

The authors thank Professor Yu. N. Demkov and Professor G. F. Drukarev for discussions and for interest in the work.

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Translated by J. G. Adashko

Application of the Faddeev equations to calculations of dissociative attachment cross sections

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(Submitted 22 December 1977)

Zh. Eksp. Teor. Fiz. 74, 2009-2016 (June 1978)

The Faddeev equations have been used to calculate the total and differential cross sections for the dissociative attachment of an electron to H_2 , HD, and D_2 molecules ($e + AB \rightarrow A^- + B$). The adiabatic approximation (at electron energies above the threshold for the dissociation of the molecule to the free atoms $A + B$) and the approximation of separable potentials (at electron energies below this threshold) are used to solve the Faddeev equations. Good agreement is achieved between theoretical calculations and experimental data on dissociative attachment.

PACS numbers: 34.80.Gs

1. INTRODUCTION

This paper is concerned with the process of dissociative attachment of an electron to H_2 , HD, and D_2 molecules ($e + AB \rightarrow A^- + B$). The reaction threshold is equal to the difference between the dissociation energy of the molecule into free atoms $A + B$ (4.48 eV in this case) and the electron affinity of the atom (0.75 eV), and amounts to 3.73 eV.

The basic approximation is that the interaction between the incident electron and the electrons and nuclei in the molecule is replaced by the interaction between the electron and each of the atoms forming the molecule. The complicated many-body problem is thus reduced to the three-body problem. This approximation is reasonable for incident electron energies below the energy corresponding to the electronic excitation of the molecule. Under these conditions, the incident electron energy can be both much greater than the dissociation energy of the molecule in its electronic ground state (4.48 eV) or comparable with it.

We shall use the Faddeev equation^[1] to solve this problem and will employ different approximations in different energy intervals. When the incident-electron energy is high enough (incident electron energy greater than the energy of dissociation of the molecule in its electronic ground state), we can use the adiabatic ap-

proximation. The set of integral equations is then much simpler and has an exact analytic solution if we use the zero-range potentials for the interaction between the electron and each of the atoms forming the molecule.^[2]

The adiabatic approximation is not valid in the region near the dissociative attachment threshold, and the use of the zero-range potential outside the framework of the adiabatic approximation is invalid.^[2] The solution for this region is, therefore, determined in the separable-potential approximation,^[3] which results in a substantial simplification of the equations (Sec. 2). The advantages and disadvantages of the various approximate potentials can be estimated by comparing such calculations with experimental data.^[4,5]

In this paper, we report the first attempt at calculations on the dissociative attachment process within the framework of the three-body problem and based on the Faddeev equations.

2. COMPUTATIONAL PROCEDURE

Let us first consider the adiabatic approximation in which the two-body potentials for the interaction of the electron and the atoms forming the molecule is taken to be the zero-range potential.

The cross section for the dissociative attachment process then has the following form^[2]:

$$d\sigma/d\Omega = (m_1/m_{23})^{1/2} |M_D|, \quad (1)$$

where

$$M_D = (2\pi)^{1/2} m_{23} \int \varphi_{12}(r) \exp[i(m_{23}/m_1)^{1/2} \mathbf{p}\mathbf{r}] F_2(r) dr,$$

φ_{12} is the wave function for the negative ion in the zero-range potential approximation, m_1 is the electron mass, m_{23} is the reduced mass of the molecule and F_2 is a function defined in the Appendix.

The fact that the ratio of the proton to the electron mass is large is useful in that it enables us to obtain an asymptotic estimate for the integral in (1) (see Appendix) which, in turn, enables us to express the dissociative attachment cross section in terms of elementary functions.

For incident-electron energies near the reaction threshold, we use nonlocal separable potentials for the interaction between the electron and the atoms. When the spin properties of the system consisting of the molecule and the incident electron are taken into account, these potentials have the form

$$V_e(r, r') = C_e g_e(r) g_e(r'), \quad V_i(r, r') = C_i g_i(r) g_i(r'). \quad (2)$$

Moreover, we use the additional assumption (in principle, not essential)

$$g_e(r) = g_i(r) = g(r),$$

which substantially simplifies the calculations. The following two functions are also used^[3]:

$$g(r) = e^{-\beta r}/r \quad (3)$$

with¹⁾

$$\beta = 0.8214, \quad C_e = -0.554, \quad C_i = 1.977 \quad (4)$$

and

$$g(r) = e^{-\beta r} \quad (5)$$

with

$$\beta = 1.235, \quad C_e = -0.261, \quad C_i = 0.620. \quad (6)$$

The choice of these parameters is described in detail.^[3]

The potential for the interaction between the heavy atoms of the molecule in the state $X^1\Sigma_g^+$ was simulated by the Morse potential

$$V(r) = D(1 - e^{-\alpha(r-r_0)})^2, \quad (7)$$

where

$$D = 0.1759, \quad \alpha = 1.1174, \quad r_0 = 1.414.$$

It is well known that, before the Faddeev equations can be solved, we must know the behavior of the two-particle T -matrix outside the mass surface. This matrix is usually obtained by solving the Lippmann-Schwinger equations. In the case of the separable potential (2), the Lippmann-Schwinger equation has an exact analytic solution and the T -matrix is obtained in separable form. The separable representation of the two-particle

T -matrix can then be used substantially to simplify the set of integral equations.

The local short-range potentials can be uniformly approximated to by the separable expression given by (2). Several methods are available for the approximate factorization of the potential: the Bubnov-Galerkin method, the Hilbert-Schmidt method, and the Bateman method.^[6]

1. In the Bubnov-Galerkin method, the approximate factorization is achieved by taking the solution of the Lippmann-Schwinger equation in the form of a linear combination of a set of linearly independent functions.

2. In the Bateman method, the local physical potential is directly approximated to by a sum of separable potentials selected in a special way.^[7]

3. The Hilbert-Schmidt method is used to approximate the two-particle matrix when an explicit solution can be found for the problem of the bound state of two particles.

We used the Bateman and Hilbert-Schmidt methods,^[7,8] to approximate the local potential (7) in our calculations. The procedure was as follows. We first constructed the factorized T -matrix and then performed the partial wave expansion and the separation of the angular variables. The result of this was that the Faddeev equations were reduced to an infinite set of coupled integral equations in one variable.

Physically, this means that the dynamic system of three interacting particles with many degrees of freedom was described by a single-particle motion in one suitably chosen variable and a set of discrete variables. This is probably justified provided the energies of the particles in the system are not too high.

In accordance with the nature of the resonance at 3.75 eV which we are investigating,^[4] only the p wave

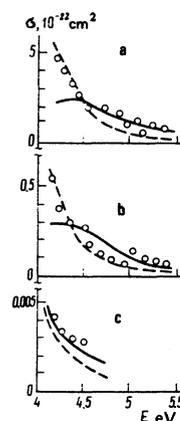


FIG. 1. Cross section for the production of negative ions during collisions between low-energy electrons and H_2 , HD, and D_2 molecules in the adiabatic approximation, using zero-range potentials: a) production of H^- from H_2 ; b) production of D^- from HD; c) production of D^- from D_2 . Points—experimental,^[4] solid curves—calculations with Morse wave functions describing the state of the target molecule, broken curves—harmonic oscillator wave functions for the target molecule.

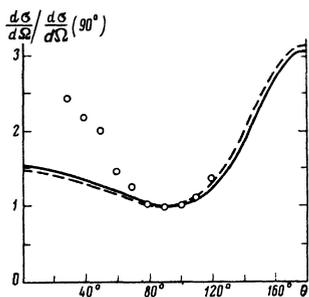


FIG. 2. Differential cross section for the production of negative ions H^- during collisions between low-energy electrons (4 eV) and H_2 molecules, calculated in the adiabatic approximation, using the zero-range potentials: points—experimental data,^[5] solid curve—calculations, using Morse wave functions for the target molecule, broken curve—calculations, using harmonic oscillator wave functions for the target molecule.

need be taken into account in the partial wave expansion. This means that the infinite set of Faddeev equations, reduces to a finite system which is then solved numerically.

We have carried out calculations of both the total and differential cross sections for the dissociative attachment of an electron to H_2 , HD, and D_2 molecules.

3. RESULTS AND DISCUSSION

The calculated total cross sections are shown in Figs. 1 and 3 and the differential cross sections in Figs. 2 and 4. We also show the experimental data reported by Schulz^[4] and Tronc *et al.*^[5] The cross sections calculated in the adiabatic approximation are shown in Figs. 1 and 2 and those obtained in the separable potential approximation in Figs. 3 and 4.

Comparison of the calculations with experimental

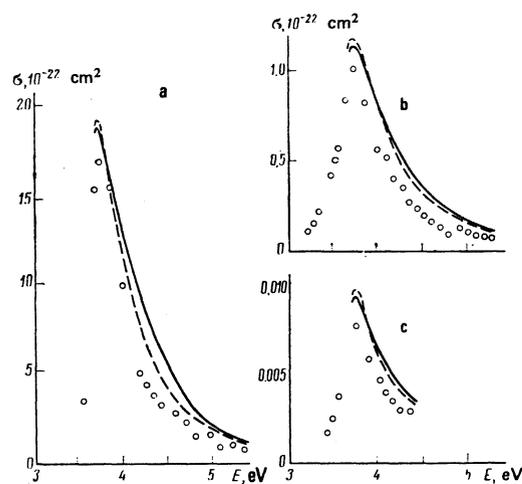


FIG. 3. Cross section for the production of H^- ions during collisions between low-energy electrons and H_2 molecules (a), D^- ions during collisions of low-energy electrons with HD molecules (b), and D^- ions during collisions of low-energy electrons with D_2 molecules (c), calculated in the approximation of separable potentials. Points—experimental,^[4] solid curves—calculated with the potential (3), broken curve—calculated with the potential (5).

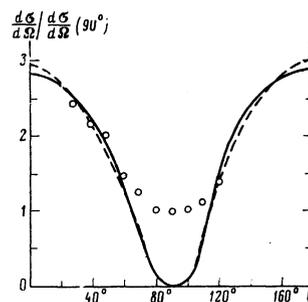


FIG. 4. Differential cross section for the production of H^- during collisions between low-energy electrons (4 eV) and H_2 molecules, calculated in the separable potential approximation. Points—experimental,^[5] solid curve—calculated with potential (3), broken curve—calculated with potential (5).

data shows that the separable potential model of the interaction between the electron and the atom produces satisfactory agreement with experiment (the cross sections agree to within an order of magnitude and the isotopic effect^[9] is confirmed). However, our calculations suffer from a number of defects:

1) the replacement of the interaction between the electron and the molecule by a short-range separable interaction prevents us from taking into account the influence of the various long-range interactions, including the polarization of the molecule by the incident electron;

2) only a finite number of partial waves was taken into account and this again introduces a definite uncertainty.

In addition to the uncertainties introduced by the model itself, there are further computational uncertainties that are also encountered in other calculations performed with the aid of Faddeev's equations. We estimate that these amount to about 0.5%.

Nevertheless, even this approximate calculation enables us to achieve satisfactory agreement with experiment.

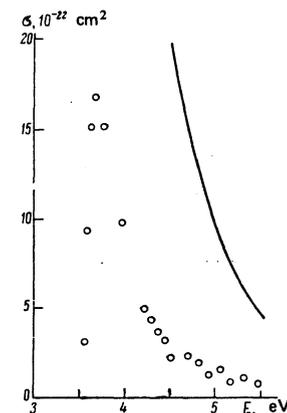


FIG. 5. Cross section for the production of H^- in collisions between low-energy electrons and H_2 molecules, calculated by the method of steepest descents.^[11] Points—experimental data,^[4] solid curve—calculated.

In order to compare our results with other methods of calculation, we have estimated the cross sections from the formulas given by Smirnov,^[10] using approximate values for the energy and the width of the quasi-stationary H_2^- term in accordance with the zero-range potential model. The results of this calculation are shown in Fig. 5. At energies below the dissociation threshold of the molecule (4.48 eV), the calculated cross sections are too high (see Fig. 5), whereas, at energies above the dissociation threshold, the agreement between experiment and calculation is much better for this model.

The authors are indebted to S. P. Merkur'ev for assistance in the numerical calculations and to the Staff of the Department of Quantum Mechanics for useful discussions.

APPENDIX

We must now consider the determination of the amplitude M_D in (1), where^[2]

$$F_2(\mathbf{r}) = \left\{ (\alpha_{12} + ip_0) \exp\left(i \frac{m_2}{m_2 + m_3} \mathbf{p}_0 \cdot \mathbf{r}\right) - \frac{1}{r} \exp\left[i \left(p_0 r - \frac{m_3}{m_2 + m_3} \mathbf{p}_0 \cdot \mathbf{r}\right)\right] \right\} \\ \times \left\{ (2\pi)^2 m_1 \left[(\alpha_{12} + ip_0) (\alpha_{12} + ip_0) - \frac{1}{r^2} \exp(2ip_0 r) \right] \right\}^{-1} \varphi_0(\mathbf{r}), \\ \varphi_0(\mathbf{r}) = \left(\frac{\alpha_0}{2\pi}\right)^{1/2} \frac{1}{r} \exp(-\alpha_0 r),$$

and φ_0 is taken in the form of the harmonic oscillator function

$$\varphi_0(\mathbf{r}) = N_h \exp[-\xi(r-r_0)^2].$$

Substituting F_2 , φ_{12} , φ_0 into the expression for M_D , we obtain

$$M_D = \frac{m_{23}}{m_1} \left(\frac{\alpha_0}{2\pi}\right)^{1/2} N_h \int \frac{\exp[-\alpha_0 r - \xi(r-r_0)^2 + i\kappa p r]}{(\alpha_{12} + ip_0)(\alpha_{12} + ip_0) - r^{-2} \exp(2ip_0 r)} \\ \times \{ (\alpha_{12} + ip_0) \exp[i(\gamma \mathbf{p}_0 \cdot \mathbf{r})] - r^{-1} \exp[i(p_0 r - \beta \mathbf{p}_0 \cdot \mathbf{r})] \} dr, \quad (\text{A.1})$$

where

$$\kappa = \left(\frac{m_{23}}{m_1}\right)^{1/2}, \quad \gamma = \frac{m_2}{m_2 + m_3}, \quad \beta = \frac{m_3}{m_2 + m_3}.$$

Using the fact that $|\mathbf{p}| \approx |\mathbf{p}_0| = p$, we can integrate with respect to the angles in (A.1):

$$\int_0^\pi \exp[i(\gamma \mathbf{p}_0 \cdot \mathbf{r} + \kappa \mathbf{p} \cdot \mathbf{r})] d\Omega = 4\pi \frac{\sin(pz_1 r)}{pz_1 r}, \\ \int_0^\pi \exp[i(\kappa \mathbf{p} \cdot \mathbf{r} - \beta \mathbf{p}_0 \cdot \mathbf{r})] d\Omega = 4\pi \frac{\sin(pz_2 r)}{pz_2 r}, \\ z_1 = (\kappa^2 + \gamma^2 + 2\gamma\kappa \cos \theta)^{1/2}, \quad z_2 = (\kappa^2 + \beta^2 - 2\kappa\beta \cos \theta)^{1/2}, \\ d\Omega = \sin \theta d\theta d\varphi, \quad \theta = \angle(\mathbf{p}, \mathbf{p}_0).$$

Since the scattering centers are identical, we have

$$\alpha_{12} = \alpha_{13} = \alpha, \quad z_1 \approx z_2 = z,$$

and hence

$$M_D = \left(\frac{\alpha_0 m_{23}}{2\pi m_1}\right)^{1/2} N_h \frac{4\pi}{p} [I_1 + iI_2], \quad (\text{A.2})$$

where

$$I_1 = \int_0^\infty \frac{[\alpha r + \cos(pr)] r \sin(pzr)}{[\alpha r + \cos(pr)]^2 + [pr + \sin(pr)]^2} \exp[-\alpha_0 r - \xi(r-r_0)^2] dr, \quad (\text{A.3})$$

$$I_2 = \int_0^\infty \frac{[pr + \sin(pr)] r \sin(pzr)}{[\alpha r + \cos(pr)]^2 + [pr + \sin(pr)]^2} \exp[-\alpha_0 r - \xi(r-r_0)^2] dr. \quad (\text{A.4})$$

Thus, to evaluate (A.2), we must investigate the integrals in (A.3) and (A.4), but these cannot be evaluated explicitly. Nevertheless, since these integrals contain the large parameter Z , we can estimate them asymptotically, for example, by the method of steepest descents,^[11] the basic idea of which is that the leading term in the asymptotic behavior of the integral

$$\int_\lambda \exp[-\eta S(r)] f(r) dr \quad (\text{A.5})$$

for $\eta \rightarrow \infty$ is

$$\left(-\frac{2\pi}{\eta S''(r^*)}\right)^{1/2} \exp[\eta S(r^*)] \left[f(r^*) + O\left(\frac{1}{\eta}\right) \right], \quad (\text{A.6})$$

where λ is a curve in the complex plane of r , the functions $f(r)$ and $S(r)$ are holomorphic in the neighborhood of λ , and r^* is the saddle point.

In our case, we have for (A.3):

$$I_1 = \text{Im} \int_0^\infty \exp[\eta S(r; \alpha_0, r_0, \xi, \eta)] f(r, \alpha, p) dr,$$

where $\eta = pz$,

$$S(r; \alpha_0, r_0, \xi, \eta) = ir - \frac{\alpha_0}{\eta} r - \frac{\xi}{\eta} (r-r_0)^2, \\ f(r, \alpha, p) = \frac{[\alpha r + \cos(pr)] r}{[\alpha r + \cos(pr)]^2 + [pr + \sin(pr)]^2}.$$

The saddle point can be determined from the condition $S'_r = 0$ and turns out to be

$$r^* = r_0 - \frac{\alpha_0}{2\xi} + i \frac{\eta}{2\xi} = a + ib.$$

From (A.5) and (A.6), we have

$$I_1 = \text{Im} \left\{ \left(-\frac{2\pi}{\eta S''(r^*)}\right)^{1/2} \exp[\eta S(r^*, \alpha_0, \xi)] \left[f(r^*, \alpha, p) + O\left(\frac{1}{\eta}\right) \right] \right\}.$$

Omitting simple although laborious algebraic manipulations, we obtain

$$I = \sqrt{\frac{\pi}{\xi}} e^{ns} \frac{B(A_2 F + B_2 G) + A(B_2 F - A_2 G)}{F^2 + G^2}$$

where

$$RS = -\frac{\eta^2}{4\xi} + \frac{\alpha^2}{4\xi} - \alpha_0 r_0, \quad IS = r_0 \eta - \frac{\eta \alpha}{2\xi}, \\ A = a_1 \cos(IS) - b_1 \sin(IS), \quad B = a_1 \sin(IS) + b_1 \cos(IS), \\ A_2 = \alpha a_1 + \cos(a, p) \text{ch}(b, p), \quad B_2 = \alpha b_1 - \sin(a, p) \text{sh}(b, p), \\ C = a_1 p + \sin(a, p) \text{ch}(b, p), \quad D = b_1 p + \cos(a, p) \text{sh}(b, p), \\ F = A_2^2 - B_2^2 + C^2 - D^2, \quad G = 2(A_2 B_2 + CD).$$

Similar calculations can also be performed for (A.4). The result is

$$I_2 = \sqrt{\frac{\pi}{\xi}} e^{ns} \frac{A(DF - CG) + B(CF - GD)}{F^2 + G^2}$$

where RS , A , B , D , C , F , and G are defined above.

We have computed the integrals in (1) using the harmonic oscillator wave function for the state of the target molecule. It is not, however, difficult to perform similar calculations with Morse-type wave functions.

¹Henceforth, we shall use the atomic system of units.

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Translated by S. Chomet

Isomerization of molecules under multiphonon vibrational and subsequent electronic excitation by laser radiation

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(Submitted 11 January 1978)

Zh. Eksp. Teor. Fiz. **74**, 2017-2026 (June 1978)

A description is given of the method used to achieve the isomerization of trans-dichloroethylene molecules under multiphoton vibrational excitation with CO₂ laser radiation, followed by excitation to an electronic state by the radiation from an excimer KrF laser. The multiphoton vibrational excitation of molecules results in a shift of the uv absorption band of trans-dichloroethylene and a sharp increase in the rate of isomerization. An examination is made of an isomerization model in which the leading mechanism is a chain reaction involving Cl atoms from the dissociation of dichloroethylene. Experimental results are found to be in satisfactory agreement with this model. Methods of increasing the selectivity of molecular isomerization by laser radiation are discussed.

PACS numbers: 33.80.Kn, 82.30.Qt, 82.30.Sw

1. INTRODUCTION

There has been considerable interest in the processes involved in the selective effect of laser radiation on matter.^[1] Discrete processes ensuring highly selective excitation of atoms and molecules have attracted particular attention. As an example of studies in this area, we note the two-step excitation and dissociation of ammonia molecules produced by infrared laser and noncoherent ultraviolet radiation^[2] and the multiphoton selective excitation of molecules by infrared laser radiation.^[3]

Laser radiation produces a great variety of selective effects in matter.^[4] Among them, selective photoisomerization of molecules is of particular interest. Isomerization is a multimolecular process not requiring collisions and is therefore expected to be highly selective.

Until quite recently, the isomerization of molecules was investigated by two traditional methods, namely, thermal excitation from the electronic ground states^[6] and excitation by noncoherent radiation to the upper electronic states.^[7] Thermal excitation is nonselective whereas the main difficulty in achieving selective isomerization of molecules in the case of noncoherent

sources of radiation is that it is difficult to produce high radiation density in a narrow spectral range.

Several methods have been proposed to achieve selective photoisomerization (see Fig. 1). The first approach (Fig. 1a) is based on the multiphoton excitation of molecules in a strong infrared field, so that the energy barrier in the electronic ground state can be overcome.^[8,9] The second approach (Fig. 1b) is based on the laser excitation of the lower electronic states of the molecules from which they can undergo transitions to the electronic ground state with a change in the isomeric form. Selective ionization is difficult to achieve in this case because, as a rule, there is a lack of resolved structures in the electronic absorption spectra. The most general approach, which is investigated in the present paper, is the stepwise excitation of molecules illustrated in Fig. 1c.

The radiation from a moderate-intensity infrared laser will excite the molecules of only one isomeric form (because of the sharp difference between the infrared absorption spectra of the isomers) in a multiphoton fashion to a number of vibrational levels. A substantial fraction of the molecules undergoes transitions to the vibrational excited states, and the uv absorption edge of