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DISSOCIATION OF VIBRATIONALLY EXCITED
MOLECULAR HYDROGEN IONS ON HYDROGEN GAS

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Dissociation of Vibrationally Excited Molecular Hydrogen
Ions on Hydrogen Gas*

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ABSTRACT

By appropriate operation of the hydrogen ion source, H_3^+ ions were obtained that have an abnormally high cross section for the dissociation reaction $H_3^+ + H_2 \rightarrow H_2^+ + H + H_2$. The cross section increases with energy from $6 \text{ \AA}^2$ at 5 keV to $10 \text{ \AA}^2$ at 50 keV. "Normal" ions gave $1.5 \text{ \AA}^2$ to $2.5 \text{ \AA}^2$ over the same range. The companion reaction of H_3^+ giving H^+ has a cross section varying from $0.5 \text{ \AA}^2$ at 5 keV to $1.6 \text{ \AA}^2$ at 35 keV. Corresponding cross sections for "vibrationally excited" ions are about $0.25 \text{ \AA}^2$ higher.

The dissociation of H_2^+ to give H^+ has a cross section of about $1.6 \text{ \AA}^2$ over the range 5 to 45 keV. The molecular ion H_5^+ has been obtained from the source. Its dissociation to H^+ with one-fifth the energy has a cross section of $3.2 \text{ \AA}^2$ at 20 keV and is independent of source condition. Excited H_3^+ may prove to be useful for transverse injection into a mirror machine.

INTRODUCTION

When atomic ions react only the relative velocity of the reactants, and short-lived electronic excitation of the ions, will affect the result. However with molecular ions the additional property, molecular vibration,

can become important. Dissociative collisions of the molecular ions H_2^+ and H_3^+ on H_2 gas provide an example of this. These reactions were studied by McClure.¹

The present work was undertaken to explore possible differences between our rf-excited ion source and McClure's Penning source. Also the effect of source condition on the extent of reaction was studied in greater detail. The reactions were studied by measuring the product ion currents directly in a Faraday cup.

The vibrational excitation cross sections for H_2 by electron impact has been recently measured by Schulz.² He finds that the cross section is $0.6 \text{ \AA}^2$ at 2 eV for the vibrational state, $v = 1$, and $0.1 \text{ \AA}^2$ at 3.4 eV for $v = 2$. Using the calculations of Hirschfelder³ heats of reaction for the production of H_3^+ can be obtained.

While it is not clear which of these reactions is dominant in forming the vibrationally excited H_3^+ ions, opportunity for excitation exists and may vary with a change in ion source parameters.

EXPERIMENTAL

Ions from an rf ion source with aperture extraction were accelerated, focused, and collimated. They then traversed a reaction region in which the pressure could be varied. The original ions and those resulting from dissociation were magnetically analyzed and detected in a Faraday cup. Figure 1 illustrates the system.

Fig. 1. Apparatus for measuring dissociation of molecular ions.

The rf source was operated at an H_2 pressure of about 5μ Hg. About 40 W of 66 Mc/sec rf power was dissipated. The distribution of ions produced and the total current were sensitive to the source magnet current. For H_3^+ , the vibrationally excited ions were obtained with a magnetic field of 495 G on axis at the surface of the source magnet. The "normal" ions were obtained at a field of 165 G. The corresponding rf voltages were 140 and 100. The complex behavior of the source will be discussed in more detail in a separate report.

Since the dissociated ions may possess a small transverse energy, the initial beam must be narrow and the detector slit wide to include all such ions. The beam was collimated to $1/16$ in. and the detector slit was $3/8$ in. wide. For ions starting at the orifice plate the detector was thus 0.8° wide and for ions near the analyzer magnet, 3° wide. The adequacy of this system to collect dissociated ions was tested directly at 15 keV using H_2^+ ions. Such a beam gave an image,⁴ on MoO_3 , $5/64$ in. wide. The corresponding image for the $H^+ E/2$ ions (those resulting from dissociation with one-half the energy) was $5/32$ in. wide, ensuring that nearly all ions would enter the detector even at lower energy. In spite of this wide detector slit the resolution for the different ions was adequate.

The ion source high voltage and the analyzing magnet field were steady to a few parts in a thousand. The voltage was measured with a precision resistor stack and a differential voltmeter. To monitor the magnet field the rectified output from a Rawson type 720 probe was smoothed and read with a digital voltmeter. By using the appropriate attenuation the mass and energy peaks gave readings that were the same at different ion energies.

The reaction region pressure was measured with a Veeco gage, which had been calibrated with a McLeod gage, and the output measured with a Keithley Model 415 pA meter for higher resolution. The ion current was plotted on the Y coordinate of an X-Y plotter as a function of reaction region pressure. In this way the line drawn by a product ion could be extrapolated to zero pressure. This eliminated any effect from source gas leakage and other background effects. Extrapolating the reactant ion current to zero pressure gave the initial ion flux. The pressure point at which measurements were made was 4.3×10^{-5} mm Hg. At this point the extent of reaction was usually less than 5%.

The data were corrected for the attenuation of the beam by charge transfer. The change in current of a product ion, $di_p = i_n \sigma_d dX$, where i is the current at position X , σ_d is the dissociation cross section, and n is the density of the H_2 molecules. When the charge transfer cross section, σ_{10} , is large compared with the σ_d , $i = i_0 e^{-n\sigma_{10}X}$, where i_0 is the ion current at the beginning of the reaction region. Substituting, $di_p = n\sigma_d i_0 e^{-n\sigma_{10}X} dX$ and integrating

$$i_p = \frac{n\sigma_d i_0}{-n\sigma_{10}} (e^{-n\sigma_{10}l} - 1)$$

gives

$$\sigma_d = \frac{i_p}{i_0} \frac{\sigma_{10}}{(1 - e^{-n\sigma_{10}l})},$$

where l is the length of the reaction region.

The reaction region pressure, acceleration potential, and ion currents were measured with an accuracy of about 2%. The various power supplies were all well regulated. In spite of this the precision of some of the resulting data was only about 10% or higher. At present it is

believed that this is caused by the instability of the rf source operating at such a low pressure.

RESULTS

Figure 2 shows the dissociation cross section, σ_d , for the reaction $H_3^+ + H_2 \rightarrow H_2^+ + H + H_2$ as a function of the H_3^+ energy. The lower (solid) curve is for a source magnet field of 165 G or less and the upper is for a field of 495 G. Some earlier runs showed points that fall close to McClure's (Penning source) data. In general, different shaped points on the curves show data taken on different days. An upward flag shows the source magnet field was high at 495 G; a downward flag shows a field of 165 G; and a down to the right flag shows no field at all, i. e., 0 G.

Figure 3 shows the same for the reaction $H_3^+ + H_2 \rightarrow H^+ + H_2 + H_2$. Here again the higher source magnetic field leads to the higher cross sections but the difference is not nearly so marked as in the reaction leading to H_2^+ .

Figure 4 shows the total cross section, σ_t , for the H_3^+ ion as obtained by measuring the attenuation of the beam. The dashed lines are calculated by summing previous⁵ values of the charge transfer cross section and the directly obtained σ_d 's just discussed. Because the attenuation measurement could not be made as accurately as the direct ones, the spread is appreciable; however many of the pairs show the higher σ_t associated with high magnetic field at the source. Most of the points fall within the limiting summations.

The dissociation $H_2^+ + H_2 \rightarrow H^+ + H + H_2$ is shown in Fig. 5. Here it should be noted that the higher magnetic field at the source, the lower the cross section. The total cross section for reactions of H_2^+ was

Fig. 2. $\sigma_d(E)$ for the reaction $\text{H}_3^+ + \text{H}_2 \rightarrow \text{H}_2^+ + \text{H} + \text{H}_2$.

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Fig. 3. $\sigma_d(E)$ for the reaction $\text{H}_3^+ + \text{H}_2 \rightarrow \text{H}^+ + \text{H}_2 + \text{H}_2$.

Fig. 4. Total cross section for attenuation of H_3^+ .

Fig. 5. $\sigma_d(E)$ for the reaction $\text{H}_2^+ + \text{H}_2 \rightarrow \text{H}^+ + \text{H} + \text{H}_2$.

obtained by measuring the attenuation of the beam. Here in Fig. 6 the points are spread out considerably but have a lower limit defined by the sum of $\sigma_{10} + \sigma_d$ for H_2^+ .

Finding H_5^+ in the source output was confirmed by also finding H^+ with one-fifth the energy. The dissociation cross section at 20 keV was found to be $3.2 \text{ \AA}^2$ and was independent of source conditions.

DISCUSSION

The ion source was operated at such a pressure, $5 \mu \text{ Hg}$, that the mean free path of a hydrogen ion would be about 11 cm, which is on the same order as the length of the source tube. Since vibrational de-excitation can take place during collision with an H_2 molecule, the effect of the increased source magnetic field may be to guide the ions to the exit orifice. Thus there is less chance for de-excitation. As another factor, when the source field is 960 G, a 1-eV H_3^+ ion, with the velocity perpendicular to B, will have an orbit radius comparable to the orifice diameter of the source.

In these dissociation reactions, an electric field, between the ion and the induced dipole of the hydrogen molecule, perturbs the electronic structure of the ion. If this occurs when the molecule is stretched out, dissociation is more probable. The theory of dissociation in an electric field has been discussed by Hiskes.⁶ Whether an H_2^+ or an H^+ ion splits off will depend on the angular orientation of the ion with respect to the perturbing molecule. If the vibration energy of the ion is 2 eV, the period, $\tau = h/2\text{eV} \approx 5 \times 10^{-15}$ sec. For a 15-keV H_3^+ the time T to cross a distance equal to the diameter of the $7\text{-\AA}^2$ cross section is 3×10^{-16} sec.

Fig. 6. Total cross section for attenuation of H_2^+ .

Thus it is seen that $\tau/T = 6.7$ and the internuclear distances remain fairly constant during a collision.

In any or all of these reactions, it has been shown by Hatfield and Hughes⁷ that the target hydrogen molecule may be dissociated and the Balmer lines excited. Also the fast H atoms produced may be similarly excited.

In the case of H_2^+ , source conditions which gave high dissociation cross sections for H_3^+ gave slightly low ones for H_2^+ . It is suspected that charge transfer of H_2^+ may be increasing under these circumstances and future experiments are planned to prove the point.

H_3^+ , with its large dissociation cross section when vibrationally excited, may prove to be a useful ion for transverse injection into a magnetic mirror field. Since the dissociation discussed above results from an electric field induced in the molecule, it follows that Lorentz field dissociation should be correspondingly easy.

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