

able choice of the spectral resolution  $\eta$  it is possible to narrow down substantially the lines in the transient spectrum [effects of cancellation of the registration width and the decay width (HL) or the exciting width (resonant Raman scattering)]. In addition, we have shown that the line shape also changes greatly with time. Thus, in the region of intermediate times  $t$  there can be observed oscillations on the wings of certain lines. All this is evidence of the variety of properties of quasi-line transition spectra and the large amount of information that they contain.

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<sup>1</sup>A similar narrowing of the emission line with increasing  $t$  was obtained in Ref. 2 for the particular case  $\Gamma_1 L_2 = 0$  as applied to a purely electronic OL line.

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## Excitation of molecule vibrations in resonant scattering of electrons

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A general approach is proposed for finding the cross section for vibrational excitation of molecules by slow electrons in the resonance region. The approach is based on the formalism of time-dependent perturbation theory. An expression is obtained for the cross section of vibrational excitation of diatomic molecules in the limiting case of two-atom molecules using a classical description of the motion of the nuclei in molecular particles. The calculation results obtained within the framework of various approximations are compared with one another and with the experimental data in the case of  $N_2$  molecules.

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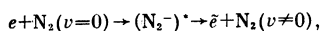
1. The possibility of formation of self-detached (resonant) states of an electron when scattered by molecules influences substantially the cross sections of their vibrational excitation in definite collision-energy ranges.<sup>1</sup> A characteristic feature of these cross sections is the peaked structure of the  $\sigma(\varepsilon)$  curves in the

indicated region of the incident-electron energies  $\varepsilon$ , when the cross sections at the maxima can exceed by several orders of magnitude the cross section in the region off resonance, where it varies smoothly with  $\varepsilon$ . The indicated peaks of the cross-section curves can vary greatly in shape and range from very broad ones

(of the order of 10 eV and more) to medium ones (several eV) and very narrow ones, and they can come either in groups or be solitary and far from one another (in the case of the  $N_2$  molecule, for example, they are observed in the range  $\varepsilon \sim 2-20$  eV, Ref. 2).

From the phenomenological point of view, the most important parameter of the self-detached state is its lifetime  $\tau$ , which is connected with the width of the decay level  $\Gamma$  by the relation  $\tau \sim \hbar/\Gamma$ . In final analysis, the transitions between the vibrational levels of the molecule are initiated precisely by the capture of the electron by the molecule and by the increase in the time of its stay near the target, compared with the time of flight of the electron past the molecule without formation of an intermediate state of the excited molecular ion (the latter time is of the order of  $a_0(m_0/e)^{1/2}$ ). In other words the "resonant" interaction of the incident wave of the electron with the field of the molecule starts the transitions. The presently available theoretical papers make use, to one degree or another, of the relation between the lifetime  $\tau$  of these resonant states, the typical times of vibrations of the nuclei in the molecular particles, and the time of flight of the electron past the molecule without formation of an intermediate molecular-ion state. We confine ourselves henceforth to resonant states whose lifetime is comparable with the time of vibration of the nuclei and greatly exceeds the free flight time of the electron, thus, when  $\tau \geq 10^{-15}$  sec. Resonances of this type are observed at the minimal electron energy (at 2-3 eV in the case of  $N_2$ ) and are apparently single-particle resonances while the energy curves of the cross sections of the vibrational excitation of the molecules are characterized by a set of closely spaced narrow peaks.

The presently accepted explanation of this effect introduces the following reaction scheme:



i.e., it is based on the concept of the intermediate (decay) state of the negative molecular ion  $(N_2^-)^*$  ( $v$  is the number of the vibrational level).

Although more than a dozen of theoretical papers have by now been published on the description of single-particle resonance in the scattering of electrons by molecules and contain calculations of the cross sections of their vibrational excitation, it seems to us that there are still a number of fundamental questions left to be answered. This is due both to the difficulties involved in constructing a general theory of the considered process,<sup>3-5</sup> and to the insufficient development of model solutions<sup>6,7</sup> that could provide distinct limiting relations for a general theory.

Among the basic papers we must single out that of Chen,<sup>3</sup> who developed a formal theory of the scattering of slow electrons by molecules with account taken of the contribution of the intermediate (decay) states of the negative molecular ion. These states are due to resonant interaction of the incident wave of the electron with the field of the molecule in electron-excited states, and the energy of these states corresponds to poles of a certain effective scattering potential. However, the

simplifying assumptions made in the course of the derivation of an equation for the cross section of the vibrational excitation of the molecule by electron impact (for example, the assumptions that the wave function of the electron is independent of the distance between nuclei in the target nucleus, that a single isolated resonance exists, that a number of off-diagonal matrix elements of the perturbation operator vanish, that the coupling between the intermediate states of the negative molecular ion and the state of motion of the nuclei in the molecule can be neglected) do not permit a definite judgment to be made concerning the limits of applicability of the relations derived in Ref. 3, concerning the order of their approximation, and concerning the possibility of using them without including empirical parameters that characterize the widths  $\Gamma$  of the decay levels of the electron in the excited molecular ion.

Among the papers in which a model solution of the problem is analyzed, mention can be made of Ref. 7. It contains a derivation of an expression for the cross section of the vibrational excitation of the molecule, with consistent use of the concept of both "instantaneous" dynamics of the process of electron capture by the molecule and the decay of the resonant state. It was assumed there that the times of formation and decay of this state are much shorter than the lifetime  $\tau$  of the level and the period of the vibrations of the nuclei in the molecular ion. The result was an equation for the cross section of the vibrational excitation of the molecule, but without a solution of the corresponding equations of motion in the field of the molecule, using only a heuristic form of the wave function of the electron + molecule system for the special case when the width of the decay level of the ion is independent of the distance  $R$  between the nuclei,  $\Gamma(R) = \text{const}$ . However, the formula obtained in this limit for the cross section of the vibrational excitation differed from Chen's result<sup>3</sup> in that it contained a different dependence on the vibrational states of the nuclei in the molecule and in the negative molecular ion.

In the present paper we develop a general approach to the solution of the problem of determining the cross section of the vibrational excitation of molecules by slow electrons. We use a simpler technique of calculations, different from that of Ref. 3 (the Feshbach formalism of generalized Green's functions), which eliminates a number of the restrictions of the cited paper. The limiting case of a constant width  $\Gamma(R)$  of the decay level is investigated in greater detail. The cause of the contradictions between the results of the two cited articles (Refs. 3 and 7) for the cross sections of the vibrational excitation of the molecule is discussed. This is followed by construction of a theory of resonant excitation of molecules using a classical description of the motion of the nuclei in the molecular particles. The results of the quantum-mechanical and classical calculations of the cross sections of the vibrational excitation of the molecules by the electrons are compared under the condition that  $\Gamma(R)$  is constant. These data are compared with the experimental relations obtained for the cross sections of the vibrational excitation of  $N_2$  molecules by slow electrons.

2. We present the total Hamiltonian of the electron plus molecule system in the form of a sum

$$\hat{\mathcal{H}} = \hat{T} + H_0 + \hat{V},$$

where  $\hat{T}$  is the operator of the kinetic energy of the nuclei, the operator  $\hat{H}_0$  is characterized by definition by a continuous spectrum of the eigenvalues of the incident electron and by the stationary state of the negative molecular ion in the continuous spectrum, while the operator  $\hat{V}$  supplements the operator  $\hat{H}_0$  to form the complete Hamiltonian of the electron and transforms the indicated stationary state into a quasistationary (decay) state (we shall not need to write out the operator  $\hat{V}$  in detail). The Hamiltonian  $\hat{H}_0$  is characterized by the following spectrum of adiabatic eigenfunctions and eigenvalues:

$$\begin{aligned} H_0 \psi_k(r, x, R) &= U_k(R) \psi_k(r, x, R) = (U(R) + k^2/2) \psi_k(r, x, R), \\ H_0 \tilde{\psi}_b(r, x, R) &= U(R) \tilde{\psi}_b(r, x, R). \end{aligned} \quad (1)$$

Here  $R, r, x$  is the aggregate of the coordinates of the nuclei, of the electrons in the molecule, and of the incident electrons;  $\psi_k(r, x, R)$  are the solutions for the free electron,  $\tilde{\psi}_b(r, x, R)$  are the solution for the bound electron at an energy in the continuous spectrum of the molecules.

The adiabatic electronic terms  $U(R)$  and  $\tilde{U}(R)$  describe, in the zeroth Born-Oppenheimer approximation, the potential field for the motion of the nuclei:

$$(\hat{T} + U) \chi_m(R) = \varepsilon_m \chi_m(R), \quad (\hat{T} + \tilde{U}) \tilde{\chi}_n(R) = \varepsilon_n \tilde{\chi}_n(R). \quad (2)$$

Here  $\chi_m(R)$  and  $\tilde{\chi}_n(R)$  are the nuclear wave functions in the case of free and bound electrons; they are separately orthonormalized but not mutually orthogonal. The total energy of the system in the case of a free electron is  $\varepsilon_{km} = \varepsilon_m + k^2/2$ , where  $k$  is the wave vector of the incident electron. The total wave function of the electron+molecule system will be represented as an expansion in terms of the functions (1) and (2) introduced above:

$$i \frac{\partial \Psi(R, r, x, t)}{\partial t} = \hat{\mathcal{H}} \Psi(R, r, x, t), \quad (3)$$

$$\Psi(R, r, x, t) = \sum_{m'} \int A_{km'}(t) \chi_{m'} \psi_k \frac{dk}{(2\pi)^3} + \sum_{n'} B_{n'}(t) \tilde{\chi}_{n'} \tilde{\psi}_b. \quad (4)$$

Substituting the expansion (4) in Eq. (3), multiplying the obtained relations by  $\psi_k^* \chi_m$  and  $\tilde{\psi}_b^* \tilde{\chi}_n$  and integrating them with respect to  $r$  and  $R$ , we arrive at the following system of equations for the expansion coefficients:

$$i \frac{dA_{km}}{dt} = \varepsilon_{km} A_{km} + \sum_{n'} B_{n'} V_{mkn'}, \quad (5)$$

$$i \frac{dB_n}{dt} = \varepsilon_n B_n + \sum_{m'} \int A_{km'} V_{nbm'} \frac{dk}{(2\pi)^3}.$$

We seek the solutions of this system in the form

$$\begin{aligned} A_{km} &= \exp \left\{ -i\varepsilon_{km}t + \int_0^t \alpha dt' \right\} \left[ \delta(k - k_0) \delta_{m_0m} + a_{km}(t) \right], \\ B_n &= \exp \left\{ -i\varepsilon_{nm}t + \int_0^t \alpha dt' \right\} b_n(t), \end{aligned} \quad (6)$$

where  $k_0$  is the initial wave vector of the electron,  $m_0$  is the index of the initial nuclear wave function of the molecule, and  $\varepsilon_{k_0 m_0} = \varepsilon_{m_0} + k_0^2/2$ ,  $\exp \left\{ \int_0^t \alpha(t') dt' \right\}$  is the

amplitude factor, with  $\alpha \rightarrow 0$  and  $\alpha(t) \rightarrow 0$ .

Substituting (6) in (5), we obtain a system of equations for the coefficients  $a_{km}(t)$  and  $b_n(t)$ :

$$(\varepsilon_{k_0 m_0} - \varepsilon_{km} + i\alpha) a_{km} = \sum_{n'} V_{mkn'} b_{n'}, \quad (7)$$

$$(\varepsilon_{k_0 m_0} - \varepsilon_n + i\alpha) b_n = \int \sum_m V_{nbm} a_{km} \frac{dk}{(2\pi)^3} + V_{nk_0 m_0}.$$

From the first equation of (7) we get directly

$$a_{km} = \frac{1}{\varepsilon_{k_0 m_0} - \varepsilon_{km} + i\alpha} \sum_{n'} V_{mkn'} b_{n'}, \quad (8)$$

Substituting this relation in the second equation of (7) we arrive at an equation for the coefficient  $b_n$ :

$$(\varepsilon_{k_0 m_0} - \varepsilon_n + i\alpha) b_n + \sum_{n'} b_{n'} \int \sum_m \frac{V_{mkn'} V_{nbm}}{\varepsilon_{km} - \varepsilon_{k_0 m_0} - i\alpha} \frac{dk}{(2\pi)^3} = V_{nk_0 m_0},$$

or, after integrating with respect to  $k$ ,

$$(\varepsilon_{k_0 m_0} - \varepsilon_n + i\alpha) b_n + \sum_{n'} \frac{1}{2} \Gamma_{nn'} b_{n'} = V_{nk_0 m_0}, \quad (9)$$

where

$$\begin{aligned} \frac{1}{2} \Gamma_{nn'} &= \frac{1}{2} \Gamma'_{nn'} + \frac{i \Gamma''_{nn'}}{2} = \sum_m \int \frac{V_{mkn'} V_{nbm} k}{\varepsilon_{km} - \varepsilon_{k_0 m_0}} \frac{d\varepsilon_{km}}{(2\pi)^3} \\ &+ \sum_m \frac{ik_m V_{mkn'} V_{nbm}}{2\pi}, \end{aligned} \quad (10)$$

and in view of the energy conservation law we have

$$k_m^2 - k_0^2 = 2(\varepsilon_{m_0} - \varepsilon_m).$$

It is practically impossible to solve (9) in general form without assuming that  $\Gamma_{nn'} \ll |\varepsilon_{k_0 m_0} - \varepsilon_n|$ , in which case this equation can be solved by successive approximations. In the particular case when  $\Gamma'_{nn'} = \Gamma' \delta_{nn'}$  (where  $\Gamma'$  is constant) and  $\Gamma''_{nn'} = \Gamma''_{nn'}$  we have

$$b_n = \frac{V_{nk_0 m_0}}{\varepsilon_{k_0 m_0} - \varepsilon_n + i\Gamma''/2}, \quad \varepsilon_n' = \varepsilon_n - \Gamma'/2.$$

We now obtain the amplitude of the  $m_0 \rightarrow m$  transition between the vibrational states of the nuclei in a molecule, due to the interaction with the incident electron. According to (4) and (6) and recognizing that  $\alpha \rightarrow 0$ , as well as neglecting that part of the wave function which is connected with potential scattering, we represent the wave function of the system in the form

$$\begin{aligned} \Psi &= \exp \{-i\varepsilon_{k_0 m_0} t\} \left[ \chi_{m_0}(R) e^{ik_0 r} + \sum_m \int \frac{\chi_m(R) e^{ikr}}{\varepsilon_{k_0 m_0} - \varepsilon_{km} + i\alpha} \sum_n V_{mkn} b_n \frac{dk}{(2\pi)^3} \right. \\ &\quad \left. + \sum_n b_n \tilde{\chi}_n(R) \tilde{\psi}_b(r, R) \right]. \end{aligned}$$

The integral with respect to  $k$  in the next-to-last term on the left must be calculated in such a way that only the diverging wave remains:

$$\begin{aligned} \Psi &= \exp \{-i\varepsilon_{k_0 m_0} t\} \left[ \chi_{m_0}(R) e^{ik_0 r} + \sum_m \chi_m(R) \frac{\exp(ik_m r)}{2\pi r} \sum_n V_{mkm_0} b_n \right. \\ &\quad \left. + \sum_n b_n \tilde{\chi}_n(R) \tilde{\psi}_b(r, R) \right]. \end{aligned}$$

(We assume that the interaction potential  $V$  is spherically symmetrical). Thus, the cross section of the sought transition  $m_0 \rightarrow m$  turns out to be

$$\sigma_{\nu_{nm}} = 4\pi \left| \sum_n \frac{V_{mkn} b_n}{2\pi} \right|^2 \quad (11)$$

In particular, when  $\Gamma_{nn'} = \Gamma \delta_{nn'}$ , we obtain from (10) the Chen formula<sup>5</sup> for the cross section of the vibrational excitation of the molecule ( $S_{mn} = \int \chi_m^* \tilde{\chi}_n dR$ ):

$$\sigma_{\nu_{nm}} = 4\pi \sum_n \sum_{n'} \frac{|V_{km}|^2 S_{mn} S_{mn'}^* |V_{kn}|^2 S_{n'm} S_{n'm}^*}{(2\pi)^2 (\epsilon_{k_0 m_0} - \epsilon_{n'} + i\Gamma/2) (\epsilon_{k_0 m_0} - \epsilon_{n'} - i\Gamma/2)} \quad (12)$$

In order for  $\Gamma_{nn'}$  to be diagonal, it is necessary to satisfy special conditions. In fact, for a spherically symmetrical interaction potential  $V$  we get from (10)

$$\begin{aligned} \frac{1}{2} \Gamma_{nn'} &= \sum_m \int \frac{V_{mkn}^* V_{nkm} k}{\epsilon_{k_0 m_0} - \epsilon_{n'}} \frac{d\epsilon_{km}}{(2\pi)^2} + \sum_l \frac{ik_m V_{mkn}^* V_{nkm}}{2\pi} \\ &= \sum_m \int \int \int \frac{\tilde{\chi}_{n'}(R') \hat{V}_k(R') \chi_m(R') \chi_m(R) \hat{V}_k(R) \tilde{\chi}_n(R)}{(2\pi)^2 (\epsilon_{l,m} - \epsilon_{k_0 m_0})} k dR dR' d\epsilon_{km} \\ &+ \sum_m \int \int \frac{1}{2\pi} \tilde{\chi}_{n'}(R') \hat{V}_k(R') \chi_m(R') \chi_m(R) \hat{V}_k(R) \tilde{\chi}_n(R) k_m dR dR' \\ &= \int \int \tilde{\chi}_{n'}(R') I(R, R') \tilde{\chi}_n(R) dR dR', \end{aligned}$$

where we have put

$$\begin{aligned} I(R, R') &= \sum_m \int \frac{\hat{V}_k(R') \chi_m(R') \hat{V}_k(R) \chi_m(R) k d\epsilon_{km}}{(2\pi)^2 (\epsilon_{km} - \epsilon_{k_0 m_0})} \\ &+ \sum_m \frac{1}{2\pi} \hat{V}_k(R') \chi_m(R') \hat{V}_k(R) \chi_m(R) k_m. \end{aligned} \quad (13)$$

It is obvious that in order for  $\Gamma_{nn'}$  to be diagonal, it is necessary to have either  $I(R, R') = \sum_m \Gamma_{mm} \chi_m(R') \chi_m(R)$ , or  $I(R, R') = \text{const}$ . We are prevented from summing over  $m$  in the second term of (13) by the factor  $k_m = |k_0^2 + 2(\epsilon_{m_0} - \epsilon_m)|^{1/2}$ . If, however,  $V_{km} \propto C(R) k_m^{-1/2}$ , where  $C(R)$  does not depend on  $m$ , then the factor  $k_m$  is eliminated from the sum. Since

$$\sum_m \chi_m(R') \chi_m(R) = \delta(R - R'),$$

we must have  $|C(R)| = \text{const}$  to satisfy the equation  $\Gamma_{nn'} = \Gamma \delta_{nn'}$ . As to the first term in (13), it is also approximately diagonal, since the integral with respect to  $\epsilon_{km}$  is

$$\ln[(\epsilon_k + K^2 - k_0^2 - \epsilon_m) / (k_0^2 + \epsilon_m - \epsilon_m)];$$

here  $K$  is a large value of  $k$ , which cuts off the integral, so that the dependence on  $\epsilon_m$  in the integral can be neglected. Assuming that  $C(R) = \text{const} = \sqrt{\pi} \Gamma$ , we obtain in this limit from (12)

$$\sigma_{\nu_{nm}} = \frac{4\pi}{k_0^2} \sum_n \sum_{n'} \frac{\Gamma^2}{4} \frac{S_{mn} S_{mn'}^* S_{n'm} S_{n'm}^*}{(\epsilon_{k_0 m_0} - \epsilon_{n'} + i\Gamma/2) (\epsilon_{k_0 m_0} - \epsilon_{n'} - i\Gamma/2)}, \quad (14)$$

which differs from the previously obtained relation<sup>7</sup> and agrees with Chen's formula<sup>3</sup> in the case of constant  $\Gamma$ . In physical language it turns out that after the electron is captured by the molecule, the latter vibrates up to the instant of decay in such a way that complete interference is observed between the vibrational states of the ion, and the frequency of these vibrations is the same for all the states. In other words, the process of vibration of nuclei in a negative molecular ion follows the mechanism of essentially forced vibrations

with one frequency determined by the energy of the system.

As to the principal assumption of Ref. 7, that it is possible to separate the instant of formation and decay of the intermediate state of the negative molecular ion, it is from all appearances untenable, in view of the limitations imposed by the uncertainty principle. Separation of time intervals shorter than the period of the nuclei in the molecular ion destroys the state itself and disperses it over many vibrational degrees of freedom.

Although there are no limitations in principle on the possibility of using the dependence of the width of the decay level  $\bar{\Gamma}(R, R')$  on the nuclear coordinates, however, serious computational difficulties lie in the task of obtaining here clear cut analytic results. This pertains to equal degree also to Chen's paper.<sup>3</sup>

Equations (12) and (14) derived above were obtained using a single assumption, namely that the matrix elements of the interaction  $\langle \psi_k^* | \hat{V} | \tilde{\psi}_k \rangle$  and  $\langle \psi_k^* | \hat{V} | \tilde{\psi}_k \rangle$  are equal to zero and only the elements  $\langle \psi_k^* | V | \tilde{\psi}_k \rangle$  differ from zero. By a suitable canonical transformation it is always possible to see to it that this assumption is satisfied. We note also that in the course of the derivation we used nowhere the concrete form of the operator  $\hat{V}$  of the interaction of the incident electron with the molecule (the operator, however, was assumed to be spherically symmetrical), nor its smallness compared with other interactions in the system.

To show how the theory presented here compares with those based on similar ideas, we note that in our approach we use for the total wave function of the system an expansion similar to that of Fano,<sup>8</sup> who investigated resonant scattering of electrons by atoms. A generalization of this technique to the case of molecular particles is contained in a paper by Bardsley.<sup>9</sup> Our derivation, however, differs in that a time-dependent perturbation theory is used, since we must know whether the characteristic frequencies introduced in Ref. 7 appear in the solution. Bardsley's paper<sup>9</sup> is aimed primarily at the dissociative attachment and recombination of electrons, and did not go as far as to obtain an expression for the cross section of the vibrational excitation of the molecules by electron impact. This was done by Drukarev,<sup>11</sup> in part on the basis of the work of Fiquet-Fayard.<sup>10</sup> Drukarev, however, just as Bardsley, bypassed a procedure that is essential for inelastic scattering processes, namely the expansion of the wave function of the negative ion in its vibrational states. The formulas obtained for the cross sections of the vibrational excitation  $\sigma_{m_0 m}$  therefore do not contain explicitly the resonant structure (fine structure), although of course, it is there implicitly. Thus, in the practical calculations these singularities may be missed in the numerical solution of the inhomogeneous differential equations.

Fiquet-Fayard<sup>10</sup> wrote down a formula for the cross section of the vibrational excitation of molecules by electron impact, similar to Chen's formula,<sup>3</sup> but averaged over the vibrational states and considered resonances connected with rotational transitions. There-

fore, by virtue of the different symmetries of the nuclear wave functions, the formulas given in Ref. 10 do not contain the interference of the vibrational terms.

3. The general approach described above to the determination of the cross section of the vibrational excitation of molecules by electrons has led us to the conclusion that the vibrations of nuclei in the resonant state of a negative molecular ion interfere with one another up to the instant of the ion decay, which has a sudden and random character. It is of interest in this connection to analyze classically the decay of the intermediate state of a negative molecular ion, so as to establish the limiting relations for the quantum-mechanical cross section (14) of vibrational excitation of molecules.

It follows from general considerations that the conditions for the classical treatment of the motion of nuclei in a potential field of an electron subsystem in the resonant state of a negative molecular ion will be satisfied under the following conditions: a) if the Franck-Condon region of the transitions for the nuclei when the electron is captured by the molecule includes a large number of vibrational states, so that the transition is to highly excited vibration levels of the ion; b) if the dimension of the transition region with respect to the distance between nuclei is small compared with the amplitude of the vibrations of the nuclei. Under these conditions it is possible to introduce the classical probability  $\Gamma$  of the decay of the state of the negative molecular ion and find the analytic formula for the cross section of the sought process.

Figure 1 shows a diagram of the electronic terms of the molecule ( $U_0$ ) and of the negative molecular ion ( $U_1$ ), as well as a new coordinate axis  $x$ , whose origin of which is the position of the minimum of the  $U_0(R)$  curve. The point  $b$  corresponds to the largest value of the distance between nuclei in the self-detached state of the molecular ion. We assume that the transition of the system into the electronic state  $U_1$  following the capture of the electron by the molecule is instantaneous, and further assume that the nuclei move in a potential  $U_1(x)$ ,  $0 \leq x \leq b$  in accordance with the classical law. We introduce two quantities: the probability  $W(t)$  of observing the electron + molecule system in a negative-molecule-ion state at the instant of time  $t$  (connected with the coordinate of the relative position of the nuclei  $x$  by the law of classical motion) under the initial condition  $W(t=0, x=0) = 1$ , and the decay constant  $\Gamma(x)$  of the state of the negative ion into an electron and a molecule at the point  $x$ . The probability  $W(t)$  satisfies the equation<sup>2)</sup>

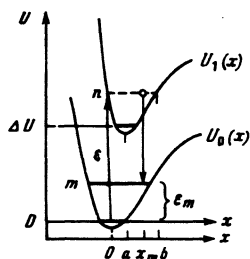


FIG. 1. Term scheme illustrating the process of formation and decay of the intermediate state of a negative molecular ion.

$$dW(t)/dt = -\Gamma(x)W(t), \quad (15)$$

so that

$$W(t) = \exp \left[ - \int_0^{t(m)} \Gamma(x) dt \right].$$

It can be shown that the function  $\Gamma(x)$  is defined at a finite number of point  $x$ , from which the decay of the system with emission of an electron and formation of a vibrationally excited molecule is possible. The corresponding values of  $x_m$  (where  $m$  is the index of the final vibrational state of the molecule) are the roots of the transcendental equation

$$U_1(x) - U_0(x) = \varepsilon - \varepsilon_m, \quad (16)$$

which is obtained if one uses the law of energy conservation in the system and the generalized Franck-Condon principal for the energy of the vibrational transition. In (16),  $\varepsilon$  is the energy of the incident electron and  $\varepsilon_m$  is the energy of the final vibrational state of the molecule after the decay of the negative molecular ion.

Analysis shows that Eq. (16) has usually one solution corresponding to positive kinetic energy of the nuclei. With a special choice of the parameters that characterize the shape of the curves of the electronic terms  $U_1(x)$  and  $U_0(x)$ , it is possible to obtain two and more solutions.

If we use for the description of the nuclear vibration the simplest model, that of the harmonic oscillator, then taking into account the coordinate system introduced above (see Fig. 1) we get

$$U_0(x) = kx^2/2, \quad U_1(x) = \Delta U + \bar{k}(x-a)^2/2,$$

where  $k$  and  $\bar{k}$  are the force constants and are connected with the nuclear-vibration frequencies  $\omega$  and  $\bar{\omega}$  by the relations  $\omega = (k/\mu)^{1/2}$  and  $\bar{\omega} = (\bar{k}/\mu)^{1/2}$ , where  $\mu$  is the reduced mass of the molecule; the parameter  $a$  represents the difference between the equilibrium distances in the molecular ion and in the molecule. In this case Eq. (16) takes the form

$$(\bar{k}-k)x^2/2 - \bar{k}ax + \varepsilon_m = 0,$$

and its solutions

$$x_m^{\pm} = \frac{\bar{k}a}{\bar{k}-k} \left[ 1 \pm \left( 1 - \frac{2\varepsilon_m(\bar{k}-k)}{\bar{k}^2 a^2} \right)^{1/2} \right],$$

should satisfy the condition  $E_{\text{kin}} = \varepsilon_m - kxm^2/2 \geq 0$ .

We proceed now to determine the probability of the decay of the electronic state of a negative molecular ion into an electron and a molecule in a specified vibrational state. Let the point  $x_m$  from which the decay of the upper state if possible be reached at the instant of time  $t$  after 10 periods of nuclear vibrations; we denote the period of the nuclear vibration between the points  $x=0$ ,  $x=b$  and  $x=0$  by  $T$ . Starting the oscillations at the point  $x=0$  and moving from left to right, the representative point will pass through the point  $x_m$  at the instant of time  $t_0(x_m), t_2 = t_0 + T, \dots, t_{2n} = t_0 + nT$ . Moving in the opposite direction, it will pass through the same point  $x_m$  at the instant  $t_1 = T - t_0(x_m), t_3 = t_1 + T, \dots, t_{2n+1} = t_1 + nT = T(1+n) - t_0$ . Since the func-

tion  $t(x)$  is multiply valued, the equation for the probability  $W(t)$  can be represented in the form

$$\begin{aligned} \frac{dW}{dx} &= \sum_n \frac{1}{|x|} \frac{dW}{dt} = \sum_n \frac{1}{|x|} \Gamma(x_n) W(t_n) \\ &= \sum_n \frac{\Gamma(x_n)}{|x|} [W(t_{2n}) + W(t_{2n+1})] = \sum_n \frac{\Gamma(x_n)}{|x|} \left\{ W(t_0) W^n(T) \right. \\ &\quad \left. + \frac{W^{n+1}(T)}{W(t_0)} \right\} = \frac{\Gamma(x_n)}{|x|} \left( \frac{W(t_0)}{1-W(T)} + \frac{W(T)}{W(t_0)} \frac{1}{1-W(T)} \right). \end{aligned} \quad (17)$$

The last equality was obtained here by taking the limit as  $n \rightarrow \infty$  and using the following property of the probability  $W(t)$ :  $W(t+T) = W(t)W(T)$ . The probabilities  $W(t_0)$  and  $W(T)$ , in view of the solution (15), take the form

$$W(t_0) = \exp\left(-\int_0^{x_m} \Gamma(x) \frac{dx}{|x|}\right), \quad W(T) = \exp\left(-2 \int_0^{\frac{1}{2}} \Gamma(x) \frac{dx}{|x|}\right).$$

If we confine ourselves to the representation of the curves of the electronic terms of the molecule and of the ion in the harmonic approximation, then the probabilities  $W(t_0)$  and  $W(T)$ , with allowance for the fact that  $|x| = \bar{\omega}[x(2a-x)]^{1/2}$ , will take the following form ( $\Gamma(x_m) = \Gamma_0$ ):

$$W(t_0) = \exp\left[-\frac{2\Gamma_0}{\bar{\omega}} \arcsin\left(\frac{x_m}{2a}\right)^{1/2}\right], \quad W(T) = \exp[-2\pi\Gamma_0/\bar{\omega}].$$

The sought solution of the vibrational excitation of the molecule by the electrons from its ground vibrational state can be represented in the form of the product

$$\begin{aligned} \sigma_{on} &= \sum_n \sigma_{on} \frac{dW}{dx} \frac{dx}{d\varepsilon} \Delta\varepsilon_m \\ &= \sum_n \sigma_{on} \frac{1(x_m)}{|x|_{x_0} d\varepsilon(x_m)/dx} \left( \frac{W(x_m)}{1-W(T)} + \frac{W(T)}{W(x_m)(1-W(T))} \right) \Delta\varepsilon_m. \end{aligned} \quad (18)$$

Here  $\sum_n \sigma_{on} = \sigma_{\text{capt}}$  is the total cross section for the capture of the electron by a molecule in the ground state,  $\Delta\varepsilon_m = (d\varepsilon_m/dm)\Delta m$  is the energy interval in the spectrum of the vibrational excitation of the molecule, and  $\Delta m \sim 1$  is a parameter that characterizes the density of the number of vibrational levels of the molecule.

To get an idea of the results of calculations by formulas (14) and (18), Fig. 2 shows the calculated values of the partial cross sections of the vibrational excitation of the  $N_2$  molecule from the ground state, while Fig. 3 shows the total excitation cross section  $\sum_m \sigma_{on}$ , where  $m$  is the number of the vibrational level of the molecule in the final state. As the partial cross section for the capture of an electron by a molecule, we used the Breit-Wigner cross section

$$\sigma_{on} = \frac{4\pi}{2m\varepsilon} |S_{on}|^2 \left(\frac{\Gamma}{2}\right)^2 / \left[ (\varepsilon - \varepsilon_n)^2 + \left(\frac{\Gamma}{2}\right)^2 \right],$$

which corresponds to a constant width  $\Gamma$  of the level.

In the calculations we used the following parameters of the adiabatic terms of the  $N_2(x^1\Sigma_g^+)$  molecule: equilibrium distance  $R_e = 1.098 \text{ \AA}$ , vibrational quantum  $\hbar\omega_e = 0.292 \text{ eV}$ . For the decay state of the molecular ion  $N_2^+(\Pi_g)$  we used the term-excitation energy

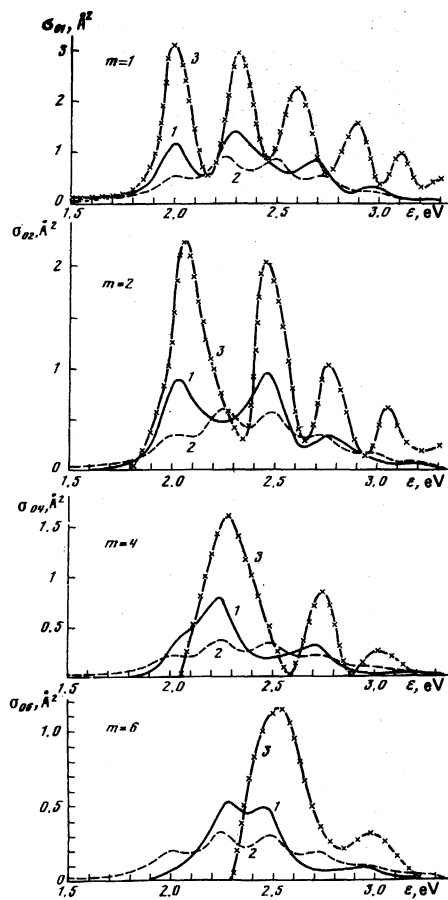


FIG. 2. Partial cross sections of vibrational excitation of the molecule  $N_2$  in collisions with electrons. The calculated values of the cross sections are compared with experimental data: curves 1—calculation by formula (14), curves 2—by formula (18), 3—experimental data from Ref. 2.

$T_0 = 2 \text{ eV}$ ,  $R_{ef} = 1.19 \text{ \AA}$ , and  $\hbar\omega_{ef} = 0.24 \text{ eV}$ , while the constant value of the level width  $\Gamma$  was taken to be  $0.2 \text{ eV}$ . The overlap integrals  $S_{mn}$  of the vibrational wave functions were calculated in the harmonic approximation. Figures 2 and 3 show also certain ex-

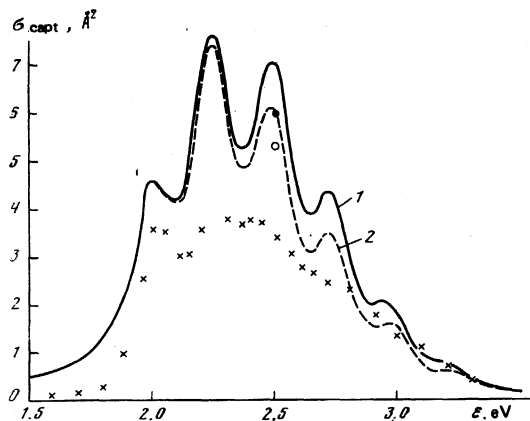


FIG. 3. Total cross section of vibrational excitation of an  $N_2$  molecule by electrons (it coincides with the total cross section of electron capture  $N_2$  molecules). Curves 1 and 2 are calculated by formulas (14) and (18), respectively; the experimental points  $\bullet$ ,  $\circ$ , and  $\times$  were taken from Refs. 13, 14, and 15, respectively. In Ref. 15 is given the total cross section of the excitation of vibrational levels with  $v = 1-8$ .

perimental plots of the cross sections of the vibrational excitation of the molecule  $N_2$  in the energy range of the incident electrons<sup>2, 13-15</sup>  $\varepsilon = 1.5-3.3$  eV.

As to the calculated cross section curves corresponding to Chen's formulas (14) and to the classical approach (18), the discrepancy between them (see Fig. 2) is apparently due to the smallness of the quantum numbers of the vibrational excitation of the negative molecular ion ( $n < 5$ ), when there is little justification for the use of the classical approximation. This is illustrated also in Fig. 3, which shows plots of the total cross section for the capture of an electron by a molecule, inasmuch as when account is taken of the contributions of all the vibrational levels of the molecules the cross sections should coincide by definition.

When it comes to a comparison of the calculation with experiment, the situation is worse. The measured values of the partial cross sections of the vibrational excitation of the  $N_2$  molecules exceed by several times the calculated ones (moreover, it is noted in Ref. 2 that the experimental cross section should apparently be increased by approximately another factor of 2). This conclusion is difficult to reconcile with Chen's quantum-mechanical formula (14) at the constant value of the width of the decay level  $\Gamma$ , inasmuch as the increase of the calculated excitation cross section can be ensured by increasing the value of  $\Gamma$ , which in turn causes a smearing of the peaked structure of the cross section. This may mean that the customarily assumed values of the width  $\Gamma$  for the state  $2\Pi_g$  of the  $N_2^-$  ion, namely<sup>16</sup> 0.7 eV, is strongly overestimated.

In conclusion, we are grateful to B. M. Smirnov for continuous interest in our work.

<sup>1</sup>Unless otherwise stipulated, we use the system of atomic units  $\hbar = m_e = e = 1$ .

<sup>2</sup>The idea of the analysis that follows is based on an approach developed in Ref. 12 in the analysis of the decay of a negative molecular ion from a repulsion term into two atomic particles.

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