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INELASTIC SCATTERING OF ELECTRONS BY MOLECULES WITH THE RENNER EFFECT

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The problem of excitation of vibrational states in triatomic linear molecules with the Renner effect is considered in the Born approximation. The problem of similar excitation of molecular ions is considered in the Born-Coulomb approximation. A "direct" nonresonance mechanism of molecule excitation is assumed. It is found that allowed scattering cross section maxima corresponding to excitation of the first three Renner states should be observable in the electron inelastic scattering energy loss spectrum. This should permit one to investigate the Renner effect in collision spectroscopy.

EXCITATION of vibrational levels of molecules in inelastic scattering of electrons was the subject of a number of recent studies,[1-4] in which the resolution of the apparatus was 10^{-2} eV at an incident-beam energy reaching 25–30 keV[1] (see also [5]). The development of instruments with such a resolution makes it possible to investigate nonadiabatic effects in molecules in electron-scattering experiments. One of the strongest and best investigated optical methods of nonadiabatic effects is the Renner effect.1) In the present paper we discuss the possible manifestations of this effect in inelastic scattering of electrons by molecules. The Renner effect takes place for Π-electronic states of linear molecules having more than two atoms. In this case the adiabatic approximation does not hold and the system of equations obtained for the wave functions of the deformation vibrations of the molecule cannot be reduced to the equations of harmonic oscillators. (For valence vibrations, neglecting anharmonicity, the equations of harmonic oscillators are obtained as before). The terms that distinguish these equations from harmonic can be characterized with the aid of the Renner parameter ϵ. Usually $\epsilon = 0.2-0.5$, so that the solution of the system can be sought in the form of a series in powers of this parameter (for details concerning the Renner effect see also [6-8]).

The scattering of electrons by Renner molecules at sufficiently high energy of the incident electrons can be regarded in the Born approximation, just as in the usual case,[9,10] using functions determined by the Renner system for the description of the electron-vibrational states. In the present paper these functions are obtained for the first three Renner excited states and are used to analyze the electron energy loss spectrum in the following cases: 1) scattering by neutral molecules without change of the electronic state; 2) scattering by neutral molecules accompanied by a transition from the electronic Σ state to the Π state; 3) scattering by an ionized molecule without a change of its ground electronic state. To calculate the cross sections in cases (1) and (2) we used the first Born approximation, taking into account only the dipole term of the expansion of the potential of the interaction between the molecule and the incident electron. In scattering by a molecular ion, the calculation of the cross sections for inelastic scattering with excitation of the first three Renner states was carried out in the Born-Coulomb approximation.[11]

1. ELECTRON-VIBRATIONAL FUNCTIONS

The deformation vibrations of a linear molecule in the electronic Π state are described by a system of equations that can be written in the following form:

$$[(\hat{H}_0 - \hat{E}_V{}^K) + \varepsilon\hat{V}]\eta_V{}^K = 0, \tag{1}$$

where $\hat{H}_0 - \hat{E}_V^K$ is a diagonal matrix with the operator $H_0(\rho, \varphi) - E_V^K$ on the diagonal, $H_0(\rho, \varphi)$ is the Hamiltonian of a two-dimensional harmonic oscillator with frequency $\omega = (\lambda/M)^{1/2}$, where M is the reduced mass of the deformation vibrations, ϵ is the Renner parameter, and $\hat{V}$ is a matrix defined by the formula2)

$$\hat{V} = \begin{pmatrix} 0 & {}^1/_2\lambda\rho^2 e^{-2i\varphi} \\ {}^1/_2\lambda\rho^2 e^{2i\varphi} & 0 \end{pmatrix}. \tag{2}$$

The functions

$$\hat{\eta}_V{}^K = \begin{pmatrix} \eta_V{}^K(\rho, \varphi) \\ \eta_V{}'^K(\rho, \varphi) \end{pmatrix} \tag{3}$$

are classified with the aid of the quantum numbers K and V, where $K = \Lambda + l$ is the projection of the total angular momentum on the molecule axis, Λ and l correspond to the projections of the electronic and vibrational angular momenta, and V is the vibrational quantum number. The total wave function of the molecule, in the zeroth order of the Born-Oppenheimer method, can be represented in the form

$$\Psi_V{}^K = \varphi^{(+1)}(r, R_0)\eta_V{}^K(\rho, \varphi) + \varphi^{(-1)}(r, R_0)\eta_V{}'^K(\rho, \varphi), \tag{4}$$

where the factors describing the translational and rota-

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1) The Renner effect was observed in optical spectra, for example, of the following molecules: CCN, CNC, BO_2, C_2H_2, N_2O^+, CO_2^+, and C_3 (see also [6]). Insofar as we know, the Renner effect has not yet been observed in collision spectroscopy.

2) We have in mind triatomic molecules; the substitution $Q_x = \rho\cos\varphi$, $Q_y = \rho\sin\varphi$ has been made for the normal coordinates Q_x and Q_y. In the case of molecules with four atoms, the system consists of two equations having a more complicated form.

tional motions have been omitted for the sake of brevity. In formula (4), $\varphi^{(\pm 1)}$ (r, R_0) are the electronic functions calculated for the equilibrium configuration of the nuclei.

We shall solve the system (1) by expanding the eigenfunctions $\hat{\eta}_V^K$ and the eigenvalues E_V^K in powers of ϵ. The lower vibrational level (V = 0, |K| = 1) coincides in first order with the unperturbed level, and in second order it is shifted by an amount $-\epsilon^2\hbar\omega/4$, remaining doubly-degenerate. For the eigenfunctions we obtain, accurate to terms of first order,

$$\hat{\eta}_0^{1} = \begin{pmatrix} \eta_{00} \\ -\varepsilon\eta_{22}/2\sqrt{2} \end{pmatrix}, \qquad \hat{\eta}_0^{-1} = \begin{pmatrix} -\varepsilon\eta_{2-2}/2\sqrt{2} \\ \eta_{00} \end{pmatrix} \tag{5}$$

where η_{Vl} are the functions of the two-dimensional harmonic oscillator.

The first excited level (V = 1, |K| = 0, 2), which is quadruply-degenerate in the absence of perturbation, splits in first order into three levels:

$$\begin{aligned} &1)\ \Sigma^+:\quad E_1^{0+} = \hbar\omega(1+\varepsilon),\\ &2)\ \Sigma^-:\quad E_1^{0-} = \hbar\omega(1-\varepsilon),\\ &3)\ \Delta:\quad E_1^{2} = E_1^{-2} = \hbar\omega. \end{aligned} \tag{6}$$

In second order, the level Δ shifts by an amount $-\epsilon^2\hbar\omega/2$. The corresponding eigenfunctions, accurate to terms of first order, are

$$\hat{\eta}_1^{0\pm} = \frac{1}{\sqrt{2}}\left[\begin{pmatrix} \eta_{1-1} \\ -\varepsilon\eta_{31}/2\sqrt{2} \end{pmatrix} \pm \begin{pmatrix} \varepsilon\eta_{3-1}/2\sqrt{2} \\ \eta_{11} \end{pmatrix}\right], \tag{7}$$

$$\hat{\eta}_1^{2} = \begin{pmatrix} \eta_{11} \\ -\varepsilon\eta_{33}/\sqrt{2} \end{pmatrix}, \qquad \hat{\eta}_1^{-2} = \begin{pmatrix} -\varepsilon\eta_{3-3}/2 \\ \eta_{1-1} \end{pmatrix}. \tag{8}$$

2. SCATTERING BY A NEUTRAL MOLECULE

The differential cross section for inelastic scattering of electrons by a molecule is determined in the first Born approximation by the formula

$$\frac{d\sigma}{d\Omega} = \left(\frac{2me^2}{k^2\hbar^2}\right)^2 \frac{k_f}{4\pi k_i}\int d\Omega_{\text{rot}}\left|\left\langle \Psi_0^{K_0}\right|\sum_{i=1}^{m} e^{-i\mathbf{k}\mathbf{r}_i} - \sum_{n=1}^{3} Z_n e^{-i\mathbf{k}\mathbf{R}_n}\left|\Psi_1^{K_1}\right\rangle\right|^2, \tag{9}$$

where $\mathbf{r}_i$ and $\mathbf{R}_n$ are respectively the coordinates of the electrons and the nuclei, reckoned from the inertia center of the molecule, Z_n are the charges of the nuclei, $\mathbf{k}_i$ and $\mathbf{k}_f$ are the momenta of the incident and scattered electrons, $\mathbf{k} = \mathbf{k}_f - \mathbf{k}_i$ is the momentum transfer, $\Psi_0^{K_0}$ and $\Psi_1^{K_1}$ are the wave functions of the ground and excited states of the molecule, and integration with respect to $d\Omega_{\text{rot}}$ corresponds to averaging over all the orientations of the molecule.[9] In the dipole approximation, formula (9) takes the form

$$\frac{d\sigma}{d\Omega} = \left(\frac{2me}{k^2\hbar^2}\right)^2 \frac{k_f}{4\pi k_i}\int d\Omega_{\text{rot}}\left|\langle\Psi_0^{K_0}|\mathbf{k}(\mathbf{P}^e + \mathbf{P}^N)|\Psi_1^{K_1}\rangle\right|^2, \tag{10}$$

where

$$\mathbf{P}^e = e\sum_{i=1}^{m}\mathbf{r}_i, \qquad \mathbf{P}^N = -e\sum_{n=1}^{3} Z_n\mathbf{R}_n$$

are the dipole moments of the electrons and nuclei, respectively.

A. Let us find the cross sections for the excitation of the first three Renner levels in the absence of an electronic transition. To this end we substitute in (10) the functions $\Psi_0^{K_0}$ and $\Psi_1^{K_1}$ defined in accordance with (4), assuming the electronic functions $\varphi^{(\pm 1)}$ to be the same in both cases, and using for the functions $\eta_0^{K_0}$ and $\eta_1^{K_1}$ the expressions (5), (7), and (8). Owing to the orthogonality of the functions $\eta_0^{K_0}$ and $\eta_1^{K_1}$, we get $\langle\Psi_0^{K_0}|)\mathbf{k}\mathbf{P}^e)|\Psi_1^{K_1}\rangle = 0$. Integrating over the electronic and nuclear coordinates in the remaining term, we find that the expression for the differential scattering cross section contains as a factor the integral $\int(1-\cos^2\gamma)\,d\Omega_{\text{rot}}$, where γ is the angle between the vector **k** and the axis of the molecule. Using the addition theorem for cos γ, we can easily show that

$$\frac{1}{4\pi}\int(1-\cos^2\gamma)\,d\Omega_{\text{rot}} = \left(1 - \frac{\cos^2\theta}{12}\right), \tag{11}$$

where θ is the scattering angle. For the total scattering cross sections we obtain the following result:

$$\sigma_{\Pi\to\Sigma^\pm} = 2\pi\frac{k_f}{k_i}\left(\frac{4}{3}\frac{me^2\alpha}{k\hbar^2}\right)^2\frac{\hbar}{M\omega}\left(1 \mp \frac{3}{4}\varepsilon\right), \tag{12}$$

$$\sigma_{\Pi\to\Delta} = 4\pi\frac{k_f}{k_i}\left(\frac{4}{3}\frac{me^2\alpha}{k\hbar^2}\right)^2\frac{\hbar}{M\omega}, \tag{13}$$

where $\alpha = (Z_2 - Z_1M_2/M_1)$. Comparing the cross sections for the transitions $\Pi \to \Sigma^+$, $\Pi \to \Delta$, $\Pi \to \Sigma^-$, we see that the ratios of the corresponding scattering cross sections are given by

$$(1 - {}^3\!/_4\varepsilon) : 2 : (1 + {}^3\!/_4\varepsilon). \tag{14}$$

Thus, in scattering of electrons by Renner molecules, three maxima should appear in the energy-loss spectrum at the location of the maximum corresponding to excitation of the deformation vibration. The distance between the neighboring maxima is $\delta \sim \epsilon\hbar\omega$, and the relative values of the cross sections are given by (14). In the cases known from optical experiments, δ = 0.01–0.03 eV. It is seen from (14) that an investigation of the electron inelastic-scattering energy-loss spectra makes it possible to determine ϵ.

B. Let us consider electron inelastic scattering accompanied by electronic excitation of the molecule from the Σ state into the Π state.[3)] To this end, we choose in (10) the function $\Psi_1^{K_1}$ in the form (4), and the function $\Psi_0^{K_0}$ in the form $\Psi_0^{K_0} = \varphi^{(0)}(\mathrm{r}, \mathrm{R}_0)\,\eta_{nl}^{(0)}(\rho, \varphi)$, where $\eta_{nl}^{(0)}$ is a function of the two-dimensional harmonic oscillator with frequency ω_0. Owing to the orthogonality of the functions $\varphi^{(0)}$ and $\varphi^{(\pm 1)}$ we have for the matrix element $\langle\Psi_0^{K_0}|(\mathbf{k}\mathbf{P}^N)|\Psi_1^{K_1}\rangle = 0$. Calculating the integrals in the remaining term, we obtain the following expressions for the excitation cross sections:

$$\sigma_{0\to 0} = \pi\left(\frac{8me^2}{3k\hbar^2}\right)^2\frac{k_f}{k_i}|J|^2A^2, \tag{15}$$

$$\sigma_{1\to\Sigma^\pm} = 2\pi\left(\frac{8me^2}{3k\hbar^2}\right)^2\frac{k_f}{k_i}|J|^2A^4(1 \pm \varepsilon B), \tag{16}$$

$$\sigma_{1\to\Delta} = 2\pi\left(\frac{8me^2}{3k\hbar^2}\right)^2\frac{k_f}{k_i}|J|^2A^4, \tag{17}$$

where the indices 0 → 0, 1 → $\Sigma^\pm$, 1 → Δ on the scattering cross sections denote that the molecule goes over from the states V = 0 and V = 1 of the deformation vibration

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[3)] The corresponding transition with excitation of the first Renner states was observed by Herzberg in the optical spectrum of acetylene [13].

of the electronic Σ state into the ground state and the Σ^+, Δ, and Σ^- states of the electronic Π state, respectively;

$$J=\pi\int\varphi^{(0)}(r,R_0)\Phi_1(\varphi_k,\rho_k,z_k)\sum_{i=1}^{m}\rho_i e^{\mp i\varphi_i'}dV_e'; \tag{18}$$

$\Phi_1 = e^{-i\varphi}\varphi^{(1)}$; φ_k, ρ_k, z_k are the cylindrical coordinates of the molecule electrons; dV_e' denotes integration over all the electronic coordinates with the exception of the cyclic coordinate φ. The constants A and B are determined by the following formulas:

$$A=2\sqrt{\omega_0\omega}\,/\,(\omega_0+\omega),\qquad B=(\omega_0-\omega)\,/\,(\omega_0+\omega). \tag{19}$$

Taking the cross section of the 0 → 0 transition as unity, we find that the cross sections of the transitions with excitation of the Renner levels Σ^+, Δ, and Σ^- are related like

$$A^2(1+\varepsilon B):A^2:A^2(1-\varepsilon B). \tag{20}$$

3. SCATTERING BY IONIZED MOLECULES

Let us consider the excitation of the first three Renner levels of an ionized molecule in the Π-electronic state. In first order of perturbation theory, the differential cross section of the transition k_i, $K_0 \rightarrow k_f$, K_1 (K is the electron-vibrational quantum number) is

$$\frac{d\sigma}{d\Omega_{K_0\to K_1}}=\frac{m^2}{4\pi^2\hbar^2}\frac{k_f}{k_i}\int|\langle\Psi^+|\hat{\mathscr{H}}|\Psi^-\rangle|^2 d\Omega_{\mathrm{rot}} \tag{21}$$

where the operator

$$\hat{\mathscr{H}}=-e^2\left(\sum_{n=1}^{3}\frac{Z_n}{|\mathbf{r}-\mathbf{R}_n|}+\frac{1}{r}+\sum_{=1}^{Z-1}\frac{1}{|\mathbf{r}-\mathbf{r}_i|}\right) \tag{22}$$

is the perturbation (**r** is the vector of the incident electron reckoned from the mass center of the molecule),

$$\Psi^+=\Psi_1^{K_1}F_{k_f}(\mathbf{r});\qquad \Psi^-=\Psi_0^{K_0}F_{k_i}(\mathbf{r}); \tag{23}$$

$\Psi_1^{K_1}$ and $\Psi_0^{K_0}$ are defined by (4), and $F_{k_i}(\mathbf{r})$ and $F_{k_f}(\mathbf{r})$ are the Coulomb functions of the continuous spectrum. In the dipole approximation, the operator $\hat{\mathscr{H}}$ is given by

$$\hat{\mathscr{H}}_d=e(\mathbf{P}_e+\mathbf{P}_N,\ \mathbf{r})\,/\,r^3. \tag{24}$$

Substituting $\hat{\mathscr{H}}_d$, Ψ^+, and Ψ^- in formula (21) and calculating the corresponding integrals, we obtain

$$\frac{d\sigma}{d\Omega_{\Pi\to\Sigma^\pm}}=\left(\frac{2me^2\alpha}{k^2\hbar^2}\right)^2\frac{k_f}{2k_i}\left(\frac{\hbar}{M\omega}\right)J_{k_ik_f}\left(1\mp\frac{3}{4}\varepsilon\right), \tag{25}$$

$$\frac{d\sigma}{d\Omega_{\Pi\to\Delta}}=\left(\frac{2me^2\alpha}{k^2\hbar^2}\right)^2\frac{k_f}{k_i}\left(\frac{\hbar}{M\omega}\right)J_{k_ik_f}, \tag{26}$$

where

$$J_{k_ik_f}=\frac{1}{4\pi}\sum_{lm,l'm',\mu}|a_{lm\,l'm'}^{1\mu}|_2|M_{ll'}^{-2}|^2|P_{l'm'}(\theta)|^2, \tag{27}$$

θ is the scattering angle

$$a_{lml'm'}^{1\mu}=\frac{(4\pi)^{5/2}}{\sqrt{3}}(-1)^\mu e^{i\varphi}[(2l+1)(2l'+1)]^{1/2}\cdot\begin{pmatrix}l & l' & 1\\ 0 & 0 & 0\end{pmatrix}\begin{pmatrix}l & l' & 1\\ m & -m & \mu\end{pmatrix} \tag{28}$$

The quantities in the parentheses are the Wigner 3j-symbols and φ is an inessential phase factor;

$$M_{ll'}^{-2}=\frac{1}{k_ik_f}\int_0^\infty F_{l'}(k_fr)\frac{1}{r^2}F_l(k_ir)\,dr, \tag{29}$$

$$F_l(k_ir)=e^{-\pi\eta/2}\frac{|\Gamma(l+1+i\eta_i)|(2k_ir)^{l+1}}{2(2l+1)!}e^{-ik_ir}$$

$$\times F(l+1-i\eta_i,\ 2l+2,\ 2ik_ir),\quad \eta_i=\frac{1}{k_i}. \tag{30}$$

It follows from (25) and (26) that the ratio of the cross sections of the transitions to the first three Renner states turn out to be the same as in the case of the neutral molecule (see (14)).

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