

SPECTROSCOPIC INVESTIGATION OF THE ELASTIC SCATTERING OF SLOW ELECTRONS BY CESIUM AND ARGON ATOMS

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Measurements were made of the shift, due to the presence of cesium and argon atoms, of the absorption lines of cesium near the edge of a series. The results were compared with the theoretically calculated amplitudes of the elastic scattering of electrons by cesium and argon atoms in the electron energy range ~0.005-0.05 eV. Extrapolation of the measured shift to the edge of the series gave the values of the cross section for the elastic scattering of electrons at zero energy.

THE spectroscopic method of determining the effective cross section for the elastic scattering of slow electrons by atoms was first proposed by Fermi.^[1] Fermi showed that an absorption line, corresponding to a transition to a level with a high value of the principal quantum number *n*, was shifted in the presence of a foreign gas by an amount

$$E = E_s + E_p = \pm \frac{\hbar^2}{m} N \sqrt{\pi\sigma_0 - 10\alpha e^2 N^{1/3}}. \quad (1)$$

Here, σ_0 is the cross section for the elastic scattering of electrons by atoms of the foreign gas at an electron energy tending to zero; *N* is the density; α is the polarizability of the foreign gas atoms. Following Fermi, we may say that the total shift of a line is governed by the sum of the shifts due to the scattering (E_s) and polarization (E_p). As a rule, $E_s > E_p$, which allows us to determine the value of σ_0 from the measured shift of a line.

Later, Firsov^[2] discussed the conditions of applicability of Eq. (1) and investigated in greater detail the polarization effect. He showed that the Fermi expression for E_s was valid only if the velocity of an atomic electron in the state with a principal quantum number *n* was so low that the main contribution to the cross section was made by the s-scattering, and the scattering phase δ_0 was much less than unity. Alekseev and Sobel'man^[3] investigated, in a more general form, the relationship between the shift and width of spectral lines near the edge of a series and the amplitude of the electron scattering by the perturbing atoms; they allowed for the scattering contribution of an arbitrary number of partial waves without any restriction on the value of the scattering phase δ_1 .

The results obtained by Alekseev and Sobel'man^[3] are as follows. If the following conditions are satisfied

$$\chi_e = \frac{\pi}{4} \alpha n N \ll 1, \quad \chi_i = \frac{\pi}{4} \alpha \frac{e^2}{\hbar V} N \ll 1, \quad (2a)$$

$$\rho_i = (\pi \alpha e^2 / 4 \hbar V)^{1/3} \ll a_0 n^2 \quad (2b)$$

(*V* is the relative velocity of the perturbing particles, and a_0 is the Bohr radius), then the scattering and polarization effects are statistically independent and they both can be considered in the impact approximation. The distribution of the intensity in a line is then described by a dispersion distribution of width γ and shift Δ :

$$\gamma = \gamma_s + \gamma_p, \quad \Delta = \Delta_s + \Delta_p, \quad (3)$$

where γ_s and Δ_s are associated with the scattering effect, and γ_p , Δ_p are due to the polarization effect,

$$\begin{aligned} \gamma_s &= N \frac{\hbar}{m} \int \left[\frac{4\pi}{q} \sum_l (2l+1) \sin^2 \delta_l \right] W(q) dq \\ &= N \frac{\hbar}{m} \int q \sigma(q) W(q) dq; \end{aligned} \quad (4)$$

$$\Delta_s = N \frac{\hbar}{m} \int \left[\frac{\pi}{q} \sum_l (2l+1) \sin 2\delta_l \right] W(q) dq. \quad (5)$$

Here, $\sigma(q)$ is the effective cross section, δ_l are the phases for the elastic scattering of an electron $\hbar q$ by a perturbing atom; $W(q)$ is the distribution function of the atomic electron velocities in the state *n*. The properties of this function were considered in detail in^[3]. The main contribution to the integrals (4) and (5) is made by the region $0 < q < 1/na_0$. If we restrict ourselves to s-scattering only and if we assume that the scattering

phase is sufficiently small, Eq. (5) reduces to the Fermi expression for E_S .

The following expressions were obtained for γ_p and Δ_p in the impact approximation

$$\gamma_p = 11.4(ae^2/2\hbar)^{2/3}V^{1/3}N, \quad \Delta_p = -^{1/2}\sqrt{3}\gamma_p. \quad (6)$$

The results obtained in [3] allow us to obtain, from the measured width and shift of the lines near the edge of a series, information on the cross section for the elastic scattering of electrons by atoms in the energy range from 0 to ~ 0.05 eV. The line width gives the value of the cross section, and the line shift gives some combination of the scattering phases for different values of l , in which each phase has its own sign. Unfortunately, both these quantities are spread over a fairly wide range of values $q \sim 1/2na_0$, and therefore it is hardly possible to determine directly the scattering phases from the line shifts. However, a comparison of the theoretically calculated phases with the measured line shifts may be useful in checking the accuracy of the calculations. In particular, Alekseev and Sobel'man's [3] calculations of the scattering of electrons by argon atoms showed that the value of the shift was very sensitive to the method of calculation.

There are many published experimental data on the shift of the absorption lines in the principal series of alkaline metals in atmospheres of various gases: He, Ne, Ar, N_2 , H_2 . [4] In one investigation, [5] a study was made of the shift of the Na lines by cesium. This study established that, at first, the shift of the lines increased along the series but then, beginning with $n \sim 15-20$, "saturation" was observed. [4] From this limiting shift, the value of the cross section σ was found using the Fermi formula.

A more detailed analysis of the published data shows that saturation is observed, in fact, only in the case of hydrogen, while in all the remaining gases (investigations were made at $n \lesssim 30$) only a slowing down of the shift is observed. The shift of the sodium lines in cesium [5] was measured only up to $n = 23$.

We investigated experimentally the behavior of cesium lines near the edge of a series in the vapor of pure cesium, measuring first only the line shift. We assumed that the resonance interaction, which did take place in this case, would not produce an additional shift because its effect was a symmetrical broadening of the lines. Moreover, the interaction constant, proportional to the oscillator strength of the resonance transition, was very small for the lines corresponding to the transitions from levels with high quantum numbers.

We investigated the absorption spectrum of cesium vapor. The edge of the principal series of cesium was at the wavelength $\lambda = 3183 \text{ \AA}$; hydrogen and krypton lamps were used as sources of the continuous spectrum. The tube containing cesium was 10 cm long and made of molybdenum glass with fused-in sapphire windows. Metallic cesium was placed in a spur, whose temperature governed the vapor density. In the working volume, the temperature was kept about 30 deg higher than that in the spur. The absorption spectra were obtained with a spectrograph of the DFS-3 type, having a dispersion of 2 $\text{\AA}/\text{mm}$. The spectrum of an iron arc, whose lines were used as standards in the measurements of the absorption line positions, was superimposed on the spectrum under investigation. The spectra were recorded at spur temperatures of about 270, 310, 350, and 400 $^\circ\text{C}$, which corresponded to cesium atom densities ranging from about 0.1 to $2.5 \times 10^{17} \text{ cm}^{-3}$.

The density of cesium atoms N was determined from the temperature of the spur using published data on the cesium vapor pressure. [6] The measurements at $T = 400^\circ\text{C}$ were reported only in Hackspill's work [7] and it was necessary to use extrapolation or calculation formulas. All the papers listed under [6] gave the same value $N = 2.5 \times 10^{17} \text{ cm}^{-3}$ at $T = 400^\circ\text{C}$. The error in the measurement of temperature, amounting to 1 deg, would alter N by 2%.

The measurements were carried out using lines with the principal quantum numbers $n = 18-47$, and in some cases, up to $n = 54$. The wavelengths of the lines were the same for the spur temperatures of 270 and 310 $^\circ\text{C}$. A marked shift of the lines was observed beginning from 350 $^\circ\text{C}$ upward. The accuracy of the measurement of the shift was 0.01 \AA , sometimes 0.02 \AA . Figure 1 shows the results obtained. The abscissa gives the quantum number n , and the ordinate the line shift in cm^{-1} at the spur temperature of 400 $^\circ\text{C}$. The vertical lines indicate the experimental scatter (averaging was carried out for three measurements).

It is evident from Fig. 1 that the shift of the lines along the series is not constant even for $n > 40$. The data for $n > 47$ are unreliable (they are represented by circles in Fig. 1) and, therefore, it is not yet possible to say anything about the behavior of the shift at higher quantum numbers. It is worth pointing out the strongly nonmonotonic nature of the curve, which exceeded the possible experimental error.

We investigated also the influence of argon on the absorption spectrum of cesium at argon pressures at which the conditions of the applicability of

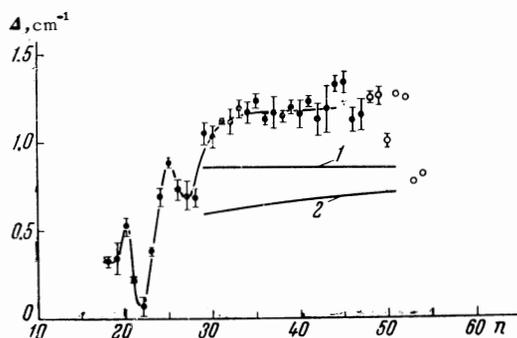


FIG. 1. Shift of the cesium lines under the influence of cesium, plotted as a function of the principal quantum number: ● — experimental data; 1 and 2 — theoretical curves.^[13]

the impact approximation (2a) were satisfied; these pressures were about 150 mm Hg. The measurements were carried out in a sealed tube 200 or 300 mm long at a sufficiently low cesium vapor density. Because of the large number of spectrograms analyzed and the high stability of the results compared with those for cesium, the error in the measurement of the shift was much less. The rms deviation from the average was less than 0.03 cm^{-1} .

Figure 2 shows the results of the measurements of the line shift. The line shift was practically constant for n from 18 to 40–50. The value of the shift at $n \sim 30$ was in good agreement with the results given in ^[8]. At $n = 10$ –15, we were able to measure both components of a doublet and found that they behaved quite differently.

At $n = 10$, the shift of the weak component was about 1.5 times less than that of the strong one. For higher values of n , the difference between the shifts of the components decreased, and at $n = 15$, the shifts of both components were equal, within the limits of the experimental error.

We shall now consider our results.

1. Shift of the cesium lines under the influence of argon. As just mentioned, the components of the cesium doublet behaved in different ways at $n < 15$. According to Fermi, the shift of a line near the limit of a series cannot depend on the properties of the absorbing atom. At $n < 15$, the orbit of an atomic electron is insufficiently large to describe its behavior in such a very simplified way. In fact, the criterion of the statistical independence of the scattering and polarization effects,^[3] given by Eq. (2b), is not obeyed: at $n \sim 15$ –17, the value of ρ_i is of the same order of magnitude as the quantity $a_0 n^2$. We go over to the region of the Van der Waals interaction of two atoms, in which the nature of each of them is important.

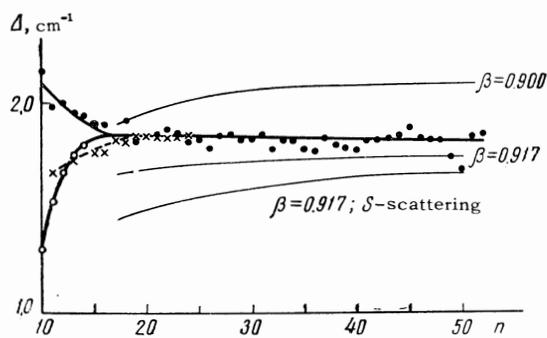


FIG. 2. Shift of the cesium lines under the influence of argon, plotted as a function of the principal quantum number n . The circles represent the experimental data of the present authors: ● — $6^2S_{1/2} - n^2P_{3/2}$ components, ○ — for $6^2S_{1/2} - n^2P_{1/2}$ components; the thin curves are theoretical curves from^[3] (β represents the Slater parameter of the atomic function of argon), × — the experimental data from^[8].

Using our experimental data, we can try to refine the criterion (2b). At $n = 15$, the measured shift is the same for both components of the doublet. With some safety margin, we may assume that the statistical independence of the scattering and polarization effects begins at $n = 17$. For argon ($\alpha = 1.65 \text{ \AA}^3$, according to ^[9]), $\rho_i = 1.8 \times 10^{-7} \text{ cm}$. When $n = 17$, $a_0 n^2 = a_0 R/E = 0.95 \times 10^{-6} \text{ cm}$. Thus, it is sufficient for $a_0 n^2$ to be five times larger than ρ_i .

A comparison of the experimental data and the results of calculations based on the phases of the elastic scattering of slow electrons by atoms has meaning only at $n \geq 15$ –17. Figure 2 shows the theoretically calculated curves taken from ^[3]. In spite of the very strong sensitivity of the calculated shift to the parameters used in the calculations, we find that even at $n \geq 50$, which corresponds to an electron energy $\lesssim 0.005 \text{ eV}$, partial waves with $l \neq 0$ make a considerable contribution to the scattering.

To estimate the cross section at zero energy by means of the Fermi formula, we must know the limiting value of the line shift at the edge of a series. We measured the value of the shift up to $n \sim 50$. With further increase in n , inelastic transitions between neighboring levels become impossible in collisions with atoms. Therefore, we were forced to extrapolate the value of the shift measured at $n \sim 50$ to $n \rightarrow \infty$. Theoretically, this extrapolation is not justified, but the experimental curve at $20 < n < 50$ is practically horizontal. If we assume that the shift at $n \sim 50$ is the limiting value of the shift at the limit of a series, we can estimate the value of σ_0 .

The shift due to the polarization effect, calculated using Eq. (6), amounts to $\Delta_p = 0.35 \text{ cm}^{-1}$ and,

therefore, the shift due to the scattering effect is $\Delta_S = 1.5 \text{ cm}^{-1}$. Hence, we obtain the limiting value of the effective cross section for the scattering of electrons at an energy approaching zero:

$$\sigma_0 = (6.8 \pm 0.8) \times 10^{-16} \text{ cm}^2.$$

2. Shift of the cesium lines under the influence of cesium. We shall estimate first of all the range of applicability of the Fermi treatment, using the refined criterion (2b). The polarizability of cesium is much greater than that of argon, $\alpha = 67.7 \text{ \AA}^3$,^[10] and, therefore, the limit of the applicability of the theory extends to higher values of n . In the Cs-Cs interaction, the limiting value is $n \sim 29-30$. The whole region of the nonmonotonic behavior of the shift (Fig. 1) falls in the range where the criterion (2b) of the statistical independence of the scattering and polarization effects is no longer obeyed. Quantitative comparison with the theory can be made only at $n \gtrsim 29-30$.

The elastic scattering phases for slow electrons incident on cesium atoms were calculated in^[11-13]. To make comparisons with our experiments, we need data on the scattering phases or the behavior of the scattering amplitude at very low energies $0 \leq q \leq 0.1$. The region near $q = 0$ is particularly important since it makes a contribution to the shift of all the lines. Unfortunately, the behavior of the scattering amplitude in the range of energies of interest to us cannot be deduced from the data given in the papers of Stone and Reitz^[11] and Karule.^[12] The necessary data are to be found only in the paper of Alekseev and Vaĩnshtein,^[13] who made a detailed comparison of the calculated results with our experimental ones.

The curves 1 and 2 in Fig. 1 are theoretical ones calculated using the scattering phases, allowing for two and one virtual p -levels in the polarization potential. The use of the adiabatic polarization potential in the calculation of the scattering phases gives a sign of the line shift which is opposite to that observed experimentally.

Thus, the experimentally measured line shift is found, in theoretical calculations, to be a quantity very sensitive to the method of calculation of the scattering phases in the region of very low energies, where the theoretical and experimental investigations of elastic scattering are very difficult.

If we again extrapolate the value of the shift measured at $n \sim 45-50$ to $n \rightarrow \infty$, as we did in the case of argon (we shall stress once again that this operation cannot be regarded as rigorously justified), we can obtain the value of σ_0 . From $\Delta_{\text{meas}} = (1.2 \pm 0.1) \text{ cm}^{-1}$, we calculate from Eq. (6) [assuming that the condition (2a) is satisfied] the shift

due to the polarization effect: $\Delta_p = 0.15 \text{ cm}^{-1}$, and for the cross section at zero energy, we obtain

$$\sigma_0 = (1.5 \pm 0.4) \cdot 10^{-13} \text{ cm}^2. \quad (7)$$

It should be mentioned that, in the case of cesium atoms at $q = 0$, there are two waves, corresponding to the symmetric and antisymmetric scattering with $l = 0$, in contrast to the case of argon, where there is only one wave. Therefore, strictly speaking, the transition from the line shift to the cross section at zero energy is impossible. In practice, however, the majority of the existing calculation methods give $f^- \gg f^+$ (antisymmetric scattering predominates) so that the result given in Eq. (7) is obviously obtained.

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