Vibrational excitation of molecules during resonance scattering of electrons

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An analytic solution is obtained within the framework of the displaced oscillator model for the vibrational transitions of molecules during resonance scattering of electrons. Limiting and special cases illustrating the properties of the excitation functions under different physically possible conditions are examined. More precise conditions are established for the validity of existing approximations (intermediate compound state and pulsed resonance scattering). Expressions are obtained for the vibrational transitions when these conditions are violated. Vibrational transitions during electron scattering by excited molecules are discussed. Resonance dissociation of diatomic molecules is investigated and, in particular, it is noted that the intermediate autoionization complex can be investigated by examining the spectrum of dissociation products. The model is generalized to the multidimensional case, and this is then used to investigate analytically the vibrational transitions in polyatomic molecules. The theory is illustrated by the example of vibrational excitation of molecular nitrogen, and the results obtained are in good agreement with experiment.

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1. Resonance scattering of electrons by molecules

$$e^-+\mathrm{AB}(v)\to(\mathrm{AB}^-)^{\mathrm{an}}\to\mathrm{AB}(v')+e^-, \tag{1}$$

which proceeds via formation of the negative ion AB^- in the autoionization state, is accompanied by a considerable change in the vibrational energy of the molecules and plays an important role in many phenomena encountered in the physics of low-temperature plasma (see, for example, Smirnov[1] and Eletskiĭ and Smirnov[2]).

The extensive experimental material that has now accumulated on these processes in the case of H_2, N_2, NO, CO, and O_2 is reported, for example, in Schulz's review.[3] Resonance vibrational excitation of diatomic molecules by electron impact has been examined theoretically by a number of authors[4–8] who used a modified form of the intermediate complex model (the ion AB^-) and, by obtaining improved values for the parameter of the model, have achieved successively better agreement between calculated cross sections and experimental results. These workers have developed general computational schemes for the solution of the problem, which can be used to take into account changes in the equilibrium distance between the nuclei[4] as well as differences between the vibrational spectra of the ion[1)] and the molecule,[5] the anharmonic nature of the vibrations,[6,7] and the dependence of the autoionization width Γ on the internuclear distance R.[7]

However, these factors are not equally important in different cases, and it is shown in the present paper that, in the case of the vibrational excitation of nitrogen, good agreement with experiment can be achieved even within the framework of the simple displaced-oscillator model for which an analytic solution of the problem can be obtained (Secs. 2 and 3). This solution covers the extensively investigated transitions from the vibrational ground state, as well as transitions between the excited states of the molecules and resonance dissociation.[3] The importance of resonance electron scattering by vibrationally excited molecules has frequently been noted in the literature (see, for example, Chen[6] and McDaniel[9]).

The approach adopted in Secs. 2 and 3 to describe diatomic molecules can readily be generalized to the multidimensional case, and this can then be used to elucidate the properties of resonance scattering of electrons by polyatomic molecules (Sec. 4).

2. Consider the resonance scattering of an electron by a diatomic molecule AB. In the approximation of an isolated parabolic term of the ion AB^- (the displaced-oscillator model[4]),

$$V_{\mathrm{AB}^-}(R)=\Delta+\omega^2(R-R_0)^2/2-i\Gamma/2 \qquad (V_{\mathrm{AB}}(R)=\omega^2R^2/2) \tag{2}$$

the amplitude $A_{vv'}(E)$ for a vibrational transition is given, apart from an unimportant factor, by[5,6]

$$A_{vv'}(E)=\Gamma\sum_{\nu}\frac{\langle v|\nu\rangle\langle\nu|v'\rangle}{E-E_\nu+i\Gamma/2}\qquad(\Gamma=\mathrm{const}). \tag{3}$$

In this expression, $|v\rangle$, $|v'\rangle$, and $|\nu\rangle$ are the nuclear wave functions in the initial, final, and intermediate states, respectively, E is the total energy of the system [$E=\varepsilon+\omega(v+\frac{1}{2})$, ε is the energy of the incident electron, $\omega(v+\frac{1}{2})$ is the vibrational energy of the molecule in the initial state, $E_\nu=\Delta+\omega(\nu+\frac{1}{2})$ is the energy of the ν-th state of the intermediate complex, $\hbar=m=1$, and m is the reduced mass of the nuclei in the molecule].

Simple analysis will show that corrections due to differences between the frequencies of vibration of the nuclei in the molecule (ω_0) and in the ion (ω) are of the order of $\delta\omega/\omega_0$ for $\alpha\lesssim 1$ and $\alpha\delta\omega/\omega_0$ for $\alpha\gg 1$.[2)] The quantity $\alpha=\omega R_0^2/2$ is the mean change in the energy of the oscillator (in units of ω) under the action of an external force which instantaneously shifts the position of

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equilibrium by the amount R_0 and $\delta\omega = |\omega_0 - \omega|$ (for example, for the nitrogen molecule, $\alpha \sim 1$ and $\delta\omega/\omega_0 = 0.17$). Corrections due to a change in the autoionization width, on the other hand, provide a contribution of $\sim (d\Gamma/dR)_{R_0}(v_0\omega)^{1/2}$ to the cross section for the process (1), where $v_0 = \max(v, v')$.

The overlap integrals for the vibrational functions of the molecule AB and the ion AB$^-$ (Franck–Condon factors) are, in this case,

$$\langle v|\nu\rangle = (-1)^{v+\nu}\left(\frac{v!}{\nu!}\alpha^{\nu-v}e^{-\alpha}\right)^{1/2} L_v^{\nu-v}(\alpha), \tag{4}$$

where $L_n^m(\alpha)$ are generalized Laguerre polynomials.

The apparent asymmetry in v and ν in (4) has the same form as for the excitation of a quantum-mechanical oscillator by a time-dependent external force [see (2.11), Chap. 6, in the monograph by Baz' *et al.*[10]]. In fact, the representation given by (4) is symmetric in the indices, i.e., it is valid for any v and ν. Using the Rodrigues formula for $L_v^{\nu-}(\alpha)$, we can write

$$\langle v|\nu\rangle \equiv (-1)^{v+\nu}\left(\frac{\alpha^{v-\nu}e^{\alpha}}{v!\,\nu!}\right)^{1/2} (\partial/\partial\alpha)^v(\alpha^\nu e^{-\alpha}). \tag{5}$$

Substituting this into the original series given by (3), we obtain

$$A_{vv'} = \hat{D}_{vv'}(\lambda, \lambda')\,\{A_{00}(\xi+v, \lambda\lambda'/\alpha)\exp[-(\lambda+\lambda')+\lambda\lambda'/\alpha]\}_{\lambda=\lambda'=\alpha}. \tag{6}$$

In this expression, $D_{vv'}(\lambda, \lambda')$ is the differential operator acting on the variables λ and λ':

$$\hat{D}_{vv'}(\lambda, \lambda') = (-1)^{v+v'}\left(\frac{\alpha^{v+v'}}{v!\,v'!}\right)^{1/2} e^{\alpha}(\partial/\partial\lambda)^v(\partial/\partial\lambda')^{v'}, \tag{7}$$

A_{00} is the amplitude for the elastic process and is given by

$$A_{00}\left(\xi+v, \frac{\lambda\lambda'}{\alpha}\right) = -i\Gamma e^{-\lambda\lambda'/\alpha}\int_0^\infty dt\exp\left\{i(\xi+v)\omega t + \frac{\lambda\lambda'}{\alpha}e^{-i\omega t}\right\}$$
$$\equiv \gamma(\xi+v)^{-1}\Phi(1, 1-\xi-v; -\lambda\lambda'/\alpha), \quad \xi = (\varepsilon-\Delta+i\Gamma/2)/\omega, \tag{8}$$

and $\Phi(a, b; z)$ is a confluent hypergeometric function.

Equation (6) establishes a single analytic relationship between the different channels for the inelastic scattering of electrons by diatomic molecules (1), and enables us to express the amplitudes for transitions, occurring during scattering by vibrationally excited molecules, in terms of amplitudes for unexcited molecules:

$$A_{vv'} = (v!\,v'!)^{1/2}\sum_{l=0}^{m}\frac{(-1)^l(s!)^{1/2}}{l!(v-l)!(v'-l)!}A_{0s}(\xi+v-l, \alpha), \tag{9}$$
$$s = v+v'-2l, \quad m = \min(v, v'),$$

where, according to (6), the amplitudes A_{0s} are given by

$$A_{0s}(z, \alpha) = \hat{D}_{0s}(\alpha, \lambda)e^{-\alpha}A_{00}(z, \lambda)|_{\lambda=\alpha}$$
$$= \gamma(s!\,\alpha^s)^{1/2}\frac{\Gamma(1-z)}{z\Gamma(1+s-z)}\Phi(1+s, 1+s-z; -\alpha). \tag{10}$$

The quantity $\Gamma(z)$ in this expression is the complete gamma-function of a complex argument.

It is important to note that (6), and also (26) and (32) (see below), can be obtained by using the integral representation of the stationary Green function for the displaced oscillator in the original expression given by (3). This approach introduces into the theory of resonance scattering of electrons the physically useful quantity

$$a_{vv'}(\tau) = \langle v|G(\tau, R, R')|v'\rangle$$

i.e., the amplitude for a transition of the nuclear subsystem during a sudden twofold change in the Hamiltonian.[11]

Equations (6) and (8)–(10) describe resonance scattering of electrons for arbitrary ratios of the energy parameters of the system, i.e., α, $\beta = 2(\varepsilon - \Delta)/\omega$, and $\gamma = \Gamma/\omega$, and enable us to investigate the transition to the limiting cases of intermediate compound states (small γ) and the resonance impulse excitation (large γ).

In the limit of small γ, the amplitude for the inelastic process (1) in the neighborhood of an isolated electron-vibrational level of AB$^-$ ($|E - E_\nu| \ll \omega$) is obviously of the form

$$A_{vv'}(E) = \frac{(\Gamma_v\Gamma_{v'})^{1/2}}{E - E_\nu + i\Gamma/2}, \tag{11}$$

where $\Gamma_v = \Gamma|\langle v\langle\nu\rangle|^2$ are the widths of the corresponding channels for the decay of the long-lived complex AB$^-$.

It is important to emphasize that the single condition $\gamma \ll 1$ will, in general, be insufficient. It follows from (6) and (8) that the validity of (11) is, to a considerable extent, determined also by the characteristic parameters α and β. Let us begin by considering small and large values of α.

For small values of α, it can be shown that (11) is valid for

$$\alpha\gamma \ll 1 \quad (\nu=0), \tag{12}$$
$$\alpha^{-\nu}(\nu-1)!\,\gamma \ll 1 \quad (\nu \geqslant 1) \tag{13}$$

where ν is the number of the resonance, i.e., the conditions for the validity of the approximation of an isolated resonance depend on the energy ε of the incident electron.

It follows from (9) and (10) that the opposite case, i.e., that of pulsed excitation of the molecule, is realized when

$$\alpha(1+w)\gamma^{-1} \ll 1, \quad \gamma \gg \max(v, v'), \tag{14}$$

which presuppose that there is no change in the position of the nuclei during the characteristic scattering time. The amplitude for the $v \to v'$ transition is of the form

$$A_{vv'} = \gamma(-1)^w\left(\frac{v_>!}{v_<!}\alpha^w\right)^{1/2}\xi^{-(1+w)},$$
$$v_> = \max(v, v'), \quad v_< = \min(v, v'), \quad w = |v-v'|. \tag{15}$$

When these conditions are violated (but α/γ is small), the amplitude given by (6) can be determined from the formula

$$A_{vv'}=\gamma\left(\frac{v_>!}{v_<!}\alpha^w\right)^{1/2}\frac{\Gamma(1-\xi)}{\xi\Gamma(1+w-\xi)}. \qquad (16)$$

Hence, it follows that, in this case, the amplitude $A_{vv'}$ for small γ has $w+1$ isolated interference maxima, the largest of which corresponds to the condition of best overlap in the region of the Franck–Condon transition. When $\gamma \gtrsim 1$, the amplitude given by (16) is a smooth function with a maximum at $\varepsilon = \Delta + \omega w$.

The case of large α corresponds to the quasiclassical motion of nuclei in the ion AB^-, and can be considered in the same way for arbitrary γ. The conditions for the validity of the compound-state and impulse-excitation approximations are then, in general, more stringent.

In fact, using the asymptotic behavior of the function $\Phi(1, 1-\xi; -\alpha)$[12] for $\alpha \gg 1$ and $|\xi - \alpha| \lesssim \alpha^{1/2}$, we obtain

$$A_{00}(\xi, \alpha)=\gamma(\pi/2\alpha)^{1/2}\exp[-(\xi-\alpha)^2/2\alpha]\{\operatorname{ctg}\pi\xi+i\operatorname{Erf}[i(\xi-\alpha)/(2\alpha)^{1/2}]\}, \qquad (17)$$

where Erf(z) is the probability integral. We note that the quasiclassical character of the motion of the nuclei enables us to take into account differences between the vibrational frequencies of the molecules AB and AB^- in (17). The difference $\xi - \alpha$ must then be replaced by $(\varepsilon + i\Gamma/2 - \Delta - \omega^2 R_0^2/2)/\omega$, and α by $\omega^2 R_0^2/2\omega_0$, where ω_0 is the vibrational frequency of the molecule AB.

The particular structure of (17) is due to the fact that there are two characteristic ranges of variation of ν which appear when the summation is carried out over the intermediate states in the original expression given by (3), i.e., $\nu\omega \approx |\varepsilon - \Delta|$ and $\nu\omega \approx \Delta + \alpha\omega$. The first term in (17) is the set of equidistant maxima with oscillation amplitude $\sim e^{-\pi\gamma}$ (in accordance with the levels of the system AB^-), the envelope of which is a Gaussian curve with a continuous maximum in the region of the vertical Franck–Condon transition ($\xi \sim \alpha$). The second term is a smooth function which falls off in accordance with a power law for large $|\xi - \alpha| \gg \alpha^{1/2}$.

For inelastic transitions, the structure of the spectrum is more complicated because the envelope then acquires additional maxima separated by $\Delta\varepsilon \sim (\alpha/w)^{1/2}$.

It is readily seen that, when $\xi \sim \alpha$ and $\gamma \ll 1$, the expression given by (17) becomes identical with Eq. (11) predicted by the theory of the compound state in the neighborhood of the isolated pole of $\cot\pi\xi$. However, on the wings of the excitation function ($\beta \ll \alpha$), the condition for the validity of (11) is

$$\gamma \ll \alpha^{\beta/2} e^{-\alpha}, \qquad (18)$$

i.e., the single condition $\gamma \ll 1$ is not, in general, sufficient to ensure that the decay of the compound state is independent of the method of its formation.

For sufficiently large γ (or, more precisely, for $\gamma \gg \alpha^{1/2}$), the formula given by (17) becomes identical to (15) with the corresponding nonadiabatic corrections in the small parameter $\alpha^{1/2}/\gamma$. When $\gamma \sim \alpha^{1/2} \gg 1$ (so that the applied force produces an appreciable shift of the nuclei of the molecule during the short lifetime of the intermediate complex AB^-), the transition amplitude is

$$A_{00}(\xi, \alpha)=-i\gamma(\pi/2\alpha)^{1/2}e^{-x^2}[1-\operatorname{Erf}(ix)] \quad (x=(\xi-\alpha)/(2\alpha)^{1/2}. \qquad (19)$$

This expression predicts the characteristic oscillating structure of the excitation functions $|A_{00}|^2$, which corresponds to interference between two waves, one of which describes the departure of particles to infinity after reflection from the potential barrier.[11]

This case does, in fact, correspond to the excitation of diatomic molecules through the steep repulsive term of the ion AB^-. Transition to an arbitrary repulsive interaction V_{AB^-}, describing the infinite motion of nuclei in the excited state, is then achieved by substituting

$$x \to \frac{(\omega_0/2)^{1/2}}{|F_{AB^-}(0)|}(\varepsilon+i\Gamma/2-V_{AB^-}(0)) \quad \left(F_{AB^-}=\frac{d}{dR}V_{AB^-}\right).$$

This result can also be obtained by using the Winans–Stueckelberg[13] approximation in the spectral representation of the Green function $G(E, R, R')$ for the wave functions of the intermediate state:

$$|\nu\rangle=|F_{AB^-}(R_\nu)|^{-1/2}\delta(R-R_\nu) \qquad (20)$$

(where R_ν is the classical turning point for states with energy E_ν). We then have

$$A_{if}=\Gamma\int dR\frac{\varphi_i(R)\varphi_f(R)}{E-V_{AB^-}(R)+i\Gamma/2}. \qquad (21)$$

In this expression, φ_i and φ_f are the wave functions of the nuclei in the initial and final states. It is clear that, in this representation, Eq. (21) is valid for any repulsive potential for which the condition for the validity of the approximation given by (20) may be regarded as satisfied3):

$$\omega_0^{-1/2}|F_{AB^-}(0)| \gg \omega_0. \qquad (22)$$

Let us now consider the intermediate case when $\alpha \sim \gamma \sim 1$ and the formation and decay of the complex AB^- leads to the most complicated interference structure on the energy dependence of the cross sections for different processes, $\sigma_{vv'}(\varepsilon)$.[3] All the characteristic features of the dependence of the cross sections on the incident electron energy and the quantum numbers v, v' can be deduced from (9)–(10).

In fact, the expression given by (10) for the amplitude $A_{0v'}$ for the vibrational excitation amplitude is the sum of two terms containing the functions $f_{v'+l}(\xi) = \Gamma(1-\xi)/\Gamma(1+v'+l-\xi)$, and it can be shown that, in the present case for which $\gamma \sim 1$, these functions have smooth maxima at $\beta = v' + l$ ($l = 0, 1, 2, \ldots$). Hence, it follows that the first interference maximum on the excitation function $|A_{0v'}(\varepsilon)|^2$ is shifted by the amount $\Delta_{v'}$, which increases with increasing number v' of the vibrational state [in the case of an elastic process, $v' = 0$, and the first maximum corresponds to the vibrational ground state of the ion AB^- and all the subsequent maxima coincide with the spectrum of the nuclear subsystem of the ion term, i.e., it follows from (8) that they lie at $\beta = l = 2k$]. All these qualitative conclusions are in complete agreement with existing experimental data. To achieve a quantitative verification of the above model for $\alpha \sim \gamma$

~1, we have used (10) to calculate the cross sections for the vibrational excitation of molecular nitrogen

$$e^-+N_2(v=0)\to N_2^-(^2\Pi_g)\to N_2(v')+e^-$$

with $\alpha=2.1$ and $\gamma=0.85$. The value of α is known with good accuracy,[3] whereas γ is subject to considerable uncertainty. The calculated values of the autoionization widths γ of the intermediate ion N_2^- for the characteristic range of motion of the nuclei lie in the range 0.6–3.3.[3] Calculations based on (10) have shown that the vibrational excitation cross sections of nitrogen are not very sensitive to the values of γ in the range 0.75–1.20. On the other hand, the best agreement with the experiment of Ehrhart and Willman[14] is achieved for $\gamma=0.85$. Figure 1 shows these results together with the data reported by Hasted and Awan[5] and the experimental results of Ehrhart and Willman.[14] The value $\gamma=0.61$ used by Hasted and Awan[5] is too low and leads to considerable discrepancy between theory and experiment. The discrepancy increases with the incident-electron energy and is due to the influence of anharmonism and the dependence of Γ on R.[7]

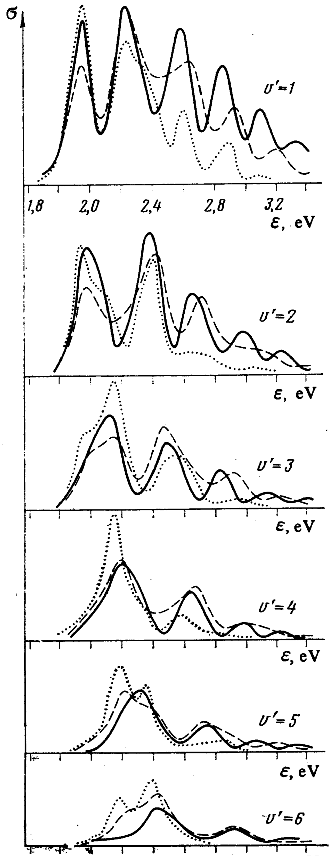

FIG. 1. Cross section $\sigma_{0v'}(\varepsilon)$ for the vibrational excitation of molecular nitrogen as a function of incident-electron energy. Solid curve—the experiment of Ehrhart and Willman,[14] points—calculations of Hasted and Awan,[5] dashed curves—cross sections calculated in this paper with $\alpha=2.1$ and $\gamma=0.85$. The cross sections are normalized to the maximum value of $\sigma_{01}(\varepsilon)$.

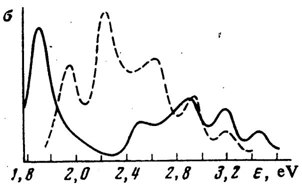

FIG. 2. Comparison of cross sections for single-quantum resonance transitions in molecular nitrogen for $v=0$ and $v=1$. Dashed curve—$\sigma_{01}(\varepsilon)$, solid curve—$\sigma_{12}(\varepsilon)$.

Equations (6) and (9) can also be used to consider transitions between vibrationally excited states of the molecules during resonance electron scattering. It is readily seen that, when $\alpha\sim1$ and $w\gg v$, the maximum contribution to (9) is provided by the term with $l=v$, so that

$$A_{vv'}=\left(\frac{v'!}{w!v!}\right)^{1/2}A_{0w}(\xi,\alpha)\qquad(w=|v-v'|),\tag{23}$$

i.e., the excitation functions do not depend on the initial state of the molecule at a fixed energy transfer. It is clear that a strong dependence of the cross sections for the inelastic transitions (1) on the number of the initial excitation is to be expected for $w\sim v$. Figure 2 shows a comparison between the cross sections for inelastic single-quantum transitions from the ground and first vibrationally excited states of molecular nitrogen, calculated with the aid of (9) and (10). It is clear that the single-quantum transition cross section $\sigma_{12}(\varepsilon)$ has a characteristic valley in a definite region of incident-electron energy, which is due to interference on intermediate vibrational levels of the ion AB⁻ (this is also reflected in the calculations reported by Chen[6]). The existence of well-defined transition regions in the case of the process (1) may have an important influence on excitation-transfer kinetics in a gas and on the electron-energy distribution function.

3. Let us now consider the role of the intermediate electron-vibrational complex AB⁻ in the resonance dissociation of diatomic molecules:

$$e^-+\mathrm{AB}\to\mathrm{AB}^-\to\mathrm{A}+\mathrm{B}+e^-\tag{24}$$

(the corresponding energies of the molecule AB, the ion AB⁻, and the quasimolecule A + B are shown in Fig. 3). The process (24) corresponds to the inelastic autoionization of the ion, the result of which is the appearance of the electronically excited quasimolecule with a repulsive interatomic interaction. Let us take the following process as a concrete example:

$$e^-+H_2(X\,^1\Sigma_g^+)\to H_2^-(^2\Sigma_g^+)\to H_2(b\,^3\Sigma_u^+)+e^-.\tag{25}$$

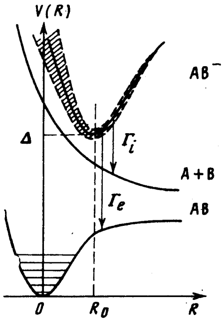

FIG. 3. Energies of the molecule AB, the ion AB⁻, and the quasimolecule A + B.

The dissociation of hydrogen during resonance exchange scattering of electrons ($\varepsilon \sim 11-12$ eV) has recently been observed[15] but, so far, such processes have not been investigated theoretically.4)

If we use the harmonic-oscillator approximation for the AB⁻ ion energy with a constant autoionization width γ, and write the wave function for the final state of the nuclei in the quasimolecule in the Winans–Stueckelberg approximation[13]

$$|E'\rangle = \varkappa(E')\,\delta(R-R_{E'})$$

(E' is the energy of relative motion of the nuclei, $R_{E'}$ is the classical turning point), we obtain

$$A_{vE'} = (\gamma_e\gamma_i)^{1/2}\sum_{\mathrm{v}}\frac{\langle v|\mathrm{v}\rangle\langle \mathrm{v}|E'\rangle}{E-E_{\mathrm{v}}+i\Gamma/2} = \hat{D}_{v0}(\lambda,0)\,e^{-\lambda}A_{0E'}(\xi+v,\lambda^2/\alpha)\,|_{\lambda=\alpha}. \tag{26}$$

The quantities γ_e and γ_i in this expression are, respectively, the elastic and inelastic autoionization widths of AB⁻ ($\gamma = \gamma_e + \gamma_i$) and $A_{0E'}$ is the amplitude for the dissociation of the vibrationally unexcited molecule

$$A_{0E'}(\xi,z) = -i\varkappa(E')\,(\gamma_e\gamma_i)^{1/2}\frac{\exp(-\alpha'-\alpha/2)}{1-\exp(2\pi i\xi)}B(\xi,z,\alpha'), \tag{27}$$

where

$$B(\xi,z,\alpha') = \int_0^{2\pi} d\eta\,\exp(i\xi\eta - 2(z\alpha')^{1/2}e^{-i\eta} - ze^{-2i\eta}/2) \qquad (\alpha'^{1/2} = (\omega/2)^{1/2}R_{E'} - \alpha^{1/2}).$$

We note that, in addition to the integral representation (26), it is possible to obtain the differential operator representation for the amplitude $A_{vE'}$:

$$\begin{gathered} A_{vE'} = a(E')\,\hat{D}_{v0}(\lambda,0)\left\{\exp\left[-\lambda + \frac{\lambda}{(2\alpha)^{1/2}}\frac{\partial}{\partial\lambda'}\right]\right. \\ \left.\times A_{00}\left(\xi+v, \frac{\lambda}{(2\alpha)^{1/2}}\frac{\partial}{\partial\lambda'}\right)e^{-\lambda'^2}\right\}_{\lambda=\alpha,\ \lambda'=\alpha'^{1/2}}, \\ a(E') = \varkappa(E')\,(\gamma_e\gamma_i)^{1/2}\exp(\alpha'-\alpha/2), \end{gathered} \tag{28}$$

which is analogous to (6) in Sec. 2.

Equations (26)–(28) together with (6) and (9) establish the analytic relationship between the different channels of resonance electron scattering, and provide us with a unified approach to the cross sections for all the possible transitions in the above system for given values of model parameters.

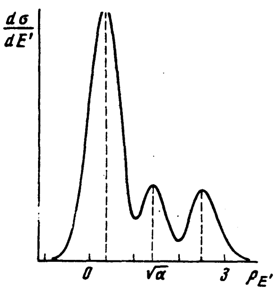

FIG. 4. Spectrum of dissociation products $d\sigma/dE' = |A_{0E'}(\rho_{E'})|^2$ at incident-electron energy corresponding to the vertical Franck–Condon transition ($\alpha = 2$, $\gamma = 1$, $\beta = 2\alpha$).

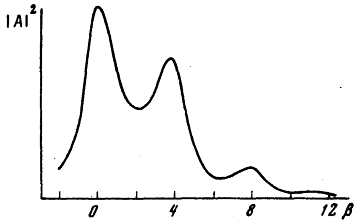

FIG. 5. Excitation function $|A_{0E'}(\beta)|^2$ as a function of the incident electron energy for $R_{E'} \sim R_0$ ($\alpha = 2$, $\gamma = 1$).

Equations (26)–(28) are substantially simplified in limiting cases. For sufficiently small γ [satisfying (12), (13), and (18) in which α plays the role of the energy shift for $\alpha' \ll 1$, and $(\alpha\alpha')^{1/2}$ is the corresponding quantity for $\alpha' \gtrsim 1$], the spectrum of the decay products in the neighborhood of the isolated ν-th level of the complex AB⁻ is

$$\frac{d\sigma}{dE'} = \frac{d\Gamma}{dE'}\frac{\Gamma_v}{(E-E_{\mathrm{v}})^2+\Gamma^2/4} \tag{29}$$

where

$$\frac{d\Gamma}{dE'} = \Gamma_i\chi_{\mathrm{v}}^2(R_{E'}). \tag{30}$$

Equation (30) suggests an interesting possibility of a direct measurement of the square of the modulus of the wave function of the nuclear subsystem of the complex AB⁻$[\chi_\nu^2(R_{E'})]$ in experiments on the resonance dissociation of molecules. This possibility can be realized in the case of the reaction given by (25) for which the conditions ensuring the validity of (20) are satisfied [unfortunately (Weingartshofer *et al.*[15]), the spectrum of electron energy losses, i.e., the spectrum of dissociation products, was not measured].

It is important to note, however, that, when $\gamma \sim 1$, the spectrum of the dissociation products is reproduced by $\chi_\nu^2(R)$ with good accuracy. This is illustrated in Fig. 4 which shows $|A_{0E'}|^2$ as a function of $\rho_{E'}$ [where $\rho_{E'} = (\omega/2)^{1/2}R_{E'}$], calculated from (27) with $\gamma = 1$ and $\alpha = 2$.5) The presence of three maxima directly reflects the fact that the region of the Franck–Condon transition ($\beta = 2\alpha$) corresponds, in this case, to the intermediate state with $\nu = 2$.

Let us now consider the properties of the excitation functions for $\gamma \sim 1$, which are of particular interest for sufficiently heavy molecules. For example, when $|R_{E'} - R_0| \ll 1/(\alpha\omega)^{1/2}$, the amplitude (27) is readily shown to be

$$A_{0E'} = \varkappa(E')\,(\gamma_e\gamma_i)^{1/2}e^{-\alpha}\xi^{-1}\Phi\left(1.1-\frac{\xi}{2};\frac{\alpha}{2}\right). \tag{31}$$

The excitation function for this part of the spectrum [i.e., $E' \sim V_{A+B}(R_0)$] and $\alpha \sim \gamma \sim 1$ exhibits interference maxima at $\varepsilon = \Delta + 2\omega k$ ($k = 0, 1, 2, \ldots$). This is illustrated in Fig. 5 which shows the dependence of the excitation function on the incident-electron energy ε calculated from (31) with $\gamma = 1$ and $\alpha = 2$.

When $\alpha' \gg 1$ (this corresponds to large and small relative energies of the dissociating nuclei of the quasi-molecule A + B), the amplitude (27), written as a function of the energy of the nuclei, decreases exponentially with increasing $R_{E'}$ (i.e., with increasing or decreasing E').

4. In conclusion, let us consider the vibrational excitation of polyatomic molecules by electron impact. The resonance (interference) structure of the excitation functions have been observed, for example, for the CO_2 molecule by Bonnes and Schulz.[16] Before we formulate the approach adopted here, we note that a situation wholly analogous to that considered here occurs in the resonance scattering of light (see, for example, Perlin[17]). It is well known that photoprocesses in polyatomic molecules can be described with a sufficient degree of completeness within the framework of the simple model of a displaced multidimensional oscillator[18,19] (the "main" model of the theory of electronic vibrational spectra of polyatomic molecules[19]). The electron binding energy in the autoionization state does not usually exceed the energy of the electronic excitation of the molecules. It is therefore natural to expect that, in general, the changes in the parameters of the vibrational subsystem in the case of electron attachment are not greater than the changes accompanying photoexcitation. These considerations justify the use of the above model in the theory of vibrational excitation of polyatomic molecules by electron impact. The approach developed in Sec. 2 can, without difficulty, be generalized to the multidimensional case.

The actual form of the dependence of the excitation function on the energy of the incident electron is determined by the values of the characteristic energy parameters Γ, ω_s, and $\alpha_s\omega_s$ (s labels the normal coordinates of the molecule), and the possible relationships between these parameters specify the physically different situations in the system. A general analysis of the excitation function is outside the scope of the present paper. We shall confine our attention to some special cases for which the methodology is essentially the same as that investigated above.

We note, to begin with, that, for small ($\Gamma \ll \omega_s$) and large ($\Gamma \gg \omega_s$) autoionization widths, the corresponding generalization of (11) and (15) to polyatomic molecules is quite obvious. Situations corresponding to the resonance scattering of electrons by polyatomic molecules under "composite" conditions, when the strong inequalities for the individual degrees of freedom are violated, are of particular interest. For example, when $\Gamma \sim \omega_1$ and $\Gamma \ll \omega_s$ ($s = 2, \ldots, N$, where N is the number of normal coordinates of the polyatomic molecule), the cross sections for processes can be shown to have the form of isolated Breit–Wigner resonances with a substructure determined by interference in the normal coordinate for which the vibrational frequency is a minimum.

When $\alpha_1 \ll 1$ for some of the normal coordinates, this type of vibration is obviously not well defined in the scattering spectrum. If, on the other hand, $\alpha_1 \ll 1$ for one of the normal coordinates, and for the others $\alpha_s \sim 1$ ($s = 2, \ldots, N$) (this case is the most characteristic for triatomic molecules for which the geometry is substantially modified when an electron is added), an irregular interference structure will in general appear against the background of the smooth envelope of the scattering spectrum.

[1)] We confine our attention mainly to the case of finite motion of nuclei in the ion AB^-.

[2)] We note that, when $\alpha \gg 1$, the problem can be solved analytically for arbitrary $\delta\omega/\omega_0$.

[3)] These results show that the correct expressions for the intramolecular transitions accompanying resonance electron scattering cannot be obtained by simple averaging of the Breit–Wigner cross section over the interatomic distances, as suggested by Smirnov[1] (p. 194).

[4)] Resonance dissociation through the repulsive term of the intermediate ion AB^- was previously considered by Golubkov *et al.*[11]

[5)] The chosen value of α is typical for most diatomic molecules.[3] For example, $\alpha_{NO} = 1.7$, $\alpha_{O_2} = 2.4$, and $\alpha_{H_2} = 2$.

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