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SPECTROSCOPY OF ATOMS AND MOLECULES

Excitation of Selenium Vapor by Slow Electrons

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Abstract—Excitation of selenium by slow electrons (2–50 eV) was studied experimentally. Emission spectra were measured in the 200–590 nm region at electron energies of 20, 30, and 50 eV. The spectra show molecular emission bands in the 300–560 nm region and Se atom lines. It was found that, at a temperature of 440 ± 5 K, selenium vapor contains polyatomic molecules, as well as a large amount of diatomic Se_2 molecules. The atomic emission lines are due to dissociative excitation of Se_2.

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INTRODUCTION

Large bodies of experimental data have been collected to date on excitation of the group I, II, III, and VIII atoms. On the other hand, the results for the group VI atoms—in particular S, Se, and Te—are scarce, which is likely due to difficulties in studies of these elements. As has been shown in several works [1–6], depending on the temperature, the vapors of these elements may contain atoms and diatomic and polyatomic molecules.

Selenium, which is a member of this group, is a rather abundant element in nature. It is used in semiconductor technology, photoelements, and UV light sources. Selenium also plays an important role in some biological processes.

In this work, we present results of studies on selenium vapor emission in the 200–590 nm spectral region upon excitation in collisions with electrons in the 2–50 eV region

EXPERIMENTAL

Excitation of selenium was studied optically in the 200–590 nm region using an MDR-2 grating monochromator which has a high light collecting efficiency. A detailed description of PC-controlled experimental setup and the measurement method and calibration procedure for the energy scale of exciting electrons is given in [7].

The electron beam of 1.5 mm in diameter emitted by an oxide cathode was produced by a four-electrode electron gun. The electron beam passed via a vapor-filled cell 12 mm in height and 10 mm in diameter and was detected by a deep Faraday cylinder. For the 3–50 eV energy region, the electron current stability after the passage via the cell was at least 3%.The monochromaticity of the electron beam energy (full width at the half maximum of the current–voltage characteristic derivative) was ~0.6 eV for a current of 25 μA. Selenium vapor entered the cell from a separate resistively heated reservoir containing Se (~5 g). The cell and reservoir were connected by a stainless steel pipe 4 mm in diameter and 60 mm in length. It allowed us to maintain the temperature of the cell and electron gun, which had their own resistive heating, by 20–30 K higher than the Se reservoir temperature to prevent Se vapor condensation in these parts of the experimental setup and provide stability of the whole system during the long term measurements. In all measurements, the Se reservoir temperature was maintained in the 440 ± 5 K region. The vacuum system was pumped by a 500-L/s oil diffusion pump. During the measurements, the residual gases pressure in the vacuum chamber was below 10^{-6} Torr and the pressure in the collision cell was 10^{-3} Torr.

The optical emission excited by collisions with electrons was monitored via quartz windows of the cell and vacuum chamber. The emission was focused on the monochromator entrance slit with use of a two-lens condenser and was recorded using an FEU-106 photomultiplier. Single photoelectron pulses were amplified, shaped by a broad band amplifier–discriminator, and then fed to a pulse counter through an interface card. Depending on the intensity of atomic lines or molecular bands, the exposure time per spectral point was 10–60 s to provide a required statistical scatter of 5–10% in the number of pulses for the maximal signal in a measuring spectrum.

The computer codes that we developed for the automatic control of the experimental measurements allow automatic recording either the Se vapor emission spectra at a fixed energy of the exciting electrons or the optical excitation function (OEF)—the dependence of the atomic line (molecular band) intensity selected with the use of the monochromator on the energy of the exciting electrons. The step in the electron energy scanning spectra can be varied from 2.5 meV to 10 eV.

In our experiments, the emission spectra in the 200–590 nm region were recorded with a spectral step of 1.2 nm and a spectral resolution of 3 nm at fixed electron energies of 20, 30, and 50 eV. The stray signal of the electron gun cathode emission was subtracted from the total signal by means of modulation of the electron beam. The dependence of the spectral sensitivity of the photomultiplier and the MDR-2 monochromator on the wavelength of recorded emission was not taken into account. The OEFs were measured by scanning the electron energies in the 2–50 eV region with a step of 150 meV.

It should be noted that special attention was given to the calibration of the electron beam energy scale. Two calibration methods were used. The first method is based on the shift of the voltage-current characteristic of the electron current to the collector, while the second uses a sharp maximum at an energy of 14.2 eV in the luminescence excitation cross section of second positive system of N_2, $\lambda = 337.1$ nm ($C^3\Pi_u \rightarrow B^3\Pi_g$) [8]. To obtain a sufficient concentration of N_2 for measuring the OEF of the $\lambda = 337.1$ nm luminescence, the pressure of residual gases in the chamber was deliberately elevated by a factor of 5. The accelerating voltage was determined from the difference in positions of this maximum on the measured OEF and its literature value [8]. This procedure allowed us to calibrate the electron beam energy scale with an accuracy of ±50 meV.

In this work, we report the first results on studies of selenium vapor excitation by electrons in the energy region from the threshold and up to 50 eV.

DISSCUSSION OF RESULTS

Figure 1 shows selenium vapor emission spectra in the 200–590 nm region recorded at fixed electron energies of 20, 30, and 50 eV.

As it was noted above, selenium vapor has a complex temperature dependent composition [4, 5] consisting of diatomic and polyatomic molecules Se_n (n = 3–8). Unfortunately, partial concentrations of these molecules in Se vapor at the temperature of our experiment, $T = 440 \pm 5$ K, cannot be readily determined. The reason for this is that the data given in numerous works, including [4, 5] are rather contradictory. Therefore, we can only assume that the broad band in the 300–560 nm region is due to emission from electronically and vibrationally excited molecules Se_n (n = 2–8). As is seen this band may be separated at least on two bands with maximums in the 310–320 and 400–420 nm regions. It should be noted that there are several peaks in the 300–560 nm region. In contrast to sulfur vapor, these peaks are poorly resolved. It appears likely that these peaks are also due to vibrationally excited selenium molecules.

First we consider the excitation of the molecular emission bands. We measured the OEFs for several spectral fragments of $\Delta\lambda = 3$ nm in width within the 300–560 nm band including its maximum and wings. Figure 2 shows the OEFs for the λ = 360, 383, 449, and 489 nm spectral regions. As is visible, the low excitation threshold is common for all spectral regions and equal to 3.7, 3.2, 2.7, and 2.5 ± 0.2 eV, respectively. This implies excitation of transitions between the low-

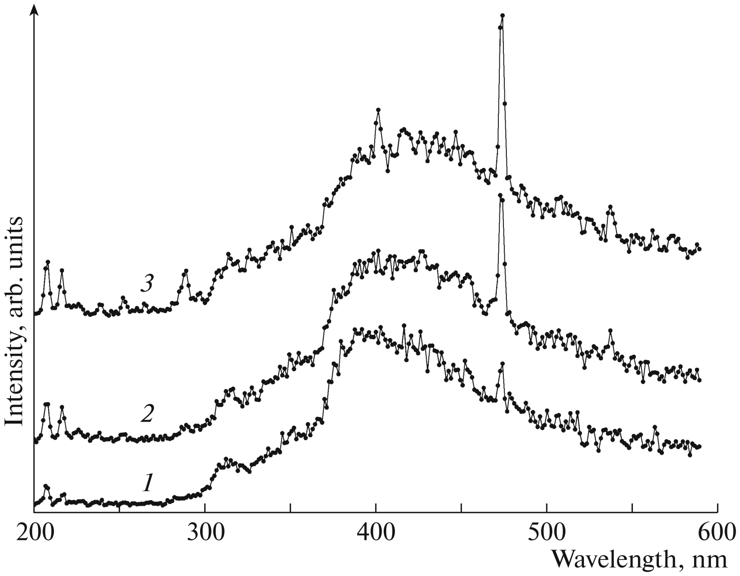

Fig. 1. Optical emission spectra of selenium vapor at energies of exciting electrons of (*1*) 20, (*2*) 30, and (*3*) 50 eV.

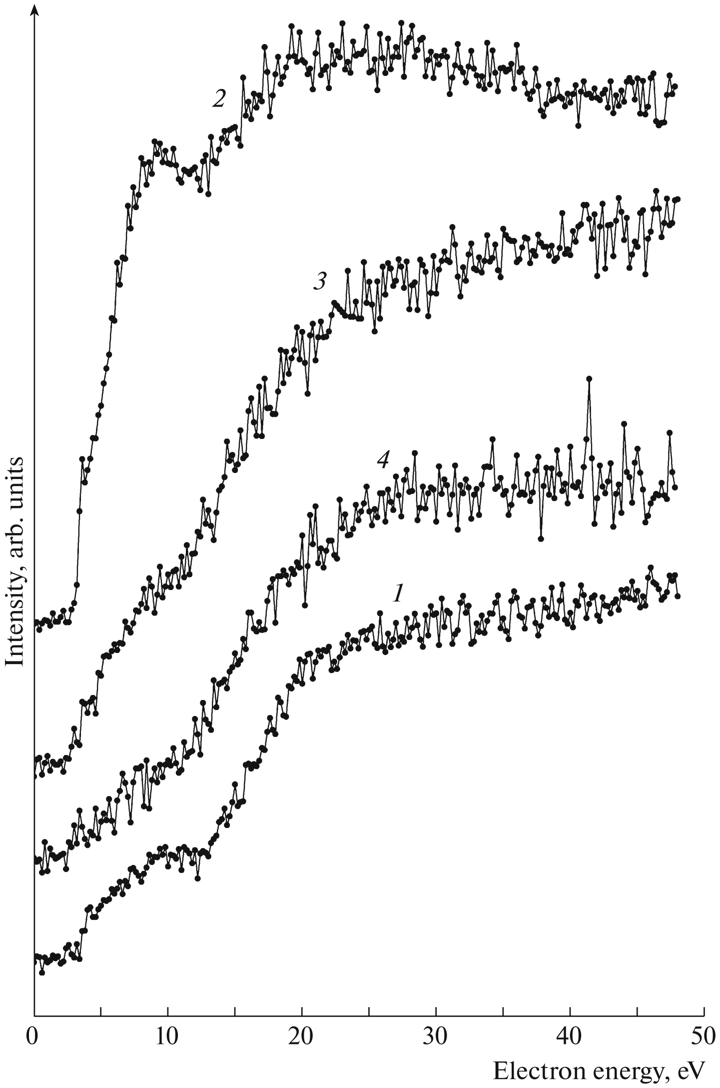

Fig. 2. Optical excitation functions of selenium molecules emission at λ = (*1*) 360, (*2*) 383, (*3*) 449, and (*4*) 489 nm.

est vibrational level of the ground electronic state of selenium molecule and its first electronically and vibrationally excited states. Near the excitation threshold, the majority of OEFs display a sharp increase with the maximum at an energy of ~10 eV and a steeper growth as the energy of the exciting electrons increases further. In the 4–15 eV energy region, the measured OEFs display structural features in some spectral regions that indicate the existence of resonance effects in the excitation mechanism of selenium molecules.

We now consider atomic spectral lines of selenium. Figure 3 shows OEFs of two resonance lines of the Se atom, λ = 207.5 nm ($4p^4\ {}^3P_2$–$4p^35s\ {}^5S_2^0$) and λ = 216.4 nm ($4p^4\ {}^3P_1$–$4p^35s\ {}^5S_2^0$), as well as lines λ = 473.1/473.9/474.2 nm ($4p^35s\ {}^5S_2^0$–$4p^36p\ {}^5P_{3,2,1}$) and λ = 536.5/537.0/537.4 nm ($4p^35s\ {}^5S_2^0$–$4p^36p\ {}^5P_{0,2,1}$). It should be noted that these spectral lines were observed by Smirnov [9] in studies of the dissociative excitation of the Se atoms. Their threshold energies are 5.97, 5.97, 8.59, and 8.62 eV, respectively. There is no molecular emission in the spectral region of the first two lines, i.e. the background intensity is zero. For the other two lines, the intensity of the background emission is significant. As expected, the OEFs of the λ = 207.5 and 216.4 nm lines, which originate from a common upper level, are nearly identical (Fig. 3). These OEFs display a well defined threshold at an energy of 9.6 ± 0.5 eV followed by a fast increase with a maximum at ~17 eV and a further increase starting at an energy of 22 eV and up to 35 eV.

Our results [9] confirm the formation of excited selenium atoms near the excitation threshold in the process

$$\mathrm{Se}_2 + \mathrm{e} \rightarrow \mathrm{Se}^* + \mathrm{Se} + \mathrm{e}', \qquad (1)$$

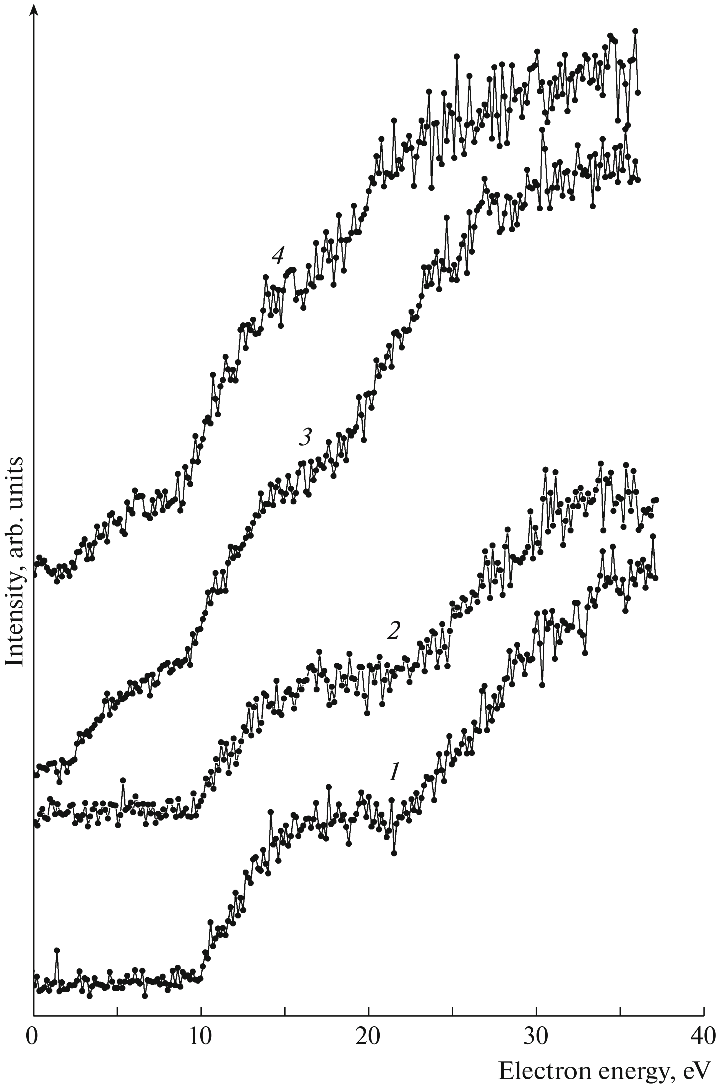

Fig. 3. Optical excitation functions of the Se atom lines λ = (*1*) 207.5, (*2*) 216.4, (*3*) 473.1/473.9/474.2, and (*4*) 536.5/537.0/536.4 nm.

which was proposed in studies of dissociative excitation of the Se atoms in collisions with electrons. The threshold of this reaction is determined by the excitation energy of the upper level of the 5.97 eV spectral line and the dissociation energy of the Se_2 molecule, which is 3.1 eV; i.e. the threshold energy is 9.07 eV. The OEFs thresholds of the λ = 207.5 and 216.4 nm lines are at 9.6 ± 0.5 eV (Fig. 3), which supports mechanism (1). On the other hand, it appears hardly possible to explain the further growth in the cross section of these lines in the energy region above ~22 eV by the process

$$Se_2 + e \rightarrow Se^* + Se^* + e' \qquad (2)$$

resulting in excitation of both atoms to the $4p^35s\ {}^5S_2$ state or another state lying high in energy, because the energy required for process (2) is well below 22 eV (15.04 eV).

The OEFs of the λ = 473.1/473.9/474.2 and λ = 536.5/537.0/537.4 nm lines (Fig. 3) have a similar character. In the energy region from the threshold at ~3.6 eV and up to ~12 eV, these OEFs mirror the OEF of the molecular emission. The further abrupt increase is due to excitation in reaction (1) of the upper levels of these lines, $4p^36p\ {}^5P_{3,2,1}$ and $4p^36p\ {}^5P_{0,2,1}$, while the increase in the energy region above 22 eV mirrors the behavior of the OEFs of the λ = 207.5 and 216.4 nm lines.

The OEF of the λ = 489 nm band (Fig. 2) appears to be the most interesting one. There is an overlap between the 300–560 nm molecular emission band (Fig. 1) and the Se atom line λ = 488.7 nm ($4p^4\ {}^3P_1$–$4p^4\ {}^1S_0$), which has an excitation threshold at 2.78 eV. The excitation threshold in our experimental OEF is at ~2.5 ± 0.2 eV, i. e. corresponds to the molecular emission threshold, while the further increase at an energy

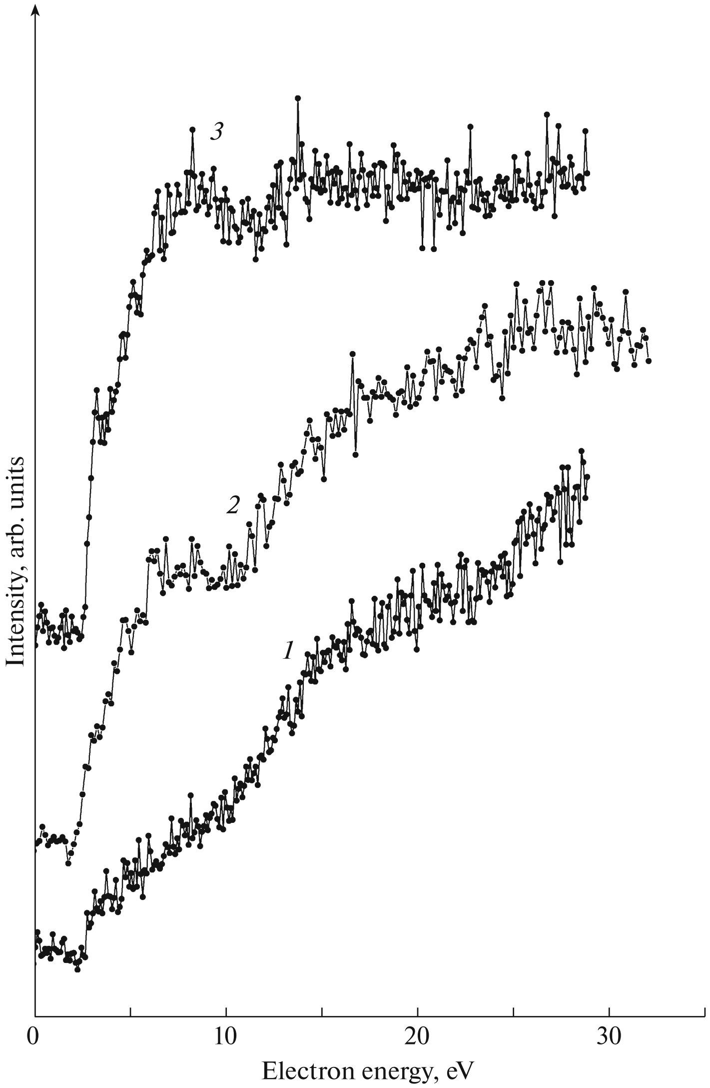

Fig. 4. Optical excitation functions of the Se atom line λ = (*1*) 473.1/.9/474.2 nm and molecular emission at λ = (*2*) 453 and (*3*) 400 nm.

of ~6 eV is another confirmation of excitation mechanism (1) because the required energy in this case is 2.78 + 3.1 = 5.88 eV.

Our studies of OEFs of atomic lines and molecular bands, as well as in some selected regions of the 300–560 nm continuous band, showed that a more detailed interpretation of the obtained results requires more highly monochromatic beam of the exciting electrons. Therefore we continued studies using a home built hypocycloidal electron monochromator (HEM) capable of providing a highly monochromatic electron beam. A detailed description of the monochromator design and operation principle is given in [10]. The design of the HEM used in the present experiments provides an electron beam in the excitation region (vapor filled cell) of ~0.3 mm in diameter and monochromaticity of 0.1–0.2 eV at a electron current of 400–800 nA. Thus, the study of electron impact excitation of selenium was continued with the use of an electron beam with a three to six times better monochromaticity in comparison with the electron beam provided by the four-electrode electron gun.

With the use of HEM we measured the OEFs of the most intense Se atomic lines and molecular emission for several selected spectral regions of the 300–560 emission band. Figure 4 shows the OEFs of the Se atom line λ = 473.1/473.9/474.2 nm and the molecular emissions at λ = 453 and 400 nm. The scanning step of the exciting electron energy was 100, 150, and 100 meV, respectively. The monochromaticity of the electron beam in measurements was 180, 200, and 110 meV, respectively.

First, we consider the OEF of the λ = 473.1/473.9/474.2 nm atomic line (Fig. 4). The behavior is similar to the OEF of this line shown in Fig. 3 and repeats the OEF of the molecular emission. However, in comparison with Fig. 3, the OEF spectrum in Fig. 4 displays more clearly the excitation threshold of the molecular "substrate" at ~2.8 eV, as well as other spectral features at energies of ~3.9, 8.6, 13.2, 16.8, and 25 eV. The presence of these structural features supports our conclusion that resonance phenomena are present in excitation mechanisms of selenium molecules.

In comparison with the OEF of the molecular emission at $\lambda = 449$ nm (Fig. 2), the OEF of the spectrally close $\lambda = 453$ nm molecular emission (Fig. 4) has a very sharp threshold at 2.3 ± 0.1 eV and rather clearly pronounced spectral features at 3.5, 5.1, 6.6, and 11.8 eV, which are hardly seen on the OEF of the $\lambda =$ 449 nm emission (Fig. 2). A similar state of affairs holds for the OEFs of the molecular emission at $\lambda =$ 400 nm (Fig. 4) and spectrally close molecular emission at $\lambda = 383$ nm (Fig. 2). The OEFs of the $\lambda =$ 400 nm emission (Fig. 4) display a sharp threshold at 2.7 ± 0.1 eV and pronounced spectral features at ~3.5, 4.8, 5.4, 8.6, 12.9, and 14 eV. One may conclude again that these spectral features on the OEFs of the molecular emissions indicate resonance phenomena in excitation mechanisms of selenium molecules. It should be also noted that the threshold energies for molecular emissions determined with the use of a highly monochromatic electron beam from the HEM are 0.4–0.5 eV below those in previous experiments.

Thus, the large body of experimental data on excitation of selenium vapor by low energy electrons collected in the course of the present study show that, at $T = 440 \pm 5$ K, selenium vapor contains virtually no Se atoms, while the main component is Se_2 molecules.

CONCLUSIONS

Electron impact excitation of selenium was studied in a vapor-filled cell with the use of the optical spectroscopy method. Emission spectra of selenium vapor were studied in the 200–590 nm spectral region at fixed energies of exciting electrons of 20, 30, and 50 eV. It was shown that, at a temperature of ~440 K, selenium vapor contain virtually no Se atoms, while the main component is the Se_2 molecules. Two broad molecular emission bands and six atomic lines were observed and attributed in emission spectra. The optical excitation functions were measured both for the atomic lines and molecular bands. With the use of a highly monochromatic electron beam, we obtained energies of excitation thresholds and structural features of OEFs with a high accuracy. This allowed us to determine excitation mechanisms of the Se atom emission lines. It was also established that the excitation of the emission from electronically and vibrationally excited molecular energy levels involves resonance processes.

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