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APPLICATION OF SOME NUCLEAR THEORY METHODS TO MOLECULAR COLLISIONS

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The concept of reduced width is introduced into the theory of molecular collisions. A method is given for calculation of the relative intensities of excitation of various vibrational and rotational levels, corresponding to a definite state of the radical produced as a result of knock-on of an atom or ion from the molecule by a fast particle. For illustration of the method, the case of the H_2O molecule is considered. The intensity of excitation of the vibrational levels of the H_2 molecule which remain after knock-on of the O atom increases exponentially with increase in the excitation energy, since it decreases for the radical OH (the H atom is knocked out). As a conclusion, the conditions for the appearance of resonances described by the Breit-Wigner formula are considered for the collision of atoms. Such a possibility is noted for the scattering of neon by neon.

INTRODUCTION

TWO essentially different types of nuclear reactions are known. In the first place, there are reactions at low energy (in the nuclear scale) of the relative motion of the colliding particles, in which resonance effects appear if the dependence of the cross section on the energy of the relative motion E_0 is measured. In this case, quasistationary excited states of an intermediate nucleus are formed and later decay. An example of such a type of reaction is the resonance capture of neutrons with energies ~ 1 MeV and below by nuclei. A second type of nuclear reaction is the "fast" (or direct) nuclear reaction which takes place without the formation of a long-lived intermediate nucleus. Reactions of this type include, for example, (p, 2p) reactions at high proton energies (much higher than the binding energy of the nucleons in nuclei). If E_0 is fixed and the intensities of the secondary particles (2p) are measured as functions of their total energy, then we obtain maxima for definite energies; these correspond to "hole" excited states of the final nucleus.

Both the values of the cross sections in resonance for reactions at low energies and the intensities of the excitation of various hole states in direct high-energy reactions of the type (p, 2p) are determined by the so-called reduced widths γ^2 of the levels.[1] The physical meaning of γ^2 amounts to the following. One can expand the wave function of the given state of the nucleus as a system of A particles in derivatives of the wave functions of the subsystem of A − B and B particles and the wave function of their relative motion. If one fixes the quantum number characterizing each of the factors and the corresponding coefficient in the expansion is denoted by $\alpha(n_{A-B}, n_B, n_{\rm rel})$, then

$$\gamma^2 \sim \sum_{n_{\rm rel}} |\alpha(n_{A-B},\ n_B,\ n_{\rm rel})|^2$$

(here n is the set of quantum numbers characterizing the given state).

There are analogs both for resonance and direct nuclear reactions in molecular collisions. The resonances of potential scattering of low energy electrons by atoms (Ramsauer effect) are well known. An analog of this effect in the nucleus is the resonance of potential scattering of nucleons at low energies (of the order of 1 MeV) by nuclei, described by the optical model of the nucleus.[2]

The fact that, as has been frequently pointed out, [3] the interatomic forces are much more powerful in scale than nuclear forces has hindered the appearance of resonances in scattering, say, of an atom by an atom. Whereas there is a single bound state for the deuteron, there are many for the molecule H_2; therefore, for excitation energies of H_2 greater than the dissociation energy of H_2, a large number of half wavelengths is contained in the region of attraction of the atoms, and the density of levels is very high; further, the levels overlap. Therefore, one must seek resonances in scattering of an atom by an atom in the noble gases, where the potential well of the interatomic interaction is shallow, so that the situation is similar to the nuclear one. As will be shown below, resonance must be expected in this case, for example, in the scattering of neon by neon.

Now we shall consider direct molecular reactions. The collisions of fast particles with molecules can lead both to knock-on of electrons (the analog of hole excitation of the nucleus) and to ejection of atoms or ions from the molecule. The fast particle can be a neutron, atom, or hydrogen ion, etc., with velocity much greater than the velocity of motion of the nuclei in the molecules or, in other words $E_0 \gg \hbar\omega_{\text{nuc}}$ (ω_{nuc} are the vibrational energy frequencies), that is, E_0 must be 50–100 eV as a minimum. Such large energies allow us to make a number of important simplifications in the theoretical analysis (impulse approximation), in particular, to neglect multiple inelastic collisions of the incident particle with the component parts of the molecule, and to consider the collision of the incident particle with the particles knocked out from the molecule as free, with instantaneous disruption of the molecular bonds.

To require that the velocities of the bombarding particles V_0 be much larger than the velocity of the electrons in the molecule V_e would not be correct if we were to consider the excitation spectrum of the residual radical for a single fixed electronic state. The condition $V_0 \gg V_e$ would be necessary if we were to consider in such fashion the relative intensities of excitation of states which differed in electronic wave functions. We note in passing that the stronger the inequality $V_0 \gg V_e$ becomes, the smaller is the relative probability of ejection from the molecule of a neutral or weakly ionized atom—"the electrons remain in place while the nucleus flies off."

In addition to the molecular knock-on reaction, one can also consider the molecular reaction of stripping where, for example, a molecule of the target "strips" an atom (ion) from the bombarding diatomic molecule Y + Z, and a hypermolecule X + Z is formed in the ground state or some excited state, while the atom (ion) Y flies past. Of course, the reverse process ("pick up") is also possible. The theory of the stripping reactions[4] also employs the concept of reduced width.

Thus the molecular stripping reaction makes it possible to investigate the excitation spectra of the hypermolecules X + Z. The molecular knock-on or stripping reactions are of most interest in those cases in which the final radical or hypermolecule is a system which is difficult to investigate by other means. In particular, in the molecular pick-up reaction, "friable" diatomic molecules can be formed, one of the atoms of which is a noble gas. Of course, very low temperatures are necessary for this case.

In the present research, knock-on of an atom or ion from the molecule by the fast particle is considered. The object of the calculation is the excitation spectrum of the radical (ionized radical) which remains after knock-on of the atom (ion) from the molecule, that is, the relative intensities of excitation of the different states of this radical. In order to illustrate the method by a concrete example, we shall consider the excitation spectra of the neutral molecules OH and H_2, which are formed when the corresponding atoms H and O are knocked out from the H_2O ground state. Here, we shall limit ourselves to the system of vibrational and rotational levels corresponding only to the lowest electron state of the final radical. Limitation to a triatomic molecule is not essential; there is no great difficulty in considering more complex molecules.

The reduced widths are computed in shell theory,[1,5] which is used in nuclear problems, and in the theory of molecular vibrations[6] in completely different fashion, inasmuch as the actual mathematical apparatus of these theories is entirely different. In the work of the authors and Smirnov,[6] the α model of the nucleus (the O^{16} nucleus as a four-atomic molecule) was considered, but actually the scheme of calculation of γ^2 is applicable to molecular problems without any change. The aim of the present paper is the use of the methods developed in [6] for investigation of molecular collisions.

1. KNOCK-ON OF AN ATOM FROM A MOLECULE BY FAST PARTICLES

1. Method of calculation. Let us consider a forced break up of the molecule X in a state with total momentum J and vibrational energy

$$E_{\text{vib}} = \hbar \sum_{\alpha} \omega_\alpha \sum_{i=1}^{f_\alpha} (v_{\alpha_i} + 1/2)$$

(for notation, see below) into the radical Y and knocked-on atom Z. The probability of finding the radical Y in the state with momentum J^0 and vibrational energy E'_{vib} (corresponding to the quantum numbers $\omega'_{\alpha'}$, $v'_{\alpha'_i}$ and $f_{\alpha'}$) will be directly proportional to the "reduced width" of the transition[1]

$$\Theta^2 = \frac{\mu_C}{\hbar^2}\rho\gamma^2 = \frac{1}{2}\rho^3 \left|\int_\sigma \Psi^*(X)\Psi_{\text{ch}}(Y)\,d\sigma\right|^2. \quad (1)$$

Here ρ is the radius of the channel, σ is the hypersurface of the channel, μ_C is the reduced mass of the bombarding particles, $\Psi(X)$ is the wave function of the molecule X, $\Psi_{ch}(Y)$ is the function of the reaction channel $X \rightarrow Y + Z$.

The concept of the channel radius can be introduced for those cases in which the forces are sufficiently short ranged in comparison with a 1/r law. For example, the interaction forces of a neutron with a nucleus and the Van der Waals forces correspond to such a class. Proceeding to the construction of wave functions, we assume the vibrations to be small, and suppose a complete distribution of rotations and vibrations.[1] The electron function is ignored ($J^0 = K$); it will be considered below.

The wave function of the axially symmetric molecule X, which is composed of different nuclei and which does not have an internal vibrational momentum, is written in the form

$$\begin{aligned}
&\Psi_X(J, M_J, K_J, \ldots, v_{\alpha_i} \ldots) \\
&= \Psi_X(J, M_J, K_J)\,\chi_X(\ldots v_{\alpha_i} \ldots, \ldots Q_{\alpha_i} \ldots) \\
&= \widetilde{D}^{J*}_{M_J, K_J}(\Omega_X) \exp\Big(-\frac{1}{2}\sum_{\alpha}\frac{\omega_\alpha}{\hbar}\sum_{i=1}^{f_\alpha} Q^2_{\alpha_i}\Big) \\
&\times \prod_{\alpha}\prod_{i=1}^{f_\alpha} H_{v_{\alpha_i}}\Big(\sqrt{\frac{\omega_\alpha}{\hbar}}\,Q_{\alpha_i}\Big) N^{\alpha}_{v_{\alpha_i}}
\end{aligned} \tag{2}$$

(in both cases Ψ_X will be the sum of such expressions). Here a generally accepted notation is used.[7] If there are several vibrations of the same symmetry of type α (for example, in H_2O: $2A + B$), then $\sum\limits_{\alpha}$ and $\prod\limits_{\alpha}$ mean summation over all these vibrations, since there will be different frequencies among them. $\sqrt{8\pi^2/(2J+1)}$ $\widetilde{D}^J_{M_J,K_J}(\Omega) = D^J_{M_J,K_J}(\alpha, \beta, \gamma)$ are the well known matrix elements of finite rotations.[8]

The channel function has the form

$$\begin{aligned}
&\Psi_{ch}(Y\,[j, m, K_K, K, l]) = \sum_{M_K+M_l=m} (KM_K, lM_l \mid jm) \\
&\times \Psi_Y(K, M_K, K_K \ldots v'_{\alpha'_i} \ldots, Q_{\alpha'_i} \ldots) \\
&\times Y_{lM_l}(\vartheta_{1ab}, \varphi_{1ab}) = \sum_{M_K+M_l=m} (KM_K lM_l \mid jm)\,\widetilde{D}^{K*}_{M_K, K_K}(\Omega_Y) \\
&\times \chi_Y(\ldots v'_{\alpha'_i} \ldots, Q'_{\alpha'_i} \ldots)\, Y_{lM_l}(\vartheta_{1ab}, \varphi_{1ab}).
\end{aligned} \tag{3}$$

Here $Y_{lM_l}(\vartheta_{lab}, \varphi_{lab})$ is the spherical harmonic which describes the angular part of the relative motion of the radical Y and the atom Z; j is the total angular momentum of the channel. The angles ϑ_{lab} and φ_{lab} refer to the laboratory system of coordinates (l.s.). The transition to the internal set of coordinates of the radical Y is brought about by the transformation

$$Y_{lM_l}(\vartheta_{1ab}, \varphi_{1ab}) = \sum_{K_l} D^{l*}_{M_l, K_l}(\Omega_Y)\, Y_{lK_l}(\vartheta, \varphi). \tag{4}$$

The integral in Eq. (1) runs over the hypersurface of the channel, i.e., the integration is carried out over all internal variables of the radical Y ($Q'_{\alpha'_i}$ and Ω_Y) and over the angles of relative motion of the radical Y and atom Z. The distance between the centers of mass of Y and Z, that is, the radius of the channel ρ, is assumed fixed. Furthermore, by regarding the molecules X and Y for the rotations as rigid systems, we can, in the case in which the internal coordinate axes of the two molecules are parallel, set $\Omega_X = \Omega_Y$.[2] After this, the overlap integral (1) is written in the form

$$\begin{aligned}
&\int_\sigma \Psi^*(X)\,\Psi_{ch}(Y)\,d\sigma \\
&= \sqrt{\frac{2K+1}{2J+1}} \sum_{K_l} (KK_{K'} lK_l \mid JK_J)\,\delta_{J,j}\delta_{M_J,m} \\
&\times \int_{\rho=\mathrm{const}} \chi^*_X(\ldots v_{\alpha_i} \ldots, Q_{\alpha_i} \ldots) \\
&\times \chi_Y(\ldots v'_{\alpha'_i} \ldots, Q'_{\alpha_i} \ldots) \\
&\times Y_{lK_l}(\vartheta, \varphi) \ldots dQ'_{\alpha'_i} \ldots \sin\vartheta\, d\vartheta\, d\varphi.
\end{aligned} \tag{5}$$

In order to carry out the computation to its conclusion, it is necessary to change over in the functions χ_X, which depend on Q_{α_i}, to the channel variables, that is, to $Q'_{\alpha'_i}$, ρ, ϑ, φ. Of course, it is not possible to do this in the general case, and one must consider concrete examples. We note only that, as is found from the relation

$$Q_{\alpha_i} = Q_{\alpha_i}(\ldots Q'_{\alpha'_i} \ldots, \rho, \vartheta, \varphi) \tag{6}$$

it is necessary to "renormalize" the function χ_X:

$$\begin{aligned}
&(\chi_X(\ldots Q_{\alpha_i} \ldots) \\
&= C^{-1}\chi_X\,[\ldots Q_{\alpha_i}(Q'_{\alpha'_i} \ldots \rho, \vartheta, \varphi) \ldots]),
\end{aligned}$$

since it was normalized in the volume $\ldots dQ_{\alpha_i} \ldots$, and not in $\ldots dQ'_{\alpha'_i} \ldots \rho^2 d\rho \sin\vartheta\, d\vartheta\, d\varphi$. As calculations show, it is not necessary to carry out the

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[1] The construction of wave functions in the presence of vibrational internal momentum, and also the account of the properties of commutative symmetry of nuclei in molecules with identical nuclei, have been treated in detail in [6].

[2] In the case in which both systems are turned toward one another, it is necessary to use the relation $D(\Omega_X) = D(\Omega)D(\Omega_Y)$.

renormalization by a direct path in the presence of small vibrations, but it suffices to consider the Jacobian of the transition (6). Expanding D in factors $D = D'\rho^2 \sin \vartheta$, we have $1/C^2 \approx D'_0$, where the index 0 denotes that all the remaining variables must be evaluated at the equilibrium position of the molecule X. For the case of small vibrations, we can substitute the linearized relations (6) [see, for example, (11)].

2. Knock-on of an atom from a triatomic molecule. The angular part of the wave function of a diatomic molecule is determined by the position of the axis of the molecule (by the two angles φ', ϑ'). These two angles correspond to a choice of Eulerian angles $\Omega_Y = (\varphi', \vartheta', 0)$, which uniquely determines the position relative to the laboratory system of a certain set of coordinates (X''', Y''', Z''') with the Z''' axis along the axis of the diatomic molecule. We call this set of coordinates (X''', Y''', Z''') the internal system of coordinates of the diatomic molecule. We determine the angle φ relative to it from (4). The difference from the case of a nonlinear radical Y lies in the fact that the angle φ now does not enter into the relation (6), but participates in the transformation of the rotation function $D^J_{M_J K_J}(\Omega_X)$ of the X molecule, with the internal system of coordinates (X_0, Y_0, Z_0), to the internal system of coordinates (X''', Y''', Z''') (see Fig. 1) of the diatomic radical Y:

$$D^J_{M_J K_J}(\Omega_X) = \sum_{K'} D^J_{K' K_J}(0, \varkappa, 0)\, D^J_{M_J K'}(\Omega_Y, \varphi).$$

The formula for the channel function (3) is easily generalized to the case in which the total electron spin of the Y radical differs from 0:

$$\begin{aligned}
&\Psi_{\mathrm{ch}}(j, m, J^0, K, l, \Lambda, J') \\
&\quad = \sum_{M'+M_l=m} (l M_l J' M' \mid jm)\, Y_{l m_l}(\vartheta_{\mathrm{lab}} \varphi_{\mathrm{lab}}) \\
&\quad \times \mid J'M'(J^0, K, \Lambda)\rangle, \\
&\mid J'M'(J^0, K, \Lambda)\rangle \\
&\quad = \sum U(K, S''(J')\, S' : J^0, S)\, (K M_K S M_S \mid J'M') \\
&\quad \times (S' M_{S'}\; S'' M_{S''} \mid S M_S)\, \chi^{S'}_{M_{S'}} \chi^{S''}_{M_{S''}} \widetilde{D}^{K*}_{M_K \Lambda}(\Omega_Y) \\
&\quad \times \chi_X(\ldots v'_{\alpha'_i} \ldots, \ldots Q'_{\alpha'_i} \ldots).
\end{aligned} \tag{7}$$

Here Λ is the projection of the orbital electron angular momentum, $\chi^{S'}_{M_{S'}}$, $\chi^{S''}_{M_{S''}}$ are the spin functions of the Z atom and the diatomic radical Y, respectively; S is the spin angular momentum of the channel; J' is some intermediate angular momentum over which it is necessary to sum (1); J^0 is the total angular momentum of the radical Y; $U(KS''(J')S':J^0S)$ are the Racah coefficients;[8] we assume that the coupling of the angular momenta in the diatomic molecule corresponds to the case b.[7]

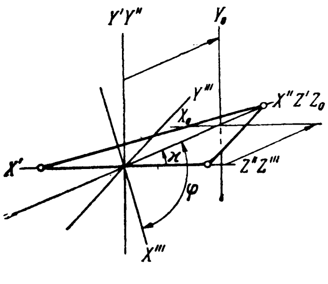

FIG. 1. (X_0, Y_0, Z_0) is the internal system of coordinates of the H_2O molecule with the set of Eulerian angles Ω_X relative to the laboratory system; (X''', Y''', Z''') is the internal set of coordinates of the H_2 radical with the set of Eulerian angles $\Omega_Y = (\varphi', \vartheta', 0)$ relative to the laboratory system; $(X''', Y''', Z''') \rightarrow (X'', Y'', Z'')$ (rotation about the Z''' axis by an angle φ; then $(X''Y''Z'') \rightarrow (X'Y'Z')$ (rotation around the Y'' axis by an angle $\varkappa$), finally, the parallel translation $(X'Y'Z') \rightarrow (X^0Y^0Z^0)$.

Substituting (7) in (1), we get, after integration over the angles and spin variables of the channel (in the case in which the total spin of the molecule X is equal to 0) $J' = K$ and

$$\begin{aligned}
&\int_\sigma \Psi^*(X)\, \Psi_{\mathrm{ch}}(Y)\, d\sigma \\
&\quad = \sum_{K'} \sqrt{\frac{2K+1}{2J+1}}\, (l K' K \Lambda \mid J K')\, D^J_{K', K_J}(0, \varkappa, 0) \\
&\quad \times U(K S''(K)\, S' : J^0 0) \\
&\quad \times \delta_{J,j} \delta_{M_J,m} \int_{\rho=\mathrm{const}} \overset{*}{\chi}_X \chi_Y(Q')\, Y_{lK'}(\vartheta, 0) \sin \vartheta\, d\vartheta\, dQ'.
\end{aligned} \tag{8}$$

Here κ is the angle between the Z' axis of the internal system of coordinates of the X molecule and the Z''' axis of the diatomic radical (see Fig. 1).

3. Knock-on of an atom of oxygen from the water molecule. We transform from the normal coordinates of the molecule H_2O — $Q^{(1)}_{A_1}$, $Q^{(2)}_{A_1}$, Q_{B_1} (in the following we use the notation Q_1, Q_2, Q_3) to the channel variables [the relation (6)]. For this purpose, it is convenient to transform first from Q_i to the internal variables q_1, q_2, q_3 (see Fig. 2):

$$Q_1 = bq_1 + a(q_2 + q_3), \qquad Q_2 = dq_1 + c(q_2 + q_3), \qquad Q_3 = e(q_2 - q_3). \tag{9}$$

In the variables q_i, the potential energy of the molecules H_2O has the form (θ is the angle between q_2 and q_3; see Fig. 2)

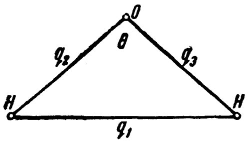

FIG. 2

$$2V = k_1 (q_2^2 + q_3^2) + k_\theta\theta^2 = k_1 (q_2^2 + q_3^2)$$
$$+ k_\theta (R_1^2 - R_2^2/4)^{-1} q_1^2,$$

where R_1 is the equilibrium distance between the atoms H and O, R_2 is the equilibrium distance between the atoms of hydrogen. In the normal coordinates Q_i, the kinetic energy T and the potential energy V have the form

$$2T = \dot{Q}_1^2 + \dot{Q}_2^2 + \dot{Q}_3^2, \qquad 2V = \omega_1^2 Q_1^2 + \omega_2^2 Q_2^2 + \omega_3^2 Q_3^2.$$

Using the experimental values[9] $R_1 = 9.58 \times 10^{-9}$ cm, $R_2 = 1.522 \times 10^{-8}$ cm, $k_1 = 7.76 \times 10^5$ dynes/cm, $k_\theta = 6.34 \times 10^{-12}$ erg, $\omega_1 = 3.01 \times 10^{14}$ sec^{-1}, $\omega_2 = 6.88 \times 10^{14}$ sec^{-1}, and $\omega_3 = 7.07 \times 10^{14}$ sec^{-1}, we find the values of the coefficients in (9):

$$a = 1.24 \cdot 10^{-12} \mathrm{g}^{1/2},\ b = 1.15 \cdot 10^{-12} \mathrm{g}^{1/2},\ c = -7.27 \cdot 10^{-13} \mathrm{g}^{1/2},$$
$$d = 3.78 \cdot 10^{-13} \mathrm{g}^{1/2}, \qquad e = 8.8 \cdot 10^{-13} \mathrm{g}^{1/2}.$$

The transition from q_i to the channel variables ρ, ϑ, φ, and r (see Fig. 3) is easily completed:

$$q_1 = r - R_2, \qquad q_2 = \sqrt{(r/2)^2 + \rho^2 - r\rho\cos\vartheta} - R_1,$$
$$q_3 = \sqrt{(r/2)^2 + \rho^2 + r\rho\cos\vartheta} - R_1. \tag{10}$$

We note that the real channel variables are ρ, ϑ, φ, and $q = r - R_2'$, where R_2' is the equilibrium distance between nuclei in the H_2 molecule; however, it will be more convenient for us to work with the variable r.

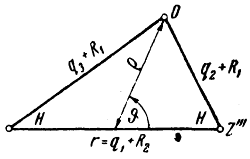

FIG. 3

Substituting (10) and (9), we get the relation (6) with the renormalization $C^{-2} = D_0'$, where

$$D' = 2e(ad - bc)\left[r/\sqrt{[(r/2)^2 + \rho^2]^2 - r^2\rho^2\cos\vartheta'}\right].$$

After linearization, we have:

$$Q_1 = x_1 r + x_2\rho + x_3, \qquad Q_2 = x_4 r + x_5\rho + x_6,$$
$$Q_3 = x_7\cos\vartheta, \tag{11}$$

where

$$x_1 = aR_2/2R_1 + b, \qquad x_4 = cR_2/2R_1 + d,$$
$$x_2 = 2a\rho_0/R_1, \qquad x_5 = 2c\rho_0/R_1,$$
$$x_3 = -[a(R_2^2/2R_1 + 2\rho_0^2/R_1) + bR_2],$$
$$x_6 = -[c(R_2^2/2R_1 + 2\rho_0^2/R_1) + dR_2],$$
$$x_7 = eR_2\rho_0/R_1.$$

The normal coordinate of the H_2 molecule has the form $Q = (r - R_2')/\sqrt{2}\,\mu$, with the corresponding frequency $\omega = 8.07 \times 10^{14}$ sec^{-1} (μ is the reciprocal of the mass of the hydrogen atom; $R_2' = 7.4 \times 10^{-9}$ cm).

Let us consider the break up of H_2O from its ground state, i.e., $J = 0$, $v_{A_1}(1) = v_{A_1}(2) = v_{B_1} = 0$ to the excited state of H_2 with the vibration number n and rotational angular momentum K ($\Lambda = 0$). Equation (8) in this case takes on the form

$$\int_\sigma \Psi^*(H_2O)\,\Psi_{ch}(H_2)\,d\sigma$$
$$= (-1)^K \int_{-\infty}^{\infty} dr \int_0^{\pi} \sin\vartheta\,d\vartheta\,\chi^*_{H_2O}(0, 0, 0, Q_1, Q_2, Q_3)$$
$$\times \chi_{H_2}(n, Q')\,Y_{K,0}(\vartheta, 0).$$

As is seen from (11) and (2), the integrand of (12) does not have any cross terms between r and ϑ in the exponents; therefore, the integrals over $d\vartheta$ and dr are separate. One can then write (12) in the form

$$\int_\sigma \Psi^*(H_2O)\,\Psi_{ch}(H_2)\,d\sigma \equiv \int_\sigma (n, K)\,d\sigma = CS_n^\rho S_K^\vartheta; \tag{13}$$

$$C = N_0^{A_1(1)} N_0^{A_1(2)} N_0^{B_1} N_0 \sqrt{D_0'}\exp\left(-\tfrac{1}{2}[C_7 + C_6\rho + C_2\rho^2]\right),$$

$$S_n^\rho = \frac{N_n}{N_0}\int_{-\infty}^{\infty}\exp\left(-\frac{1}{2}\left[C_1 r^2 + C_3 r\rho + C_5 r\right]\right)$$
$$\times H_n\left[\sqrt{\frac{\omega}{2\hbar\mu}}(r - R_2')\right]dr, \tag{14}$$

$$S_K^\vartheta = (-1)^K\int_0^{\pi}\exp\left(-\frac{1}{2}C_4\cos^2\vartheta\right)Y_{K0}(\vartheta, 0)\sin\vartheta\,d\vartheta; \tag{15}$$

where

$$\hbar C_1 = \omega_1 x_1^2 + \omega_2 x_4^2 + \omega x_8^2,$$
$$\hbar C_2 = \omega_1 x_2^2 + \omega_2 x_5^2, \qquad \hbar C_3 = 2(\omega_1 x_1 x_2 + \omega_2 x_4 x_5),$$
$$\hbar C_4 = \omega_3 x_7^2, \qquad \hbar C_5 = 2(\omega_1 x_1 x_3 + \omega_2 x_4 x_6 + \omega x_8 x_9),$$
$$\hbar C_6 = 2(\omega_1 x_2 x_3 + \omega_2 x_5 x_6), \quad \hbar C_7 = \omega_1 x_3^2 + \omega_2 x_6^2 + \omega x_9^2.$$

As is seen from (15), S_K^ϑ differs from 0 only for even K. This corresponds to the fact that the total spin of the nuclei of the H_2 molecule must be equal to 0 (J = 0 corresponds to the para-state of the water molecule). S_K^ϑ, S_n^ρ are reduced from K = n = 0 to the error integral, while for values of K and n different from 0, they correspond to differentiation over the parameter.

Finally, we get from (13) and (1)

$$\Theta^2_{K,n}(\rho) = \tfrac{1}{2}\rho^3 |C(\rho) S_n^\rho S_K^\vartheta|^2.$$

The value of the channel radius is chosen at the maximum of the "reduced width." In the given case, the value $\rho_{\max} = 6.77 \times 10^{-9}$ cm was obtained; S_n^ρ was computed for n = 0, 1, 2, 3, 4; S_K^ϑ for K = 0, 2, 4, 6, 8. The dependence of $|S_n^\rho|^2$ and $|S_K^\vartheta|^2$ is shown in relative scale in Figs. 4 and 5.

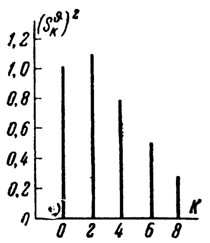

FIG. 4. Distribution of the relative intensities of the rotational states of the final H_2 radical.

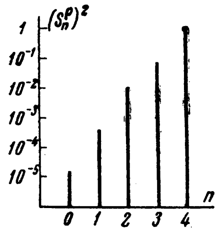

FIG. 5. Distribution of the relative intensities of the vibrational states of the final H_2 radical.

It should be noted that the cross section of the knock-on reaction is directly proportional not to Θ^2, but to $|\int \Theta(\rho)\, d\rho|^2$, if the conditions of the experiment are such that q = 0 (q is the momentum transferred to the radical Y). However, because of the presence of the sharp maximum in the dependence $\Theta(\rho)$, the width of which changes slightly from level to level (see Fig. 6), $\Theta^2(\rho_{\max})$ for sufficiently small q (for the choice of the angle θ_1 and θ_2, see A.4) excellently describes the dependence of the cross section on the excitation energy of the remainder. The dependence $\Theta(\rho)$ is determined explicitly in the given case by $C(\rho)$ and $S_n^\rho(\rho)$ and the integration over $d\rho$ presents no great difficulties.

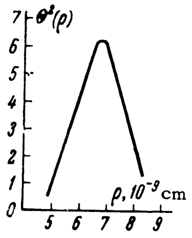

FIG. 6. Dependence of $\Theta^2(\rho)$ in relative units for n = 0. For n = 1, 2, 3, 4, the dependence of $\Theta^2(\rho)$ has the same character. $\rho_{\max}$ lies between 6.77 and 6.50×10^{-9} cm, while the width of the hump varies from 2.2 to 2.0×10^{-9} cm.

Table I. Distribution of the relative intensities of the vibrational and rotational excitations of the final H_2 radical

K	n				
	0	1	2	3	4
8	$3.45\cdot10^{-6}$	$1.19\cdot10^{-4}$	$2.06\cdot10^{-3}$	$1.76\cdot10^{-2}$	0,25
6	$6.63\cdot10^{-6}$	$2.29\cdot10^{-4}$	$3.96\cdot10^{-3}$	$3.38\cdot10^{-2}$	0,48
4	$1.06\cdot10^{-5}$	$3.67\cdot10^{-4}$	$6.34\cdot10^{-3}$	$5.42\cdot10^{-2}$	0,77
2	$1.52\cdot10^{-5}$	$5.25\cdot10^{-4}$	$9.07\cdot10^{-3}$	$7.75\cdot10^{-2}$	1.1
0	$1.38\cdot10^{-5}$	$4.77\cdot10^{-4}$	$8.24\cdot10^{-3}$	$7.04\cdot10^{-2}$	1.0

The reduced widths for n = 1, 2, 3, 4 and K = 0, 2, 4, 6, 8 are shown in Table I in relative scale. As is seen from these results, the probability of excitation increases with increase in n, and the maximum probability takes place in the continuous spectrum. This is explained by the fact that R_2' is approximately two times smaller than R_2.

4. Knock-on of an atom of hydrogen from the water molecule. It follows from (8) that in this case one should have $\Lambda = 0$; therefore, the radical OH is not found in the ground electron state (Π state) but is found in the first excited electron state (Σ state). This prohibition is connected with the adiabatic character of the motion.

As was the case in Sec. 3, one must transform from the normal coordinates Q_i of H_2O to the channel variables ρ, ϑ, φ and r, the determination of which in the case of break-up to O and OH is seen from Fig. 7. Transforming as above, first from Q_i to q_i, and then by means of Fig. 7 from the q_i to the channel variables, we obtain relations similar to those of (11) with different x_i, and formulas for the overlap integral (8) similar to (13)—(15), in which the quantities C_i are connected with the corresponding x_i by bilinear relations of the type (15).

In the expression obtained for the overlap integral, division into factors similar to what was done in Eq. (13) no longer takes place. Therefore, the calculation is somewhat more involved, although it contains nothing new in principle. The results are

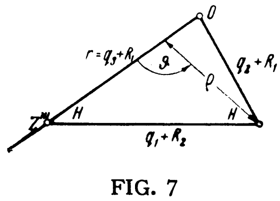

FIG. 7

shown in Table II and Fig. 8. In the numerical calculation, use was made of the following experimental values of the frequency of the radical OH (ω) and the equilibrium distance between the nuclei in this radical (R_2'): $\omega = 5.98 \times 10^{14}$ sec^{-1}, $R_2' = 1.0121 \times 10^{-8}$ cm.[9] The value 9.83×10^{-9} cm was obtained for $\rho_{\max}$ in this case.

Table II. Distribution of the relative intensities of the vibrational and rotational excitations of the final OH radical

K	J_0	$n=0$	$n=1$	$n=2$	$n=3$	$n=4$
0	$^1/_2$	7.90	0,317	3.09	0.225	1,014
1	$^1/_2$ $^3/_2$	0.438 0.876	0,0511 0.1022	0.270 0,540	0.0502 0.1004	
2	$^3/_2$ $^5/_2$	1.310 1.970	0.324 0.486	0,504 0,756	0.332 0,498	
3	$^5/_2$ $^7/_2$	0,720 0.960	0.0448 0,0598	0.453 0,604	0.0431 0.0571	
4	$^7/_2$ $^9/_2$	0,0875 0,1094	0.291 0.363	0.0078 0.0098		
5	$^9/_2$ $^{11}/_2$	0.1980 0.238	0,527 0.633			
6	$^{11}/_2$ $^{13}/_2$	0,1223 0.1427				

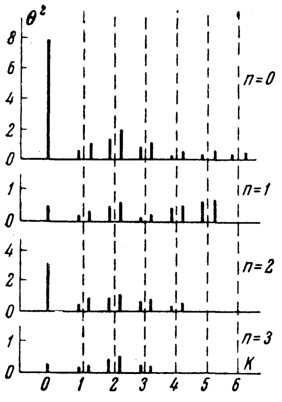

FIG. 8. Distribution of the relative intensities of the vibrational and rotational excitations of the final OH radical. The left column of each doublet corresponds to $J^0 = K - \frac{1}{2}$, the right to $J^0 = K + \frac{1}{2}$.

As we see, the excitation curves corresponding to knock-on of O and knock-on of H are completely different, because of the fact that there is a bond between O and H in the H_2O molecule but not between H and H. Thus a study of the excitation curve of the residual radical can give information as to the character of the interatomic forces in the original molecule.

The experiment which makes it possible to obtain information on the reduced widths is the following.[10] Two counters (C_1, C_2) are arranged for coincidence as is shown in Fig. 9, while the angles θ_1 and θ_2 are determined by the requirement that the momentum transferred to the residual radical be equal to 0. The counting rate is measured as a function of the total energy recorded by the counters. The energy resolution must be sufficiently high to separate the peaks corresponding to the neighboring vibrational states of the residual radical. It is impossible to resolve the separate rotational levels, in particular, because of the thermal motions of the molecules of the "target" (the target must be gaseous and sufficiently thin), so that the entire rotational band corresponding to the given vibrational state is recorded integrally. The temperature achieved by the gas is determined by the distance between the neighboring vibrational levels ΔE, so that one has $kT \ll \Delta E$ (usually the ΔE for the molecules of the target and the residual radical are comparable).

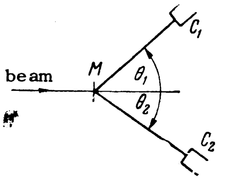

FIG. 9

In the calculation given above, the initial state of the molecule was its ground state. In fact, if $T \neq 0$ (but $kT \ll \Delta E$), it is necessary to average over the rotational excitations of the initial molecules. However, inasmuch as the rotational and vibrational variables are separated in the integrals, all the conclusions on the relative intensity of excitation of the different vibrational states remain unaltered.

II. MOLECULAR RESONANCE REACTIONS

As was pointed out in the introduction, the problem of Breit-Wigner resonances in the collisions of atoms is important for collisions of atoms of noble gases that are both identical (for example, Ne–Ne), and also nonidentical (for example He–Ar). It is not excluded that such a problem can exist also for systems of the type He–O, etc. We limit ourselves to analysis of collisions of identical atoms only, inasmuch as there is no information on the interaction in systems of different atoms (precisely this would be given by a study of scattering resonances).

For molecules of He_2, the potential well is so shallow that there is no single bound state;[11] s is the phase for scattering of He by He and will pass through $\pi/2$ for $E \approx 3–5 \times 10^{-4}$ eV (in the center of mass system), but there is no clearly expressed resonance cross section in this case, inasmuch as the condition $|\mathbf{k}_0| \gg |\mathbf{k}|$ is not satisfied in this case, where $\mathbf{k}_0$ is the wave vector inside the region of attraction and $\mathbf{k}$ is that outside this region.[12]

For the molecule Ne_2, as data on the interatomic potential show,[13] (data obtained from analysis of experimental data on crystalline Ne, on gaseous Ne at high temperatures, etc) there exists a single bound vibrational state with coupling energy $\sim 1 \times 10^{-3}$ eV. The rotational levels corresponding to the state, beginning with $L \approx 6$, pass into the region of positive energies of the system and, thanks to the presence of a centrifugal barrier, will be realized in the form of sharp resonance peaks in the curve of the energy dependence of the scattering cross section. In the quasistationary states with $L \approx 10$, the energy E_0 of the relative motions of the atoms at infinity will be equal to $\approx 1 \times 10^{-3}$ eV, i.e., approximately one half of the height of the centrifugal barrier. All these resonances have reduced widths equal to the Wigner limit.[1]

For the molecule Ar, there are four or five bound vibrational states,[13,14] and the density of levels for excitations close in energy to the dissociation energy will be markedly greater than for Ne_2. But for energies $\sim 1 \times 10^{-3}$ eV above the dissociation threshold, it is evidently still possible to speak of isolated resonances. The difference mentioned in the potentials of interaction of He–He, Ne–Ne, Ar–Ar, etc., also lead to the result that He in general does not have a crystalline phase, and that the temperature of crystallization increases with increase in A for the other noble gases.

It is of course very difficult to study the scattering of an atom by an atom at an energy of $\sim 1 \times 10^{-3}$ directly by experiment; however, the resonances discussed above will play an important role in the process of adhesion of atoms of noble gases onto a molecule in atomic beams at low temperatures[15] (1×10^{-3} eV ≈ 10°K): in the presence of quasistationary states in the corresponding region ($E_0 \sim kT$) the probability of adhesion is increased sharply. A similar situation is well known in astrophysics.[16] For $T \sim 10^8$ °K ($kT \sim 10^4$ eV) an important role in the energy balance in stars is played by thermonuclear reactions of the adhesion of α particles in nuclei of the type C^{12} or O^{16}, where this process is strongly accelerated because of the presence in the system $\alpha + \alpha$ of a quasistationary S state for $E_0 \approx +90$ keV (the ground state of Be^8), and also by the presence of a quasistationary s state with large reduced width in the system

$$Be^8 + \alpha(C^{12*}) \quad \text{for } E_0 = +280 \text{ keV}.$$

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