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Electron exchange between a dipole-bound anion and a polar molecule and dimer formation in dipole-bound anions

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We consider collision between a dipole-bound molecular anion and a neutral polar molecule and show that the excess electron can bind two neutral molecules into a dimer. Using a variational approach similar to the Heitler-London model of H_2^+ ion, we obtain the energy terms of such a dimer. Their difference determines the cross section of electron transfer from the anion to the neutral molecule in quasiclassical near-resonant Born-Oppenheimer approximation. We obtain for the cross section an analytical expression containing the weak (logarithmic) factor depending on the molecular dipole moment and the collision velocity. With the prelogarithmic factor proportional to inverse binding energy of the electron in the molecular anion, such weak dependence on the collision velocity is somewhat similar to the expressions appearing in the hard-sphere collision model. However the large logarithmic factor connected with long-range dipole-dipole interaction between the colliding molecules contradict to the hard-sphere approximation even for qualitative description of the charge transfer. Our analytical calculations are in a good accordance with the results of a recent experiment [Y. Liu, M. Cannon, L. Suess, F. B. Dunning, V. E. Chernov, and B. A. Zon, Chem. Phys. Lett. **433**, 1 (2006)].

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I. INTRODUCTION

Dipole-bound anions (DBAs) have been attracting great, both experimental and theoretical, interests [1–3]. Almost any neutral molecule with dipole moment $d>2.5$ D can form DBA, i.e., bind an extra electron due to its dipole potential. As a rule, the electron is bound in a diffused orbital with large (about of tens of angstroms) size and weak (about of tens of meV) binding energy [4], and this fact suggests that DBAs should possess high reactivity.

There are several types of charge-transfer reactions involving DBA. The DBA themselves are formed under collisions of polar molecules with Rydberg atoms, which also contain an electron in a diffused weakly bound orbital. The capture of such "essentially free" electron can result in formation of long-lived valence-bound anions [5–10]. Electron transfer in collisions between CH_3CN^- DBA ($d=3.92$ D) and nonpolar targets such as SF_6 and CCl_4 (which are able to capture free low-energy electrons) can also be treated in terms of capture of the essentially free dipole-bound electron [11]. Another type of charge-transfer reactions can be collision between two polar molecules with dipole moments large enough to bind the electron. An example of such charge transfer is the reaction

$$CH_3CN^- + CH_3NO_2 \to CH_3CN + CH_3NO_2^- \qquad (1)$$

studied in Ref. [12]. The measured cross-section values of $\simeq 10^{-12}$ cm cannot be predicted using rough hard-sphere approximation. Indeed, it implies that the hard-sphere radius is $\simeq 60$ Å, which is more than twice greater than the mean-square radius of the excess electron orbital. This work presents a simple but consistent theory of charge-transfer reactions between two polar molecules and shows that the cross section of such reactions differ from the hard-sphere approximation by a logarithmic factor, which is large for common values of dipole moments and velocities of the colliding molecules and is due to the long-range character of the dipole interaction.

As it was mentioned above, the main role in charge transfer is played by intermolecular distances comparable with the electron localization radius in a DBA. For typical DBAs moving with thermal velocities $v \sim 10^5$ cm/s, the collision time is about $\simeq 10^{-12}-10^{-13}$ s. Strictly speaking, such values of the collision time require taking into account different effects of molecular geometry. Indeed, the molecular rotations have the same order of the temporal period. Moreover, the same orders of value (in energy scale) are inherent to the inversion splitting, which forms molecular dipole moment. We remind that, due to the *P* invariance of the electromagnetic interaction, the dipole moment is zero in the stationary states of a quantum system, and it appears, as a classical object, only due to an interaction of this quantum system with the fields of other, classical or quantum, systems. A well-known manifestation of this fact is the maser effect on ammonia molecular beam. Another example, quantum anomalies in Rydberg spectra of polar molecules, is considered in Ref. [13].

Thus the calculation of charge-transfer probability in collisions of polar molecules with thermal velocities is a rather complicated problem. At the same time, most of theoretical studies of DBA are limited to large-scale *ab initio* calculations [3] that give only the numerical electron affinity values. Some model-potential calculations, although yielding rea-

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sonable results for one-photon photodetachment from DBA [14], are hard to use for the description of collisions between DBA and neutral molecules. More simple analytical theories can give the electronic affinity as a function of the DBA dipole moment only numerically [4] and are not able to calculate adequately the cross sections of charge-transfer reactions [15].

Recently a simple analytical model suitable for the description of DBA structure (electronic affinity as a function of the DBA dipole moment) and interactions with photons was proposed in Ref. [16]. After some modifications, we apply this model to a quantitative study of charge-transfer reactions in collisions of DBA with neutral polar molecules on the basis of quasiclassical near-resonant charge exchange calculation technique of the general collision theory [17].

II. MODEL: ADIABATIC TERMS OF A MOLECULAR DIMER BOUND BY AN EXCESS ELECTRON

For simplicity, the complex angular dependence of an electron in the field of two dipoles can be neglected, and each molecule can be considered as a source of spherically symmetric dipole potential (the atomic units are used throughout the work)

$$V_{\text{spher dip}}(\boldsymbol{r}) = -d_{\text{eff}}/r^2. \tag{2}$$

Here the effective dipole moment d_{eff} is somewhat less than the true dipole moment of the molecule, d, but, as it will be shown below, the charge-transfer cross section depends on d_{eff} slow (logarithmically). Such "spherical approximation" was used by many authors (see, for instance, Refs. [18–20]).

With the above-mentioned spherically symmetric interaction of the outer electron with two molecules a and b, the Hamiltonian of the system in Born-Oppenheimer approximation can be written in the center-of-mass reference frame as [17]

$$H = -\frac{1}{2M}\Delta_{\boldsymbol{R}} + H_{\text{el}} + U(\boldsymbol{R}), \tag{3}$$

$$H_{\text{el}} = -\frac{1}{2}\Delta_r + V_a(r_a) + V_b(r_b). \tag{4}$$

Here M is the reduced mass of the molecules a and b, vectors $\boldsymbol{r}_{a,b}$ point to the electron from the molecules a and b correspondingly, and R is the separation between molecules. The intermolecular interaction $U(\boldsymbol{R})$ can be neglected for large R values which determine the charge-transfer cross section (see discussion below). The potentials $V_{a,b}$ have form (2).

It is convenient to express solutions of Schrödinger equation with Hamiltonian (3) in terms of the "quasimolecular" adiabatic functions χ_m^a and χ_n^b

$$\Psi(R,\boldsymbol{r}) = \sum_m F_m^a(R)\chi_m^a(\boldsymbol{r},R) + \sum_n F_n^b(R)\chi_n^b(\boldsymbol{r},R), \tag{5}$$

which satisfy

$$H_{\text{el}}\chi^{a,b}(\boldsymbol{r},R) = E_{a,b}(R)\chi^{a,b}(\boldsymbol{r},R). \tag{6}$$

The subscripts m,n enumerate the eigenvalues of Hamiltonian (4), while the subscripts a,b indicate the asymptotic behavior

$$\chi_m^a(\boldsymbol{r},R\to\infty) \sim \phi_m^a(\boldsymbol{r}_a),$$

$$\chi_n^b(\boldsymbol{r},R\to\infty) \sim \phi_n^b(\boldsymbol{r}_b) \tag{7}$$

of the quasimolecular functions: at large distances R, they turn into "quasi-atomic" functions, which are simply the wave functions of an electron bound by the molecules a or b,

$$\left[-\tfrac{1}{2}\Delta_{\boldsymbol{r}} + V_{a,b}(r)\right]\phi_{m,n}^{a,b}(\boldsymbol{r}) = \varepsilon_{m,n}^{a,b}\phi_{m,n}^{a,b}(\boldsymbol{r}). \tag{8}$$

In fact, $\varepsilon^{a,b}$ are the electron affinities of the molecules a,b in the correspondent electronic states.

In the two-state approximation, we assume that the electron initially bound by the molecule a in the state $|m\rangle$ is captured by the molecule b into the state $|n\rangle$, so that the sums in Eq. (5) disappear. In quasiclassical approximation, one finds the following expression for the cross section of such charge-transfer reaction [17]:

$$\sigma_a^b = 2\pi\int_0^\infty \left|\int_{-\infty}^{\infty} L_a^b(R)e^{-i\Delta(Z)}dZ\right|^2 p\,dp,$$

$$L_a^b(R) = \int d\boldsymbol{r}_a\, \chi_n^b(\boldsymbol{r}_b,R)\left.\frac{\partial\chi_m^a(\boldsymbol{r}_a,R)}{\partial Z}\right|_{\boldsymbol{r}_a=\text{const}},$$

$$R^2 = p^2 + Z^2,$$

$$\Delta(Z) = \frac{1}{v}\int_{-\infty}^{Z}[E_a(R') - E_b(R')]dZ'. \tag{9}$$

Here v is the velocity of relative motion of the colliding molecules and p is the impact parameter.

The adiabatic terms $E_{a,b}(R)$ and the quasimolecular wave functions $\chi^{a,b}(\boldsymbol{r},R)$ can be found with the help of a variation procedure similar to that used in the Heitler-London theory of H_2^+ ion [21]. We find the solutions of Eq. (6) in the form

$$\chi(\boldsymbol{r},R) = c_a(R)\phi^a(\boldsymbol{r}_a) + c_b(R)\phi^b(\boldsymbol{r}_b). \tag{10}$$

Introducing the matrix elements

$$V_{aa} = \langle\phi^a(r_a)|V_b(r_b)|\phi^a(r_a)\rangle,$$

$$V_{bb} = \langle\phi^b(r_b)|V_a(r_a)|\phi^b(r_b)\rangle,$$

$$V_{ab} = \langle\phi^a(r_a)|V_a(r_a)|\phi^b(r_b)\rangle,$$

$$V_{ba} = \langle\phi^b(r_b)|V_b(r_b)|\phi^a(r_a)\rangle,$$

$$S = \langle\phi^b(r_b)|\phi^a(r_a)\rangle = \langle\phi^a(r_a)|\phi^b(r_b)\rangle,$$

we obtain the secular equation

$$\begin{vmatrix} (\varepsilon_a - E) + V_{aa} & (\varepsilon_b - E)S + V_{ab} \\ (\varepsilon_a - E)S + V_{ba} & (\varepsilon_b - E) + V_{bb} \end{vmatrix} = 0 \tag{11}$$

that should give two adiabatic terms $E_{a,b}(R)$ and two functions $\chi(\boldsymbol{r},R)$ which then should be combined into two linear combinations to satisfy Eqs. (7).

For simplicity, we restrict our further consideration to the resonant case of two molecules with equal dipole moments: $V_a(r) \equiv V_b(r) = V(r)$, $\varepsilon_a = \varepsilon_b = \varepsilon$, $\phi^a(r) = \phi^b(r) = \phi(r)$. Then the solutions of Eq. (6) can be divided into symmetric χ_+ and antisymmetric χ_- as follows:

$$\chi_\pm \leftrightarrow \pm \chi_\pm \quad \text{at } a \leftrightarrow b,$$

with the corresponding symmetric and antisymmetric adiabatic terms $E_\pm(R)$.

Then in the above Heitler-London approximation, one has $V_{aa} = V_{bb}$, $V_{ab} = V_{ba}$, and the secular equation (11) easily yields the symmetric and the antisymmetric wave functions

$$\chi_\pm = \frac{\phi(r_a) \pm \phi(r_b)}{\sqrt{2(1 \pm S)}} \tag{12}$$

and adiabatic terms $E_\pm(R)$

$$E_\pm = \varepsilon + \frac{V_{aa} \pm V_{ab}}{1 \pm S} \tag{13}$$

corresponding to $c_a = \pm c_b$ in Eq. (10). Expression (9) for the cross section is simplified [17] as follows:

$$\sigma = 2\pi \int_0^\infty p \sin^2 \xi(p) dp, \tag{14}$$

$$\xi(p) = \frac{1}{v} \int_0^\infty [E_-(\sqrt{Z^2 + p^2}) - E_+(\sqrt{Z^2 + p^2})] dZ. \tag{15}$$

Thus for the further calculations one needs to know the adiabatic terms $E_\pm(R)$.

Spherically symmetric solutions of Eq. (8) has the following form [16]:

$$\phi(\boldsymbol{r}) = \frac{N}{\sqrt{4\pi}} \frac{\varkappa}{\sqrt{r}} K_{\mathrm{i}s}(\varkappa r), \tag{16}$$

$$N = \left(\frac{2 \sinh \pi s}{\pi s} \right)^{1/2} = \left(\int_0^\infty \lambda K_{\mathrm{i}s}^2(\lambda) d\lambda \right)^{-1/2}, \tag{17}$$

where K is McDonald function. The electron wave function $\phi(\boldsymbol{r})$ depends on the parameters $\varkappa = \sqrt{-2\varepsilon}$ and s. The latter is related to eigenvalues of the Schrödinger equation with the *angle-dependent* point-dipole potential [16]

$$V_{\mathrm{dip}}(\boldsymbol{r}) = -(\boldsymbol{d} \cdot \boldsymbol{r})/r^3. \tag{18}$$

The radial Schrödinger equation for the outer electron in DBA includes the spherical potential (2) with $2d_{\mathrm{eff}} = s^2 + 1/4$ [16]. For typical dipole moments $d_{\mathrm{eff}} \simeq d$; moreover, the final expression (26) for the cross section depends on d logarithmically. This fact suggests that the spherical approximation (2) should be reasonable as well for the description of charge-transfer process.

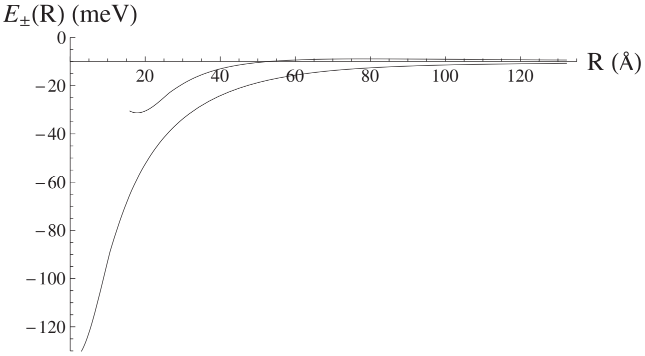

FIG. 1. Adiabatic terms E_+ (lower curve) and E_- (upper curve) for $d=4$ D, $\varepsilon = -10$ meV.

With the account for Eq. (16), the matrix elements involved in Eq. (13) have the following form:

$$S = \frac{\varkappa^2 N^2}{4\pi} \int d\tau \frac{K_{\mathrm{i}s}(\varkappa r_a) K_{\mathrm{i}s}(\varkappa r_b)}{\sqrt{r_a r_b}}, \tag{19}$$

$$V_{ab} = -\frac{d\varkappa^2 N^2}{4\pi} \int d\tau \frac{K_{\mathrm{i}s}(\varkappa r_a) K_{\mathrm{i}s}(\varkappa r_b)}{r_a^2 \sqrt{r_a r_b}}, \tag{20}$$

$$V_{aa} = -\frac{d\varkappa^2 N^2}{4\pi} \int d\tau \frac{K_{\mathrm{i}s}^2(\varkappa r_b)}{r_a^2 r_b}. \tag{21}$$

Here $d\tau$ stands for the phase volume element (see Appendix A where an asymptotic calculation of the above integrals is presented).

To avoid the divergence of integrals (20) and (21) at $r_a \to 0$, the point-dipole potential (2) should be regularized at the origin. The simplest way of such a regularization is the "nonpenetrative point-dipole" model [16], i.e., $V(r < r_0) = \infty$, where r_0 is the effective radius of the neutral molecular core. Thus in calculating integrals (20) and (21), we assumed that $r_a > r_0$. It can be shown that the integrals depend on r_0 slowly ($\propto \ln \varkappa r_0$).

III. RESULTS AND DISCUSSION

The adiabatic terms are shown in Fig. 1. Since the charge transfer takes place at large R, we do not need their behavior for intermolecular distances much less than the effective radius of the excess electron orbital, ϕ. On the other hand, the radial dependence of real molecular potential is substantially different from the point-dipole potential (2) at small distances. Moreover, in the Heitler-London approach, it is of no sense to consider the terms at small R. Indeed, for small R the adiabatic terms $E_\pm(R)$ should converge to the energies of the first two states of the "united DBA." However, such states cannot be described in terms of the basis set (10). As a result, $E_-(R)$ blows up at $R \to 0$ due to $S \to 1$ in the denominator of Eq. (13); and $E_+(R \to 0)$ tends to a value on the order of $-d\varkappa^2$, which has absolutely no connection with the ground-state energy of the united anion [16].

Nevertheless, even in such rough approximation, Fig. 1 demonstrates a simple, but remarkable fact: since $E_+(R)$ is

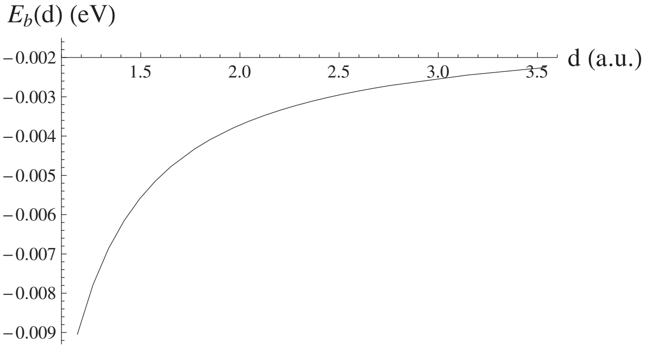

FIG. 2. Electron binding energy E_b in dimer as a function of dipole moment d.

negative for all R, there exists a bound state of a DBA dimer, i.e., a pair of neutral molecules bound by a common excess electron (in full analogy with two protons bound into H_2^+ ion by a common electron). The structure of such complexes has been studied since recent years by *ab initio* methods and by numerical solution of Schrödinger equation with model Hamiltonians (see, for instance, [22,23], and references therein). Simple qualitative analysis shows that the dimer can be formed at intermolecular distance $R_{\mathrm{dimer}} \simeq 2/\varkappa$. We remind that $1/\varkappa$ is the order of the DBA geometric size; for the molecules involved into reaction (1), $1/\varkappa \simeq 30$ a.u. $\simeq 15$ Å. The binding energy of such dimeric state $E_{\mathrm{dimer}} \lesssim \varepsilon$. In our simple model these values may depend also on the parameters of the intermolecular repulsion potential $U(R)$ (e.g., Lennard-Jones potential). Note again that in the Heitler-London approximation the exact information on $U(R)$ behavior is not important for the calculation of the charge-transfer cross section, since it drops out the difference $E_+ - E_-$ between the adiabatic terms.

Also, it can be easily shown within our model that the dependence of electron binding energy E_b in dimer on dipole moment d is very simple. Thus, for example, Fig. 2 shows electron binding energy E_b in dimer as a function of d for the case of electron binding energy in monomer $\varepsilon = -10$ meV. This curve was obtained using Eqs. (19)–(21).

As it was mentioned above, the charge transfer takes place at large intermolecular distances $R \gg 2/\varkappa$. Therefore we can use asymptotic approximations (A6), (A9), and (A12) for the matrix elements (19)–(21) to express the difference of terms (13) at large R,

$$E_- - E_+ = 2\frac{SV_{aa} - V_{ab}}{1 - S^2} \simeq \frac{2Ad\varkappa}{R}e^{-\varkappa R}. \tag{22}$$

Changing the variables according to $\sqrt{Z^2 + p^2} = R$, $ZdZ = RdR$ reduces Eq. (15) to the form

$$\xi(p) = \frac{2Ad\varkappa}{v}\int_p^\infty \frac{e^{-\varkappa R}dR}{\sqrt{R^2 - p^2}} = \frac{2Ad\varkappa}{v}K_0(\varkappa p) \simeq \gamma\frac{e^{-\varkappa p}}{\sqrt{\varkappa p}}, \tag{23}$$

where

$$\gamma = \sqrt{2\pi}\frac{Ad\varkappa}{v}, \tag{24}$$

and the last expression in Eq. (23) is obtained by using the asymptotic behavior of the McDonald function at large p.

Substitution of Eq. (23) into Eq. (14) gives

$$\sigma = \frac{2\pi}{\varkappa^2}\int_0^\infty dx\, x \sin^2\left(\frac{\gamma e^{-x}}{\sqrt{x}}\right). \tag{25}$$

For the molecules CH_3CN and CH_3NO_2 studied in the experiment [12], we assume their average dipole moment $d = 3.7$ D $= 1.46$ a.u., then Eq. (A9) yields $A \simeq 8.7$. For these molecules $\varepsilon = -0.017$ eV $= -6.2 \times 10^{-4}$ a.u., $\varkappa = \sqrt{-2\varepsilon} = 0.035$ a.u. At room temperature $T = 300$ K and molecular mass $M \simeq 10^4 m_e$ the relative velocity $v \simeq \sqrt{2k_B T/M} \simeq 4.6 \times 10^{-4}$ a.u. $\simeq 10^5$ cm/s. Thus $\gamma \simeq 2 \times 10^3 \gg 1$ can be considered as large parameter, so the integral in Eq. (25) can be calculated asymptotically (for the details, see Appendix B). So we obtain the following simple expression for the charge-transfer cross section (with convenient units used in the second expression):

$$\sigma \simeq \frac{\pi}{2\varkappa^2}\ln^2\gamma = \frac{\pi\hbar^2}{4m_e|\varepsilon|}\ln^2\left(\frac{Ade\sqrt{2\pi m_e|\varepsilon|}}{\hbar^2 v}\right). \tag{26}$$

For the above-mentioned experimental data, Eq. (26) yields the cross section $\sigma \simeq 7.83 \times 10^4$ a.u. $= 2.19 \times 10^{-12}$ cm^2. Note that the numerical calculation of the integrals in Eqs. (14) and (15), i.e., without using the asymptotics from Eq. (22), leads to a close value $\sigma = 1.72 \times 10^{-12}$ cm^2. Note that our earlier estimate $\sigma \simeq 1.6 \times 10^{-12}$ cm^2 given in Ref. [12] was obtained based on an approximation of the difference $E_-(R) - E_+(R)$ similar to our asymptotic formula (22) with $A = 2$. It seems that such a choice of A value is more adequate to approximate $E_-(R) - E_+(R)$ at not very large R for the particular dipole moment $d = 3.7$ D value, while our expression (A9) is asymptotically exact for $R \to \infty$ and depends on d explicitly. The measured value $\sigma = 1.4 \times 10^{-12}$ cm^2 reported in Ref. [12] is somewhat less than our theoretical estimates. But given the fact that we used very rough model, one can consider the presented theory to explain the experiment adequately. To make a more detailed comparison with the experiment, one needs measurement of the cross section as a function of the dipole moment and/or the binding energy of the colliding dipolar molecules that seems to be a rather challenging task for the experimentalists.

Physically, it is interesting to compare expression (26) with the corresponding expression for the cross section of elastic scattering (for slow collisions) in the hard-sphere framework [17] as follows:

$$\sigma_{\mathrm{hs}} = 4\pi R_{\mathrm{hs}}^2, \quad Mv \ll 1/R_{\mathrm{hs}}, \tag{27}$$

where R_{hs} is an effective radius of the colliding molecules. On one hand, similarly to the hard-sphere scattering, the cross section (26) displays weak (logarithmical) dependence on the relative velocity v of the colliding molecules. If considered in hard-sphere approximation (27), the charge transfer is characterized by the effective radius

$$R_{\mathrm{hs}} = \frac{1}{2\sqrt{2}\varkappa}\ln(\gamma/\gamma_0), \tag{28}$$

which comprises large logarithmic factor ln γ. Then expression (28) can be treated as a manifestation of the long-range character of the dipole interaction, which leads to the above-mentioned difference of the measured cross-section value from the rough estimates based on the hard-sphere approximation (27). On the other hand, this difference can be connected with slowness of the molecules' translational motion. In fact, according to Eq. (24), γ appearing in Eq. (26) or Eq. (28) is the well-known Massey parameter [17]. This parameter is large for adiabatic collisions when the molecule velocity v is much less than the characteristic "intradimer" velocity defined as the product of the characteristic dimer size $1/\varkappa$ by the characteristic difference $Ad\varkappa^2$ between the dimer's electronic terms. While such adiabatic condition is valid for many chemical reactions, in charge transfer between polar molecules the Massey parameter is large also due to long-range character of the dipole interaction, which results in large $1/\varkappa$ values.

In conclusion, we theoretically considered near-resonant charge-transfer reaction between two polar molecules; each of which is able to capture an excess electron in dipole-bound state. The obtained simple analytical formula (26) gives a good agreement with recent experimental data and contains explicitly the cross-section dependence on the dipole moment of the molecules. We also point out that the formation of dimers of such molecules bound by the excess electron is possible.

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APPENDIX A: ASYMPTOTIC APPROXIMATIONS OF MATRIX ELEMENTS

In this appendix we derive the asymptotic approximations for integrals (19)–(21). It is convenient to use spherical coordinates centered at the "a" molecule with the z axis directed along the $\boldsymbol{R}$ vector. The following notations are used: $\nu=\cos\theta$, $r'=\sqrt{r^2+R^2-2rR\nu}$, $\rho=\varkappa r$, $\rho'=\varkappa r'$, $L=\varkappa R$, and $l_0=\varkappa r_0$.

We start with S as follows:

$$\begin{aligned} S &= \frac{\varkappa^2 N^2}{2}\int_{-1}^{1} d\nu \int_{r_0}^{\infty} dr \frac{r^{3/2}}{\sqrt{r'}} K_{is}(\varkappa r) K_{is}(\varkappa r') \\ &= \frac{N^2}{2}\int_{-1}^{1} d\nu \int_{r_0}^{\infty} d\rho \frac{\rho^{3/2}}{\sqrt{\rho'}} K_{is}(\rho) K_{is}(\rho'). \end{aligned} \tag{A1}$$

We use the asymptotic behavior

$$K_{is}(\lambda) \sim \sqrt{\frac{\pi}{2\lambda}}e^{-\lambda}, \quad \lambda \to +\infty \tag{A2}$$

of McDonald function and the following notation: $\nu=\cos\theta$, $r'=\sqrt{r^2+R^2-2rR\nu}$, $\lambda=\varkappa r$, $L=\varkappa R$, and $l_0=\varkappa r_0$. We start with S as follows:

$$S = \frac{\varkappa^2 N^2}{2}\int_{-1}^{1} d\nu \int_{r_0}^{\infty} dr \frac{r^{3/2}}{\sqrt{r'}} K_{is}(\varkappa r) K_{is}(\varkappa r'). \tag{A3}$$

Then we substitute $K_{is}(\varkappa r')$ in Eq. (A3) by asymptotics (A2). Indeed, if R is large, $\varkappa r'$ is large elsewhere except in the neighborhood of the "b" molecule, where $r \simeq R$, $\nu \simeq 1$. But this neighborhood gives exponentially small contribution into the value of integral (A3) due to the $K_{is}(\varkappa r)$ multiplier. Then we have

$$\begin{aligned} S &\simeq N^2\sqrt{\frac{\pi\varkappa^3}{8}}\int_{r_0}^{\infty} dr\, r^{3/2}K_{is}(\varkappa r)\int_{-1}^{1} d\nu \frac{\exp(-\varkappa r')}{r'} \\ &\simeq \frac{N^2}{R}\sqrt{\frac{\pi\varkappa^3}{8}}\int_{r_0}^{\infty} dr\, r^{1/2}K_{is}(\varkappa r)\int_{|R-r|}^{R+r} \exp(-\varkappa r')dr' \\ &\simeq \frac{N^2}{R}\sqrt{\frac{\pi\varkappa}{8}}\int_{r_0}^{\infty} dr\, r^{1/2}K_{is}(\varkappa r)[e^{-\varkappa|R-r|} - e^{-\varkappa(R+r)}], \\ &\simeq \frac{N^2}{R}\sqrt{\frac{\pi\varkappa}{2}}\Bigg\{ e^{-\varkappa R}\int_{r_0}^{R} dr\, r^{1/2}K_{is}(\varkappa r)\sinh(\varkappa r) \\ &\quad + \sinh(\varkappa R)\int_{R}^{\infty} dr\, r^{1/2}K_{is}(\varkappa r)e^{-\varkappa r}\Bigg\}. \end{aligned} \tag{A4}$$

The second integral in Eq. (A4) has an additional exponential smallness and thus should be omitted in the first approximation,

$$\begin{aligned} S &\simeq \sqrt{\frac{\pi}{2}}\frac{N^2 e^{-L}}{L}\int_{l_0}^{L} d\lambda\, \lambda^{1/2}K_{is}(\lambda)\sinh(\lambda) \\ &\simeq \sqrt{\frac{\pi}{2}}N^2 e^{-L}\frac{d}{dL}\int_{l_0}^{L} d\lambda\, \lambda^{1/2}K_{is}(\lambda)\sinh(\lambda)\Bigg|_{L\to+\infty} \\ &\simeq \sqrt{\frac{\pi}{8}}N^2 e^{-L}L^{1/2}K_{is}(L)e^{L}\big|_{L\to+\infty} \end{aligned} \tag{A5}$$

$$= \frac{\pi N^2}{4}e^{-L}, \tag{A6}$$

since the integral in Eq. (A5) diverges proportionally to L as $L \to \infty$.

Let us consider the next matrix element (20),

$$V_{ab} = -\frac{d\varkappa^2 N^2}{2}\int_{-1}^{1} d\nu \int_{r_0}^{\infty} dr \frac{K_{is}(\varkappa r)K_{is}(\varkappa r')}{\sqrt{rr'}}. \tag{A7}$$

Its asymptotic approximation can be calculated in a way completely similar to that used for S. Since the power of r in

Eq. (A7) is by 2 less than that in Eq. (A3), we can directly obtain instead of Eq. (A5),

$$V_{ab} \simeq -\sqrt{\frac{\pi}{2}}\frac{d\varkappa^2 N^2 e^{-L}}{L}\int_{l_0}^{L}\frac{d\lambda}{\lambda^{3/2}}K_{is}(\lambda)\sinh(\lambda). \tag{A8}$$

Since the integral in Eq. (A8) converges at its both upper and lower limits, we can assume $l_0=0$, $L\to\infty$ and use for the resulting integral the expression in terms of hypergeometric functions available in Ref. [24]. After some simplifications, one yields

$$V_{ab} = -\frac{A d\varkappa^2}{L}e^{-L}, \quad A = \frac{4\sinh \pi s}{s(4s^2+1)}. \tag{A9}$$

Note that both results (A6) and (A9) can be obtained also by calculating the integrals in elliptic coordinates.

The remaining matrix element (21)

$$\begin{aligned} V_{aa} &= -\frac{d\varkappa^2 N^2}{2}\int_{-1}^{1}d\nu\int_{r_0}^{\infty}dr\frac{rK_{is}^2(\varkappa r)}{r'^2} \\ &= -\frac{d\varkappa^2 N^2}{2}\int_{l_0}^{\infty}d\lambda\;\lambda K_{is}^2(\lambda)\int_{-1}^{1}\frac{d\nu}{\lambda^2+L^2-2L\lambda\nu} \end{aligned} \tag{A10}$$

$$= -\frac{d\varkappa^2 N^2}{2L}\int_{l_0}^{\infty}d\lambda\;\lambda K_{is}^2(\lambda)\ln\left|\frac{L+\lambda}{L-\lambda}\right|. \tag{A11}$$

In the $\lambda \lesssim L$ domain one can insert the Taylor approximation $\ln\left|\frac{L+\lambda}{L-\lambda}\right| \simeq \frac{2\lambda}{L}$ into integral (A11). But this approximation can be leaved also for the $\lambda \gtrsim L$ domain since this domain makes an exponentially small contribution into the value of integral (A11). Then assuming $l_0\to 0$ and using Eq. (17) we obtain for large L

$$V_{aa} \simeq -\frac{d\varkappa^2}{L^2}. \tag{A12}$$

This result follows immediately from Eq. (A10) under rough change $r'\to R$.

Figures 3–5 show the matrix elements $S(R)$, $V_{ab}(R)$, and $V_{aa}(R)$ calculated numerically according Eqs. (19)–(21) correspondingly (dots) compared with the asymptotic expressions (A6), (A9), and (A12) given by solid lines. For convenience, the $L=\varkappa R$ values are specified in the upper frames. General considerations suggest that asymptotic formulas should be valid for $L \gg 1$; however, the figures show a good agreement between the asymptotics and the numerical calculations for L as low as $\gtrsim 1-3$ for $V_{ab,aa}(R)$ and $L \gtrsim 5$ for $S(R)$. Note that the obtained asymptotic approximation for $V_{ab}(R)$ is somewhat better than that for $S(R)$; this can be explained by the different contributions of the above-mentioned singularity domain $r\simeq R$, $\nu \simeq 1$ into the integrals in Eqs. (A4), (A7), and (A10). This contribution was omitted in deriving the above asymptotic expressions due to its exponential smallness $\sim\exp(-\varkappa R)$ at large R. However, this contribution has additional smallness for V_{ab} and V_{aa} due to powers of r in the denominators of integrands in Eqs. (A7) and (A10).

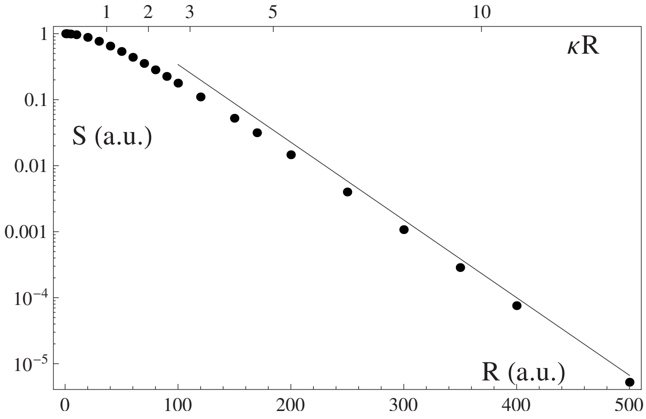

FIG. 3. $S(R)$ calculated numerically [Eq. (19), dots] and asymptotically [Eq. (A6), solid line] in logarithmic scale; d=4 D, ε=−10 meV.

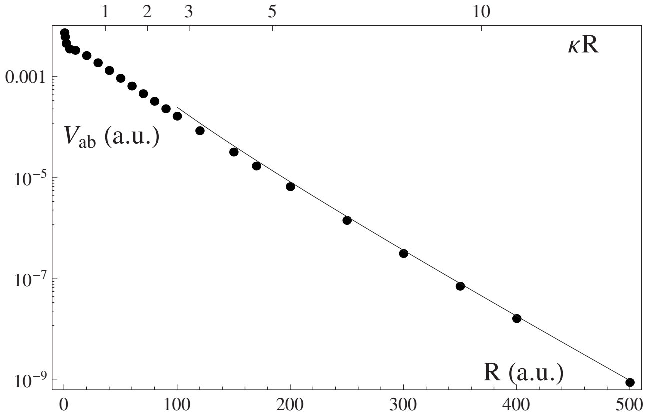

FIG. 4. $V_{ab}(R)$ calculated numerically [Eq. (20), dots] and asymptotically [Eq. (A9), solid line] in logarithmic scale; d=4 D, ε=−10 meV.

APPENDIX B: ASYMPTOTIC APPROXIMATION FOR THE CROSS SECTION

In this appendix we derive the asymptotic expression (26) of the cross section. For large γ, the monotonically decreas-

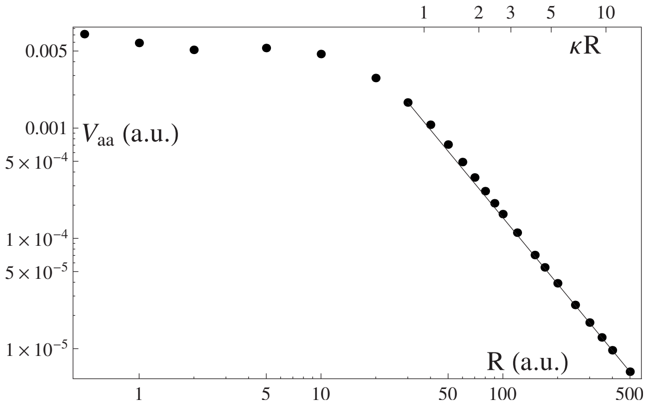

FIG. 5. $V_{aa}(R)$ calculated numerically [Eq. (21), dots] and asymptotically [Eq. (A12), solid line] in double logarithmic scale; d=4 D, ε=−10 meV.

ing (with x) argument of the sine in Eq. (25) can be considered large until it becomes (at some $x=x_0$) equal to some value $\gamma_0 \simeq 1$,

$$\frac{\gamma e^{-x_0}}{\sqrt{x_0}} = \gamma_0. \tag{B1}$$

Due to the large argument of the sine for $x < x_0$, one can change $\sin^2$ to $\frac{1}{2}$ and neglect the contribution of the $x > x_0$ domain into integral (25) as follows:

$$\sigma \simeq \frac{\pi x_0^2}{2\varkappa^2}. \tag{B2}$$

The value of x_0, in turn, can be found from Eq. (B1) asymptotically,

$$x_0 \simeq \ln(\gamma/\gamma_0). \tag{B3}$$

To find the unknown parameter γ_0, we fit the dependence $\sigma(\gamma)$ in Eq. (25) by the asymptotic approximations (B2) and (B3). Such a fitting is shown in Fig. 6; the obtained best-fit value $\gamma_0=0.97$ practically coincides with the previously suggested $\gamma_0=1$ used in our final formulas (26).

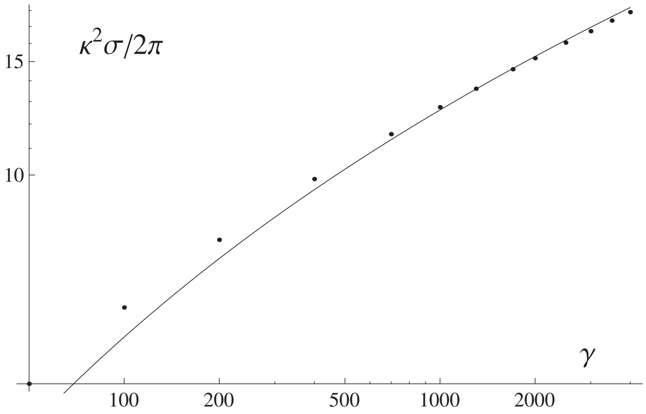

FIG. 6. $\varkappa^2\sigma(\gamma)/2\pi$ calculated numerically [Eq. (25), dots] and asymptotically [Eqs. (B2) and (B3) with $\gamma_0=0.97$, solid line].

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