

# Influence of Repeller Potential on Ion–Molecule Reactions in H<sub>2</sub>S and CH<sub>4</sub> Mixtures

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Ion–molecule reactions initiated by electron impact in the hydrogen sulfide–methane mixtures have been studied by means of quadrupole mass spectrometer with a high-pressure ion source. The total gas pressure of investigated mixtures was changed from 0.7 to 33.3 Pa. Influence of repeller potential on ion–molecule reactions have been studied. The repeller potential was changed in the range 2–12 V. Measurements were performed for different concentrations of methane and hydrogen sulfide in the mixture (from 10% H<sub>2</sub>S + 90% CH<sub>4</sub> to 90% H<sub>2</sub>S + 10% CH<sub>4</sub> with 10% increment). The major ion–molecule reactions have been identified. The primary ions C<sup>+</sup>, CH<sup>+</sup>, CH<sub>2</sub><sup>+</sup>, CH<sub>3</sub><sup>+</sup>, CH<sub>4</sub><sup>+</sup>, S<sup>+</sup>, HS<sup>+</sup>, H<sub>2</sub>S<sup>+</sup> produced in gas by the electrons with the energy of 300 eV and secondary CH<sub>5</sub><sup>+</sup>, C<sub>2</sub>H<sub>5</sub><sup>+</sup>, H<sub>3</sub>S<sup>+</sup>, H<sub>2</sub><sup>34</sup>S<sup>+</sup>, H<sub>3</sub><sup>34</sup>S<sup>+</sup>, CHS<sup>+</sup>, CH<sub>3</sub>S<sup>+</sup>, S<sub>2</sub><sup>+</sup>, HS<sub>2</sub><sup>+</sup>, H<sub>2</sub>S<sub>2</sub><sup>+</sup> and H<sub>3</sub>S<sub>2</sub><sup>+</sup> from the ion–molecule reactions were observed. Relative intensities for primary and secondary ions are presented as a function of potential of repeller electrode and concentration of methane in the mixture.

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## 1. Introduction

Investigations of ion–molecule reactions in pure hydrogen sulfide [1–6] and methane [7–15] and also in the mixture of H<sub>2</sub>S with CH<sub>4</sub> were performed using various mass spectrometric techniques and methods [16–19].

One of the criteria that helps to distinguish between primary and secondary ions arising in ion–molecule processes, is different dependence of ion intensity on the gas pressure. The other one is based on the fact that probability of interaction between primary ions and neutral molecules that leads to ion–molecule reactions decreases with the decreasing residence time in the ion chamber. Residence time can be changed by changes of the repeller potential. The influence of that potential on ion–molecule reactions efficiency for the examined mixtures of hydrogen sulfide and methane has been determined.

Methane and hydrogen sulfide are important trace impurities of atmospheric air. These gases are emitted to the atmosphere as a consequence of natural biomass degradation (decay of proteins), biomass burning and motor exhaust. Sulfur compounds contribute to acidity of atmospheric rains. As many other atmospheric contaminants H<sub>2</sub>S and CH<sub>4</sub> can undergo ion–molecule reactions in the upper layer of the earth atmosphere. Reconstruction of these reactions in laboratory conditions and knowledge about reaction mechanisms can be very important for monitoring and protection of the earth atmosphere [20].

## 2. Experimental

Measurements of ion–molecule reactions in the mixtures of hydrogen sulfide with methane were performed

by means of the quadrupole mass spectrometer with a special high-pressure ion source constructed in the Institute of Physics in Lublin. The instrument and techniques were described previously [21–23]. Hydrogen sulfide and methane used in experiment, supplied by Praxair and Merck were of the best available purity (99.8% and 99.99%, respectively). Total gas pressure inside the collision chamber of the ion source was changed by means of a precision sapphire valve and controlled by the MKS Baratron capacitance manometer scaled in mTorr. The quadrupole mass spectrometer is able to perform ion mass analyses in the range from 1 to 400 u. The detection system of this spectrometer consists of the Balzers 16 stage electron multiplier. Hydrogen sulfide and methane mixtures were made in the independent inlet system and then supplied directly to the ion source collision chamber. The differential vacuum system was applied to separate ion source and analyzer regions evacuation. The high-speed diffusion pump 2000 l/s was used to evacuate the ion source region and 800 l/s diffusion pump for analyzer evacuation. Mass spectrometer is equipped in special computer interface for data collection and data analyses. In order to correct the errors resulting from ion discrimination effects in different regions of the mass spectrometer, the ion transmission coefficient on the ion path from the ion source to the collector of an electron multiplier was determined [24].

During the measurements the gas pressure inside the collision chamber of the ion source was fixed at 1.3 Pa.

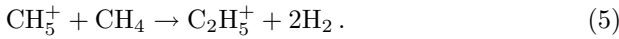
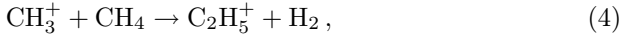
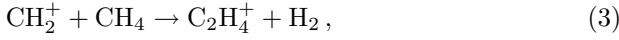
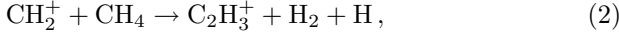
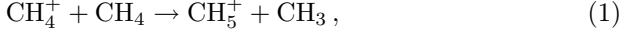
The concentration of methane in mixtures with hydrogen sulfide ranged from 10% to 90% (at 10% increments). Primary ions were produced by electrons emitted from the rhenium thermocathode and after that formed in a beam by the system of ion source electrodes and then accelerated to the energy of 300 eV. Considering that all measurements were performed at high pressure inside the ion source, energy of the electrons bombarding the

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gas should be higher than this corresponding to maximum values of ionization cross-section for investigated fragments. The multiple collisions of ionizing electrons with molecules are the reason for such selection of their energy. The repeller potential has been changed from 2 to 12 V.

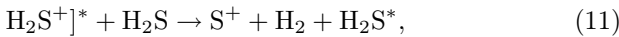
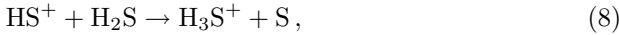
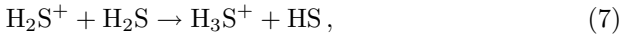
### 3. Results and discussion

For high pressure of methane inside the ion source collision chamber, the primary ions  $\text{CH}_2^+$ ,  $\text{CH}_3^+$  and  $\text{CH}_4^+$  react with molecules of methane and the secondary ions are produced according to the following reactions [7–15]:

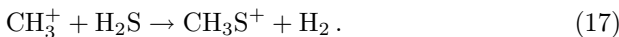
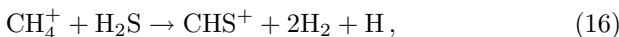
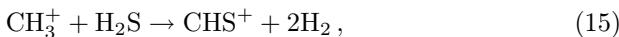
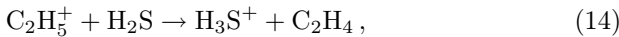


At relatively low pressure of pure hydrogen sulfide inside the ion source collision chamber the main primary ions  $\text{S}^+$  ( $m/q = 32$ ),  $\text{HS}^+$  ( $m/q = 33$ ) and  $\text{H}_2\text{S}^+$  ( $m/q = 34$ ) were observed. When the pressure gradually grows, primary ions start to react with neutral molecules of hydrogen sulfide to form secondary ions. As the result of interactions between primary  $\text{H}_2\text{S}^+$  ions and neutral  $\text{H}_2\text{S}$  molecules the following ions were observed:  $\text{H}_3\text{S}^+$  ( $m/q = 35$ ),  $\text{H}_3^3\text{S}^+$  ( $m/q = 37$ ),  $\text{S}_2^+$  ( $m/q = 64$ ),  $\text{HS}_2^+$  ( $m/q = 65$ ),  $\text{H}_2\text{S}_2^+$  ( $m/q = 66$ ) and  $\text{H}_3\text{S}_2^+$  ( $m/q = 67$ ).

Ion–molecule processes observed for pure hydrogen sulphide can be presented by the following reactions [1–5]:



In the mixtures of hydrogen sulfide and methane, the following ion–molecule processes can take place according to the reaction scheme [16, 18, 19]:



Relative ion currents for the observed ions as a function of repeller potential are presented in Figs. 1–3. The results of ion–molecule reactions for two selected concentrations of methane (Fig. 1 — 20% and Fig. 2 — 80%) in the mixtures with hydrogen sulfide are shown in Figs. 1

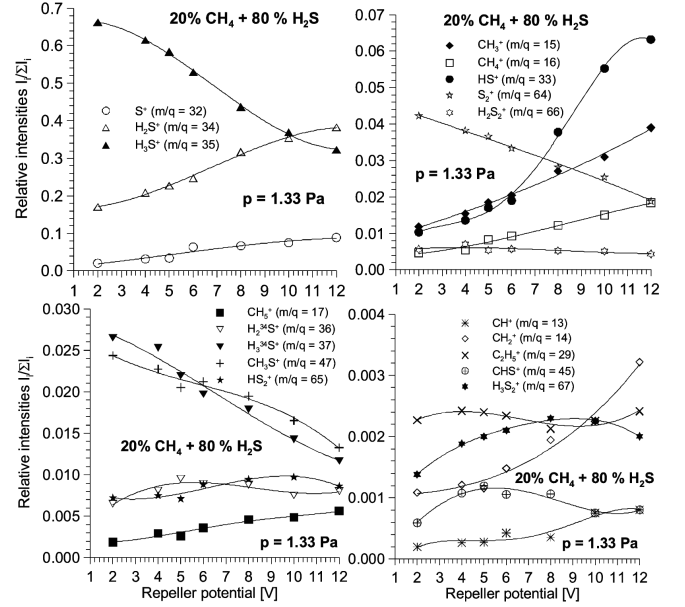


Fig. 1. Relative ion current intensities as a function of repeller potential at the constant total gas pressure 1.3 Pa for 20% concentration of methane in the mixture with hydrogen sulfide.

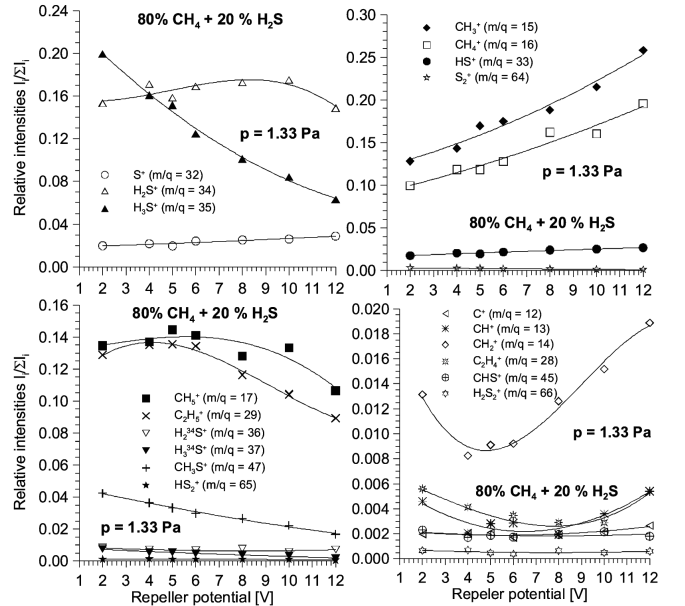


Fig. 2. As in Fig. 1, but for 80% concentration of methane.

and 2. The total gas pressure, for all measurements presented here, was 1.3 Pa. The repeller potential was varied over the range 2–12 V.

As a result of ion–molecule reactions (1), (4) and (5) in methane,  $\text{CH}_5^+$  and  $\text{C}_2\text{H}_5^+$  ions were observed. As the repeller potential increases, the probability of secondary collisions decreases (relative efficiency of reactions (1), (4) and (5) decreases).

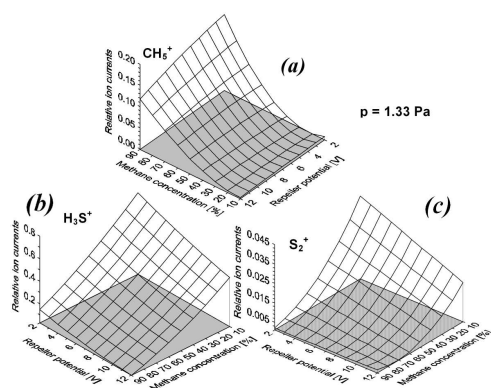


Fig. 3. Relative currents for the secondary ions (a)  $\text{CH}_5^+$ , (b)  $\text{H}_3\text{S}^+$  and (c)  $\text{S}_2^+$  as a function of repeller potential for all examined concentrations of methane in the mixtures with hydrogen sulfide at the total gas pressure 1.3 Pa. The repeller potential was varied over the range 2–12 V.

$\text{H}_3\text{S}^+$  ions were produced as a result of ion–molecule reactions ((7), (12)–(14)). The relative ion current of  $\text{H}_3\text{S}^+$  decreases (see reactions (13) and (14)) as the residence time of secondary  $\text{CH}_5^+$  and  $\text{C}_2\text{H}_5^+$  ions decreases. Residence time reductions were caused by the increase of repeller potential.

From the results presented in Figs. 1–3, there can be seen decrease in relative intensities of the secondary ions  $\text{CH}_5^+$  and  $\text{C}_2\text{H}_5^+$  (see Figs. 1 and 2) and increase for  $\text{H}_3\text{S}^+$  and  $\text{S}_2^+$  ions with the drop of methane concentration in the mixtures.

Figure 3 presents the relative currents for the secondary ions (a)  $\text{CH}_5^+$ , (b)  $\text{H}_3\text{S}^+$  and (c)  $\text{S}_2^+$  as a function of repeller potential for all examined concentrations of methane in the mixtures with hydrogen sulfide at the total gas pressure 1.3 Pa.

#### 4. Conclusions

In the earlier work [19], the authors presented the results of ion–molecule reactions in the mixtures of hydrogen sulfide with methane as a function of total gas pressure. One of the methods used for distinguishing between the primary and secondary ions is that based on the change of repeller potential. In this work the influence of repeller potential on the primary  $\text{C}^+$ ,  $\text{CH}^+$ ,  $\text{CH}_2^+$ ,  $\text{CH}_3^+$ ,  $\text{CH}_4^+$ ,  $\text{S}^+$ ,  $\text{HS}^+$  and  $\text{H}_2\text{S}^+$  and secondary  $\text{CH}_5^+$ ,  $\text{C}_2\text{H}_5^+$ ,  $\text{H}_3\text{S}^+$ ,  $\text{H}_2^{34}\text{S}^+$ ,  $\text{H}_3^{34}\text{S}^+$ ,  $\text{CHS}^+$ ,  $\text{CH}_3\text{S}^+$ ,  $\text{S}_2^+$ ,  $\text{HS}_2^+$ ,  $\text{H}_2\text{S}_2^+$  and  $\text{H}_3\text{S}_2^+$  ions production was examined for the mixtures of methane with carbon tetrafluoride. The results obtained here are complementary to those presented before [19].

The compositions of the mixtures were changed from 10%  $\text{H}_2\text{S}$  + 90%  $\text{CH}_4$  to 90%  $\text{H}_2\text{S}$  + 10%  $\text{CH}_4$  with 10% methane increment and the repeller potential was varied over the range 2–12 V. The total gas pressure, for all measurements of repeller influence on ion–molecule reactions presented here, was fixed at 1.3 Pa.

From the results presented on the semi-three-dimensional plots (see Fig. 3) there can be seen that par-

allel to the increasing repeller potential, drop for  $\text{CH}_5^+$ ,  $\text{H}_3\text{S}^+$  and  $\text{S}_2^+$  ions is observed. The results obtained for all investigated mixtures indicate that with the decrease of the methane concentration the growth of relative secondary  $\text{H}_3\text{S}^+$  and  $\text{S}_2^+$  and drop of  $\text{CH}_5^+$  ion current intensities are observed.

The obtained results are complementary to those presented by the authors in the earlier work and are very useful for distinguishing between primary and secondary ions observed in experiment [19].

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