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Formation of negative ions in collisions between Rydberg atoms and neutral particles

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We present a theoretical description of the formation of weakly bound ($E_b \sim 0.1$–10 meV) negative ions in collisions of Rydberg atoms with neutral atoms or molecules. Using the adiabatic approximation for the collision, we obtain an analytical expression for the formation cross section. It is shown that the cross section has a sharp peak in its dependence on the principal quantum number of the Rydberg electron. This result is in agreement with the experimental studies. We obtain a simple analytical expression that relates the peak position and the binding energy of the negative ion. This expression generalizes the empirical law previously established by Desfrançois [Phys. Rev. A **51**, 3667 (1995)]. Comparison of our calculations with the experimental data on dipole-bound anion formation shows that the obtained formula can be used for determination of binding energies of weakly bound negative ions from Rydberg electron transfer reactions with good accuracy.

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I. INTRODUCTION

Fermi and Teller [1] were the first to predict that a fixed point dipole can bind an electron provided that the dipole moment is larger than 1.625 D. This result has been used over the last 20 years in experimental and theoretical studies of dipole-bound anions (DBA), that is, molecular negative ions in which the excess electron is bound to the neutral molecule due to its dipole moment (see reviews [2,3] and recent works [4,5]).

One of the basic processes of DBA creation for experimental studies is charge-exchange collision between an excited Rydberg atom and a polar molecule. The probability of this reaction should be expected to be large due to the small binding energy of the Rydberg electron. The formation of DBAs with binding energies $E_b \sim 1$–10 meV has been studied in Refs. [6,7]. The cross sections of the anion formation were shown to be strongly dependent on the principal quantum number n of Rydberg atoms, peaking sharply at a certain value of $n = n_{\max}$. Such a sharp sensitivity has also been observed in Ca$^-$ ion formation ($E_b \simeq 20$ meV) produced by similar charge-exchange collisions between ground-state Ca atoms and Ne Rydberg atoms [8]. The characteristic of these reactions is that the following relation (in a.u.) is fulfilled at the maximum of the cross sections as a function of the Rydberg quantum number n:

$$E_b \ll \frac{1}{2n_{\max}^2}. \tag{1}$$

This inequality means that the charge-exchange process is strongly nonresonant since the cross section reaches its maximum value when the binding energy of the Rydberg atom is much larger than that of the created negative ion. The following empirical law has been established [7] that relates E_b and $n_{\max}$:

$$E_b \simeq \frac{0.84}{n_{\max}^{2.8}}, \tag{2}$$

where Eq. (1) follows for $n \gg 1$. Relation (2) has been used in a series of works [7,9,10] for determination of DBA binding energies and has been proven to be quite accurate.

Numerical calculations of DBA formation cross sections were carried out within the framework of the multistate Landau-Zener model [7]. In Ref. [11] the cross section of the reaction of Ca$^-$ ion formation was numerically calculated using the decay model. According to this model, the negative ion can decay due to the electric field of the positive core of the Rydberg atom. As applied to the Ca$^-$ formation, both models agree well with experiments with regard to the value of $n_{\max}$, but differ substantially from each other in the predicted values of the cross section. In the latter case, a comparison with experiment is difficult because one usually measures relative rather than absolute formation cross sections. The close-coupling calculations [12] of the Ca$^-$ formation have shown that the decay model describes quite well both the peak position and the absolute value of the cross section as a function of Rydberg quantum numbers n.

A common drawback of the above mentioned numerical calculations is that they are not able to clarify the physical meaning and the validity conditions of the useful empirical relation (2). In the present work we show that condition (1) together with the requirement for the collision to be adiabatic enable us to perform analytical calculations of negative ion formation in charge-exchange reactions between Rydberg atoms and neutral atoms or molecules. As a result, we obtain an approximate expression that determines $n_{\max}$ for given values of the anion binding energy E_b and the relative collision velocity v. Also, an approximate formula for calculating E_b for given $n_{\max}$ and v is obtained that generalizes the empirical law (2). This formula seems important because it can be used for direct determination of the binding energy of weakly bound negative ions from Rydberg electron transfer reactions with good accuracy. The results of calculations with the obtained analytical expressions are shown to be in good agreement with the experimental data. [It should be noted that investigation of Rydberg states has recently become especially actual in relation to important scientific and technological applications (see, for instance, Refs. [13–15] and references therein).]

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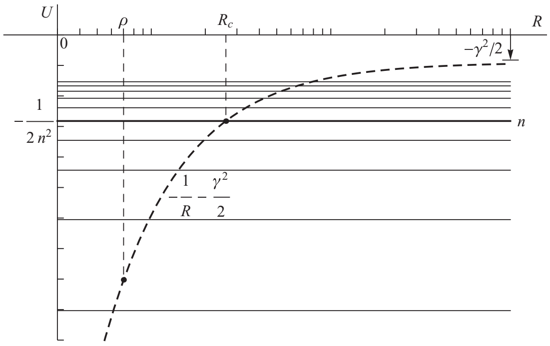

FIG. 1. Diabatic potential curves for the system of the colliding particles in reaction (3) as a function of the internuclear distance R at a fixed impact parameter ρ. The solid lines correspond to covalent terms H_{11}, and the dashed line corresponds to the ionic term H_{22}. R_c is the transition point from the initial ns covalent term to the ionic term.

Atomic units will be used throughout this paper, unless explicitly stated otherwise.

II. GENERAL EXPRESSIONS FOR PROBABILITY OF NEGATIVE ION FORMATION

We consider the charge transfer reaction in collisions between Rydberg atoms in ns states and neutral particles (atoms or molecules) in ground states,

$$A^*(ns) + B \to A^+ + B^-. \tag{3}$$

We assume that the negative ion B^- has only the ground-state energy level with the angular momentum $l = 0$ (the s state) and the binding energy $-E_b$ ($E_b > 0$). It should be noted that in the case of DBAs the angular momentum l of the excess electron is not conserved due to nonspherical symmetry of the dipole potential. Nevertheless, the spherically symmetric approximation for DBAs may be regarded as acceptable, its accuracy is discussed in Refs. [16,17]. The effect of nonspherical symmetry of the dipole potential on the charge-exchange process in collisions of polar molecules has been considered in Refs. [18,19].

The energies H_{11} and H_{22} of the covalent and ionic diabatic states, which correspond to the localization of the electron in the Rydberg atom and the negative ion, respectively, are

$$H_{11} = -\frac{1}{2n^2}, \quad H_{22} = -\frac{\gamma^2}{2} - \frac{1}{R}. \tag{4}$$

Here $\gamma = \sqrt{2E_b}$ and R is the distance between the colliding particles. Equations (4) are accurate up to the terms of the order of $O(R^{-1})$.

In the approximation of straight-line trajectories the time dependence of R has the form

$$R(t) = \sqrt{\rho^2 + v^2t^2}. \tag{5}$$

Here ρ is the impact parameter and v is the velocity of relative motion of the colliding particles.

The neutral particle B can capture the electron initially localized in the Rydberg atom to form a negative ion. It can occur at the point $R = R_c$, where the initial covalent potential curve crosses the ionic curve (Fig. 1). Equating $H_{11} = H_{22}$, we obtain

$$R_c = \frac{1}{-\gamma^2/2 + 1/2n^2}. \tag{6}$$

Since in the collision the particles pass through the crossing point $R = R_c$ twice (Fig. 1), the total probability of negative ion formation for a fixed impact parameter ρ is

$$P = p_n W_1 + (1 - p_n) p_n W_2. \tag{7}$$

Here p_n is the probability of the initial capture of the electron into the ionic state and $W_{1,2}$ are the probabilities for the negative ion to survive if it is formed after the first or the second passing through the crossing point $R = R_c$, respectively. The first term in Eq. (7) corresponds to the negative ion formation as the particles approach each other, and the second term is responsible for negative ion formation as the particles move away from each other.

III. DECAY MODEL

In the next step we will calculate the survival probabilities $W_{1,2}$ that appear in Eq. (7). The electron of the negative ion can make a transition to the Rydberg atom energy levels at each crossing point that the particles pass through in the collision (Fig. 1). Since the spectrum of Rydberg states is dense, such a transition can be described as tunneling of the electron from the short-range potential of the neutral particle to the quasicontinuous spectrum of the states in the field of the positive ion [20–22]. We will refer to this picture for the electron transition from the negative ion to the Rydberg atom as the decay model. In this model it is possible to define a decay probability per unit time $\Gamma(R)$. Then the probabilities $W_{1,2}$ are given by the exponential decay law

$$W_{1,2} = \exp\left[-\int_{\mp t_c}^{\infty} \Gamma(R(t))dt\right], \tag{8}$$

where $\mp t_c$ are the instants of the first ("$-$" sign) and the second ("$+$" sign) passing through the point $R = R_c$. We note that, in accordance with Eq. (5), the instant of the closest approach, when $R = \rho$, has been chosen as a time reference point, that is, $R(0) = \rho$.

Using the substitution $t = \sqrt{R^2 - \rho^2}/v$, which follows from Eq. (5), we change from integration over t to integration over R in Eq. (8). As a result, we obtain

$$W_1 = \exp\left(-\int_{\rho}^{Rc} \Gamma \frac{dR}{v_r}\right) \exp\left(-\int_{\rho}^{\infty} \Gamma \frac{dR}{v_r}\right), \tag{9}$$

$$W_2 = \exp\left(-\int_{Rc}^{\infty} \Gamma \frac{dR}{v_r}\right). \tag{10}$$

Here $v_r = v\sqrt{1 - \rho^2/R^2}$ is the component of the relative velocity along the internuclear axis.

In the decay model, the electron tunnels through the potential barrier in the Coulomb field of a positive ion (Fig. 2). Under the conditions of the problem studied, variation of the electric field along the path of the electron through the barrier can be neglected, that is, the negative ion decay can be considered to occur in a uniform electric field. To prove this we note that condition (1) implies the relation

$$n^2\gamma^2 \ll 1, \tag{11}$$

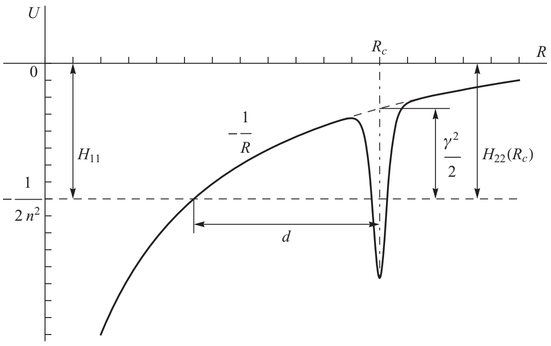

FIG. 2. The potential energy of the electron that tunnels from the negative ion to the Rydberg atom, along the internuclear axis. The positive ion is located at the point $R = 0$, d is the tunneling length, the internuclear distance $R = R_c$.

which holds near the maximum of the cross section as a function of the Rydberg principal quantum number n. Using inequality (11), Eq. (6) for R_c can be rewritten approximately as

$$R_c \simeq 2n^2(1+\gamma^2 n^2). \tag{12}$$

This relation has a clear physical meaning: the distance R_c at which the electron can pass from the Rydberg atom to the negative ion almost coincides with the radius of the Rydberg atom. As is seen from Fig. 2, the tunneling length d is determined at $R = R_c$ by the condition

$$\frac{1}{R_c - d} = \frac{1}{2n^2}.$$

Substituting here Eq. (12) for R_c, we obtain

$$d = R_c - 2n^2 \simeq 2n^4\gamma^2 \ll R_c. \tag{13}$$

From Eq. (13) it follows that at $R = R_c$ the electron tunnels in a uniform electric field with the strength $F = 1/R_c^2$. The corresponding probability per unit time for an s electron of a negative ion has the form [23,24]

$$\Gamma = \frac{\mathcal{A}^2 F}{4\gamma^2}\exp\left(-\frac{2\gamma^3}{3F}\right). \tag{14}$$

Here $\mathcal{A}$ is the normalization factor in an asymptotic behavior of the s electron wave function at large distances [25]

$$\psi(r) \simeq \frac{\mathcal{A}}{\sqrt{4\pi}r}e^{-\gamma r}, \quad r\gamma \gg 1. \tag{15}$$

For a weakly bound electron, it is convenient to represent $\mathcal{A}$ in the form

$$\mathcal{A} = \mathcal{B}\sqrt{2\gamma},$$

where the coefficient $\mathcal{B} \sim 1$. When $\mathcal{B} = 1$, the electron in a negative ion is described by the wave function (15) in the whole space.

Equation (14) can be used for description of the negative ion decay not only at the point $R = R_c$, but also in a narrow interval of R values around this point, $|R - R_c| \ll R_c$, where the uniform-field approximation also holds. The substitution of the corresponding electric field strength $F = 1/R^2$ in Eq. (14) gives

$$\Gamma(R) = \frac{\mathcal{A}^2}{4\gamma^2 R^2}\exp\left(-\frac{2}{3}R^2\gamma^3\right). \tag{16}$$

As it will be shown below, expression (16) leads to the result that the negative ion decay mainly takes place at distances $|R - R_c| \ll R_c$, that is, in the region where (16) is applicable. Thus we can assume that Eq. (16) gives a complete description of the negative ion decay.

Expression (16) is correct if $R^2\gamma^3 \gg 1$, which corresponds to a small tunneling probability. For description of the negative ion decay in the neighborhood of the point $R = R_c$ it is sufficient to satisfy the condition $R_c^2\gamma^3 \gg 1$. It follows from Eqs. (11) and (12) that $R_c \simeq 2n^2$. Therefore, the condition $n^2\gamma^2 \ll 1$ for the uniform field approximation to be valid is equivalent to $R_c\gamma^2/2 \ll 1$. To use formula (16) it is necessary to satisfy both conditions

$$R_c\gamma^2/2 \ll 1, \quad R_c^2\gamma^3 \gg 1 \tag{17}$$

simultaneously. We show below that, for thermal collision velocities, conditions (17) are satisfied at the cross section maximum $n = n_{\max}$ in a wide range of γ values.

IV. LANDAU-ZENER MODEL FOR NEGATIVE ION FORMATION

In this section we calculate the capture probability p_n from Eq. (7). Since the probability p_n corresponds to the transition between the initial covalent curve and the ionic curve, it can be obtained from the following simplified Landau-Zener formula [26] (see also Ref. [27]):

$$p_n = 1 - \exp\left(-\frac{2\pi|H_{12}(R_c)|^2 R_c^2}{v_{rc}}\right), \tag{18}$$

where H_{12} is the potential of the one-electron exchange interaction between the ionic state and the initial covalent state, and $v_{rc} = v\sqrt{1-\rho^2/R_c^2}$ is the radial velocity v_r at $R = R_c$.

The decay model can be used for description of the electron transfer from the negative ion to the Rydberg atom if the transition probability at each crossing between the ionic and covalent curves is sufficiently small, so that the electron has a negligible chance to return back into the negative ion from quasicontinuum of the Rydberg states, that is, so that the irreversibility of the decay holds. In particular, we must have $p_n \ll 1$. We make the assumption, which will be confirmed by the result, that the condition $p_n \ll 1$ does hold. Then the exponential in Eq. (18) is close to 1, and, expanding it in a series, we obtain

$$p_n \simeq \frac{2\pi|H_{12}(R_c)|^2 R_c^2}{v_{rc}}. \tag{19}$$

To calculate $H_{12}(R_c)$ we use an approximate expression, obtained in Refs. [28,29], for the potential of the exchange interaction between negative and positive ions at large internuclear distances $R\gamma \gg 1$. In our case of the s electron transition, it has the form

$$H_{12}(R_c) = \frac{\mathcal{A}}{2}\chi_{ns}(R_c), \tag{20}$$

where $\chi_{ns}(R)$ is the radial wave function of the ns Rydberg state. We note that the condition $R_c\gamma \gg 1$ for expression (20) to be valid is satisfied automatically if conditions (17) hold since $R_c^2\gamma^3/R_c\gamma^2 = R_c\gamma$.

Since the principal quantum number n of the Rydberg electron is high, we can use for $\chi_{ns}(R_c)$ the quasiclassical approximation [25]

$$\chi_{ns}(R_c) = \frac{c_n}{2R_c\sqrt[4]{\frac{1}{n^2}-\frac{2}{R_c}}}\exp\left(-\int_{2n^2}^{R_c}\sqrt{\frac{1}{n^2}-\frac{2}{r}}\,dr\right),$$
$$c_n^2 = 2/\pi n^3. \tag{21}$$

The integral appearing in Eq. (21) can be calculated as

$$\int_{2n^2}^{R_c}\sqrt{\frac{1}{n^2}-\frac{2}{r}}\,dr = R_c\left(\frac{1}{n^2}-\frac{2}{R_c}\right)^{1/2} - n\ln\left[\frac{R_c}{n^2}-1+\frac{R_c}{n}\left(\frac{1}{n^2}-\frac{2}{R_c}\right)^{1/2}\right]. \tag{22}$$

Using Eqs. (6), (11), and (12), Eq. (22) can be simplified to

$$\int_{2n^2}^{R_c}\sqrt{\frac{1}{n^2}-\frac{2}{r}}\,dr \simeq \frac{4}{3}\gamma^3 n^4.$$

In the pre-exponential factor in Eq. (21) we replace $1/n^2 - 2/R_c$ by γ^2 in accordance with Eq. (6). The final result for χ_{ns} is

$$\chi_{ns}(R_c) = \frac{1}{R_c\sqrt{2\pi\gamma n^3}}\exp\left(-\frac{1}{3}R_c^2\gamma^3\right). \tag{23}$$

In the exponent in Eq. (23) the replacement of n by R_c has been carried out by using relation (12).

Substituting Eq. (23) into Eq. (20), and then Eq. (20) into expression (19), we finally obtain for the capture probability

$$p_n = \frac{\mathcal{A}^2}{4\gamma n^3 v_{rc}}\exp\left(-\frac{2}{3}R_c^2\gamma^3\right). \tag{24}$$

V. CALCULATIONS OF THE TOTAL CROSS SECTION

Taking into account Eq. (7), the total cross section of negative ion formation can be written as

$$\sigma = 2\pi\int_0^{Rc}\rho P(\rho)\,d\rho = 2\pi\int_0^{Rc}p_n(W_1+W_2)\rho\,d\rho. \tag{25}$$

Here we have used the above-stated inequality $p_n \ll 1$.

It is follows from Eqs. (9) and (10) that the expression for W_1 can be rewritten in the form

$$W_1 = \exp\left[-2\int_\rho^{Rc}\Gamma(R)\frac{dR}{v_r}\right]W_2. \tag{26}$$

According to Eq. (25), the lower limit of integration in Eq. (26) varies from 0 to R_c. As shown in the Appendix, for $R_c^2\gamma^3 \gg 1$ the exponent in Eq. (26) decreases rapidly with decreasing ρ from the value $\rho = R_c$, that is, with increasing the interval of integration. This fact enables us to neglect W_1 in comparison with W_2 in Eq. (25). Physically, it means that almost all negative ions which were formed at the first passing through the point $R = R_c$ decay as they move from $R = R_c$ to $R = \rho$ and back.

Next we consider the integral

$$\int_{Rc}^{\infty}\Gamma(R)\frac{dR}{v_r}, \tag{27}$$

which appears in Eq. (10) for W_2. For $R_c^2\gamma^3 \gg 1$, according to Eq. (16), $\Gamma(R)$ decreases fast as R increases from the value $R = R_c$, corresponding to the lower limit of integration in Eq. (27). Therefore, the main contribution to integral (27) is given by a narrow region near the point $R = R_c$. The width δR of the region is determined by variation of the exponent in Eq. (16) by a quantity of the order of $O(1)$. Then for $R_c^2\gamma^3 \gg 1$ we obtain the estimate

$$\delta R \sim \frac{1}{2R_c\gamma^3}. \tag{28}$$

From this relation and the condition $R_c^2\gamma^3 \gg 1$, it is follows that $\delta R/R_c \ll 1$. Thus, the negative ion decay mainly takes place near the transition point $R = R_c$.

We assume that the velocity v_r is constant in the segment δR and equal to the value v_{rc}. We also neglect the variation of the pre-exponential factor in expression (16) for $\Gamma(R)$ in this segment. Then we can approximately calculate the integral (27). Putting $R = R_c(1+u)$, we obtain

$$\int_{Rc}^{\infty}\Gamma(R)\frac{dR}{v_r} \simeq \frac{\mathcal{A}^2 e^{-\frac{2}{3}R_c^2\gamma^3}}{4\gamma^2 R_c v_{rc}}\int_0^{\infty}e^{-\frac{2}{3}R_c^2\gamma^3 u(2+u)}du \simeq \frac{3\mathcal{A}^2}{16\gamma^5 R_c^3 v_{rc}}\exp\left(-\frac{2}{3}R_c^2\gamma^3\right). \tag{29}$$

In the calculation it has been taken into account that for $R_c^2\gamma^3 \gg 1$ only values $u \lesssim 1/(R_c^2\gamma^3) \ll 1$ contribute to the integral over u.

Substituting Eq. (29) in expression (10) for W_2 and using formula (24) for p_n, and neglecting W_1 in comparison with W_2, we can represent the cross section (25) as

$$\sigma = \frac{\pi\mathcal{B}^2R_c^2}{n^3 v}e^{-\frac{2}{3}R_c^2\gamma^3}\int_0^1\exp\left(-\frac{3}{8}\frac{\mathcal{B}^2 e^{-\frac{2}{3}R_c^2\gamma^3}}{\gamma^4 R_c^3 v x}\right)dx. \tag{30}$$

Replacing n in front of the integral by $\sqrt{R_c/2}$ in accordance with Eq. (12) and denoting $\alpha \equiv (2/3)R_c^2\gamma^3$, we bring the previous expression for σ to the form

$$\sigma = \frac{6^{1/4}2\pi\mathcal{B}^2}{v\gamma^{3/4}}\alpha^{1/4}e^{-\alpha} \times \int_0^1\exp\left(-\frac{\sqrt{2}}{4\sqrt{3}}\frac{\sqrt{\gamma}\mathcal{B}^2}{v}\frac{e^{-\alpha}}{\alpha^{3/2}}\frac{1}{x}\right)dx. \tag{31}$$

Figure 3 shows the cross section (31) as a function of the principal quantum number n of Rydberg atoms for $\gamma = 10^{-2}$ a.u., $\mathcal{B} = 1$, and $v = 10^{-4}$ a.u. The resonant behavior of the dependence $\sigma(n)$ is explained by the competition between two processes, which occur mainly in the neighborhood of the transition point $R = R_c$: (i) the capture of the Rydberg electron into the negative ion and (ii) its decay in the Coulomb field of the positive ion. We also plotted in Fig. 3 the Gaussian curve obtained by the least-squares fitting of the

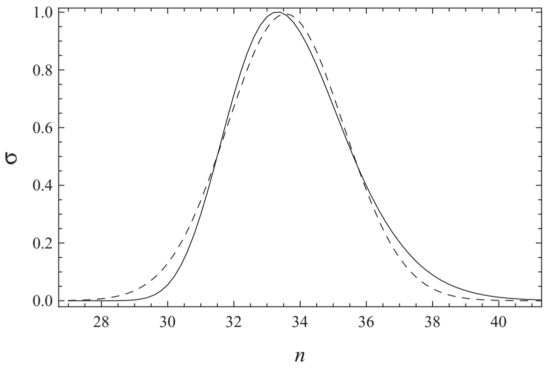

FIG. 3. Solid line: the cross section of the negative ion formation normalized to unity as a function of the Rydberg principal quantum number n for $\gamma = 10^{-2}$ a.u., $\mathcal{B} = 1$, and $v = 10^{-4}$ a.u. Dashed line: the Gaussian curve which gives the least-squares approximation of the cross section curve.

cross section curve. As can be seen, the two curves differ markedly, which is mainly related to the asymmetry of the function $\sigma(n)$.

VI. DEPENDENCE OF THE CROSS SECTION ON REACTION PARAMETERS

The cross section (31) reaches its maximum at the value of n determined by the condition

$$\frac{d\sigma}{dn} = \frac{\partial\sigma}{\partial\alpha}\frac{d\alpha}{dn} = 0. \tag{32}$$

Since $d\alpha/dn = (4/3)\gamma^3 dR_c/dn \simeq (16/3)\gamma^3 n \neq 0$, condition (32) is reduced to the equation $\partial\sigma/\partial\alpha = 0$. For $\alpha \gg 1$, in a computation of $\partial\sigma/\partial\alpha$ in the first nonvanishing order of α^{-1}, it is sufficient to differentiate in expression (31) only the exponentials that appear in the terms $\alpha^{1/4}e^{-\alpha}$, $e^{-\alpha}/\alpha^{3/2}$. As a result, condition (32) is transformed into the equation

$$\int_0^1 e^{-\delta/x}\left(\frac{\delta}{x} - 1\right)dx = 0, \tag{33}$$

where

$$\delta(\alpha) = \frac{\sqrt{2}}{4\sqrt{3}}\frac{\sqrt{\gamma}\mathcal{B}^2}{v}\frac{e^{-\alpha}}{\alpha^{3/2}}.$$

A numerical evaluation of Eq. (33) gives $\delta(\alpha) \simeq 0.61$. Thus we have the following relation at the cross section maximum:

$$\frac{e^{-\alpha}}{\alpha^{3/2}} = 3.0\frac{v}{\sqrt{\gamma}\mathcal{B}^2}. \tag{34}$$

For given values of γ and v, Eq. (34) enables us to find the value of R_c that corresponds to the cross section maximum and hence to obtain the value of $n_{\max}$. Conversely, given values of $n_{\max}$ and v, we can calculate γ from Eq. (34), taking into account that $R_c \simeq 2n_{\max}^2$ in accordance with Eq. (12).

To calculate $n_{\max}$ approximately, we note that in the adiabatic approximation, when $v/\gamma \ll 1$, the inequality $v/\sqrt{\gamma} \ll 1$ holds if $\gamma \ll 1$. Therefore, we have a small parameter on the right-hand side of Eq. (34), so that it can be solved by iteration. To do this we represent Eq. (34) in the form

$$\alpha = \ln\mu - \tfrac{3}{2}\ln\alpha,$$

where we have introduced the parameter $\mu = \sqrt{\gamma}\mathcal{B}^2/(3v) \gg 1$. Assuming that in the zeroth approximation $\alpha = \ln\mu$, we get after the first iteration

$$\alpha = \ln\mu - \tfrac{3}{2}\ln\ln\mu. \tag{35}$$

Substituting the expression $\alpha = (2/3)R_c^2\gamma^3$ for α in Eq. (35), and replacing, in accordance with Eq. (12), R_c by $2n_{\max}^2$, we finally obtain

$$n_{\max} \simeq \frac{0.78(\ln\mu)^{1/4}}{\gamma^{3/4}}\left(1 - \frac{3}{8}\frac{\ln\ln\mu}{\ln\mu}\right), \quad \mu = \frac{\sqrt{\gamma}\mathcal{B}^2}{3v}. \tag{36}$$

To determine the binding energy $\gamma^2/2$ for given v and $n_{\max}$, we rewrite Eq. (34) in such a form that it does not contain γ on its right-hand side:

$$\frac{e^{-\alpha}}{\alpha^{4/3}} = \frac{2.8}{\mathcal{B}^2}R_c^{1/3}v. \tag{37}$$

From Eq. (11) we have the inequality $n \lesssim 1/\gamma$, which enables us to estimate the right-hand side of Eq. (37) as follows: $R_c^{1/3}v \simeq (2n^2)^{1/3}v \sim n^{2/3}v \lesssim nv \lesssim v/\gamma$. In the adiabatic approximation $v/\gamma \ll 1$, and consequently the right-hand side of Eq. (37) is small, so that we can solve Eq. (37) by iteration. Proceeding in exactly the same way as in the derivation of formula (36), we obtain from Eq. (37) the following expression for the negative ion binding energy:

$$E_b = \frac{\gamma^2}{2} \simeq \frac{0.26(\ln\eta)^{2/3}}{n_{\max}^{8/3}}\left(1 - \frac{8}{9}\frac{\ln\ln\eta}{\ln\eta}\right), \quad \eta = \frac{0.28\mathcal{B}^2}{n_{\max}^{2/3}v}. \tag{38}$$

Now we will show that the relations obtained are in agreement with the assumption which have been made in deriving formulas (19) and (25), that is, that the probability $p_n \ll 1$ in the neighborhood of the cross section maximum. To this end, we substitute the expression for $\exp[-(2/3)R_c^2\gamma^3]$ from Eq. (34) into formula (24) for p_n. This enables us to get the following estimate:

$$p_n \sim \frac{R_c^3\gamma^4}{n^3} \simeq 8n^3\gamma^4,$$

where the relation $R_c \simeq 2n_{\max}^2$ has been used. For Rydberg atoms with a principal quantum number $n \gtrsim 10$, we obtain, using inequality (11), $8n^3\gamma^4 = 8(n^2\gamma^2)^2/n \ll 1$, which proves the assumption made.

VII. RESULTS AND DISCUSSION

To compare $n_{\max}$ and E_b values obtained by using formulas (36) and (38) with experimental data and results of previous calculations, we use results of Ref. [7], where the process of DBA formation in collisions of several polar molecules with Xe Rydberg atoms was studied. In Table I the experimental values $n_{\max}^{(1)}$ are given for the Rydberg electron principal quantum number at which the formation cross section for various DBAs reaches its maximum. The binding energies $E_b^{(1)}$ indicated in Table I have been adjusted in Ref. [7] so as to achieve the best fit of the experimental and numerically calculated cross

TABLE I. Comparison of $n_{\max}$ and E_b values obtained by using analytical expressions (36) and (38) with the experimental data and the results of numerical calculations of Ref. [7] for the reaction of DBA formation in collisions between Rydberg atoms and polar molecules. The $\mathcal{B}$ values are calculated from the data of Ref. [7].

	Reference [7]			This work	
Molecule	$n_{\max}^{(1)}$	$E_b^{(1)}$ (meV)	$\mathcal{B}$	$n_{\max}^{(2)}$	$E_b^{(2)}$ (meV)
Acetonitrile	13	18.6	2.21	13.1	18.6
Acrylonitrile	15–16	10.8	2.19	15.9	11.4
Cyclohexanone	19	5.78	1.73	19.5	6.09
TFMB[a]	22–23	3.73	1.73	22.8	3.81
Cyclopentanone	24	3.18	1.70	24.1	3.17
Acetone	24–25	2.97	1.66	24.7	2.97
2-Butanone	28–29	1.89	1.64	29.0	1.94
Cyclobutanone	29	1.88	1.66	29.1	1.86
Butanal	33	1.29	1.59	33.1	1.28
Pivaldehyde	34	1.20	1.56	33.9	1.17
Acetaldehyde	41–42	0.70	1.53	41.1	0.67

[a] Trifluoromethylbenzene.

section curves. The numerical calculations were carried out by using the multistate Landau-Zener model. The binding energies thus obtained are compared in Table I with the values $E_b^{(2)}$ calculated by means of formula (38), the values $n_{\max}^{(1)}$ and $\mathcal{B}$ from Table I being used for $n_{\max}$ and $\mathcal{B}$ in (38), respectively. We assume the relative collision velocity $v = 5.5 \times 10^{-4}$ a.u. $= 1.2 \times 10^5$ cm/s, which corresponds to the mean collision energy 350 meV reported in [6]. Theoretical values $n_{\max}^{(2)}$ are also given in Table I for the Rydberg electron principal quantum number at the maximum of the cross sections. These values were calculated by using formula (36) with $E_b^{(1)}$ for the binding energy.

As can be seen from Table I, the results of numerical calculations [7] within the framework of the multistate Landau-Zener model agree well with those obtained here by using the decay model for description of the electron transfer from anions to Rydberg atoms. This indicates that both models are equivalent in the neighborhood of the cross section maximum. In a significant deviation from the maximum, one of the conditions (17) for validity of our theory is violated. Therefore, far from the cross section maximum, calculations within the multistate Landau-Zener model is expected to be more accurate.

The empirical relation (2) has been obtained in [7] by approximating the dependence of the values $E_b^{(1)}$ on $n_{\max}^{(1)}$ (see Table I). Expression (38) for E_b enables us to understand the origin of this empirical relation. Indeed, as is seen from Table I, in the experiment [7] $n_{\max} \simeq 10$–40, which leads, at the velocity $v \sim 10^{-4}$ a.u., to variation of the coefficient before $1/n_{\max}^{8/3} \simeq 1/n_{\max}^{2.7}$ in Eq. (38) by about 15% of its maximum value, the change of $\mathcal{B}$ being taken into account. Thus we can write $E_b \simeq \mathrm{const}/n_{\max}^{2.7}$, and this is very close to the empirical law (2).

It follows from Eq. (2) that $n_{\max}$ does not depend on the relative velocity v of the colliding particles. However, in accordance with Eq. (36), such a dependence, though weak, must exist. A weak dependence of $n_{\max}$ on v has indeed been observed experimentally [9,30], and its character is similar to that predicted by formula (36): as the relative velocity of the colliding particles decreases, $n_{\max}$ shifts in the direction of bigger values.

In Ref. [7], numerical results are also presented for DBA formation rate constants $k = v\sigma$ at the cross section maximum, where $n = n_{\max}$. The values reported vary from 1.6×10^{-8} cm^3/s for acetonitrile to 14×10^{-8} cm^3/s for acetaldehyde. A similar computation by using Eq. (30) for the cross section σ gives, at the velocity $v = 1.2 \times 10^5$ cm/s, $k = 3.1 \times 10^{-8}$ cm^3/s for acetonitrile and $k = 12 \times 10^{-8}$ cm^3/s for acetaldehyde. This should be considered as good agreement with [7] in view of the many approximations which have been made in our calculations.

Expressions (30), (36), and (38) for σ, $n_{\max}$, and E_b are valid under conditions (17). At the cross section maximum we can write them by using Eq. (35) for $\alpha = (2/3)R_c^2\gamma^3$, in the form

$$\sqrt{\gamma}\left(\ln\frac{\sqrt{\gamma}}{3v}\right)^{1/2} \ll 1, \quad \ln\frac{\sqrt{\gamma}}{3v} \gg 1. \qquad (39)$$

For a given relative velocity v of the colliding particles, the first of conditions (39) gives an upper limit, while the second gives an lower limit for the permissible values of γ. Conditions (39) must be supplemented by the requirements that the electron of the negative ion is weakly bound, that is, $\gamma \ll 1$, and the collision is adiabatic, which implies $\gamma \gg v$. It is the latter condition that gives the lower limit for the values of γ at thermal collision velocities $v \sim 10^5$ cm/s $\simeq 4.6 \times 10^{-4}$ a.u. since the second of conditions (39) still holds when $\gamma/v \sim 1$, provided that $\gamma \ll 1$. As a result, we obtain that at velocity $v = 4.6 \times 10^{-4}$ a.u. our theory is applicable for γ values lying in a range $\sim 10^{-3}$–10^{-2} a.u., which corresponds to negative ion binding energies $E_b \sim 0.1$–10 meV. For lower values of E_b the adiabatic approximation is violated; for bigger values of E_b the assumption that the negative ion decays in a uniform electric field breaks down because of violation of condition (11).

The expressions (36) and (38) for $n_{\max}$ and E_b can be shown to remain valid even for a nonzero orbital angular momentum l of the electron in the Rydberg atom before the collision, provided that $l \ll n$, and $l \sim 1$, where n is the principal Rydberg quantum number. These conditions hold in all the experiments referred above, in which Rydberg atoms were initially excited in states with angular momentum $l \leqslant 3$. Expression (30) for σ retains its form for $l \neq 0$ if σ means a cross section averaged over the projection of the Rydberg electron angular momentum on the internuclear axis. A special consideration is required for the case when the Rydberg electron is captured by neutral particles in a state with $l \neq 0$, for example, for the reaction of Ca$^-$ ion formation [8].

VIII. CONCLUSION

We have theoretically considered the formation of negative ions in collisions between Rydberg atoms and neutral particles (atoms or molecules) which are able to capture an excess electron. Using condition (11), which means that the formation of the negative ion takes place at the boundary of the Rydberg atom, and the requirement for the collision to be adiabatic with respect to the motion of the electron in the negative ion, we have calculated the formation cross section in an analytical form. It is shown that the cross section as a function of the principal quantum number n of Rydberg atoms has a sharp maximum at a certain value of $n = n_{\max}$ which is strongly correlated to the binding energy E_b of the negative ions. The analytical expressions (36) and (38) linking E_b and $n_{\max}$ are obtained. We point out that in accordance with Eq. (38) the negative ion binding energy E_b depends only slightly on the relative collision velocity v and the asymptotic coefficient $\mathcal{B}$. It is the reason why the simple empirical law (2) established in Ref. [7] appears to be quite accurate for determination of DBA binding energies. The expression (38) for E_b generalizes the empirical law (2). It can be used for determination of binding energies of DBA and other weakly bound negative ions (both atomic and molecular) through measurements of the cross section of Rydberg electron transfer reactions. The obtained expressions are shown to be applicable to negative ions with binding energies $E_b \sim 0.1$–10 meV.

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APPENDIX: ESTIMATION OF THE SURVIVAL PROBABILITY W_1

To prove that the survival probability W_1 can be neglected in comparison with W_2, we will show that, if conditions (17) hold, the exponential factor in expression (26) for W_1 decreases fast as ρ decreases from the value $\rho = R_c$, at which the factor is unity. To this end, we consider the integral in the exponent in Eq. (26),

$$I(\rho) = \int_{\rho}^{Rc} \Gamma(R)\,\frac{dR}{v_r}. \tag{A1}$$

Since $R_c^2\gamma^3 \gg 1$, the inequality $\rho^2\gamma^3 \gg 1$ holds for values of ρ that satisfy $(R_c - \rho)/R_c \ll 1$. For the same reason as in the derivation of estimate (28), the condition $\rho^2\gamma^3 \gg 1$ means that the main contribution to integral (A1) is given by a region of width $\delta\rho \sim 1/(\rho\gamma^3) \sim 1/(R_c\gamma^3)$ near the lower limit $R = \rho$ of integration. Consequently, for $R_c - \rho \gtrsim \delta\rho$ we can replace the upper limit R_c in Eq. (A1) by infinity. For $\rho^2\gamma^3 \gg 1$, the integral obtained may be calculated approximately to give

$$I(\rho) \simeq \sqrt{\frac{3\pi}{2}}\,\frac{\mathcal{A}^2}{8\gamma^{7/2}\rho^2 v}\exp\left(-\frac{2}{3}\rho^2\gamma^3\right). \tag{A2}$$

Since $\rho < R_c$, from Eq. (A2) we get the inequality

$$I(\rho) > I(R_c) \sim \frac{\mathcal{A}^2}{\gamma^{7/2}R_c^2 v}\exp\left(-\frac{2}{3}R_c^2\gamma^3\right). \tag{A3}$$

Substituting the expression for $\exp[-(2/3)R_c^2\gamma^3]$ from Eq. (34) into (A3) we obtain

$$I(\rho) \gtrsim R_c\gamma^{3/2} \gtrsim 1 \tag{A4}$$

since $R_c^2\gamma^3 \gg 1$. Estimate (A4) is valid for values of ρ in the range

$$\frac{1}{R_c^2\gamma^3} \lesssim \frac{R_c - \rho}{R_c} \ll 1. \tag{A5}$$

These inequalities are consistent due to the condition $R_c^2\gamma^3 \gg 1$.

From relations (A4) and (A5) it follows that the exponential $\exp[-2I(\rho)]$ in Eq. (26) becomes small even on a slight deviation of ρ from R_c, and this proves the prime assertion.

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