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*Note.* The prediction made in the present paper that drift can occur in an isotropic mixture in which the role of the buffer gas is played by one of the isotopes has recently been experimentally confirmed by Panfilov *et al.* [*JETP Lett. Fiz.* **33**, 80 (1981) in the isotopic mixture  $^{12}\text{CH}_3\text{F} + ^{13}\text{CH}_3\text{F}$ . From the experimental data Panfilov *et al.* determined the relative collision frequency difference, and found it to be equal to  $\Delta\nu/\nu = 10^{-2} - 10^{-3}$ . The theoretical estimate, carried out by us on the basis of (1.4) and the assumption that  $\Delta\nu \sim \sigma_{\text{ex}}^{\pm}$ , given the same order of magnitude for  $\Delta\nu/\nu$ .

Translated by A. K. Agyei

## Quasiclassical representation for the cross sections for vibrational excitation of molecules by slow electrons

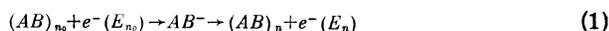
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(Submitted 1 August 1980)  
*Zh. Eksp. Teor. Fiz.* **80**, 982-991 (March 1981)

Approximate (quasiclassical) formulas are derived which allow the computation of the cross section for vibrational excitation of a diatomic molecule in the ground vibrational state in a resonance collision with a slow electron. A numerical comparison of these formulas with Herzenberg's quantum-mechanical calculation for the case of the scattering of an electron of energy  $\sim 2.3$  eV by molecular nitrogen is carried out. A comparison with experiment shows that the formulas of the present paper are almost as accurate as the results of the exact calculation.

PACS numbers: 34.80.Gs

The vibrational excitation of diatomic molecules by slow electrons has been the subject of many experimental and theoretical investigations (see, for example, Schulz's<sup>1</sup> and Lane's<sup>2</sup> review articles). It is well known that the majority of the experimental data are well accounted for (both qualitatively and quantitatively) within the framework of the idea that the molecular-ion states, which determine the resonance character of the inelastic processes, are quasistable states. It is assumed that there is formed as a result of the interaction of an electron with a molecule in the ground vibrational state  $n_0$  an intermediate negative ion that decays into the final reaction products<sup>1</sup>:



(the electron energies are indicated in the brackets, and the energy conservation law for "molecule + electron" system relates  $E_{n_0}$  and  $E_n$ :

$$E = E_{n_0} + \epsilon_{n_0} = E_n + \epsilon_n,$$

where  $\epsilon_n$  is the energy of the molecule in its  $n$ th vibrational state).

If the lifetime of the group  $AB^-$  is short compared to the vibration period of the molecule  $AB$ , then the energy dependence of all the processes exhibits normal resonance. If, on the other hand, the lifetime of the group is comparable to the period of the molecular vibrations, then the absorption and emission of the electron in the process (1) occur at different internuclear

distances, and there appear in the resonance curve oscillations connected with interference phenomena in the motion of the nuclei.

A method for the theoretical investigation of the processes of inelastic resonance electron scattering by diatomic molecules has been proposed by a number of authors.<sup>3-6</sup> The basic equation in this theory is a Schrödinger-type inhomogeneous equation that, after the separation of the angular dependences, assumes the following form:

$$\left( -\frac{1}{2M} \frac{d^2}{dR^2} + W(R) - E \right) \xi(R) = -\zeta_0(R) V(R). \quad (2)$$

Here  $M$  is the reduced mass of the atoms constituting the molecule;  $R$  is the internuclear distance;  $W(R)$  is the molecular-ion term [it becomes quasistationary at  $R$  less than some  $R_1$ :  $W(R) = U_I(R) + i\Gamma(R)/2$ , where  $\Gamma(R) > 0$  is the width of this term];  $V(R)$  is the auto-ionization amplitude of the molecular ion:  $V(R) = [4\pi^2\Gamma(R)/mk(R)]^{1/2}$ , where  $k(R) = [2m(U_I(R) - U(R))]^{1/2}$  is the momentum of the electron emitted by the molecule at an internuclear distance of  $R$ ;  $U$  denotes the term of the neutral molecule and  $m$  is the electron mass. The function  $\xi(R)$ , determined by Eq. (2) with natural boundary conditions, is the wave function for the nuclear motion in the molecular ion;  $\zeta_0(R)$  is the wave function for the nuclear motion in the initial (i. e., ground) vibrational state of the molecule.

To determine the cross section for the process (1),

we must compute the integral

$$\sigma_{0 \rightarrow n} = \frac{v_n m^2}{v_0 8\pi^2} \left| \int \xi_n(R) \zeta_n(R) V(R) dR \right|^2, \quad (3)$$

where  $\xi_n(R)$  is the wave function of the vibrational motion of the nuclei in the final state of the molecule,  $v_0$  and  $v_n$  are the initial and final electron velocities respectively.

The main physical assumption used in the derivation of Eq. (2) is the assumption that the relaxation of the electron shell of the  $AB^-$  group is a fast one when all the electrons of this group are considered on an equal basis.<sup>6</sup> Another approach to the investigation of the processes under discussion, which is based on a system of tight-binding equations (formally equivalent to the complete Schrödinger equation for the "molecule + electron" system), requires the separation of the incoming electron from the shell of the group, with the result that the re-establishment of its equality to the other electrons requires the consideration of a large number of states. The unnaturalness of such a separation is manifested in the slow convergence of the results as the number of equations of the system is increased.<sup>7</sup>

The quantities  $U_I(R)$  and  $\Gamma(R)$ , entering into Eq. (2), can be computed only for the simplest systems, e. g., for the  $N_2$  molecule<sup>8,9</sup>; therefore, in the majority of cases these quantities are parametrized. The computational method based on Eq. (2) has been used to investigate the vibrational excitation of the molecules  $N_2$  (Refs. 4 and 10), CO (Ref. 11), and  $CO_2$  (Refs. 12 and 13). In all the indicated papers this equation was numerically integrated with a properly chosen  $W(R)$  function. Although we do not encounter any fundamental difficulties in this approach, we nevertheless have to deal with rapidly oscillating functions, and this complicates the computations.

The problem is solved exactly in Ref. 14 for the particular case in which  $U(R)$  and  $U_I(R)$  are parabolic functions with the same frequency and the term is of constant width. A similar exactly soluble model has also been constructed by Domcke and Cederbaum.<sup>13</sup> These two models give only a qualitative agreement with experiment, since the assumption that the term width is independent of the internuclear distance does not, as pointed out in Ref. 4, allow us to correctly reproduce the experimental results.

In the present paper we offer an analytical, though approximate (quasiclassical) representation for the cross sections for inelastic excitation of a molecule from the ground vibrational state. This representation does not assume significant limitations on the term  $W(R)$ , does not contain integration operations involving rapidly oscillating functions (the importance of the exclusion of this operation is pointed out in Ref. 15), and it is fairly graphic from the physical point of view. Strictly speaking, the analytical expressions proposed for the cross sections for the inelastic processes are valid only in the asymptotic region  $M \gg 1$ , where their accuracy can be assessed only after the next term in the asymptotic expansion has been analyzed. There-

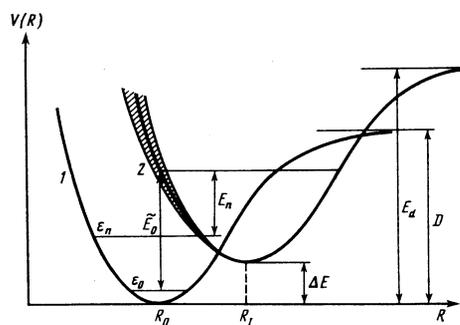


FIG. 1. Potential energy of the neutral molecule (1) and the real part of the molecular ion's energy (2) as functions of the internuclear distance. The hatched area conditionally indicates the width arising to the left of the point of intersection of the potential curves.

fore, to verify the accuracy of the formulas proposed below, we carried out a comparison of the results obtained on their basis with the results of Ref. 14; the accuracy of the quasiclassical formulas turned out to be fairly good.<sup>16</sup>

It is well known that the quasiclassical approximation leads to graphic—from the physical point of view—results. In the present case the inelastic electron scattering process can be regarded as occurring in three stages: the capture of the electron by the molecule with the formation of a compound system, the motion of this system (in the non-eigenstate), and its dissociation. The capture of an electron by a molecule in its ground state occurs in the vicinity of the equilibrium point  $R_0$  of the molecule, and its probability  $|I_1|^2$  is determined by the overlap integral for the wave functions of the ground state of the molecule and the state of the molecular ion. This probability has a maximum at an electron energy close to  $\bar{E}_0$  (Fig. 1), and can, in the simplest case, be represented by the square of the Airy function [see (17)]. The decay of the compound system into the channel connected with the  $n$ -th vibrational state of the molecule occurs in the vicinity of the point of intersection of the molecular ion's term lowered by the magnitude of the energy of the outgoing electron and the neutral molecule's term; the probability  $|I_2|^2$  for this process is determined by the corresponding Franck-Condon factor. The motion of the compound system from the "point" of its formation to the "point" of its dissociation occurs in a state corresponding to forced oscillations. Therefore, the final formula (its derivation is given below)

$$\sigma_{0 \rightarrow n} = \frac{v_n m^2}{v_0 8\pi^2} \frac{|I_1|^2 |I_2|^2}{|Q|^2} \quad (4)$$

contains the denominator

$$|Q(E)|^2 = \frac{1}{4M^2} \left| \sin \left( \int_{a^-}^{b^-} [2M(E-W)]^{1/2} dz - \frac{\pi}{2} \right) \right|^2 \quad (5)$$

( $a^-$  and  $b^-$  are the left and right turning points for a compound system moving with energy  $E$  in the potential well  $W(R)$ ,  $a^-$  being a complex point).

Let us consider the effect of the above-indicated factors on the behavior of the vibrational-excitation cross

section as a function of the energy  $E$ . The factors  $|I_1|^2$  and  $|Q|^{-2}$  are not related with the final-channel number, and this dependence is entirely concentrated in the factor  $|I_2|^2$ . The dependence of  $|I_1|^2$  on the energy  $E$  determines the behavior of the cross section averaged over its oscillations. These oscillations are determined by the factors  $|Q|^{-2}$  and  $|I_2|^2$ . If the width of the term is small, then the equation  $Q=0$  has roots located near the real axis (these roots are evidently determined by the Bohr-Sommerfeld condition). Therefore, the cross section for small  $\Gamma$  has the ordinary Breit-Wigner anomalies in the neighborhood of the auto-ionization levels of the molecular ion. For large  $\Gamma$  the expression for  $Q^{-1}$  can be expanded in a series in powers of the quantity

$$\exp\left(-\text{Im}\int_{a^-}^{b^+} [2M(E-W)]^{1/2} dz\right),$$

the  $k$ -th term of this expansion representing the probability for decay of the system after completing  $k/2$  complete vibrations. This representation corresponds to the "boomerang" model.<sup>4,10</sup> For large  $\Gamma$  the denominator in (4) does not have a significant influence on the oscillations of the cross sections, and the structure of the cross sections is determined by the Franck-Condon factor  $|I_2|^2$ . Physically, the oscillations of this factor are due to the interference of the states corresponding to the decay of the compound system as it moves in the vicinity of the decay point in opposite directions. These oscillations have been discussed both in connection with the boomerang model<sup>3,4</sup> and in the adiabatic theory,<sup>17</sup> as well as in the particular problem of the escape of the term across the tilted boundary of the continuous spectrum.<sup>18</sup> The transition from the Breit-Wigner behavior of the cross sections to the observed behavior is qualitatively discussed in Drukarev's monograph.<sup>19</sup>

Let us now proceed to the derivation of the formula (4), which is the main result of the present paper. Let us consider the inhomogeneous equation (2), which determines the radial wave function for the nuclear motion in the molecular ion, and construct the corresponding Green function. To do this, we introduce the functions  $\chi_1$  and  $\chi_2$  satisfying the equation

$$\left[-\frac{1}{2M}\frac{d^2}{dR^2} + W(R) - E\right]\chi_i(R) = 0; \quad i=1,2 \quad (6)$$

and the boundary conditions:  $\chi_1=0$  for  $R=0$  and  $\chi_2 \rightarrow 0$  as  $R \rightarrow \infty$ . The latter condition implies that the total energy of the system is lower than the energy  $E_d$  of dissociation of the molecular ion (see Fig. 1), we do not consider the process of dissociative attachment.

The Green function for Eq. (2) can be represented in the form

$$G(R, R') = \chi_1(R_-)\chi_2(R_+)/Q(\chi_1, \chi_2),$$

where

$$Q(\chi_1, \chi_2) = \frac{1}{2M}(\chi_1'\chi_2 - \chi_1\chi_2')$$

is the Wronskian of the functions  $\chi_1$  and  $\chi_2$ . The Green function allows us to represent the solution (2) in the

following form:

$$\xi(R) = - \int_{-\infty}^{\infty} G(R, R') \xi_0(R') V(R') dR'$$

[the value of the lower integration limit is of little importance because of the rapid decrease of the function  $G(R, R')$  to the left of the turning point of the compound system]. For the  $0 \rightarrow n$  transition cross section we obtain

$$\begin{aligned} \sigma_{0 \rightarrow n} &= \frac{v_n}{v_0} \frac{m^2}{8\pi^3} \left| \int dR V(R) \xi_n(R) \int dR' G(R, R') V(R') \xi_0(R') \right|^2 \\ &= \frac{v_n}{v_0} \frac{m^2}{8\pi^3} |I|^2 |Q|^{-2}. \end{aligned} \quad (7)$$

Let us express the integral  $I$  in (7) in terms of the functions  $\chi_1$  and  $\chi_2$ :

$$\begin{aligned} I &= \int_{-\infty}^{\infty} dR \xi_n(R) V(R) \left[ -\chi_2(R) \int_{-\infty}^R V(R') \chi_1(R') \xi_0(R') dR' \right. \\ &\quad \left. - \chi_1(R) \int_R^{\infty} V(R') \chi_2(R') \xi_0(R') dR' \right]. \end{aligned} \quad (8)$$

The molecular ion's auto-ionization amplitude  $V(R)$ , which is an adiabatic characteristic of the system, does not depend on the large parameter  $M$ , and is a slowly varying function of the internuclear distance. In view of the localized character of  $\xi_0(R)$ , the integrals over  $R'$  give a steplike function. On the other hand, the integral over  $R$  will, because of the relatively rapid oscillation of the functions  $\xi_n$  and  $\chi_i$ , be determined by the saddle point—the Franck-Condon transition point  $z_{FC}$  ( $z_{FC}$  is complex). We shall assume that this point lies to the right of  $R_0$  and is sufficiently far from it. (This is an additional, though quite a natural, assumption; we shall adhere to it in the present paper.)

Let us, on account of the foregoing, retain only the first term in (8), extending the integration range to infinity<sup>2)</sup>:

$$I = -I_1 I_2; \quad (9)$$

$$I_1 = \int_{-\infty}^{\infty} dR' \xi_0(R') V(R') \chi_1(R'), \quad (10)$$

$$I_2 = \int_{-\infty}^{\infty} dR \xi_n(R) V(R) \chi_2(R). \quad (11)$$

The integral  $I_1$  is evidently connected with the compound-state formation process;  $I_2$ , with the decay of the state.

Let us construct the functions  $\chi_1$  and  $\chi_2$  introduced above with the aid of the WKB method.<sup>20</sup> To apply this method, we must construct the asymptotic solution to the equation in the vicinity of its turning points. Equation (6) has two (generally speaking, complex) turning points. In the case depicted in Fig. 1, one of the turning points is located on the real axis, and corresponds to the right stopping point of the molecular ion; the second turning point turns out to be shifted into the lower half-plane. If, on the other hand, the minimum of the molecular ion's term is shifted into the instability region, then, for a sufficiently low total energy,  $E$ , of the system, the right turning point also leaves the real axis and goes into the upper half-plane. Figure 2 shows the disposition of the turning points for the case depicted in

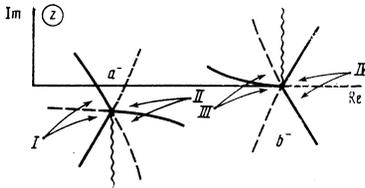


FIG. 2. Position of the turning points of Eq. (6) in the  $z$  plane in the case corresponding to Fig. 1. The local behavior of the Stokes lines (the dashed lines) and the conjugate Stokes lines (the solid lines) is shown. The wavy lines indicate the branch cuts in the complex plane.

Fig. 1, together with the various asymptotic region separated by the Stokes lines.

The functions  $\chi_1$  and  $\chi_2$  that are of interest to us can be obtained by continuing the solutions to (2) that decrease in the sectors I and IV, respectively. As a result, we obtain the following representation for these functions:

$$\chi_1(z) = \begin{cases} \frac{1}{2} [2M(W-E)]^{-1/2} \exp\left(\int_a^- z [2M(W-E)]^{1/2} dz\right), & z \in \text{I}, \\ [2M(E-W)]^{-1/2} \cos\left(\int_a^- z [2M(E-W)]^{1/2} dz - \pi/4\right), & z \in \text{II}, \end{cases}$$

$$\chi_2(z) = \begin{cases} [2M(E-W)]^{-1/2} \cos\left(\int_z b^- [2M(E-W)]^{1/2} dz - \pi/4\right), & z \in \text{III}, \\ \frac{1}{2} [2M(W-E)]^{-1/2} \exp\left(\int_z b^- [2M(W-E)]^{1/2} dz\right), & z \in \text{IV}. \end{cases} \quad (12)$$

Here  $a^-$  and  $b^-$  are the left and right stopping points (see Fig. 2). The Wronskian for these functions can be computed at the intersection of the regions II and III; the calculation leads to the expression

$$Q(\chi_1, \chi_2) = -\frac{1}{2M} \sin\left(\int_a^- b^- [2M(E-W)]^{1/2} dz - \frac{\pi}{2}\right).$$

As the wave function of the ground state, we can naturally choose the normalized wave function of the ground state of an oscillator:

$$\zeta_0 = \left(\frac{M\omega}{\pi}\right)^{1/4} \exp\left(-\frac{M\omega}{2}(R-R_0)^2\right) \quad (13)$$

( $\omega$  is the vibration frequency of the molecule). We shall assume the wave function of the final state to be quasi-classical:

$$\zeta_n(R) = \frac{(2\omega M/\pi)^{1/4}}{[2M(\epsilon_n - U)]^{1/4}} \cos\left(\int_z^b [2M(\epsilon_n - U)]^{1/2} dz - \frac{\pi}{4}\right). \quad (14)$$

Here  $b$  is the right turning point in the molecule's well and  $\epsilon_n$  is the final-state energy of the molecule.

Let us substitute the representations (13) and (14) into (10) and (11). The integral  $I_2$  is computed by the method of steepest descent:

$$I_2 = \frac{(2\omega M/\pi)^{1/4} V(z_{FC})}{2[2M(E-W(z_{FC}))]^{1/2}} \left(\frac{2\pi}{\Psi''(z_{FC})}\right)^{1/2} \cos\left(\Psi(z_{FC}) - \frac{\pi}{4}\right), \quad (15)$$

$$\Psi(z) = \int_z^b [2M(E-W)]^{1/2} dz - \int_z^b [2M(\epsilon_n - U)]^{1/2} dz,$$

and the saddle point  $z_{FC}$  is determined from the equation  $\epsilon_n - U(z_{FC}) = E - W(z_{FC})$ , i. e., for a small  $W(R)$  term width it is close to the point of intersection of this term with the molecule's potential curve raised by the magnitude of the energy of the emitted electron.

The computation of the integral  $I_1$  is a more complex problem. We can, depending on the total energy  $E$  of the system, distinguish three cases of electron capture by the molecule.

1)  $E < \bar{E}_0 + \epsilon_0$  (see Fig. 1). In this case the molecular ion is formed in the region that, classically, is forbidden to it. The probability for the process in this region is exponentially small because of the barrier factor.

2)  $E > \bar{E}_0 + \epsilon_0$  (see Fig. 1). After the capture, a compound system is formed at a point far from a turning point in the region of classically allowed motion. Numerical computations show that the contribution of this energy region to the total inelastic cross section is fairly small.

3) The intermediate case  $E \sim \bar{E}_0 + \epsilon_0$ , in which the electron energy is such that the molecular ion is formed in the vicinity of a turning point. This case is the most important. It is precisely this case that we shall discuss in detail; the remaining cases have already been investigated.<sup>16</sup>

To compute the integral  $I_1$  in this case, we need a sufficiently exact representation for the function  $\chi_1$ . Its expression in terms of the Airy function, which is connected with the linear interpolation of the term  $W(R)$ , is the simplest of such representations. It is possible to apply two such interpolations: one connected with the expansion of  $W(R)$  around the point  $R_0$ ; the other, with the expansion of  $W$  around the stopping point,  $a^-$ , of the compound system. Below we carry out the computations for the latter case; the formulas for the first case are similar.

Let us limit ourselves to the first two terms in the expansion of  $W(R)$  around the point  $a^-$ :

$$W(R) = W(a^-) - F(R - a^-). \quad (16)$$

(Here  $F = -dW/dR|_{R=a^-}$ .)

By replacing  $\chi_1$  by the appropriate Airy function, we can compute the integral  $I_1$  in the explicit form

$$I_1 = CV(R') \exp\left\{\frac{F^2}{3M\omega^3} + \frac{a^- - R_0}{\omega} F\right\} \Phi(\eta), \quad (17)$$

where  $\Phi(\eta)$  is the Airy function of the shifted argument

$$\eta = (2MF)^{1/2} \left(\frac{F}{2M\omega^2} + a^- - R_0\right).$$

The coefficient  $C$  is determined by comparing the expression (17) with the result of the  $I_1$  computation in the subbarrier region.<sup>16</sup> We obtain for it the expression

$$C = \frac{2^{1/2} \pi^{1/4}}{M^{-1/2} \omega^{-1/2} F^{-1/2}}.$$

In deriving the formula (17), we assumed that  $V(R)$  is a smoothly varying function of its argument [ $V(R)$  was assumed to be a constant in the comparison of the calculations carried out in Ref. 16 with the results of Ref. 14]; the value of  $R'$  for small  $E$  lies between  $R_0$  and  $a^-$ .

We shall return to this question in the discussion of specific calculations; it will become clear then that the problem of the ambiguity in the choice of  $R'$  is less crucial in the case of higher  $E$ .

The representation (4) was varied by using it to compute the cross sections for vibrational excitation of the  $N_2$  molecule. These cross sections have been repeatedly computed before, and the results closest to the experimental data were obtained by means of a numerical integration of Eq. (2).<sup>10</sup> The molecule's terms and the real part of the molecular ion's term were given as follows:

$$U(R) = U(R_0) + D\{1 - \exp[-\beta(R - R_0)]\}^2; \quad \beta = (M/2D)^{1/2}\omega; \quad (18)$$

$$U_i(R) = U_i(R_i) + D_i\{1 - \exp[-\beta_i(R - R_i)]\}^2; \quad \beta_i = (M/2D_i)^{1/2}\omega_i.$$

In these formulas  $\omega$  and  $\omega_i$  are the vibration frequencies and  $D$  and  $D_i$  are the dissociation energies of the molecule and the ion respectively;  $D_i = E_d - \Delta E$  (see Fig. 1).

The function  $\Gamma$  for the case under consideration of the  ${}^2\Pi_g$  resonance of  $N_2^+$  can be represented in the form<sup>10</sup>

$$\Gamma(R) = \Gamma(R_0) \frac{k(R)v_l[k(R)\rho]}{k(R_0)v_l[k(R_0)\rho]},$$

where  $v_l$  is the barrier factor; in the present case  $l = 2$  and

$$v_2(x) = \frac{x^4}{9 + 3x^2 + x^4};$$

$\rho$  is the ion "radius" (the distance from the center of mass starting from which the centrifugal potential predominates over the Coulomb and polarization interactions between the electron and the molecule).

The parameters of the problem, which were taken from Ref. 11, have the following values:  $R_f - R_0 = 0.0825 \text{ \AA}$ ,  $\Delta E = U_f(R_f) - U(R_0) = 1.912 \text{ eV}$ ,  $\Delta\hbar\omega = \hbar\omega - \hbar\omega_f = 0.049 \text{ eV}$ ,  $\hbar\omega_f = 0.244 \text{ eV}$ ,  $D_f = 11.961 \text{ eV}$ ,  $\Gamma(R_0) = 0.54 \text{ eV}$ , and  $\rho = 1.41 \text{ \AA}$ .

It was found in the course of the computations with the formulas (4) and (18) that the position of the minima and maxima in the cross sections, as determined by the "free play" in the factors  $|I_2|^2$  and  $|Q|^2$ , agrees well with Ehrhardt and Willmann's<sup>21</sup> experimental data and the results of Dubé and Herzenberg's<sup>10</sup> calculations. On the other hand, the relative magnitude of the maxima and minima turns out to be sensitive to the type of interpolation chosen for the molecular ion's term in the  $I_1$  computation. For  $E = \tilde{E}_0 + \epsilon_0$ , this integral is determined by a broader range of variation of the internuclear distance  $R$  than is the case for the integral  $I_2$ , since the compound system formed upon the capture of the electron moves more slowly at the initial moment than at the moment of its decay.

In Fig. 3 we present the results of the calculations for  $N_2$  with  $V$  computed at the turning point  $a^-$ , and compare them with the exact quantum-mechanical calculation.<sup>10</sup> The agreement between the results can be considered to be satisfactory. It is not difficult to estimate the effect of the factor  $V(R')$  as a function of  $R'$ . For low  $E$  (within the limits of the first peak),  $|V(a^-)|^2$  differs from  $|V(R_0)|^2$  by 20%. This is the maximum

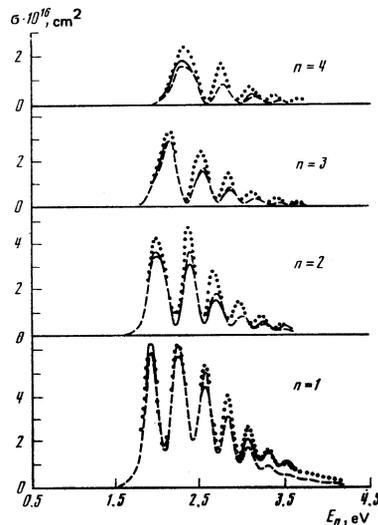


FIG. 3. Dependence of the vibrational-excitation cross sections,  $\sigma_{0 \rightarrow n}$ , for the nitrogen molecule on the energy of the incoming electron for  $n = 1-4$ ; the dashed curves represent the results of the calculations performed in Ref. 10 (the  $\sigma_{0 \rightarrow n}$  curves are normalized on the basis of the  $\sigma_{n \rightarrow 0}$  values given in Ref. 10 with allowance for the principle of detailed balance); the solid lines are the curves computed from the formula (4) of the present paper (the curves have been drawn in those regions where they deviate from the dashed curves); the dotted curves are Ehrhardt and Willmann's<sup>21</sup> experimental curves.

error (let us recall that the point  $R'$  lies between  $R_0$  and  $a^-$ ), and can be reduced if we use the linear approximation for  $V(R)$ .

In conclusion, let us point out that we can, within the framework of the method, raise the accuracy of the computation of the factor  $I_1$  by using in the determination of  $\chi_1$  a quadratic interpolation for  $W(R)$ . Let us also note that it is possible to compute with the aid of the proposed method the cross sections for transitions between the excited vibrational states.

The authors are grateful to G. F. Drukarev for constant interest in the work.

- 1) It is assumed that the electronic state of the molecule is the ground state; in the course of the scattering this state remains unchanged.
- 2) It is not difficult to show that the error that this extension gives rise to is small.

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Translated by A. K. Agyei

## Investigation of excitation transfer in the system He( $2^3S_1$ ) + Ne( $2^1S_0$ ) by the method of optical orientation of atoms

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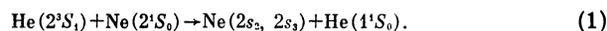
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The method of optical orientation of atoms has been used to investigate the process of excitation transfer from helium atoms in the triplet metastable state to neon atoms. It turns out that this process has a cross section of  $\sigma = 0.35 \text{ \AA}^2$  at  $T = 300 \text{ K}$  and  $\sigma = 0.06 \text{ \AA}^2$  at  $T = 178 \text{ K}$ . Analysis of the experimental data within the framework of the Rosen-Zener-Demkov model allows the determination of the He-Ne system's exchange-interaction potential, which has the form  $\Delta = 8000 \exp(-1.38R)$ .

PACS numbers: 34.20.Fi, 34.50.Ez

### 1. INTRODUCTION

Metastable triplet helium atoms with an excitation energy of 19.82 eV can ionize by collisions at thermal relative-motion energies all atoms except neon, whose ionization potential is 21.56 eV. But the metastable helium atoms lose their excitation in the neon case too. This happens as a result of the transfer of the excitation energy of the  $2^3S_1$  helium state to the nearby  $2s_2$  and  $2s_3$  levels of neon (electronic configuration  $2p^54s$ ):



This process is one of the principal processes that occur in the course of pumping in an infrared helium-neon laser, and quite a large number of papers have been devoted to the determination of its reaction rate.<sup>1-10</sup> The study of this reaction is also of interest from the point of view of the fact that it is not a strictly resonance process: the  $2s_2$  and  $2s_3$  neon levels respectively lie 0.039 and 0.058 eV below the  $2^3S_1$  helium level.

Apropos of the data available in the literature on the magnitude of the reaction rate of the excitation-transfer process (1), we should note two facts:

1) The experiments were performed largely at room temperature. A summary of the data obtained by the various authors is given in Table I, where we give the values of the reaction rate and cross section, given, as usual, by the formulas

$$\sigma = C/2^{\frac{1}{2}} \bar{v}, \quad \bar{v} = (8kT/\pi\mu)^{\frac{1}{2}}, \quad (2)$$

where  $\mu$  is the reduced mass of the He-Ne system. It can be seen from Table I that the data of the various

authors differ considerably from each other.

Temperature investigations have been carried out by Jones *et al.*<sup>5</sup> in the 77-400-K temperature range, Lindinger *et al.*<sup>7</sup> in the 300-800 K range, and Arathoon<sup>8</sup> in the 140-340 K range. It turns out that the reaction rate decreases sharply with decreasing temperature. At the same time, these authors report significantly differing values for both the reaction rate and its rate of change with temperature.

2. In all the experiments, except Beterov and Chebotayev's,<sup>4</sup> the afterglow of a decaying helium-neon plasma was studied. The reaction rate of the process (1) was found by comparing the decay constants of the  $2^3S_1$  helium state (i.e., the rates of decrease of the metastable triplet helium atom concentration in the afterglow) for pure He and a He-Ne mixture. The concentration of the He\*( $2^3S_1$ ) atoms in the afterglow is determined by

TABLE I. Results of experimental investigations of the process of excitation transfer He\* to Ne at  $T = 300 \text{ K}$ .

	$C, 10^{-12} \text{ cm}^3\text{-sec}^{-1}$	$\sigma, \text{ \AA}^2$
Phelps <sup>1</sup>	0.31	0.22
Javan <i>et al.</i> <sup>2</sup>	0.54±0.07	0.37±0.05
Benton <i>et al.</i> <sup>3</sup>	0.39±0.08	0.28±0.06
Beterov and Chebotayev <sup>4</sup>	0.52	0.38
Jones <i>et al.</i> <sup>5</sup>	0.43±20%	0.31±20%
Schmeltekopf <i>et al.</i> <sup>6</sup>	0.385±30%	0.28±30%
Lindinger <i>et al.</i> <sup>7</sup>	0.36±30%	0.26±30%
Arathoon <sup>8</sup>	0.72	0.52
Lee and Collins <sup>9</sup>	<0.7	<0.51
Ernie and Oskam <sup>10</sup>	0.43	0.31