

Vibrational-rotational excitation of polar molecular ions by charged particles

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The problem of excitation of rotations and vibrations of polar molecular ions by charged particles is considered in the quasiclassical approximation. The particles move along hyperbolic trajectories, the inelastic transitions being induced by charge-dipole interactions and are considered within the framework of the exponential approximation for the scattering matrix. An interesting point is that in a rotating reference system, the series in the argument of the exponential (the Magnus series) is cut off after the first term in the zeroth approximation with respect to the adiabaticity parameter $\langle\omega\rangle\tau_c$. In this way, an exact expression can be found for the scattering matrix elements. Calculations are carried out for both the differential and the total excitation cross sections for polar molecular ions excited by charged particles. The results of a numerical calculation of the cross section for rotational excitation of the CH^+ ion ($j_i = 0 - j_f = 1$) by electrons are compared with the results of other authors. The limits of applicability of the theory are discussed.

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INTRODUCTION

As is well known, the excitation of vibrational-rotational states of molecules is the basic mechanism by which slow charged particles lose energy in molecular gases. The cross sections with which such processes of excitation of vibrations and rotations of molecules take place are of significant interest in the study of low-temperature plasma if there is a large number of molecules and molecular ions in the latter. The vibrational-rotational excitation of neutral molecules in collisions with electrons^{1,2} and ions^{3,4} have been studied intensively, both theoretically and experimentally. However, the excitation of molecular ions by charged particles is more difficult to study experimentally, and only a few theoretical communications exist on this subject.

Within the framework of the Born-Coulomb approximation, Boikova and Ob'edkov⁵ were the first to consider the problem of dipole and quadrupole excitations of molecular ions by electrons. The rotational excitation of the CH^+ ion by electrons was considered in this approximation in the work of Chu and Dalgarno.⁶ The expressions for the cross sections, obtained in quantum formalism, are very cumbersome. Therefore, a much simpler quasiclassical method has been applied in a number of researches,⁷⁻⁹ a method that yields nothing in accuracy to the quantum mechanical one.^{3,9} The transition probability has been considered in first-order perturbation theory with use of a Coulomb trajectory for the relative motion of the pair of colliding particles.

This paper treats the vibrational-rotational excitation of polar molecular ions in collisions with charged particles in terms of the quasiclassical method, with use of an exponential approximation for the scattering matrix. The essence of the method is as follows: the scattering matrix is represented in the form e^{-iA} ,

where A is a Hermitian operator, perhaps expanded in a series of time-dependent integrals of the Hamiltonian interaction commutators (the Magnus expansion).¹⁰ It is noteworthy that in the rotating system of coordinates, for the interaction of the type charge-dipole, the series in the argument of the exponential is cut off at the first term, enabling us to find an exact analytic expression for the elements of the scattering matrix in the nonadiabatic limit.

The condition of quasiclassical behavior of the scattering in a Coulomb field is satisfied if the relative angular momentum of the pair of colliding particles is large: $L = Mva/\hbar = Z_1Z_2e^2/\hbar v \gg 1$, where a is the characteristic length (cf. Ref. 11, pp. 214, 596). This condition sets an upper limit on the energy of relative motion: $E \leq 13.6(Z_1Z_2)^2M/m[\text{eV}]$, where Z_1 is the charge of the molecular ion, Z_2 is the charge of the emerging particle, M is their reduced mass, m is the mass of the electron. In what follows, we shall assume that the kinetic energy E greatly exceeds the quantum $\hbar\langle\omega\rangle$, where $\langle\omega\rangle$ is the characteristic frequency corresponding to the internal motion of the molecule. The first condition is necessary and the second sufficient to introduce the trajectory and neglect contributions due to in-

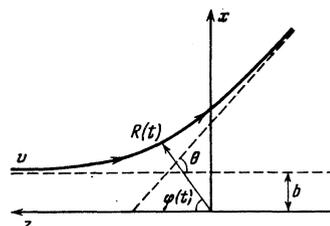


FIG. 1. Classical trajectory of a charged particle in the Coulomb field of a molecular ion. The origin coincides with the center of mass of the system.

elastic processes. The developed theory is valid in the nonadiabatic limit, i.e., the following inequality should hold: $\beta = \langle \omega \rangle a / v \ll 1$. The latter condition is the most stringent in the case of Coulomb repulsion, since one should have $\beta \ll 1/2\pi$ (see Eq. (2.7) below).

In first section of the work, a formula is obtained for the elements of the scattering matrix with account of only the dipole term in the interaction potential. In the second and third sections, results are given of calculations of the differential and total cross sections, both in the case of purely rotational excitations and in the case in which an effective excitation of vibrations of the molecular ions take place along with the excitation of the rotations.

1. THE SCATTERING MATRIX

We consider the excitation process

$$M^+(n_i, m_i) + A^+ \rightarrow M^+(n_f, m_f) + A^+,$$

where j_i, m_i are the rotational angular momentum and its projection on the preferred axis before scattering, n_i is the vibrational quantum number; j_f, m_f, n_f are the corresponding quantum numbers after scattering. For definiteness, we consider the collision of positively charged ions. The case of attraction is considered similarly. We assume the particle A^+ to be structureless. In the anisotropic part of the interaction operator, we take into account only the dipole term

$$V = Z_2 e \frac{\mathbf{dR}}{R^3}, \quad (1.1)$$

where R is the distance between the mass centers of the particles, \mathbf{d} is the dipole moment of the molecular ion (relative to the mass center of the molecule).

Let the vector \mathbf{R} lie in the plane $\mathbf{x} \cdot \mathbf{z}$ that is perpendicular to the orbital momentum \mathbf{L} . We direct the \mathbf{z} axis along the relative velocity \mathbf{v} , the \mathbf{x} axis along the impact parameter b (see the drawing). The transition from the rotating system of coordinates is accomplished with the help of the finite rotation operator $\exp(-i\varphi(t)J_y)$ (Ref. 12, p. 26). Here $\varphi(t)$ is the angle between the \mathbf{z} axis and the radius vector $\mathbf{R}(t)$. We set the time $t=0$ as the instant of closest approach, so that $\varphi(-\infty)=0$ and $\varphi(+\infty)=\pi-\theta$, where θ is the scattering angle.

In the zeroth approximation in $\langle \omega \rangle \tau_c$, where τ_c is the characteristic time of interaction, we get the following equation for the evolution operator:

$$i\hbar \frac{\partial}{\partial t} U(t, -\infty) = V(t)U(t, -\infty) + \hbar\varphi(t)[J_y, U(t, -\infty)]. \quad (1.2)$$

We shall seek a solution of Eq. (1.2) in the form

$$U(t, -\infty) = e^{-iA(t)} \exp(i\varphi(t)J_y), \quad A(-\infty) = 0. \quad (1.3)$$

Substituting (1.3) in (1.2), we get

$$i\hbar \frac{\partial}{\partial t} e^{-iA(t)} = [V(t) + \hbar\varphi(t)J_y] e^{-iA(t)}. \quad (1.4)$$

In the rotating system of coordinates with the \mathbf{z} axis directed along the radius vector \mathbf{R} , we get $dR - d_z R$ and, consequently, $\varphi(t) = bv/R^2$ and $V = Z_2 e d_z / R^2$ depend on the time in the same fashion—a unique feature of the charge-dipole interaction. We therefore verify directly

that the commutators

$$[V(t) + \hbar\varphi(t)J_y, V(t') + \hbar\varphi(t')J_y] = 0 \quad (1.5)$$

vanishes at different instants of time and the series in the argument of the exponential (the Magnus series) is cut off at the first term. With account of (1.3) and (1.4), we find the exact expression for the scattering operator ($S = U(+\infty, -\infty)$):

$$S = \exp \left[-i\varphi \left(J_y + \frac{Z_2 e d_z}{\hbar b v} \right) \right] \exp(i\varphi J_y), \quad (1.6)$$

where we have introduced the expression $\varphi = \varphi(+\infty) = \pi - \theta$. Thus, the scattering operator is a function of the orbital momentum and the scattering angle and does not depend on the other characteristics of the trajectory.

Let

$$\hat{a} = -i\varphi J_y, \quad \hat{b} = -iZ_2 e d_z / \hbar b v.$$

We consider a generating function of the form (see also Ref. 13)

$$Q(t) = e^{\hat{a} + \hat{b}t} e^{-\hat{a}t} = \sum_{n=0}^{\infty} \frac{t^n}{n!} Q_n, \quad (1.7)$$

where \hat{a} and \hat{b} do not commute, but $[\hat{b}, [\hat{a}, \hat{b}]] = 0$, i.e., all commutators in which \hat{b} is encountered more than once vanish. Differentiating n times both sides of Eq. (1.7), we find a recurrence relation for the coefficients Q_n :

$$Q_n = [\hat{a}, Q_{n-1}] + b Q_{n-1}, \quad Q_0 = 1. \quad (1.8)$$

The first few coefficients are given in the Appendix.

On the other hand, an exponential of the sum of two non-commuting operators can be displayed in the form of an infinite product of exponentials.^{10,14} We proceed in the following fashion:

$$\begin{aligned} Q(t) &= \exp(\hat{a}t/2) \exp(\hat{b}t/2) \exp(\hat{b}t) \exp(c_2 t^2) \exp(c_3 t^3) \dots \\ &\dots \exp(-\hat{a}t/2) \exp(-\hat{a}t/2) \\ &= \exp(\hat{a}t/2) \exp(q_1 t) \exp(q_2 t^2) \dots \exp(-\hat{a}t/2). \end{aligned} \quad (1.9)$$

Comparing the expansion coefficients in (1.7) and (1.9) as $t \rightarrow 0$, we find

$$q_1 = \hat{b}, \quad q_2 = \frac{1}{2}[\hat{a}, [\hat{a}, \hat{b}]]; \quad c_2 = -\frac{1}{2}[\hat{a}, \hat{b}], \quad c_3 = \frac{1}{6}[\hat{a}, [\hat{a}, \hat{b}]] \quad (1.10)$$

and so on.

It is convenient to introduce more suitable notation for the commutators $[\hat{a}, \hat{b}]$ with increasing number \hat{a} :¹⁴

$$\{\hat{a}^n, \hat{b}\} = \hat{b}, \quad \{\hat{a}^1, \hat{b}\} = [\hat{a}, \hat{b}], \quad \{\hat{a}^2, \hat{b}\} = [\hat{a}, [\hat{a}, \hat{b}]], \quad (1.11)$$

so that

$$\{\hat{a}^{n+1}, \hat{b}\} = [\hat{a}, \{\hat{a}^n, \hat{b}\}], \quad \{\hat{a}^n, \{\hat{a}^m, \hat{b}\}\} = \{\hat{a}^{n+m}, \hat{b}\}. \quad (1.12)$$

It is shown in the Appendix that if $[\hat{b}, [\hat{a}, \hat{b}]] = 0$, then there exists a simple formula in the general case, for arbitrary q_n :

$$q_n = \frac{\{\hat{a}^{n-1}, \hat{b}\}}{2^{n-1} n!}, \quad n=1, 3, \dots \quad (1.13)$$

Returning to our problem, we note that $[J_y, [J_y, z]] = z$ and, consequently, $\{\hat{a}^{n-1}, \hat{b}\} \propto \varphi^{n-1} d_z$. It remains to make use of the formal theory developed above (see Eqs. (1.7)–(1.13)), to obtain the result of interest to us. In the final form, the scattering operator has the following form in the dipole approximation:

$$S = \exp\left(-\frac{i\varphi J_y}{2}\right) \exp\left(-i\frac{2Z_2ed}{\hbar\nu a} \sin\frac{\theta}{2} \cos\gamma\right) \exp\left(\frac{i\varphi J_y}{2}\right), \quad (1.14)$$

where γ is the angle between \mathbf{d} and the \mathbf{z} axis in the rotating system of coordinates. In the derivation of (1.14), use was made of the connection between the impact parameter and the scattering angle in the Coulomb field (Ref. 15, p. 70):

$$b = a \operatorname{ctg} \frac{\theta}{2}, \quad a = \frac{Z_1 Z_2 e^2}{2E}. \quad (1.15)$$

We now discuss the region of applicability of the formula (1.14). First, in the anisotropic part of the interaction operator

$$V_a = \sum_{k=1} V_k(r, R) P_k(\cos\gamma) \quad (1.16)$$

we have neglected the quadrupole term ($k=2$), a correct procedure if $\delta_1 \gg \delta_2$, where

$$\delta_1 = \frac{1}{\hbar} \int_{-\infty}^{+\infty} \frac{Z_2 e d}{R^2} dt, \quad \delta_2 = \frac{1}{\hbar} \int_{-\infty}^{+\infty} \frac{Z_2 e Q}{R^3} dt. \quad (1.17)$$

Here Q is the quadrupole moment of the molecular ion. The corresponding integrals are calculated in elementary fashion, so that we obtain

$$\frac{\delta_2}{\delta_1} = \frac{Q}{ad} f(\theta), \quad f(\theta) = \frac{2 \operatorname{tg}(\theta/2)}{\pi - \theta} \left[1 - \frac{\pi - \theta}{2} \operatorname{tg} \frac{\theta}{2} \right]. \quad (1.18)$$

The function $f(\theta)$ reaches its maximum value at $\theta = \pi$ (backward scattering) and is equal to $f(\pi) = 1/3$. Thus, if we require

$$Q/3ad \ll 1, \quad (1.19)$$

then the contribution of the quadrupole interaction can be neglected throughout the entire range of scattering angles.

Second, the adiabatic parameter $\langle \omega \rangle \tau_c$ should be small. In each case, we can expect that if the condition $\beta = \langle \omega \rangle a / v \ll 1$ is satisfied with a good deal to spare, then the boundary of the region of non-adiabaticity will have little effect on the calculation of the cross sections, at least for weakly excited vibrational-rotational states. The conditions enumerated above are well satisfied if we consider the excitation of a heavy molecular ion, possessing a large dipole moment, by a light charged particle. If the excitation is produced by heavy particles, say protons, then it can be shown that only for the low-lying vibrational levels (or even pure rotation) will the entire set of conditions be incontrovertibly satisfied.

Keeping this circumstance in mind, we shall consider the molecule as a rotating harmonic oscillator. We can then write

$$\mathbf{d} = d(r_e) + d^{(v)}(r_e) \mathbf{x} = d_e \left(1 + \mu_1 \frac{\mathbf{x}}{r_e} \right), \quad \mu_1 = \frac{r_e d^{(v)}(r_e)}{d_e}, \quad (1.20)$$

where d_e is the dipole moment of the ion at the equilibrium distance between the nuclei r_e : $\mathbf{x} = \mathbf{r} - \mathbf{r}_e$ is the vibrational coordinate. We introduce the notation

$$\alpha = \mu_1 \left(\frac{B_e}{\hbar \omega_e} \right)^{1/2} \delta \sin \frac{\theta}{2}, \quad \delta = \frac{2Z_2 e d_e}{\hbar \nu a}, \quad (1.21)$$

where $B_e = \hbar^2 / 2\mu r_e^2$ is the rotational constant, ω_e is the frequency of vibration. The elements of the scattering matrix, after integration over the vibrational coordin-

ates, have the following form:

$$\begin{aligned} \langle n_i, j_i, m_i | S | n_j, j_j, m_j \rangle &= \left(\frac{n_{<}}{n_{>}} \right)^{1/2} \sum_{m_{ij}} d_{m_{ij}}^{n_{<}} \left(\frac{\varphi}{2} \right) d_{m_{ij}}^{n_{>}} \left(\frac{\varphi}{2} \right) \\ &\times \int d\Omega Y_{j_i, \mu_i}^*(\Omega) Y_{j_j, \mu_j}(\Omega) (-i\alpha \cos \gamma)^s \\ &\times \exp\left(-i\delta \sin \frac{\theta}{2} \cos \gamma - \frac{\alpha^2}{2} \cos^2 \gamma\right) L_{n_{<}}^s(\alpha^2 \cos^2 \gamma). \end{aligned} \quad (1.22)$$

Here $s = |n_j - n_i|$, $n_{>}$ ($n_{<}$) is the greater (lesser) of the numbers n_i, n_j ; L_n^s are the Laguerre polynomials, d^J are the finite rotation matrices (Ref. 12, p. 68).

For further progress, we need the formulas

$$\exp\left(-\frac{\alpha^2}{2} \cos^2 \gamma\right) = \sum_{J=0}^{\infty} [J^s] S_J(\alpha) P_J(\cos \gamma), \quad (1.23)$$

where the expansion coefficients of this function in a series in the Legendre polynomials are given by the expression

$$S_J(\alpha) = \exp\left(-\frac{\alpha^2}{4}\right) \sum_{lm} (-1)^l \begin{pmatrix} l & l & J \\ 0 & 0 & 0 \end{pmatrix} \begin{pmatrix} l & l & J \\ m & -m & 0 \end{pmatrix} i_l \left(\frac{\alpha^2}{4} \right), \quad (1.24)$$

and also

$$\begin{aligned} &(-i\alpha \cos \gamma)^s \exp\left(-i\delta \sin \frac{\theta}{2} \cos \gamma\right) L_{n_{<}}^s(\alpha^2 \cos^2 \gamma) \\ &= \sum_{k=0}^{n_{<}} \frac{1}{k!} \binom{n_{>}}{n_{<} - k} \alpha^{2k+s} \sum_{L=0}^{\infty} (-i)^L [L^s] j_L^{(2k+s)} \left(\delta \sin \frac{\theta}{2} \right) P_L(\cos \gamma). \end{aligned} \quad (1.25)$$

The result (1.24) is obtained with the help of the well known formula of the d -function of doubled argument and the integral of the product of three d -functions (Ref. 12, pp. 77, 84). The expression in the round brackets in (1.24) is the $3j$ symbol. In both equations (1.24) and (1.25), we have used the standard notation

$$j_l(x) = \left(\frac{\pi}{2x} \right)^{1/2} J_{l+1/2}(x), \quad i_l(x) = \left(\frac{\pi}{2x} \right)^{1/2} I_{l+1/2}(x), \quad (1.26)$$

and also $[J^2] = 2J + 1$, setting $[J] = (2J + 1)^{1/2}$; $j_L^{(s)}(x)$ is the s -th derivative of this function with respect to its argument.

Substituting the Eqs. (1.23), (1.25), in (1.22), we obtain

$$\begin{aligned} \langle n_i, j_i, m_i | S | n_j, j_j, m_j \rangle &= (-1)^{m_i} [j_i j_j] \left(\frac{n_{<}}{n_{>}} \right)^{1/2} \sum_{k=0}^{n_{<}} \frac{1}{k!} \binom{n_{>}}{n_{<} - k} \\ &\times \alpha^{2k+s} \sum_{JLMQ} (-i)^L [J^2 L^2 \kappa^2] \begin{pmatrix} j_i & \kappa & j_j \\ -m_i & q & m_j \end{pmatrix} \begin{pmatrix} j_i & \kappa & j_j \\ 0 & 0 & 0 \end{pmatrix} \begin{pmatrix} J & L & \kappa \\ 0 & 0 & 0 \end{pmatrix}^2 \\ &\times d_{q0}^{\kappa} \left(\frac{\varphi}{2} \right) S_J(\alpha) j_L^{(2k+s)} \left(\delta \sin \frac{\theta}{2} \right). \end{aligned} \quad (1.27)$$

Formula (1.27) for the elements of the scattering matrix is accurate within the framework of the semiclassical method. Under the assumptions made relative to the collision mechanism, it gives the answer to the stated problem in the most general form.

2. RIGID-ROTATOR APPROXIMATION

In the quasiclassical picture of the description of the excitation process, we assume that the emerging charged particle moves along a hyperbolic trajectory in the Coulomb field of the molecular ion (see the draw-

ing). The differential cross section of the scattering is given by the Rutherford formulas (Ref. 15, p. 70)

$$d\sigma_{cl} = \frac{a^2 d\omega}{4\sin^4(\theta/2)} = \frac{2\pi a^2 d(\sin(\theta/2))}{\sin^2(\theta/2)}. \quad (2.1)$$

By virtue of our assumptions ($\hbar\langle\omega\rangle/E \ll 1$ and $L \gg 1$), nonadiabatic transitions do not affect the trajectory of the particle and the differential cross section of the $i \rightarrow f$ transition is defined as

$$d\sigma_{if} = \frac{1}{|j_i|^2} \sum_{m_i, m_f} |\langle n_{if}, m_i | S | n_{ij}, m_j \rangle|^2 d\sigma_{cl}. \quad (2.2)$$

If $n_i = n_f = 0$, then we are dealing with purely rotational excitation. Simple estimates show that for electrons the parameter α is small ($|\alpha| \ll 1$) over practically the entire range of energies in which the developed theory is valid. For heavy charged particles, the condition $|\alpha| \ll 1$ is satisfied only at low energies—below the threshold of excitation of the vibrations. Therefore, the formulas given below for heavy particles have a limited region of applicability with respect to the energy. The most radical situation $\alpha = 0$ corresponds to the rigid-rotator approximation. Inserting the elements of the scattering matrix (1.27) with $\alpha = 0$ in (2.2), we find the differential cross section of transition excitation $j_i \rightarrow j_f$ ($i \neq f$):

$$d\sigma(j_i \rightarrow j_f) = |j_i|^2 \sum_{\kappa} [\kappa^2 \begin{pmatrix} j_i & j_f & \kappa \\ 0 & 0 & 0 \end{pmatrix}]^2 j_i^2 \left(\delta \sin \frac{\theta}{2} \right) d\sigma_{cl}. \quad (2.3)$$

The expression for the total cross section of the transition, obtained upon integration over all scattering directions, reduces to quadrature. For example, in the case of the transition $0 \rightarrow j$ ($j = 2, 3, \dots$)

$$\sigma(0 \rightarrow j) = \frac{8\pi}{3} \left(\frac{Z_1 e d_e}{\hbar v} \right)^2 \left[\frac{2j+1}{j(j^2-1)(j+2)} - 3(2j+1) \int_0^{\pi} \frac{dx}{x^2} j_i^2(x) \right]. \quad (2.4)$$

The integral on the right of Eq. (2.4) is calculated numerically without any special difficulty. So far as the transition $0 \rightarrow 1$ is concerned, the differential cross section behaves in the limit $\theta \rightarrow 0$ as $\theta^{-1} d\theta$ and the total cross section diverges logarithmically at the lower limit (i.e., as $b \rightarrow \infty$). The problem of divergence arises also in the case of excitation of neutral molecules by charged particles.¹⁶

The situation resolves into the following: the basic contribution to the cross section σ_0 is made by distant collisions, in which the curving of the trajectory takes place weakly. And, although the parameter β is small as before, the parameter $\beta\varepsilon$, where ε is the eccentricity of the orbit, can be as large as desired. Since $\beta\varepsilon$ represents the ratio of the collision time to the period of rotation of the nuclei, the nonadiabatic condition for the process is violated. However, this occurs at such impact parameters b_0 at which it is known beforehand that perturbation theory holds.

In order to estimate correctly the trajectories both with $b \leq b_0$ and with $b > b_0$, we proceed in the following fashion. We carry out the change in variables in (2.1):

$$\sin \frac{\theta}{2} = \frac{1}{\varepsilon} = \left(1 + \frac{b^2}{a^2} \right)^{-1/2}. \quad (2.5)$$

Further, we so choose b_0 that $\delta/\varepsilon_0 \ll 1$, but still $\beta\varepsilon_0$

$\ll 1$. We can then write

$$\sigma_{01} = 6\pi a^2 \int_1^{\infty} \varepsilon d\varepsilon j_1^2 \left(\frac{\delta}{\varepsilon} \right) + 2\pi a^2 \int_{\varepsilon_0}^{\infty} \varepsilon d\varepsilon P_{01}(\varepsilon). \quad (2.6)$$

where $P_{0,1}(\varepsilon)$ is the transition probability calculated by perturbation theory:^{8,9}

$$2\pi a^2 \int_{\varepsilon_0}^{\infty} \varepsilon d\varepsilon P_{01}(\varepsilon) = \frac{2\pi^3}{3} \left(\frac{Z_1 e d_e}{\hbar v} \right)^2 e^{-2\pi\beta} [\text{ip}\varepsilon_0 H_{\text{ip}}^{(1)}(\text{ip}\varepsilon_0) H_{\text{ip}}^{(1)'}(\text{ip}\varepsilon_0)]. \quad (2.7)$$

The factor $e^{-2\pi\beta}$ arises because of the Coulomb barrier in the case of repulsion. In the case of attraction, it is absent. The difference disappears in the situation to which we refer: $\beta \ll 1$ ($e^{-2\pi\beta} \approx 1$).

At small values of δ/ε_0 and $\beta\varepsilon_0$, both integrals in (2.6) depend on these parameters logarithmically. Therefore, at $b \sim b_0$, the regions of applicability of both theories overlap and ε_0 is eliminated from the final calculation:

$$\sigma(0 \rightarrow 1) = \frac{8\pi}{3} \left(\frac{Z_1 e d_e}{\hbar v} \right)^2 \left[\frac{7}{4} - 2C + \ln \left(\frac{\hbar v^2}{2Z_1 e d_e \omega} \right) - 9 \int_0^{\pi} \frac{dx}{x^2} j_1^2(x) \right]. \quad (2.8)$$

Here $C = 0.577\dots$ is Euler's constant, ω is the frequency of the rotational transition $0 \rightarrow 1$. In the limit $\delta \ll 1$ both expressions (2.8) and (2.7) are identical if we set $\varepsilon_0 = 1$ in the latter and assume that $\beta \ll 1$. It follows from the above analysis that the expression in front of the logarithm should be large.

The differential cross section of excitation from the level j_i to all the others is the sum over all $j_k \neq j_i$ in (2.3). The identity

$$\sum_{\kappa=0}^{\infty} [\kappa^2] j_i^2 \left(\delta \sin \frac{\theta}{2} \right) = 1 \quad (2.9)$$

follows from the unitarity of the S matrix (see Eq. (1.27) with $\alpha = 0$). By virtue of this, we obtain

$$d\sigma_r(j_i) = |j_i|^2 \sum_{\kappa} [\kappa^2 \begin{pmatrix} j_i & j_i & \kappa \\ 0 & 0 & 0 \end{pmatrix}]^2 [\delta_{\kappa 0} - j_i^2 \left(\delta \sin \frac{\theta}{2} \right)] d\sigma_{cl}. \quad (2.10)$$

We find the following expression for the total excitation cross section:

$$\sigma_r(j_i) = \sigma_r(0) - |j_i|^2 \sum_{j=2}^{2j_i} \left(\begin{matrix} j & j & j \\ 0 & 0 & 0 \end{matrix} \right)^2 \sigma(0 \rightarrow j), \quad (2.11)$$

where

$$\sigma_r(0) = \frac{8\pi}{3} \left(\frac{Z_1 e d_e}{\hbar v} \right)^2 \left[\frac{25}{12} - 2C + \ln \left(\frac{\hbar v^2}{2Z_1 e d_e \omega} \right) - \frac{5}{4\delta^2} + \frac{3\sin^2 \delta}{4\delta^4} + \frac{\sin 2\delta}{4\delta^3} - \frac{\sin^2 \delta}{2\delta^2} - \frac{\sin 2\delta}{2\delta} + \text{ci}(2\delta) \right]. \quad (2.12)$$

Here $\text{ci}(x)$ is the cosine integral (Ref. 17, p. 942). The result (2.12) is obtained directly with the help of Eqs. (2.4), (2.8) and (2.9). The summation in (2.11) is taken over even j . In the case of odd j , the $3j$ -symbol vanishes.

We also calculate the cross section for the rotational momentum transfer

$$\sigma_n(j_i) = \int (1 - \cos \theta) d\sigma_r(j_i). \quad (2.13)$$

Because of the presence of the term $1 - \cos \theta$ under the integral, the integrand falls off rapidly as $\theta \rightarrow 0$ and no

divergence occurs. After cumbersome calculations, we obtain

$$\sigma_{\alpha}(j_i) = \sigma_{\alpha}(0) - 4\pi a^2 [j_i^2] \sum_{\kappa=2}^{2j_i} [\kappa^2] \begin{pmatrix} j_i & j_i & \kappa \\ 0 & 0 & 0 \end{pmatrix}^2 g_{\alpha}(\delta). \quad (2.14)$$

where

$$\sigma_{\alpha}(0) = 4\pi a^2 \left[\frac{\sin^2 \delta}{2\delta^2} + \frac{\sin 2\delta}{2\delta} + \ln 2\delta - \text{ci}(2\delta) - \frac{3}{2} + C \right], \quad (2.15)$$

and by $g_{\alpha}(\delta)$ we designate the integral ($\kappa \neq 0$)

$$g_{\alpha}(\delta) = \int_0^{\delta} \frac{dx}{x} j_{\alpha}^2(x) = \frac{1}{2\kappa(\kappa+1)} - \int_0^{\delta} \frac{dx}{x} j_{\alpha}^2(x). \quad (2.16)$$

In principle, the integrals in Eqs. (2.4) and (2.16) can be obtained analytically, but the resulting expressions are so cumbersome (even in the case $\kappa=2$) that they are practically useless. It is much more convenient to estimate these integrals numerically.

It is seen from the expressions (2.12) and (2.15) that the plots of the cross sections as functions of energy have such a shape that a complex oscillating structure is superposed on a smooth curve. The amplitude of the oscillations falls off with increase in the energy and the frequency increases since $\delta \propto E^{1/2}$. The oscillating structure of the cross sections appears because of the presence of interference between the competing inelastic channels in the scattering. We emphasize that this is essentially a nonadiabatic effect. The interference develops between energetically close channels if they are separated from each other by no more than \hbar/τ .

3. APPROXIMATION OF A ROTATING HARMONIC OSCILLATOR

Let us consider the collision of a charged particle with a polar molecular ion, accompanied by excitation of combined vibrational rotational transitions. The excitation of the oscillations takes place effectively in the nonadiabatic limit, i.e., the condition $\bar{\beta} \ll 1$ should hold also for vibrational frequencies. As before, we assume that $\hbar\langle\omega\rangle/E \ll 1$, i.e., the transferred energy is less than the initial. The differential cross section of the excitation of the vibrational-rotational transition $n_i j_i - n_f j_f$, obtained from (2.2) and (1.27), can be written as

$$d\sigma(n_i j_i \rightarrow n_f j_f) = [j_f^2] \frac{n_{<}}{n_{>}} \sum_{k, k_1=0}^{n_{<}} \frac{1}{k! k_1!} \begin{pmatrix} n_{>} \\ n_{<} - k \end{pmatrix} \begin{pmatrix} n_{>} \\ n_{<} - k_1 \end{pmatrix} \times \alpha^{2(k+k_1)} \sum_{J, L, J_1, L_1} i^{L-L_1} G_{\alpha}(JL|J_1 L_1) \begin{pmatrix} j_i & j_f & \kappa \\ 0 & 0 & 0 \end{pmatrix}^2 \times S_J(\alpha) S_{J_1}(\alpha) j_i^{(2k_1)} \left(\delta \sin \frac{\theta}{2} \right)_{j_i}^{(2k_1)} \left(\delta \sin \frac{\theta}{2} \right)_{j_f} d\sigma_{cl}, \quad (3.1)$$

where

$$G_{\alpha}(JL|J_1 L_1) = [J^2 L^2 J_1^2 L_1^2 \kappa^2] \begin{pmatrix} J & L & \kappa \\ 0 & 0 & 0 \end{pmatrix}^2 \begin{pmatrix} J_1 & L_1 & \kappa \\ 0 & 0 & 0 \end{pmatrix}^2. \quad (3.2)$$

We note that in (3.1), $i \neq f$, i.e., at $n_i = n_f$ the rotational momenta $j_i \neq j_f$ and vice versa.

If the final rotational state of the molecular ion is not fixed, then, summing in (3.1) over all j_f including the value $j_f = j_i$, we obtain the differential cross section of excitation of the vibrational transition $n_i - n_f$. In the nonadiabatic limit, it does not depend on the value of

the rotational momentum preceding the collision, since the expansion coefficients S_J do not depend either on the value of the initial or of the final rotational momenta. With the help of Eqs. (1.24), (1.25), and using the property of completeness of the Legendre polynomials and the important formula (Ref. 12, p. 76)

$$\sum_L [L^2] \begin{pmatrix} J & L & \kappa \\ 0 & 0 & 0 \end{pmatrix}^2 P_L(\cos \gamma) = P_J(\cos \gamma) P_{\kappa}(\cos \gamma), \quad (3.3)$$

we find

$$d\sigma(n_i \rightarrow n_f) = \frac{n_{<}}{n_{>}} \int_0^{\pi} \sin \gamma d\gamma (\alpha \cos \gamma)^{2n} \exp(-\alpha^2 \cos^2 \gamma) \times [L_{n_{<}}(\alpha^2 \cos^2 \gamma)]^2 d\sigma_{cl}. \quad (3.4)$$

Let us investigate an important case: the excitation of a molecular ion from its ground vibrational state by a charged particle. In this case, the differential cross section of the transition is expressed in terms of a confluent hypergeometric function (Ref. 17, p. 954)

$$d\sigma(0 \rightarrow n) = \frac{\alpha^{2n}}{n!(2n+1)} \Phi\left(n + \frac{1}{2}, n + \frac{3}{2}; -\alpha^2\right) d\sigma_{cl}. \quad (3.5)$$

We obtain the following expression for the total cross section of excitation of the vibrational transition $0 - n$:

$$\sigma(0 \rightarrow n) = \frac{2\pi a^2 w^n}{n!(2n+1)} \int_0^1 dx x^{2n-3} \Phi\left(n + \frac{1}{2}, n + \frac{3}{2}; -wx^2\right) = \frac{\pi a^2}{n!} \int_0^1 \frac{dx}{x^2} (-1)^n \frac{\partial^n}{\partial t^n} \left[\left(\frac{\pi}{wt} \right)^{1/2} \Phi(x(wt)^{1/2}) \right]_{t=1}, \quad (3.6)$$

where

$$w = \mu^2 (B_e / \hbar \omega_e) \delta^2, \quad (3.7)$$

$\Phi(x)$ is the probability integral (Ref. 17, p. 944).

Simple transformations lead to the following result:

$$\sigma(0 \rightarrow n) = \frac{\pi a^2}{n!} [F_n(0, 1) - F_n(1, 1)], \quad n = 2, 3, \dots, \quad (3.8)$$

where $F_n(0, 1) = w/3$,

$$F_n(x, t) = (-1)^n \frac{\partial^n}{\partial t^n} F(x, t), \quad (3.9)$$

$$F(x, t) = \frac{1}{3x^3} \left(\frac{\pi}{wt} \right)^{1/2} \Phi(x(wt)^{1/2}) + \frac{\exp(-wtx^2)}{3x^2} + \frac{wt}{3} \text{Ei}(-wtx^2). \quad (3.10)$$

Here $\text{Ei}(-x)$ is the integral exponential function (Ref. 17, p. 939).

At small w , the $0 - n$ transition cross section behaves as

$$\sigma(0 \rightarrow n) = \frac{\pi a^2 w^n}{n!} \sum_{k=0}^{n-1} \frac{(-1)^k w^k}{k!(2n+2k+1)(n+k-1)}, \quad (3.11)$$

while in the other limiting case the dependence on w becomes universal:

$$\sigma(0 \rightarrow n) = \pi a^2 w / 3(n!), \quad (3.12)$$

since $F_n(1, 1)$ vanishes at large values of the parameter w . In the first case ($w \ll 1$) the cross section depends on the energy as E^{n-2} , while in the second case ($w \gg 1$) the dependence is universal $-E^{-1}$.

The differential cross section of the vibrational transition $0 - 1$ behaves as $\theta^{-1} d\theta$ at small scattering angles and the total cross section diverges logarithmically at

the lower limit. Proceeding in the same fashion as in the derivation of Eq. (2.8), we find

$$\sigma(0 \rightarrow 1) = \frac{2\pi a^2}{3} \left[\frac{w}{3} + \frac{e^{-w}}{2} - \frac{1}{4} \left(\frac{\pi}{w} \right)^{1/2} \Phi(w^{1/2}) + \frac{w}{2} \text{Ei}(-w) + w \ln \left(\frac{2\gamma^{-1/2}}{\beta w^{1/2}} \right) \right] \quad (3.13)$$

In Eq. (3.13), $\gamma = e^C = 1.781 \dots$; $\beta = \omega a/v$, where ω is the frequency of the vibrational transition 0-1. The region of applicability of Eq. (3.13) is limited by the condition that the expression under the logarithm sign be large.

We note that $1/\beta w^{1/2} \propto E$ i.e., at large w , the cross section depends on the energy as $E^{-1} \ln E$.

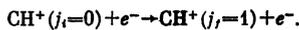
4. DISCUSSION OF THE RESULTS

In the derivation of the existing formulas, we have made several assumptions. The most significant of them is the condition of the nonadiabatic nature of the process, i.e., the collision should be brief in comparison with the period of motion of the nuclei of the molecular ion:

$$\beta = \frac{\omega a}{v} = 1.8 \frac{Z_1 Z_2 \omega}{E^{1/2}} \left(\frac{M}{m} \right)^{1/2} \ll 1.$$

Here ω and E are expressed in electron volts. As is seen from this expression, the excitation by heavy particles (in comparison with electron excitation) will be nonadiabatic under the condition that the energy of the heavy particle be greater than the electronic energy by an order of magnitude. If, at a specified energy, the condition $\beta \ll 1$ holds in the case of Coulomb attraction, then in the case of repulsion we should have $\beta \ll (2\pi)^{-1}$, which is equivalent to an increase in energy by a factor of 3.4.

We consider a specific example:



The threshold value of the energy of this reaction is $\omega = 0.00351$ eV. Data are given in Table I of the calculation of the differential cross-section $d\sigma_{0,1}/d\sigma$. The calculation was carried out from the formulas (see (2.3))

$$\frac{d\sigma_{0,1}}{d\sigma} = \frac{12}{q_0^2} j_i^2(0,67q_0), \quad j_i(x) = \frac{\sin x - x \cos x}{x^2}, \quad (4.1)$$

TABLE I. Differential cross sections (in units of a_0^2 of excitation of the rotational transition 0-1 of CH^+ in collisions with electrons (q is in atomic units)).

q	$d\sigma_{0,1}/d\sigma, a_0^2$		q	$d\sigma_{0,1}/d\sigma, a_0^2$		q	$d\sigma_{0,1}/d\sigma, a_0^2$	
	formula (4.1)	[11]		formula (4.1)	[11]		formula (4.1)	[11]
$E=0.01$ eV								
5.27(-3) *	1.74(4)	1.73(4)	1.52(-3)	2.57(5)	4.74(-4)	2.66(6)	2.65(6)	3.40(5)
7.72(-3)	8.09(3)	3.08(3)	2.58(-3)	8.83(4)	8.81(4)	1.33(-3)	3.38(5)	3.40(5)
8.94(-3)	6.03(3)	6.02(3)	4.71(-3)	2.65(4)	2.65(4)	3.88(-3)	3.97(4)	3.97(4)
1.02(-2)	4.63(3)	4.66(3)	8.96(-3)	7.32(3)	7.32(3)	7.28(-3)	1.13(4)	1.13(4)
1.50(-2)	2.14(3)	2.13(3)	1.53(-2)	2.51(3)	2.50(3)	1.75(-2)	1.95(3)	1.95(3)
1.99(-2)	1.22(3)	1.22(3)	1.85(-2)	1.72(3)	1.71(3)	3.45(-2)	5.02(2)	5.01(2)
2.47(-2)	7.90(2)	7.88(2)	4.70(-2)	2.66(2)	2.67(2)	5.49(-2)	1.98(2)	1.98(2)
2.96(-2)	5.50(2)	5.51(2)	8.48(-2)	8.17(1)	8.16(1)	8.55(-2)	8.15(1)	8.15(1)
3.44(-2)	4.07(2)	4.06(2)	1.23(-1)	3.88(1)	3.90(1)	2.69(-1)	8.20(0)	8.18(0)
3.93(-2)	3.12(2)	3.12(2)	1.42(-1)	2.91(1)	2.92(1)	3.92(-1)	3.84(0)	3.84(0)
4.44(-2)	2.44(2)	2.47(2)	1.61(-1)	2.26(1)	2.27(1)	4.83(-1)	2.50(0)	2.50(0)
4.90(-2)	2.01(2)	2.01(2)	1.70(-1)	2.03(1)	2.03(1)	5.45(-1)	1.96(0)	1.96(0)
$E=0.10$ eV								
$E=1.01$ eV								

*This notation means 5.27×10^{-3} .

TABLE II. Total excitation cross section of the rotational transition 0-1 of CH^+ in collisions with electrons.

E, eV	$\sigma_{0,1}, \text{\AA}^2$				E, eV	$\sigma_{0,1}, \text{\AA}^2$					
	formula (2.8)	[1]	[1]	[11]		formula (4.4)	formula (2.8)	[1]	[1]	[11]	formula (4.4)
0.00351	-	7409	7403	0.0	7408	0.31	157	173	174	271	172
0.005	-	4809	-	-	4801	0.40	135	142	145	220	140
0.007	-	3835	3826	3592	3826	0.50	118	121	124	183	121
0.010	-	2619	2728	-	2724	0.61	103	105	108	155	104
0.017	-	1675	1669	2402	1668	0.75	90	91	93	129	90
0.028	-	1071	1072	-	1072	1.01	73	73	75	100	73
0.045	130	709	719	1239	715	2.04	43	43	44	55	43
0.072	240	491	496	873	493	3.00	32	-	-	39	32
0.10	244	370	381	675	376	4.00	26	-	-	31	26
0.20	196	229	235	390	231	5.00	21	-	-	25	21

where

$$q_0 = 2k_i \sin \frac{\theta}{2}, \quad q = |\mathbf{k}_i - \mathbf{k}_f| \approx q_0 \left(1 - \frac{\omega}{E} \right)^{1/2}. \quad (4.2)$$

In Ref. 18, the differential cross section of this process was calculated in the Glauber approximation (the eikonal approximation). As is seen from Table I, the results of both methods are practically identical even at energies of 0.01 eV. Thus, in the limit $E \gg \omega$ our method is equivalent to the Glauber approximation, but, in contrast with the latter, the calculation of the differential cross section $d\sigma_{0,1}/d\sigma$ according to Eq. (4.1) is much simpler of cf. Eqs. (18), (19) in Ref. 18).

Table II gives the data of a calculation of the total excitation cross section of the rotational transition 0-1 according to the formula (2.8) at different energies. Data on $\sigma_{0,1}$ obtained in the Born-Coulomb approximation,⁶ in the quasiclassical approximation,⁸ and in the eikonal approximation¹⁸ are given for comparison. As is seen from Table II, the quantum-mechanical and semiclassical methods give approximately the same results in the region of their applicability ($\delta \ll 1$). Hence the theory predicts that the cross section is maximal at the threshold and falls off monotonically with increase in the energy. In contrast with Refs. 6 and 8, the cross section $\sigma_{0,1}$ calculated in Ref. 18 vanishes at the threshold, owing to the inapplicability of the eikonal approximation near the threshold. The comparison indicates the excellent agreement of our data with the calculations of Refs. 6 and 8 in the limit $\beta \ll 1$. However, already at $\beta = 0.2$ ($E = 0.10$ eV) the condition of applicability of the formula (2.8) is violated and the divergence becomes considerable. At $\beta > 1$, the expression (2.6) [and also (2.8)] loses any meaning. In this case, a rather accurate approximation for the excitation cross section of the rotational transition 0-1 can be obtained if the phase in the expression (2.6) is replaced by

$$\Delta = \frac{\pi \beta \delta \varepsilon}{2} \left\{ [H_{10}^{(1)}(i\beta\varepsilon)]^2 - \frac{\varepsilon^2 - 1}{\varepsilon^2} [H_{10}^{(1)}(i\beta\varepsilon)]^2 \right\}^{1/2} \quad (4.3)$$

and ε_0 is allowed to become infinite:

$$\sigma_{0,1} = 6\pi a^2 \int_0^\infty \varepsilon j_i^2 \left(\frac{\Delta}{\varepsilon} \right). \quad (4.4)$$

At $\delta \ll 1$ the result of perturbation theory (2.7) follows directly from the expression (4.4), and at $\beta \ll 1$, the result of the nonadiabatic theory (2.8). Table II illustrates the accuracy of the formula (4.4). The function $H_{10}^{(1)}(ix)$ was approximated by its limiting value at $\beta \ll 1$ ($\beta \gg 1$) and at larger values of the argument.

Equation (3.13) for the excitation cross section of the vibrational transition 0-1 can be modified in analogous fashion. It is of interest to note that in the calculation of the anharmonicity in vibrations of nuclei, a similar modification is required for the transitions 0-n with $n \geq 2$. The fact is that the divergence that is characteristic for the transition 0-1 as $\theta \rightarrow 0$ in the harmonic approximation appears in all transitions without exception. It appears in first order in w , since the matrix element $\langle 0 | x | n \rangle^2 \sim x_e^{n-1}$ is different from zero in the anharmonic approximation. Here x_e is the anharmonicity constant.

Within the framework of applicability of our theory we can obtain a better expression for the excitation cross section of the vibrational transition 0-n ($n \geq 2$) if we carry out its symmetrization, i.e., replace v by $(v_i v_f)^{1/2}$ and multiply by the factor v_f/v_i .⁸ The cross section symmetrized in similar fashion satisfies the detailed balancing principle.

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APPENDIX

We now derive Eq. (1.13) of the text. It is useful to write out the first coefficients of the expansion (1.7) rewriting them in the notation of (1.11):

$$Q_1 = \{\hat{a}^2, \hat{b}\}, Q_2 = \{\hat{a}^3, \hat{b}\} + \{\hat{a}^2, \hat{b}^2\},$$

$$Q_3 = \{\hat{a}^4, \hat{b}\} + 3/2 \{\hat{a}^3, \hat{b}^2\} + \{\hat{a}^2, \hat{b}^3\}. \quad (\text{A.1})$$

The latter equality is written with account of the fact that $2\hat{b}[\hat{a}, \hat{b}] = [\hat{a}, \hat{b}^2]$, since $[\hat{b}, [\hat{a}, \hat{b}]] = 0$. Further, differentiating both sides of Eq. (1.9) n times, we obtain, at $t=0$,

$$Q^{(1)}(0) = \{\hat{a}^2, q_1\}, Q^{(2)}(0) = \{\hat{a}^3, q_1\} + \{\hat{a}^2, q_1^2\}, \quad (\text{A.2})$$

$$Q^{(3)}(0) = 3/2 \{\hat{a}^3, q_1\} + 3/2 \{\hat{a}^2, q_1^2\} + \{\hat{a}^2, q_1^3\} + 6\{\hat{a}^2, q_2\},$$

generally,

$$Q^{(n)}(0) = \sum_{k=0}^{n-1} \frac{(n-k)!}{2^k} \binom{n}{k} \{\hat{a}^k, q_{n-k}\} + \sum_{k=1}^{n-1} \sum_{p=0}^{n-k-1} \frac{1}{2^p} \binom{n}{p} \{\hat{a}^p, q_{n-p}^k\} + \dots \quad (\text{A.3})$$

The structure of the omitted terms is greatly complicated with increase in n . It is not difficult to see by comparing (A.1) with (A.2) that the sum of all commutators of the type $\{\hat{a}^m, q_{n-k}^m\}$ with $m=1$ should be equal to $\{\hat{a}^{n-1}, \hat{b}\}$, i.e., the following equality should hold:

$$\sum_{k=0}^{n-1} \frac{(n-k)!}{2^k} \binom{n}{k} \{\hat{a}^k, q_{n-k}\} = \{\hat{a}^{n-1}, \hat{b}\}. \quad (\text{A.4})$$

We emphasize that the equality (A.4) is valid if and only if

$$[\hat{b}, [\hat{a}, \hat{b}]] = 0 \quad (\text{A.5})$$

and all other commutators in which \hat{b} is encountered more than once vanish. For example, in the general case we would have had

$$q_3 = 1/2 \{\hat{a}^2, \hat{b}\} - 1/2 \{\hat{a}^3, \hat{b}^2\} + \hat{b} \{\hat{a}^2, \hat{b}\} \quad (\text{A.6})$$

and the assertion made before formula (A.4) would have been untrue. For arbitrary n , by virtue of the relation (A.5), we have

$$q_n = f(n) \{\hat{a}^{n-1}, \hat{b}\}, n=1, 3, \dots \quad (\text{A.7})$$

Substituting (A.7) in (A.4), we obtain

$$\sum_{k=0}^{n-1} \frac{(n-k)!}{2^k} \binom{n}{k} f(n-k) = 1. \quad (\text{A.8})$$

The prime on the sum indicates that the summation is carried out over such k for which $n-k$ is an odd number. Let

$$f(n-k) = \frac{p}{(n-k)! 2^{n-k}}, \quad (\text{A.9})$$

where we choose p from the normalization condition (A.8). Since

$$\sum_{k=0}^{n-1} \binom{n}{k} = 2^{n-1} \quad (\text{A.10})$$

(see Ref. 17, p. 17), we find that $p=2$ and, with account of (A.9) and (A.7), we obtain the result (1.13) given in the text.

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