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Figure 1

Figure 1: Figure 1

Abstract

Full Text

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Dissociation Cross Sections of H_2^+ Ions from Methane and *n*-Butane at Various Electron Energies

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In studying the dissociation of H_2^+ ions obtained by electron impact from various hydrogen-containing molecules, it was found (^{6}) that these ions dissociate on collision with atoms with larger cross sections than do H_2^+ ions from hydrogen. This circumstance is naturally connected with the difference in the distribution over vibrational levels of H_2^+ ions from hydrogen-containing molecules and directly from hydrogen (^{1,6}). In the present communication the results of a study of the dissociation of H_2^+ ions from methane and *n*-butane, obtained at various energies of the ionizing electrons in the source, are briefly presented.

A detailed description of the experimental method is given in work (^{2}). The dissociation cross sections were determined on a double mass spectrometer. In the collision chamber there was neon at a pressure of $\sim 10^{-4}$ mm Hg (the pressure was measured with a McLeod gauge). The energy of the H_2^+ ions was 3.8 keV. The pressure of the initial gas in the ion source was usually $\sim 2{\cdot}10^{-5}$ mm Hg. The random error over the entire range of variation of the electron energy, except for very low energies (below 28 eV), did not exceed 7%. At the indicated kinetic energy of H_2^+ ions, discriminations are possible in the instrument which may lead to a systematic underestimation of the measured value of the cross section (for more details see (^{2})); however, they do not prevent determination of the character of the dependence of the dissociation cross section on the electron energy.

Fig. 1. Dependence of the dissociation cross section of H_2^+ and D_2^+ (crosses) ions on the variation of the electron energy with a magnetic field of ~ 100 gauss in the ionization region

In Fig. 1 (curve 1) is shown the dependence of the cross section of the process $H_2^+ \to H^+ + H^0$, which takes place in the collision chamber as a result of single

Fig. 2. Dependence of the current of H_2^+ ions from methane on electron energy

Figure 2: Fig. 2. Dependence of the current of H_2^+ ions from methane on electron energy

collisions of H_2^+ ions with neon atoms, on the electron energy in the ion source. The H_2^+ ions were formed by dissociative ionization of methane molecules in the source under the action of a beam of nonmonochromatized electrons. The dissociation cross section at an energy of 20 eV is approximately $0.7 \cdot 10^{-16}$ cm^2. This value agrees within the limits of error with the dissociation cross section of H_2^+ ions from hydrogen under analogous conditions (^{6}). Beginning at electron energies of approximately 28 eV, the measured dissociation cross section rises sharply and reaches a value of $2.5 \cdot 10^{-16}$ cm^2. Thus, when the energy is changed from 28 to 70 eV, the dissociation cross section in this case increases

by a factor of 3.5, whereas changing the electron energy from 20 to 70 eV in the ionization of hydrogen leads to an increase in the dissociation cross section of H_2^+ by only about 30% (^{2}).

Similar results were obtained with deuteromethane CD_4. The dissociation cross section of D_2^+ ions also increases sharply beginning at electron energies of about 28 eV and changes with the change in electron energy in the same way as in the case of H_2^+ from CH_4. The increase in the dissociation cross section with increasing electron energy is caused, first, by an increase, beginning at 28 eV, in the number of H_2^+ ions in the beam with a considerably higher vibrational excitation than below 28 eV, and, second, by an increase of this excitation with electron energy. Figure 2 shows the dependence of the current of H_2^+ ions from methane on the electron energy. A distinct break can be seen at approximately 28 eV, where the process of formation of H_2^+ ions with large vibrational excitation begins. Another small break at 35 eV is apparently due to the appearance of the process of formation of H_2^+ ions that have still higher vibrational excitation. Comparing Figs. 1 and 2, the following may be noted. Beginning at 60 eV the current of H_2^+ ions slowly decreases, whereas the cross section continues to grow. This can be explained by an increase in the degree of excitation of H_2^+ ions from methane with increasing electron energy.

Fig. 2. Dependence of the current of H_2^+ ions from methane on electron energy

The formation of H_2^+ ions from methane with increased population of the upper vibrational levels may occur both as a result of dissociation of highly excited CH_4^+ ions and during dissociation of doubly charged CH_4^{2+} ions, stable states of which have not been observed. However, when H_2^+ ions are formed by the decay of the doubly charged ion CH_4^{2+}, for example in the process $CH_4^{2+} \to CH_2^+ + H_2^+$, these ions can acquire appreciable kinetic energy, which will reduce their content in the beam of H_2^+ ions entering the collision chamber and, consequently, will reduce their contribution to the increase in the dissociation cross section.

In an electronic transition, according to the Franck–Condon principle, the position and velocity of the nuclei practically do not change. Using the corresponding data for methane molecules (3), one may assume the formation of H_2^+ ions approximately on the fifth vibrational level. However, because of the difference between the electronic shells of the methane molecule and ion, during the dissociation time, which is at least $\sim 10^{-13}$ s, the nuclei, moving in the field corresponding to the new electronic configuration, acquire kinetic energy. This leads to the fact that the resulting H_2^+ ions are in fact apparently on higher vibrational levels. The data of work (4) confirm this conclusion. An approximate estimate of the degree of vibrational excitation of H_2^+ ions from methane can be made by considering the energetics of the methane dissociation process, which is given in work (5). It is shown there that, from the energy point of view, the most probable mechanism for the formation of H_2^+ is $CH_4^+ \to C + 2H + H_2^+$ (at least at electron energies close to the appearance potential of H_2^+ ions from methane, which according to that work is approximately 28 eV). In this case about 2 eV goes into excitation of the dissociation products and kinetic energies of the fragments. Consequently, this value is also the upper limit of the excitation energy

excitation of the H_2^+ ions, which may thus be at the 10–11th vibrational level. It must be noted, however, that this is a rather rough estimate, since the quantities used in the calculation are not very accurate. Moreover, as was stated above, the distribution over vibrational excitation changes with the electron energy.

The characteristic dependence of the dissociation cross section of H_2^+ ions on electron energy, shown in Fig. 1 for the case of dissociative ionization of methane (or deuteromethane), is not an exception. Similar behavior is also exhibited by the dissociation cross section of H_2^+ ions formed from *n*-butane (curve 2) and ethylene. The measured value of the cross section in the case of formation of H_2^+ ions from *n*-butane at electron energies in the range 25–35 eV is $0.8 \cdot 10^{-16}$ cm^2. With increasing electron energy the cross section grows and at an energy of 100 eV becomes $\sim 1.75 \cdot 10^{-16}$ cm^2. The mechanism of formation of H_2^+ ions in the dissociative ionization of the *n*-butane molecule may differ from the mechanism of their formation from methane. The difference should consist in an increase of the contribution of the statistical mechanism to the formation of H_2^+ in the first case, owing to the relatively greater complexity of the *n*-butane molecule. It is natural to suppose that, with increasing excitation energy of the initial molecular ion of *n*-butane, the excitation energy of the fragment ion H_2^+ formed from it may also increase.

Superposition of a weak magnetic field ($\sim$ 100 gauss) on the ionization region for focusing the electron beam leads to a decrease in the measured cross sections by 10–15%. This may be due to an increase in the residence time of the ions in the source, which leads to some deactivation of them.

The results presented show that the distribution over vibrational states in a beam of H_2^+ ions obtained from hydrogen-containing molecules changes when the dissociation conditions of the initial molecular ion are changed. With increasing excitation energy of the molecular ion, the population of the upper vibrational levels of the fragment H_2^+ ions increases.

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Note: Figure translations are in progress. See original paper for figures.