

EXCITATION OF THE ROTATIONAL LEVELS OF DIATOMIC MOLECULES BY ELECTRON
IMPACT IN THE ADIABATIC APPROXIMATION

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A formula is obtained in the adiabatic approximation for the cross sections of excitation of rotational and vibrational states of diatomic molecules by electron impact, the formula being valid for incident electrons with energies appreciably exceeding the energy of the vibrational-rotational state of the molecule. The inelastic transition cross section is expressed in terms of the elastic scattering phases, calculated earlier by Fisk. Specific calculations of the cross sections are carried out for the rotational transitions $L \rightarrow L$, $L \rightarrow L \pm 2$, $L \rightarrow L \pm 4$ of N_2 , O_2 , and H_2 molecules in the ground electronic and vibrational states, for incident electrons with energies between 0 and 25 eV. The results of the calculations are in agreement with experimental data on measurements of the total scattering cross sections and of the vibrational excitation cross sections, and also with the data on determination of the losses of energy by slow electrons.

1. INTRODUCTION

A large number of experimental works, carried out twenty to thirty years^[1-6] ago and very recently,^[7-10] have been devoted to an investigation of processes which occur during the passage of a beam of electrons through a molecular gas. Numerous experiments indicate that the basic losses of energy by slow electrons are associated with inelastic processes, particularly with the excitation of rotational and vibrational states of the molecules. The inelastic losses appreciably exceed the losses associated with elastic collisions, even if the energy of the electrons is below the threshold of vibrational excitation. This has led various investigators to the idea that the effective cross sections for the excitation of rotational states of molecules by collisions with electrons may have a large value, in spite of the enormous difference in the masses of the colliding particles. However, measurements of the values of these cross sections have, up to the present time, still not been carried out. In connection with this, definite interest has developed in the theoretical investigation of the processes of rotational excitation of molecules.

The first attempt in this direction was proposed by Massey in 1932.^[11] Subsequent work dates back only to the last ten years.^[12-19] In all of these articles except the one by Mjolsness and Sampson,^[18] the Born approximation is used to calculate the ex-

citation cross section. In those cases when the authors take as the interaction energy of an electron with a molecule a potential energy whose form is valid over all distances, their calculations are applicable under the usual conditions of the Born approximation.^[13,14] In other cases,^[15-19] the potential selected is one which correctly describes the interaction only at large distances (dipole, quadrupole, polarization, or Coulomb interaction). Assuming this potential to be equal to zero at small distances and applying the Born approximation, the authors deduce a proof to the effect that their obtained values for the cross sections are valid for energies of the incident electrons below a few tenths of an electron volt (such an upper limit appears because of various approximations used during the calculations). The results of a calculation according to the method of distorted-waves are given in^[18], and only insignificantly change the results of the article by Gerjuoy and Stein.^[15]

In the present article we use the adiabatic approximation method, which enables us to calculate the cross sections for excitation of vibrational and rotational states of diatomic molecules for electron energies beginning with a few tenths of an electron volt and above. On the basis of this method, the cross sections for various rotational transitions in molecules of nitrogen, oxygen, and hydrogen are calculated for incident electrons with energies from 0 to 25 eV. It is indicated how one

can compare the results of the present calculation with known experimental data.

2. ADIABATIC APPROXIMATION

The adiabatic approximation, well known in the literature under the name Born-Oppenheimer approximation, is a fundamental method of solving the problem of bound molecular states. The possibility of using this approximation in collision theory is obvious from the following simple considerations. Let us consider the collision of a light structureless particle (mass m) with a heavy particle (mass M , we shall call it the target). If $\lambda = m/M \ll 1$, and the energy of the incident particle considerably exceeds the internal energy of the target, then during the effective collision time τ neither the relative distribution of the internal parts of the target nor the interaction potential will be able to change appreciably. Therefore, to the first approximation one can consider the collision problem as the scattering of a particle by a given potential which depends on the internal coordinates of the target as a parameter. The cross section for elastic scattering of the particle will furthermore depend on this same parameter. In the next approximation, one can take the change of the target's internal state into account.

In recent years the adiabatic approximation has been successfully used to solve a number of problems in nuclear scattering theory.^[20,21] An examination of this approximation from the point of view of the general assumptions of the quantum theory of scattering was carried out by Chase.^[22] In 1959 Massey^[23] pointed out the possibility of using the adiabatic approximation in connection with the scattering of electrons by molecules. However, the general expression (independent of the nature of the colliding particles) obtained by him for the inelastic scattering cross section differs from the expression given by Chase and usually used in nuclear scattering theory. In addition, Massey did not indicate the conditions for applicability of the expression obtained by him. The adiabatic approximation will be formulated below in a manner similar to that used by Chase, but for excitation of vibrational and rotational levels of diatomic molecules upon collision with light particles.

We shall assume that during the collision the electronic state of the molecule does not change, and it remains in its ground state. Let us write the Schrödinger equation for the wave function of the colliding particles in the center of mass system of "molecule + particle" in the form

$$\left[-\frac{\hbar^2}{2m} \Delta_r - \frac{\hbar^2}{2M} \Delta_R - E - \varepsilon + U(R) + V(\mathbf{r}, \mathbf{R}) \right] \times \psi(\mathbf{r}, \mathbf{R}) = 0, \quad (1)$$

where \mathbf{r} and \mathbf{R} denote, respectively, the radius vectors of particles with reduced masses m and M :

$$m = m_1(M_1 + M_2) / (m_1 + M_1 + M_2);$$

$$M = M_1 M_2 / (M_1 + M_2);$$

M_1 and M_2 are the masses of the molecular nuclei; m_1 is the mass of the incident particle; E is the relative kinetic energy of the particle and the molecule; ε is the internal energy of the molecule; $U(R)$ is the effective interaction energy of the nuclei with each other; $V(\mathbf{r}, \mathbf{R})$ is the effective interaction energy of the particle and the molecule, whose form depends on the electronic state of the molecule.

As in the Born-Oppenheimer approximation, we seek a solution of Eq. (1) in the form

$$\psi_A(\mathbf{r}, \mathbf{R}) = F(\mathbf{r}, \mathbf{R}) \varphi(\mathbf{R}), \quad (2)$$

where $\varphi(\mathbf{R})$ is the wave function of the nuclei, satisfying the equation

$$\left[-\frac{\hbar^2}{2M} \Delta_R + U(R) - \varepsilon \right] \varphi(\mathbf{R}) = 0. \quad (3)$$

Substituting expression (2) into Eq. (1) and using Eq. (3), we obtain the following equation for $F(\mathbf{r}, \mathbf{R})$:

$$\left[-\frac{\hbar^2}{2m} \Delta_r + V(\mathbf{r}, \mathbf{R}) - E \right] F = \frac{\hbar^2}{2M} \left(\Delta_R + 2 \frac{\nabla_R \varphi}{\varphi} \nabla_R \right) F. \quad (4)$$

We seek a solution of the last equation in the form of an expansion in powers of the small parameter $\lambda = m/M$:

$$F = F^{(0)} + \lambda F^{(1)} + \dots \quad (5)$$

Following Chase, one can show that if the number of possible excited states $\varphi_n(\mathbf{R})$ is bounded, then $F^{(1)}$ does not depend on λ . Therefore, in the zero-order approximation with respect to λ , $F = F^{(0)}$ and is determined from the following equation:

$$\left[-\frac{\hbar^2}{2m} \Delta_r + V(\mathbf{r}, \mathbf{R}) - E \right] F = 0 \quad (6)$$

with the boundary condition:

$$F(\mathbf{r}, \mathbf{R}) \longrightarrow e^{i\mathbf{k}\mathbf{r}} + \frac{f(\mathbf{n}, \mathbf{R})}{r} e^{i\mathbf{k}\mathbf{r}}. \quad (7)$$

Then using the exact expression

$$f_{0n}(\mathbf{n}) = \frac{m}{2\pi\hbar^2} \int \varphi_n^*(\mathbf{R}) e^{-i\mathbf{k}\mathbf{n}\mathbf{r}} V(\mathbf{r}, \mathbf{R}) \psi(\mathbf{r}, \mathbf{R}) d\mathbf{r} d\mathbf{R}, \quad (8)$$

for the inelastic transition amplitude, but with the wave function (2) of the adiabatic approximation, we obtain the following expression for the amplitude of the transition $0 \rightarrow n$ between two states of the molecule in the adiabatic approximation:

$$f_{0n}^A(\mathbf{n}) = \int \varphi_n^*(\mathbf{R}) f(\mathbf{n}, \mathbf{R}) \varphi_0(\mathbf{R}) d\mathbf{R}. \quad (9)$$

The following conditions are used in the derivation of formula (9):^[22]

$$kr_0 \Delta E / E \ll 1, \quad \text{if} \quad kr_0 \gg 1, \quad (10)$$

$$\Delta E / E \ll 1, \quad \text{if} \quad kr_0 \leq 1, \quad (11)$$

where ΔE is the greater of the following two energies: the energy transferred and the energy of the vibrational-rotational state of the molecule; E is the smaller of the particle energies before and after the collision; r_0 is a characteristic distance for the interaction of an electron with a molecule; k is the wave number of the incident particle.

Thus, in the adiabatic approximation the inelastic transition amplitude is determined as the matrix element of the elastic scattering amplitude $f(\mathbf{n}, \mathbf{R})$ for a potential $V(\mathbf{r}, \mathbf{R})$ with a given value of the parameter \mathbf{R} and a definite orientation with respect to the direction of the incident particle. It is easy to see that the adiabatic approximation goes over into the Born approximation, if the elastic scattering amplitude is determined from the Born approximation.

3. ELASTIC SCATTERING AMPLITUDE

An exact solution of the problem of elastic scattering by a non-spherically symmetric potential is possible only for some special choice of this potential, enabling us to separate the variables in the Schrödinger equation. In the case when the scattering system has cylindrical symmetry, separation of variables is possible in spheroidal coordinates, provided the potential in these coordinates has the form

$$V(\xi, \eta) = [a(\xi) + b(\eta)] / (\xi^2 - \eta^2), \quad (12)$$

where ξ and η are prolate spheroidal coordinates (see, for example,^[24] $a(\xi)$ and $b(\eta)$ are arbitrary functions of the corresponding variables.

The method for solving the problem of elastic scattering by a potential of the form (12) with $b(\eta) = 0$ is analogous to the usual method of partial waves for scattering by a spherically symmetric potential. This method was first applied to the scattering of electrons on diatomic molecules by Stier^[25] and Fisk,^[26] and later to the scattering

of neutrons by nonspherical nuclei by Inopin.^[21] It will be assumed below that one can represent the interaction potential of an incident particle with a molecule in the form

$$V(\xi, \eta) = a(\xi) / (\xi^2 - \eta^2). \quad (13)$$

Since the method of solving the problem does not impose any limitations on the function $a(\xi)$, except $\xi^{-2}a(\xi) \rightarrow 0$ as $\xi \rightarrow \infty$, in the vast majority of cases one can select the form of $a(\xi)$ for each specific case so that the potential (13) corresponds in the best way to the actual potential (see Sec. 5 below).

In the coordinate system whose z axis coincides with the axis of symmetry of the potential, the amplitude for elastic scattering by a potential of the form (13) has the form^[21,26]

$$f(\nu_0, \nu, \mathbf{R}) = \frac{2\pi}{ik} \sum_{lm} [\exp(2i\delta_{lm}) - 1] J_{lm}^*(c, \nu_0) J_{lm}(c, \nu); \quad (14)$$

here ν_0 and ν are unit vectors characterizing, respectively, the directions of the incident and scattered particle fluxes; \mathbf{k} is the wave vector of an incident particle; $c = (1/2)kR$; $\delta_{lm}(c)$ is the scattering phase which depends on the specific form of $V(\xi, \eta)$;

$$J_{lm}(c, \nu) = \sum_n s_{nm}^l(c) Y_{nm}(\nu) \quad (15)$$

are orthonormalized spheroidal angular functions, where $Y_{nm}(\nu)$ are normalized spherical functions:

$$s_{nm}^l(c) = (-1)^m \left[\sum_r |b_{rm}^l|^2 \right]^{-1/2} b_{nm}^l, \\ b_{nm}^l(c) = \left[\frac{2n+1}{2} \frac{(n-|m|)!}{(n+|m|)!} \right]^{-1/2} d_{n-|m|}^{l-|m|}(c), \\ s_{nm}^l(0) = \delta_{nl}. \quad (16)$$

In the last equation, δ_{nl} is the Kronecker delta function. The quantities $d_{n-|m|}^{l-|m|}$ are defined in the article by Flammer.^[24] The parity of the summation indices n (or r) coincides with the parity of the quantum number l , and the summation starts with the value of n (or r) equal to m or $m+1$. The number m takes values from $-l$ to $+l$. We note that the vector \mathbf{R} , determined by the properties of the potential, enters into the expression for the amplitude $f(\nu_0, \nu, \mathbf{R})$ as a parameter.

4. EXCITATION OF ROTATIONAL AND VIBRATIONAL LEVELS

Formula (9) given above is valid for the excitation of rotational and vibrational states if the effective collision time τ is considerably less than the vibrational period ω^{-1} : $\omega\tau \ll 1$. We shall assume that high vibrational states are excited with small

probability. In this case the wave function for the relative motion of the nuclei in a molecule has the form

$$\varphi(R) = \varphi_v(R) Y_{LM}(\omega), \quad (17)$$

where v , L , and M are, respectively, vibrational and rotational quantum numbers, and ω denotes the angular coordinates of the molecule.

Using Eq. (9), we obtain the following expression for the amplitude for scattering of a particle in the direction ν with the molecular transition $vLM \rightarrow v_1L_1M_1$:

$$f_{vLM}^{v_1L_1M_1} = \frac{2\pi}{ik} \sum_{lm} \int V_{lm}^{vv_1} A_{LMlm}^{L_1M_1} R^2 dR, \quad (18)$$

where

$$V_{lm}^{vv_1}(R) = [\exp(2i\delta_{lm}) - 1] \varphi_v(R) \varphi_{v_1}^*(R),$$

$$A_{LMlm}^{L_1M_1}(\mathbf{v}, R) = \sum_{nn'} Q_{LMnm}^{L_1M_1n'}(\mathbf{v}) s_{nm}^l s_{n'n}^l,$$

$$Q_{LMnm}^{L_1M_1n'}(\mathbf{v}) = \int Y_{LM}(\omega) Y_{L_1M_1}^*(\omega) Y_{n'm}^*(\mathbf{v}_0) Y_{nm}(\mathbf{v}) d\omega; \quad (19)$$

$d\omega$ is an element of solid angle.

Changing from a coordinate system attached to the molecule to the system of coordinates associated with the direction of motion of the incident particle (the z axis is along the direction of motion), and carrying out transformations similar to those carried out in the article by Inopin,^[21] we obtain

$$Q_{LMnm}^{L_1M_1n'}(\mathbf{n}) = (-1)^m \sum_{\lambda\mu} \frac{2n' + 1}{2\lambda + 1} (n'n0\mu|\lambda\mu) \times (n'nm - m|\lambda0) B_{LM\lambda\mu}^{L_1M_1} Y_{n\mu}^*(\mathbf{n}), \quad (20)$$

where \mathbf{n} is a unit vector in the direction of scattering in the new coordinate system: $(n'n0\mu|\lambda\mu)$ and $(n'nm - m|\lambda0)$ are Clebsch-Gordan coefficients;

$$B_{LM\lambda\mu}^{L_1M_1} = \int Y_{L_1M_1}^*(\omega) Y_{LM}(\omega) Y_{\lambda\mu}(\omega) d\omega = \left[\frac{(2L+1)(2\lambda+1)}{4\pi(2L_1+1)} \right]^{1/2} \times (L\lambda00|L_10) (L\lambda M\mu|L_1M_1) \delta_{M_1, M+\mu}. \quad (21)$$

Substituting the expression for $B_{LM\lambda\mu}^{L_1M_1}$ into Eq. (20), we obtain

$$Q_{LMnm}^{L_1M_1n'}(\mathbf{n}) = (-1)^m \left[\frac{(2n'+1)(2L+1)}{4\pi(2L_1+1)} \right]^{1/2} \times Y_{n, M_1-M}^*(\mathbf{n}) \sum_{\lambda} K_{LM\lambda m}^{L_1M_1n'n'}, \quad (22)$$

$$K_{LM\lambda m}^{L_1M_1n'n'} = (n'n0M_1 - M|\lambda M_1 - M) (n'nm - m|\lambda0) \times (L\lambda00|L_10) (L\lambda MM_1 - M|L_1M_1).$$

Using the usual expression for the transition cross section in terms of the amplitude, averaging over

the projections M of the initial orbital momentum L , and summing over M_1 , we obtain the following expression for the cross section of the transition from the state vL to the state v_1L_1 with scattering of the particle in the direction \mathbf{n} :

$$\sigma_{vL}^{v_1L_1}(\mathbf{n}) = \frac{1}{2L+1} \sum_{MM_1} \sigma_{vLM}^{v_1L_1M_1}(\mathbf{n}), \quad (23)$$

$$\sigma_{vLM}^{v_1L_1M_1}(\mathbf{n}) = \frac{\pi}{k^2} \frac{2L+1}{2L_1+1} \times \left| \sum_{lmn'n'} (-1)^m (2n'+1)^{1/2} K_{LM\lambda m}^{L_1M_1n'n'} u_{v_1lm}^{v_1n'n'} Y_{n, M_1-M}^*(\mathbf{n}) \right|^2, \quad (24)$$

$$u_{v_1lm}^{v_1n'n'} = \int [\exp(2i\delta_{lm}) - 1] \varphi_v \varphi_{v_1}^* s_{nm}^l s_{n'n}^l R^2 dR. \quad (25)$$

It is easy to obtain the total cross section by integrating expression (23) over the angles. In the form (24) the expression for the cross section appears to be rather complicated. But, under certain simplifying assumptions, one can reduce it to a form from which numerical results can be obtained fairly simply, and the dependence of the cross section on L and L_1 is expressed in analytic form. It turns out that for comparatively small values of $c = (1/2)kR$, the coefficients $s_{nm}^l(c)$ do not differ appreciably from unity if $n = l$, but are equal to zero for $n \neq l$.^[24] Therefore, for $c \lesssim 2$ one can set $s_{nm}^l(c) = \delta_{nl}$ (Kronecker delta function) and $s_{n'm}^l(c) = \delta_{n'l}$ with a large degree of accuracy. Using these equalities and integrating expression (24) over angles, for the total cross section we obtain

$$\sigma_{vL}^{v_1L_1} = \frac{\pi}{k^2} \frac{1}{2L+1} \sum_{lmn'n'} (-1)^{m+m'} (2l+1) u_{v_1lm}^{v_1n'n'} u_{v_1l'm'}^{v_1n'n'} T_{LL'l}^{\lambda\lambda'}, \quad (26)$$

$$u_{v_1lm}^{v_1n'n'} = \int [\exp(2i\delta_{lm}) - 1] \varphi_v \varphi_{v_1}^* R^2 dR, \quad (27)$$

$$T_{LL'l}^{\lambda\lambda'} = \sum_{MM_1} (l0M_1 - M|\lambda M_1 - M) (L\lambda MM_1 - M|L_1M_1) \times (l0M_1 - M|\lambda' M_1 - M) (L\lambda' MM_1 - M|L_1M_1). \quad (28)$$

Taking into account the symmetry relations for the Clebsch-Gordan coefficients, their connection with Racah coefficients, and the orthogonality relation for Racah coefficients,^[27] for $T_{LL'l}^{\lambda\lambda'}$ we obtain

$$T_{LL'l}^{\lambda\lambda'} = \frac{2L_1+1}{2l+1} \delta_{\lambda\lambda'}. \quad (29)$$

Finally, using the last equation, we obtain the final expression for the cross section of the transition $vL \rightarrow v_1L_1$:

$$\sigma_{vL}^{v_1L_1} = \frac{\pi}{k^2} \sum_{lm} (L\lambda00|L_10)^2 \times \left| \sum_m (-1)^m u_{v_1lm}^{v_1n'n'} (lm - m|\lambda0) \right|^2. \quad (30)$$

If $L = 0$ in the initial state, then it is not necessary to assume that the value of c is small. In this case, an expression for the differential cross section for excitation of rotational levels was obtained in the article by Inopin^[21] during an investigation of the scattering of neutrons by nonspherical nuclei. A completely analogous expression may be obtained in our case:

$$\sigma_{v_0}^{v_1 L_1} = \frac{\pi}{k^2} \sum_{nn'} \left| \sum_{lm} (-1)^m (n'nm - m |L_1 0) u_{v_1 n n'}^{v_1 n n'} \right|^2. \quad (31)$$

It is easy to see that if we set $L = 0$ in formula (30) and $s_{nm}^L = \delta_{nL}$ in formula (31), then these two formulas agree.

One can easily show that if $u_{v_1 L_1 m}^{v_1} = u_{v_1 L_1 -m}^{v_1}$, then transitions are allowed only between rotational states of the same parity. Since the last equality is realized only in the case of invariance of the potential with respect to reflection in a plane perpendicular to the axis of the molecule and passing through its center of mass, then the selection rule stated above corresponds to a general classification of the rotational states of molecules containing identical nuclei. In the spherically symmetric case

$$u_{v_1 l m}^{v_1} = u_{v_1 l}^{v_1}, \quad \sum_m (-1)^m (l m - m | \lambda 0) = (-1)^l (2l + 1)^{-1/2} \delta_{\lambda 0},$$

and transitions are possible only between states with the same L :

$$\sigma_{v_1 L}^{v_1 L_1} = \frac{\pi}{k^2} \sum_l (2l + 1) |u_{v_1 l}^{v_1}|^2 \delta_{LL_1}. \quad (32)$$

Summation of expression (30) with respect to the rotational quantum number of the final state, using the orthogonality relation for the Clebsch-Gordan coefficients, gives

$$\sum_{L_1} \sigma_{v_1 L}^{v_1 L_1} = \frac{\pi}{k^2} \sum_{im} |u_{v_1 im}^{v_1}|^2 = \sigma_{v_1 v_1}, \quad (33)$$

i.e., the sum over the rotational quantum number L_1 of the cross sections for the transitions $v_1 L \rightarrow v_1 L_1$ does not depend on the initial rotational state and is equal to the cross section for the corresponding vibrational excitation without change of the ground ($L = 0$) rotational state. If it is assumed that the cross sections of vibrational excitation are small, and if a molecule in the ground vibrational state v is considered, then

$$u_{v_1 im}^v \approx \exp[2i\delta_{im}(R_0)] - 1,$$

where R_0 is the equilibrium distance between the nuclei. In this case the sum of all cross sections for rotational transitions from a given state L is equal to the cross section for elastic scattering on a given potential with classical averaging over orientations of the molecule, and again the sum

does not depend on the initial state L :

$$\sum_{L_1} \sigma_{LL_1} = \frac{4\pi}{k^2} \sum_{lm} \sin^2 \delta_{lm} = \overline{\sigma_{el}}. \quad (34)$$

In the last formula and everywhere below, the cross section for the elastic transition $L \rightarrow L$ is included in the sum of the rotational transitions.

5. EXCITATION OF ROTATIONAL STATES OF THE MOLECULES N_2 , O_2 , AND H_2 BY ELECTRON IMPACT

In this section we shall illustrate the application of the method to the specific example of excitation of the rotational states of hydrogen, oxygen, and nitrogen molecules by collisions with electrons. We shall assume that in the collision process the molecule remains in its ground electronic and ground vibrational states. It is clear from expression (30) that in this case, in order to calculate the rotational transition cross sections, it is sufficient to know the phases δ_{lm} for the elastic scattering of electrons at the equilibrium internuclear distance R_0 .

The problem of determining the phases δ_{lm} for the scattering by a potential of the form (13) was solved by Fisk,^[26] who investigated electron scattering by N_2 , O_2 , and H_2 molecules. Fisk assumed a model potential for the interaction of the electron with a molecule, starting from the conditions for best agreement between given statistical calculations and experimental data:

$$V(\xi, \eta) = \frac{8Z}{R} \frac{\xi}{\xi^2 - \eta^2} f(\xi),$$

$$f(\xi) = \begin{cases} 1 - \frac{\xi_0}{\xi} \left(\frac{\xi - 1}{\xi_0 - 1} \right)^2, & \xi < \xi_0, \\ 0, & \xi > \xi_0 \end{cases}, \quad (35)$$

where R is the experimental value of the equilibrium internuclear distance, Z is the effective charge associated with a certain parameter β by the relation $\beta^2 = (1/4)ZR\xi_0$. $\xi_0 = 2$ for molecules of H_2 , N_2 , and O_2 , and the value of β is equal, respectively, to 0.6, 1.32, and 1.35. The atomic system of units is used in formula (35). Correctness of the choice for the potential is confirmed by the good agreement between the elastic scattering cross sections calculated by Fisk and the experimental data in all three cases. Therefore, there is no need here to dwell in more detail on a discussion of the choice for the potential.

In connection with the limitation imposed on the magnitude of c during the derivation of formula (30), the latter is applicable in the interval of incident electron energies below ~ 25 eV. For

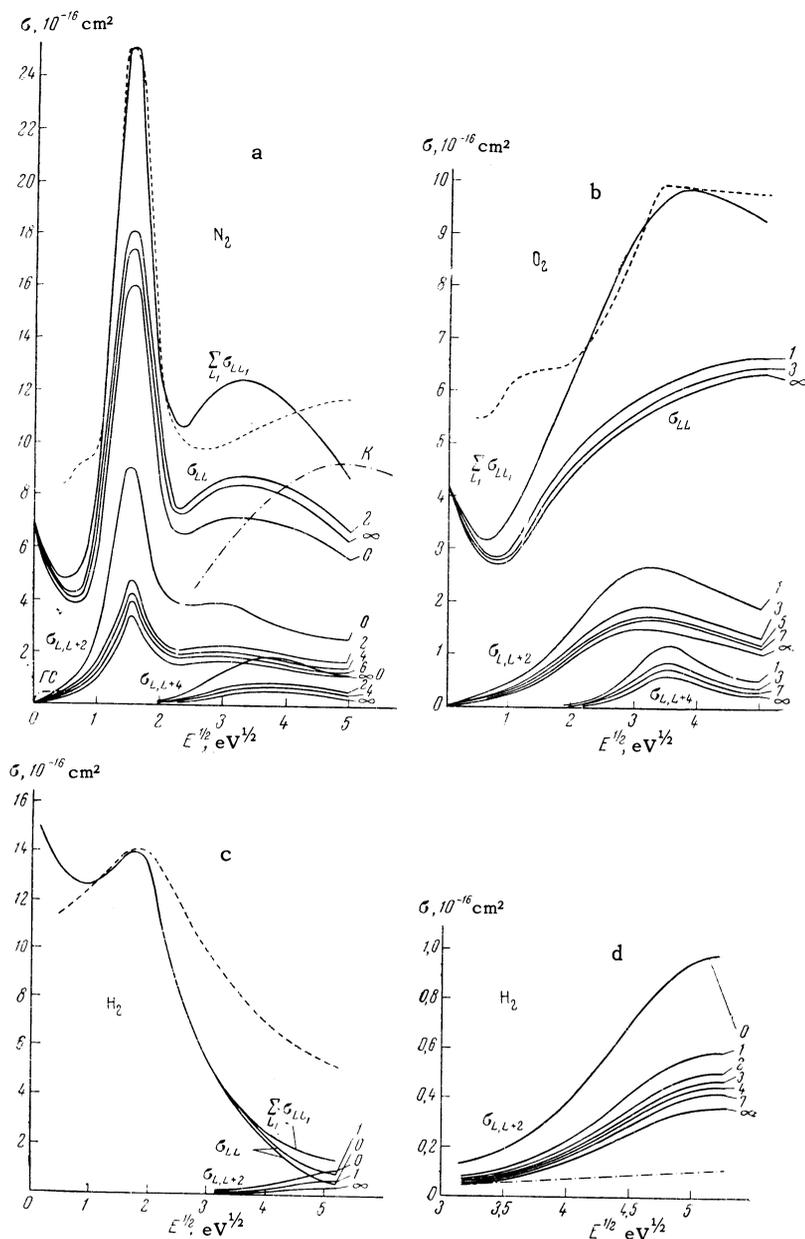


FIG. 1

larger energies, one can perform the calculation using the Born approximation. From formula (30) it is not difficult to obtain numerical values for the cross sections of various rotational transitions, if the appropriate expression for the scattering phase deduced by Fisk^[26] is used. It was found that in the interval of electron energies indicated above, the cross sections for the transitions $L \rightarrow L_1$ decrease markedly with deviation of L_1 from the initial state L . Therefore, the dependence of the cross sections on the velocity of the electrons is given in Fig. 1 only for the transitions $L \rightarrow L$, $L \rightarrow L + 2$, and $L \rightarrow L + 4$. (E is the kinetic energy of an incident electron.) In addition, the total cross sections corresponding to formula (34) and coin-

iding with the elastic scattering cross sections calculated by Fisk, and experimental values for the total scattering cross sections (the dotted curves)^[3, 4, 26] are shown in Figs. 1a, 1b, and 1c. On Fig. 1d in expanded scale are given only the cross sections $\sigma_{L, L+2}$ for hydrogen, since the values of $\sigma_{L, L+4}$ are very small in this case. Even values of L correspond to para-hydrogen, and odd values correspond to ortho-hydrogen. Curves corresponding to even values of the orbital quantum number (the ortho modification of N_2^{14}) are given for the N_2 molecule. In the case of the para modification, the behavior of the curves is similar to that shown in Fig. 1a. The ground electronic state of O_2^{16} corresponds to only odd values of the

orbital angular momentum.^[28] The vertical column of numbers to the right of the curves corresponds to different values of L for a given type of transition. It is easy to obtain the cross sections for the inverse transitions from the relation $\sigma_{L, L_1} = (2L + 1)\sigma_{L_1, L}/(2L + 1)$ (we neglect the difference in energies of the incident and scattered electrons). The energy dependence of the cross section σ_{02} , calculated in the Born approximation for H_2 by Carson^[14], is indicated by the dot-dashed curve in Fig. 1d. The large difference between this curve and the curves of the adiabatic approximation is explained in the first place by the fact that a different potential was chosen to describe the interaction, and in the second place by the fact that the Born approximation is not valid for such small incident electron energies. We note that in the case of nitrogen, the value of the cross section σ_{02} at the maximum (Fig. 1a) agrees with the corresponding value calculated by Kerner^[13] in the Born approximation using an interaction potential close to that calculated by Hund^[29] by a statistical method (curve K, Fig. 1a). However, the maximum cross section obtained by Kerner lies in the region of higher energies (23 eV). Such a discrepancy is again explained by the nonvalidity of the Born approximation in the indicated energy region.

The dot-dashed lines on Fig. 1a represent the values of the cross section σ_{02} for N_2 (the curve labelled GS) obtained by Gerjuoy and Stein,^[15] also in the Born approximation. Moreover, upon expansion of the interaction potential in inverse powers of distance, only one term corresponding to the quadrupole interaction was left. In such an approximation, only the transitions $L \rightarrow L \pm 2$ are different from zero. The formula obtained by Gerjuoy and Stein has the form

$$\sigma_{L, L+2} = \frac{16\pi Q^2 k_1}{45 k_0} c_{L, L+2}^{(2)},$$

$$c_{L, L+2}^{(2)} = \frac{3}{2} \frac{(L+1)(L+2)}{(2L+1)(2L+3)}, \quad (36)$$

where k_0 and k_1 are the wave numbers of the electron in the initial and final states, respectively, Q is the experimentally determined value of the molecular quadrupole moment in atomic units. $\sigma_{L, L+2}$ is also expressed in atomic units. As the authors indicate, formula (36) is valid only for electron energies below ~ 0.6 eV. In this energy region, from expression (30) one can obtain

$$\sigma_{L, L+2} = c_{L, L+2}^{(2)} \sigma_{02}. \quad (37)$$

Thus, the dependence on L of the cross sections for the transitions $L \rightarrow L + 2$ is the same in expressions (36) and (37). An essential difference, how-

ever, becomes apparent in the different velocity dependence of the cross sections. This dependence is shown in Figs. 1a and 1b for σ_{02} from formula (37), but in practice the magnitude of the cross section, determined by expression (36), does not depend on the velocity (with the exception of the region near threshold, where formula (36) is incorrect).

For practical purposes, one can indicate two more formulas which are applicable to the calculation of rotational transition cross sections for electron energies $\lesssim 25$ eV, and which are obtained from the general formula (30) by using the phases calculated by Fisk:

$$\sigma_{L, L+2} = c_{L, L+2}^{(2)} \sigma_{02} + c_{L, L+2}^{(4)} \sigma_{04}, \quad (38)$$

$$\sigma_{L, L+4} = c_{L, L+4}^{(4)} \sigma_{04}, \quad (39)$$

where the quantity $c_{L, L+2}^{(2)}$ is defined above,

$$c_{L, L+2}^{(4)} = \frac{5}{2} \frac{L(L+1)(L+2)(L+3)}{(2L-1)(2L+1)(2L+3)(2L+7)},$$

$$c_{L, L+4}^{(4)} = \frac{35}{8} \frac{(L+1)(L+2)(L+3)(L+4)}{(2L+1)(2L+3)(2L+5)(2L+7)}.$$

The values of σ_{02} and σ_{04} for N_2 and H_2 are given in Figs. 1a and 1d.

6. COMPARISON WITH EXPERIMENT

Since experimental data with regard to direct determination of the cross sections for excitation of rotational states are unknown to us, it is necessary to apply various indirect methods. If it is assumed that, in the energy interval for which the above mentioned results are valid, the probability for excitation of vibrational states gives a small contribution to the total scattering cross section, then the sum of the cross sections $\sum_{L_1} \sigma_{L, L_1}$, calculated from expression (30) and averaged over the rotational states L , must approximately coincide with the experimental value of the total scattering cross section. The first assumption is confirmed by the recent measurements of Schulz for nitrogen,^[7] which give for the total cross section of vibrational excitation a value an order of magnitude smaller than the total cross section for rotational transitions. The total cross section for the scattering of electrons on molecules was measured in many articles,^[3-6] but since the values of the cross sections for the rotational and vibrational excitations were not known, then usually they were assumed to be small and the total cross section was considered to be elastic. As is evident from Fig. 1, the cross sections of the rotational transi-

tions are comparable with the elastic transition cross section. Therefore, it is necessary to compare not the elastic scattering cross section σ_{LL} but the total cross section of rotational transitions (including the elastic transition $L \rightarrow L$ as well) with the measured cross section. As is evident from Eq. (34), $\sum_{L_1} \sigma_{LL_1}$ does not depend on L .

Therefore, in a comparison with experiment, there is no necessity to average this sum over the initial distribution of rotational states. A comparison of the total scattering cross sections (experiment and theory) for N_2 , O_2 , and H_2 molecules is shown correspondingly in Figs. 1a–1c. Experimental values^[3,4,26] are indicated by dotted lines.

Another possible method of comparison consists of an evaluation of the energy losses associated with the passage of electrons through a molecular gas, when the energy of the electrons is so small that the losses are basically associated with the excitation of rotational states. We immediately find that in our case such a comparison may only be qualitative in nature, since the region near the threshold for vibrational excitations is just the lower limit for applicability of the adiabatic approximation. The average energy loss per unit time of an electron beam, due to the excitation of rotational states, can be expressed in the form

$$-\frac{dE}{dt} = v \sum_{LL_1} n_L \sigma_{LL_1} \Delta E_{LL_1}, \quad (40)$$

where v is the velocity of the electrons (assuming that $mv^2/2 \gg \Delta E_{LL_1}$, we shall regard it as constant); ΔE_{LL_1} is the energy difference between the two rotational levels L_1 and L ; n_L is the relative density of molecules existing in the state L at a given temperature. Using the expression $E_L = BL(L+1)$, where B is the rotational constant, and including the transitions $L \rightarrow L \pm 2$, which are most important at low electron energies, we obtain

$$-dE/dt = 6nv\sigma_{O_2}B, \quad (41)$$

where n is the total density of molecules.

The ratio of the total losses to the elastic will be

$$\lambda' = 1 + 6 \frac{B}{E} \frac{\sigma_{O_2}}{\sigma_{LL}} \frac{M}{2m}, \quad \overline{\sigma_{LL}} = \frac{1}{n} \sum_L n_L \sigma_{LL}, \quad (42)$$

where m is the electron mass, M is the mass of the whole molecule. The dependence of the quantity λ' on the electron energy E is given in Fig. 2 for nitrogen. Curves 1 and 4 correspond to average energy losses, determined by measuring the drift velocity of electrons in molecular nitrogen under the action of an electric field. Curve 4 is taken from the book by Massey and Burhop,^[30] and

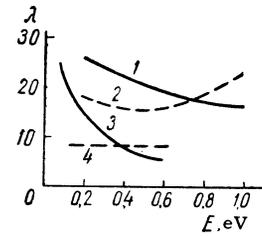


FIG. 2

curve 1 from the data of Crompton and Sutton.^[31] Here the average value of the electron's energy is plotted along the axis of abscissas. Curve 3 corresponds to the above mentioned calculations by Gerjuoy and Stein,^[15] and curve 2 corresponds to the results of the present article. As is evident from the Figure, the average value of the energy losses, calculated on the basis of formula (30), does not differ very much from the experimental data.^[30]

A tendency towards an increase in the value of λ' to the side of very small electron energies is observed in both indicated cases. One can explain the discrepancy between the theoretical and experimental curves by the remark cited above with regard to the limit for applicability of the adiabatic approximation at low energies. It is easy to explain the increase of the experimental curve towards the side of larger energies by an increasing contribution coming from excitation of vibrational states. The measured values of the energy losses in oxygen appreciably exceed the calculated values, and therefore are not given. It is easy to understand this, if the following fact is taken into account: the excited electronic levels nearest to the ground state of the O_2 molecule lie altogether at ~ 1 eV above the ground level, and among the electrons possessing an even lower average energy, there are many such whose energy is greater than 1 eV and which thus introduce a significant contribution to the cross section.

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