Relation between Electron Exchange and Nuclear Vibrations in the $\text{H}_2^+ + \text{H}_2^+ \rightarrow \text{H}_3^+ + p$ Exothermic Ion–Molecular Reaction

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Abstract—The effective cross section for the $\text{H}_2^+ + \text{H}_2^+ \rightarrow \text{H}_3^+ + p$ reaction in the energy range 5.7–11.5 eV is measured by the split beam method. The maximum of the cross section at an energy of ~8 eV is related to the production of the $\text{H}_4^{++}$ compound system. The reaction threshold $W_{\text{thr}} = 5$ eV provides evidence in favor of the classical model of the $\text{H}_2^+$ ion with the charge fixed on one of the nuclei throughout the collision event. © 2001 MAIK “Nauka/Interperiodica”.

1. INTRODUCTION

Investigations of the energy levels of molecules consisting of multielectron atoms showed that $ab\text{ initio}$ calculations by the antisymmetrical molecular orbital (ASMO) method provide correct results only for the intermolecular interaction of atoms in a stable structure and fail when atoms and molecules interact at long distances typical of both the production of an intermediate compound in ion–molecular reactions and the formation of electronically excited or excimer molecules [1]. Using the example of an oxygen molecule, it was shown that, in calculating the atomic interaction at distances longer than the size of a stable molecule, the best results are obtained by taking into account not only atomic orbitals of an oxygen atom but also orbitals of $\text{O}^-$ and $\text{O}^+$ ions. Here, exchange effects turn out to be of minor importance [2].

Based on the above approach, the diatomic molecular compound (DMC) method [3, 4] has been developed, in which the interatomic interaction of chemically defined structures is of primary importance, whereas electron exchange between identical atoms is of little significance. The method was successively used in studying not only multielectron atomic compounds but also simple structures, such as $\text{H}_3^+$, $\text{H}_4^+$, and $\text{H}_5^{++}$ [5].

Strictly speaking, in studying electronically excited molecules and ion–molecular reactions, a chemical approach is taken in which orbitals that can occur as the distance between the nuclei constituting a molecule approaches infinity are assumed to be the basic ones. In other words, atomic constituents of a molecular structure should not change their properties drastically. In particular, in molecular ions (such as $\text{H}_2^+$ or $\text{H}_3^+$), only a successive transfer of an electron from one nucleus to another is possible, rather than a uniform distribution of the electron density among the nuclei. The uniform distribution of the electron density can only be a next order effect in terms of a small parameter equal to the ratio of the chemical bond energy to the ionization energy of the atomic structure.

In this paper, it is shown that studying the threshold behavior related to Coulomb repulsion in exothermic ion–molecular reactions makes it possible to verify the validity of the chemical approach and relate the electron exchange between nuclei to the excitation of molecular vibrations. As an example, we will consider an ion–molecular reaction that proceeds in pair collisions of $\text{H}_2^+$ ions.

According to modern theoretical views, among the four possible channels for the ion–molecular reaction,

$$\text{H}_2^+ + \text{H}_2^+ \rightarrow \begin{cases} \text{H}_2^+ + \text{H} + p & -2.65 \text{ eV} \quad (1) \\ \text{H} + p + \text{H} + p & -5.30 \text{ eV} \quad (2) \\ \text{H}_2 + p + p & -0.82 \text{ eV} \quad (3) \\ \text{H}_3^+ + p & +3.18 \text{ eV} \quad (4) \end{cases}$$

the latter two must proceed via the formation of the intermediate $\text{H}_4^{++}$ compound [3, 6], whereas channels (1) and (2) may be direct processes. Previous studies [7, 8] showed that channels (1) and (2) could not provide the observed probability of proton production at relative kinetic energies of $W \sim 7$ eV [9]. Therefore, at such energies, channel (4) should be of major importance because, during the decay of the intermediate compound, an exothermic channel prevails, all other factors being the same. Although channel (4) is exothermic, the need to overcome the Coulomb barrier makes it very sensitive to the mutual orientation of the colliding lin-
ear molecular \( H_2^+ \) ions because, in order to form an intermediate compound, the ions must approach each other to the distance \( R \sim 10^{-8} \) cm (comparable with the molecular size), at which atomic electron clouds can overlap.

The measured effective cross section for reaction (4) (on the order of \( 10^{-16} \) cm\(^2\)) indicates that the formation of an \( H_2^+ \) ion proceeds via an intermediate state, thus providing evidence in favor of Firsov’s theoretical approach [10], proposed for the description of similar ion–molecular reactions. On the other hand, such a cross-section value points to the importance of this reaction for applications, because an appreciable number of \( H_2^+ \) ions in intense \( H_2^+ \) or proton beams extracted from a gas-discharge ion source increase the energy consumption and, therefore, decrease the efficiency of this source.

The paper is organized as follows. The concept of the experiment is described in Section 2, and the experimental setup and the method for recording the reaction under study are described in Section 3. The results of measurements are presented in Section 4 and discussed in Section 5 based on Firsov’s theoretical concept with allowance for the DMC method, which has been developed in connection with studies of other ion–molecular reactions and excimer molecules. It is shown that the Coulomb threshold for reaction (4) depends on the molecular model used—the chemical model or the quantum mechanical one, in which the electron cloud is distributed uniformly between the two nuclei of an \( H_2^+ \) ion. Based on the probability of \( H_2^+ \) ion production measured at interaction energies of the colliding \( H_2^+ \) ions of several electronvolts, it is concluded that the chemical approach not only serves as a successful semiempirical calculation procedure but also adequately describes the processes occurring over time intervals much shorter than the period of nuclei vibrations, whereas the exchange of electron clouds between the nuclei correlates with these vibrations.

2. DESCRIPTION OF THE EXPERIMENT

The measurements were carried out by the split beam method (see [8] for details). To ensure collision events, a ribbon-shaped ion beam is split into two and then is focused so that the ion trajectories of the newly formed beams intersect in the focal region at a small angle \( \varphi \). In the center-of-mass frame, the total kinetic energy of the colliding ions \( W \) (the interaction energy) is significantly less than their energy \( E \) in the laboratory frame. For equal ion masses, we have

\[
W = \frac{1}{2} \varphi^2 E. \tag{5}
\]

Therefore, it is possible to carry out measurements in an energy range of several electronvolts for particle beams with energies of several kiloelectronvolts, which greatly facilitates the experiment.

The probability of an inelastic process is determined from the production rate of the new particles (which will be referred to as “effect particles”) in the beams after they have crossed each other. If \( \varphi < 10^5 \), which is easily achieved, the effective cross section of the process is independent of \( \varphi \) (within an accuracy of 0.5%) and is equal to (see [8])

\[
\sigma = n_{\text{eff}} V_0 h / I_1 I_2, \tag{6}
\]

where \( n_{\text{eff}} \) is the production rate of the effect particles, \( V_0 \) is the velocity of the beam particles in the laboratory frame, \( I_1 \) and \( I_2 \) are the beam currents, and \( h \) is the beam height in the intersection region. The fact that the cross section of the process is almost independent of \( \varphi \) implies that, at small intersection angles, an uncertainty in the measured value of \( \sigma \) depends only slightly on the shape and horizontal dimensions of the beam intersection region (at a constant particle density in beams over the height \( h \) and, according to formula (6), is only determined by the scatter in the particle energies in the beams:

\[
\Delta \sigma / \sigma = \Delta E / 2E = \Delta V_0 / V_0. \tag{7}
\]

The angular spread (together with the scatter in energies) affects, according to formula (5), only the scatter in the interaction energies

\[
\Delta W / W = \Delta E / E + 2 \Delta \varphi / \varphi. \tag{8}
\]

In our experiments, the angle \( \varphi \) was equal to 4°.

To separate the ion–molecular reaction out of all the processes occurring in the focal region, the \( H_2^+ \) ions were recorded. It was taken into account that their energy was higher than that of \( H_2^+ \) ions by a factor of 1.5, because both the magnitude and direction of the ion velocity remained almost unchanged in the laboratory frame.

3. EXPERIMENTAL SETUP

The experiments were carried out in the DIVO facility [8]. The system for separating and recording the secondary particles was substantially modified. A schematic of the experimental setup is shown in Fig. 1.

Molecular hydrogen ions were produced in an RF ion source \( S \). Then, they were extracted and an ion beam was formed by a lens system \( L \). A magnet monochromator \( M \) separated \( H_2^+ \) ions out of the total ion flow, formed the beam, and directed it into a high-vacuum (\( p \approx 10^{-7} \) torr) chamber HVC. At the entrance to the chamber, a diaphragm \( D_1 \) with two slits (2 mm in width and 8 mm in height) was installed, which split the primary ion beam into two beams (\( I_1 \) and \( I_2 \)). To adjust the position of the focal region of the primary beam at diaphragm \( D_1 \), quadrupole lenses \( QL \) and vertical...