Direct and Resonance Rotational Excitation of Molecules by Slow Electrons*†

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(Received 2 August 1965; revised manuscript received 10 January 1966)

The theory of electron scattering by molecules is presented in terms of Feshbach's projection-operator formalism with special attention to the problem of molecular rotational excitation. The absolute orders of magnitude and the energy dependence of the cross section for resonance rotational excitation are calculated for the (N_2,e) system. The characteristic multipeak structure for resonance elastic scattering and vibrational excitation is again found for resonance rotational excitation. A comparison of the calculated results with experimental measurements is made for peak positions in the cross section for resonance elastic scattering, which may be considered as a special case of resonance rotational excitation (i.e., $\Delta l_0=0$). Cross sections for simultaneous rotational and vibrational excitation of N_2 are also calculated. The total partial cross sections for resonance vibrational excitation are then obtained as a sum of all the corresponding partial cross sections with different allowed rotational transitions. The energy dependence of the newly obtained vibrational excitation cross section compares favorably with experimental observations.

I. INTRODUCTION

THE problem of rotational excitation has been actively studied[1-5] not only because it is a fundamental scattering problem but also because it is an important energy-loss mechanism for slow electrons in molecular gases. Gerjuoy and Stein[2] pointed out that the long range of the interaction between an electron and the quadrupole moment of a molecule is the origin of the large energy losses observed in laboratory swarm experiments. Later, Dalgarno and Moffett[3] added the contribution due to polarization force to the rotational excitation and pointed out that this may in some cases result in a decrease in the cross section. There are discrepancies between results of these calculations, based upon the Born approximation with the higher order terms in the potential neglected, and analysis of swarm data.[6] Recently, a number of papers appeared pointing out the importance of the distortion effects on the incident electron.[4,5] In all these studies, the possible resonance rotational excitation was not considered. In the present paper, we consider the possible resonance excitation mechanism and the effects of its interference on the direct excitation mechanisms for rotational excitation.

The plan of the paper is as follows: In Sec. II, the theory for electron scattering by molecules[7] is presented in terms of Feshbach's projection-operator formalism[8] with considerations of Fermi-Dirac statistics for the N electrons. In Sec. III, we illustrate how this theory may be applied to the problem of rotational excitation of molecules by slow electron impact. Various approximations that may be of use are examined in some detail. The theory is then applied to the scattering of electrons by nitrogen molecules in Sec. IV. The absolute orders of magnitude and the energy dependence of the cross section for direct and resonance rotational excitation are calculated for the (N_2,e) system. A comparison of the results with experimental measurements is made for peak positions in the cross section for resonance elastic scattering which may be considered as a special case of resonance rotational excitation (i.e. $\Delta l_0=0$). The effects on vibrational excitation due to the degrees of freedom provided by possible accompanying rotational transitions are discussed. The total partial cross sections for resonance vibrational excitation are then obtained as a sum of all the corresponding partial cross sections with different allowed rotational transitions. The energy dependence of the newly obtained vibrational excitation cross section is then compared with that observed experimentally.

II. PROJECTION-OPERATOR FORMALISM OF THE THEORY

The Schrödinger equation for an N-electron system consisting of an incident electron and a target diatomic molecule ab having N_0 ($N_0=N-1$) molecular electrons is in relative coordinates with respect to the center of mass of the nuclei[9]

$$H\Upsilon=E\Upsilon \tag{2.1}$$

with

$$H=K_0(\mathbf{r}_0)+V_0(\mathbf{r}_0,\mathbf{r},\mathbf{R})+H_{ab}(\mathbf{r},\mathbf{R}), \tag{2.2}$$

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[9] Atomic units are used through this paper except where indicated otherwise.

$$V_0(\mathbf{r}_0,\mathbf{r},\mathbf{R}) = \sum_{i=1}^{N_0} |\mathbf{r}_0-\mathbf{r}_i|^{-1} - \frac{Z_a}{r_{0a}} - \frac{Z_b}{r_{0b}}, \qquad (2.3)$$

where $\mathbf{r}_0$ and $\mathbf{r}$ (denoting $\mathbf{r}_1, \mathbf{r}_2 \cdots \mathbf{r}_{N_0}$ collectively) are the incident and molecular electron coordinates, respectively, K_0 is the kinetic energy operator of the incident electron, V_0 is the interaction potential of the incident electron with the target molecule, H_{ab} is the Hamiltonian for the target molecule, Υ is the total wave function for the scattering system (ab,e) having the total energy E as the eigenvalue, and finally the $\mathbf{r}_0$'s (i.e. $\mathbf{r}_{0a}$ and $\mathbf{r}_{0b}$) are the position vectors of the incident electron with respect to the two nuclei having the Z's as their charges.

It is assumed that the unperturbed molecule is described by the set of Schrödinger equations

$$H^{\mathrm{el}}(\mathbf{r},\mathbf{R})\Phi_n(\xi,\mathbf{R}) = \mathcal{E}_n(\mathbf{R})\Phi_n(\xi,\mathbf{R}), \quad (2.4)$$

$$\{-(2\mu)^{-1}\nabla_{\mathbf{R}}{}^2+\mathcal{E}_n(\mathbf{R})\}\chi_{\gamma_n}(\mathbf{R}) = \mathcal{E}_{\gamma_n}\chi_{\gamma_n}(\mathbf{R}), \quad (2.5)$$

with

$$H^{\mathrm{el}}(\mathbf{r},\mathbf{R}) = \frac{1+M_a+M_b}{2(M_a+M_b)}\sum_{i=1}^{N_0}\nabla_i{}^2+U^{\mathrm{el}}(\mathbf{r},\mathbf{R}), \quad (2.6)$$

where the ξ's denote the assembly of the coordinates (i.e. the $\mathbf{r}$'s) and spin projections of the electrons, H^{el} is the Born-Oppenheimer electronic Hamiltonian, $\mu=M_aM_b/(M_a+M_b)$, ∇^2 is the Laplacian operator, and U^{el} is the potential energy of the molecular electrons. The Hamiltonian for the target molecule takes the approximate form

$$H_{ab} = -(2\mu)^{-1}\nabla_{\mathbf{R}}{}^2+H^{\mathrm{el}}(\mathbf{r},\mathbf{R}). \quad (2.7)$$

Both the electronic wave functions Φ_n and the nuclear wave functions χ_{γ_n}, having the respective eigenvalues $\mathcal{E}_n(\mathbf{R})$ and $\mathcal{E}_{\gamma_n}$, form a complete orthonormal set in their corresponding spaces with variables r and R, respectively.

In dealing with subexcitation electron impact where no electronic excitation is energetically allowed, it is desirable to project out from the total wave function Υ the open channels in which the target molecule remains in a ground electronic state and to treat the remaining part of the total wave function as a field for generating effective potentials in the new Hamiltonian for the projectile electron. That is, we want to construct a projection operator P such that

$$P\Upsilon(\xi_0,\xi,\mathbf{R}) = \sum_{\gamma_0}\chi_{\gamma_0}(\mathbf{R})\mathcal{C}\{\psi_{\gamma_0}(\xi_0)\Phi_0(\xi,\mathbf{R})\}, \quad (2.8)$$

where $\mathcal{C}$ is the antisymmetrization operator operating only on electrons, and the ψ's are the channel wave functions of the incident electron. The appropriate projection operator takes the form

$$P = P_0^{\mathrm{el}}P_0^{\mathrm{nu}}, \quad (2.9)$$

where P^{el} is the electronic projection operator and P^{nu} is the nuclear projection operator.

The electronic projection operator P^{el} capable of projecting out from the total wave function Υ the anti-symmetrized electronic wave function representing a projectile electron with the target molecule in its ground electronic state has the general appearance[8]

$$P_0^{\mathrm{el}} = \mathcal{C}|\Phi_0\rangle[1+\mathcal{O}_0(\xi_0,\xi_0')]\langle\Phi_0|\mathcal{C}, \quad (2.10)$$

where $\mathcal{O}_0(\xi_0,\xi_0')$ is the auxiliary electronic projection operator. The nuclear projection operator P^{nu} capable of projecting out from the total wave function Υ all the energetically allowed nuclear states associated with the ground electronic state has the form

$$P_0^{\mathrm{nu}} = \sum_{\gamma_0} P_{\gamma_0} = \sum_{\gamma_0}|\chi_{\gamma_0}\rangle\langle\chi_{\gamma_0}|, \quad (2.11)$$

where P_{γ_0}'s are the elementary nuclear projection operators, and γ_0 sums over all the energetically allowed nuclear states associated with the ground electronic state. This implies that the remaining Hilbert space $1-P$ still contains a component of ground electronic state Φ_0 associated with excited nuclear states which are not summed over in Eq. (2.11). The auxiliary electronic projection operator $\mathcal{O}_0(\xi_0,\xi_0')$ appearing in Eq. (2.10) is expressed in terms of solutions of an inhomogeneous integral equation of the Fredholm type[8]; its complexity increases with the number of electrons. For two-electron scattering systems, we have the following simple expression for $\mathcal{O}_0$,

$$\mathcal{O}_0(\xi_0,\xi_0') = -\tfrac{1}{2}|\Phi_0(\xi_0)\rangle\langle\Phi_0(\xi_0)|. \quad (2.12)$$

Operating on the total wave function $\Upsilon(\xi_0,\xi,\mathbf{R})$ by the projection operator given by Eqs. (2.9), (2.10), and (2.11), we obtain the desired equation [Eq. (2.8)] with the channel wave functions ψ_{γ_0} defined uniquely as

$$\psi_{\gamma_0}(\xi_0) = \langle\chi_{\gamma_0}(\mathbf{R})\Phi_0(\xi)|\Upsilon(\xi_0,\xi,\mathbf{R})\rangle + \langle\chi_{\gamma_0}(\mathbf{R})\Phi_0(\xi)|\mathcal{O}(\xi_0,\xi_0')|\Upsilon(\xi_0',\xi,\mathbf{R})\rangle. \quad (2.13)$$

In performing the scalar products in Eq. (2.13), we integrate over the coordinates which are common to both sides of the scalar products.

Now, let the complementary orthogonal components of $P\Upsilon$ be denoted by $Q\Upsilon$, then $Q=1-P$. Operating on Eq. (2.1) with P and Q, we obtain[10]

$$(E-PHP)P\Upsilon = PHQ\Upsilon, \quad (2.14a)$$

$$(E-QHQ)Q\Upsilon = QHP\Upsilon. \quad (2.14b)$$

Solving Eq. (2.14b) for $Q\Upsilon$ and substituting into Eq. (2.14a), we obtain[8]

$$(T_0+\mathcal{V}-E)P\Upsilon = 0, \quad (2.15)$$

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[10] We note that the coupling matrix elements found in the Born-Oppenheimer separation are contained in Eqs. (2.14), since more explicitly we have, for example,

$$HP\Upsilon = \sum_{\gamma_0}\{[K_0(\mathbf{r}_0)+V(\mathbf{r}_0,\mathbf{r},\mathbf{R})+\mathcal{E}_{\gamma_0}]\chi_{\gamma_0}(\mathbf{R})\psi_{\gamma_0}(\xi_0)\Phi_0(\xi,\mathbf{R}) - \frac{1}{2\mu}$$
$$\times[2\{\nabla_{\mathbf{R}}\Phi_0(\xi,\mathbf{R})\}\cdot\nabla_{\mathbf{R}}+\{\nabla_{\mathbf{R}}{}^2\Phi(\xi,\mathbf{R})\}]\chi_{\gamma_0}(\mathbf{R})\psi_{\gamma_0}(\xi_0)\}.$$

with

$$T_0 = P(K_0 + H_{ab})P, \qquad (2.16)$$

$$\mathcal{V} = PV_0P + PHQ(E - QHQ)^{-1}QHP. \qquad (2.17)$$

The last term in Eq. (2.17) is the nonlocal effective potential generated by $Q\Upsilon$. Equation (2.15) is identical to Eq. (2.22) in Paper I,[7] except now Eq. (2.15) is properly antisymmetrized. We may divide the potential into two components: $\mathcal{V} = \mathcal{U} + \mathcal{U}'$. The first component $\mathcal{U}$ gives rise to the direct scattering which represents the propagation of a projectile electron in the field of the target molecule in its ground electronic state and which includes both the effects of distant resonance and exchange scattering. The second component $\mathcal{U}'$ gives rise to the resonance scattering which represents compound state formation involving excited states of the target molecule.

The transition matrix $T_0(\gamma_0 \rightarrow \gamma_0')$ describing transitions from the incident channel γ_0 (the initial nuclear state) to channel γ_0' (the final nuclear state) with the electronic state of the target molecule remaining in its ground state is[11]

$$T_0(\gamma_0 \rightarrow \gamma_0') = \langle \Pi_0^{(-)}(\gamma_0') | \mathcal{U} | \psi_0^{(+)}(\gamma_0) \rangle$$
$$+ \langle \psi_0^{(-)}(\gamma_0') | \mathcal{U}'F | \psi_0^{(+)}(\gamma_0) \rangle \qquad (2.18)$$

with

$$\mathcal{U} = \mathcal{V} - \mathcal{U}', \qquad (2.19)$$

$$\mathcal{U}' = \sum_m' PHQ | \Psi_m \rangle (E - W_m)^{-1} \langle \Psi_m | QHP, \qquad (2.20)$$

$$F = 1 + (E - T_0 - \mathcal{U} + i\eta)^{-1}\mathcal{U}'F, \qquad (2.21)$$

$$P\psi_0^{(+)} = P\Pi_0^{(+)} + (E - T_0 + i\eta)^{-1}\mathcal{U}P\psi_0^{(+)}, \qquad (2.22)$$

where the prime on $\sum$ denotes that only those compound states Ψ_m having comparable energies with the given energy of the system may be included in the summation.

The differential partial cross section for the transition $\gamma_0 \rightarrow \gamma_0'$ can now be expressed in terms of the transition matrix

$$d\sigma(\gamma_0 \rightarrow \gamma_0') = (2\pi)^{-3}\frac{k_{\gamma_0'}}{k_{\gamma_0}}|T_0(\gamma_0 \rightarrow \gamma_0')|^2 d\Omega_f \qquad (2.23)$$

with

$$k_{\gamma_0'}^2 = k_{\gamma_0}^2 + 2(\mathcal{E}_{\gamma_0} - \mathcal{E}_{\gamma_0'}), \qquad (2.24)$$

where k_{γ_0} and $k_{\gamma_0'}$ are the initial and final wave numbers of the projectile electron, and $d\Omega_f = \sin\theta_f d\theta_f d\phi_f$ is the scattered solid angle. Since the cross section is not a linear function of the transition matrix, we have therefore not only the direct and resonance scattering contributions but also the contribution due to their interference to consider. Hence, we have

$$\sigma(\gamma_0 \rightarrow \gamma_0') = \sigma_d(\gamma_0 \rightarrow \gamma_0') + \sigma_r(\gamma_0 \rightarrow \gamma_0')$$
$$+ \sigma_i(\gamma_0 \rightarrow \gamma_0') \qquad (2.25)$$

with

$$\sigma_d(\gamma_0 \rightarrow \gamma_0') = (2\pi)^{-2}\left(\frac{k_{\gamma_0'}}{k_{\gamma_0}}\right) \int |\langle \Pi_0^{(-)}(\gamma_0') | \mathcal{U} | \psi_0^{(+)}(\gamma_0) \rangle|^2 d\Omega_f, \qquad (2.26)$$

$$\sigma_r(\gamma_0 \rightarrow \gamma_0') = (2\pi)^{-2}\left(\frac{k_{\gamma_0'}}{k_{\gamma_0}}\right) \int |\langle \psi_0^{(-)}(\gamma_0') | \mathcal{U}'F | \psi_0^{(+)}(\gamma_0) \rangle|^2 d\Omega_f, \qquad (2.27)$$

$$\sigma_i(\gamma_0 \rightarrow \gamma_0') = (2\pi)^{-2}\left(\frac{k_{\gamma_0'}}{k_{\gamma_0}}\right) \int 2\,\mathrm{Re}\{\langle \Pi_0^{(-)}(\gamma_0') | \mathcal{U} | \psi_0^{(+)}(\gamma_0) \rangle \langle \psi_0^{(-)}(\gamma_0') | \mathcal{U}'F | \psi_0^{(+)}(\gamma_0) \rangle\} d\Omega_f, \qquad (2.28)$$

where σ_d, σ_r, and σ_i correspond to the direct, resonance, and interference contributions to the cross section, and Re signifies the real part of the quantity in { }. Unless the interference is negligible, the cross section is not an additive quantity.

III. ROTATIONAL EXCITATION OF MOLECULES

1. Direct Rotational Excitation

The direct transition matrix appearing in the cross section for direct excitation given by Eq. (2.26) is

$$\langle \Pi_0^{(-)}(\gamma_0') | \mathcal{U} | \psi_0^{(+)}(\gamma_0) \rangle$$
$$= \langle P\Pi_0^{(-)}(\gamma_0') | \mathcal{U} | P\psi_0^{(+)}(\gamma_0) \rangle, \qquad (3.1)$$

where, in obtaining the right-hand side of Eq. (3.1), the Hermitian and idempotent properties of the projection operator are used. Now, utilizing the definition of the projection operator P given by Eq. (2.8), we have

$$P\Pi_0^{(-)} = \sum_{\gamma_0} \chi_{\gamma_0}(R)\,\mathcal{C}\{\Pi_{\gamma_0}^{(-)}(\xi_0)\Phi_0(\xi,R)\}, \qquad (3.2)$$

$$P\psi_0^{(+)} = \sum_{\gamma_0} \chi_{\gamma_0}(R)\,\mathcal{C}\{\psi_{\gamma_0}^{(+)}(\xi_0)\Phi_0(\xi,R)\}, \qquad (3.3)$$

where Π_{γ_0} and ψ_{γ_0} are the unperturbed and distorted channel wave functions, respectively. This permits us to define, for transitions from nuclear state γ_0 to state γ_0', the direct transition matrix

$$T_d(\gamma_0 \rightarrow \gamma_0') = \langle \chi_{\gamma_0'}(\mathbf{R}) | \alpha_{\gamma_0'\gamma_0}(R,\hat{R}) | \chi_{\gamma_0}(\mathbf{R}) \rangle \qquad (3.4)$$

with

$$\alpha_{\gamma_0'\gamma_0}(R,\hat{R}) = \langle \mathcal{C}\{\Pi_{\gamma_0'}^{(-)}(\xi_0)\Phi_0(\xi,R)\} | \mathcal{U} |$$
$$\times \mathcal{C}\{\Phi_0(\xi,R)\psi_{\gamma_0}^{(+)}(\xi_0)\}\rangle \qquad (3.5)$$

where $\hat{R} = \mathbf{R}/R$ is the unit vector and $\alpha_{\gamma_0'\gamma_0}(R,\hat{R})$ is the

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[11] Since the antisymmetrization operator $\mathcal{C}$ commutes with P, $\mathcal{U}$, and $\mathcal{U}'$, it is not difficult to see that for the purpose of calculating the transition matrix, it is sufficient to antisymmetrize only the initial state $\psi_0^{(+)}(\gamma_0)$.

effective potential responsible for the nuclear excitation. Various orders of distorted channel wave functions can now be obtained by considering the corresponding terms in the expansion of the potential $\mathfrak{U}$ weighted by the molecular electronic wave function Φ_0. In terms of such distorted channel wave functions, the cross section for direct rotation excitation may be evaluated to the corresponding order of accuracy in the distorted wave approximation.[12]

It is sometimes more convenient, however, to define an equivalent direct scattering potential $\mathfrak{U}F_d$ so that

$$\alpha_{\gamma_0'\gamma_0}(R,\hat{R}) = \langle \mathfrak{a}\{\Pi_{\gamma_0'}{}^{(-)}(\xi_0)\Phi_0(\xi,\mathbf{R})\} | \mathfrak{U}F_d |$$
$$\times \mathfrak{a}\{\Phi_0(\xi,\mathbf{R})\Pi_{\gamma_0}{}^{(+)}(\xi_0)\}\rangle \quad (3.6)$$

with

$$F_d = 1 + (E - T_0 + i\eta)^{-1}\mathfrak{U}F_d. \quad (3.7)$$

Equation (3.7) is derived with the help of Eq. (2.22). The series generated by F_d for direct transition matrix is the well known Born series. Since for a given energy all the bound states of the scattering system are removed, this series does not have convergence difficulties.[13] In general, the expression for $\alpha(R,\hat{R})$ is very complicated and difficult to evaluate. We therefore define an average direct scattering potential $\mathfrak{U}_d$ so that

$$\alpha_{\gamma_0'\gamma_0}(R,\hat{R}) = \langle \Pi_{\gamma_0}{}^{(-)} | \mathfrak{U}_d(r_0,R,\hat{R}) | \Pi_{\gamma_0}{}^{(+)}\rangle. \quad (3.8)$$

In principle, $\mathfrak{U}_d$ can be obtained from Eq. (3.6) by integrating over all the molecular electron volumes. Since $\mathfrak{U}F_d$ appearing in Eq. (3.7) is nonlocal, $\mathfrak{U}_d$ is necessarily nonlocal.

If we neglect for the moment the nonlocality effects and assume that $\mathfrak{U}_d(r_0,R,\hat{R})$ possesses a multipole expansion,[14] we obtain

$$\mathfrak{U}_d(\mathbf{r}_0,R,\hat{R}) = \mathfrak{U}_d{}^{(0)}(\mathbf{r}_0,R,\hat{R})$$
$$+ (r_0)^{-1}\sum_i (q_j(R)/r_0{}^j)P_j(\hat{r}_0,\hat{R}), \quad (3.9)$$

where the q's are the various electric moments for a fixed nuclear configuration, the $P_j(\hat{r}_0,\hat{R})$'s are the Legendre polynomials and $\mathfrak{U}_d{}^{(0)}(\mathbf{r}_0,R,\hat{R})$ is the remainder of the averaged direct scattering potential. This expansion presupposes, of course, that the projectile electron can never penetrate closer than the molecule

size, since the requirement $r_i/r_0 < 1$ for all molecular electrons must be satisfied. Although it still deserves further study, this approximation, however, accounts for the most essential features for direct rotational excitation.

In dealing with the problem of rotational excitation, the vibrational motion is assumed to remain in its initial state; and the vibrational wave functions may be eliminated first by integrating over R^2dR. Thus we obtain, for direct rotational excitation of a diatomic molecule in Σ states, the transition matrix

$$T_d(l_0m_0 \to l_0'm_0') = \langle Y_{l_0'm_0'}(\hat{R})\Pi_{\gamma_0}{}^{(-)}(\xi_0) | \langle \mathfrak{U}_d(\mathbf{r}_0,\hat{R})\rangle$$
$$\times | \Pi_{\gamma_0}{}^{(+)}(\xi_0)Y_{l_0m_0}(\hat{R})\rangle \quad (3.10)$$

with

$$\langle \mathfrak{U}_d(\mathbf{r}_0,\hat{R})\rangle = \langle \mathfrak{U}_d{}^{(0)}(\mathbf{r}_0,\hat{R})\rangle$$
$$+ \sum_j (\langle q_j\rangle/r_0{}^{j+1})P_j(\hat{r}_0,\hat{R}), \quad (3.11)$$

$$\langle A\rangle \equiv \int_0^\infty |X_{v_0}|^2 A R^2 dR, \quad (3.12)$$

where for definiteness the nuclear states γ_0 and γ_0' are labeled explicitly as $v_0 l_0 m_0$ and $v_0' l_0' m_0'$, respectively, and the nuclear vibrational and rotational wave functions are denoted, respectively, by $X_{v_0}(R)$ and $Y_{l_0m_0}(\hat{R})$. For Σ states, the rotational wave functions are simple spherical harmonics. Thus, approximate cross sections for direct rotational excitation can be evaluated from Eq. (2.26) with the transition matrix approximated by Eq. (3.10), provided we know the averaged electric moments $\langle q_i\rangle$.

2. Resonance Rotational Excitation

The resonance transition matrix appearing in Eq. (2.27) is formidable in its complexity. In application we must rely upon meaningful simplifications. For our present purposes, we adopt the isolated resonance model,[15] which is capable of accounting for the most essential features of resonance elastic scattering and resonance vibrational excitation.[16]

In the framework of the isolated resonance model, the transition matrix takes the form

$$T_r(\gamma_0 \to \gamma_0') = \langle \psi_0{}^{(-)}(\gamma_0') | \mathfrak{U}'F | \psi_0{}^{(+)}(\gamma_0)\rangle = \{\langle \psi_0{}^{(+)}(\gamma_0') | PHQ | \Psi_m\rangle(E - W_m - R_m)^{-1}\langle \Psi_m | QHP | \psi_0{}^{(+)}(\gamma_0)\rangle\}.$$

Assuming that the resonance field is effectively generated by an electronic target state, say n, we have for the compound state

$$\{Q_{\gamma_n}HQ_{\gamma_n} - \mathcal{W}_{\gamma_n}{}^{(m)}\}Q_{\gamma_n}\Psi_m(\gamma_n) = 0 \quad (3.13)$$

[12] M. L. Goldberger and K. M. Watson, Collision Theory (John Wiley & Sons, Inc., New York, 1964); T. Y. Wu and T. Ohmura, Quantum Theory of Scattering (Prentice-Hall, Inc., Englewood Cliffs, New Jersey, 1962).

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with

$$Q_{\gamma_n}\Psi_m = \sum_{\gamma_n} \chi_{\gamma_n} \mathcal{C}\{\psi_{\gamma_n}{}^{(m)}(\xi_0)\Phi_n(\xi,\mathbf{R})\}, \tag{3.14}$$

where Q_{γ_n} is the component of Q capable of projecting onto the target electronic state n, and $\psi_{\gamma_n}{}^{(m)}$ is the compound channel wave function.

This permits us to write for $T_r(\gamma_0 \rightarrow \gamma_0')$:

$$T_r(\gamma_0 \rightarrow \gamma_0') = \sum_{\gamma_n} \{\langle P\psi_0{}^{(-)}(\gamma_0')|H|Q_{\gamma_n}\Psi_m(\gamma_n)\rangle(E - \mathcal{W}_{\gamma_n}{}^{(m)} - \mathcal{R}_{\gamma_n}{}^{(m)})^{-1}\langle Q_{\gamma_n}\Psi_m(\gamma_n)|H|P\psi_0{}^{(+)}(\gamma_0)\rangle\} \tag{3.15}$$

with

$$\mathcal{R}_{\gamma_n}{}^{(m)} = \Delta_{\gamma_n}{}^{(m)} - i\tfrac{1}{2}\Gamma_{\gamma_n}{}^{(m)}, \tag{3.16}$$

$$\Delta_{\gamma_n}{}^{(m)} = \langle Q_{\gamma_n}\Psi_m(\gamma_n)|HP\mathcal{P}(E - T_0 - \mathcal{U} + i\eta)^{-1}PH|Q_{\gamma_n}\Psi_m(\gamma_n)\rangle, \tag{3.17}$$

$$\Gamma_{\gamma_n}{}^{(m)} = (2\pi)^{-2}\sum_{\gamma_0}\int |P\psi_0{}^{(-)}(\gamma_0)|H|Q_{\gamma_n}\Psi_m(\gamma_n)|^2 k_{\gamma_0} d\Omega_f, \tag{3.18}$$

where $\Delta_{\gamma_n}{}^{(m)}$ is energy shift in the position of resonance from $\mathcal{W}_{\gamma_n}{}^{(m)}$, and $\Gamma_{\gamma_n}{}^{(m)}$ is the half-width of the resonance. It is convenient to define a quantity $\mathcal{E}_{\gamma_n}{}^{(m)}$ in place of $\mathcal{W}_{\gamma_n}{}^{(m)}$

$$\mathcal{E}_{\gamma_n}{}^{(m)} = \mathcal{W}_{\gamma_n}{}^{(m)} + \mathcal{E}_n(R_e{}^{(n)}) - \mathcal{E}_{\gamma_n}, \tag{3.19}$$

where $\mathcal{E}_n(R_e{}^{(n)})$ is the nth electronic energy of the target molecule evaluated at its equilibrium internuclear distance $R_e{}^{(n)}$, and $\mathcal{E}_{\gamma_n}$ is the total energy of the target molecule in its γ_nth nuclear state of the nth electronic state.

Interchanging the order of integration in Eq. (3.15), we obtain, with the help of Eq. (3.14), the transition matrix

$$T_r(\gamma_0 \rightarrow \gamma_0') = \sum_{\gamma_n} \{\langle \chi_{\gamma_0'}|\alpha_{\gamma_0'\gamma_n}(\mathbf{R},\Omega_f)|\chi_{\gamma_n}\rangle(E - E_{\gamma_n}{}^{(m)} + i\tfrac{1}{2}\Gamma_{\gamma_n}{}^{(m)})^{-1}\langle \chi_{\gamma_n}|\alpha_{\gamma_n\gamma_0}{}^*(\mathbf{R},\Omega_0)|\chi_{\gamma_0}\rangle\} \tag{3.20}$$

with

$$\Gamma_{\gamma_n}{}^{(m)} = \sum_{\gamma_0}\frac{k_{\gamma_0}}{4\pi^2}\int |\langle \chi_{\gamma_0}|\alpha_{\gamma_0\gamma_n}(\mathbf{R},\Omega_f)|\chi_{\gamma_n}\rangle|^2 d\Omega_f, \tag{3.21}$$

$$E_{\gamma_n}{}^{(m)} = \mathcal{W}_{\gamma_n}{}^{(m)} + \Delta_{\gamma_n}{}^{(m)} = \mathcal{E}_{\gamma_n}{}^{(m)} + \Delta_{\gamma_n}{}^{(m)} + \mathcal{E}_{\gamma_n} - \mathcal{E}_n(R_e{}^{(n)}), \tag{3.22}$$

$$\alpha_{\gamma_n\gamma_0}{}^*(\mathbf{R},\Omega_0) = \langle \mathcal{C}\{\psi_{\gamma_n}{}^{(m)}\Phi_n\}|H|\mathcal{C}\{\Phi_0\psi_{\gamma_0}{}^{(+)}\}\rangle, \tag{3.23a}$$

$$\alpha_{\gamma_0'\gamma_n}(\mathbf{R},\Omega_f) = \langle \mathcal{C}\{\psi_{\gamma_0'}{}^{(-)}\Phi_0\}|H|\mathcal{C}\{\Phi_n\psi_{\gamma_n}{}^{(m)}\}\rangle, \tag{3.23b}$$

where Ω_0 and Ω_f are the incident and scattered solid angles of the projectile electron.

The effective potentials, the α's, responsible for the resonance nuclear excitation are formidably complicated. For rotational excitation of homonuclear diatomic molecules in Σ states, the effective potential may be approximated by

$$\alpha_{\gamma_n\gamma_0}{}^*(\mathbf{R},\Omega_0) \cong (\tfrac{4}{5}\pi)^{1/2}\alpha_{0v_0}{}^*(R,\Omega_0)\sum_{m'} Y_{2m'}(\hat{R}), \tag{3.24a}$$

$$\alpha_{\gamma_0'\gamma_n}(\mathbf{R},\Omega_f) \cong (\tfrac{4}{5}\pi)^{1/2}\alpha_{v_0'0}(R,\Omega_f)\sum_{m'} Y_{2m'}{}^*(\hat{R}), \tag{3.24b}$$

where the vibrational states are explicitly labeled by the v_0's and the Y's are the spherical harmonics. Substituting this expression into Eqs. (3.20) and (3.21) and the resultants into Eq. (2.27), we obtain, for resonance rotational excitation, the cross section

$$\sigma_r(l_0 \rightarrow l_0') = \frac{\beta_{v_0}{}^2}{16\pi^3}\left(\frac{k_{v_0 l_0'}}{k_{v_0 l_0}}\right)\frac{1}{2l_0+1}\sum_{m_0 m_0'}\left|\sum_{v_n l_n}\frac{C_{l_n}(l_0'l_0 m_0'm_0)|\langle \chi_{v_0}|\chi_{v_n}\rangle|^2}{E - E_{v_n l_n}{}^{(m)} + i\tfrac{1}{2}\Gamma_{v_n l_n}{}^{(m)}}\right|^2 \tag{3.25}$$

with

$$k_{v_0 l_0'}{}^2 = k_{v_0 l_0}{}^2 + 2(\mathcal{E}_{v_0 l_0} - \mathcal{E}_{v_0 l_0'}), \tag{3.26}$$

$$\beta_{v_0} = \int |\alpha_{v_0'0}(R_e{}^{(0)},\Omega_f)|^2 d\Omega_f, \tag{3.27}$$

$$C_{l_n}(l_0'l_0 m_0'm_0) = \tfrac{4}{5}\pi \sum_{m_n}\langle Y_{l_0'm_0'}(\hat{R})|Y_{2,m_n-m_0'}{}^*(\hat{R})|Y_{l_n m_n}(\hat{R})\rangle\langle Y_{l_n m_n}(\hat{R})|Y_{2,m_n-m_0}(\hat{R})|Y_{l_0 m_0}(\hat{R})\rangle$$

$$= (2l_n+1)[(2l_0'+1)(2l_0+1)]^{1/2}$$

$$\times \begin{pmatrix} l_0' & 2 & l_n \\ 0 & 0 & 0 \end{pmatrix}\begin{pmatrix} l_n & 2 & l_0 \\ 0 & 0 & 0 \end{pmatrix}\sum_{m_n=-l_n}^{l_n}\begin{pmatrix} l_0' & 2 & l_n \\ -m_0' & m_0'-m_n & m_n \end{pmatrix}\begin{pmatrix} l_n & 2 & l_0 \\ -m_n & m_n-m_0 & m_0 \end{pmatrix}, \tag{3.28}$$

where we have averaged the cross section over the initial states m_0 and summed over the final states m_0', made the approximation $|\alpha_{0v_0}*(R_e{}^{(0)},\Omega_0)|^2\cong\beta_{v_0}/4\pi$ with the incident angles Ω_0 arbitrarily chosen, and finally adopted the Wigner's "$3j$" symbols for the Clebsch-Gordan coefficients[17] appearing in Eq. (3.28). In deriving Eq. (3.25), the α's have been taken outside of the R integrals because they vary slowly and most of their contribution to the integration comes from a narrow range of the internuclear separation $R=R_e{}^{(0)}$, the equilibrium distance of the ground state of the diatomic molecule.

The total width given by Eq. (3.21) takes for approximation (3.24) the form

$$\Gamma_{v_n l_n m_n}{}^{(m)}=\sum_{v_0 l_0}\frac{\beta_{v_0}k_{v_0 l_0}}{4\pi^2}|\langle X_{v_0}|X_{v_n}\rangle|^2(2l_0+1)(2l_n+1)\begin{pmatrix}l_0 & 2 & l_n\\0 & 0 & 0\end{pmatrix}^2\sum_{m_0}\begin{pmatrix}l_0 & 2 & l_n\\-m_0 & m_0-m_n & m_n\end{pmatrix}^2. \tag{3.29}$$

To remove the weak dependence of the total width on nuclear states m_n, we averaged, in Eq. (3.25), the width over m_n. Applying the operator $(2l_n+1)^{-1}\sum_{m_n}$ to Eq. (3.29), we obtain

$$\Gamma_{v_n l_n}{}^{(m)}=\sum_{v_0 l_0}\frac{\beta_{v_0}k_{v_0 l_0}}{4\pi^2}(2l_0+1)\begin{pmatrix}l_0 & 2 & l_n\\0 & 0 & 0\end{pmatrix}^2|\langle X_{v_0}|X_{v_n}\rangle|^2. \tag{3.30}$$

Now, the approximate cross section for resonance rotational excitation can be calculated from Eq. (3.25) with the β's estimated from the total width (3.30).

Because of the coefficients C_{l_n}, we have the following selection rules for resonance transitions between l_0 and l_0' rotational states:

$$\Delta l_0\equiv l_0'-l_0=0,\ \pm2,\ \pm4. \tag{3.31}$$

Thus, for two-quantum rotational excitation and de-excitation, we have from Eq. (3.25)

$$\sigma_r(l_0\to l_0\pm2)=(\beta_{v_0}{}^2/16\pi^3)\left(\frac{k_{v_0,l_0\pm2}}{k_{v_0 l_0}}\right)(2l_0+1)^{-1}\sum_{m_0 m_0'}\left|\sum_{v_n}\left\{\frac{C_{l_0}(l_0\pm2,l_0 m_0'm_0)|\langle X_{v_0}|X_{v_n}\rangle|^2}{E-E_{v_0 l_0}{}^{(m)}+i\frac{1}{2}\Gamma_{v_n l_0}{}^{(m)}}\right.\right.$$
$$\left.\left.+\frac{C_{l_0\pm2}(l_0\pm2,l_0 m_0'm_0)|\langle X_{v_0}|X_{v_n}\rangle|^2}{E-E_{v_n,l_0\pm2}{}^{(m)}+i\frac{1}{2}\Gamma_{v_n,l_0\pm2}{}^{(m)}}\right\}\right|^2; \tag{3.32}$$

and for four-quantum rotational excitation and de-excitation,

$$\sigma_r(l_0\to l_0\pm4)=\frac{\beta_{v_0}{}^2}{16\pi^3}\left(\frac{k_{v_0,l_0\pm4}}{k_{v_0 l_0}}\right)\frac{1}{2l_0+1}\sum_{m_0 m_0'}|C_{l_0\pm2}(l_0\pm4,l_0 m_0'm_0)|^2\left|\sum_{v_n}\frac{|\langle X_{v_0}|X_{v_n}\rangle|^2}{E-E_{v_n,l_0\pm2}{}^{(m)}+i\frac{1}{2}\Gamma_{v_n,l_0\pm2}{}^{(m)}}\right|^2. \tag{3.33}$$

IV. ROTATIONAL EXCITATION OF NITROGEN MOLECULES

A model calculation of resonance rotational excitation of N_2 is carried out from Eq. (3.25), treating the averaged with $\Gamma_{00}{}^{(m)}$, the electronic resonance energy $(\mathcal{E}_{00}{}^{(m)}+\Delta_{00}{}^{(m)})$, and the excited field of the target molecule as adjustable parameters. The procedure of the calculation is identical to that used in paper II[16] in which the resonance energy $E_{\gamma_n}{}^{(m)}$ [Eq. (3.22)] is now approximated by

$$E_{v_n l_n}{}^{(m)}=\mathcal{E}_{00}{}^{(m)}+\Delta_{00}{}^{(m)}+(v_n+\tfrac{1}{2})\omega_e{}^{(n)}-(v_n+\tfrac{1}{2})^2\omega_e{}^{(n)}$$
$$\times X_e{}^{(n)}+l_n(l_n+1)[B_2{}^{(n)}-(v_n+\tfrac{1}{2})\alpha_e{}^{(n)}], \tag{4.1}$$

where $\omega_e{}^{(n)}/2$ is the zero-point energy of the corresponding harmonic oscillator, $X_e{}^{(n)}$ is the anharmonicity constant, $B_e{}^{(n)}$ is the rotational constant, and $\alpha_e{}^{(n)}$ is the vibration-rotation coupling constant. The nuclear vibrational wave functions are approximated by the

Morse anharmonic wave function. The coefficients C_{l_n}, involving the Clebsch-Gordan coefficients, are evaluated using the tables provided by Rotenberg et al.[18]

In Fig. 1, the cross section for resonance elastic scattering which agrees fairly well with the previous calculation[15] using harmonic wave functions, is plotted as a function of the incident electron energy. For $\Gamma_{00}{}^{(m)}=0.152$ eV and $\mathcal{E}_{00}{}^{(m)}+\Delta_{00}{}^{(m)}=1.89$ eV, the calculated cross section for $\Delta l_0=0$ is indistinguishable from that calculated for $\Delta v_0=0$ obtained as a special case for vibrational excitation.[16] A comparison of the maxima and minima of the resonance elastic cross section with those observed experimentally[19] is displayed in Table I. The agreement is very good on the whole. In the experimentally observed curve, the first

[17] See for example, A. Messiah, *Quantum Mechanics* (North-Holland Publishing Company, Amsterdam, 1962), Vol. II.

[18] M. Rotenberg, R. Bivins, N. Metropolis, and J. K. Wooten, Jr., *The 3-j and 6-j Symbols*, (The Technology Press, MIT, Cambridge, Massachusetts, 1959).

[19] G. J. Schulz, in *Atomic Collision Processes* edited by M. R. C. McDowell (North-Holland Publishing Company, Amsterdam, 1964), p. 124.

TABLE I. Comparison of the experimental and theoretical maxima and minima in the cross section for elastic resonance scattering of electrons by N_2 molecules.

Identifica-tion for the maxima and minima	Electron energy (eV)			
	Maxima		Minima	
	Exper-imental[a]	Theoretical	Exper-imental[a]	Theoretical
1	1.92	1.98	2.04	2.09
2	2.16	2.22	2.29	2.36
3	2.46	2.47	2.59	2.60
4	2.69	2.70	2.82	2.86

[a] Reference 19.

peak at the low energy side is, however, larger then the second peak in contradiction to the calculated curve (Fig. 1). This is due to the direct elastic scattering which is not included in the calculated curve. Since the latter scattering does not affect the positions of the resonance peaks, the agreement obtained in Table I is very encouraging.
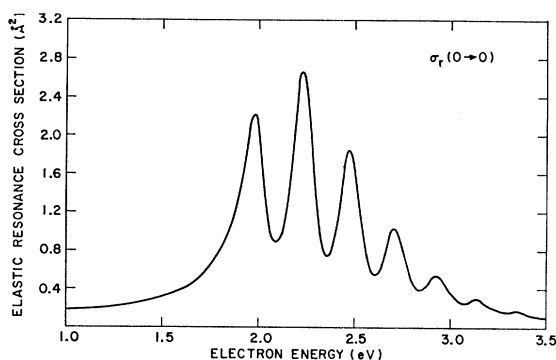

FIG. 1. Calculated cross section for elastic resonance scattering of electrons by N_2 molecules as a function of the incident electron energy.

The results of our calculation for resonance rotational excitation of N_2 are shown in Figs. 2 and 3. Figure 2 shows the resonance excitation function for the excitation of ground rotational state $l_0 = 0$ to the second- and fourth-excited rotational states $l_0' = 2$, 4. Excitations from the first excited rotational state $l_0 = 1$ to the third- and fifth-rotational state $l_0' = 3$, 5 are shown in Fig. 3. The characteristic multipeak structure[20] for resonance elastic scattering and vibrational excitation is again found for resonance rotational excitation. In addition, we observe for each case a tail for the cross section, extending towards the low energy region.

In this model calculation, we have made the tacit assumptions for the resonance structure of the scattering system that in the energy region pertinent to the present problem only an isolated compound state is primarily of importance and that this compound state is formed largely as a result of virtual excitations of target states. In Paper II,[16] we have found that the set

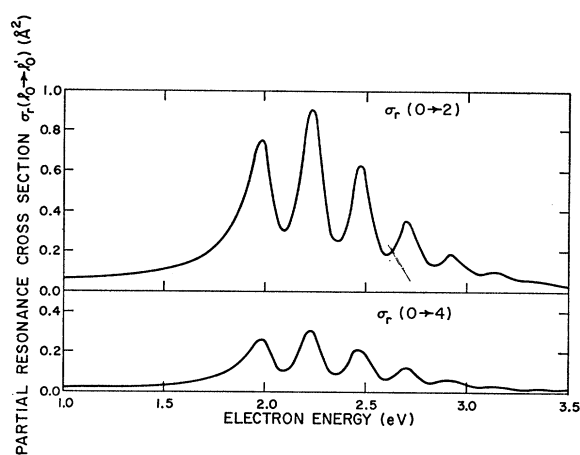[20] G. J. Schulz, Phys. Rev. **125**, 229 (1962); **135**, A988 (1964).

FIG. 2. Energy dependence of the partial cross sections for the resonance rotational excitation of the ground state N_2 molecule by slow electron impact.

of molecular constants needed for the excited field of the target molecule is very similar to that of the $x^1\Sigma_g^-$ state of N_2. It was misleading to interpret this finding as an indication that the excited field of the target molecule is generated solely by the $x^1\Sigma_g^-$ state of N_2. Rather, it should be interpreted that the similarity between the set of constants and that of the $x^1\Sigma_g^-$ state is coincidental. *The set of molecular constants thus really describes an effective molecular field created by virtual excitations of the target molecule in which the projectile electron propagates.* It should be noted that the Q-projected subspace (i.e., the subspace involving virtual excitation of the target molecule, $Q = 1 - P$) also contains a substantial component of the ground electronic state of the target molecule with excited nuclear vibrational and rotational states [see Eqs. (2.9) and (2.11)].

Since calculations for direct rotational excitation have been carried out by several workers,[1-5] we will not repeat them here but merely investigate briefly the
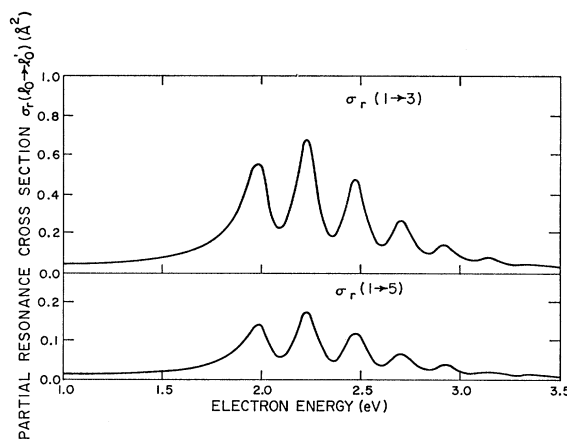

FIG. 3. Energy dependence of the partial cross sections for the resonance rotational excitation of the first excited rotational state of the N_2 molecule by slow electron impact.
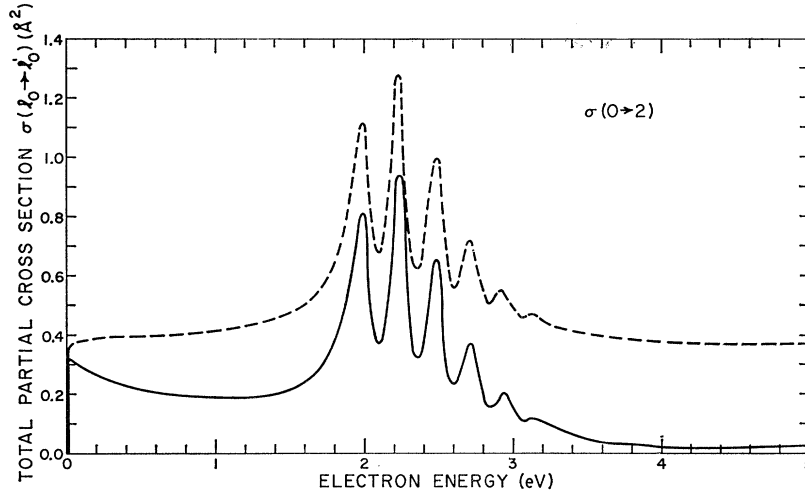
FIG. 4. Energy dependence of the partial cross sections for two-quantum rotational excitation of N_2 molecules by slow electron impact. (Interference effects due to direct and resonance excitations are neglected.) The solid curve indicates that the cross section for direct excitation is taken from Dalgarno and Moffett's calculation and the dashed curve indicates the cross section from Gerjuoy and Stein.

effects due to interference between the direct and resonance excitations. If, following Dalgarno and Moffett,[3] we approximate the averaged direct scattering potential Eq. (3.11) by

$$\langle \mathfrak{U}_d(\mathbf{r}_0, \hat{R}) \rangle \cong 2(q/r_0{}^3 + \alpha'/2r_0{}^4) P_2(\hat{r}_0, \hat{R}), \quad (4.2)$$

the direct transition matrix elements take the expression

$$\mathcal{T}_d(l_0 m_0 \rightarrow l_0' m_0')$$
$$= -(32\pi^2/5)\langle Y_{l_0' m_0'}(\hat{R}) | Y_{2,\,m_0-m_0'}{}^*(\hat{R}) | Y_{l_0 m_0}(\hat{R}) \rangle$$
$$\times \{\tfrac{1}{3}q + (\tfrac{1}{32}\alpha'\pi)k_{l_0' l_0}\} Y_{2,\,m_0-m_0'}(\Omega) \quad (4.3)$$

with

$$k_{l_0' l_0} = (k_{v_0 l_0'}{}^2 + k_{v_0 l_0}{}^2 - 2k_{v_0 l_0'}k_{v_0 l_0}\cos\theta)^{1/2}, \quad (4.4)$$

where q is the quadrupole moment of N_2, α' is the nonspherical portion of the polarizability of N_2, including both parallel and perpendicular polarization $[\alpha' = \tfrac{2}{3}(\alpha_{||} + \alpha_\perp)]$, and finally $\Omega = (\theta, \phi)$, includes the angles between the scattered and the incident direction of the electron.

Substitution of the transition matrix elements $\mathcal{T}_d$ and $\mathcal{T}_r$ as approximated by Eqs. (4.3) and (3.20), respectively, into Eq. (2.28) yields with the help of approximation (3.24)

$$\sigma_i(l_0 \rightarrow l_0') = 8/(5\pi)^{1/2}\left(\frac{k_{v_0 l_0'}}{k_{v_0 l_0}}\right)$$

$$\times \sum_{v_n l_n} \frac{C_{l_n}'(l_0' l_0) | \langle \chi_{v_0} | \chi_{v_n} \rangle |^2}{(E - E_{v_n l_n}{}^{(m)})^2 + \tfrac{1}{4}(\Gamma_{v_n l_n}{}^{(m)})^2} \quad (4.5)$$

with

$$C_{l_n}'(l_0' l_0) = \left(\frac{2l_0 + 1}{2l_0' + 1}\right)^{1/2}\begin{pmatrix} l_0' & 2 & l_0 \\ 0 & 0 & 0 \end{pmatrix} \sum_{m_0, m_0'} (-)^{m_0 + 1}$$

$$\times \{\lambda_{m_0' m_0}(E - E_{v_n l_n}{}^{(m)}) + \tfrac{1}{2}\zeta_{m_0' m_0}\Gamma_{v_n l_n}{}^{(m)}\}$$

$$\times C_{l_n}(l_0' l_0 m_0' m_0)\begin{pmatrix} l_0' & 2 & l_0 \\ -m_0' & m_0' - m_0 & m_0 \end{pmatrix}, \quad (4.6)$$

$$\lambda_{m_0' m_0} = \int \text{Re}\{f(k_{v_0 l_0} m_0 m_0'\Omega)\} d\Omega, \quad (4.7)$$

$$\zeta_{m_0' m_0} = \int \text{Im}\{f(k_{v_0 l_0} m_0 m_0'\Omega)\} d\Omega, \quad (4.8)$$

$$f(k_{v_0 l_0} m_0 m_0'\Omega) = (\tfrac{1}{3}q + (\tfrac{1}{32}\alpha'\pi)k_{l_0' l_0})Y_{2,m_0'-m_0}(\Omega)$$
$$\times \alpha_{0v_0}{}^*(R_e{}^{(0)}\Omega_0)\alpha_{v_0'0}(R_e{}^{(0)}\Omega_f), \quad (4.9)$$

where in Eq. (4.5) we have averaged the interference cross section over initial states m_0 and summed over the final states m_0'.

From the coefficient C_{l_n}', we observe that in the framework of the present approximation, the interference for four-quantum excitation is zero. Any interference which may be of importance should appear in the two-quantum excitation. Unfortunately, we do not know at the present a reliable method for estimating quantities λ and ζ. In Fig. 4, we plot the sum of direct and resonance cross sections for two-quantum rotational excitation without consideration of the interference effects. The direct excitation cross section is calculated from approximation Eq. (4.3), taking the experimental values $-1.1ea_0{}^2$ (or -1.48 Debye Å) and $4.18a_0{}^3$ respectively[21,22] for the quadrupole moment and the nonspherical polarizability of N_2. For comparison, we also included in Fig. 4 the case where the nonspherical polarization term is omitted for the direct excitation cross section.[2] The distortion effects on the direct excitation are not included in Fig. 4, since it has been shown[5] that they are very sensitive to the approximate potential used in the investigations.

We thus conclude that in problems concerning slow electron scattering by molecules, one may distinguish two types of scattering: the direct and resonance scattering. In the direct scattering, the projectile

[21] J. D. Poll, Phys. Letters 7, 32 (1963).
[22] M. Born, Optik (Julius Springer-Verlag, Berlin, 1933).

FIG. 5. Energy dependence of the partial cross section for simultaneous resonance, vibrational and rotational excitations of ground state N_2 molecules by slow electron impact.
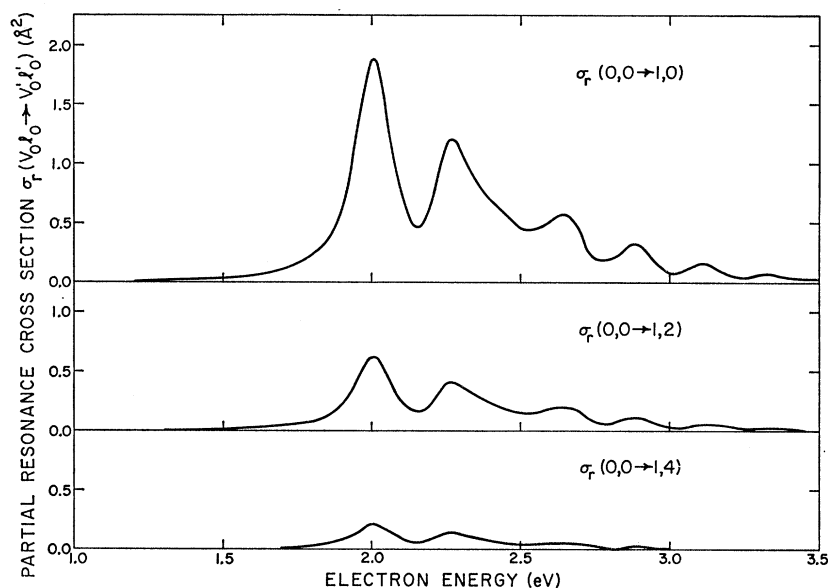
electron propagates (except for distant resonance) mainly in the unexcited field of the target molecule, tolerating comparatively smaller distortion; but, in the resonance scattering, the projectile electron propagates in the excited field of the target molecule, suffering
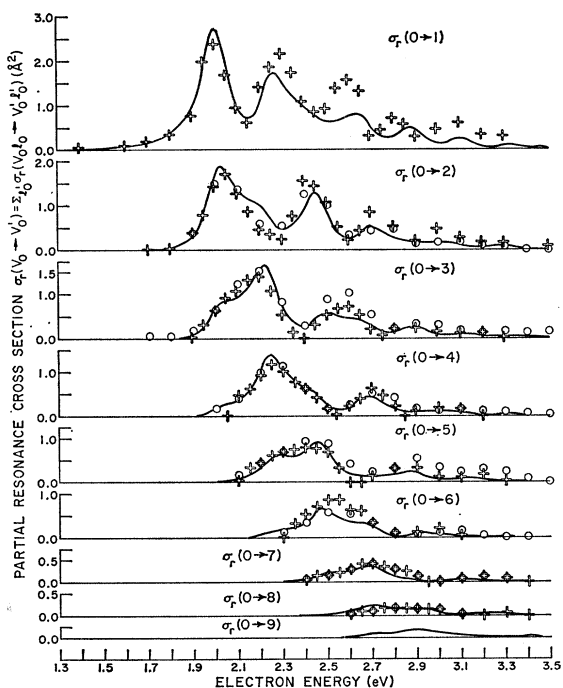

FIG. 6. Energy dependence of the partial cross section for the excitation of the ground state N_2 molecule to various excited vibrational states by slow electron impact. The circles and the crosses are the experimental data of Schulz measured at the forward angle and at an angle of 72 deg, respectively. These experimental data are normalized to our calculated values by a single scale factor.

considerable distortion in forming compound states. This classification is, however, not unique, since the distant resonance in the direct scattering may become rapid varying resonance scattering as the incident electron energy reaching into the appropriate energy region. Also this classification does not distinguish the broad potential resonance from the direct scattering. Nevertheless, this classification of direct and resonance scattering is physically desirable and mathematically convenient.

It is of interest to discuss the effects on resonance vibrational excitation due to the extra degrees of freedom provided by possible rotational transitions. Thus for a given vibrational excitation, we may have possible accompanying rotational transitions $v_0 l_0 \rightarrow v_0' l_0$, $v_0 l_0 \rightarrow v_0', l_0 \pm 2$, $v_0 l_0 \rightarrow v_0', l_0 \pm 4$ (see Fig. 5). Since the rotational level spacings are within the uncertainty of electron beam width used in measuring vibrational excitation, it is reasonable to assume that the observed cross sections for vibrational excitation are given by

$$\sigma_r(v_0 \rightarrow v_0') = \sum_{j=0}^{2} \sigma_r(v_0 l_0 \rightarrow v_0', l_0 + 2j)$$

$$+ \sum_{\substack{j=0 \\ 2j < l_0}}^{2} \sigma_r(v_0 l_0 \rightarrow v_0', l_0 - 2j). \quad (4.10)$$

A comparison of the calculated vibrational excitation cross section from Eq. (4.10) with that measured by Schulz[20] is given in Fig. 6. The increase in the magnitude of the cross section shown in Fig. 6 results in a rise of the calculated total virbational excitation cross section [i.e., $\sum_{v'} \sigma_r(0 \rightarrow v')$] from 3.52 Å^2 to 5.13 Å^2 at 2.2 eV which is consistent with the analysis of the swarm data.[6]