

ATOMIC SPECTROSCOPY

Spin-Exchange Broadening of Magnetic-Resonance Line of Potassium Atoms

E. B. Aleksandrov*, M. V. Balabas*, A. K. Vershovskii*,
A. I. Okunevich**, and N. N. Yakobson*

* "Vavilov State Optical Institute" All-Russia Scientific Center, St. Petersburg, 190034 Russia

** Ioffe Physicotechnical Institute, St. Petersburg, 194021 Russia

Received January 14, 1999

Abstract—New measurements of spin-exchange cross sections in ground-state potassium atoms are performed. Direct measurements are made of variation of the linewidth of the magnetic-resonance transition $F = 2, m_F = -2 \leftrightarrow m_F = -1$ versus the potassium vapor density. The vapor density was measured by light absorption of a single-frequency laser tuned to the center of the D_1 -line (769.9 nm). The measured cross section is $3.55(0.25) \text{ cm}^2$.

INTRODUCTION

Cross sections of spin-exchange collisions for potassium atoms have been obtained previously in the experiments from the dark decay of the hyperfine polarization produced by optical pumping [1] and also from the linewidth of electron paramagnetic resonance (EPR) [2] in a strong polarizing magnetic field. The results of these measurements are strongly different (by approximately a factor of two), and their direct comparison is hampered since the experiments in [1, 2] were performed at different temperatures and in different magnetic fields, for which the spin-exchange cross sections were measured.

Similar measurements can be performed in weak magnetic fields using optical orientation by selecting isolated lines of the magnetic resonance spectrum. Transitions of the microwave range ($\Delta F = \pm 1$) are convenient due to simplicity of selection of isolated lines even at Earth's magnetic fields. Among these transitions is, first of all, the so-called 0-0 transition, whose broadening is virtually unaffected by the magnetic field nonuniformity. However, the microwave (MW) transitions require buffer gases to reliably suppress the Doppler broadening; the buffer gas contributes to the broadening, which, in combination, makes it much more difficult to single out the spin-exchange component of the linewidth. For this reason, we preferred to use the radio-frequency (RF) transitions $\Delta F = 0, \Delta m_F = \pm 1$, whose spectrum, for the potassium atom, proves to be completely resolved, even in sub-Earth's magnetic fields in cells without buffer gases with the paraffin-coated walls [3].

The difference between this paper and [1] is, basically, that we directly measured concentration of the potassium vapor using optical absorption at the center of the D_1 -line, while our predecessors used the tabu-

lated values of the temperature dependence of the saturated vapor density.

We combined the new measurements of the spin-exchange cross section in potassium atoms with determination of the smallest magnetic resonance linewidth, which is of applied interest since it is among the main factors controlling the ultimate resolving power of the potassium magnetometer, which exhibits, at present, the highest metrological performance [4].

RESULTS AND DISCUSSION

Calculation of the spin-exchange cross section, based on the linewidth of isolated transitions, should use a detailed spin-exchange theory. A large number of theoretical studies have been published to date [5–10] that describe the spin exchange. They all give the same result, under the assumption that collisions occur with the conservation of the total electron spin of the colliding atoms, which is usually justified with a high accuracy when the temperature is not too low. Using this assumption and neglecting nonlinear terms in the spin-exchange rate equations, which is justified at small atomic polarization, the evolution of non-diagonal elements (elements of coherence) of the density matrix $f_{FmF'm'}$ of identical alkali-metal atoms with the nuclear spin I can be described by the equation

$$\left(\frac{\partial}{\partial t} f_{FmF'm'}\right)_{\text{ex}} = -\gamma_{\text{ex}} Z_{FmF'm'} f_{FmF'm'}, \quad (1)$$

where

$$Z_{FmF'm'} = \sum A_{FmF'm'}(L) Z_{FF'}(L), \quad (2)$$

$$A_{FmF'm'} = \frac{2L+1}{2F'+1} (C_{L\Delta F m'}^{F'm'})^2, \quad (3)$$

$$Z_{FF'}(L) = (1 - \delta_{L,1})P_{FF'}(0, 1) + \sum_{K=1}^{2I} P_{FF'}(K, L), \quad (4)$$

$$P_{FF'}(K, L) = 3(2K+1)(2F+1)(2F'+1) \left\{ \begin{matrix} 1/2 & I & F \\ 1/2 & I & F' \\ 1 & K & L \end{matrix} \right\}^2. \quad (5)$$

Equations (2)–(5) containing the Klebsch–Gordan coefficients and $9j$ -symbols [11] are taken from [8], where the most compact formula has been obtained for the quantity $(\gamma_{\text{ex}} Z_{FmF'm'})$ corresponding to spin-exchange contribution to the linewidth of the $Fm \rightarrow F'm'$ resonance transition.

The constant γ_{ex} in (1) is expressed through the spin-exchange cross section σ_{ex} as

$$\gamma_{\text{ex}} = Nv\sigma_{\text{ex}}, \quad (6)$$

where N is the atomic concentration and $v = 4\sqrt{k_B T / \pi M_A}$ is the average velocity of the relative motion of the atoms (k_B is the Boltzmann constant, T is the temperature, and M_A is the mass of the atom). The spin-exchange cross section σ_{ex} is determined by the expression

$$\sigma_{\text{ex}} = \left\langle \frac{\pi}{k^2} \sum_{l=0}^{\infty} (2l+1) \sin^2[\delta_0(l) - \delta_1(l)] \right\rangle, \quad (7)$$

where k is the wave vector, l is the angular momentum of the relative motion of atoms, and $\delta_s(l)$ are phases of partial scattering by the singlet ($S=0$) and triplet ($S=1$) potentials of the alkaline molecule. The broken brackets in (7) denote averaging over the Maxwell distribution of the relative atomic velocities.

It follows from (2)–(5) that the matrix $Z_{FmF'm'}$ from (1) is symmetric with respect to the permutation of pairs of indices and sign inversion of the subscripts m and m' : $Z_{FmF'm'} = Z_{F'm'Fm}$ and $Z_{FmF'm'} = Z_{F-mF'-m'}$. For the case of nuclear spin $I = 3/2$, among 30 elements of this matrix (for the transitions with $\Delta F = 0, \pm 1, \Delta m = 0, \pm 1$), there are only three independent elements for the RF transitions and four for the MW transitions. Numerical values of these elements are given in Table 1.

Table 1

$\Delta F, \Delta m$	$\Delta F = 0$ (RF transitions)			$\Delta F = 1$ (MW transitions)			
	$22, 21$	$21, 20$	$11, 10$	$22, 11$	$21, 11$	$21, 10$	$20, 10$
$Fm, F'm'$	22, 21	21, 20	11, 10	22, 11	21, 11	21, 10	20, 10
$192Z_{FmF'm'}$	54	63	69	92	108	76	60

As follows from Table 1, the spin-exchange widths of the RF transitions, in conformity with the theory, are close to each other, differing by a factor of 1.3 from the smallest to the greatest. For this reason, in the experiments, we restricted ourselves to measuring the width of the line $m = -2 \leftrightarrow m' = -1$, which is the strongest in our conditions.

The spin-exchange broadening was measured in the conventional single-beam configuration of optical orientation with detection of the signal of coherence (see, for example [4]). As the pump sources, a HF potassium electrodeless lamp with a filter for selecting the potassium D_1 -line or an injection laser stabilized by nonlinear resonance in the D_1 absorption line of potassium vapor in an auxiliary cell [4, 12] was used in these experiments with close efficiencies. The light of the source transmitted through a circular polarizer was directed to the main cell with potassium vapor. The cell was shaped as a sphere, 150 mm in diameter, with paraffin-coated walls. The potassium metal was placed into a side arm separated from the cell volume by a glass diaphragm with a calibrated aperture of 1 mm in diameter. After manufacturing, the cell was subjected to the procedure of coating ripening [1] which consisted in its being kept, for several days, under the temperature of 60°C (as the coating ripens, both the potassium vapor density in the cell and the spin relaxation time increase to saturation). The temperatures of the cell and of the side arm were measured independently. The light transmitted through the cell was detected by a silicon photodetector. The optical axis was directed at an angle of 30° to the vector of the dc magnetic field. The HF field was excited by a coil with its axis directed normal to the plane containing the optical axis and the dc field vector. The dc field was produced by a system of coils and stabilized to within 50 μT using a cesium quantum magnetometer.

The signal detected in the transmitted light was the signal of coherence, i.e., it was the light intensity modulated at the frequency of the ac field. In the field 50 μT , all six lines of the transitions $\Delta F = 0, \Delta m_F = \pm 1$ for ^{39}K are totally resolved. For the chosen sign of circular polarization of the light, the strongest resonance was the one with the highest frequency $m_F = -2 \leftrightarrow m_F = -1$. All the measurements were performed at this resonance. The resonance was recorded upon sweeping the RF-field frequency with the lock-in amplification technique. The phase of the reference signal for the lock-in amplifier was chosen so that the resonance looked like a symmetric dispersion-like curve. The width Δf of the resonance was defined as a half of the distance between the extrema of the curve in frequency units. The intrinsic linewidth Δf_0 was determined by extrapolating Δf to zero values of the pump light intensity and of the RF field amplitude. The transverse relaxation rate Γ (relaxation of coherence) is related to the measured linewidth by the formula $\Gamma = 2\pi\Delta f_0$.

The relaxation of coherence of the potassium atoms occurs in the volume of the cell (due to spin-exchange collisions between the atoms), on the surface of the cell, and due to atoms going away from the volume to the side arm of the cell. These two latter contributions can be found by extrapolating the potassium atom concentration to zero when the volume relaxation is removed.

One of the most important problems in measurements of this kind is related to the determination of the potassium atom concentration. The conventional method of measuring concentration by the temperature of saturated vapors, in this case, needs to be additionally justified, since in our experimental conditions, a dynamic equilibrium is established between the processes of arrival of potassium atoms from the side arm through the diaphragm and the processes of irreversible absorption of the potassium atoms by the paraffin coating of the cell. For this reason, the concentration of vapors in the cell volume should be lower than that of saturated vapors in the side arm. Special measurements of the relaxation time of the potassium vapor density in the cell, with the access of atoms from the side arm being blocked, have shown that the vapor absorption rate abruptly increases with increasing temperature of the cell surface [13]. In [1], the D_1 -line absorption of potassium in the operation cell was compared with that in a similar cell, but with its inner walls (also paraffin-coated) covered with a sputtered potassium metal. It was supposed that the saturated potassium vapor pressure was established in this cell. A deficiency of about 20% in the potassium vapor density in the operation cell has been found. By using the same comparison, we have found a constant excess of 26% in the vapor density for the cell without a coating as compared with the vapor density in the cell with paraffin-coated walls in the temperature range 315–343 K (Fig. 1). The experimental dependences were approximated by the function $\log \kappa = A - B/T$, where κ is the absorption index in cm^{-1} and T is the absolute temperature. For both cells, the constant B was found to be equal to 38.6 ± 0.3 . The constant A for the cell with the coating was 10.16 ± 0.05 , and the constant for the glass cell was 10.37 ± 0.08 (in the vicinity of 70°C , a jump of the potassium vapor density in the cell, presumably related to melting of the paraffin film, was observed).

Unlike the authors of [1], we were not sure that the vapor density in the reference cell with uncoated walls corresponded to the saturated vapor density. In addition, the literature data on saturated vapor density of solid potassium are few and differ substantially (by about 30%) between themselves [5, 14]. At the same time, we had every reason to trust measurements of the optical density of the potassium vapor, since we used a single-frequency injection laser stabilized exactly at the center of the D_1 -line (769.9 nm) as a light source in this study (in contrast to [1]) rather than a resonance lamp with its characteristic broad (Doppler) spectral lines

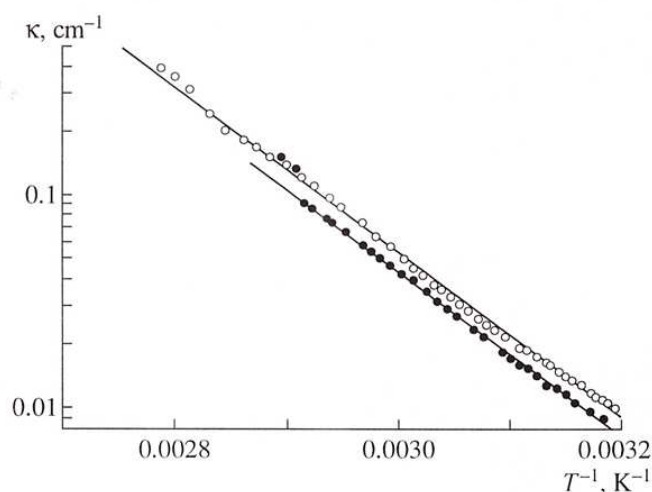


Fig. 1. Temperature dependence of the absorption coefficient of cells with potassium vapors at the center of the D_1 -line. Solid lines: logarithmic approximation (see the text). (○) glass cell, (●) paraffin-coated cell.

and uncertainties of their lineshapes. The laser frequency was stabilized using the nonlinear absorption resonance in the middle of the interval between two extreme hyperfine components of the D_1 -line [12].

The resulting data on optical density allowed us to directly calculate the potassium vapor density (N) using the well-known relations [15]

$$\kappa = \frac{2}{\Delta\nu_D} \sqrt{\pi \ln 2} \frac{e^2}{mc} N f \delta_{hfs},$$

where $\Delta\nu_D$ is the Doppler linewidth expressed through the transition frequency ν_0 (in Hz), temperature T , and atomic weight M (in atomic units); e , m , and c are the electron charge, its mass, and light velocity,

$$\Delta\nu_D = 7.16 \times 10^{-7} \nu_0 \sqrt{\frac{T}{M}}.$$

In the interval 20 – 54°C , the Doppler width varies from 765 to 808 MHz. The oscillator strength (f) was taken to be 0.35. The presence of a hyperfine structure of the spectral line reduces the spectral density of absorption at the line center, which is taken into account by the factor δ_{hfs} . In the case of potassium, this reduction is insignificant due to smallness of the hyperfine splitting compared with the Doppler width (Fig. 2). The figure shows mutual arrangement in the frequency scale of the hyperfine structure components of D_1 -line of ^{39}K (solid lines) and ^{41}K (dashed lines) [16]. The heights of the vertical lines are proportional to intensities of the relevant components. Their positions in the frequency scale, with respect to the line a ($4^2S_{1/2}, F=2 \leftrightarrow 4^2P_{1/2}, F'=1$), are as follows, respectively (in MHz) [17]: b ($F=2 \leftrightarrow F'=2$)—55.6, c ($F=1 \leftrightarrow F'=1$)—461.7,

Table 2

$T, ^\circ\text{C}$	Γ, Hz	$\kappa \times 10^3, \text{cm}^{-1}$	$N \times 10^{-8}, \text{cm}^{-3}$	$\kappa' \times 10^3, \text{cm}^{-1}$	$N' \times 10^{-8}, \text{cm}^{-3}$	$N'' \times 10^{-8}, \text{cm}^{-3}$
20	0.04 (0.03)	1.06	1.31	0.90	1.34	2.4
24	0.05	1.6	1.97	1.37	2.03	3.8
28	0.05	2.4	2.93	2.04	3.03	6.1
36	0.06 (0.07)	5.2	6.31	4.41	6.57	14.8
42	0.13 (0.11)	9.06	10.95	7.66	11.44	27.7
45	0.13	11.9	14.3	10.02	14.97	37.7
46	0.16 (0.17)	13	15.6	10.95	16.36	41.9
50	0.22	18.4	22.0	15.50	23.19	62.1
54	0.35	25.9	30.96	21.77	32.60	91.6

$d (F = 1 \leftrightarrow F' = 2)$ —517.3. Similarly, a' —328.6, b' —359, c' —582.6, and d' —613.

The laser frequency ν_l was stabilized to the middle of the distance between the lines a and d . In this case,

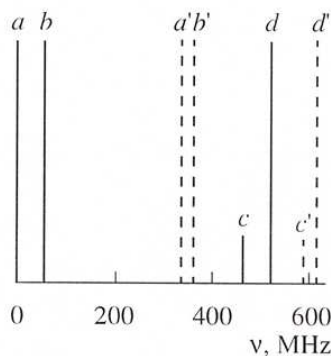


Fig. 2. Mutual position of the hyperfine structure components of the D_1 -line of the potassium atom for the ^{39}K (solid lines) and ^{41}K (dashed lines) isotopes.

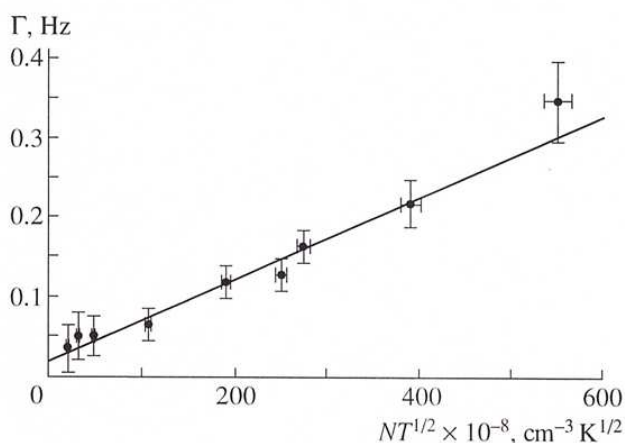


Fig. 3. Dependence of intrinsic linewidth of the magnetic resonance on the potassium atom concentration.

the decrease in the optical density, when shifting from the center of the Doppler line with no hyperfine structure, is determined by the factor

$$\delta_{hfs} = \frac{\sum_j I_j \exp \left[-4 \left(\frac{\nu_j - \nu_l}{\Delta \nu_D} \right)^2 \ln 2 \right]}{\sum_j I_j}$$

In this expression, ν_j denotes the frequency of the j th component with the intensity I_j . According to the results of calculations, δ_{hfs} does not essentially differ from unity, varying in the temperature range 20–54°C from 0.763 to 0.785.

Table 2 contains initial data of the experiment: cell temperature (t), resonance line halfwidth (Γ),¹ absorption index of potassium vapor at the line center (κ), and the calculated concentration N . For comparison, in the last column we give concentration of the potassium saturated vapor (N'') according to the data of [14], reduced by 26%, i.e., assuming that the vapor pressure in the reference cell without paraffin coating corresponds to that of the saturation. As is seen, the concentrations N'' and N differ by a factor of 2 or 3. Such a significant difference made us use additional data on absorption of the laser light (tuned this time to the center of the D_1 -line of ^{41}K). The appropriate values of the absorption index (κ') are also presented in Table 2, together with the concentrations N' calculated from these values. As could be expected, the values κ' proved to be systematically lower than the values κ . At the same time, the values of the calculated concentrations N' coincided with the concentrations N to within 5%. Note that when the cell was illuminated by the laser beam tuned almost exactly to the weaker hyperfine component of the ^{39}K line, slightly higher values of the concentrations were obtained. This is important since it allows us to rule out the assumption about optical pumping by the laser

¹ The linewidths in parentheses are obtained for reverse motion of the cell temperature and characterize the spread of the measured values.

Table 3

Experiment				Theory			
$\sigma_{\text{ex}} \times 10^{14}, \text{cm}^2$	T, K	$B \times 10^4, \text{T}$	source	$\sigma_{\text{ex}} \times 10^{14}, \text{cm}^2$	T, K	$B \times 10^4, \text{T}$	source
2.7 ± 0.7	315–340	0.5	[1]*	1.41	500	0	[16]
				1.34	1000		
				1.25	3000		
$1.45^{+0.12}_{-0.19}$	600	3375	[2]**	1.5	540	0	[19]
				4.88	300		
3.55 (0.25)	293–327	0.5	This work**	4.76	405	0	[18]
				4.68	500		
				4.62	540		

*The cross section was determined from the decay of (\mathbf{SI}) .

**The cross section was determined from the linewidth of the $(2,-2) \longleftrightarrow (2,-1)$ transition.

beam.² Such a pumping could, in principle, have resulted in understated values of the concentration, but repumping between the hyperfine sublevels in potassium is small in any conditions because of the smallness of the hyperfine splitting. In addition, when the pump line is detuned from the line center to its wing, one should expect an increase in the pump efficiency which could reduce the measured concentration. However, this is not the case. Since almost identical data about concentration of the vapor have been obtained from the measurements of absorption in different parts of the line profile, we will use, in what follows, only the data about concentrations obtained by direct measurements of optical density of the potassium vapor.

Figure 3 shows the dependence of the resonance line half-width on the product $X = NT^{1/2}$. Approximation of this dependence by the straight line $\Gamma = \Gamma_0 + \sigma Nv = \Gamma_0 + CX$ allows one to estimate the limiting linewidth $\Gamma_0 = 0.016$ (0.009) Hz and quantity $C = 5.26(0.38) \times 10^{-12}$ Hz/(cm⁻³ T^{1/2}) characterizing the cross section of the process $\sigma = 2\pi C / \{4[k_B / (\pi M_A)^{1/2}]\} = 1.00(0.07) \times 10^{-14}$ cm².

Going back to the cross section σ_{ex} , using (1) and (6), we obtain

$$\sigma_{\text{ex}} = 192\sigma/54 = 3.55(0.25) \times 10^{-14} \text{cm}^2.$$

It is of interest to compare the results of measuring the value σ_{ex} with the data of other authors presented in Table 3. As follows from this table, the value of the cross section obtained by us exceeds the value σ_{ex} given in [1] by 33%. This difference is likely to be caused by an overstated concentration of potassium atoms, which is supported by our data (Table 2). The value σ_{ex} from [2], as seen in Table 3, is smaller than that obtained in the present paper by a factor of 2.5. Such a significant

discrepancy cannot result from inaccuracy in determination of the potassium atom concentration, since, in that paper, the concentration of potassium atoms was determined by comparing the signals of microwave absorption for potassium atoms and for a known quantity of Cu⁺⁺ ions in copper sulfate. The reason for the difference between our result and that of [2] is likely to be related to a significant difference in the temperatures and magnetic fields. As for the temperature, it follows from the theory developed in [16, 18] that the cross section decreases with temperature but not so strongly as to explain the above discrepancy between the measured cross sections. The main factor that can substantially decrease the cross section is the high magnetic field used in [2].

Comparison of the cross sections obtained by us with the values σ_{ex} computed in [16, 18, 19] shows that our estimate of the cross section lies approximately in the middle between the results of studies [16, 19], in which the cross section was calculated in a semiclassical way, and the results of [18], in which the cross section was calculated by the quantum method for small values of l ($l \leq 147$) and by the semiclassical method for large l ($l > 147$).

REFERENCES

- Grossetete, F. and Brossel, J., *Compt. Rend.*, 1967, vol. 264, pp. 381–384.
- Ressler, N.V., Sands, R.H., and Stark, T.E., *Phys. Rev.*, 1969, vol. 184, no. 1, pp. 102–118.
- Aleksandrov, E.B., Bonch-Bruевич, V.A., Provotorov, S.V., and Yakobson, N.N., *Opt. Spektrosk.*, 1985, vol. 58, no. 3, pp. 953–954.
- Aleksandrov, E.B., Balabas, M.V., Pazgalev, A.S., Vershovskii, A.K., and Yakobson, N.N., *Laser Phys.*, 1996, vol. 6, no. 2, pp. 244–251.
- Grossetete, F., *J. Phys. (Paris)*, 1964, vol. 25, no. 4, pp. 383–396.

²This assumption has not been verified in the course of the experiments.

6. Grossetete, F., *J. Phys.* (Paris), 1968, vol. 29, nos. 5–6, pp. 456–466.
7. Pinard, M and Laloë, F., *J. Phys.* (Paris), 1980, vol. 41, no. 8, pp. 769–797.
8. Okunevich, A.I., *Opticheskaya orientatsiya atomov i molekul* (Optical Orientation of Atoms and Molecules), Leningrad, 1987, pp. 65–76.
9. Okunevich, A.I., *Opt. Spektrosk.*, 1994, vol. 77, no. 2, pp. 178–186.
10. Okunevich, A.I., *Opt. Spektrosk.*, 1995, vol. 79, no. 5, pp. 718–728.
11. Varshalovich, D.A., Moskalev, A.N., and Khersonskii, V.K., *Kvantovaya teoriya uglovogo momenta* (Quantum Theory of the Angular Momentum), Leningrad, 1975.
12. Aleksandrov, E.B., Balabas, M.V., Vershovskii, A.K., Ivanov, A.E., Yakobson, N.N., Velichanskii, V.L., and Senkov, N.V., *Opt. Spektrosk.*, 1995, vol. 78, no. 2, pp. 325–333.
13. Balabas, M.V. and Bonch-Bruевич, V.A., *Pis'ma Zh. Tekh. Fiz.*, 1993, vol. 19, no. 7, pp. 6–8.
14. Nesmeyanov, A.N., *Davlenie para khimicheskikh elementov* (Vapor Pressure of Chemical Elements), Moscow: Akad. Nauk SSSR, 1961.
15. Frish, S.E., *Opticheskie spektry atomov* (Optical Spectra of Atoms), Moscow: Nauka, 1963, p. 393.
16. Smirnov, V.M. and Chibisov, M.I., *Zh. Eksper. Teor. Fiz.*, 1965, vol. 48, no. 3, pp. 939–945.
17. Radzig, A.A. and Smirnov, V.M., *Reference Data on Atoms, Molecules, and Ions*, Berlin: Springer-Verlag, 1985.
18. Chang, C.K. and Walker, R.H., *Phys. Rev.*, 1969, vol. 178, no. 1, pp. 198–204.
19. Dalgarno, A. and Rudge, M.H.R., *Proc. R. Soc. (London)*, 1965, vol. A286, no. 1407, pp. 519–524.

Translated by V. Zapasskii