Ionization of a highly excited (Rydberg) atom and attachment of an ultraslow electron to an SF₆ molecule

I. M. Beterov, G. L. Vasilenko, B. M. Smirnov, and N. V. Fateev

Institute of Heat Physics, Siberian Branch of the Academy of Sciences of the USSR, Novosibirsk

Selective three-stage laser excitation of an atomic beam was used to determine the rate constants of collisional quenching by SF_6 molecules of Rydberg (np series) states of sodium with the principal quantum numbers $n = 23$–40. It was found that the main contribution to the quenching came from the ionization producing an ion pair. The rate constant of the process was independent of n and amounted to $\overline{K} = (4.4 \pm 0.2) \times 10^{-7} \, cm^3/sec$. This was in agreement with the results obtained for the ns and nd series of Rb and for the nf series of Xe with different orbital momenta, confirming the validity of the semiclassical description of the electron motion. A critical analysis of the data on the rate constants of the attachment of slow electrons obtained by direct methods gave $K \leqslant (2.6 \pm 0.4) \times 10^{-7} \, cm^3/sec$. An analysis was also made of the possible reasons for the observed difference between the values of the electron attachment rate constants obtained by different methods.

1. INTRODUCTION

Ionization of highly excited (Rydberg) atoms and collisions with other atoms and molecules can provide information on the processes of collisions of slow electrons with atomic particles. When a highly excited atom collides with an electronegative molecule, an investigation of the rate of ionization of this atom makes it possible to analyze the nature of the process by which an ultraslow electron becomes attached to a molecule. Investigations of this kind have been made earlier[1,2] (see also Ref. 3) and they demonstrate a rough agreement between the cross sections for electron attachment to the molecule, both obtained by direct measurements and reconstructed from the ionization cross sections of highly excited atoms colliding with molecules. However, a more detailed analysis shows that there is some discrepancy between these values. In tackling this problem we need above all more reliable and accurate data on the ionization cross sections of highly excited atoms. We therefore measured the ionization cross sections of highly excited p-state sodium atoms colliding with SF_6 molecules. In combination with the data on the ionization of highly excited xenon atoms in the f state[1] and highly excited rubidium atoms in the s and d states,[2] this makes it possible to obtain reliable information on the attachment of an electron to an SF_6 molecule at ultralow energies. An analysis of these data and a comparison with the results of direct measurements at higher energies can provide a more detailed picture of this process.

We shall consider the process of ionization during collisions of highly excited atoms with other atoms or molecules. The cross section of this process is given by the formula[4,5]

$$\sigma_{ion} = \left\langle \frac{\int |\mathbf{v} - \mathbf{v}_a| \, d\sigma}{v_a} \right\rangle . \tag{1}$$

Here, v_a is the relative velocity of the nuclei, v is the velocity of a weakly bound electron at a given point in space, $d\sigma$ is the cross section for the collision of an electron with a molecule when the scattering of an electron results in breaking of its initial bond. The angular brackets denote averaging over the distance from the nucleus. Equation (1) implies that the size of the region where the scattering occurs is small compared with the size of a highly excited atom. We can then employ the semiclassical description of the electron motion. It should be pointed out that Eq. (1) is obtained also using the impulse approximation, developed by Matsuzawa.[6] We can show[7] that in the range of validity of the semiclassical approximation the initial assumptions in the semiclassical and impulse approximations are the same.

We shall transform Eq. (1) to fit the conditions of the investigations reported below. Firstly, at thermal collision velocities we have $v_a \sim 10^5 \, cm/sec$, whereas for the principal quantum number $n \sim 100$ the electron velocity is $v \sim 10^6$ cm/sec, so that we have $v_a \ll v$. Consequently, the ionization rate constant becomes

$$K_{ion} = \langle K_e(v) \rangle, \tag{2}$$

where $K_e(v)$ is the rate constant of collisions of an electron with a molecule resulting in breaking of the initial bond. Secondly, the main process of this type is the attachment of an electron to a molecule, i.e., we can substitute $K_e = K_{att}$ in Eq. (2). Therefore, measurements of the ionization rate constant of a highly excited atom give in this case the rate constant K_{att} of electron attachment to a molecule averaged over the velocities of an electron in a highly excited atom.

2. APPARATUS AND EXPERIMENTAL METHOD

Rydberg Na(np) atoms ($n > 17$) were formed in an atomic beam by a three-stage excitation procedure $3S_{1/2} \to 3P_{3/2} \to 5S_{1/2} \to nP_{1/2,3/2}$ (Fig. 1) using time-synchronized radiation from two pulsed dye lasers emitting at wavelengths $\lambda = 589$ nm and 615 nm, and radiation of a pulsed color-italic center (F_2^-) LiF laser operating at wavelengths 1.08–1.28 μ. This made it possible to excite the atoms of Na to Rydberg states with $n \geqslant 17$ right up to the ionization limit ($\lambda_{III} = 1.21 \, \mu$) at a high (up to 10 kHz) repetition frequency of the pulses, which simplified greatly an analysis of the experimental results. We used the apparatus shown schematically in Fig. 2. The dye lasers were pumped synchronously with radiation representing the second harmonic of
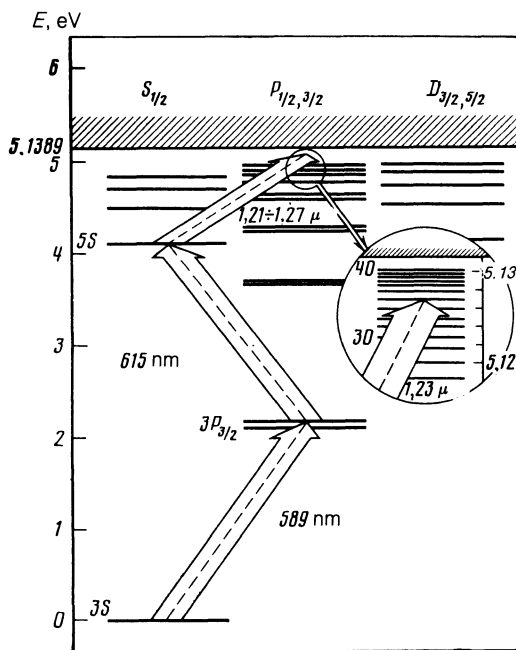
FIG. 1. Active levels of Na.

a YAG:Nd laser ($\lambda = 532$ nm) operating at a pulse repetition frequency 3.5 kHz and characterized by an average output power of 3 W. The first excitation stage ($\lambda_I = 589$ nm) was due to radiation from a dye laser utilizing a solution of rhodamine 6G in ethylene glycol characterized by an emission line of width < 0.1 nm and an average output power of 10 mW. The dye laser providing the excitation for the second stage ($\lambda_{II} = 615$ nm) utilized a solution of rhodamine B. The average output power of this laser was 5 mW and the line width was 0.08 nm. The optical systems of these lasers were described by us earlier.[8]

The third stage involved excitation with radiation from a tunable laser utilizing the F_2^- color centers in an LiF crystal, which was pumped with the second harmonic of a Q-switched YAG:Nd laser ($\lambda = 1.06\mu$) operating at the same (3.5 kHz) pulse repetition frequency. The LiF:F_2^- crystal
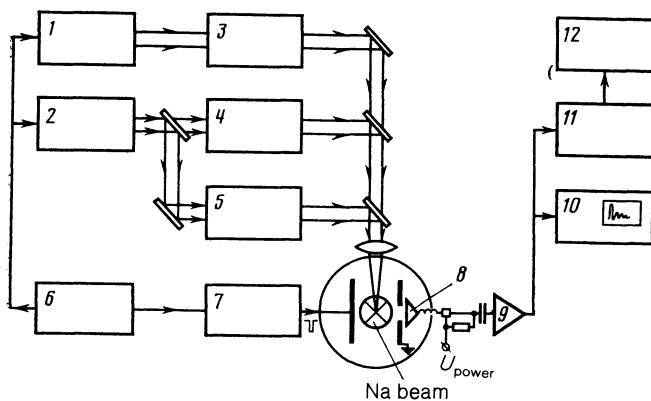

FIG. 2. Schematic diagram of the apparatus: 1) YAG:Nd laser, $\lambda = 1.064$ μ; 2) YAG:Nd laser with intracavity frequency doubling to $\lambda = 532$ nm; 3) laser with F_2^- color centers in an LiF crystal, $\lambda = 1.08$–1.28μ; 4) dye laser, $\lambda = 589$ nm; 5) dye laser, $\lambda = 615$ nm; 6) master oscillator; 7) generator of electric field pulses; 8) VÉU-6 secondary electron multiplier; 9) wide-band amplifier; 10) oscilloscope; 11) pulse counter and discriminator; 12) graph plotter.

was 10 cm long and the color centers were created by γ rays from a ^{60}Co source at the Institute of Nuclear Physics of the Uzbek Academy of Sciences. A three-mirror resonator with a V-like configuration and a diffraction grating as a dispersive component ensured continuous tuning of the emission frequency of the color-center laser in the range 1.28–1.08 μ and the line width was < 0.3 nm, which ensured selective excitation of the Rydberg states of Na from the $5S_{1/2}$ state right up to the $n \approx 40$ levels. The average power of the LiF:F_2^- laser was ~ 100 mW at the maximum of the laser emission band and the pulse duration was ~ 150 nsec. The pulses from the three lasers were synchronized optically using a wide-band photodetector and the final matching was ensured employing an electric signal due to field ionization.

In these experiments we used a thermal beam of Na atoms colliding in the working chamber with SF_6 molecules which acted as a target gas. The atomic beam was formed by the effusion of Na vapor from a slit (0.5×3 mm) of a heated source the temperature of which was measured with a calibrated thermocouple. The concentration of atoms in the interaction region was 10^7 atoms/cm^3, which corresponded to a beam source temperature of 470 K. The beam was collimated by a stop 0.5 mm in diameter located at a distance of 4 cm from the beam source slit. The region crossed by the atomic beam and the working chamber were pumped out using oil diffusion pumps, which ensured that the residual pressure was 3×10^{-6} Torr. The molecules of the SF_6 target gas were introduced into the working chamber with the aid of a needle leak valve. The pressure was measured employing a calibrated (against SF_6) ionization tube of the PMI-2 type and was found from

$$P = (P_{\text{meas}} - P_0)/2.7,$$

where P_{meas} is the reading of a vacuum gauge and P_0 is the residual gas pressure. The coefficient 2.7 was determined by the method of a constant flow rate.[9]

Atoms were excited to the Rydberg states in an interaction region located at a distance of 13 cm from the slit of the atomic beam source. The interaction region was a parallel-plate capacitor with copper electrodes 33 mm in diameter separated by a gap of 7.5 mm. One of the plates had an aperture 10 mm in diameter for the extraction of charged particles and it was covered by a metal grid.

A pulsed electric field of up to 2 kV/cm intensity, applied to the capacitor plates, made it possible to detect effectively the excited atoms by the method of selective field ionization.[10] The electrons and negative ions formed as a result of field ionization were recorded using a VÉU-6 channel electron multiplier.

The multiplier signal due to the charged particles passed through an amplifier and reached either an oscilloscope or a pulse counter with an amplitude discriminator and a control switch. This made it possible to record pulses at a given moment in time, selected using an external pulse generator synchronized with the laser pump pulses. The duration of a gate pulse was selected so as to ensure separate recording of the electron and negative-ion currents formed as a result of collisional ionization up to a given moment in time.

Variation of the time delay τ between the electric field pulses relative to the exciting laser pulses enabled us to deter-
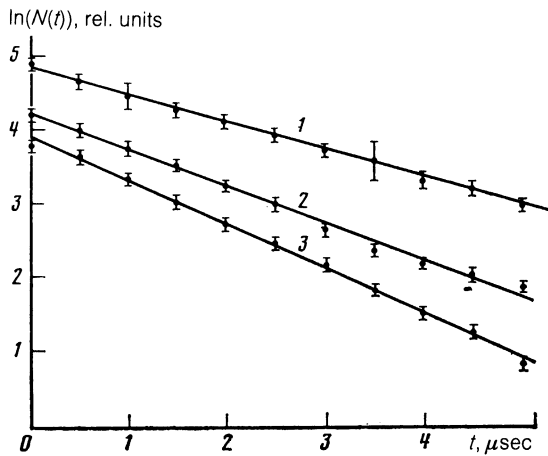
FIG. 3. Time dependences of the population of the 26p level: 1) in the absence of SF_6 from the working chamber, $P_0 = 3 \times 10^{-6}$ Torr; 2) SF_6 pressure $P = 0.94 \times 10^{-5}$ Torr; 3) $P = 1.6 \times 10^{-5}$ Torr.

mine the dependence of the signal on τ, which gave the density of the Rydberg atoms with given values of n as a function of time $N_n(\tau)$ (Fig. 3). This dependence was readily approximated by an exponential function. In the absence of the target gas the argument of the exponential function was practically the same for all the levels with $n = 24$–41. The slope of these curves should be determined by effective time spent by a Rydberg atom in the recording zone, which was governed by radiative decay, collisional or field quenching, and time taken for the atom to leave the recording region (transit time):

$$1/\tau_{\text{eff}} = 1/\tau_r + 1/\tau_q + 1/\tau_t. \tag{3}$$

It is known that radiative lifetimes of highly excited states are long and can be estimated from the approximate formula[11]

$$\tau_r = \tau_0 n^\alpha \tag{4}$$

where for the P series of Na we have $\tau_0 = 8.35$ nsec and

$\alpha = 3.11$. The values obtained from Eq. (4) are in agreement with the calculations reported in Ref. 12, which moreover allow for the reduction in the lifetime because of stimulated transitions under the action of thermal radiation.[13] An analysis of the results reported in Ref. 12 demonstrated that thermal radiation reduces the radiative lifetime of the np levels of sodium with $n > 20$ by a factor of 3–4 on the average. According to our estimates the radiative lifetime for the 28p level at $T \approx 300$–500 K should be $\tau_p \approx 76\,\mu$sec, which is more than order of magnitude higher than the average time spent by the Rydberg atoms in the recording zone. In our geometry this time was $\approx 2.6\,\mu$sec for a one-dimensional Maxwellian distribution of the velocities of the Na atoms with a temperature $T \approx 500$ K, equal to the temperature of the atomic beam source, and it was in agreement with the results of direct measurements.

Introduction of an electronegative target gas at a pressure of 5×10^{-5} Torr resulted in effective quenching of the Rydberg atoms. The rate constant of collisional quenching was found from the formula

$$K_q \approx \frac{1}{N_{\text{tg}}} \frac{\tau_t - \tau_{\text{eff}}}{\tau_t \tau_{\text{eff}}}, \tag{5}$$

where N_{tg} is the density of the molecules of the target gas in the interaction region. The effective lifetime τ_{eff} was deduced from the signal for two different delays τ_1 and τ_2 (N_1 and N_2):

$$\tau_{\text{eff}} = \Delta t \ln(N_1/N_2), \tag{6}$$

where $\Delta T = \tau_2 - \tau_1$. For simplicity in the subsequent analysis we selected $\Delta t = 2\,\mu$sec. The $\tau_1 = 3\,\mu$sec delay ensured avoidance of a background electrical signal due to the charges created in the interior as a result of three-stage photoionization of Na. The ratio N_2/N_1 was determined from ~ 60 measurements accumulated in 1 sec; this was followed by averaging over all the points, which made it possible to increase the precision of the measurements of the rate constant of collisional quenching to 15–20%.
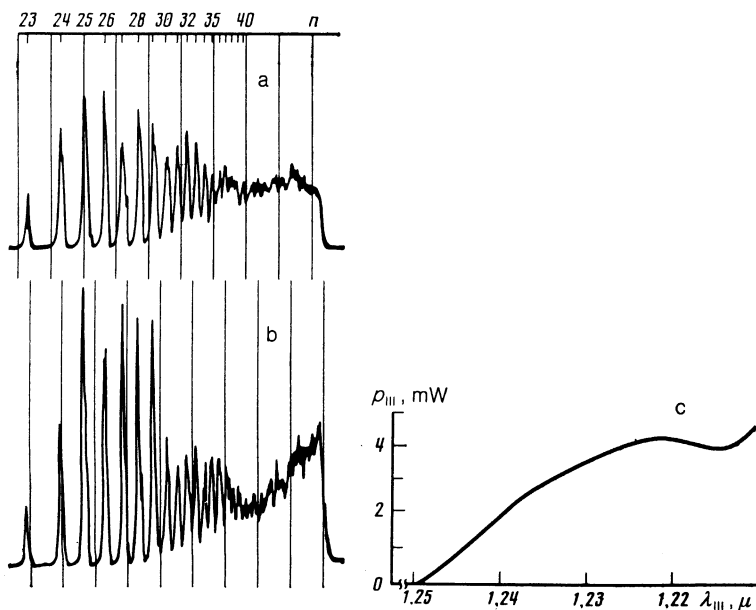

FIG. 4. a) Spectrum of the field ionization of the np series of Na. b) Collisional ionization spectrum. c) Dependence of the power of the third stage of excitation (with LiF:F_2^- laser radiation) on the wavelength.

19   Sov. Phys. JETP **66** (1), July 1987

Beterov *et al.*   19

TABLE I. Rate constants K_q of collisional quenching of highly excited np series of Na by SF_6 molecules.

n	K_q, 10^{-7} cm^3/sec	n	K_q, 10^{-7} cm^3/sec
24	4.40±0.34	33	4.63±0.76
25	4.36±0.65	34	4.33±0.43
26	4.37±0.62	35	4.17±0.52
27	4.99±0.09	36	4.46±0.83
28	4.52±0.80	37	3.97±0.39
29	4.32±0.67	38	4.71±0.78
30	4.39±0.65	39	4.36±0.69
31	4.60±0.43	40	4.76±1.62
32	4.10±0.56	41	4.85±0.86

We also carried out experiments involving direct observations of the formation of negative SF_6^- ions as a result of ionization of SF_6 by collisions with the Rydberg Na atoms. The negative particles were extracted by a pulsed electric field of intensity (~ 100 V/cm) insufficient for the field ionization of the Rydberg atoms with $n = 20$–40. A pulse of negative SF_6^- ions delayed by $\sim 1.5\,\mu$sec was then observed. The delay was due to the transit time of the negative ions traveling to the collector. Figure 4 shows the excitation spectrum of the Rydberg states of Na obtained by the collisional ionization method. For comparison, this figure includes also the spectrum recorded by the field ionization method.

Table 1 gives the results of our measurements of the rate constant of the collisional quenching of the np series of Na by the molecules of SF_6.

3. DISCUSSION OF RESULTS

The results of our determination of the ionization rate constant of the highly excited Na(np) atoms characterized by $n = 24$–40 and colliding with SF_6 molecules are presented in Fig. 5. This figure includes also the ionization rate constants of Xe(nf) for $n = 25$–40, of Rb(ns) for $n = 49$–62, and of Rb(nd) for $n = 38$–106, reported in Refs. 1 and 2. An analysis of these data leads to the following conclusions.

The results obtained for the ionization of states of atoms with different moments are similar. This follows from Eq. (1) because if the motion of an electron is semiclassical, its scattering by a molecule is determined by the electron energy and is independent of its spatial distribution, i.e., of the momentum of the highly excited electrons in an atom. More-

over, the results of the measurements reported for different atoms are similar and the discrepancies between them are less than the random error in each measurement. For example, if we ignore the random error governed by the statistics of the measurements, we find that the average value of the ionization rate constant deduced from our results is, in units of 10^{-7} cm^3/sec, 4.4 ± 0.2 according to our results, 4.0 ± 0.3 according to Ref. 1, and 4.2 ± 0.4 according to Ref. 2. Such an agreement confirms the validity of each of the measurements and makes it possible to reduce the error of the final results.

It follows from these measurements that the ionization rate constant of a highly excited atom colliding with an SF_6 molecule is independent of the principal quantum number of the state. If we assume that this dependence is given by $K_{ion} \propto n^\alpha$, then an analysis of all the data in Fig. 5 gives $\alpha = -0.2 \pm 0.2$ for the power exponent, i.e., within the limits of the experimental error we can assume that this exponent is zero. Then, averaging the results of all three investigations (ignoring the random error in each set of measurements) gives

$$K_{ion} = (4.2 \pm 0.4) \cdot 10^{-7} \text{ cm}^3/\text{sec} . \tag{7}$$

In addition to the ionization rate constant of these highly excited atoms, it is important to consider the information on the products of the investigated process. Measurements indicate that the products of ionization of the process Na(np) + SF_6 are Na$^+$ and SF_6^-. Special measurements indicated that a relative value of the electron current considered as a component of the negative charge current is zero (within an error of up to 10%) for the products of the process. This means that the quantity K_e in Eq. (2) is identical with the rate constant of the attachment of an electron to a molecule. Therefore, the result obtained (7) means that in the energy range 0.8–15 MeV the rate constant of the attachment of an electron to an SF_6 molecule is independent of the electron energy and amounts to $(4.2 \pm 0.4) \times 10^{-7}$ cm^3/sec. The quenching of the autoionizing state of the resultant SF_6^- ion occurs in the field of a positive ion.

We shall now analyze the information on the process of attachment of a free electron to an SF_6 molecule, which had been investigated on many occasions.[14,15] It is known[15,16] that at low electron energies this process produces SF_6^- and at electron energies in the range of 1 eV the reaction products
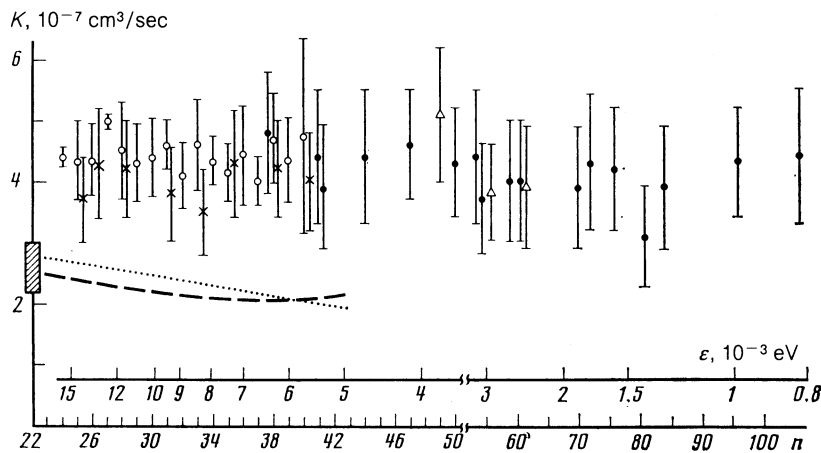

K, 10^{-7} cm^3/sec

FIG. 5. Ionization rate constants of highly excited atoms colliding with SF_6 molecules: O) our results for Na(np), where $n = 24$–40 [$\overline{K} = (4.4 \pm 0.2) \times 10^{-7}$ cm^3/sec]; ✕) results taken from Ref. 1 for Xe(nf), $n = 25$–40 [$\overline{K} = (4.0 \pm 0.3) \times 10^{-7}$ cm^3/sec]; △) results taken from Ref. 2 for Rb(nd), $n = 38$–106 [$\overline{K} = (4.2 \pm 0.4) \times 10^{-7}$ cm /sec]; ▲) results taken from Ref. 2 for Rb(ns), $n = 49$–62 [$\overline{K} = (4.3 \pm 0.7) \times 10^{-7}$ cm^3/sec]. The rate constants of the attachment of an electron to an SF_6 molecule are shown as follows: the dotted line represents formation of slow electrons as a result of photoionization of xenon and the dashed line[15] represents the case of photoionization of xenon; the ordinate gives the value for thermal energies.

are F^- and SF_5^-. A negative SF_6^- ion formed as a result of attachment of an electron of thermal energy is an autoionizing state. Quenching of this state by collisions with atoms and molecules transfers it to a stable state.[1)] At thermal energies the rate constant of the attachment of an electron to an SF_6 molecule, averaged over the Maxwellian distribution of electrons for different quenching gases, has the following value (in units of $10^{-7}\,cm^3/sec$) depending on the source of data: 3.1 (Refs. 18 and 19); 2.1 (Refs. 20 and 21); 2.2 (Refs. 22 and 23); 2.6 (Ref. 24); 2.7–2.8 (Ref. 25); 2.8 (Ref. 26); 2.3 (Ref. 27). Statistical averaging of these data on the attachment rate constant at room temperature gives $K = (2.6 \pm 0.4) \times 10^{-7}\,cm^3/sec$. Measurements reported in Refs. 20 and 21 for different quenching atoms and molecules demonstrate that the results depend weakly on the nature of the quenching particle.

The absence of a temperature dependence of the rate constant of the attachment of an electron to an SF_6 molecule in the temperature range 293–523 K was established in Ref. 23. The rate constants of the attachment of an electron to a SF_6 molecule obtained in Ref. 9 at temperatures 200, 300, 455, and 590 K were 3.1, 3.1, 4.5, and 4.0 in units of 10^{-7} cm^3/sec.

This information applies to the equilibrium conditions during the process when the electron temperature is equal to the temperature of the internal degrees of freedom of the molecule. The additional information applies to the attachment cross sections obtained when the electron energy exceeds the thermal energy. The measurements carried out in Ref. 25 for an electron energy ε amounting to a fraction of an electron volt give the dependence of the cross section for the attachment of an electron to the SF_6 molecule as a function of the energy: $\sigma \propto \varepsilon^{-1.12}$. If these data are extrapolated to thermal energies, the rate constant of the attachment at these energies is found to be $2.4 \times 10^{-7}\,cm^3/sec$.

The attachment of an electron to an SF_6 molecule was investigated also on several occasions at low energies.[28,29,25] Slow electrons were formed by the photoionization of xenon[29] or krypton[25] atoms, which made it possible to improve the electron energy resolution to 5–9 meV. These measurements gave the relative values of the attachment cross sections at various energies and they were then "fitted" to the available data for thermal energies.

The results were approximated by the authors of these papers using strange energy dependences, which gave an incorrect asymptotic behavior of the cross section. However, if we confine ourselves to extrapolation of the attachment cross section to low energies, exceeding the scatter of the electron energies, we find that the rate constant for the attachment of an electron to an SF_6 molecule decreases, according to Refs. 29 and 25, on reduction in the energy.

It should be pointed out that the threshold law for the attachment cross section obeying the Wigner rule[14,30] is $\sigma \propto \varepsilon^{-1/2}$ i.e., the attachment rate constant is independent of the energy in the limit of low energies. These results[28,29,25] show that the rate constant for the attachment of an electron to an SF_6 molecule is independent of the electron energy at low collision energies (below the thermal range) and does not exceed the value of this constant obtained at thermal energies and amounting to $(2.6 \pm 0.4) \times 10^{-7}\,cm^3/sec$.

Comparison demonstrates that the data on the rate constants of the attachment of an electron to an SF_6 molecule at low energies deduced from the ionization cross sections of highly excited atoms differ from the rate constants of the attachment at thermal energies obtained by direct measurements. This difference is equal to four errors for each of these quantities. Such a discrepancy can be explained in two ways. Firstly, we can assume that at thermal energies the attachment rate constant does not reach its asymptotic value where the constant ceases to depend on the electron energy. We should then ignore the results of measurements reported in Refs. 28, 29, and 25 and assume that they are not sufficiently accurate. Secondly, we may conclude that the quenching of the autoionizing states of SF_6 experiencing the influence of a positive ion during ionization of highly excited atoms colliding with SF_6 molecules is more effective than the quenching under the influence of atoms or molecules. This means that the processes of the capture of an electron by an SF_6 molecule when it collides with a free electron and with a "quasi-free" electron in a Rydberg atom have different final products: a negative $(SF_6^-)^*$ ion in vibrationally excited states with different lifetimes in the case of the autoionization (preionization) process. The fact that the lifetime of an autoionizing state $(SF_6^-)^*$ depends on the energy of the incident electron has been confirmed recently by direct measurements involving the capture of SF_6^- ions in a quadrupole trap.[31] Therefore, a more effective stabilization of an excited $(SF_6^-)^*$ ion in the field of a positively charged Na^+ nucleus should increase the rate constant of the attachment process, which is indeed observed experimentally. It should be pointed out that in this case calculations of the type reported in Refs. 32 and 33, based on a simple model of dissociative detachment, become unacceptable. Therefore, we have to conclude the observed discrepancy is not due to a simple difference between the measurement methods, but is the result of a difference between the physical processes themselves. It should be pointed out that this is manifested particularly strongly in the experimental investigations of collisional ionization in the range of intermediate values of the principal quantum number n, but these results will be reported separately.

4. CONCLUSIONS

Laser excitation of Rydberg states, in contrast to electron impact,[34] has high selectivity in respect of the states, ability to carry out experiments at low particle densities, and feasibility of transit-time mass spectrometry with high spatial and temporal resolution. This increases the reliability of the results and makes it possible to obtain more detailed information on the process. In the case under discussion the results obtained in a study of the attachment of a slow electron to an SF_6 molecule and of the ionization of highly excited atoms by collisions with SF_6 demonstrate a divergence between the electron-attachment rate constants obtained on the basis of these two approaches. Although experiments have confirmed the validity of the semiclassical description of an electron in a Rydberg atom, such an electron is only "quasifree" so that the products of the reaction of formation of negative molecular ions are different for free and bound electrons.

[1)]The lifetime of an autoionizing state of SF_6^- exceeds 25 μsec (Refs. 14 and 17).

21   Sov. Phys. JETP **66** (1), July 1987

Beterov *et al.*   21

[1]G. W. Foltz, C. J. Latimer, G. F. Hildebrandt, F. G. Kellert, K. A. Smith, W. P. West, F. B. Dunning, and R. F. Stebbings, J. Chem. Phys. **67**, 1352 (1977).

[2]B. G. Zollars, C. Higgs, F. Lu, C. W. Walter, L. G. Gray, K. A. Smith, F. B. Dunning, and R. F. Stebbings, Phys. Rev. A **32**, 3330 (1985).

[3]B. M. Smirnov, Usp. Fiz. Nauk **131**, 577 (1980) [Sov. Phys. Usp. **23**, 450 (1980)].

[4]B. M. Smirnov, in *Physics of Weakly Ionized Gases* [in Russian], Nauka, Moscow (1972), p. 131.

[5]B. M. Smirnov, in: *Physics of Electronic and Atomic Collisions* (Proc. Ninth Intern. Conf., Seattle, 1975, ed. by J. S. Risley and R. Geballe), University of Washington Press, Seattle, Wash. (1976), p. 701.

[6]M. Matsuzawa, J. Electron Spectrosc. **4**, 1 (1974).

[7]B. M. Smirnov *Excited Atoms* [in Russian], Energoatomizdat, Moscow (1982).

[8]I. M. Beterov, V. L. Kurochkin, and N. V. Fateev, Khim. Fiz. **1**, 957 (1982).

[9]I. M. Beterov and N. V. Fateev, Khim. Fiz. **3**, 1669 (1984).

[10]G. I. Bekov, V. S. Letokhov, and V. N. Mishin, Zh. Eksp. Teor. Fiz. **73**, 157 (1977) [Sov. Phys. JETP **46**, 81 (1977)].

[11]A. N. Klyucharev and N. N. Bezuglov, *Processes of Excitation and Ionization of Atoms by the Absorption of Light* [in Russian], Leningrad State University (1983).

[12]C. E. Theodosiou, Phys. Rev. A **30**, 2881 (1984).

[13]T. F. Gallagher and W. E. Cooke, Phys. Rev. Lett. **42**, 835 (1979).

[14]B. M. Smirnov, *Negative Ions* [in Russian], Atomizdat, Moscow (1978).

[15]H. Massey, *Negative Ions*, 3rd ed., Cambridge University Press (1976).

[16]J. H. Mullen, J. M. Madson, and L. N. Medgyesi-Mitschang, Proc. IEEE **59**, 605 (1971).

[17]R. N. Compton, L. G. Christophorou, G. S. Hurst, and P. W. Reinhardt, J. Chem. Phys. **45**, 4634 (1966).

[18]B. H. Mahan and C. E. Young, J. Chem. Phys. **44**, 2192 (1966).

[19]D. Smith, N. G. Adams, and E. Alge, J. Phys. B **17**, 461 (1984).

[20]F. J. Davis and D. R. Nelson, Chem. Phys. Lett. **3**, 461 (1969).

[21]F. J. Davis and D. R. Nelson, Chem. Phys. Lett. **6**, 277 (1970).

[22]R. W. Fessenden and K. M. Bansal, J. Chem. Phys. **53**, 3468 (1970).

[23]F. C. Fehsenfeld, J. Chem. Phys. **53**, 2000 (1970).

[24]K. G. Mothes and R. N. Schindler, Ber. Bunsenges. Phys. Chem. **75**, 936 (1971).

[25]L. G. Christophorou, D. L. McCorkle, and J. G. Carter, J. Chem. Phys. **54**, 253 (1971).

[26]J. A. Ayala, W. E. Wentworth, and E. C. M. Chen, J. Phys. Chem. **85**, 3989 (1981).

[27]R. W. Crompton and G. N. Haddad, Aust. J. Phys. **36**, 15 (1983).

[28]J. M. Ajello and A. Chutjian, J. Chem. Phys. **71**, 1079 (1979).

[29]A. Chutjian, Phys. Rev. Lett. **46**, 1511 (1981).

[30]E. P. Wigner, Phys. Rev. **73**, 1002 (1948).

[31]M. Vedel, J. Andre, G. Brincourt, Y. Zeraga, G. Werth, and J. P. Schermann, Appl. Phys. B **34**, 229 (1984).

[32]C. E. Klots, Chem. Phys. Lett. **38**, 61 (1976).

[33]A. Chutjian, J. Phys. Chem. **86**, 3518 (1982).

[34]H. Hotop and A. Niehaus, J. Chem. Phys. **47**, 2506 (1967).

Translated by A. Tybulewicz