Cross section of excitation of molecular vibrational levels by electron impact

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The Breit-Wigner formula for the cross section for the excitation of a molecule by electron impact via formation of an intermediate autoionization state of a negative ion is generalized to include the case when the width of the autoionization level is small in comparison with the vibrational quantum of the negative ion. Use is made of the absence of transitions between vibrational levels of a negative ion during its lifetime, and also of the physical conditions for the formation and decay of the ion. For the case when the width of the autoionization level is independent of the nuclear configurations of the negative ion, an expression is obtained for the cross section of the transition between the vibrational levels of the negative ion at an arbitrary ratio of the level width to the vibrational quantum of the ion.

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1. This paper is devoted to a calculation of the cross section for the excitation of the vibrational levels of a molecule by electron impact. This process takes place effectively only if an autoionization state exists for the negative ion made up of the colliding electron and molecule. The decay of this autoionization state can lead to formation of a molecule in a vibrationally excited state. In the case when the width of the autoionization level is small in comparison with the distance between the vibrational levels, the cross section of the considered transition can be obtained in accordance with the Breit–Wigner theory (see[1–4]).

The existing theories of vibrational excitation of molecules by electron impact[5–9] either contain the assumption that the width of the autoionization level of the negative ion is small in comparison with the energy difference between the neighboring vibrational levels (implicitly or explicitly), or are of semi-empirical character.1) In this paper we use the physical character of the formation and decay of the negative ion of the molecule, so that the Breit–Wigner theory can be extended to include the more general case when the width of the autoionization level is comparable with the distance between the vibrational levels of the negative ion (but is small in comparison with energy of the incident electron).

2. Before we examine the dynamics of the electron-molecule collision process, let us consider the singularities of the character of the interaction of an electron with a molecule. We shall operate within the framework of the Born–Oppenheimer approximation, according to which the wave function of a system can be represented in the form of the product of the nuclear wave function by the electron wave function, the latter being dependent on the configuration of the nuclei as a parameter. Excluding the electron motion, we find that the electron energy, which depends on the nuclear configuration, plays the role of a potential in which the nuclei move. By the same token, we shall continue the discussion in the language of electronic terms, which are shown in Fig. 1 for a diatomic molecule and its electronic term. We consider furthermore, for the sake of simplicity, a diatomic molecule, although the results are equally valid for a polyatomic molecule.

We thus have an electronic term of a molecule that goes over, following capture of an electron, to the electronic term of the autoionization state of the negative ion. Each of the terms has a vibrational structure, and the state of the negative ion is characterized by a width $\Gamma(R)$ that depends on the distance R between the nuclei. However, since the negative-ion decay is due to an electronic transition, this characteristic does not influence the positions of the vibrational terms. The width of the autoionization level is always much less than the excitation energy of the autoionization state, for only then does the level width have a meaning.

The width $\Gamma(R)$ of the autoionization level of the negative ion is significantly altered when the distance between the nuclei is shifted by an amount of the order of atomic dimensions. The amplitude of the nuclear vibration in the molecule is much smaller than atomic dimensions. If it is therefore assumed that the equilibrium distances between the nuclei in the molecule and in the negative ion are close to one another, then $\Gamma(R)$ is independent of the internuclear distance in the region of the transition. We shall focus our attention henceforth on just this case.

3. We now trace the character of the formation and

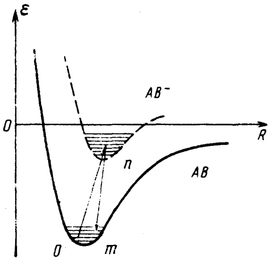

FIG. 1. Vibrational excitation of a molecule by electron impact via formation of an intermediate autoionization negative-ion state; 0 and m are the initial and final vibrational states of the molecule, and n is the intermediate state of the negative ion.

decay of the autoionization state. We note that each of these transitions occurs at an instant of a strong interaction of the electron with the molecule, and the time of such a transition is of the order of atomic times, i.e., much less than the average lifetime of the autoionization state or the characteristic time of vibration of the nuclei. Electron capture on an autoionization level, as well as the decay of the autoionization state, has therefore a sudden and random character. Capture of the electron produces a sudden change in the Hamiltonian—the potential energy in the Schrödinger equation for the nuclei. In contrast to typical problems of the theory of sudden perturbation, however, we have here also a simultaneous change of the nuclear wave function. This is determined by the dependence of the electron capture cross section on the nuclear configuration.

We are faced thus with the following problem. The electron is suddenly captured by a molecule in a vibrational state 0. The result is a negative ion with a certain distribution over the vibrational states. The corresponding vibrational level of the negative ion will be labeled n. The excitation energy of this level from the initial vibrational state of the molecule is equal to ε_n, and the nuclear wave function is $\Phi_n(R)$. The produced negative ion decays suddenly after a certain time. Our problem is to find the cross section of this process, which in final analysis transfers the molecule to the level m.

4. Let us construct the wave function of the autoionization state of the negative ion. Let f_{0n} be the probability amplitude of electron capture by the n-th vibrational level. Then at the instant of the capture the suitably normalized nuclear wave function is equal to

$$\sum_n f_{0n}\Phi_n(R),$$

and at a time t following the capture it is given by

$$\Psi(t)=\sum_n f_{0n}\Phi_n(R)\exp\left(-\frac{i\varepsilon_n t}{\hbar}\right). \tag{1}$$

This wave function is accurate to within a phase shift that is the same for the different vibrational states of the ions, and therefore makes it possible to take into account the interference of the states in the course of the decay of the negative ion. The wave function (1) has the dimension of a transition amplitude. The capture cross section, as follows from (1), is

$$\sigma_{\text{capt}}=4\pi\sum_k |\langle\Phi_k|\Psi(0)\rangle|^2=4\pi\sum_k |f_{0k}|^2. \tag{2}$$

We now trace the character of the decay of the autoionization state. Obviously, the amplitude of the conversion of a negative ion in a vibrational state n into a molecule on a vibrational level m following sudden decay of the negative ion is equal to the overlap integral of the corresponding nuclear functions $S_{mn}=\langle\varphi_m(R)|\Phi_n(R)\rangle$, where $\varphi_m(R)$ is the nuclear wave function of the molecule. Thus, if the decay of the negative ion occurs at an instant t after its formation, then we have for the nuclear wave function of the molecule after the ion decay

$$\Psi_{\text{mol}}=\sum_{n,m} f_{0n}S_{nm}\varphi_m(R)\exp\left(-\frac{i\varepsilon_n t}{\hbar}\right). \tag{3}$$

Formula (3) allows us to determine the cross section of the transition of the molecule into the vibrational state m. Namely, if the decay of the autoionization states occurs at a time t after its formation, then the cross section of the transition to the m-th vibrational level is, according to (3),

$$\sigma_{0m}(t)=4\pi|\langle\varphi_m(R)|\Psi_{\text{мол}}\rangle|^2=4\pi\sum_{n,n'} f_{0n}f_{0n'}^{*}S_{nm}S_{n'm}^{*}\exp\left[\frac{i(\varepsilon_{n'}-\varepsilon_n)t}{\hbar}\right]. \tag{4}$$

In particular, using the relation

$$\sum_m S_{nm}S_{n'm}^{*}=\delta_{nn'},$$

we obtain from (4) the formula (2) for the capture cross section. This quantity, as can be expected from general considerations, does not depend on the instant of the decay.

If it is assumed that the wave function of the system remains unchanged during the lifetime of the autoionization state of the negative ion, then we obtain (this corresponds to the decay of the autoionization state at $t=0$)

$$\sigma_{0m}(0)=4\pi\left|\sum_n f_{0n}S_{nm}\right|^2.$$

This formula, with account taken of the concrete expression for the capture amplitude, was obtained by Chen[5] by a method more complicated than the one considered here (to be sure, we assume that Γ is constant). However, since Chen's formula does not take into account the evolution of the system during the lifetime of the autoionization state of the negative ion, it is incorrect. We shall obtain below for the cross section of the process in question a formula that takes this effect into account.[2)]

Let us average the cross section (4) over the decay time. The probability that the autoionization state will decay in the time interval from t to $t+dt$ is, by virtue of the definition of the level width, equal to $e^{-\Gamma t/\hbar}\hbar^{-1}\Gamma\,dt$. This yields for the excitation cross section of the m-th vibrational level

$$\sigma_{0m}=\int_0^\infty e^{-\Gamma t/\hbar}\frac{\Gamma\,dt}{\hbar}\sigma_{0m}(t)=4\pi\sum_{n,n'}\frac{\Gamma f_{0n}S_{nm}f_{0n'}^{*}S_{n'm}^{*}}{\Gamma+i(\varepsilon_n-\varepsilon_{n'})}. \tag{5}$$

5. The derived formula allows us to take into account of the interference of the nuclear states of the negative ion of the molecule at the instant of decay. This effect is essential if the width of the autoionization level is comparable with the distance between the neighboring vibrational levels of the negative ion. On the other hand, if the width of the level is small in comparison with the distance between the vibrational levels, then electron capture will occur mainly only on one vibra-

tional level. In this case we can average in (4) the oscillating function $\exp[i(\varepsilon_{n'} - \varepsilon_n)t/\hbar]$ with respect to time. This allows us to restrict the sum over n' to only one term, $n'=n$. After integrating with respect to time we arrive at the following expression for the molecule excitation cross section:

$$\sigma_{0m}=4\pi\sum_n |f_{0n}|^2|S_{nm}|^2. \tag{6}$$

In the obtained formula, the first factor is the probability of electron capture on the autoionization level, the second factor is the probability that the decay of the autoionization state leads to formation of a molecule in a given vibrational state. There is no interference of the states in this case, since the system lives long enough in the autoionization state, and "forgets" the history of its formation by the time it decays.

6. We determine now the amplitude f_{0n} of electron capture in a given vibrational autoionization state of the negative ion. If the width of the autoionization level is small in comparison with the distance between the vibrational levels of the negative ion, then the capture takes place in only one state and the sought capture amplitude is determined by the Breit–Wigner formula[4]

$$f_{0n}=\frac{\hbar}{(2m\varepsilon)^{1/2}}\frac{S_{0n}\Gamma/2}{\varepsilon-\varepsilon_n+i\Gamma/2} \tag{7}$$

where ε is the electron energy and m is the electron mass. In the more general case we obtain this quantity from the detailed-balancing principle, assuming a constant width of the autoionization level.

Let the negative ion be on the n-th vibrational level and let it decay. We determine the energy distribution of the emitted electrons for the case when the molecule is produced in the initial vibrational state. We use here the natural physical assumption that there are no transitions between the vibrational states of the negative ion in the course of its decay. Then the dependence of the wave function on the time is given by

$$\psi_n(t)\sim\exp(-i\varepsilon_n t/\hbar-\Gamma t/2\hbar),$$

where the width Γ of the autoionization level does not depend on the number of the level. It follows therefore that the decay amplitude that characterizes the distribution of the emitted electrons with respect to the energies ε is of the form

$$f_n\sim(\varepsilon-\varepsilon_n+i\Gamma/2)^{-1}.$$

This quantity is proportional to the Fourier component of the wave function of the negative ion.

On the basis of the detailed-balancing principle we find that the amplitude of the capture of electrons with energy ε on the n-th vibrational level is proportional to the quantity

$$f_{0n}\sim(\varepsilon-\varepsilon_n+i\Gamma/2)^{-1}. \tag{8}$$

This dependence can take place for any ratio of the width of the autoionization level and at any distance between neighboring level if Γ is constant. In the limit when the width of the autoionization level is small, we obtain formula (7) for the decay amplitude. It follows therefore that formula (7) for the decay amplitude is valid at any ratio of the width of the autoionization level and to the distance between the neighboring vibrational levels. When this is taken into account, formula (5) for the excitation cross section of the m-th level of the molecule by electron impact, at a constant width of the autoionization level, takes the form

$$\sigma_{0m}=\frac{\pi\hbar^2}{2m\varepsilon}\sum_{n,n'}\frac{\Gamma}{\Gamma+i(\varepsilon_n-\varepsilon_{n'})}\frac{\Gamma S_{0n}S_{nm}}{\varepsilon-\varepsilon_n+i\Gamma/2}\frac{\Gamma S^*_{0n'}S^*_{n'm}}{\varepsilon-\varepsilon_{n'}-i\Gamma/2}. \tag{9}$$

Formula (9) leads to the following integral relations:

$$\int\sigma_{0m}\varepsilon\,d\varepsilon=\frac{\pi^2\hbar^2}{m}\sum_{n,n'}\frac{\Gamma^3 S_{0n}S^*_{0n'}S_{nm}S^*_{n'm}}{(\varepsilon_n-\varepsilon_{n'})^2+\Gamma^2} \tag{10a}$$

$$\int\sigma_{\text{capt}}\varepsilon\,d\varepsilon=\sum_m\int\sigma_{0m}\varepsilon\,d\varepsilon=\frac{\pi^2\hbar^2}{m}\Gamma. \tag{10b}$$

In the limit when the autoionization level width is small ($\Gamma \ll |\varepsilon_n - \varepsilon_{n'}|$) formula (9) yields, in accord with (6),

$$\sigma_{0m}=\frac{\pi\hbar^2}{2m\varepsilon}\sum_n\frac{\Gamma^2|S_{0n}|^2|S_{nm}|^2}{(\varepsilon-\varepsilon_n)^2+\Gamma^2/4}=\sum_n\sigma^{(n)}_{\text{capt}}|S_{nm}|^2, \tag{11}$$

where $\sigma^{(n)}_{\text{capt}}$ is the partial cross section for electron capture on the n-th vibrational level of the negative ion, and $|S_{nm}|^2$ is the probability of the decay of the negative ion with transition between the considered vibrational states. In this limit, the integral relation (10a) for the vibrational excitation cross section is transformed into

$$\int\sigma_{0m}\varepsilon\,d\varepsilon=\frac{\pi^2\hbar^2}{m}\Gamma\sum_n|S_{0n}|^2|S_{nm}|^2.$$

7. We consider another limiting case, when the width of the autoionization level exceeds the difference of the neighboring vibrational levels, and the distance between the turning points for neighboring vibrational levels is small in comparison with the amplitude of the vibration of the molecule nuclei. In this case the wave function of the nuclei in the negative ion can be written in the form[15]

$$\Phi_n(R)\approx[\hbar\omega/U'(R_n)]^{1/2}\delta(R-R_n),$$

where $U(R)$ is the potential curve of the negative ion, $U'(R_n)$ is its derivative at the turning point, $\hbar\omega$ is the energy difference of the neighboring vibrational level, and R_n is the turning point for the n-th level and satisfies the relation $U(R_n)=\varepsilon_n$. With the aid of this expresion we obtain $S_{0n}=[\hbar\omega/U'(R_n)]^{1/2}\varphi_0(R_n)$ and, taking the high level density into account, we can replace in (9) the summation over n by integration over dR_n:

$$\sum_n\to\int\frac{U'(R_n)\,dR_n}{\hbar\omega}.$$

Using the obtained relations in formula (9), we reduce the latter to the form

$$\sigma_{0m}=\frac{\pi\hbar^2}{2m\varepsilon}\int\frac{\Gamma^3 dR\,dR'\,\varphi_0(R)\varphi_0^*(R')\varphi_m(R)\varphi_m^*(R')}{\{\Gamma+i[U(R)-U(R')]\}[\varepsilon-U(R)+i\Gamma/2][\varepsilon-U(R')-i\Gamma/2]}. \tag{12}$$

In particular, for the electron capture cross section we obtain

$$\sigma_{\text{capt}}=\sum_m\sigma_{0m}=\frac{\pi\hbar^2}{2m\varepsilon}\int\frac{\Gamma^2|\varphi_0(R)|^2\,dR}{[\varepsilon-U(R)]^2+\Gamma^2/4}. \tag{13}$$

This expression has a simple physical meaning. Namely, the cross section of electron capture into an autoionization state is represented as a sum of partial capture sections at each distance. We note that formulas (12) and (13) are valid also in the case when the autoionization state of the negative ion corresponds to a repulsion potential curve.

8. We thus obtain a generalization of the Breit–Wigner formula for the excitation cross section of a molecule by electron impact to include the case when the autoionization-level width is comparable with the vibrational quantum $\hbar\omega$. We note that the formula obtained for the vibrational-transition cross section satisfies the detailed-balancing principle[16]

$$\varepsilon\sigma_{0m}(\varepsilon)=\varepsilon'\sigma_{m0}(\varepsilon'),$$

where ε and ε' are the energies of the incident electron in the corresponding reaction channel, and $\varepsilon-\varepsilon'$ coincides with the energy difference between the m-th and the initial vibrational levels.

Let us compare the result with those of the earlier approaches. Our scheme of the process consists of three stages: fast capture of the electron, the spreading of the packet of vibrational states of the negative ion during the lifetime of this ion, and rapid decay of the negative ion into a molecule and an electron. If we exclude the second stage, which leads to interference of the vibrational states, then we arrive at Chen's formula[5] for the cross section of the vibrational excitation of the molecule, which is usually taken as the basis of concrete calculations for vibrational excitation of molecules. Chen's formula corresponds to decay at the zeroth instant of time in formula (4). It is valid in practice only in the case of a very small or very large width of the autoionization level in comparison with the energy difference between the neighboring vibrational levels, for under this condition the interference between the vibrational states is inessential. In the general case, however, Chen's formula is in principle incorrect.

9. The foregoing analysis pertains to the case when the width Γ of the autoionization level does not depend on the nuclear configuration in the quasimolecule. We regard an extension of the result to more general case, when there is such a dependence, as a rather complicated task. In the general case the matrix element of the interaction operator corresponding to electron capture and to decay of the autoionization state depends on the distance between the nuclei as a parameter. The employed description of each of the three stages of the considered process (and particularly the latter) therefore becomes invalid. To illustrate the complexity of the transition to the general case, we present the expression for the excitation cross section within the framework of the Breit–Wigner theory,[1–3] when the level width is small in comparison with the magnitude of the vibrational quantum, and the cross section of the transition can be obtained in second order perturbation theory. Under these conditions the cross section for the excitation of the vibrational level by electron impact is

$$\sigma_{0m}=\frac{\pi\hbar^2}{2m\varepsilon}\sum_n\left|\frac{(\Gamma^{1/2})_{0n}(\Gamma^{1/2})_{nm}}{\varepsilon-\varepsilon_n+i\Gamma_n/2}\right|^2. \tag{14}$$

Here $(\Gamma^{1/2})_{0n}=\langle\varphi_0(R)|\Gamma^{1/2}|\Phi_n(R)\rangle$ is the matrix element taken between the vibrational states of the molecule and the negative ion, and $\Gamma_n=\langle\Phi_n(R)|\Gamma|\Phi_n(R)\rangle$ is the average width for the given vibrational level of the negative ion. This formula goes over into (11) in the case of constant Γ. It does not make it possible, however, to extend formula (9) in simple fashion to the general case, since formulas (11) and (14) do not provide for an unambiguous transition from a constant value of the level width to matrix elements associated with this quantity. In this respect the second limiting case, when the width of the autoionization level is large, becomes physically understandable. Transitions with capture and release of an electron take place then with the distance between nuclei unchanged.[15]

(1) The width of the autoionization level of a quasimolecule usually exceeds the energy of the vibrational quantum. Thus, for the autoionization state $H_2^-(^3\Sigma^+)$ the width of the autoionization level is[10–12] $\Gamma=3$ eV, for the ion $N_2^-(^2\Pi_g)$ we have $\Gamma=0.7$ eV,[10–12] and the distance between the vibrational levels of the ion is $\hbar\omega=0.24$ eV[11–13]; for the $CO^-(^2\Pi)$ ion we have $\Gamma=0.4$ eV[10–12] and for the $NO_2^-(^2\Sigma^+)$ ion $\Gamma=0.7$ eV.[14]

(2) This effect is due to interference between different vibrational states for the autoionization state of the negative ion. We note that for associative attachment of an electron to a molecule via formation of an autoionization negative-ion state ($e+AB\rightarrow(AB^-)^{**}\rightarrow A^-+B$) this effect is inessential, since each of the molecule negative-ion state with a different nuclear energy is dispersed independently and there is no interference between the states.

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