TABLE V. Principle absorption energy for some hydrocarbons.[a]

Species	Benzene	Naphthalene	Anthracene
Calculated	6.90	5.69	5.20
Observed	6.75	5.63	5.24

[a] All energies in eV.

the region subjected to experimental studies. We have not calculated oscillator strengths for the corresponding transitions, but we expect that, in general, they should be small due to the strong mixing of configurations in the theory.[1] The principle absorption peak in the spectrum is given very accurately by the present theory as is shown in Table V.

Pariser[27] found it possible to give a further classifica-

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[27] R. Pariser, J. Chem. Phys. 24, 250 (1956).

tion of the states of even alternant hydrocarbons. His results are dependent upon the dispersion law for quasi-particle energies. The present theory does not give rise to such a classification.

The research reported is an attempt to show that Green's function methods could be used with advantage in molecular theory, and we hope to elaborate the approach further.

ACKNOWLEDGMENTS

Dissociation of Molecular Hydrogen Ions Enhanced by Ion-Source Operation*

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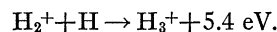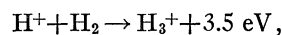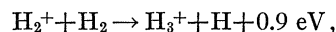
(Received 15 March 1965)

The cross section for the dissociation reaction $H_3^+ + H_2 \rightarrow H_2^+ + H + H_2$ increased by a factor of about 4 when the rf ion-source magnet field was raised. This increase is attributed to H_3^+ ions in high vibrational states. The energy dependence of the cross section was measured. Excited ions increased from 6 Å^2 at 5 keV to 10 Å^2 at 50 keV, whereas the normal ions increased from 1.5 to 2.5 Å^2 over the same energy range. The companion reaction cross section, for H_3^+ producing H^+, was 0.5 Å^2 at 5 keV increasing to 1.6 Å at 35 keV. Cross sections were about 0.25 Å^2 higher for excited ions than for normal ions. The cross section for dissociation of H_2^+ to H^+ was about 1.6 Å^2 from 5 to 45 keV. H_5^+ was detected; its dissociation to H^+ with one-fifth the energy gave a cross section of 3.2 Å^2 at 20 keV, independent of source condition. Excited H_3^+ may be a useful ion for transverse injection into a magnetically confined plasma.

INTRODUCTION

THERE are cases where investigators may obtain differing cross sections for dissociation or charge transfer because their molecular ions have varied distributions of vibrational states. Such a change in the dissociation of H_3^+ and H_2^+ was detected by McClure[1] when he changed his Penning ion-source conditions. The dissociation of H_2^+ was also studied by McGowan and Kerwin.[2] The present work investigates changes in dissociation when an rf-excited ion source is employed. Such data are required in interpreting experiments in which fast neutral products are detected; from these experiments electron-capture cross sections may be obtained.[3] In addition, the present work studies in more detail the effect of source parameters on dis-

sociation. Fast charged products from both H_3^+ and H_2^+ with energies from 5 to 50 keV have been measured as currents after magnetic analysis.

In the ion source, H_2^+ is formed by electron ionization. McGowan and Kerwin[2] have shown the increase in subsequent collisional dissociation that results from increasing the source electron energy. With H_2^+ the Franck-Condon principle puts an upper bound on the vibrational level that can be reached. With H_3^+, however, the excess energy of formation can excite the higher vibrational states. Three of the possible reactions forming H_3^+ follow. The heats of formation were calculated using the results of Hirschfelder.[4]

$$H_2^+ + H_2 \rightarrow H_3^+ + H + 0.9 \text{ eV},$$

$$H^+ + H_2 \rightarrow H_3^+ + 3.5 \text{ eV},$$

$$H_2^+ + H \rightarrow H_3^+ + 5.4 \text{ eV}.$$

The first reaction has been studied by Stevenson and

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[1] G. W. McClure, Phys. Rev. 130, 1852 (1963).
[2] J. M. McGowan and L. Kerwin, Can. J. Phys. 42, 972 (1964).
[3] E. S. Chambers, Lawrence Radiation Laboratory, Livermore, Report No. UCRL-6987 Rev. 1 (unpublished).

[4] J. D. Hirschfelder, J. Chem. Phys. 6, 795 (1938).

Schissler.[5] The last would result in dissociation unless a third body were available to accept the excess energy. The second is questionable without a third body.

EXPERIMENTAL

Fast ionic dissociation products resulting from the collisions of H_3^+ and H_2^+ with H_2 molecules were measured as currents after magnetic analysis. Figure 1 illustrates the system. The reactant and product ion "spectrum" is shown in Fig. 2, where E refers to the initial ion energy and the fractions of E indicate the mode of dissociation.

The previously described[6] rf-excited ion source was operated at 5×10^{-3} Torr of H_2. About 40 W of 66-Mc/sec power was dissipated. Currents of the ions produced and their ratios were sensitive to the source magnet field. For H_3^+, vibrationally excited ions were produced by a source magnet field of 495 G. "Normal" ions were obtained at 165 G. The excited H_3^+ ions have also been observed[6] to produce a higher-than-normal secondary electron yield on Cu-Be.

The plasma from the source flows through the aperture and is then extracted by the full accelerating voltage. The einzel lens is exaggerated in Fig. 1. It is 2.8 in. between the source aperture and the ground electrode collimator plate.

For H_2^+ the electronic excitation from the ground state $^2\Sigma_g$ to the $^2\Sigma_u$ state is the lowest energy mode that leads to dissociation. For an H_2^+ produced by ionization of H_2 the lowest vibration state is $v=0$. The minimum electronic excitation required to excite to the $^2\Sigma_u$ state will occur when the two nucleons are at their maximum separation. The potential-energy curves show that the resulting separated atoms will have only 2.8 or 1.4 eV
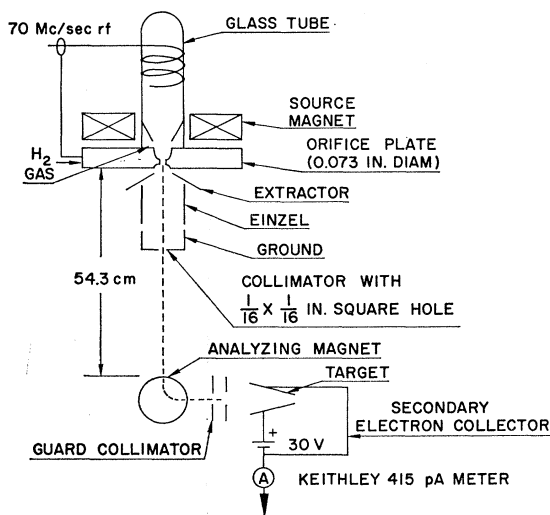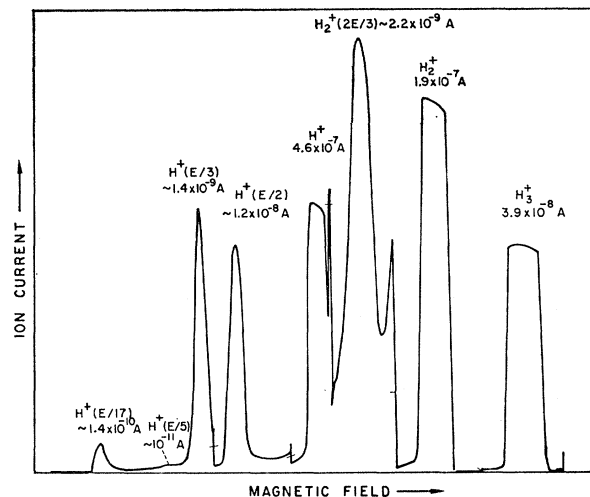

FIG. 2. "Spectrum" of reactant and product ions.

each. For H_2^+ ions in higher vibration levels the corresponding separation energies will be smaller, as discussed by McGowan and Kerwin.[2] For an unfavorable orientation of the H_2^+ ion the separation energy spreads the beam. However, for a 10-keV ion the maximum spread is only 0.7° each side of center. The beam was collimated to $\frac{1}{16}$ in. and the detector slit was $\frac{3}{8}$ in. wide. For collisions near the orifice plate the detector is 0.8° wide and for collisions near the analyzer magnet, 3° wide. The collection adequacy was tested directly using 15-keV H_2^+ ions. By placing a plate coated with molybdenum trioxide at the detector collimator, a blue image of MoO_2 $\frac{5}{64}$ in. wide was obtained. An image of the dissociation product $H^+(E/2)$ was $\frac{5}{32}$ in. wide, ensuring that nearly all ions would enter the detector even at lower energy. This width showed that the ions with maximum transverse energy, discussed above, were comparatively small in number. In spite of this wide detector, Fig. 2 shows adequate resolution of the species.

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.

The reaction-region pressure was measured with a Veeco ionization gage which had been calibrated with a McLeod gage. The collector current of the Veeco gage was measured with a Keithley model 415 pA meter for higher resolution. Matheson prepurified hydrogen was added to the reaction region at a central box. The pump was also connected with this box. Thus the gas pressure was constant throughout the reaction region except for hydrogen coming from the source. Ion current, after magnetic analysis, was plotted on the Y coordinate of an $X-Y$ plotter as a function of reaction-region
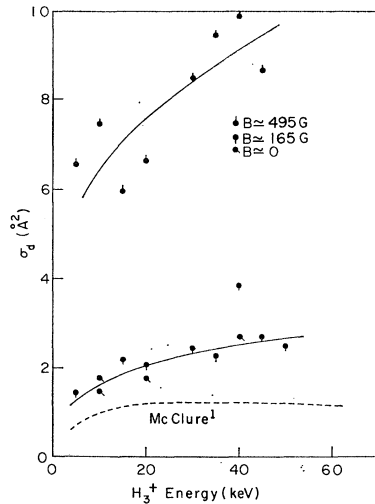

FIG. 1. Apparatus for measuring dissociation of molecular ions.

[5] D. P. Stevenson and D. O. Schissler, J. Chem. Phys. 29, 282 (1958).

[6] E. S. Chambers, Rev. Sci. Instr. 36, 41 (1965).

FIG. 3. Dissociation cross section for production of fast H_2^+ from H_3^+ ions in H_2 gas showing the effect of source magnet field.

pressure. In this way the line drawn by a product ion could be extrapolated to zero pressure. This eliminated product ions caused by source gas leakage and any extraneous current from scattering of reactant ions. Extrapolating the reactant ion-current curve to zero pressure gave the initial ion flux. This same curve was used to measure attenuation of the beam. The pressure point at which measurements were made was 4.3×10^{-5} mm Hg. At this point the dissociation of the beam was usually less than 5%.

As a first approximation with H_2^+, the dissociation cross section σ_d may be obtained from the initial H_2^+ current i_0, the H^+ product current i_p, the H_2 gas density n, and the reaction-region length l. However, there are a number of complications that arise. The H_2^+ ions are reduced in number by electron capture as they travel through the reaction region. The product H^+ ions from dissociation are also attenuated by electron capture. Dissociative ionization produces two H^+ ions instead of one as in a simple dissociation.

The attenuation of the beam by electron capture was corrected for by using the equation

$$\sigma_d = \frac{i_p \sigma_{10}}{i_0 [1 - \exp(-n\sigma_{10} l)]},$$

where σ_{10} is the electron-capture cross section for $H_2^+ \rightarrow H_2$. For the conditions of these experiments the correction is about 5%.

The loss of H^+ by electron capture can be corrected by using an equation that is identical to the one above. At 15 keV the two cross sections are almost the same so that this error is also about 5%. This correction was not made; however, it is partly compensated for by the dissociative ionization $H_2^+ \rightarrow 2H^+$. The effect of this was estimated by an extended extrapolation of Guidini's[7] work, which gave $\sigma_i/(\sigma_d + \sigma_i) = 0.23$ at 15 keV, where σ_i

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[7] J. Guidini, *Atomic Collision Processes* (North-Holland Publishing Company, Amsterdam, 1964), p. 751.

is the dissociative ionization cross section. The additional H^+ ion per H_2^+ ion yields an apparent cross section which is 12% higher than the total dissociation cross section. Since the extrapolated ratio may not be correct it is not incorporated in the results. Hence the final results presented may be about 7% high, due to leaving out this correction for dissociative ionization and the partially compensating correction for loss of H^+ by electron capture.

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 accuracy of some of the resulting data was only about ±10%. At present it is believed that this is caused by the instability of the rf source operating at such low pressure.

RESULTS

Figure 3 shows σ_d, the dissociation cross section per molecule, for the reaction $H_3^+ + H_2 \rightarrow H_2^+ + H + H_2$ as the function of the H_3^+ energy. The lower (solid) curve is for a source magnet field of 165 G or less and the upper curve is for a field of 495 G. 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, zero G. The McClure curve is based on his $\sigma(H_2^+)$. The specific reaction written above is based on the detection of H_2^+ when H_3^+ reacts with H_2. The fate of H_2 was not determined. A similar remark applies to the reaction in the following paragraph.

Figure 4 shows the cross section for the companion reaction $H_3^+ + H_2 \rightarrow H^+ + H_2 + H_2$. Here again the higher source magnet field leads to the higher cross sections but the difference is not nearly so marked as in the reaction producing H_2^+. The McClure curve is based on his $\sigma(H^+)$. Thus his curve and the present data may be slightly high when interpreted as σ_d because of dissociative ionization. The same applies to the H_2^+ dissociation discussed below.
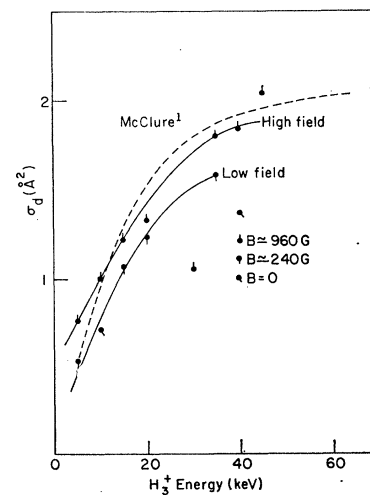

FIG. 4. Dissociation cross section for production of fast H^+ from H_3^+ in H_2 gas, showing the effect of source magnet field.
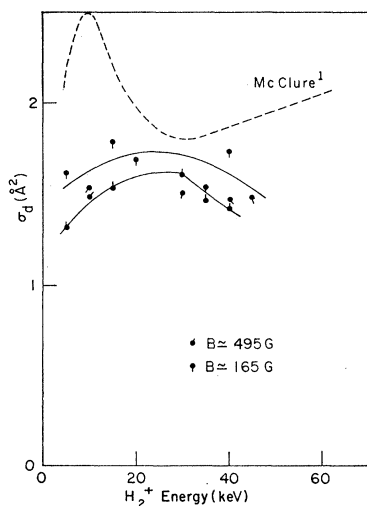
FIG. 5. Dissociation cross section for production of fast H^+ from H_2^+ in H_2 gas, showing the effect of source magnet field.

The dissociation $H_2^+ + H_2 \rightarrow H^+ + H + H_2$ is shown in Fig. 5. Here the data suggest that the higher the magnetic field at the source, the lower the cross section.

Finding H_5^+ in the source output was confirmed by also finding H^+ with one-fifth the energy. This indicates a possible reaction $H_5^+ + H_2 \rightarrow H^+ + 3H_2$. Obviously other dissociation reactions may occur. The dissociation cross section at 20 keV was found to be 3.2 $Å^2$ and was independent of source conditions. Dawson and Tickner[8] also detected H_5^+.

DISCUSSION

The ion source was operated at a pressure of 5×10^{-3} Torr, so 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. A strong source magnet field prevents collisions with the wall and guides the ions down toward and through the exit orifice. This reduces the number of collisions between the ions and gas molecules and hence may reduce vibrational de-excitation.[9] This may explain the difference in ion character as the magnetic field is varied.

In these dissociation reactions, an electric field between the ion and the induced dipole of the hydrogen molecule perturbs the electronic structure of the molecular ion. If this occurs when the molecular ion is stretched out, dissociation is more probable. The theory of dissociation in an electric field has been discussed by Hiskes.[10] 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 E of the ion is 2 eV, the period $\tau = h/E \approx 5 \times 10^{-15}$ sec. For a 15-keV H_3^+, the time T to cross a distance equal to the diameter of the 7 $Å^2$ cross section is 3×10^{-16} sec. Thus it is seen that $\tau/T = 16.7$ and the internuclear distances remain fairly constant during a collision.

In Fig. 3 the lower McClure curve may represent the ions that are close to the ground state, while the lowest curve of the present work may be partially excited.

In any or all of these reactions, it has been shown by Hatfield and Hughes[11] that the target hydrogen molecule may be dissociated and the Balmer lines excited. Also, the fast H atoms may be similarly excited.

In the case of H_2^+ (Fig. 5), source conditions which gave high dissociation cross sections for H_3^+ gave slightly low ones for H_2^+. It is suspected that charge transfer for H_2^+ may be increasing under these circumstances, and future experiments are planned to investigate this possibility. Cause of the differences from McClure's curve is not understood.

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 probably results from an electric field induced in the molecule, it follows that Lorentz force-field dissociation will also be increased.

ACKNOWLEDGMENTS

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[9] T. L. Cottrell and J. C. McCoubrey, *Molecular Energy Transfer in Gases* (Butterworths Scientific Publications Ltd., London, 1961).

[10] J. R. Hiskes, Phys. Rev. **122**, 1207 (1961).

[11] L. L. Hatfield and R. H. Hughes, Phys. Rev. **131**, 2557 (1963).