

# Analysis of the outlook for using narrow-band spontaneous emission sources for atmospheric air purification

K.A. Boyarchuk, A.V. Karelin, R.V. Shirokov

**Abstract.** The outlook for using narrow-band spontaneous emission sources for purification of smoke gases from sulphur and nitrogen oxides is demonstrated by calculations based on a nonstationary kinetic model of the  $N_2 - O_2 - H_2O - CO_2 - SO_2$  mixture. The dependences of the mixture purification efficiency on the UV source power at different wavelengths, the exposure time, and the mixture temperature are calculated. It is shown that the radiation sources proposed in the paper will provide better purification of waste gases in the atmosphere. The most promising is a  $KrCl^*$  lamp emitting an average power of no less than 100 W at 222 nm.

**Keywords:** purification of smoke gases, photodissociation of molecules, excimer lamps.

## 1. Introduction

We analyse in this study the possibility of intensifying purification of industrial smoke gases from hazardous impurities using spontaneous radiation sources. It is known that the presence of chemically active radicals OH, HO<sub>2</sub>, O, and N in an air mixture facilitates the extraction of the NO, NO<sub>2</sub>, SO<sub>2</sub>, H<sub>2</sub>S and other impurities from the mixture. In this connection it is interesting to attempt to increase the concentration of required radicals in a mixture with the help of external radiation sources with properly chosen parameters.

In this paper, we propose to perform the efficient photodissociation of H<sub>2</sub>O molecules in a mixture with the formation of OH radicals (the dissociation energy is 5.12 eV) using the  $KrCl^*$  (222 nm),  $ArF^*$  (192 nm), and  $Xe_2^*$  (172 nm) excimer lamps, whose radiation can also directly produce the photodissociation of the SO<sub>2</sub> molecule. These radiation sources were proposed for the purification of smoke gases long ago [1]; however, to our knowledge, neither theoretical nor experimental studies were performed in this field.

## 2. Description of the model

The nonstationary kinetic model of the  $N_2 - O_2 - H_2O - CO_2 - SO_2$  mixture, which was developed using the PLASER program package [2], allows us to observe the temperature dependences of different components of a model mixture after its excitation by different radiation sources. At present there exist many kinetic models developed for studying the plasmachemistry of atmospheric air. However, as far as we know, models taking into account many components and allowing the solution of a great number of kinetic equations are absent. As a rule, only simple nitrogen–oxygen or oxygen–water mixtures were considered (see, for example, Refs [3–7]). In addition, most of the models available at present were developed for the only theoretical problem and were not tested experimentally.

The main problems involved in the development of models of complex mixtures are related to a great number of components in the mixture (i.e., the necessity to take into account a great number of plasmachemical reactions) and the calculation interpretation of many relaxation channels of the excited mixture. A change in the type and parameters of the excitation source in the mixture composition leads to substantial variations in the excitation and relaxation channels of the mixture. Along with well-known relaxation channels of air-like mixtures, there exist quite exotic plasmachemical relaxation processes whose role in the purification of smoke gases was unknown earlier. For example, the testing of the model [8] in experiments on purification of even simple mixtures by an electron beam revealed that ions and electrons in the plasma being formed appreciably affect the conversion processes involving hazardous impurities.

The model developed in Ref. [8] represents now a bank of constants for more than 3000 plasmachemical reactions, which are used to simulate the kinetics of the Earth atmospheric air and a variety of air-like mixtures irradiated by a hard ioniser (from solar rays to high-energy gamma quanta). Because the computational ability of the PLASER program package is limited, it is necessary to select a limited number of reactions for each specific problem (no more than 1700) for a limited number of components (no more than 120) of the excited mixture.

In this paper, the model is supplemented by photochemical reactions of dissociation and excitation of the main components of the mixture by UV radiation from excimer lamps. The photodissociation cross sections were taken from Refs [9, 10] and partially calculated as in Ref. [11].

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Received 7 March 2003

Kvantovaya Elektronika 33 (12) 1107–1110 (2003)

Translated by M.N. Sapozhnikov

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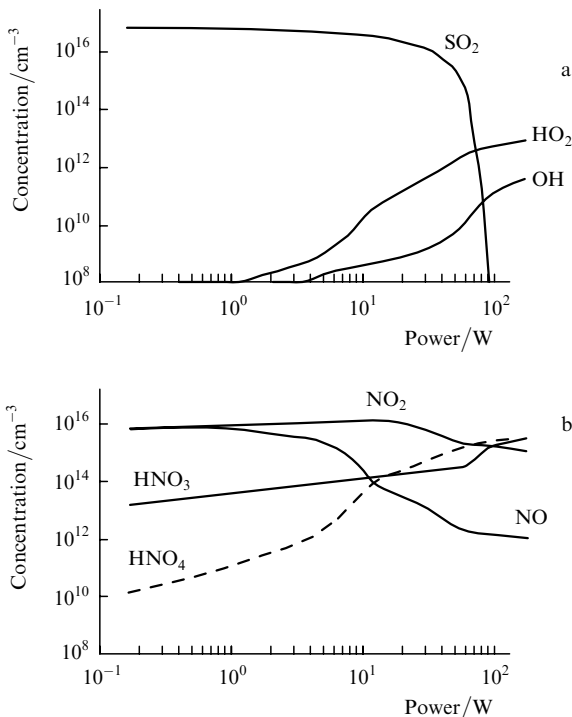
Because the role of electrons and ions is not significant in this situation, the number of components studied was substantially reduced [we considered molecules  $N_2$ ,  $H_2O$ ,  $O_2$ ,  $CO_2$ ,  $CO$ ,  $NO$ ,  $NO_2$ ,  $NO_3$ ,  $N_2O_5$ ,  $N_2O$ ,  $N_2^*(A)$ ,  $N_2^*(B)$ ,  $N_2^*(C)$ ,  $O_3$ ,  $HO_2$ ,  $H_2$ ,  $OH$ ,  $H_2O_2$ ,  $HNO$ ,  $HNO_2$ ,  $HNO_3$ ,  $HNO_4$ ,  $O_2^*(^1\Delta)$ ,  $CH_2O$ ,  $CHO$ ,  $CN$ ,  $SO_2$ ,  $SO_3$ ,  $SO_4$ ,  $SO$ ,  $H_2S$ ,  $HS$ ,  $H_2SO_4$ ,  $HSO_3$ ,  $SNO_4$ ,  $HSO$ ,  $HSO_4$ ,  $HSO_5$ ,  $H_2S_2O_6$ ,  $HSNO_5$ ,  $HSNO_6$ , and atoms  $O$ ,  $N$ ,  $H$ ,  $O^*(^1D)$ ,  $O^*(^1S)$ ,  $N^*(^2D)$ ,  $C$ ,  $S$ ], which allowed us to consider a greater number of reactions between the neutral and excited components of the mixture.

### 3. Results of calculations

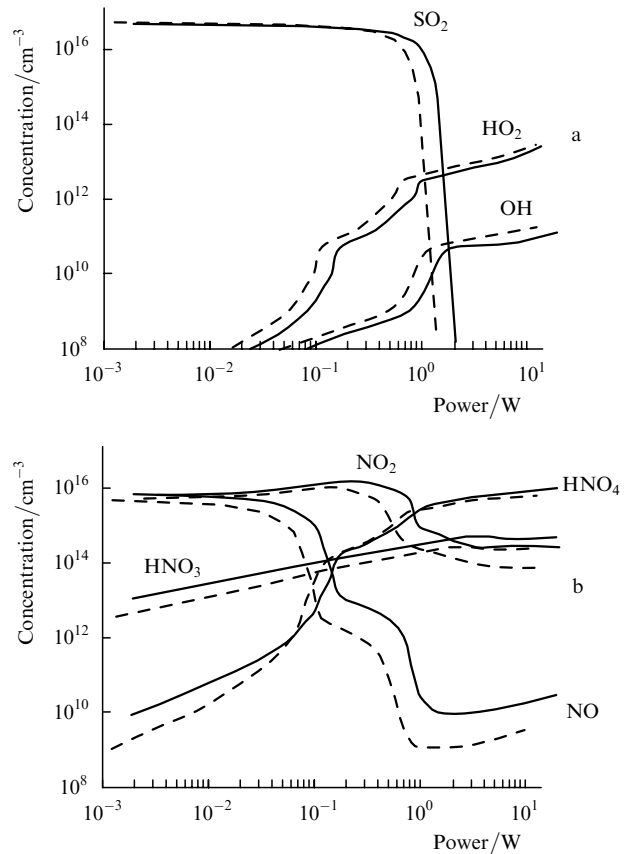
We performed calculations demonstrating the possibilities of the method proposed for purification of smoke gases. We considered cylindrical excitation sources of length 1 m and diameter 3 cm.

The volume of a gas irradiated by a lamp was determined by the absorption coefficient of the exciting radiation in the mixture. Radiation at a wavelength of 172 nm is mainly absorbed by nitrogen and water vapours (the total absorption coefficient  $k$  for the model mixture was  $\sim 12 \text{ cm}^{-1}$ ), at 192 nm by nitrogen ( $k = 1.5 \text{ cm}^{-1}$ ), and at 222 nm by the  $SO_2$  and  $NO_2$  molecules ( $k = 0.03 \text{ cm}^{-1}$ ) [10].

Figures 1 and 2 show the dependences of the maximum concentrations of the  $OH$ ,  $HO_2$  radicals and of the residual concentration of the  $NO$ ,  $NO_2$ ,  $HNO_3$ , and  $HNO_4$  molecules in the model mixture after its irradiation by pulsed lamps for 100 s [the initial concentration of  $SO_2$  was  $5 \times 10^{16} \text{ cm}^{-3}$  (1850 ppm) and  $10^{16} \text{ cm}^{-3}$  (370 ppm) for  $NO$  and  $NO_2$ ] on the radiation power under the conditions typical for smoke gases: 80 % of  $N_2$ , 5 % of  $O_2$ , 10 % of



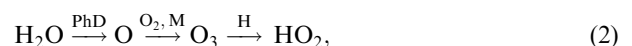
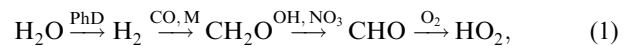
**Figure 1.** Dependences of the concentrations of  $OH$ ,  $HO_2$ , and  $SO_2$  (a),  $NO$ ,  $NO_2$ ,  $HNO_3$ , and  $HNO_4$  (b) on the 222-nm radiation power of a  $KrCl^*$  lamp.



**Figure 2.** Dependences of the concentrations of  $OH$ ,  $HO_2$ , and  $SO_2$  (a),  $NO$ ,  $NO_2$ ,  $HNO_3$ , and  $HNO_4$  (b) on the 192-nm radiation power of a  $ArF^*$  lamp (solid curves) and the 172-nm radiation power of a  $Xe_2^*$  lamp (dashed curves).

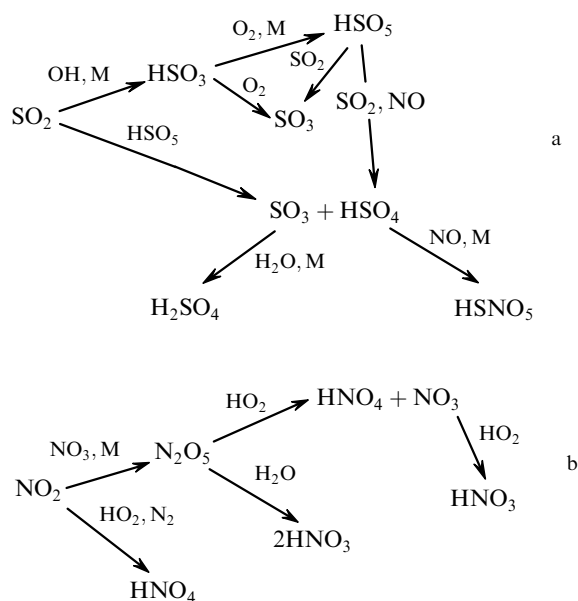
$H_2O$ , 3.7 % of  $CO_2$  and the mixture temperature equal to  $60^\circ C$ .

One can see that the efficiency of purification from hazardous impurities depends on the source power. The efficiency of the mixture purification from the  $NO$ ,  $NO_2$ , and  $SO_2$  molecules has a threshold nature, the threshold being most pronounced for the  $SO_2$  molecule. The concentration of  $OH$  radicals at which  $SO_2$  molecules are rapidly transformed to sulphuric acid was approximately  $2 \times 10^{10} \text{ cm}^{-3}$  in all cases. The concentration of  $HO_2$  molecules at which the  $NO$  molecules were efficiently removed was the same. The  $OH$  radicals were produced in the mixture upon its direct irradiation [due to photo-dissociation (PhD) of water vapours]. The  $HO_2$  radicals were produced via the channels



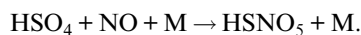
where  $M$  is an arbitrary third particle. The concentrations of formaldehyde and carbon monoxide (which were initially absent in the mixture and were produced during irradiation) exceeded  $10^{16} \text{ cm}^{-3}$  and the concentration of  $CHO$  was greater than  $10^8 \text{ cm}^{-3}$ .

Figure 3a shows the scheme of conversion of sulphur oxides. The intermediate products are the  $SO_3$  and  $HSO_4$



**Figure 3.** Schemes of the main conversion channels for SO<sub>2</sub>, NO (a), and NO<sub>2</sub> (b) molecules.

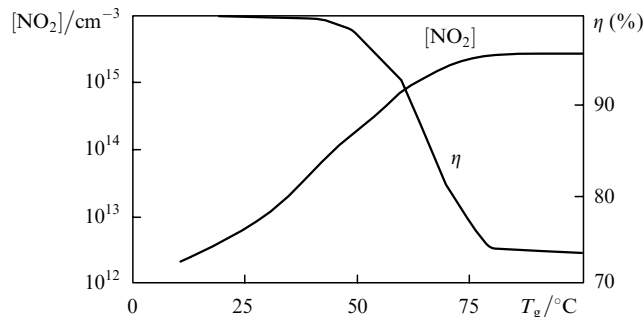
molecules, and the final products are sulphuric acid and HSNO<sub>5</sub> molecules. The OH radicals and oxygen and water molecules serve as intermediaries. Nitrogen monoxide was most efficiently removed from the mixture in the presence of sulphur oxides with the formation of HSNO<sub>5</sub> molecules (Fig. 3a) in the reaction



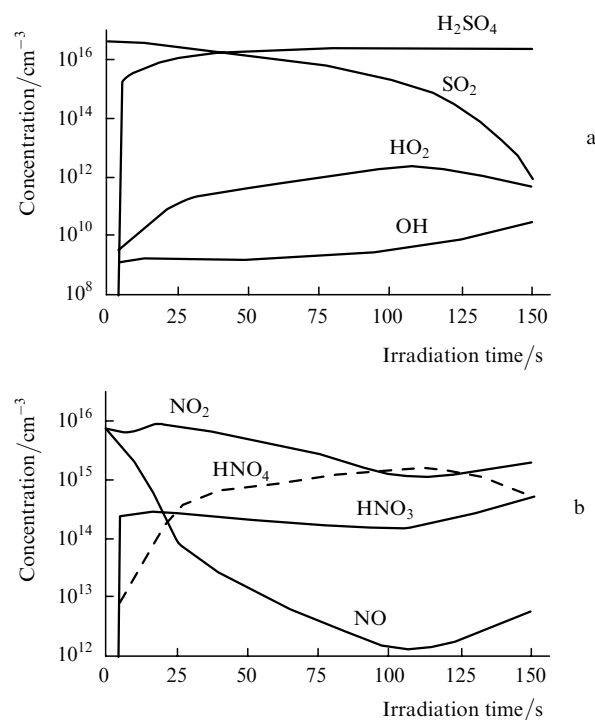
It is difficult to say anything about the further destiny of the HSNO<sub>5</sub> molecules, even their phase state being unknown under the given conditions. The H<sub>2</sub>SO<sub>4</sub>, HNO<sub>3</sub>, and HNO<sub>4</sub> acids are removed, as a rule, from the mixture under industrial conditions by adding ammonia to smoke gases, which neutralises, in the presence of water and oxygen vapours, these acids to ammonia sulphates and nitrates in the solid state.

Nitrogen dioxide is transformed to the HNO<sub>3</sub> and HNO<sub>4</sub> acids with the participation of the HO<sub>2</sub> radicals (Fig. 3b). In this case, the reaction of the N<sub>2</sub>O<sub>5</sub> molecules with water vapours is the main channel of conversion of NO<sub>2</sub> molecules to the acids. Note that at high temperatures of the irradiated mixture, the reaction of reverse decomposition of the N<sub>2</sub>O<sub>5</sub> molecules into NO<sub>2</sub> and NO<sub>3</sub> efficiently competes with the above reaction. Figure 4 demonstrates the influence of the mixture temperature on the efficiency  $\eta = 1 - [\text{NO}_2]/[\text{NO}_2]_0$  (where  $[\text{NO}_2]$  and  $[\text{NO}_2]_0$  are the final and initial concentrations) of removal of NO<sub>2</sub> molecules by the 222-nm radiation from a KrCl\* lamp.

Figure 5 shows the dependences of the concentration of the mixture components of interest to us on the time of irradiation by a 50-W KrCl\* lamp. One can see that the NO concentration is reduced for the first 50 s, whereas to remove sulphur oxides, either a longer irradiation time is required (when the OH concentration increases) or a greater irradiation power. The conversion of NO<sub>2</sub> molecules is weak, but it can be enhanced by lowering the temperature of smoke gases.



**Figure 4.** Dependences of the residual concentration of NO<sub>2</sub> and the efficiency  $\eta$  of mixture purification from nitrogen oxide by the 222-nm radiation from a KrCl\* lamp on the mixture temperature  $T_g$ .

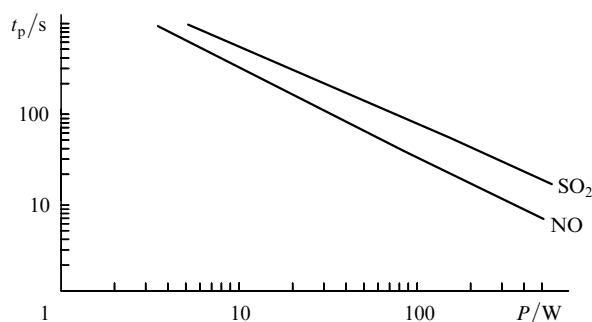


**Figure 5.** Dependences of the concentrations of OH, HO<sub>2</sub>, SO<sub>2</sub>, H<sub>2</sub>SO<sub>4</sub> (a) and NO, NO<sub>2</sub>, HNO<sub>3</sub>, and HNO<sub>4</sub> (b) on the time of irradiation by a KrCl\* lamp at 222 nm.

The choice of the parameters of radiation sources and of their geometry is determined (along with the mixture temperature and composition) by the size of the irradiated volume and the propagation velocity of the mixture through the volume. If the efficiency of mixture purification from a hazardous impurity is characterised by the reduction of the concentration of this impurity by three orders of magnitude, then the time of irradiation of a mixture by a KrCl\* lamp at 222 nm is inversely proportional to the radiation power  $P$  (Fig. 6):  $t_p \sim P^{-A}$  ( $A > 0$ ). For example, for  $P = 100$  W, the efficient conversion of nitrogen monoxide and sulphur oxide can be performed for 30 and 70 s, respectively.

#### 4. Conclusions

Based on the nonstationary kinetic model of the N<sub>2</sub>–O<sub>2</sub>–H<sub>2</sub>O–CO<sub>2</sub>–SO<sub>2</sub> mixture, we have calculated in detail the kinetics of processes in the air mixture containing hazard-



**Figure 6.** Times  $t_p$  of irradiation required for the efficient conversion of  $\text{SO}_2$  and  $\text{NO}$  molecules as functions of the 222-nm radiation power of a  $\text{KrCl}^*$  lamp.

ous impurities. We have demonstrated theoretically the possibility of using narrow-band spontaneous radiation sources for purification of smoke gases. The efficiency of mixture purification from sulphur and nitrogen oxides was calculated as a function of the UV irradiation power at different wavelengths, the irradiation time, and the mixture temperature. The basic mechanisms of the removal of hazardous impurities from smoke gases are revealed and studied. It is shown that the use of radiation sources proposed in the paper will result in a better purification of hazardous waste gases in the atmosphere. It is found that during the purification of smoke gases by radiative-plasmochemical methods, the  $\text{HSNO}_5$  molecules are produced in the mixture, whose stability and properties in air are unknown. It is shown that the mixture volume that can be subjected to purification drastically increases with the wavelength of the radiation source, and at the same time the requirements to the power and time of irradiation of the mixture are increased. The most promising is a 222-nm  $\text{KrCl}^*$  lamp with the average power of no less than 100 W.

**Acknowledgements.** This work was supported by the Russian Foundation for Basic Research (Grant Nos 00-02-17140 and 02-02-06118) and by International Scientific and Technology Centre (Grant No. 1270).

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