ЖЭТФ, 2015, том 148, вып. 3 (9), стр. 435–443

ELECTRON ATTACHMENT TO THE SF_6 MOLECULE

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Received January 21, 2015

Various models for transition between electron and nuclear subsystems are compared in the case of electron attachment to the SF_6 molecule. Experimental data, including the cross section of electron attachment to this molecule as a function of the electron energy and vibrational temperature, the rate constants of this process in swarm experiments, and the rates of the chemionization process involving Rydberg atoms and the SF_6 molecule, are collected and treated. Based on the data and on the resonant character of electron capture into an autodetachment ion state in accordance with the Breit–Wigner formula, we find that intersection of the molecule and negative ion electron terms proceeds above the potential well bottom of the molecule with the barrier height 0.05–0.1 eV, and the transition between these electron terms has both the tunnel and above-barrier character. The limit of small electron energies ε for the electron attachment cross section at room vibrational temperature takes place at $\varepsilon \ll 2$ meV, while in the range 2 meV $\ll \varepsilon \ll 80$ meV, the cross section is inversely proportional to ε. In considering the attachment process as a result of the interaction between the electron and vibrational degrees of freedom, we find the coupling factor f between them to be $f = aT$ at low vibrational temperatures T with $a \approx 3 \cdot 10^{-4}$ K^{-1}. The coupling factor is independent of the temperature at $T > 400$ K.

DOI: 10.7868/S0044451015090011

1. INTRODUCTION

Electron attachment to complex or polyatomic molecules proceeds via the electron capture in an autodetachment term, and the Born–Oppenheimer approximation is applicable if this process proceeds effectively, such that the nuclear configuration varies weakly in the course of the electron capture. Subsequent development of a formed autodetachment state is determined by evolution of a slow nuclear system. But the complexity of molecules leads to a specific character of this process. First, several autodetachment states of the negative ion with a low excitation energy usually exist, and these states can be responsible for the electron capture. Interaction and intersections of these autodetachment electron terms with the molecular term lead to a high efficiency of the process of electron capture. Second, complex molecules have many vibrational degrees of freedom, and their excitation in the course of evolution of the electron–molecule system determines an irreversible character of the development of this system. Third, electronegative complex molecules have stable states of negative ions, and the surplus energy in formation of these states goes to vibration degrees of freedom and is subsequently transfered to gas molecules in collisions with them. All this increases the role of measurements in the analysis of electron attachment processes.

Electron attachment to molecules proceeds via formation of autodetachment states of a negative ion of this molecule. Various aspects of this process are studied in detail and are analyzed both in books [1–4] and in reviews [5–8] as a result of transitions between electron terms of the initial molecule and the forming negative ion. Electron attachment to a complex molecule includes three stages: the electron capture in an autodetachment term of the negative ion, the development of this autodetachment state, and formation of the final state of this system. Because of the resonant character of this process, it proceeds efficiently at thermal and lower electron energies if the autodetachment term of the negative ion intersects the molecular electron term near its bottom. This is more probable for complex molecules because they have several autodetachment terms of the negative ion that correspond to the ground electron state of the molecule. A high efficiency of this process allows using this molecule to protect power electric systems from breakdown. Be-

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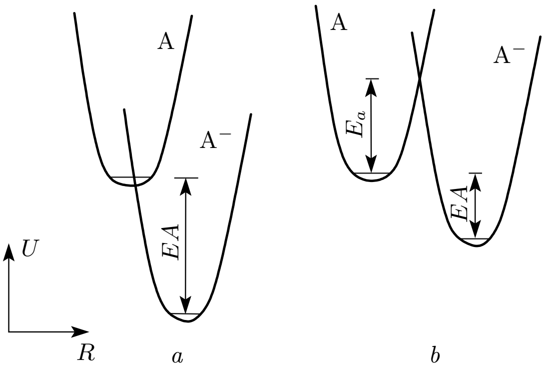

Fig. 1. Electron terms: (a) the dependence of the potential energy U of electrons on the reduced coordinate R for a molecule A and its negative ion A$^-$ in the case of effective electron attachment to the molecule and (b) this process with a high activation energy E_a. EA is the molecule electron affinity

low, we consider the electron attachment process for the SF_6 molecule involving slow electrons where this process is effective. This case is of interest in practice and therefore there is rich information about this process. Treatment of the results of experiments gives us the detailed understanding of this process. This is the goal of this paper.

The rate of electron attachment to complex molecules and the final channel of this process are determined by the parameters of autodetachment electron terms through which this process proceeds. According to our experience, contemporary computer methods do not allow calculating reliably, especially as concerns the width of autodetachment levels. Hence, this information may be extracted from treatment of experimental data; below, we analyze experimental results for electron attachment to the SF_6 molecule from this standpoint. The behavior of electron terms is represented in Fig. 1 for the two limit cases of this process. In the first case, electron capture proceeds effectively and the rate constant of formation of negative ions exceeds that constructed from atomic parameters. In the second case, on the contrary, electron capture in an autodetachment state is hampered, but the formed autodetachment state of the negative ion is characterized by a large lifetime because its electron term is separated from the molecular term by a potential barrier. Below, we analyze the two limit cases separately.

2. BEHAVIOR OF AUTODETACHMENT TERMS OF SF_6^-

We focus on the molecule that is characterized by advantageous parameters of electron terms and, therefore, by a large cross section of the electron attachment process at small electron energies. In considering the behavior of electron terms of this molecule and its negative ion, we are guided by the SF_6 case. As regards electron terms of the negative ion SF_6^-, we note that in the ground state of the SF_6 molecule, the sulfur atom is located in the center and fluorine atoms are located in vertices of an octahedron. The octahedral symmetry of the electron wave function of the SF_6 molecule includes the symmetry with respect to transformations of both reflection with respect to three symmetry planes passing through the squares with four fluorine atoms in vertices, and rotation through $\pi/2$ about any of the three symmetry axes passing through opposite fluorine atoms and the sulfur atom. If we take the total number of transformations to be the number of configurations of the nuclei with respect to a given nucleus, it is equal to the number of permutations of the other five nuclei, i. e., the number of such transformations is $5! = 120$.

We construct the wave function of the negative ion SF_6^- in the form

$$\Psi = \sum_{i=1}^{6} a_i \psi_i, \qquad (2.1)$$

where ψ_i corresponds to electron location on the ith fluorine atom. We can make six different combinations of the wave functions, and because this number is smaller than the total number of nuclear configurations, some electron states of the negative ion are degenerate. We can extract the symmetric state from the electron terms of the negative ion SF_6^- resulting from addition of an electron to the SF_6 molecule in the ground electron state, and the coefficients a_i are identical for this state. The wave function of this state, Eq. (2.1), is conserved under any octahedral transformation. Evidently, the electron wave function of the SF_6 molecule in the ground state is symmetric under octahedral transformations, and hence the symmetric state of the negative ion corresponds to the addition of an s-electron to the SF_6 molecule. The other five electron states of the negative ion are antisymmetric under some octahedral transformations, i. e., wave function (2.1) changes sign under some of these transformations. Because the number of these states is less than the number of octahedral transformations, these states are degenerate when fluorine atoms are located in octahedral vertices. If one fluorine atom is removed from the molecule center, there are two antisymmetric states degenerate by energy, and when it is located far from the molecule center, the negative ion consists of two pairs, $SF_5^- + F$ or $SF_5 + F^-$, which increases the number of electron terms.

We note the existence of a stable state of the SF_6^- negative ion. Because the symmetric state is the lowest state of the negative ion, evidently, an s-electron is captured in the autodetachment state of SF_6^- that is stable under other configurations of nuclei. Hence, the capture of a slow electron by the SF_6 molecule is accompanied by the development of the forming autodetachment state toward the stable negative ion. Hence, the capture of an s-electron by the SF_6 molecule leads to the formation of the negative ion SF_6^-, whereas if the electron momentum is higher, the channels of electron capture are $SF_5^- + F$ or $SF_5 + F^-$, and these channels may be locked at thermal electron energies.

Thus, the capture of a slow s-electron by the SF_6 molecule leads to the formation of the symmetric state of the SF_6^- negative ion according to the scheme

$$e + SF_6 \to SF_6^-, \tag{2.2}$$

and the subsequent development of this ion goes toward a stable negative ion by simultaneous variation of distances of all the fluorine atoms from the center. We note that although this motion does not excite antisymmetric vibrations of fluorine atoms, such vibrations arise from the interaction of this atom motion with molecular rotation. Indeed, the molecule rotational momentum is conserved in the course of the atom motion, and therefore simultaneous motion of fluorine atoms in the radial direction can cause both a change of the rotational energy of the molecule and the excitation of antisymmetric vibrations.

Thus, this analysis exhibits that the negative ion is characterized by two electron terms at least, which are symmetric and antisymmetric under octahedral transformations. The symmetric state corresponds to a stable negative ion, and the degeneracy of the antisymmetric state is removed if the fluorine nuclear configuration becomes nonsymmetric. In addition, removing one fluorine atom from the SF_5 radical leads to a degeneracy due to formation of two pairs $SF_5 + F^-$ and $SF_5^- + F$. Hence, in the case of electron attachment to the SF_6 molecule, many autodetachment states of the negative ion SF_6^- may be formed.

3. ATTACHMENT OF SLOW ELECTRONS TO THE SF$_6$ MOLECULE AT ROOM TEMPERATURE

We first consider electron attachment to the SF_6 molecule in the case where a stable negative ion is formed and the process proceeds with a high rate. Acounting for the resonant character of the electron attachment to a molecule, we use a general formula for the electron attachment cross section based on the Breit–Wigner formula [9–11]:

$$\sigma_{at} = \frac{\pi\hbar^2}{2m_e\varepsilon}\int\frac{\Gamma(R)^2\,|\varphi(R)|^2\,dR}{[\varepsilon-\varepsilon_R]^2+\Gamma^2(R)/4}. \tag{3.1}$$

Here, m_e is the electron mass, ε is the electron energy, R is the nuclear coordinate that is responsible for this process, ε_R is the autodetachment state energy, $\Gamma(R)$ is the width of the autodetachment term, and $\varphi(R)$ is the molecular wave function at the beginning. In the limit of low electron energies, under the assumption that $\Gamma(R) = \text{const}$ and under optimal conditions, the cross section of electron attachment to a molecule has the form

$$\sigma_{at} = \frac{A}{\varepsilon}, \quad \varepsilon_1 \ll \varepsilon \ll \varepsilon_2. \tag{3.2}$$

Although this dependence follows from formula (3.1) in the case of a strong electron–molecule interaction, it is justified by measurements [12–14].

We assume a strong interaction at the electron attachment to a molecule and determine the parameters in formula (3.2) in the SF_6 case on the basis of experimental data. The boundaries of this dependence for the SF_6 molecule are on the basis [13, 14] $\varepsilon_1 \approx 2$ meV and $\varepsilon_2 \approx 80$ meV, and the parameter A in formula (3.2) is $A = 5.8\,\text{Å}^2\cdot\text{eV}$ according to measurements [12] and $A = 7.1\,\text{Å}^2\cdot\text{eV}$ according to [15, 16]. Hence, based on formula (3.2), we have the rate of electron attachment to a molecule

$$k_{at} = \frac{2A}{\sqrt{\pi m_e T_e}}, \tag{3.3}$$

where T_e is the electron temperature. At low electron energies, the energy dependence for the electron attachment cross section has the form [11, 17]

$$\sigma_{at} \sim \frac{1}{\sqrt{\varepsilon}}, \tag{3.4}$$

and the rate constant of the electron attachment process $k_0 = v\sigma_{at}$ does not depend on the electron velocity v or its energy ε. We use the energy dependence for the cross section of this process in the form

$$\sigma_{at} = \frac{A}{\sqrt{\varepsilon^2+\varepsilon\varepsilon_1}}, \tag{3.5}$$

which is transformed in the limit cases into formulas (3.2) and (3.4). In particular, we hence have the rate constant at zero electron energy

$$k_0 = A\sqrt{\frac{2}{m\varepsilon_1}}, \tag{3.6}$$

and this formula connects the parameters that describe the process rate in the limit cases. Averaging the rate constant over the Maxwell distribution function of electrons, we obtain

$$k_{at} = \frac{k_0}{\sqrt{1+\pi T_e/4\varepsilon_1}}. \tag{3.7}$$

This formula can be rewritten in the form

$$k_{at}(T_e, T) = A(T)\sqrt{\frac{8}{\pi m_e T_e}}\,\frac{1}{\sqrt{1+4\varepsilon_1/\pi T_e}}, \tag{3.8}$$

where T is the nuclear or vibrational temperature. In the limit of high electron temperatures, this formula gives

$$k_{at}(T_e, T) = A(T)\sqrt{\frac{8}{\pi m_e T_e}}, \quad T_e \gg \varepsilon_1. \tag{3.9}$$

Important information about the process under consideration follows from measurements with ultraslow electrons formed in a photoelectron source of electrons in two-step laser ionization of metastable argon atoms formed in a gas discharge plasma. Such a scheme [18, 19] provides a high resolution up to 0.1 meV. This method is used for measuring the electron attachment to the SF_6 molecule at low electron energies [13, 14, 20, 21]. In particular, the experimental rate constant is independent of the electron energy ε starting from $\varepsilon \approx 2$ meV; in the zero energy limit and at room vibration temperature, its value is given by [13, 14]

$$k_0 = (5.4 \pm 0.8)\cdot 10^{-7}\ \mathrm{cm^3/s}. \tag{3.10}$$

Another information follows from the chemionization process

$$\mathrm{A}^* + \mathrm{SF}_6 \to \mathrm{A}^+ + \mathrm{SF}_6^-, \tag{3.11}$$

where A^* is a highly excited (Rydberg) atom state. Taking experiments [22–28] with the electron binding energy approximately equal to 10 meV, we obtain the result of statistical treatment of these measurements:

$$k_{at} = (4.3 \pm 0.3)\cdot 10^{-7}\ \mathrm{cm^3/s}. \tag{3.12}$$

Because the behavior of a weakly bound electron is similar to that of a free electron, this rate constant is close to the electron attachment rate constant at low electron energies.

Statistical averaging of the experimental data in [16, 29–46] for electron attachment to the SF_6 molecule at room temperature leads to the rate constant

$$k_{at} = (2.3 \pm 0.4)\cdot 10^{-7}\ \mathrm{cm^3/s}. \tag{3.13}$$

This coincides, within the accuracy limit, with the precise measurements [40, 42], where $k_{at} = (2.27 \pm 0.07) \times \times 10^{-7}$ cm^3/s. We note that the rate constant of electron attachment at the electron energy $\varepsilon = 0.2$ eV and room temperature of molecular oscillations is $k_{at} = = (9 \pm 1)\cdot 10^{-8}$ cm^3/s if we use the value in (3.2) and expand it to higher electron energies using formula (3.2) in accordance with measurements in [47, 48]. In addition, measurements in a magnetized plasma at this electron energy and room vibrational temperature of molecules give $k_{at} = (8 \pm 2)\cdot 10^{-8}$ cm^3/s [49]. It hence follows that the higher boundary of formula (3.2) $\varepsilon_2 > 200$ meV. Evidently, $\varepsilon_2 \approx 300$ meV because at this energy the character of the attachment process varies [50].

From formula (3.3), we find the parameter A in formula (3.2): $A = 8 \pm 1\,\text{Å}^2\cdot\text{eV}$. With the results of measurements [12, 15, 16] added to this, we obtain

$$A = 7 \pm 2\,\text{Å}^2\cdot\text{eV}. \tag{3.14}$$

The indicated measurements of the rate constants for electron attachment to the SF_6 molecule allows determining a typical energy ε_1 in formula (3.5), if we use formula (3.6) and rate constant (3.10) in the limit of zero electron energy at room vibrational temperature. It follows from formula (3.6) with (3.14) taken into account that

$$\varepsilon_1 = 6 \pm 2\ \text{meV}. \tag{3.15}$$

This value of the rate constant justifies the method for determining the parameter ε_1 because the rate constant (3.10) corresponds to the electron energy $\varepsilon = = 2$ meV that is below ε_1, and according to formula (3.5) at the electron energy $\varepsilon = 2$ meV, the attachment cross section differs from its asymptotic value by approximately 10 %. In addition, we note that the transition from dependence (3.2) to (3.4) with a decreasing electron energy proceeds in a wide range of electron energies. Hence, the statement that the Wigner law holds at electron energies below 5 meV has a qualitative character.

We can increase the accuracy of the value ε_1 if we include the rate constant (3.12) of the chemionization process (3.11) into consideration. In this case, a bound electron of a highly ionized atom attaches to the SF_6 molecule in a region of the Coulomb interaction between the electron and the atomic core. In this region, the average kinetic electron energy is equal to the ionization potential of this highly ionized atom, which is equal 10 meV on average under the conditions of measuring the rate constants of the chemionization process, whose average values at room temperature of SF_6 molecules are given in formula (3.11). Then using formula (3.8) and parameters (3.14) and (3.15), we can obtain the rate constant of chemionization process (3.11) as $k_{at} = (4.4 \pm 1.2) \cdot 10^{-7}$ cm^3/s in accordance with measured values (3.12).

We summarize the results obtained. We are based on Breit–Wigner formula (3.1) for the cross section of electron attachment to the SF_6 molecule, assuming that the resonance is in the accessible region of nuclear location. At small electron energies, the cross section is given by (3.4) [17], and this transition proceeds at $\varepsilon \ll \Gamma$. We have found the parameters of the attachment cross section (3.5) in the range $\varepsilon \sim \Gamma$ or $\varepsilon \ll \Gamma$ at room vibrational temperature of molecules.

We can glance at the problem from another standpoint. Indeed, although we proceed from the resonant character of the electron–molecule interaction in accordance with Breit–Wigner formula (3.1), a model of a strong electron–molecule interaction is used in reality after averaging over the nuclear configuration. This model is similar to the models in [51–55], which account for a certain character of electron–molecule interactions. But this model is based on experimental results that correspond to more general conditions. By restricting to room vibrational temperature only, we obtain that this process is independent of the molecular parameters. In this case, the cross section depends on the electron energy only. Far from the threshold, the attachment cross section σ_{at} is inversely proportional to electron energy (3.2) and has a threshold dependence (3.4). Assuming the electron–molecule interaction to be separated into electron and molecular parts and the molecular part to be identical at any electron energies, we use the experimental data to find the behavior of the attachment rate constant at room temperature in accordance with formulas (3.7) and (3.8) with parameters (3.14) and (3.15), and k_0 in accordance with formula (3.10).

4. TEMPERATURE DEPENDENCE FOR THE RATE OF ELECTRON ATTACHMENT

In considering the electron attachment process to the SF_6 molecule at room vibrational temperature and separating the electron and nuclear degrees of freedom, we cannot obtain information about the role of nuclear motion in this process because it is identical at different electron energies if the process proceeds at room temperature. A temperature dependence of the rate of this process allows understanding the role of nuclear configurations in this process, which consists in both excitation of molecule vibrations and positioning electron terms for the molecule and its negative molecular ion. We first transform formula (3.1) in the case of a strong electron–molecule interaction if the negative ion term intersects the molecular term not far from the bottom of the molecular potential curve (see Fig. 1). Assuming the width $\Gamma(\mathbf{R})$ of the autodetachment level to be relatively small (where $\mathbf{R}$ refers to the nuclear configuration), we can consider the autodetachment state as a bound one. Approximating the autodetachment term energy $E(\mathbf{R})$ by a straight line, after integrating cross section (3.1) over nuclear configurations, we obtain [2]

$$\begin{gathered}\sigma_{at}(\varepsilon) = \frac{\pi^2\hbar^2}{m_e\varepsilon} f,\\ f(\varepsilon) = \Gamma(R_\varepsilon)\frac{dR}{dE}|\varphi(R_\varepsilon)|^2 e^{-\zeta},\\ \zeta = \int\limits_{R_\varepsilon}^{R_c} \frac{\Gamma(R')\,dR'}{\hbar v_R},\end{gathered} \tag{4.1}$$

where R_ε is the nuclear coordinate along the reaction path that provides the resonance at an electron energy ε, $E(R)$ is the energy of the autodetachment state at a given nuclear configuration, $\varphi(R_\varepsilon)$ is the nuclear wave function of the molecule at an indicated coordinate, R (R') is the coordinate along the reaction path, and R_c is the coordinate where the electron terms of the molecule and the negative ion intersect. Formula (4.1) describes interaction of an electron with an absorption center, and the possibility to consider an autodetachment state as a bound state (or a smallness of $\Gamma(R_\varepsilon)$) requires the smallness of the coupling factor $f \ll 1$. We note that the coupling factor in the SF_6 case at room temperature is $f = 0.077$ [2].

We thus consider the process of electron attachment to a molecule as a result of electron scattering on an absorption center, where electron–molecule interaction is reduced to the coupling factor f that accounts for properties of an autodetachment state of the negative ion. Therefore, the temperature dependence of the coupling factor gives information about the parameters of the molecular and autodetachment terms of the negative ion. Below, we take the survival probability $\exp(-\zeta)$ of the autodetachment state during evolution of the negative ion to the stable state to be one, i. e., we assume the electron attachment process to be efficient. Using the harmonic character of the molecule oscillation, we use (4.1) to obtain the rate constant of the electron attachment process

$$
\begin{gathered}
k_{at}(\varepsilon) = A\sqrt{\frac{8}{\pi m_e \varepsilon}}\left[1-\exp\left(-\frac{\hbar\omega}{T}\right)\right]^{-1} \times \\
\times \sum_n |\varphi_n(R_{\varepsilon,n})|^2 \exp\left(-\frac{\hbar\omega n}{T}\right), \\
E(R_{\varepsilon,n}) = \varepsilon + \hbar\omega n.
\end{gathered}
\tag{4.2}
$$

For simplicity, we assume the normal molecule oscillation along the reaction coordinate and the harmonic character of these oscillations. Comparison of formula (4.2) with experimental data for the electron attachment rate constant at various molecule temperatures gives information about the behavior of electron terms for the molecule and the negative ion. We first represent the data for the temperature dependence of the electron attachment rate constant.

In analyzing the temperature dependence of the electron attachment rate constant, we note that the experimental data in [41, 56–60] relate to identical electron and molecular temperatures. In particular, according to [41], the electron attachment rate constant to the SF_6 molecule is 3.1, 3.1, 4.5, 4.0 in units of 10^{-7} cm^3/s at the respective temperatures 205, 300, 455, and 590 K. Measurements in [56] at the temperatures 300, 411, and 545 K give the respective electron attachment rate constants 2.3, 3.1, and 2.2 in units of 10^{-7} cm^3/s. According to [57], we have $k_{at}(300\ \mathrm{K}) = 2.9 \cdot 10^{-7}$ cm^3/s and $k_{at}(73\ \mathrm{K}) = 1.2 \cdot 10^{-7}$ cm^3/s. In addition, at high temperatures, we have $k_{at}(670\,\mathrm{K}) = 2.0 \cdot 10^{-7}$ cm^3/s and $k_{at}(700\,\mathrm{K}) = 1.7 \cdot 10^{-7}$ cm^3/s. The accuracy of the above and other measurements of the temperature dependence is restricted and does not allow us to determine precisely the parameters of the autodetachment electron term with respect to the molecular electron term. But the above information shows an important tendency in the behavior of this rate constant.

The main problem in the analysis of the temperature dependence for experimental rate constants k_{at} is its high experimental error. Nevertheless, the sum of experimental data leads to certain conclusions about positions of the electron terms for the SF_6 molecule and its negative ion. In Fig. 2, we give the values of the coupling factor f at different temperatures in accordance with its definition in (4.1). Introducing the coupling factor f, we separate the electron and vibrational degrees of freedom in expressions for the cross section or the rate constant of electron attachment to the molecule, and the coupling factor includes vibrational degrees of freedom. In particular, the rate constant of electron attachment to the SF_6 molecule according to formula (3.8) is given by

$$
k_{at} = \frac{2\pi\hbar^2}{m_e}\sqrt{\frac{2\pi}{m_e T_e}}\,\frac{1}{\sqrt{1+4\varepsilon_1/\pi T_e}}\,f. \tag{4.3}
$$

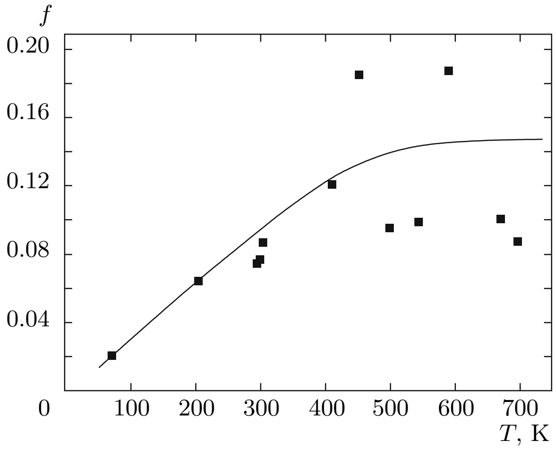

Fig. 2. Temperature dependence of the coupling factor f in formula (4.1) that accounts for the contribution of molecular oscillations to the rate constant of electron attachment to the SF_6 molecule. The solid curve is a rough approximation of this dependence $f = 3 \cdot 10^{-4}T – 10^{-7}T^2$, where T is expressed in K

In formula (4.3), we thus relate the rate constant of electron attachment to the SF_6 molecule with the coupling factor f.

We can analyze the temperature dependence for the coupling factor f. At low molecular temperatures T ($T < 100$ K), if the molecule is in the ground vibrational state, the coupling factor is independent of the temperature. The same occurs at high temperatures, where intersection of the molecular term and the autodetachment negative ion is attained. The coupling factor increases as the temperature increases because the terms intersect outside the region of classical location of the nuclei, i. e., positions of electron terms of the SF_6 molecule and its negative ion in the autodetachment state have the form as shown in Fig. 3.

It is convenient to approximate the coupling factor in accordance with the character of its temperature dependence by the formula

$$
f = f_0\,\frac{1-\exp(-E_1/T)}{1-\exp(-E_2/T)}. \tag{4.4}
$$

In this case, the coupling factor f is independent of the temperature in the limits of low and high temperatures, and has a jump at moderate temperatures. The

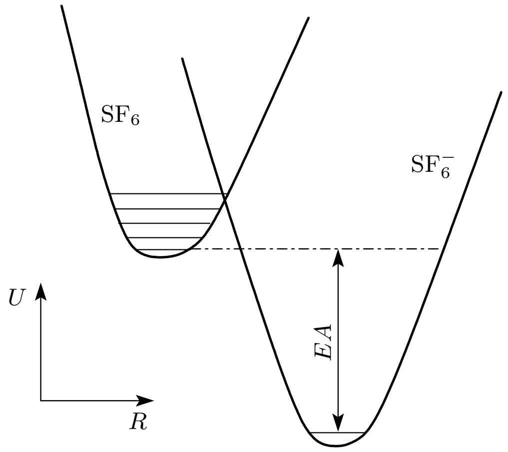

Fig. 3. Behavior of electron terms as a function of the reduced molecular coordinate for electron attachment to the SF_6 molecule

value E_1 is a typical energy of molecule vibrations, and the energy E_2 is of the order of the excitation energy needed to reach the intersection of electron terms of the molecule and its negative ion, but it is not the activation energy because of the tunnel character of transition in formulas (4.1) and (4.2).

In particular, the following parameters in formula (4.4) are suitable for approximating the experimental data in Fig. 2: $f_0 = 0.017$, $E_1 = 70$ K, and $E_2 = 900$ K. For these parameters, in accordance with formula (4.4), we have $f(50\text{ K}) = 0.02$, $f(300\text{ K}) = 0.08$, and $f(700\text{ K}) = 0.13$ which corresponds to the data in Fig. 2. Nevertheless, the accuracy of this approximation is not satisfactory. Indeed, the data of measurements in [41] and [56] in the temperature range 450–550 K differ by up to a factor of 2. Therefore, the average values f of different measurements are characterized by an error of 30–50 %. In particular, according to measurements in [41] and [56], the electron attachment rate constant has a maximum at a temperature in the range 400–450 K, whereas the approximating dependence (4.4) with suitable parameters leads to a monotonous temperature dependence of the coupling factor. In addition, in the limit of low electron and molecule temperatures, the above experimental data yield $k_{at}(T \to 0) = (1.4 \pm 0.5) \cdot 10^{-7}\ \text{cm}^3/\text{s}$.

5. CONCLUSION

As we see, the treatment of experimental data both gives reliable numerical parameters for the electron attachment process to the SF_6 molecule and allows understanding the relation between various models of this process. In considering electron attachment to the SF_6 molecule as the interaction between a fast (electron) and slow (vibration) subsystems, we can obtain a viable method to analyze this process as a result of transition between electron terms (or the potential energy surfaces) of the SF_6 molecule and its negative ion SF_6^-. Assuming this interaction to be weak, we introduce the coupling factor f between these subsystems that is responsible for this interaction, and analyzing the experimental data confirms the interaction weakness. As a result, the process of electron attachment to the SF_6 molecule can be considered as the electron interaction with an absorption center.

In addition, the above analysis of experimental data for the electron attachment to the SF_6 molecule allows relating various quantum models for various aspects of this process. Indeed, taking this process as a result of resonant electron capture in an autodetachment level and describing this process on the basis of the Breit–Wigner formula, in the limit of low electron energies ε compared with the width Γ of the autodetachment level, we obtain the Wigner formula for the electron attachment cross section $\sigma_{at}(\varepsilon) \propto 1/\sqrt{\varepsilon}$ after averaging over parameters of the electron capture. In the other limit case $\varepsilon \gg \Gamma$, the electron attachment cross section is $\sigma_{at}(\varepsilon) \propto 1/\varepsilon$. In addition, for the Maxwell distribution function of electrons, we go to the chemical model of electron attachment to the SF_6 molecule with the activation energy $E_a \approx 0.05$–0.1 eV.

The study was supported by the Russian Science Foundation (Grant No. 14-50-00124).

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