

# Spectrum of the two-photon absorption in collisions of hydrogen atoms with neutral particles in the zero-range potential approximation

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An analytic expression of the optical spectrum is obtained for the two-photon absorption in collisions of hydrogen atoms in the ground state with a particle  $Y$ , the electron interaction with which is approximated by a  $\delta$ -function potential. A convenient analytic representation is found for the matrix elements of transitions between the states of the molecular system. The nuclear part of the problem is solved by using the Landau-Zener formula. Using the results of calculations based on this theory, an analysis of the dependence of the two-photon absorption spectrum on the only parameter in the theory, the electron- $Y$  scattering length, could be made. It was thus shown that the intensity distribution in the two-photon absorption spectrum is significantly different from the case of single-photon absorption. In addition to the well-known squared field parameter  $\mathcal{E}_0^2$  determining the smallness of the two-photon absorption, there appears in this theory a large parameter, partially compensating for the smallness of  $\mathcal{E}_0^2$ . This work also expands the class of problems for which an exact quantum solution can be found.

## 1. INTRODUCTION

During the past two decades, the collisions between atoms and molecules, accompanied by absorption or emission of photons, have been intensely investigated both experimentally and theoretically.<sup>1-7</sup> One of the most interesting classes of reactions of this type consists of elementary processes in which a photon is absorbed by the colliding complex, an inert gas atom or a halogen molecule or compound  $X_2$ . In such a process, an exchange reaction<sup>8-13</sup>



or other dynamically allowed processes may occur.<sup>14,15</sup> The absorption bands corresponding to these processes usually are in the vacuum-UV region. The experiments are therefore difficult, particularly if the radiation source is a laser. Such processes can be studied in principle if one uses a doubled wavelength laser inducing two-photon absorption. In such a case, the reaction dynamically equivalent to (1) is



The study of a reaction of this type was first reported in Ref. 16. Clearly, the absorption coefficient should increase proportionally to the light intensity. One might also expect its magnitude to be small compared to the single photon process, as determined by the factor  $\mathcal{E}_0^2$  (Ref. 1), where  $\mathcal{E}_0$  is the amplitude of the electric vector of the electromagnetic field. However, under usual experimental conditions even in the case of powerful pulsed lasers,  $\mathcal{E}_0^2 \ll 1$  a.u. ( $0.5 \times 10^{10}$  V/cm). Nevertheless, in a number of circumstances, the two-photon collision processes are quite promising. This is because in order to realize two-photon processes of type (2) one needs radiation sources in the near UV range, and this allows the use of industrial excimer lasers which are both powerful and reliable.

Yet, the elementary processes involving two-photon absorption are still very little investigated. Even in the case of the simplest typical models, there is no theory capable to describe the dependence of the cross section or of the absorption coefficient on wavelength. This is precisely the problem

solved in the present work. Our purpose is to develop for two-photon absorption spectra for atomic collisions, a theory which might be subsequently extended to atomic-molecular processes of type (2). In the following, we shall analyze the problem of the optical spectrum corresponding to two-photon absorption in a colliding complex of the type  $H + Y$ . Within the framework of the proposed model, the electronic part of the problem is reduced to the study of the electron motion in the field of two centers,  $H^+$  and  $Y$ , and interaction potential with  $Y$  will be approximated by a  $\delta$ -function. The fundamental idea of using potentials with zero radius goes back to Fermi.<sup>17</sup> The only parameter of the problem is the electron scattering length in the field of the neutral particle  $Y$ . The nuclear part of the problem is solved by using the Landau-Zener linear model. The single-photon absorption problem in a reaction of type  $H + Y + \hbar\omega \rightarrow (HY)^*$  was solved in Refs. 18 and 19.

## 2. PROBABILITY OF TWO-PHOTON ABSORPTION IN ATOMIC COLLISIONS

An important first step in solving any problem of finding an absorption spectrum is an analysis of the states between which the transition takes place. The states of the  $HY$  system in the zero-range potential approximation are well known<sup>20</sup> (see also Presnyakov's article in Ref. 21). They are found by solving the transcendental equation

$$\Phi(n, R) = -a_n^{-1}, \quad (3)$$

in which the function  $\Phi(n, R)$  has the expression

$$\Phi(n, R) = \frac{2\Gamma(1-n)}{n} \left\{ \left[ \frac{n^2}{2R} - \frac{1}{4} \right] M_{n, n/2} \left( \frac{2R}{n} \right) W_{n, n/2} \left( \frac{2R}{n} \right) + M'_{n, n/2} \left( \frac{2R}{n} \right) W'_{n, n/2} \right\}. \quad (4)$$

In (4),  $R$  is the distance between the centers  $H^+$  and  $Y$ ,  $n = (-2E)^{-1/2}$  is the energy parameter,  $E(R)$  is the electron energy and depends parametrically on the distance  $R$ ,  $\Gamma$  is the gamma function, and  $M_{n, 1/2}$  and  $W_{n, 1/2}$  are the Whittaker functions. In the problem under consideration, a transi-

tion with the absorption of one photon occurs at distances  $R \gg 1$  a.u. In this case, the ground state term  $|i\rangle$  is horizontal, and the wave function of the external electron coincides with the wave function of an unperturbed hydrogen atom. The perturbed state  $|f\rangle$  of the molecular system  $HY$  after photon absorption can be found by solving Eq. (3) numerically. The next step in solving the problem under consideration, concerning the two-photon spectrum of the collision process

$$H + Y + 2\hbar\omega - (HY) \quad (5)$$

involves the solution of the Schrödinger equation

$$i \frac{\partial \Psi}{\partial t} = H \Psi, \quad (6)$$

with

$$H = H_0 + V, \quad (7)$$

in which  $H_0$  is the Hamiltonian of the molecular system, and  $V$  is the interaction between the molecular system and the electromagnetic field and is given by the expression

$$V = \vec{\mathcal{E}} \mathbf{d}, \quad (8)$$

$$\mathcal{E} = \mathcal{E}_0 \cos \omega t. \quad (9)$$

Here  $\mathbf{d}$  is the dipole moment transition operator,  $\vec{\mathcal{E}}$  the electric field vector,  $\omega$  the circular frequency, and  $t$  the time. Let us write the wave function as

$$\Psi = \sum_i a_i(t) \varphi_i, \quad (10)$$

where  $\varphi_i$  are the wave functions of the molecular system and depend parametrically on the distance  $R$ . These functions are eigenfunctions of the Hamiltonian  $H_0$  and are independent of time:

$$H_0 \varphi_i = U_i(R) \varphi_i. \quad (11)$$

The eigenvalues  $U_i(R)$  are the electronic levels of the molecular system. Substituting (10) into the Schrödinger equation (6), and neglecting the operator for nonadiabatic coupling (see below), we obtain for the amplitudes the system of differential equations

$$i \dot{a}_j = a_j U_j + \sum_{k \neq j} a_k V_{jk}. \quad (12)$$

The field is omitted from the diagonal matrix elements, so that they coincide with the energy levels. The set of subscripts  $(k, j)$  is, in principle, infinite. Let  $|i\rangle$  be the state before collision of the quasimolecule  $HY$ . The system of differential equations (12), with the initial condition  $a_k(t \rightarrow -\infty) \rightarrow \delta_{ki}$ , describes the evolution in time of the state amplitudes. The probability of transition from the state  $|i\rangle$  to a state  $|f\rangle$  is given by the quantity  $|a_f(\infty)|^2$ . The substitution

$$a_k = b_k \exp\left(-i \int_{-\infty}^t dt U_k\right)$$

leads to the system

$$i \dot{b}_k = \sum_{i \neq k} b_i V_{ki} \exp\left[i \int_{-\infty}^t dt (U_k - U_i)\right], \quad (13)$$

which can be solved by successive approximations. In the zeroth approximation,  $|b_k| = |a_k| = \delta_{ki}$ , and in the first approximation with  $k \neq j$  we have

$$i \dot{b}_k = V_{ki} \exp\left[i \int_{-\infty}^t dt (U_k - U_i)\right]. \quad (14)$$

Substituting in Eq. (14) the explicit expression for the matrix element  $V_{ki}$ , and using Eqs. (8) and (9), we find that in first order of perturbation theory

$$b_k(t) = -\frac{i}{2} (\vec{\mathcal{E}}_0 \mathbf{d}_{ki}) \left( \int_{-\infty}^t \exp\left[i \int_{-\infty}^{\tau} dt_1 (U_k - U_i + \omega)\right] d\tau + \int_{-\infty}^t \exp\left[i \int_{-\infty}^{\tau} dt_1 (U_k - U_i - \omega)\right] d\tau \right). \quad (15)$$

We now assume that one-photon transitions are not possible due to the absence of a corresponding resonance. Incidentally, we omit from the integrand in Eq. (15) the points where the phase is stationary, i.e., where

$$U_k - U_i \pm \omega = 0. \quad (16)$$

The method of stationary phase<sup>23</sup> allows us to find the asymptotic values of the integrals in Eq. (15), in the limit of fast variations of the phase:

$$b_k(t) = -\frac{1}{2} \mathcal{E}_0 \mathbf{d}_{ki} \left\{ \frac{\exp\left[i \int_{-\infty}^t (U_k - U_i + \omega) dt_1\right]}{U_k - U_i + \omega} + \frac{\exp\left[i \int_{-\infty}^t (U_k - U_i - \omega) dt_1\right]}{U_k - U_i - \omega} \right\}. \quad (17)$$

Due to the absence of stationary phase points,  $|b_k(\infty)| = \delta_{ki}$ . In the second order of perturbation theory, we must replace the amplitudes on the right-hand side of (13) by the amplitudes  $b_i$  in the form given in Eq. (15) in first order. We thus obtain four terms, only one of which has a stationary phase point defined by the equality

$$U_j - U_i - 2\omega = 0. \quad (18)$$

Evaluating the integral by the stationary-phase method, we obtain

$$W = |b_f(\infty)|^2 = \frac{2\pi |V_{if}|^2}{\Delta F v}, \quad (19)$$

which is the transition probability for passing through the stationary-phase point  $R_\omega$ , which is the intersection of the energy of the initial state raised by  $2\hbar\omega$  with the energy of the final state  $|f\rangle$ . The quantities  $\Delta F$  and  $v$  are respectively, the relative energy slope and velocity at the point  $R_\omega$ ,

$$V_{if} = \frac{\mathcal{E}_0^2}{4} \sum_j \frac{(\mathbf{nd}_{ji})(\mathbf{nd}_{ij})}{U_j - U_i - \omega}; \quad n = \frac{\vec{\mathcal{E}}_0}{\mathcal{E}_0}. \quad (20)$$

The expressions (19) and (20) have obvious physical interpretations. The expression (19) for the transition probability for the passing through the intersection point coincides with Landau's formula.<sup>24</sup> The transition matrix element is a

product of the square of the field and the polarizability of the molecular system by an alternating field frequency  $\omega$ . The quantity  $|V_{if}|^2$  must be averaged over the angle between the vectors  $\mathbf{n} = \mathcal{E}_0/\mathcal{E}_0$  and  $\mathbf{d}_{ji}, \mathbf{d}_{jf}$ . The states  $|i\rangle$  and  $|f\rangle$  between which the transition takes place correspond to zero projections of the external-electron angular momentum along the internuclear direction. This is due to the fact that, in the zero-range potential approximation, only such states are different from the state of the isolated hydrogen atom. Therefore,

$$(\mathbf{nd}_{ij})(\mathbf{nd}_{jf}) = d_{ij}^0 d_{jf}^0 n_0^2 + d_{ij}^{-1} d_{jf}^1 n_{+1} n_{-1} + d_{ij}^1 d_{jf}^{-1} n_{-1} n_{+1}, \quad (21)$$

where  $d_{ij}^+, d_{ij}^-, n_+,$  and  $n_-$  are covariant cyclical coordinates. It can be easily seen that upon substitution of the expression (21) in the sum over  $j$  from Eq. (20), the second and third terms yield identical contributions.

Setting

$$n_0 = \cos \theta, \quad n_+ = -2^{-1/2} \sin \theta e^{i\varphi}, \quad n_- = 2^{-1/2} \sin \theta e^{-i\varphi}, \quad (22)$$

and taking into account the fact that  $V_{if}$  is a real quantity, we have

$$V_{if} = \frac{\mathcal{E}_0^2}{4} \left\{ \cos^2 \theta \sum_j \frac{d_{ij}^0 d_{jf}^0}{U_j - U_i - \omega} - \sin^2 \theta \sum_j \frac{d_{ij}^1 d_{jf}^{-1}}{U_j - U_i - \omega} \right\}. \quad (23)$$

Hence, replacing the quantities  $\cos^4 \theta, \sin^4 \theta, \cos^2 \theta$  and  $\sin^2 \theta$  by their average values, we obtain

$$|V_{if}|^2 = \frac{\mathcal{E}_0^4}{16} |S_{if}|^2, \quad (24)$$

where

$$|S_{if}|^2 = \frac{1}{5} (S_0)^2 - \frac{4}{15} S_0 S_1 + \frac{8}{15} (S_1)^2, \quad (25)$$

$$S_0 = \sum_j \frac{d_{ij}^0 d_{jf}^0}{U_j - U_i - \omega}, \quad (26)$$

$$S_1 = \sum_j \frac{d_{ij}^1 d_{jf}^{-1}}{U_j - U_i - \omega}. \quad (27)$$

Although the quantities  $S_0$  and  $S_1$  have similar expressions, they are essentially different from a calculational viewpoint. This is because the sum in  $S_0$  is taken over the levels of the molecular system  $HY$ , whereas the sum in  $S_1$  is restricted to those levels  $j$  for which the component of the external-electron angular momentum along the internuclear direction is unity. These are states of the hydrogen atom which are not affected by the presence of a  $\delta$ -interacting center  $Y$ . At large distances between centers, the states  $|j\rangle$  as well as  $|f\rangle$  in the sum for  $S_0$  also become hydrogen states.

### 3. EFFECTIVE TWO-PHOTON TRANSITION OPERATOR

We shall now examine the problem of calculating the sums  $S_0$  and  $S_1$ . Since they will be analyzed in the same manner, let us introduce the notation

$$S_k = \sum_j \frac{d_{ij}^k d_{jf}^{-k}}{U_j - U_i - \omega}, \quad k=0, 1. \quad (28)$$

Expanding  $S_k$  in a power series in  $\omega$ , we obtain

$$S_k = \sum_{j,m} \frac{d_{ij}^k d_{jf}^{-k}}{U_j - U_i} \left( \frac{\omega}{U_j - U_i} \right)^m. \quad (29)$$

Setting

$$\frac{d_{ij}^k}{(U_j - U_i)^m} = (b_m^k)_{ij}, \quad (30)$$

we may write

$$S_k = \sum_m \omega^m (b_{m+1}^k d^{-k})_{if}. \quad (31)$$

Consequently, should the operators  $b_m^k$  be known explicitly, the problem of calculating the sum  $S_k$  reduces to the calculation of the matrix elements  $(b_{m+1}^k d^{-k})_{ij}$  and a subsequent summation over  $m$ . The sum (31) is fairly rapidly convergent, so that it will be sufficient to calculate only the first few terms. The advantage of working with the representation (31) rather than with the sum  $S_0$  of Eq. (26) is that the energy levels in the sum (26) have no analytic expressions and, as mentioned before, they must be found by solving the transcendental equation (4). Moreover, the sum (26) implies an integration over the continuous spectrum, making the evaluation of  $S_k$  even more difficult.

To find  $b_1^k$  we introduce the auxiliary operator  $C_1^k$ , which by definition is such that

$$C_1^k = d^k. \quad (32)$$

Then

$$\frac{d}{dt} (C_1^k)_{ji} = (d^k)_{ji} \quad (33)$$

and

$$d_{ji}^k = C_{ji}^k i (U_j - U_i). \quad (34)$$

Clearly, up to a constant, the operator  $C^k$  is none other but the desired operator  $b_1^k$ :

$$C_1^k = -i b_1^k. \quad (35)$$

To find  $C_1^k$  explicitly, we use the known expression for the time derivative of an operator:

$$d^k |i\rangle = i (H_0 C_1^k - C_1^k H_0) |i\rangle. \quad (36)$$

or, because of the relation (35),

$$d^k |i\rangle = (H_0 b_1^k - b_1^k H_0) |i\rangle. \quad (37)$$

Similarly, we can find a recurrent relation between any two consecutive operators  $b_m^k$  and  $b_{m+1}^k$ :

$$b_m^k |i\rangle = (H_0 b_{m+1}^k - b_{m+1}^k H_0) |i\rangle. \quad (38)$$

Introducing

$$b_m^k = b_m n_k, \quad (39)$$

and substituting for  $|i\rangle$  the wave function of the hydrogen ground state, we can write (see also Ref. 24, § 77):

$$b_m = -1/2 b_{m+1}'' - b_{m+1}'/r + b_{m+1}' + b_{m+1}/r^2. \quad (40)$$

By definition,

$$b_0 = r, \quad (41)$$

where  $r$  is the distance from the electron to the nucleus  $H^+$ .

The solution can be found in the form of a power series in  $r$  :

$$b_m = \sum_s \alpha_s^m r^s. \quad (42)$$

Substitution of the series (42) in the differential equation (40) leads to a system of equations for the coefficients  $\alpha_s^m$

$$-\frac{(s+1)(s+4)}{2} \alpha_{s+2}^{m+1} + (s+1) \alpha_{s+2}^{m+1} - \alpha_s^m = 0, \quad (43)$$

from which one can find all necessary coefficients. To this end, we start with  $m = 0$ ; since it follows from (41) that  $\alpha_s^0 = \delta(s, 1)$ , we can rewrite the system (43) as

$$-\frac{(s+1)(s+4)}{2} \alpha_{s+2}^1 + (s+1) \alpha_{s+1}^1 - \delta(s, 1) = 0. \quad (44)$$

The operators we seek must be regular at the origin. This implies that  $\alpha_0^m = 0$ . Moreover, the series (42) should not diverge too strongly for large  $r$ , because this would make the matrix elements of Eq. (39) divergent. Hence, necessarily, starting with some  $m$ , function of  $s$ , all coefficients  $\alpha_s^m$  must be equal to zero, i.e.,  $b_m$  must be polynomials. We begin the solution of (44) with  $s = 1$ . Setting  $\alpha_3^1 = 0$  (only such a choice of  $\alpha_3^1$  converts the series (42) for  $b_1$  into a polynomial), we obtain  $\alpha_2^1 = 1/2$ . Substituting this value in (44) and setting  $s = 0$ , we find that  $\alpha_1^1 = 1$ . Therefore,  $b_1 = r + r^2/2$ . Given the values just found for  $\alpha_2^1$  and  $\alpha_1^1$ , it follows that

$$\alpha_3^1 = \delta(s, 1) + 1/2 \delta(s, 2).$$

in which  $\delta_{ij}$  is the Kronecker symbol. We can thus write the relation (43) in the form

$$-\frac{(s+1)(s+4)}{2} \alpha_{s+2}^2 + (s+1) \alpha_{s+1}^2 - \delta(s, 1) - 1/2 \delta(s, 2) = 0. \quad (45)$$

Starting with Eq. (45) for  $s = 2$ , and setting  $\alpha_4^2 = 0$ , we find that  $\alpha_3^2 = 1/6$ . Switching to  $s = 1$ , we obtain  $\alpha_2^2 = 11/12$ , and for  $s = 0$ ,  $\alpha_1^2 = 11/6$ . Consequently,

$$b_2 = \frac{11}{6} r + \frac{11}{12} r^2 + \frac{1}{6} r^3.$$

Continuing this iterative procedure, we can find the rest of the operators  $b_m$ , which turn out to be polynomials of degree  $m + 1$ , with no free terms. The numerical values of the coefficients which determine the needed operators are given in the Appendix. A direct verification, using the explicit expressions found for  $\alpha_s^m$ , confirms the validity of the relation (30) that we used to formulate the problem of finding the operators  $b_m$ . The expansion (42) for the effective operator for two-photon transitions, as well as the method described above, can likewise be used to solve other problems relating to two-photon absorption.

#### 4. ANALYTIC REPRESENTATION OF THE ABSORPTION SPECTRUM

Using Landau's formula (19) for the transition probability through the intersection point of the ground state energy raised by  $2\hbar\omega$  with the energy of the perturbed state, one can also obtain other statistical characteristics of the process under consideration. For this purpose, one must first integrate with respect to the impact parameter  $\rho$ , to calculate the

total cross-section:

$$\sigma_\omega = 2\pi \int_0^\infty d\rho \rho W(\rho, \mathcal{E}_0, \omega) \quad (46)$$

for the collision process

$$H + Y \rightarrow (HY)^*. \quad (47)$$

It is understood here that the reaction (47) occurs with the absorption of two photons, although the formal dependence on the light field is implicit in the cross section  $\sigma_\omega$ , which depends parametrically on  $\mathcal{E}_0$  and  $\omega$ . Nevertheless, this representation is convenient, because it allows the use of other relations corresponding to collision processes taking place in the absence of light. In particular, by using the cross section  $\sigma_\omega$ , one can calculate the field-dependent velocity rate

$$K_\omega = \langle \sigma_\omega v_\infty \rangle, \quad (48)$$

in which the angle brackets indicate averaging over velocities with a Maxwell-Boltzmann distribution, and  $v_\infty$  is the relative velocity of the colliding particles at infinity. The number of reactions of type (47) per unit time is

$$\frac{d[HY^*]}{dt} = K_\omega [H][Y]. \quad (49)$$

The quantity  $d[HY^*]/dt$  can be easily related to the optical properties of the medium. The most convenient and, in the case of photon absorption during atomic collisions, traditionally most utilized concept is that of reduced absorption coefficient,  $q$ . This quantity can be evaluated by dividing the absorption coefficient of the medium, in  $\text{cm}^{-1}$  units, by the product  $[H][Y]$  of the particle concentrations. If the concentrations are given in  $\text{cm}^{-3}$ , the reduced absorption coefficient is in  $\text{cm}^5$ . The number of reactions per unit volume and per unit time is given in terms of the reduced absorption coefficient  $q$  by the relation

$$\frac{d[HY^*]}{dt} = \frac{1}{2} q [H][Y] \frac{J}{\omega}, \quad (50)$$

in which  $J$  is the energy flux density,

$$J = \mathcal{E}_0^2 c / 8\pi. \quad (51)$$

$c$  is the velocity of light, and  $J/\omega$  is the number of photons passing per unit time through a unit area in a surface perpendicular to the light beam. The factor one-half in Eq. (50), indicates that there are two absorbed photons. Comparing expressions (49) and (50) and using the explicit expression for  $K_\omega$ , we have

$$\frac{q}{\mathcal{E}_0^2} = \frac{8\pi^2 \omega}{c} \sum_\omega \frac{|S_{if}|^2 R_\omega^2}{\Delta F(R_\omega)} \left\langle \left( 1 - \frac{U_i(R_\omega)}{E_v} \right)^2 \right\rangle. \quad (52)$$

The sum in (52) is taken over all quasicrossing points, and  $E_v$  is the kinetic energy of the colliding particles. Formula (52) is similar to the expression for the absorption coefficient in the case of single-photon absorption:

$$q = \frac{16\pi^3 \omega}{3c} \sum_\omega \frac{R_\omega^2}{\Delta F(R_\omega)} |d_{if}(R_\omega)|^2 \left\langle \left( 1 - \frac{U_i(R_\omega)}{E_v} \right) \right\rangle. \quad (53)$$

However, unlike (53), formula (52) contains the quantity

$|S_{if}|^2$ , the explicit representation of which will be detailed below.

Let us set in the expression (31)

$$b_{n+1}^0 d^0 = \cos^2 \theta b_{n+1} r, \quad b_{n+1}^1 d^{-1} = -\frac{1}{2} \sin^2 \theta b_{n+1} r,$$

and use the wave function of the hydrogen atom ground state

$$|i\rangle = 2 \exp(-r) Y_{00}, \quad (54)$$

as well as the wave function of the final state

$$|f\rangle = C(E, R) G(\mathbf{r}, \mathbf{R}). \quad (55)$$

Here  $G$  is the Coulomb Green's function,<sup>25,26</sup> and  $C$  a normalization factor determined from the condition that

$$|\langle f|f\rangle|^2 = 1. \quad (56)$$

The coefficient  $C$  was found in Ref. 19:

$$C = \left[ \frac{n^3}{2\pi} \frac{\partial}{\partial n} \Phi(n, R) \right]^{-1/2}, \quad (57)$$

where  $\Phi(n, R)$  is given by the relation (4). The Coulomb Green's function can be written as a series in partial waves:

$$G(\mathbf{r}, \mathbf{R}) = \frac{1}{\gamma r R} \sum_l f_{1l}(r_>) f_{2l}(r_<) \left( \frac{2l+1}{4\pi} \right)^{1/2} Y_{l0}(\mathbf{n}), \quad (58)$$

$$f_{1l}(r) = (2\gamma)^{-1/\gamma+l+1} r^{l+1} \exp(-\gamma r) U(-1/\gamma+l+1, 2l+2, 2\gamma r), \quad (59)$$

$$f_{2l}(r) = \frac{(2\gamma)^{1/\gamma+l+1} \Gamma(-1/\gamma+l+1)}{(2l+1)!} r^{l+1} \exp(-\gamma r) M(-1/\gamma+l+1, 2l+2, 2\gamma r). \quad (60)$$

In these expressions,  $U$  and  $M$  are confluent hypergeometric functions,<sup>22</sup> and  $r_<$  ( $r_>$ ) is the smaller (larger) of the distances  $r$  and  $R$ . The quantities  $S_0$  and  $S_1$ , which according to (25) generate the expression for  $|S_{if}|^2$ , can be written as

$$S_0 = \frac{C}{3\gamma R \pi^{1/2}} \sum_n \omega^n (R_0^{n+1} + 2R_2^{n+1}), \quad (61)$$

$$S_1 = \frac{C}{3\gamma R \pi^{1/2}} \sum_n (R_2^{n+1} - R_0^{n+1}). \quad (62)$$

where

$$R_l^{n+1} = f_{1l}(R) \int_0^R dr r^2 b_{n+1} e^{-r} f_{2l}(r) + f_{2l}(R) \int_R^\infty dr r^2 b_{n+1} e^{-r} f_{1l}(r) \quad (63)$$

and  $l = 0, 2$ . The final expression for the reduced absorption coefficient can be obtained by following the approach described in Ref. 19. Writing

$$\Delta F = \left| \frac{\Gamma(1-n)}{n^2 R^2} M_{n, 1/2} \left( \frac{2R}{n} \right) W_{n, 1/2} \left( \frac{2R}{n} \right) \left[ \frac{\partial}{\partial n} \Phi(n, R) \right]^{-1} \right| \quad (64)$$

and substituting (64) in (52), we obtain

$$\frac{q}{\mathcal{E}_0^2} = \frac{8\pi^3 \omega}{C} \sum_\omega \frac{|P_{if}(R_\omega)|^2 R_\omega^3 n^2}{|M_{n, 1/2}(2R/n) W_{n, 1/2}(2R/n) \Gamma(1-n)|} \quad (65)$$

in which

$$|P_{if}|^2 = \frac{1}{5} P_0^2 - \frac{4}{15} P_0 P_1 + \frac{8}{15} P_1^2, \quad (66)$$

$$P_0 = \left( \frac{2}{n^3} \right)^{1/2} \frac{1}{3\gamma R} \sum_n \omega^n (R_0^{n+1} + 2R_2^{n+1}), \quad (67)$$

$$P_1 = \left( \frac{2}{n^3} \right)^{1/2} \frac{1}{3\gamma R} \sum_n \omega^n (R_0^{n+1} - R_2^{n+1}). \quad (68)$$

Introducing the notation

$$Q_l = \sum_n \omega^n R_l^{n+1}, \quad l=0, 2. \quad (69)$$

we can rewrite

$$P_0 = \frac{(2\gamma)^{1/2}}{3R} (Q_0 + 2Q_2), \quad (70)$$

$$P_1 = \frac{(2\gamma)^{1/2}}{3R} (Q_2 - Q_0). \quad (71)$$

Substituting the expressions (70) and (71) into (66), we have

$$|P_{if}|^2 = \frac{2\gamma}{9R^2} \left[ Q_0^2 + \frac{4}{5} Q_2^2 \right]. \quad (72)$$

Using in formula (63) the explicit expression (42) for  $b_{n+1}$  and then substituting the explicit expression for  $R_l^{n+1}$  into (69), we find, interchanging the order of summation over  $n$  and  $s$ ,

$$Q_l = \sum_{l=1}^N [f_{1l}(R) J_{1l}(s, R, \gamma) + f_{2l}(R) J_{2l}(s, R, \gamma)] |F_s|. \quad (73)$$

where

$$|F_s| = \sum_{n=l-1}^{n=\infty} \omega^n \alpha_n^{n+1}. \quad (74)$$

$$J_{1l}(s, R, \gamma) = \int_0^R dr r^{l+2} e^{-r} f_{2l}(r),$$

$$J_{2l}(s, R, \gamma) = \int_R^\infty dr r^{l+2} e^{-r} f_{1l}(r), \quad (75)$$

$$l=0, 2.$$

In general, exact calculation of  $J_{1l}$  and  $J_{2l}$  requires numerical integration. However, one can obtain approximate analytic expressions of these quantities. The presence of the rapidly decreasing factor  $\exp(-r)$  in (75) allows us to extend the limit of integration in the first integral to infinity, and neglect the second integral, i.e.,

$$J_{1l} \approx I_{1l}, \quad J_{2l} = 0. \quad (76)$$

Here

$$I_{1l} = \int_0^\infty dr r^{l+2} \exp(-r) f_{2l}(r). \quad (77)$$

Using in (77) the explicit expression (60) of  $f_{2l}$ , we obtain (see Ref. 24, Appendix f)

$$I_{s,l} = \frac{(2\gamma)^{l+l+1} \Gamma(-1/\gamma+l+1) \Gamma(l+s+4)}{(2l+1)! (1+\gamma)^{s+l+4}} \times {}_2F_1(-1/\gamma+l+1, l+s+4, 2l+2, 2\gamma/(1+\gamma)) \quad (78)$$

in which  ${}_2F_1$  is the hypergeometric function. The second and third arguments of the hypergeometric function are integers. Using then the known relations between contiguous hypergeometric functions,<sup>22</sup> with second and third arguments different from unity, and also the formulae for the hypergeometric functions with identical second and third arguments, when  $F(a,b;b;z) = (1-z)^{-a}$ , we can express  $r^{n+1}$  in terms of elementary functions, to obtain an analytic expression, which has, however, a rather complicated form.

Formula (66) yields the reduced absorption coefficient in atomic units, and the result has the dimensions of the fifth power of length. To express the result in units of  $\text{cm}^5$ , usually adopted in experiments, one must multiply the result of (65) by the factor  $(0.529 \times 10^{-8})^5 = 4.14 \times 10^{-42}$ .

## 5. RESULTS

In Figs. 1–3 we show the quantity  $q/\mathcal{E}_0^2$  as a function of the energy of the state into which the transition takes place.

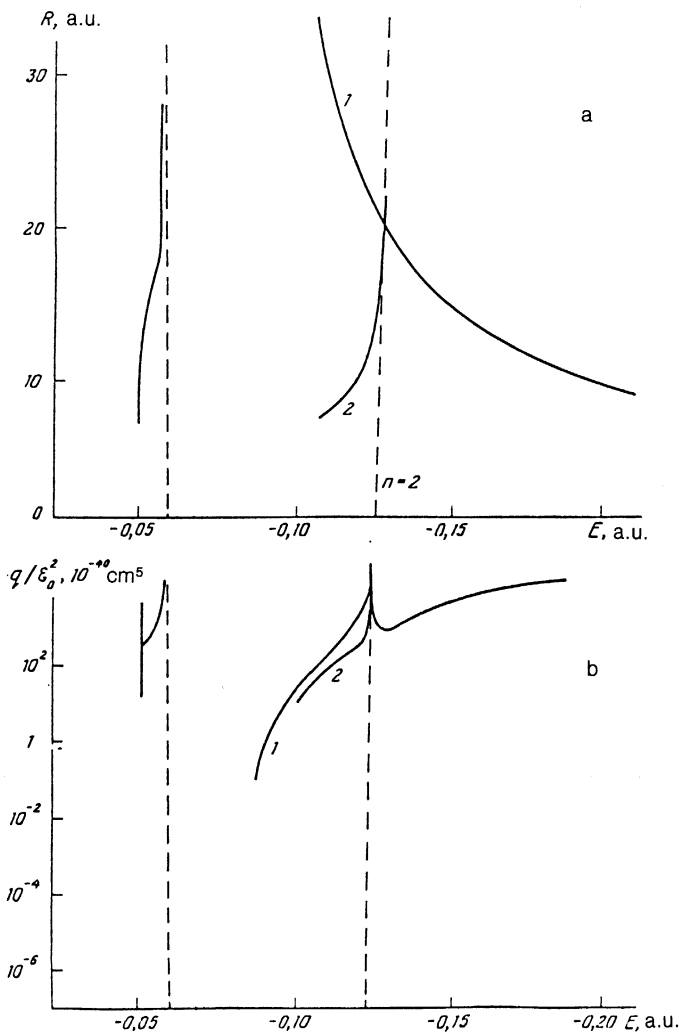


FIG. 1. a—States of the  $H + Y$  system in the zero-range potential approximation ( $a_0 = 2.61$ ); b—Dependence of the reduced absorption coefficient, divided by the square of the field magnitude on the energy of the state into which the transition takes place.  $\mathcal{E}_0$  in a.u.

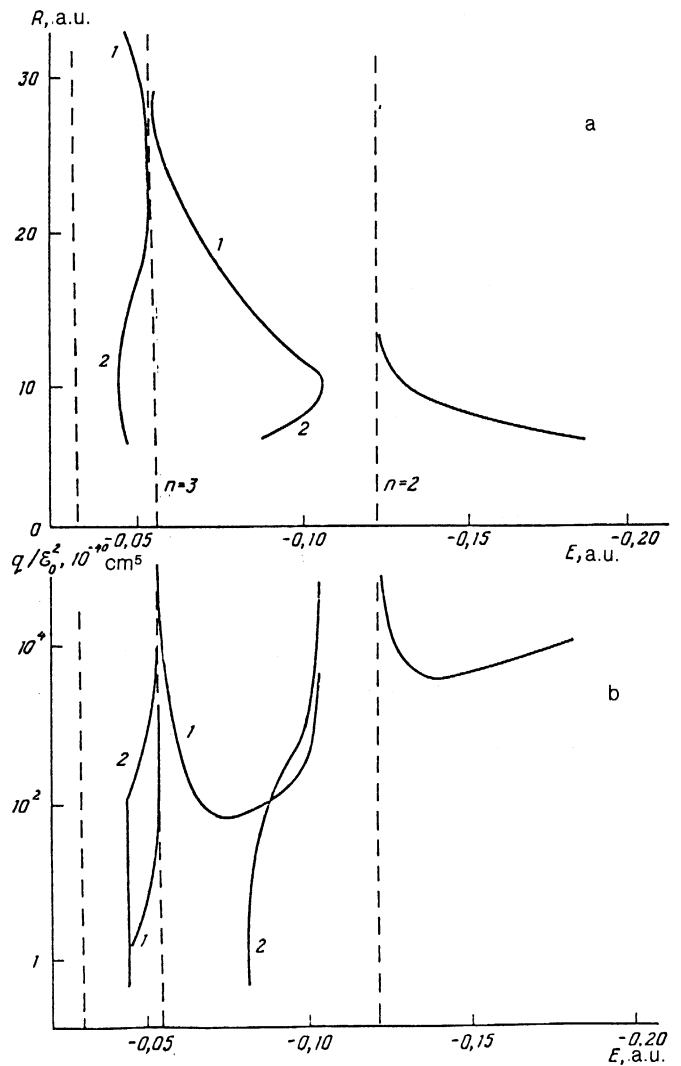


FIG. 2. Same as Fig. 1, but with  $a_0 = 5.22$ .

In the same figures we also indicate the energy levels of the corresponding states of the  $H + Y$  system. Comparing these results with those obtained<sup>19</sup> for single photon absorption, one can note both similarities and significant differences. The similarities primarily consist in the presence of so-called satellite lines near the points of equal slope of the states between which the transition occurs. Formally, these points are due to the vanishing of the denominator in (65). The shapes of the comparable functions are considerably different. While in the short-wavelength portion of the spectrum the results for two-photon absorption exceed the intensity of the one-photon spectrum by several times, or by an order of magnitude, in the long-wavelength region of the spectrum we see differences of two to four orders of magnitude, depending on the scattering length.

The calculations of  $q/\mathcal{E}_0^2$  as functions of energy were done with various numbers  $N$  of operators  $b_m$ . By taking into account the first three ( $N = 3$ ) operators, in the short wavelength region of the spectrum, one obtains an accuracy of about 20%, but this accuracy becomes worse in the long-wavelength region. However, if one considers the first eight operators  $b_m$ , the errors do not exceed a few percentage points over the entire spectrum.

The computing time is primarily determined by repeat-

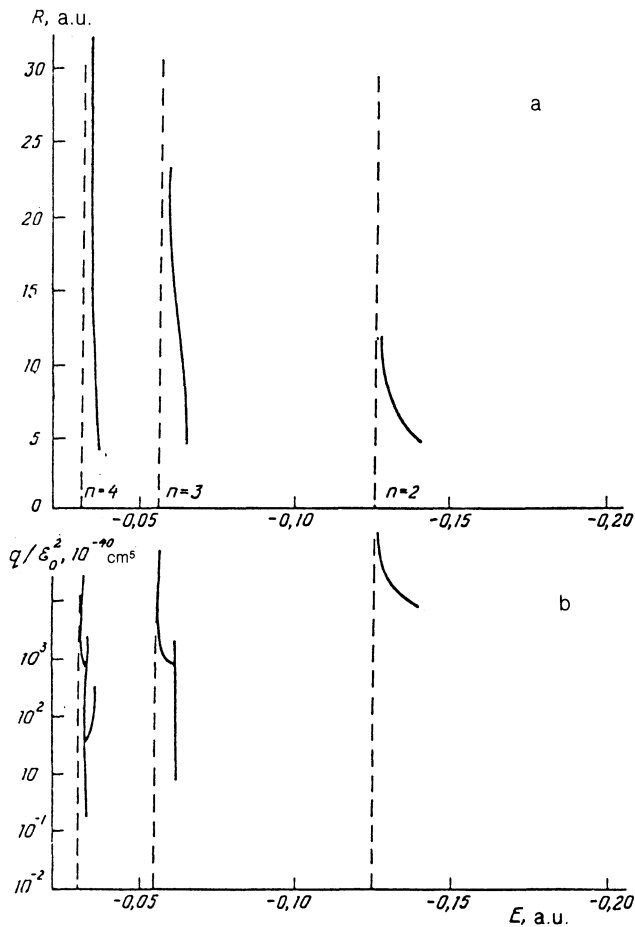


FIG. 3. Same as Fig. 1, but with  $a_0 = -1.2$ .

ed evaluation of integrals of type (75). If instead one uses the analytic formulae (76)–(78), the computing time can be reduced by an order of magnitude. However, the possibility of using these formulae depends strongly on the spectral range. Moreover, the validity of the analytic expressions becomes questionable as the power of  $r$  increases, since ever increasing distances  $r$  come from which are not correctly represented by the analytic expression (78) make the main contributions to the integrals. As mentioned above, in the short wavelength portion of the spectrum one may consider a smaller number of operators  $b_m$ , so that in this region the analytic expressions are more likely to be valid. On the contrary, the need to consider a larger number of operators  $b_m$  for long wavelengths makes the use of analytic expressions inapplicable in the long-wave portion of the spectrum.

## 6. CONCLUSIONS

In the case of a two-photon absorption spectrum, the quantity of interest is the reduced absorption coefficient  $q$ , which is proportional to  $\mathcal{E}_0^2$ , so that the intensity is determined by this small parameter. In order to obtain the reduced absorption coefficient, the ratio  $q/\mathcal{E}_0^2$ , shown in Figs. 1–3 as a function of wavelength, must be multiplied by a factor  $\mathcal{E}_0^2$ . In experiment,  $\mathcal{E}_0 \ll 1$ . As a rule, even when powerful pulsed lasers are used,  $\mathcal{E}_0$  is smaller than an atomic unit by several orders of magnitude. The possibility of performing experiments involving two-photon absorption in atomic-molecular collisions may thus appear doubtful. Nev-

ertheless, as our calculations represented in Figs. 1–3 have shown, in certain regions the small two-photon absorption intensity may be partially compensated for (up to four orders of magnitude) by the large values of the ratio  $q/\mathcal{E}_0^2$ , which in the case of two-photon absorptions is much larger than the reduced absorption coefficient for one-photon absorption. An additional possibility of compensating for the small intensity of the two-photon transition intensity is related to the wavelength doubling of the pump radiation. Since the radiation intensity in this type of experiments is usually detected indirectly, more often than not by fluorescence intensity of the products, working at lower frequencies may allow the use of more appropriate and more powerful lasers, thereby lowering the intensity requirement by orders of magnitude. As a result, the two-photon experiments appear competitive with the one-photon experiments, and from the viewpoint of the theory presented here these processes may successfully complement each other.

The main condition for the applicability of the present approximate theory is that the range of the electron-neutral particle  $Y$  potential be small ( $\rho_0 \sim 1$  a.u.) as compared to the electron wavelength in the vicinity of  $Y$ , i.e.,

$$\rho_0 \ll (2|E+1/R|)^{-1/2}. \quad (79)$$

Another assumption is the disregard of nonadiabatic transitions. Strictly speaking, the system of differential equations (12) should be written in the form

$$i\dot{a}_j = a_j \bar{U}_j + \sum_{k \neq j} a_k \bar{V}_{jk}, \quad (80)$$

where

$$\bar{U}_j = U_j - i \langle \varphi_j | \dot{\varphi}_j \rangle, \quad (81)$$

$$\bar{V}_{jk} = V_{jk} - i \langle \varphi_j | \dot{\varphi}_k \rangle. \quad (82)$$

The term  $\langle \varphi_j | \dot{\varphi}_j \rangle$  in the diagonal matrix elements (81) is smaller than  $U_j$ , because the quantity

$$\dot{\varphi}_j = \frac{\partial \varphi_j}{\partial R} \dot{R}$$

contains the parameter  $\dot{R}$ , the relative approach velocity of the nuclei ( $\dot{R} \sim 10^{-4} - 10^{-3}$  a.u.). Although this small parameter appears also in the non-diagonal matrix elements  $\langle \varphi_i | \dot{\varphi}_k \rangle$ , it may not formally be neglected in (12) compared with  $V_{jk}$ , because the latter is proportional to  $\mathcal{E}_0$ , a quantity for which there is no lower bound, so that  $\langle \varphi_i | \dot{\varphi}_k \rangle$  may very well be larger than  $V_{jk}$ . Nonetheless, formulae (17) and (19) may still remain valid without allowance for the non-adiabatic coupling parameter. Indeed, when going from (12) to (17), an additional third term of the form

$$- \int d\tau \langle \varphi_i | \dot{\varphi}_k \rangle \int_{-\infty}^{\tau} dt (U_k - U_i)$$

appears in (15). Furthermore, in second order of perturbation theory, substituting in the right-hand side of (13) the quantities  $b_i$  containing non-adiabatic contributions and  $\bar{V}_{jk}$  as given in (82), we obtain not four, but nine terms. Yet, not more than one of these terms have a stationary-phase point defined by Eq. (18). This is due to the fact that the characteristic variation time of the non-diagonal elements is determined by the collision time of the particle  $H$  and  $Y$ , which is

$\tau_c \sim 10^{-13} - 10^{-14}$  s. The possibility of neglecting non-adiabatic effects is determined, as in the theory of collisions without participation of the light field by the Massey parameter, which in our case is  $\omega\tau_c$ . Hence, the adiabatic approximation holds if

$$\omega\tau_c \gg 1. \quad (83)$$

The solution of the nuclear part of the problem was based on the Landau-Zener model, which, however, breaks down in the neighborhood of the points where the relative slope of the energy terms vanishes (satellite atomic lines). The analysis of the problem at these points requires a more detailed investigation, using known methods of collision theory.

## APPENDIX

The coefficients  $\alpha_n^m$  of the expansion (42)

| n  | m      |        |        |        |           |
|----|--------|--------|--------|--------|-----------|
|    | 1      | 2      | 3      | 4      | 5<br>1e+4 |
| 0  | 1.0    | 0      | 0      | 0      | 0         |
| 1  | 1.0    | 0,50   | 0      | 0      | 0         |
| 2  | 1,8333 | 0,9177 | 0,1667 | 0      | 0         |
| 3  | 3,9861 | 1,9931 | 0,4306 | 0,0417 | 0         |
| 4  | 9,3599 | 4,6799 | 1,0748 | 0,1368 | 83,333    |
| 5  | 22,918 | 11,459 | 2,7117 | 0,3839 | 329,17    |
| 6  | 57,557 | 28,778 | 6,9276 | 1,0360 | 1023,0    |
| 7  | 146,94 | 73,468 | 17,876 | 2,7610 | 2940,2    |
| 8  | 379,31 | 189,65 | 46,475 | 7,3286 | 8170,5    |
| 9  | 986,89 | 493,44 | 121,52 | 19,432 | 22325     |
| 10 | 2582,3 | 1291,1 | 319,08 | 51,532 | 60438     |

| n  | m         |           |           |           |            |            |
|----|-----------|-----------|-----------|-----------|------------|------------|
|    | 6<br>1e+4 | 7<br>1e+4 | 8<br>1e+4 | 9<br>1e+4 | 10<br>1e+8 | 11<br>1e+8 |
| 0  | 0         | 0         | 0         | 0         | 0          | 0          |
| 1  | 0         | 0         | 0         | 0         | 0          | 0          |
| 2  | 0         | 0         | 0         | 0         | 0          | 0          |
| 3  | 0         | 0         | 0         | 0         | 0          | 0          |
| 4  | 0         | 0         | 0         | 0         | 0          | 0          |
| 5  | 13,889    | 0         | 0         | 0         | 0          | 0          |
| 6  | 63,790    | 1,9841    | 0         | 0         | 0          | 0          |
| 7  | 217,08    | 10,353    | 0,2480    | 0         | 0          | 0          |
| 8  | 662,12    | 38,240    | 1,4457    | 0,0276    | 0          | 0          |
| 9  | 1916,9    | 123,36    | 5,7544    | 0,1772    | 27,557     | 0          |
| 10 | 5393,5    | 371,71    | 19,575    | 0,7554    | 193,45     | 2,5052     |

Note: The coefficients in the columns marked  $1e+4$  ( $1e+8$ ) have been multiplied by  $10^4$  ( $10^8$ ).

<sup>1)</sup> We use atomic units.

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