ELECTRON-IMPACT EXCITATION OF GAS-PHASE SULFUR

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Optical emissions of gas-phase sulfur induced by low-energy electrons were studied experimentally in the range 270–550 nm. Molecular bands in the range 280–480 nm and lines of S atoms formed mainly via dissociative excitation of S_2 molecules were observed in the spectrum. Optical excitation functions for the 19 most intense atomic and ionic spectral lines and molecular bands in the range 2–50 eV were measured.

Keywords: electron, atom, molecule, excitation, dissociation.

Introduction. Molecular states of sulfur (S_2, S_3, …, S_8) were mainly observed during vaporization of S from the condensed state into the gas phase at 350–750 K [1, 2]. However, mass spectroscopic investigations in our laboratory of the ionization of gas-phase S in the range 300–700 K showed that S_2 and S_8 in addition to a small amount of S atoms and fewer S_n molecules ($n = 3–7$) dominated the mass spectrum. Therefore, it seemed interesting to study optical emission stimulated by collisions of low-energy (2–50 eV) electrons with gas-phase S. Sulfur is incorporated into several amino acids (cysteine, methionine), vitamins (biotin, thiamine), and enzymes [4]. Redox reactions involving it supply energy for chemical syntheses. Sulfur occurs also in the atmosphere of several cosmic objects. It is a very common element in the universe and interstellar space [5]. Finally, S is a powerful source of optical radiation in the far-UV and near-VUV spectral regions [6]. All this is responsible for the continuing interest in various physical and chemical properties of S.

Herein we present results from a study of optical emission in the range 270–550 nm that was stimulated in collisions of low-energy electrons (2–50 eV) with gas-phase S.

Experimental. Excitation of S was studied using an optical method with an MDR-2 high-aperture diffraction monochromator in the range 270–550 nm on an automated apparatus. The apparatus and procedures for measuring and calibrating the beam energy of exciting electrons were described in detail [7]. The beam diameter was 1.5 mm for electrons emitted by an oxide cathode. The beam was formed by a four-electrode electron gun, passed through a gas-filled cell 12 mm high and 10 mm in diameter, and was detected by a deep Faraday cup. The energy of electrons in the beam (full width at half-height of the distribution maximum of differentiated voltammetric characteristics) was ~0.5 eV at 20 μA. Gas-phase S was fed into the collision cell from a separate resistance-heated reservoir loaded with S (~5 g) through a thin-walled tube 4 mm in diameter and 60 mm long. This enabled the temperatures of the collision cell, electron beam, and Faraday cup, which had their own independent resistance heaters, to be maintained 20–30 K above the temperature of the S reservoir. Thus, condensation of gas-phase S on the components of the aforementioned electron-optical system was avoided. The S reservoir temperature for all measurements was maintained within 335 ± 2 K. The vacuum chamber was evacuated using an oil pump at 500 L/s. The residual gas pressure in the vacuum chamber during the measurements was <10^{-6} Torr.

Emission resulting from collisions of electrons and gas-phase S passed through quartz windows of the collision cell and vacuum chamber, was focused using a dual-lens condenser onto the input slit of the MDR-2 diffraction monochromator (grating 1200 lines/mm, reverse dispersion 2 nm/mm), and was detected by an FEU-106 photoelectron multiplier. Single FEU photoelectron pulses were pre-amplified, shaped by a broad-band amplifier-discriminator, fed through an interface card into a pulse counter, and stored in a PC. The signal at each measurement point was accumulated for 10–60 s of exposure depending on the intensity of the emitted spectral lines or molecular bands in order to ensure that the measurement accuracy was better than 5–10% at the emission maximum.

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Application programs developed by us allowed S emission spectra at fixed energies of bombarding electrons and with a given rotation of the monochromator diffraction grating drum to be recorded automatically. Also, energy dependences of the emission intensity of isolated lines, bands, or spectral regions, i.e., optical excitation functions (OEF), were measured. The bombarding electron energy for OEF measurements could be scanned in steps from 2.5 meV to 10 eV.

Emission spectra of S in the range 270–550 nm were recorded by scanning wavelength in steps of 0.548 nm and spectral resolution $\Delta\lambda = 2$ nm with fixed exciting electron energies of 8, 20, and 50 eV. Background emission from the electron-gun cathode that impinged on the FEU was subtracted from the total signal by modulating the exciting electron beam. The spectral sensitivity of the FEU and the spectral characteristics of the monochromator transmission were not considered. Electron energy during OEF measurements was scanned in the given range (2–45 eV) in steps of 150 or 200 meV. Portions of the OEF before the threshold were scanned in steps of 100 meV for more precise measurements.

Special attention was paid to calibrating the energy of the exciting electron beam. This was done in two ways. These used the shift of the voltammetric characteristics of the electron current on the collector and the sharp maximum at 14.2 eV in the excitation cross section of the spectral band for the second positive system of molecular N_2 at $\lambda = 337.1$ nm ($C^3\Pi_u \rightarrow B^3\Pi_g$) [8]. The OEF of this band (the vacuum in the chamber was artificially degraded by ~5 times so that the residual gases provided the concentration of N_2 molecules required for the measurements) was measured in order to perform the second method. The difference between the energy positions of the maximum of the OEF measured by us and that determined before [8] yielded the contact potential difference between the cathode and the electron detector. This procedure allowed the energy of the electron beam to be calibrated to ±50 meV.

Results and Discussion. Emission spectra of S were measured in the range 270–550 nm with bombarding electron energy 8, 20, and 50 eV. Energy dependences of the emission intensity of 19 atomic spectral lines and molecular S bands in various spectral regions ($\lambda = 282.9$, 290, 293, 336.9, 376, 393.3, 407, 414.2–415.3, 419.3, 423, 425, 447.8, 456, 468, 469.4–469.6, 501, 514, 527.9, and 543–545 nm) were studied in detail in the energy range 2–45 eV. The S reservoir temperature was varied from 320 to 380 K with the shape of the emission spectra remaining practically unchanged. Figure 1 shows that the emission spectra were rather complicated. A large number of well resolved lines and bands was observed already at exciting-electron energy 8 eV on the background of continuous emission in the range 280–480 nm. The intensity of the continuous component of the emission spectrum increased considerably as the bombarding-electron energy increased. Also, new discrete lines appeared, especially in the range 480–550 nm. Because the excitation threshold of S atomic spectral lines in the spectral region was >8 eV, it was concluded that the emission spectrum for $E_{ex} = 8$ eV was related to excitation of S molecules. Considering the rather large distance between separate spectral lines, it could be assumed with high probability that this spectrum was due to excitation of S_2 molecules with S atomic lines superimposed on it for electron energies 20 and 50 eV.

Spectral lines (nm) of atomic S could be identified in the emission spectra at 469.41/469.5/469.63 ($3s^23p^35p^5$ $P_{1,2,3}$–$3s^23p^34s^5$ S_2^0) and 527.81/527.86/527.89 ($3s^23p^35p^3$ $P_{2,1,0}$–$3s^23p^34s^3$ S_1^0). The excitation thresholds of these lines were 9.16 and 9.21 eV. Several lines of S^+ were also identified at $\lambda = 393$, 414.2/414.5/415.3, and 542.8/543.2/545.3 nm. The excitation thresholds of these lines were 19.4, 18.88/18.86/18.84, and 15.94/15.89/15.86 eV, respectively. It should be noted that the lines for S and S^+ that were observed by us in addition to strong bands of S_2 ($B^3\Sigma_u^- - X^3\Sigma_g^-$) were present in emission spectra of gas-phase S in a high-voltage (3–5 kV) discharge [9]. Using those results [9], we identified seven spectral emissions of S_2 molecules at $\lambda = 282.9$, 290, 293, 336.9, 394, 419.3, and 447.8 nm.

OEF of 19 spectral lines, molecular bands, and portions of the continuous band emission at 280–480 nm were also studied. Energy dependences for excitation of seven emissions in isolated portions of the continuous emission band at 280–480 nm, both at the narrow maximum, e.g., $\lambda = 501$ nm ($\Delta\lambda = 3$ nm) and in the broader spectral range, e.g., $\lambda = 419$–428 nm ($\Delta\lambda = 9$ nm), in addition to the aforementioned atomic and ionic lines and molecular bands in various portions of the continuous spectrum were measured.

As mentioned above, a small amount of S atoms and S_n molecules ($n = 2$–8) was present in gas-phase S at ~335 K [1, 2]. Therefore, it was complicated to associate unambiguously the observed spectra with an actual molecule. Furthermore, the probability of forming the excited states of these species could differ by many times, even an order of magnitude, through the interaction of electrons at a given energy with the various species [9]. Nevertheless, an analysis of the results indicated that the observed spectral lines were most probably due to decay of S_2 excited states. This could be confirmed firstly by mass spectrometric studies in our laboratory of gas-phase S ionization [3]. It was shown that S_2 and to a lesser extent S_8 dominated in the gas phase at 300–700 K. Secondly, the threshold excitation energy of one of the lower states of molecular S was ~4 eV in a study of the peri-threshold excitation of gas-phase S in control experiments using electron spectroscopy and a hypocycloidal electron spectrometer. This agreed well with energy thresholds for molecular emissions in portions of
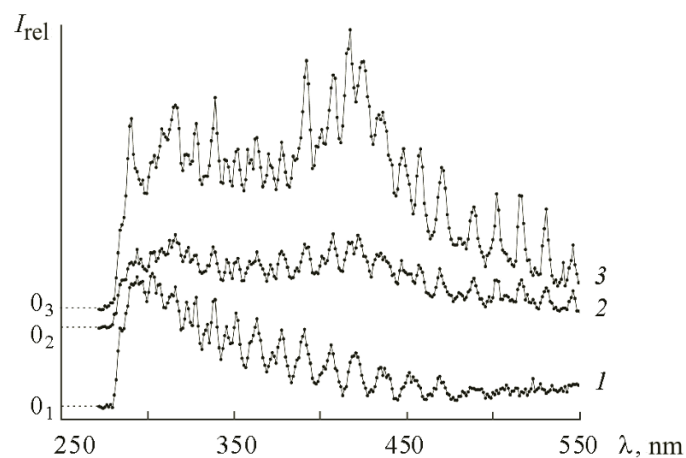
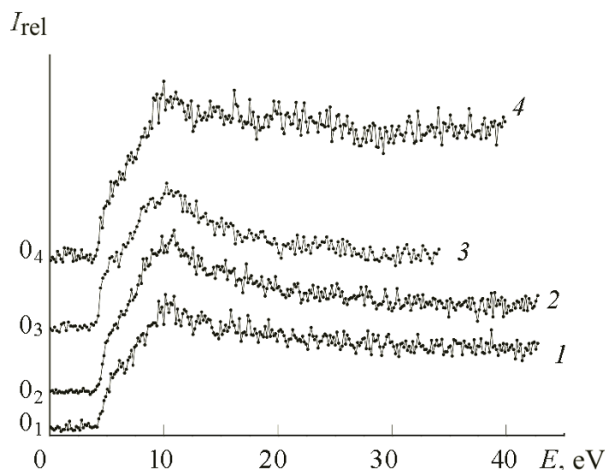Fig. 1. Optical emission spectra of gas-phase S for exciting-electron energies 8 (1), 20 (2), and 50 eV (3).

Fig. 2. Optical excitation functions of S_2 spectral emissions: $\lambda = 282.9$ (1), 290 (2), 293 (3), and 336.9 nm (4).

the continuous emission band at 280–480 nm ($\lambda = 282.9$, 290, 293, and 336.9 nm) in the OEF that were measured by us (Fig. 2). It is noteworthy that the shape of emission spectra measured by us reproduced well the characteristic spectrum of S_2 with clearly resolved vibrational states.

Excited states of S_2^* could also be formed by decomposition of S_8 molecules during interaction with electrons. However, the molecular dissociation energy had to be considered in this instance. For example, the reaction

$$e^-(E) + S_8(X) \rightarrow 4S_2(X) + e^-(E_s),$$
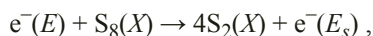
where X is the molecular ground state without excitation of vibrational levels; E_s, the kinetic energy of the scattered electron, had dissociation energy 4.35 eV [10]. Therefore, the continuous emission band at 280–480 nm in spectra with exciting-electron energies 20 and 50 eV was much stronger than that in the spectrum with energy 8 eV, where the energy was less than the total energy of S_8 molecular dissociation and subsequent excitation of S_2 molecules.

Figure 2 shows that all OEF of molecular emissions had a sharp excitation threshold at 4.3 ± 0.3 eV, a rapid rise of excitation cross section up to ~5–6 eV (where a maximum was observed), a further increase of the cross section with a maximum at ~10 eV, and a subsequent drop of the excitation cross section with increasing bombarding-electron energy.
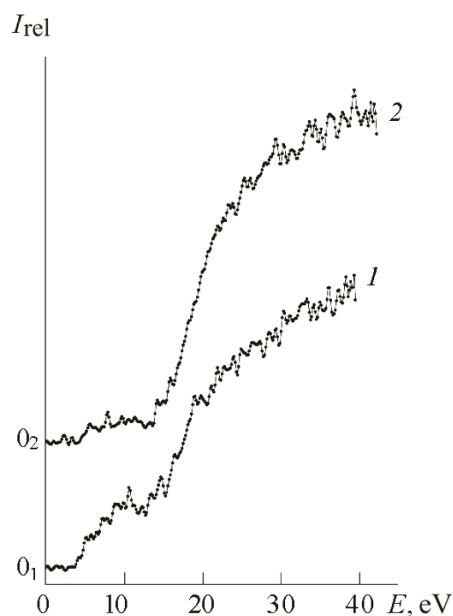
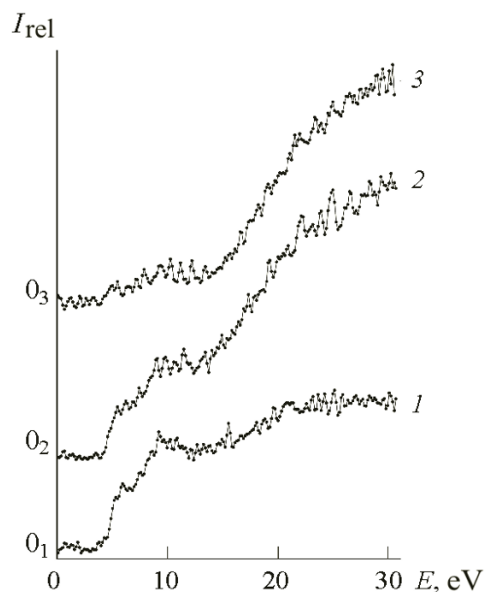Fig. 3. Optical excitation functions of S atomic spectral lines: λ = 469.4/469.5/469.6 (1) and 527.86/89 nm (2).

Fig. 4. Optical excitation functions of S$^+$ spectral lines: λ = 393.3 (1), 414.2/414.5/415.3 (2), and 542.8/543.2/545.3 nm (3).

The nature of the OEF of these emissions was typical for excitation of molecular triplet states [10, 11]. Triplet excited states of S_2^* ($A'^3\Delta_u$, $A^3\Sigma_u^+$, $B'^3\Pi_g$, and $B^3\Sigma_u^-$) were observed at 2.93, 3.03, 4.84, and 5.03 eV in calculations using an R-matrix method [12]. Several features indicative of resonances were observed in the published energy dependences of the excitation of these states after a sharp rise of the cross section [12]. The energy dependence of excitation of the $B'^3\Pi_g$-state, i.e., the $X^3\Sigma_g^- \rightarrow B'^3\Pi_g$ transition, was closest in shape and nature to our OEF. Let us emphasize that several resonance features could also be noticed in our OEF near the threshold. Therefore, we plan to make new measurements using an electron beam with a narrower energy range ($\Delta E \sim 0.1$–0.2 eV). This will make it possible to determine more clearly the energies of these features and; therefore, their nature.

Figure 3 shows OEF for atomic S spectral lines at 469.4/469.5/469.6 and 527.86/89 nm. The excitation energy thresholds for them were 9.16 and 9.21 eV. The first OEF had a rather distinct threshold at ~4.3 eV and a less distinct threshold at ~13.6 eV. Maxima and inflections at 10–15 eV were also observed. Emission spectra (Fig. 1) showed that this line had an underlying component, i.e., the continuous spectrum due to excitation of vibronic levels of molecular S, as mentioned above. Thus, the OEF threshold at ~4.3 eV was indicative of excitation of molecular S vibronic levels. The underlying component was practically absent in the OEF of the spectral line at 527.86/89 nm, which was located on the tail of the continuous emission band at 280–480 nm. Its excitation threshold at ~13.6 eV was rather clearly visible. The experimentally observed excitation thresholds were shifted from the true spectroscopic excitation thresholds of these lines by ~4.4 eV. Therefore, it was concluded that excitation near the threshold of the initial levels of these atomic S spectral lines occurred according to:

$$S_2 + e \rightarrow S^* + S + e ,$$

i.e., corresponded to dissociative excitation of a S atom. The effectiveness of this process increased with increasing bombarding-electron energy up to 25–30 eV.

Figure 4 shows OEF of S$^+$ spectral lines at 393.3, 414.2/5/415.3, and 542.8/543.2/545.3 nm. Their excitation threshold energies were 19.4, 18.88/18.86/18.84, and 15.94/15.89/15.86 eV, respectively. The first two lines were located in the region of the continuous emission band at 280–480 nm that was due to excitation of molecular S vibronic levels. Like for the atomic lines (Fig. 3), the excitation threshold at ~4.3 eV was clearly resolved in OEF of these ionic lines. Then, both OEF showed a sharp intensity increase up to ~5 eV and complicated behavior and several inflections and maxima at ~7, 9, and 18–25 eV.

TABLE 1. Relative Intensities of S and S$^+$ Spectral Lines and S$_2$ Bands for Exciting-Electron Energy 50 eV

S aggregate state	λ, nm	Excitation threshold energy, eV	Intensity, rel. units
S	469.41/.5/.63	9.16	0.45
	527.81/.86/.89	9.21	0.27
S$^+$	393.3	19.4	0.96
	414.2/.5/415.3	18.88/.86/.84	1.0
	542.8/543.2/545.3	15.94/.89/.86	0.21
S$_2$	282.9	4.3 ± 0.3	0.4
	290.0	4.3 ± 0.3	0.95
	293.0	4.3 ± 0.3	0.68
	336.9	4.3 ± 0.3	0.9

The complicated nature of the OEF of these spectral lines and the weak appearance of the true excitation thresholds of their initial levels were also due to overlap of strong S$_2$ molecular bands at $\lambda = 393.8$ and 419.3 nm.

The underlying component was practically absent and the threshold of its excitation could be clearly observed at ~15.8 eV in OEF of the spectral line at $\lambda = 542.8/543.2/545.3$ nm, which was located on the tail of the continuous emission band at 280–480 nm. The emission intensity after the excitation threshold increased smoothly up to ~28 eV without any features in the OEF.

The intensities of the spectral lines and bands of gas-phase S, the OEF of which are shown in Figs. 2–4, were normalized. For this, we used known effective excitation cross sections for spectral lines of atomic Hg at 250–580 nm [13]. OEF of 15 spectral lines of atomic Hg were measured in this range in an experiment set up specially by us with parameters that were analogous to those for the experiment with S. This enabled the emission intensities of excited gas-phase S to be normalized. Table 1 presents the results for the strongest line at $\lambda = 414.2/.5/415.3$ nm.

Conclusions. Excitation of gas-phase S by electron impact was studied using optical spectroscopy and a gas-filled cell. Emission spectra of gas-phase S were studied in the range 270–550 nm with excitation by electrons of energy 8, 20, and 50 eV. It was shown that gas-phase S at ~335 K contained mainly S$_n$ molecules ($n = 2$–8) and fewer S atoms.

OEF of 19 spectral lines of atomic, ionic, and molecular bands and emissions of portions of the continuous emission band at 280–480 nm were studied. Of these, five atomic and seven ionic lines and seven molecular bands were identified. It was found that the broad continuous emission band at 280–480 nm was a set of narrow lines and resulted from emission of excited vibronic states of S$_2$ molecules. The OEF of atomic and ionic spectral lines and molecular bands and emissions of portions in the range 2–50 eV were measured. Intensities of these spectral lines and bands were normalized. Excitation energy thresholds of the observed spectral lines and bands were determined. Excitation mechanisms of atomic spectral transitions were established. The most effective excitation mechanism for S atoms was dissociation of S$_2$ molecules by electron impact with subsequent excitation of the atoms.

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