Band emission spectrum of Ar_2 molecule in the region of the argon $\lambda=1048$ Å($^1P_1-^1S_0$) resonance line

É. T. Verkhovtseva, V. I. Yaremenko, E. A. Katrunova, and Ya. M. Fogel'

Physico-technical Institute of Low Temperatures, Ukrainian Academy of Sciences
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An unresolved system of bands of the transition $^1\Sigma_u^+(0_u^+)\to{}^1\Sigma_g^+(0_g^+)$ of the Ar_2 molecule was observed for the first time in the emission spectrum of a supersonic argon jet excited by an electron beam, on the long-wave side of the $\lambda=1048$ Å($^1P_1-^1S_0$) resonance line. It is shown that the main contribution to the population of the $^1\Sigma_u^+(0_u^+)$ state is made by electron interactions with diatomic and polymer argon molecules.

On the basis of Mulliken's theoretical paper[1] and experimental investigations of the absorption spectrum of molecular argon in the vacuum ultraviolet (VUV) region,[2] the potential curve of the excited electronic state of the argon molecule $^1\Sigma_u^+(0_u^+)$ with the limit of dissociation $^1P_1+{}^1S_0$ has approximately the form shown in Fig. 1. The minima of the potential curves of the considered state $^1\Sigma_u^+(0_u^+)$ and of the ground state $^1\Sigma_g^+(0_g^+)$ correspond approximately to identical intermolecular distances. This means that, according to the Franck-Condon principle, the band system produced in the transition $^1\Sigma_u^+(0_u^+)\to{}^1\Sigma_g^+(0_g^+)$ should have an appreciable intensity and should be located on the long-wave side of the argon $\lambda=1048$ Å resonance line ($^1P_1-{}^1S_0$ transition).

In spite of the indicated circumstances, the band system in question was not observed in the radiation of gas-discharge VUV sources. In[2] this system was registered only in the absorption spectrum of molecular argon. We have therefore searched for the band system of the $^1\Sigma_u^+(0_u^+)\to{}^1\Sigma_g^+(0_g^+)$ transition in the region of the $\lambda=1048$ Å line in the emission of a gas-jet VUV source.[3]

Figure 2 shows the spectra of a supersonic argon jet excited by electron beam in the region 1040–1060 Å at various temperatures T_0 of the gas entering the nozzle.[1)] As follows from the figure, in the temperature interval $\Delta T_0=250$–400 °K, on the long-wave side of the $\lambda=1049$ Å line, emission is observed with an intensity maximum at $\lambda=1052$ Å. Outside the indicated temperature interval, the intensity of the considered emission becomes small, and at $T_0>450$ °K there is no emission with $\lambda_{max}=1052$ Å in the radiation.

According to the data of[4], the absorption spectrum of molecular argon in the VUV region, in the system of bands produced by transitions of molecules between vibrational levels of the ground state $^1\Sigma_g^+(0_g^+)$ and the excited state $^1\Sigma_u^+(0_u^+)$ with a limit of dissociation $^1P_1+{}^1S_0$, the maximum intensity is possessed by the band with

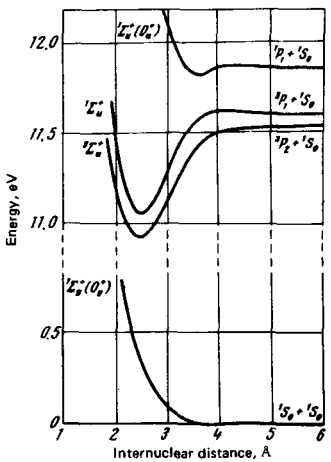

FIG. 1. Potential curves of certain lower states of the Ar_2 molecule.

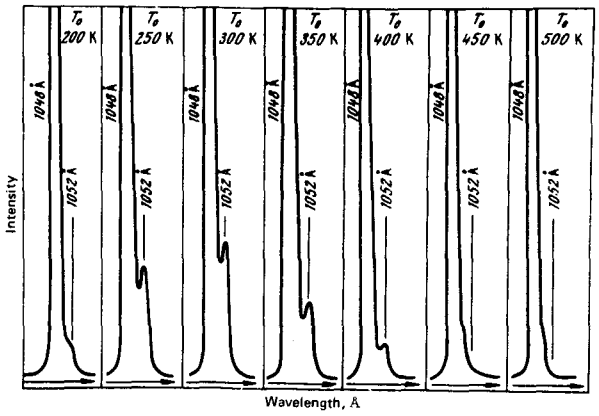

FIG. 2. Emission spectrum of argon jet in the 1040—1060 Å region at various gas temperatures T_0 at the entrance to the nozzle. Electron energy ≈1 keV; current density ≈0.3 A/cm^2; gas pressure at entrance to nozzle 1 atm; the particle concentrations at the point where the jet is excited varies in the range (1 to 3)×10^{17} cm^{-3} in the temperature interval T_0 = 500 to 200 °K.

edge wavelength λ = 1052 Å. There is therefore every reason to assume that the emission with the maximum intensity at λ = 1052 Å, observed in the emission spectrum of an argon jet, is an unresolved system of bands of the $^1\Sigma_u^+(0_u^+) \rightarrow {}^1\Sigma_g^+(0_g^+)$ transition of the Ar_2 molecule.

On the basis of the result of a study[5] of the changes occurring in the spectrum of the VUV emission of a gas-jet source, which occur when the temperature and pressure of the argon entering the nozzle are varied, one can suggest certain reasons why the emission of the $^1\Sigma_u^+(0_u^+) \rightarrow {}^1\Sigma_g^+(0_g^+)$ band system can be observed only in a definite temperature interval ΔT_0. When an electron beam passes through a supersonic jet, the excited Ar_2^* molecules in the $^1\Sigma_u^+(0_u^+)$ state are produced in the following elementary processes[5]:

$$Ar_2(^1\Sigma_g^+) + e \rightarrow Ar_2^*(^1\Sigma_u^+) + e \qquad (I)$$

$$Ar_n + e \rightarrow Ar_2^*(^1\Sigma_u^+) + Ar_{n-2} + e \qquad (II)^{2)}$$

$$Ar^*(^1P_1) + 2Ar(^1S_0) \rightarrow Ar_2^*(^1\Sigma_u^+) + Ar(^1S_0). \qquad (III)$$

As shown in[5], at $T_0 > 450$ °K the concentration of the Ar_2 and Ar_n molecules in the jet is small, and the excited molecules are produced mainly by the process III. However, in view of the low gas pressure in the jet (approximately several tenths of 1 mm Hg), the process III plays a negligible role in the population of the $^1\Sigma_u^+(0_u^+)$ electronic state. This is precisely why there is no emission with $\lambda_{max} = 1052$ Å in the emission of the argon jet at $T_0 > 450$ °K. When T_0 is decreased from 450 to 300 °K, the concentration of the diatomic and light polymer molecules in the jet is greatly increased. At $T_0 < 300$ °K, the number of indicated molecules decreases because of their transformation into more complicated polymer formations, which subsequently develop into microscopic liquid-argon drops that solidify into single crystals at lower temperatures.[5-7] Since the temperature dependences of the intensity of the emission with $\lambda_{max} = 1052$ Å and of the concentration of the diatomic and light polymer molecules are correlated, the appearance in the jet of Ar_2^* in the $^1\Sigma_u^+(0_u^+)$ state can be attributed to processes I and II.

The absence of a system of bands of the transition $^1\Sigma_u^+(0_u^+) \rightarrow {}^1\Sigma_g^+(0_g^+)$ in the emission spectra of gas sources is apparently due to strong self-absorption of the emission in question, caused by the high gas pressure (approximately several hundred mm Hg). The results of the present study show that it is preferable to use a gas-jet source of light rather than a gas-discharge source in the investigation of certain emissions in the radiation spectra of noble gases.

[1)] Details of the experimental technique can be found in[3-5].

[2)] The existence in the argon jet of diatomic Ar_2 molecules and polymer Ar_n molecules produced via adiabatic expansion of the gas leaving the nozzle has been established by mass-spectrometer investigations.[6,7]

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