so that the shape of the resonance must be modified to the normal Doppler-broadened shape as prescribed by Bethe[9] and appropriate here for a rigid molecule. In summary, a resonance shape taking account of molecular vibration was calculated beginning with the Doppler-broadened resonance shape defined by Bethe for the rigid molecule which was displaced by the energies in the table, weighted by the probability factors of the table, and added together.

To facilitate a comparison with experiment, this resonance shape was then compared with the shape which one would obtain in a solid uranium oxide target as prescribed by Jackson and Lynn.[10] The ratio of the U_3O_8 to the UF_6 case is shown as the solid line in Fig. 2. The dashed line of the figure shows a calculation of the shape for U_3O_8 divided by the prediction for a rigid molecule of UF_6. The differences with the solid are due to recoil and Doppler broadening associated with the larger gas target mass ($A = 352$). The position and shape of the resonance in the solid is shown at the bottom of the figure for reference. The comparison of the curves indicates the large error resulting from ignoring the change of internal excitation of the molecule.

IV. EXPERIMENT

To compare the prediction with theory, measurements of the total cross section for U_3O_8 and for an equivalent thickness of UF_6 were carried out. The U_3O_8 sample was prepared by mixing a small portion of U_3O_8 with aluminum powder which yielded a thickness of 8.56×10^{-5} at./b corresponding to a peak transmission of 0.5 at the 6.67 eV resonance.

A UF_6 gas sample was prepared by filling a steel container 30 cm long with UF_6 gas at a pressure of 72 Torr. At this pressure and at room temperature all the UF_6 will exist in the gas phase. Also, this pressure yielded approximately the same thickness of ^{238}U as the solid sample.

The measurements were made on the NBS linac using a neutron flight path from neutron

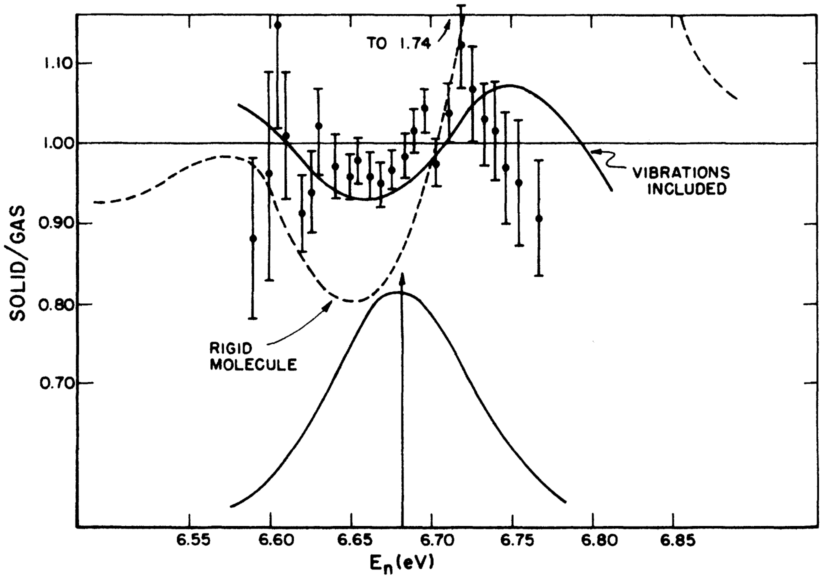

FIG. 2. The points show the ratio of the measured resonance shape of a gas to that for a solid. The upper solid line is the result of the calculation of this ratio with vibrational transitions included. The dashed line is the same ratio under the assumption of a rigid molecule. The lower solid line is included to show the shape and position of the 6.67 eV resonance in ^{238}U.

source to detector of 69 m. The samples were placed 5 m from the neutron source. The samples were 20 cm in diameter and the collimated neutron beam was 15 cm in diameter at the sample. The detector was a 12.7-cm diameter, 2.5-cm thick slab of 6% enriched lithium glass directly attached to an 8854 photomultiplier. The beam is collimated to 10 cm at the detector. The flight tube contains appropriate collimators to prevent inscattering. The linac was operated at 126 MeV with an average electron current of 18 μA, 360 pulses per second, with a pulse width of about 60 nsec. The neutrons were generated in a tungsten target with an external moderator of polyethylene 2.5 cm thick. The neutron resolution function is approximately 6 meV wide at 6.6 eV. The data were collected using a time interval meter having 256 nsec resolution, which represents about 2 meV resolution at 6.6 eV neutron energy. The observed full width at half maximum (FWHM) of the 6.6 eV line in ^{238}U was 111 meV (about 36 channels). Linac runs of about 20 h produced about 7000 counts per channel at 6.6 eV. For analysis the data were grouped eight channels at a time.

Transmission measurements were completed and transformed to cross sections. The ratio of the solid to the gas was then calculated and the results plotted in Fig. 2. The uncertainties shown are derived from the statistical uncertainty of the two transmissions. The shift in energy between the two measurements is less than 2 mV. The agreement between theory and experiment is not perfect but is satisfactory in view of the approximations in the application of Eq. (19).

SUMMARY

In this paper we believe we have demonstrated for the first time the significance of taking into account the change in internal excitation of a free molecule upon absorption of a neutron. The calculation is, of course, distinctly different from that required for slow neutron inelastic scattering measurements. The effect depends approximately on the ratio of the mass of peripheral nuclei to the central nucleus for centrosymmetric molecules. For this reason the effect for other molecules can be much larger than for UF$_6$.

A thorough exploration of this class of phenomena should include a study of noncentrosymmetric molecules including diatomic molecules where the full treatment must include both vibrations and rotations and the interactions between them. Qualitatively it appears that the probability of induced transitions might be significantly higher for such molecules.

ACKNOWLEDGMENTS

The authors wish to acknowledge helpful discussions with M. Danos of the NBS on the physics of the interaction, and with D. Jackson and R. S. McDowell of the Los Alamos Scientific Laboratory on the properties of UF$_6$. We also wish to thank J. C. Browne of the Lawrence Livermore Laboratory (LLL) and R. G. Johnson of the University of Pennsylvania for their help in attempting a comparison of capture for the gas and solid ^{238}U carried out at the LLL linac.

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