

Threshold behavior of the cross sections for scattering of electrons by polar molecules

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The behavior of the cross sections for elastic and inelastic scattering of electrons by polar molecules near the threshold of the inelastic process is considered for the energy range in which a decisive role is played by the electron-dipole interaction. The possibilities of observing resonances and threshold anomalies in the cross sections are discussed. Some experimental data are interpreted in the light of the results.

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1. INTRODUCTION

An analytical approach to the discussion of scattering of an electron by a nonrotating molecule has been worked out in^[1-3]. The effects produced by the long-range interaction of an electron with an immobile dipole become apparent in the range of energies at which, on the one hand, the de Broglie wavelength of the electron is large compared with the radius of the short-range forces and, on the other hand, the molecule can be regarded as nonrotating during the time of collision.

The effects of the long-range action should become apparent also in inelastic scattering, if the formulated conditions are satisfied by the electron energy in some i -th channel, i. e., (see^[3])¹⁾

$$jD_i^h/I_i \ll E_i \ll 1/r_0^2, \quad (1)$$

where j is the rotational quantum number of the molecule, D_i and I_i its dipole moment and moment of inertia in the i -th channel, and r_0 the radius of short-range action.

In view of the appearance of a number of experimental papers^[4-7] on the threshold behavior of cross sections in the presence of electron-dipole interaction in the channel that is opening, interest is arising in developing a multi-channel theory of the scattering of electrons by polar molecules at near-threshold energies, which is the aim of the present work.

2. MULTICHANNEL THEORY OF SCATTERING

We consider the scattering of an electron by a molecule, taking into account the coupling of n different vibrational or electronic states. The strong-coupling equations describing scattering are (disregarding exchange)

$$(\Delta + k_i^2)\psi^i(r) = 2 \sum_{j=0}^n \psi^j(r) V_{ij}(r), \quad (2)$$

where V_{ij} are the matrix elements of the electron-molecule interaction. If the first inequality in (1) is satisfied, the molecule can be regarded as nonrotating, the matrix elements have an asymptotic form

$$V_{ij} \sim g_{ij}(\theta, \varphi)/r^2, \quad r \rightarrow \infty, \quad (3)$$

and in a spherical coordinate system whose polar axis is directed along the axis of the molecule we have $g_{ii}(\theta, \varphi) = D_i \cos \theta$, where D_i is the dipole moment of the i -th state. Regarding the molecule in each channel as nonrotating, we do not separate the various rotational channels, which corresponds to the "hybrid theory" of Chandra and Temkin.^[8]

We use next the same approach as in^[3]. We assume that at $r > r_0$ the interaction is described by the matrix (3), while at $r < r_0$ its explicit form is unknown. For $r > r_0$ we write the i -th channel electron wave function corresponding to the incident wave in channel i' in the form

$$\psi^{ii'} = \sum_{m_i m_i'} A_{v, i'} \frac{u_{v v'}^{ii'}(r)}{r} Q_{v'}^i(\cos \theta) e^{i m_i \varphi}, \quad (4)$$

where $Q_{v'}^i(\cos \theta)$ is the solution of the equation

$$\frac{1}{\sin \theta} \frac{d}{d\theta} \left(\sin \theta \frac{dQ_{v'}^i}{d\theta} \right) + \left[\left(2D_i \cos \theta - \frac{m_i^2}{\sin^2 \theta} \right) + \lambda_{v'} (\lambda_{v'} + 1) \right] Q_{v'}^i = 0, \quad (5)$$

introduced in Ref. 3, ν numbers the eigenvalues of that equation, and m_i is the projection of the electron angular momentum on the molecule axis. In virtue of the conservation of the total angular momentum we have

$$m_i + \Lambda_i = m_i' + \Lambda_i,$$

where Λ_i is the projection of the molecule's angular momentum. Substitution of (4) into (2) leads to the following system of equations for $u_{v v'}^{ii'}$:

$$\left[\frac{d^2}{dr^2} - \frac{\lambda_{v'} (\lambda_{v'} + 1)}{r^2} + k_i^2 \right] u_{v v'}^{ii'} = \frac{2}{r^2} \sum_{j \neq i} \sum_{\nu} \beta_{v \nu}^{ij} u_{\nu v'}^{j i'}, \quad (6)$$

where $\beta_{v \nu}^{ij}$ are angular integrals whose explicit form is inessential for the present discussion.

The solutions of Eqs. (6) will be written in the form of the linear combination

$$u_{v v'}^{ii'} = \varphi_{v v'}^{(-) ii'} - \sum_{\nu j} \varphi_{v \nu}^{(+ij)} \delta_{\nu v'}^{j i'}, \quad (7)$$

where the functions $\varphi^{(\pm)}$ are defined by the asymptotic expression

$$\varphi_{\nu\nu'}^{(\pm)it'} \sim \delta_{\nu\nu'} \delta_{it'} k_i^{-1/2} \exp\{\pm i(k_i r - \lambda_{\nu\nu'} \pi/2)\}, \quad r \rightarrow \infty. \quad (8)$$

By requiring that the difference $\psi^{it'} - \delta_{it'} \exp(ik_i r)$ contain a diverging wave only, we obtain expressions for the coefficients A_i^t and the scattering amplitude. The latter has the form

$$f_{it'}(\xi, \varphi_0, \theta, \varphi) = \frac{i}{k_i^{1/2}} \sum_{\nu\nu'} \left[\frac{\delta_{\nu\nu'} \delta_{it'}}{k_i^{1/2}} Q_{\nu\nu'}^{it'}(\cos \xi) - \exp\left\{i\pi \left(m_{\nu\nu'} - \frac{\lambda_{\nu\nu'} + \lambda_{\nu\nu'}}{2}\right)\right\} \frac{S_{\nu\nu'}^{it'}}{k_i^{1/2}} Q_{\nu\nu'}^{it'}(-\cos \xi) \right] \times \exp\{i(m_{\nu\nu'} \varphi - m_{\nu\nu'} \varphi_0)\} Q_{\nu\nu'}^{it'}(\cos \theta), \quad (9)$$

where the angles ξ, φ_0 characterize the direction of the incident beam in the spherical coordinate system considered.

From the conditions of conservation of the total particle flux follows the unitarity of the matrix

$$S' = e^{-i\pi\lambda/2} S e^{-i\pi\lambda/2},$$

where λ is a diagonal matrix with the elements $\lambda_{\nu\nu}^t$. The matrices S and S' are symmetric with respect to time reversal.

If only one scattering channel is present, the same formula for the amplitude is obtained as in^[3], except that the elements s_{ν} introduced there are replaced by $S_{\nu\nu}$ in (9); the latter are connected with the s_{ν} by the relations

$$A_{\nu}(\xi) s_{\nu}(\xi) = \sum_{\nu'} A_{\nu'}(\xi) S_{\nu\nu'}.$$

In order to determine the elements of the S matrix we will first find representations for the solutions of the radial equations (6). Wave functions of channels with different energies are coupled in the system (6). In this case Damburg^[9] and Gaillitis^[10] have shown that a coupling of the form α_{ij}/r^2 between a channel i and an opening channel j is equivalent to the appearance of the diagonal potential β^2/r^4 in the channel j , where $\beta^2 = \alpha_{ij}^2/(k_i^2 - k_j^2)$. The potential β^2/r^4 leads to unimportant corrections to the cross sections in the near threshold energy region, if there is a long-range action αr^{-2} in the channel j . The small magnitude of the coefficient β^2 , which ensures the absence of an anomalous increase of the correction terms, is connected, in the case of transitions between different electronic states of the molecule, with the rather large distance between the terms (of the order of several electron-volts), and in the case of transitions between different vibrational states it is connected with the smallness of the coupling coefficient $\alpha_{ij} \sim M^{-1/2}$, where M is the reduced mass of the molecule. Therefore the coupling in the right-hand sides of the equations in (6) can be neglected and the solutions determined by the equality (8) take the form

$$\varphi_{\nu\nu'}^{(\pm)it'} = \pm \delta_{\nu\nu'} \delta_{it'} (\pi r/2)^{1/2} H_{\lambda_{\nu\nu'}^t + 1/2}^{(1,2)}(k_i r), \quad (10)$$

where $H_{\lambda_{\nu\nu'}^t + 1/2}^{(1,2)}$ is a Hankel function.

We now write (7) in matrix form and we match the

functions $\psi^{it'}$ with the wave functions for $r < r_0$ with the help of the Wigner R matrix.^[11] Then, using the representations of Hankel functions for small values of the argument, we obtain a formula analogous to that derived for the one-channel case^[3]:

$$S = 1 + 2ik_i^{1/2} [\sin \pi(\lambda + 1/2)]^{1/2} (M + e^{-i\pi(\lambda + 1/2)} k_i^{2\lambda + 1})^{-1} [\sin \pi(\lambda + 1/2)]^{1/2} k_i^{\lambda + 1/2}. \quad (11)$$

The matrix M is a meromorphic function of the energy, and may be regarded as constant in the vicinity of the threshold in the first approximation. The M matrix is symmetric and real in the absence of complex λ . Otherwise the following equalities take place:

$$M^{(11)*} M^{(11)} = 1, \quad M^{(11)*} M^{(12)} = -i M^{(12)*}, \\ M^{(21)*} M^{(21)} = -2 \operatorname{Im} M^{(22)}, \quad M^{(21)*} M^{(11)} = i M^{(21)},$$

where $M^{(11)}$ denotes a submatrix composed of elements $M_{\nu\nu'}^{it'}$, such that the corresponding $\lambda_{\nu\nu}^t$ and $\lambda_{\nu\nu'}^{t'}$ are complex, while $\lambda_{\nu\nu}^t$ and $\lambda_{\nu\nu'}^{t'}$ are real for the elements of the submatrix $M^{(22)}$, while $M^{(12)}$ and $M^{(21)}$ contain "mixed" elements.

We will apply the formulas (9) and (11) to the analysis of concrete processes. For simplicity we will consider the two-channel case. Assume that the condition (1) is satisfied for $i = 1$ and the wave number k_0 of the initial channel may be regarded as varying slowly near the threshold. Then we have for the elements of the S matrix in the first approximation

$$S_{\nu\nu'}^{00} = \delta_{\nu\nu'} + 2i \left(\frac{\rho_{\nu\nu'}}{\eta + z_i} + \xi_{\nu\nu'} \right), \\ S_{0\nu'}^{10} = \frac{2i\tau_{\nu} k_i^{\lambda_0^t + 1/2}}{\eta + z_i}, \quad S_{00}^{11} = 1 + \frac{2ik_i^{2\lambda_0^t + 1} \sin \pi(\lambda_0^t + 1/2)}{\eta + z_i}, \quad (12) \\ S_{\nu\nu'}^{10} = 0 \text{ at } \nu > 0, \quad S_{\nu\nu'}^{11} = \delta_{\nu\nu'} \text{ at } (\nu, \nu') \neq (0, 0),$$

where $z_i = \exp\{-i\pi(\lambda_0^t + 1/2)\} k_i^{2\lambda_0^t + 1}$. The parameters $\rho_{\nu\nu'}$, $\xi_{\nu\nu'}$, τ_{ν} , and η , which depend on the short-range action, have the symmetry properties $\rho_{\nu\nu'} = \rho_{\nu'\nu}$, $\xi_{\nu\nu'} = \xi_{\nu'\nu}$, because of unitarity they are not independent.

The formulas (12) hold both for $D < D_{cr}$ (when λ_0^t is real) and for $D > D_{cr}$ (when $\lambda_0^t = -\frac{1}{2} + i\mu$). For $D = D_{cr}$ (as $\lambda_0^t = -\frac{1}{2}$) transition to the limit in the formulas (12) yields for the denominators an energy dependence of the form $d\eta/d\lambda = \pi i + 2 \ln k$.

From (9) and (12) we have for the scattering amplitudes

$$f_{00}(\omega) = a_{00}(\omega) + \frac{b_{00}(\omega)}{\eta + z_i}, \quad (13)$$

$$f_{10}(\omega) = b_{10}(\xi, \varphi_0) \frac{k_i^{\lambda_0^t} Q_{\nu\nu'}^{it'}(\cos \theta) e^{im_{\nu\nu'} \varphi}}{\eta + z_i}, \quad (14)$$

where ω denotes the set of angles $\xi, \varphi_0, \theta, \varphi$. The amplitude for elastic scattering in the first channel ($i = 1$) has the same form as in the absence of inelastic processes,^[3] with the difference that η is determined not by one but by two real parameters. Knowledge of the parameters $\rho_{\nu\nu'}$, $\xi_{\nu\nu'}$, τ_{ν} is required for the determination of the angular dependence of f_{00} as well as the dependence

of f_{10} on ξ .

Within the framework of the considered model of a nonrotating molecule, the total cross section σ_{11} diverges, and if $D_0 \neq 0$, then σ_{00} diverges as well. To remove the divergences, it is necessary to regularize the cross section according to a procedure proposed in Ref. 3.

We consider next the case when the energy difference between the channels is sufficiently small so that the condition (1) is satisfied also for the zeroth channel, as is the case, for example, upon excitation of vibrational levels. In this case the theory yields the angular dependence of all amplitudes.²⁾ For instance, the excitation amplitude is of the form

$$f_{10}(\omega) = B_{10} \frac{k_1^{\lambda_1} k_0^{\lambda_0} Q_0^0(-\cos \xi) Q_0^1(\cos \theta) e^{i(m_0 \varphi - m_1 \varphi_0)}}{C + B_0 z_0 + B_1 z_1 + z_0 z_1}, \quad (15)$$

where B_{10} , B_0 , B_1 , and C are constants.

In concluding this chapter we point out that the form of formulas (13) and (14) does not depend on the specific physical nature of the zeroth channel. This may be, for example, the channel of scattering of a photon by a negative molecular ion. Then formula (14) yields the threshold behavior of photodetachment.

3. RESONANCES AND THRESHOLD SINGULARITIES

Observation of resonance effects in the elastic-scattering cross section in an opening channel is difficult, since this cross section is anomalously large owing to the large number of partial waves contributing to it. On the other hand, the cross sections of the remaining processes may be not as large if the dipole moments of the other channels are small (or, in particular, zero). Furthermore, the cross sections for transition to a new channel are determined solely by the lower (in λ) partial wave. These processes are therefore more interesting from the viewpoint of observation of resonances and threshold singularities.

We shall examine these phenomena in more detail. It follows from (14) that at $D_i < D_{cr}$ the cross section σ_{10} increases abruptly near the threshold (the more abruptly the closer λ_0^1 is to $-\frac{1}{2}$), while at $D_i > D_{cr}$ it is finite at the threshold (taking into account the restriction that follows from (1)) and oscillates. The cross sections of all the other processes are also oscillating both above and below the threshold. In reality the oscillations are observed if there is room for even one period in the range of applicability of the theory (1), as is the case for $D_i > 3$ a. u. These oscillations are noticeable only below the threshold of the new channel. Above the threshold the resonances in the elastic scattering cross section σ_{11} will be masked by the large magnitude of that cross section. The oscillations in the cross sections σ_{00} and σ_{11} yield a relative contribution of the order $e^{-\pi\mu}$, $\mu = \text{Im} \lambda_0^1$ above the threshold, which is very small at $D_1 > 1$ a. u. These considerations are confirmed by calculations of scattering by the hydrogen atom, carried out by strong coupling methods. As follows from the work of Gailitis and Damburg,^[13] the energy dependence of

the amplitude for scattering of an electron by a hydrogen atom near the excitation threshold is analogous to that obtained in the formulas (13) and (14). Calculation^[14,15] indicates the presence of resonances in the cross sections for elastic-scattering from the ground state below the excitation threshold of the levels $2s$, $2p$ and in the cross section for excitation of the levels $2s$, $2p$ below the excitation threshold of the states $3s$, $3p$, $3d$. No oscillations were noticeable above the threshold, however. The physical meaning of below-threshold oscillations is obvious. These are Feshbach resonances caused by the existence of bound states in the dipole field.

We will now touch upon the problem of resonances in the case $D < D_{cr}$. The S matrix elements (12) have poles whose positions are determined by the roots of the equation

$$\eta + \exp\{-i\pi(\lambda_0^1 + 1/2)\} k_1^{2\lambda_0^1 + 1} = 0.$$

If we let the channel coupling go to zero, then for $\eta < 0$ the root whose phase is contained between 0 and 2π lies on the upper imaginary semiaxis of the complex k_1 plane, i. e., it corresponds to a bound state. As the coupling is switched on, a Feshbach resonance appears below the threshold; it is narrow if $\text{Im}\eta$ is small. It follows from (13) that the resonant amplitude varies slowly on the left and rapidly on the right of the peak, i. e., it has an asymmetric shape (the same applies to the resonances in the case $D_1 > D_{cr}$). If $\text{Re}\eta > 0$ the resonance is absent. The possibility of the presence of resonant peaks above the threshold also follows from the formulas (13) and (14). Like the below-threshold resonances they are of asymmetric shape.

We examine further the energy dependence of cross sections if the resonance is caused by short-range forces. In this case a polar term has to be separated out in the R matrix, and the energy dependence of the parameter η has the form

$$\eta = (E - E_0) / \Gamma, \quad (16)$$

where Γ is a small-modulus quantity if the resonance is narrow. Substitution of (16) into (12) yields the usual Breit-Wigner formula, its energy shift and width depending on the long-range action. For instance, if $D < D_{cr}$ at energies above the threshold energy, and in the case of weak coupling between channels, when E_0 and Γ may be regarded as real, we obtain proportionality of the cross sections to the factor

$$\Gamma^2 / [(E - E_0 + \Gamma \text{Re} z_1)^2 + (\Gamma \text{Im} z_1)^2].$$

If D_1 is close to D_{cr} , it is more convenient to write the expansion of (16) for $\eta + 1$ rather than for η , and then take it into account that $\Gamma^{-1} \rightarrow 0$ as $D \rightarrow D_{cr}$.

If $D \rightarrow D_{cr}$, the width of the resonance above the threshold increases in proportion to $e^{-\pi\mu}$. Therefore for $D \gtrsim 1$ a. u. neither pure dipole resonances nor resonances caused by short-range action should be observed above the threshold.

The cross sections of all the processes that take place below the threshold have breaks and jumps analogous to those discovered by Wigner^[16] and Baz'^[17] for short-range forces and by Gallitis and Damburg^[14] for the case of scattering by the hydrogen atom. For instance, for $D < D_{cr}$ the differential cross section for elastic scattering has the form

$$\sigma_{00} = c_1 + \frac{c_2 + 2\kappa \operatorname{Re} c_3}{|\eta|^2 + \kappa^2 + 2\kappa \operatorname{Re} \eta}, \quad k_i^2 < 0, \\ \sigma_{00} = c_1 + \frac{c_2 + 2\kappa \operatorname{Re} \{c_3 \exp[-i\pi(\lambda_0^2 + 1/2)]\}}{|\eta|^2 + \kappa^2 + 2\kappa \operatorname{Re} \{\eta \exp[-i\pi(\lambda_0^2 + 1/2)]\}}, \quad k_i^2 > 0, \quad (17)$$

where $\kappa = |k_1|^{2j+1}$, and c_1, c_2, c_3 are angle-dependent quantities.

A characteristic circumstance is that, in contrast to the Wigner-Baz' case, the breaks and jumps of (17) do not vanish, generally speaking, at any scattering angle, this being due to the fact that all partial waves contribute to the anomaly.

If $D > D_{cr}$, a jump is observed at the threshold. In a real situation, because of rotation the cross section undergoes a jump not at one point, but in a region whose dimensions are of the order of $jD_1^{1/2}/I_1$.

4. ON THE POSSIBILITIES OF COMPARISON WITH THE EXPERIMENT

Wong and Schulz^[4] investigated experimentally elastic scattering and excitation of vibrational levels of the CO molecule near the threshold of excitation of the electronic state $\sigma^3\Pi$, whose dipole moment $D = 0.544$ a. u. is large in comparison with the dipole moment of the ground state. Singularities, named dipole-dominated resonances by the authors, were discovered in the excitation thresholds of the vibrational levels ($v = 0, 1, 2$). Wong and Schulz reject the interpretation of these features as Wigner-Baz' breaks,^[16,17] since they should vanish at the scattering angle 90° , but this is not observed experimentally. But an interpretation of these features as breaks in (17) is possible, as the latter do not vanish at any angle. The singularities may also be interpreted as Feshbach resonances (Wong and Schulz reject this interpretation for some reason). Low energy resolution does not allow a choice between these possibilities. Both interpretations are in agreement with the proportionality, established by Wong and Schulz, between a resonant amplitude and a product of Franck-Condon overlap integrals.

Rohr, Linder and Seng^[5,6] have studied the excitation of vibrational levels of the polar molecules HCl, HF and H₂O near the threshold. A characteristic feature of the results is the presence of a strong and sharp resonance peak in the excitation cross section. This phenomenon cannot be described within the framework of the theory expounded, since formulas (14) and (15) yield an anisotropic distribution of scattered electrons, which contradicts the experimental data. The reason of inapplicability of the formulas (14) and (15) lies in too small a value of the energy moment I at a considerable contribution to the process from large j molecules,

which renders the theory inapplicable in the resonance region (see (1)). For its description the strong-coupling method must be applied to scattering by a rotating molecule.

Hotop and Patterson^[7] have measured the cross sections for photodetachment of an electron from the ions OH⁻ and OD⁻ near the threshold. In the region considered by them the formula (14) is suitable only for lower rotational levels, while the contribution to the process yields about ten rotational levels. Therefore the threshold law for the photodetachment cross section averaged over j should have a form intermediate³⁾ between (14) and Wigner's law.^[16] In fact, Hotop and Patterson, using the law $\sigma_{10} \sim k_1^{1/2}$ for all j (but taking into account the change of threshold energy with changing j), obtain an averaged cross section that is in good agreement with the experiment.

We wish further to point out that a quantitative comparison of the theory with experiment could be carried out once data become available on differential cross sections for excitation in the energy region satisfying (1), namely either in the case of a small energy differences between channels, so that (15) may be applied, or in the case of oriented molecules. In the latter case

$$\sigma_{10} \sim [Q_\nu(\cos \theta)]^2.$$

The function Q_ν was studied by Gaponov, Demkov *et al.*^[18] in the problem of the behavior of a polar molecule in an electric field. For large values of $\tau = 2IDF$, where F is the intensity of the field, the wave function of that problem is approximately equal to

$$(8\tau)^{\nu/2} \exp\left\{-\frac{\theta^2}{2}\left(\frac{\tau}{2}\right)^{1/2}\right\} \quad (\nu=0, m_1=0).$$

Consequently in our problem (when $\tau = 2D_1$) at large D_1 the angular distribution of scattered electrons will be sharply anisotropic, directed along the vector \mathbf{D} . The physical significance of this result is obvious: the electrons emitted in the direction of \mathbf{D} do not have to overcome a potential barrier. This conclusion was reached previously by Baz' and Gol'danskii^[19] in a study of the behavior of the cross section of the ion-molecular reaction



by analysis of a simple model.

It must be pointed out, however, that the results above cannot be applied directly to ion-molecular reactions, since the condition of applicability of the theory which for the process (18) takes the form

$$\frac{j(D_{AB}m_B)^{1/2}}{I_{AB}} \ll E \ll \frac{1}{m_B r_0^2},$$

is not fulfilled in any energy interval at values of D_{AB} appreciably different from zero.

- ¹Atomic units are used in this paper.
²To obtain the dependence of the amplitudes on the scattering angle, it is necessary to change over to a coordinate system in which the polar axis is directed along the incident beam (see, e.g., Ref. 12).
³The dipole moment of OH equals 0.65 a.u. $> D_{cr}$, therefore the cross section that follows from (14) is finite at the threshold.

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Photoionization of molecules from the ground and selectively-excited states by radiation from a vacuum-ultraviolet H₂ laser

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Photoionization laser spectroscopy based on the use of vacuum ultraviolet lasers is reviewed. Descriptions are given of the design and parameters of a hydrogen VUV laser. Experiments are described on the single-photon ionization of dimethylaniline and methylaniline molecules in the region of 1600 Å, and the ionization of NO molecules by radiation in the region of 1200 Å. The two-step photoionization technique has been used to investigate the kinetics of predissociation of H₂CO molecules excited to the ¹A₂ electronic state by a pulse from a nitrogen laser. Two-step photoionization of NO₂ molecules with radiation transformation on the first step has been investigated in the range 4470-4570 Å. The feasibility of a highly sensitive and highly selective method of detecting polyatomic molecules is examined.

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1. INTRODUCTION

Substantial success has recently been achieved in the development of lasers operating in the vacuum-ultraviolet part of the spectrum (VUV). The short-wave limit of laser radiation is at present at about 400 Å, and the spectral range 1000 ≤ λ ≤ 2000 Å has now become accessible to the practical application of laser methods.^[1,2] The high energy of the laser photon in this range opens up new possibilities for physics experiments.

One of the most promising areas for the application of short-wave lasers is photoionization laser spectroscopy of molecules.^[3] The method of two-step selective photoionization of molecules, used in conjunction with the VUV laser, opens up new possibilities for the detection of infrared absorption events with probability close to unity. This relies on measurements of the ionization

current. There is particular interest in the possibility of using a laser detector of complex molecules, based on the two-step photoionization of molecules followed by the mass spectrometry of the resulting ions. The practical realization of this possibility would essentially result in a laser detector of trace amounts of complex molecules, and the solution of one of the more difficult problems in physics.^[4]

There is, therefore, considerable interest in the study of one- and two-step ionization of molecules. Since the ionization energy of most molecules lies in the range 8-12 eV, the VUV laser must be used, even in the two-step scheme, after excitation of the intermediate electronic state of the molecule. Experiments in this area were impeded by the absence of suitable lasers in the VUV band. Laser radiation has so far been used mainly for the step photoionization of atoms with relatively low