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Merged Beam Studies of the Dissociative Recombination of H_3^+ and H_2^+

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This report is intended to provide an update on the progress of an ongoing investigation into the recombination of electrons with hydrogenic molecular ions, namely, H_2^+ and H_3^+. Recombination is of major importance in determining the physical and chemical state of plasmas such as are found in H^- ion sources. Molecular ions are usually created with considerable internal energy in the form of vibrational and rotational excitation. Under this condition such ions generally exhibit large recombination rates [1] and will represent a significant loss mechanism for low energy electrons in the discharge. These electrons are needed for attachment to vibrationally excited H_2 molecules in order to produce H^-.

Theoretical [2,3] and experimental studies [4] of recombination made in recent years have raised a number of questions regarding the influence of vibrational excitation of the recombining ions on the reaction rate and indeed concerning the identity of the actual recombination mechanism.

This program of study is intended to provide a clear understanding of the mechanism and the behaviour of electron $-H_2^+$ and electron $-H_3^+$ recombination for ions in both low and excited vibrational states. This knowledge should be useful for determining optimal source operating conditions for H^- production.

H_3^+ recombination

Over the past year studies of H_3^+ ions have been performed using ions prepared in a radiofrequency trap ion source. Measurements of the dissociative excitation of H_3^+ ions are carried out concurrently with the recombination measurements and allow the internal energies of the ions to be determined. We have been able to produce H_3^+ ions with only the $v = 0$ and 1 levels populated and have found that they display a recombination cross section given by $2.17 \times 10^{-16}(E_{cm})^{-0.57}$ below 0.03 eV and $3.23 \times 10^{-17}(E_{cm})^{-1.15}$ above. This corresponds to a rate coefficient of $\sim 1 \times 10^{-8} cm^3 s^{-1}$ at 300K, which is consistent with published results of Adams et al [4] although it is much higher than a more recent upper limit of $2 \times 10^{-11} cm^3 s^{-1}$ which they have claimed [5]. Michels and Hobbs [3] have predicted that the curve crossing with the repulsive state through which H_3^+ will recombine occurs in the vicinity of $v = 3$.

A manuscript currently in preparation, which describes our measurements in detail, has been submitted for publication and is included in Appendix A.

Work is in progress to bring a new merged beam experiment, MEIBE II on line. This is capable of operating at much lower pressures than the original MEIBE I apparatus. Once operational, this will be used for studying the branching ratio for the decay channels following H_3^+ recombination. Preliminary measurements of this have been published previously [6] however the poor signal to background ratio encountered prevented a detailed examination of the process.

Given our ability to control and measure the internal energy of the H_3^+ ions it will be very interesting to see how the branching ratio varies with vibrational state. It has been suggested (R. Johnsen, 1987, Private Communication) that e-H_3^+ (v = 0) recombination may proceed via the formation of a long lived H_3 molecule which subsequently decays radiatively. This decay process has been examined recently by Kulander and Light (6,7]. Studies of the branching ratio will tell us if indeed this channel is important to the overall recombination process.

It is also our intention to study the branching ratio for the isotopic forms of H_3^+ namely HD_2^+ and D_3^+.

H_2^+ Recombination

The dissociative attachment of electrons to vibrationally excited H_2 is the primary mechanism for the formation of H^- ions in the gas phase. an analogous reaction to this is the dissociative recombination of H_2^+ ions. The primary difference between the two processes is due to the presence of Rydberg states of H_2 lying below the H_2^+ ground state. These states have a great influence on the recombination since they can participate in the electron capture via the indreict mechanism [8] namely: -

$$e + H_2^+ \rightarrow H_2^R \rightarrow H_2^{**} \rightarrow H^* + H.$$

Furthermore, curve crossings to these Rydberg states from the repulsive H_2^{**} state lead to the formation of electronically excited product H atoms.

H_2^+ ions are an important constituent of the hydrogen plasma at low densities and like H_3^+ they will act as a sink for low energy electrons. The H_2^+ ion is also especially important to fundamental studies of electron-ion recombination as it is amenable to theoretical calculations and is a good testbed for studies concerning the role of the indirect process. The curve crossing to the repulsive H_2^{**} through which the direct recombination proceeds, i.e.

$$e + H_2^+ \rightarrow H_2^{**} \rightarrow H^* + H$$

occurs in the vicinity of v = 2. For H_2^+ in the v = 0 and 1, the indirect process will play a major role in the recombination. A number of calculations of H_2^+ recombination via both the direct and indirect mechanisms have been performed by Giusti et al [9], Nakashima et al [10] and by Hickman [11]. The former two studies, using a Multichannel Quantum Defect Theoretical (MQDT) approach predict that interference between the direct and indirect processes will be destructive leading to resonant dips in the cross section vs energy curve. Hickman, using a Configuration Interaction (CI) approach however predicts constructive interference leading so resonant enhancement of the cross section.

A preliminary measurement of e-H_2^+ recombination has been made using the MEIBE I apparatus and very narrow deep window resonances are evident in the results. A manuscript describing these measurements has also been submitted for publication and is given in Appendix B.

This measurement is very significant for two reasons. (a) It is the first clear indication that Rydberg states play a major role in the recombination process. Since the molecular ions are prepared in only two vibrational states a direct comparison with theoretical calculations is possible. (b) This is the first time that the high energy resolution of a merged beam experiment has been demonstrated directly. it can be seen from Fig. 3, Appendix B that there is a very narrow resonance at 0.1 eV collisions energy that is less than 20 meV wide. The instrumental resolution therefore is better than this value. This opens up the field of high resolution electron ion recombination studies and it will be interesting to search for these resonances not only in hydrogen but in other ions as well. It also shows that it is indeed valid to use the merged beam technique to study collisions at energy down to <10 meV.

it must be stressed that these results are preliminary and much more effort is called for in order to provide a close test of theory. In particular many more data points must be taken using automatic energy scanning methods in order to properly identify and characterize these resonances. This study will be conducted during the next contract period.

HeH^+ and He^+ measurements

In discussions with David Smith and Nigel Adams in England it was learned that the recent value of $\alpha = 2 \times 10^{-11} cm^3 s^{-1}$ for H_3^+ recombination quoted by them is arrived at by introducing a hydrogen/helium mixture into their flow apparatus so that their afterglow is dominated by HeH^+ and He^+. They find no difference in the decay rate of electrons than when the afterglow is dominated by H_3^+. He^+ certainly can only recombine radiatively at thermal temperatures and HeH^+ has been predicted to have a very low recombination rate so Smith and Adams [5] have quoted the predicted radiative recombination rate of He^+, $(2 \times 10^{-11} cm^3 s^{-1})$ as their H_3^+ recombination rate.

This technique is a cause for concern to two reasons.

(a) The recombination rate for HeH^+ has not been determined experimentally.

(b) It is not clear if the FALP technique is sufficiently sensitive to make such a close comparison.

In order to clear up at least one of these concerns the recombination of HeH^+ will be examined using the merged beam technique during the next contract period.

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APPENDIX

A

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Merged Beam Studies of the Dissociative Recombination of H_3^+ Ions with low internal energy.

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ABSTRACT

Cross sections for the dissociative recombination of H_3^+ ions with low internal energy have been obtained using the merged beam technique. Dissociative excitation measurements have confirmed that only the v = 0 and 1 states were present in the ion beam. The resulting cross sections can be expressed in the form $2.17 \times 10^{-16} E_{cm}^{-0.57} (cm^2)$ for E_{cm} below 0.03 eV and $3.23 \times 10^{-17} E_{cm}^{-1.15} (cm^2)$ above.

The dissociative recombination of H_3^+ is a process of great importance to the physical and chemical state of ionized hydrogen plasmas. Such plasmas are encountered in planetary ionospheres, interstellar clouds, ion sources and fusion reactors. When molecular hydrogen is ionized the H_2^+ ions rapidly react with neutral H_2 gas to form H_3^+ via the reaction:

$$H_2^+(v) + H_2 \rightarrow H_3^+ + H \qquad - - 1.$$

For H_2^+ (v=0) this reaction is exothermic by 1.68 eV.

The ionization of H_2 by energetic electrons or photons however yields H_2^+ ions with all 19 available vibrational states populated (1). Since H_2^+ has no dipole moment the radiative lifetime of these states is ~10^6 seconds (2) so that in practice the exothermicity of reaction (1) will be greater. Experimental studies by Leventhal & Friedman (3) have shown that the bulk of this exothermicity appears in the form of internal excitation of the H_3^+ ions which are formed with on average about 2 eV of internal energy. A calculation of the initial populations of individual vibrational states of H_3^+ formed via reaction 1 has been performed by Anicich and Futrell (4) using a statistical approach and the results are tabulated in Table I. Unlike H_2^+ however, H_3^+ ions are susceptible to collisional de-excitation (5) so the populations of excited vibrational states will decrease with time the rate depending upon the collision frequency.

TABLE I

Calculated population distribution of the vibrational energy of H_3^+ ions formed from reaction 1 prior to de-excitation. (Anicich and Futrell, 1983/84)

V	POPULATION	ENERGY (eV)
0	0.0341	0.0
1	0.0919	0.372
2	0.1601	0.744
3	0.2197	1.116
4	0.2303	1.488
5	0.1387	1.860
6	0.0796	2.232
7	0.0299	2.604
8	0.0109	2.976
9	0.0037	3.348
10	0.0010	3.720
11	0.0001	4.092

An important question for the modelling of hydrogen plasmas concerns the fate of the H_3^+ ions formed via reaction (1). It has always been assumed (6) that H_3^+ decays via dissociative recombination with electrons, i.e.

$$H_3^+ + e \rightarrow H_2 + H \qquad \text{-- 2a}$$

$$\rightarrow H + H + H \qquad \text{-- 2b}$$

A number of measurements of this process have been made using both microwave afterglow (7,8), inclined beams (9), merged beams (10,11) and electron beam trap techniques (12). These measurements all agreed with each other to within a factor of two and they all pointed to the process having a large room temperature rate coefficient of $\sim 2 \times 10^{-7}$ $cm^3 s^{-1}$. Measurements of the individual cross sections for reactions 2a and 2b were made by Mitchell et al (13) who showed that reaction 2b dominated reaction 2a by about a factor of two.

Theoretical studies of H_3^+ recombination however indicated that for ions in low vibrational states, the recombination rate should in fact be quite small (14,15). The reason for this can be seen from Figure 1. The direct dissociative recombination of H_3^+ must proceed via an initial capture into the lowest available $^2A_1$ resonance state of H_3 which is repulsive for low internuclear separations. In this way the potential energy of the system is rapidly converted to kinetic energy leading to a stabilization of the recombination. Although the asymptotic limit of the $^2A_1$ state is actually H_2^+ + H^- it has been shown (16) that in fact these products represent only a small fraction of the total recombinations. Curve crossing transitions between this state and singly excited neutral states of H_3 leads to the formation of neutral products.

It can be seen from Figure 1 that the $^2A_1$ state intersects the ground $^1A_1$ state of H_3^+ at about 1 eV above the v = 0 level. It must be expected therefore that direct dissociative recombination of H_3^+ in low vibrational states should be very slow and Michels and Hobbs (15) have argued that indirect dissociative recombination involving initial capture into a vibrationally excited rydberg state followed by transition to the $^2A_1$ resonance state and subsequent dissociation, is also unlikely because of the poor overlap.

This prediction was confirmed recently by studies of H_3^+ recombination in a flowing afterglow apparatus (17). It was found that H_3^+ ions exhibited an initial rapid decay rate followed by a much slower decay, after about 0.5ms. The reason for this rate change was interpreted as being due to the collisional de-excitation of higher vibrational states of H_3^+ in the high pressure (0.5-1.0 torr) environment of the afterglow. The H_3^+ ions initially formed with high internal energy exhibit a large recombination rate but once de-excited the rate diminishes dramatically. Adams et al gave an upper limit to the recombination rate of $2 \times 10^{-8} cm^3 s^{-1}$ at 95°K. More recently, however, this has been revised down to the very low figure of 2 x $10^{-11}cm^3s^{-1}$ (18). These results have stirred considerable controversy not only because they disagree with previous measurements but also because they require a dramatic re-examination of models of physical systems such as the Jovian atmosphere, (19), and interstellar chemistry (20,21).

Previous merged beam measurements (10,11,13) made in this laboratory were performed with ions formed in a conventional rf ion source. The mean residence time of ions in the source has been estimated to be ~30 μ secs and under these conditions it is estimated that about 60% of the ions were vibrationally excited. It is not surprising therefore that these ions displayed large recombination cross sections.

Recently a new ion source has been installed in the Van de Graaff accelerator which is used as the injector into the merged beam experiment. This source uses the method of ion trapping to confine ions for times sufficient to cause collisional de-excitation. The present paper describes measurements of H_3^+ electron recombination using ions which have been demonstrated to be in vibrational states v = 0 and 1 only.

EXPERIMENTAL

The ion source used in this study has been described elsewhere (22) so only a brief description will be given here. Ions formed by electron impact are confined by a radio frequency field to move within a U shaped channel. At the end of this channel they exit the source through an octupole lens.

An earthed aperture sits in front of this lens and the body of the source is maintained at a positive potential to assist in the extraction. Previous studies of Collision Induced Dissociation of H_3^+ -He collisions (23) showed that this source was indeed capable of producing H_3^+ ions with low internal energy.

The ion source is mounted in the terminal of a 400 KeV Van de Graaff accelerator. After acceleration the ions are magnetically mass analyzed and injected into the merged electron ion beam apparatus which has been described in detail elsewhere (10). Inside this apparatus, which is maintained at a pressure of 10^{-9} torr, the beam is deflected to eliminate neutrals formed via charge exchange in the beam line and then passed through the interaction region. The electron beam is formed from an indirectly heated barium oxide cathode and accelerated to a velocity close to that of the ions and in a direction initially parallel to that of the ion beam. For these measurements an ion energy of 400 KeV and electron energies in the range 25-75 eV were used. The electrons are merged with the ions using a trochoidal analyzer which employs an axial magnetic field and a transverse electric field to shift the electrons from their initial path to a parallel but offset path. The latter is arranged to coincide with the ion beam. The beams interact over a distance of 8.6 cms and the overlap of the two beams is measured using three equispaced scanners (24).

Following the interaction, the electron beam is deflected into a faraday cup using a second trochoidal analyzer and its intensity is measured. The ion beam is electrostatically deflected into a second faraday cup. The undeflected neutral products formed in the interaction region are detected using an energy sensitive surface barrier detector. Products from reaction 2 arrive almost simultaneously at the detector and hence appear as a single full beam-energy particle.

At higher collision energies, the reactions

$$e + H_3^+ \rightarrow (H+H) + H^+ + e \qquad --3$$

$$e + H_3^+ \rightarrow H + H_2^+ + e \qquad --4$$

yield H_2 molecules, or H atom pairs and individual H atoms which appear with 2/3 and 1/3 of the full beam energy respectively. Single channel analyzers are used to select the signals arising in the three channels so that they can be counted separately. Hence reactions 2, 3 and 4 can be studied individually. Interaction of the ion beam with the background gas in the interaction region also leads to neutral products in each of the three channels. These signals are distinguished from true signals arising from electron-ion collisions by modulating the electron beam and counting in and out of phase with the modulation using pairs of gated scalers. The difference in the scaler counts gives the true signal.

The collision cross section is determined using the expression: -

$$\sigma = \frac{C_j e^2}{I_i I_e L} \left| \frac{v_i \cdot v_e}{v_i - v_e} \right| F$$

where C_j is the neutral count rate for channel j, I_i, I_e, v_i, v_e are the ion and electron currents and velocities respectively, L is the length of the interaction region, e, the electronic charge and F is the effective collision area (24).

The centre of mass collision energy is given by

$$E_{cm} = (E_e^{\frac{1}{2}} - E_+^{\frac{1}{2}})^2$$

where $E_+ = E_e \cdot m_e/m_i$ and E_i, E_e are the ion and electron energies. In practice the ion energy is held fixed and E_{cm} is varied by varying E_e. In related studies (25) of the recombination of H_2^+ ions, sharp resonances have been seen and the width of these indicate that the energy resolution of the apparatus is better than 20 meV at low energies.

DISSOCIATIVE EXCITATION MEASUREMENTS

Measurements of the threshold for the dissociative excitation process: -

$$e + H_3^+ ({}^1A_1, v) \rightarrow H_3^+ ({}^3E') \qquad -- 4$$

$$\rightarrow H + H_2^+ + e$$

can be used to determine the internal energy of the H_3^+ ions (28). The ${}^1A_1 \rightarrow {}^3E'$ transition is illustrated in figure 2 which shows potential energy curves calculated by Kawaoka and Borkman (26).

These agree closely with earlier calculations by Schaad and Hicks (27). It can be seen that for H_3^+ ($v = 0$), this process is endothermic by about 15.1 eV. As the internal energy of the H_3^+ ions is raised, the excitation threshold moves to lower energies. Since the $^1A_1 \rightarrow {}^3E'$ transition is optically forbidden it proceeds via electron exchange and so only displays a sizeable cross section close to threshold, falling off rapidly at higher energies.

Measurements of reaction 4 were performed for H_3^+ ions formed under a variety of source conditions and the results of these measurements are shown in Figure 3a - 3d. It can be seen from Figure 3a that ions formed in a conventional rf ion source have states higher than $v = 4$ populated, as expected. By using an rf trap source and by varying the source pressure and extraction voltage it is possible to cool the ions in a controlled fashion.

In the absence of a Franck-Condon analysis for transitions involving states in both D_{3h} (symmetric stretch) and C_{2v} (assymmetric stretch), the indicated thresholds for the excited vibrational states must be considered approximate. The results indicate that the ion trap source operating at a low pressure (10mtorr) produces H_3^+ ions with $v = 0, 1, 2$ and 3 (fig. 3b) populated and increasing the pressure to 30mtorr results in the quenching of the $v = 3$ state (Fig. 3c). By reducing the extraction voltage to a low value and thus allowing the ions to remain for a longer period in the trap it is possible to quench the $v = 2$ state (fig. 3d). It should noticed that the threshold in the latter case appears below the $v = 0$ threshold but above that ascribed to $v = 1$ using the potential curves shown in Fig. 2. A double peaked structure is evident though and this would imply that excitation from the $v = 1$ level is occurring. Clarification of this point awaits the Franck–Condon analysis mentioned above.

Assuming that $v = 1$ is present and that the excitation cross section varies little for the $v = 0$ and $v = 1$ levels, then it would appear that these states are approximately evenly populated.

DISSOCIATIVE RECOMBINATION MEASUREMENTS

Cross sections for the dissociative recombination of H_3^+ ions are illustrated in Figure 4. The curves marked a, b, c and d correspond to measurements made using ions formed under varying source conditions leading to the excitation functions as shown in figs. 3a - 3d. It can be seen that for the case of H_3^+ ($v = 0, 1$) the cross section is reduced by about a factor of 13 from that measured for ions obtained from a conventional rf source. This cross section can be expressed in the form $\sigma = 2.17 \times 10^{-16} E_{cm}^{-0.57}$ (cm^2) for E_{cm} below 0.03eV and $3.23 \times 10^{-17} E_{cm}^{-1.15}$ (cm^2) above.

It is possible to estimate a rate coefficient $\alpha(T_e)$ for the recombination using the expression: -

$$\alpha(T_e) = \int_0^\infty \frac{8\pi m_e E_{cm}}{(2\pi m \; kT \;)^{3/2}} \cdot \sigma(E_{cm}) \exp(-E_{cm}/kT_e) dE_{cm}$$

Evaluation of this expression involves a linear extrapolation of our measured data to lower energies although this assumes that the form of the cross section energy dependance does not change greatly outside our measured energy range. The cross section displays a change of energy dependance at 0.03 eV which complicates this analysis. By assuming linear dependances above and below this it is possible to obtain an approximate value for α. The resulting rate coefficient for H_3^+ ions with v = 0 and v = 1 populated varies from $2 \times 10^{-8} cm^3 s^{-1}$ at 100 K to 1×10^{-8} at 1000 K.

It can be seen that our findings reflect the earlier conclusion of Adams et al that the recombination rate is substantially reduced due to the poor overlap with the dissociating state for vibrationally cool ions. More recently Smith and Adams ( ) have revised their estimate for the upper limit for the recombination rate to $2 \times 10^{-11} cm^3 s^{-1}$ at 300K but this result is difficult to reconcile with our measurements. Even if complete de-excitation of H_3^+ is achieved in the FALP technique (and this is inferred not measured), it is difficult to believe that the rate coefficient for H_3^+ (v = 0) is three orders of magnitude smaller than for H_3^+ (v = 1).

Figure 5 shows the variation of the recombination cross section at 0.01 ev as a function of source pressure and extraction and it can be seen that a plateau is reached at the lowest value. At this point the cross section is independent of source conditions suggesting that either it has become rather insensitive to the vibrational state population or that further de-excitation cannot be achieved.

It has been suggested (Johnsen, 1987 private communication) that the method of measuring the rate coefficient might explain the discrepancies between the measurements.

In the FALP technique, a langmuir probe is used to measure the rate of change of H_3^+ concentration while in the merged beam experiment the neutrals following the recombination are detected. It may be that the recombination of H_3^+ $(v = 0)$ with electrons does not proceed via a dissociative path but rather through a process in which long lived H_3 rydberg molecules are formed. These may subsequently decay via radiation emission (29). It is possible that such an entity might appear as an ionized H_3^+ molecule to a Langmuir probe due to potential electron ejection at the probe surface.

In the merged beam case, it takes approximately 10^{-7} seconds for the neutral products to reach the detector and so such a rydberg molecule would have to be stable against autoionization for at least that time. In future studies the branching ratio for the various possible decay channels following the recombination will be measured in an effort to elucidate this problem.

Footnote: A recent reanalysis of the measurements of H_3^+ recombination by Biondi and co-workers indicates that contamination of the afterglow by CH_5^+ ions may explain their high measured rate coefficients (Johnsen - private communication 1987).

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FIGURE CAPTIONS

1. Potential energy curves for H_3^+ and H_3 in C_{2v} symmetry. (Michels and Hobbs, 1984).
2. Potential energy curves for the ground and excited states of H_3^+ in D_{3h} symmetry. (Kawaoka and Borkman, 1971).
3. Cross sections for the dissociative excitation process:-

$$e + H_3^+ \rightarrow H_3^+(^3E^1) \rightarrow H + H_2^+ + e.$$

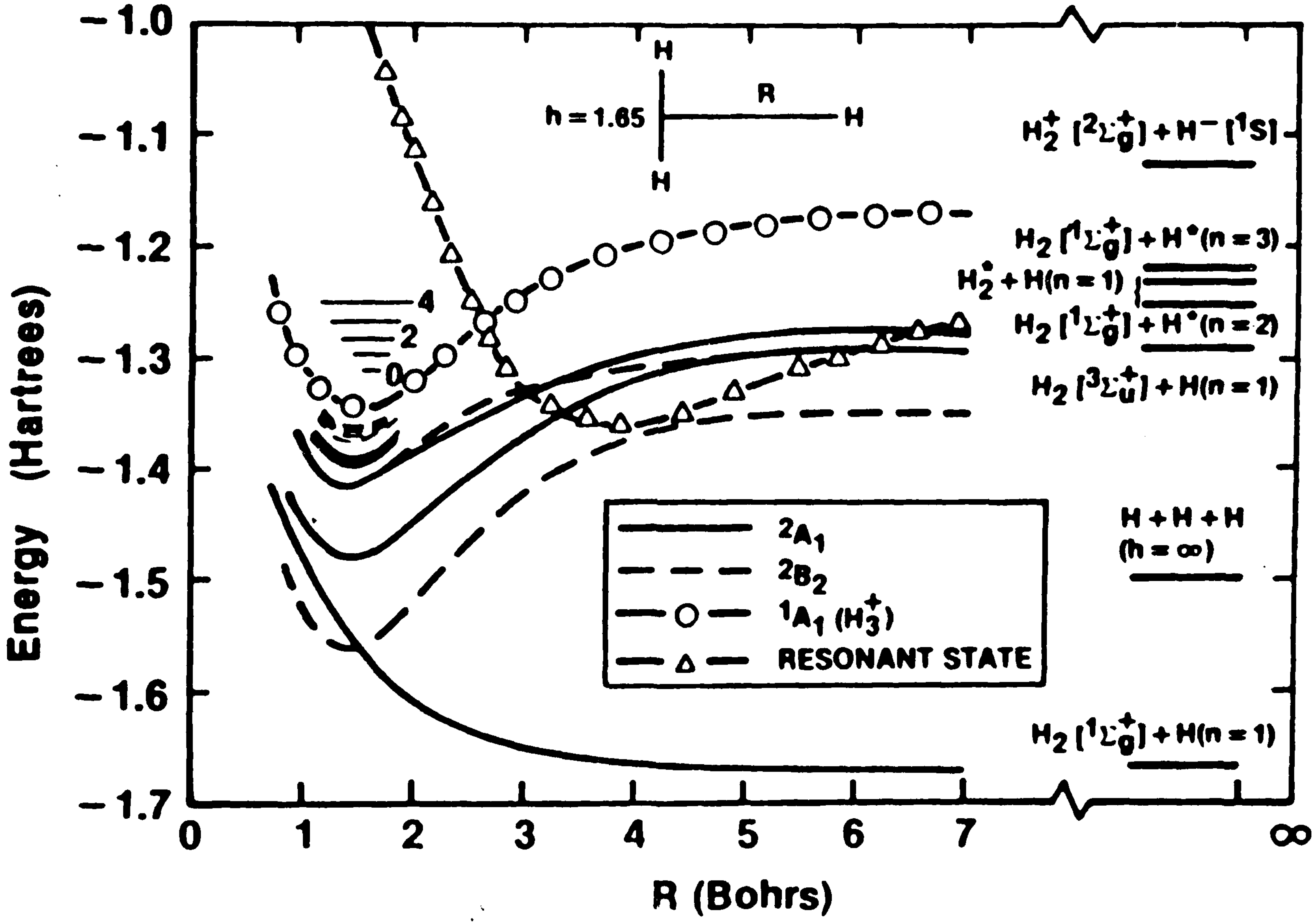
   (a) Ions produced in conventional rf source at 100mtorr pure H_2.

   (b) Ions produced in trap ion source at 10mtorr; pure H_2.

   (c) Trap ion source, 30mTorr; pure H_2.

   (d) Trap ion source, 70mtorr, low extraction 10:3:1 H_2:Ar:He mixture.

4. Cross sections for e - H_3^+ recombination. The four curves shown here were measured using ions formed under conditions which yielded the corresponding four excitation functions shown in fig. 3.
5. Variation of the e - H_3^+ recombination cross section measured at 0.01 eV, as a function of source pressure and extraction voltage (arbitrary units).



Energy (Hartrees)
−1.0
−1.1
−1.2
−1.3
−1.4
−1.5
−1.6
−1.7
0
1
2
3
4
5
6
7
∞
R (Bohrs)
h = 1.65
H
H
R
H
4
2
0
$H_2^+\ [^2\Sigma_g^+] + H^-\ [^1S]$
$H_2\ [^1\Sigma_g^+] + H^*(n=3)$
$H_2^+ + H(n=1)$
$H_2\ [^1\Sigma_g^+] + H^*(n=2)$
$H_2\ [^3\Sigma_u^+] + H(n=1)$
H + H + H
(h = ∞)
$H_2\ [^1\Sigma_g^+] + H(n=1)$
$^2A_1$
$^2B_2$
$^1A_1\ (H_3^+)$
RESONANT STATE

Fig.1.

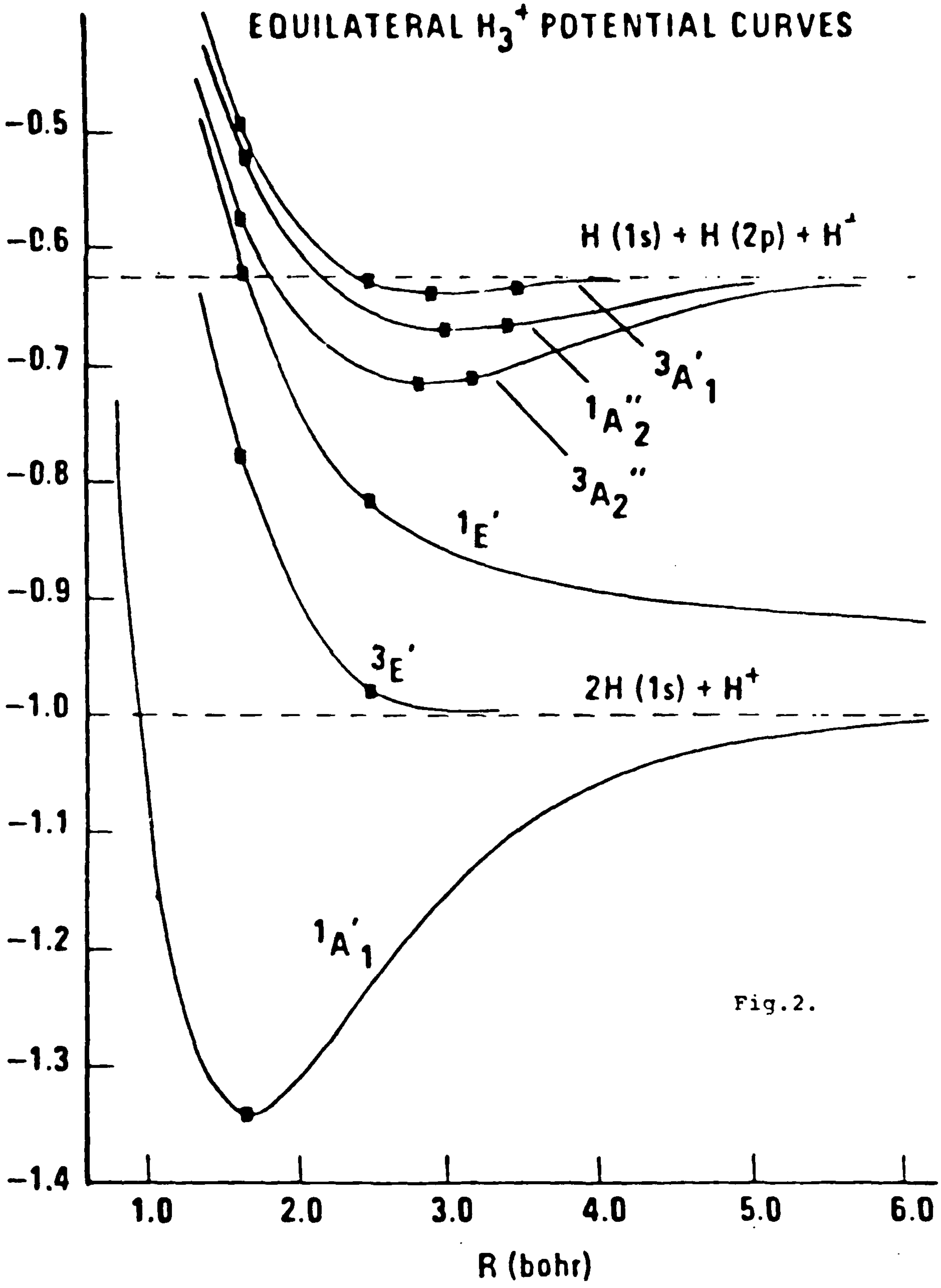

EQUILATERAL H_3^+ POTENTIAL CURVES
-0.5
-0.6
-0.7
-0.8
-0.9
-1.0
-1.1
-1.2
-1.3
-1.4
E (hartree)
1.0
2.0
3.0
4.0
5.0
6.0
R (bohr)
H (1s) + H (2p) + H^+
2H (1s) + H^+
$^3A'_1$
$^1A''_2$
$^3A_2''$
$^1E'$
$^3E'$
$^1A'_1$

Fig.2.

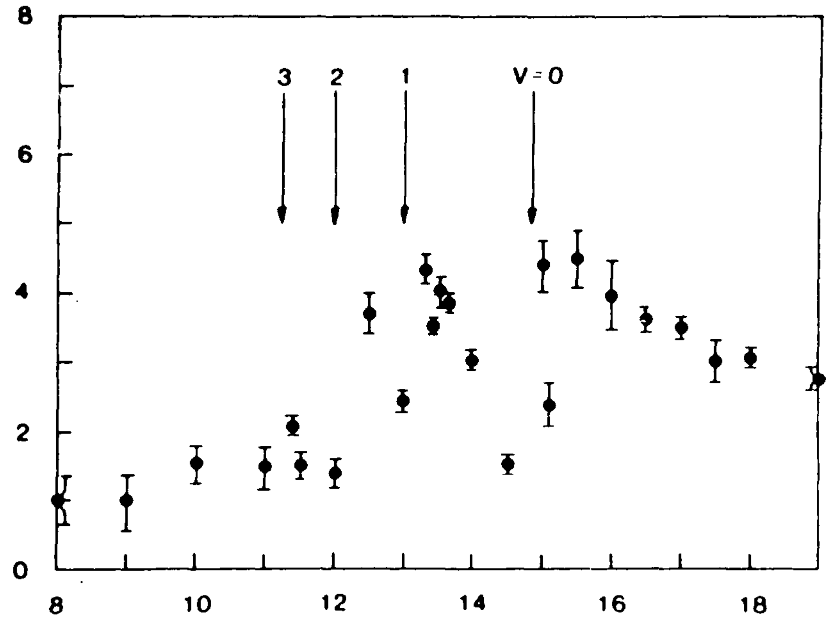


Fig.3a.

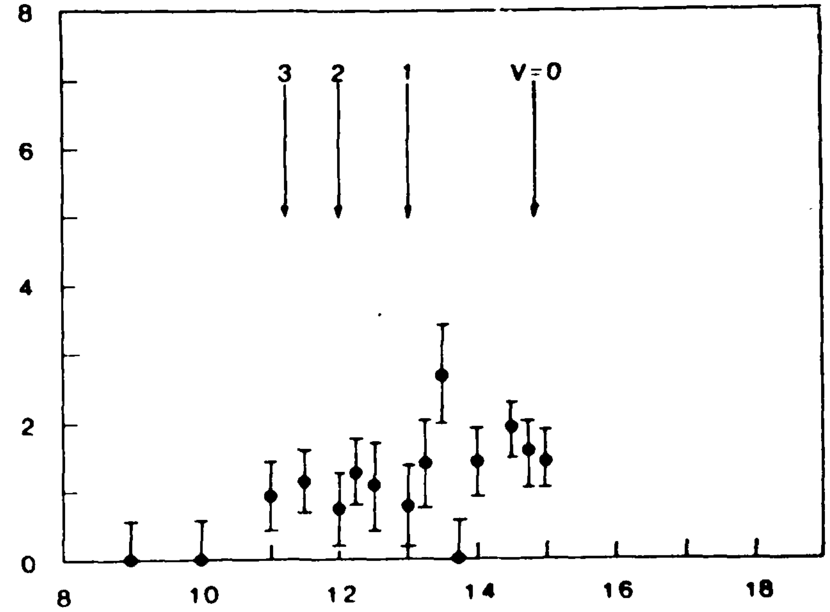
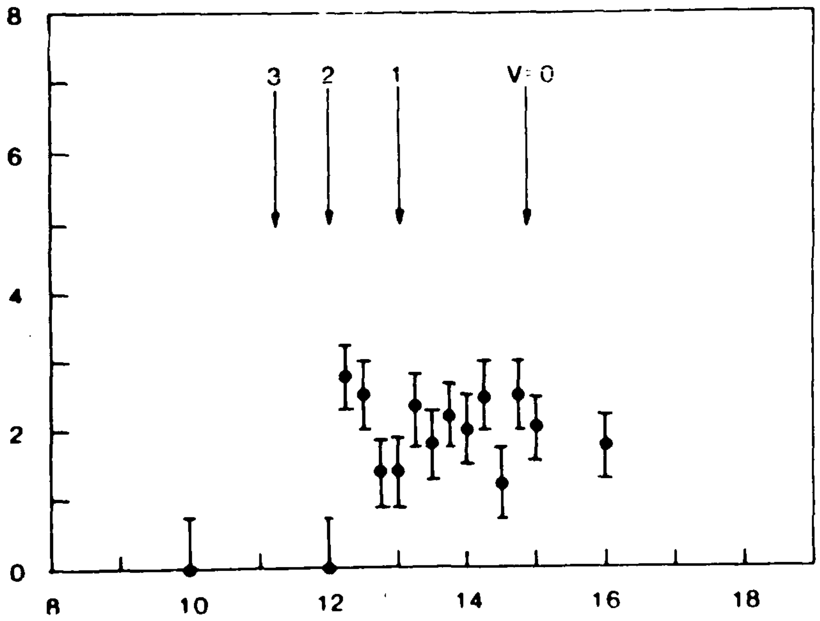
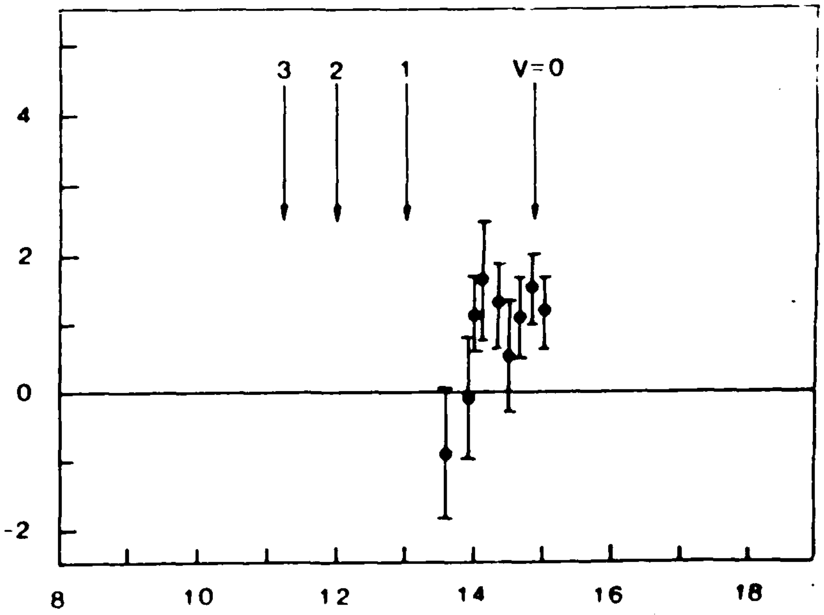


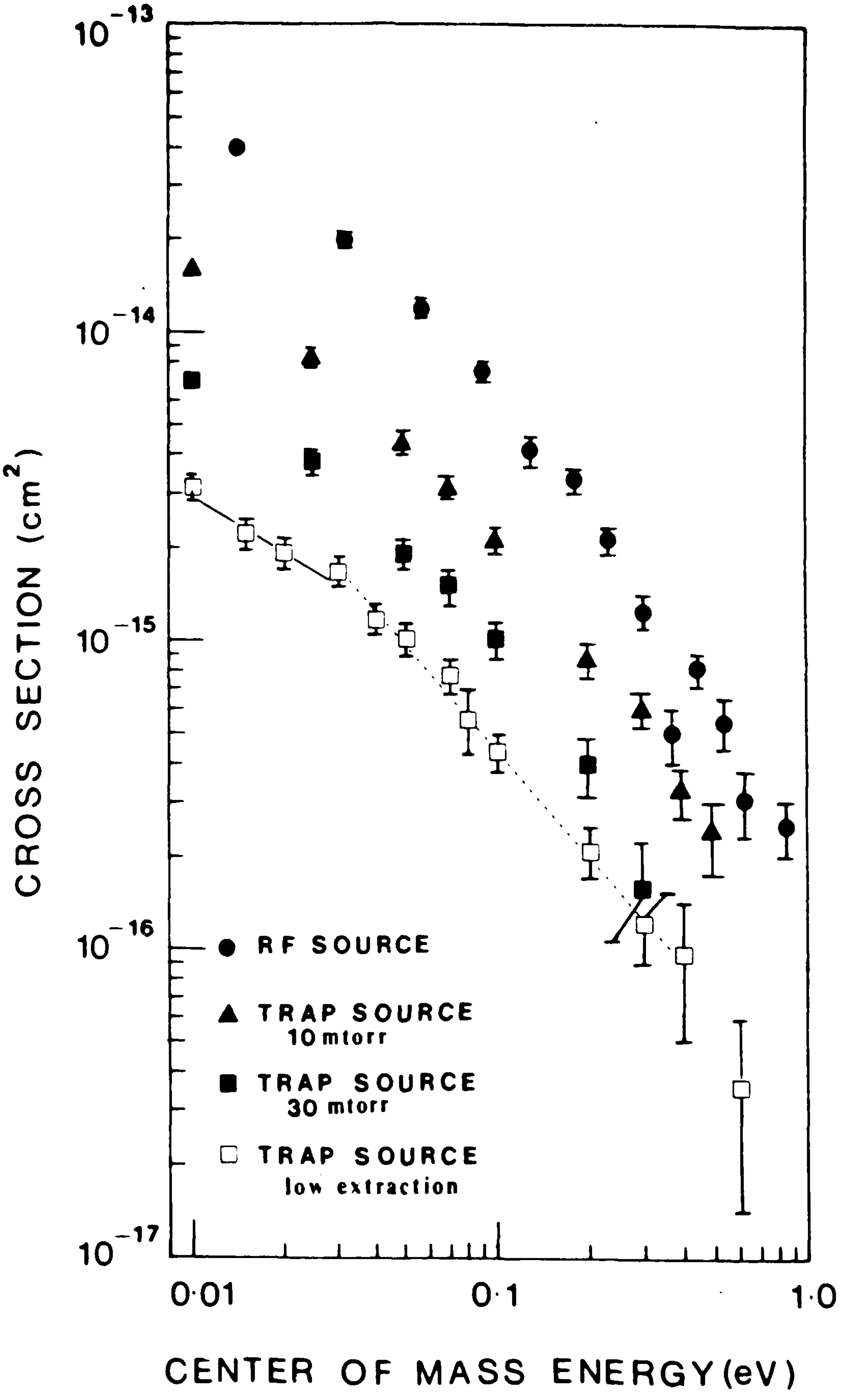
Fig.3b

CENTER OF MASS ENERGY (eV)

CROSS SECTION ($\times 10^{-17} cm^2$)







10^{-13}
10^{-14}
10^{-15}
10^{-16}
10^{-17}
CROSS SECTION (cm^2)
● RF SOURCE
▲ TRAP SOURCE 10 mtorr
■ TRAP SOURCE 30 mtorr
□ TRAP SOURCE low extraction
0·01
0·1
1·0
CENTER OF MASS ENERGY(eV)

Fig.4.

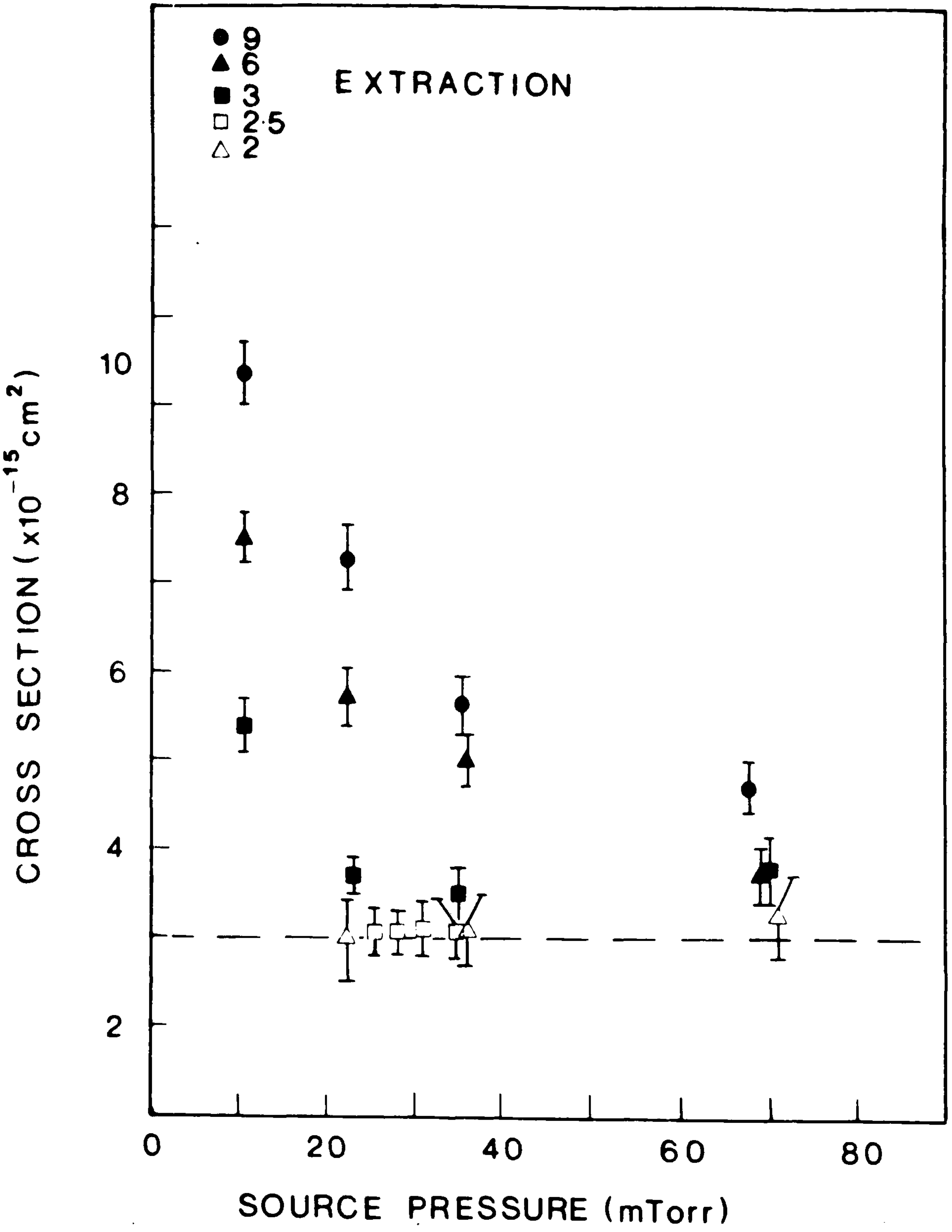

● 9
▲ 6
■ 3
□ 2·5
△ 2
EXTRACTION
CROSS SECTION ($\times10^{-15}$cm^2)
10
8
6
4
2
0
20
40
60
80
SOURCE PRESSURE (mTorr)

Fig.5.

APPENDIX

B

The Dissociative Recombination of H_2^+ in low vibrational states

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ABSTRACT

Dissociative recombination cross sections for H_2^+ ions with only v = 0 and 1 significantly populated have been measured using the merged beam technique. Narrow resonances associated with indirect capture have been found. A comparison with recent theoretical calculations is given

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The recombination of molecular ions with electrons is a rich area of study of great significance to many branches of physics and chemistry. Over the years the field has given rise to considerable controversy as different experimental techniques have yielded widely differing results for apparently the same molecular ion. Theoretical predictions for recombination processes have often been tentative and usually have raised more questions than they answered. A number of reviews of developments in this area have been given[1].

The biggest problem with studying molecular ion recombination lies in the fact that molecules are fundamentally complex.

Often more than one state is available into which the electron can be captured. Following capture these states must pass through a manifold of Rydberg states. Curve crossings to these states give rise to neutral products and these considerations make theoretical analyses difficult. From an experimentalist's point of view the major problem arises from the fact that molecular ions are usually formed with considerable vibrational excitation. Excited vibrational states can often however be quenched by collision with neighbouring molecules and this means that the population of vibrational states is a function of the environment within which the ions are formed.

The H_2^+ ion being the simplest molecular system is amenable to calculation and offers the best choice for a direct comparison between theory and experiment.

The potential energy curves involved in the dissociative recombination of H_2^+ are shown in figure 1. For low energy electrons and H_2^+ ions with low internal energy, only the $^1\Sigma_g^+$ state of H_2 is available for direct electron capture. This repulsive state is autoionizing at small internuclear separation but being repulsive the potential energy of the system falls rapidly as the H atoms move apart. Once the system is below the ionization potential of H_2 it can no longer autoionize and the recombination is stabilized. At very large r the $^1\Sigma_g^+$ state tends asymptotically to a limit corresponding to $H^+ + H^-$. It has been shown however that recombinations leading to ion pair formation account for less than 0.1% of all recombinations[2] so curve crossings to states with neutral atom limits must dominate the dissociation process. Some experimental work has been performed to identify the recombination products[3] but there is a complete absence of theoretical analysis of the decay channels. A number of calculations of the $^1\Sigma_g^+$ state have been performed[4] and it can be seen that it crosses the ion ground $X^2\Sigma_g^+$ state in the vicinity of the $v = 2$ level. For H_2^+ ions with $v < 2$, direct dissociative recombination will be reduced.

Besides the direct process it is also possible for electrons to be captured initially into excited autoionizing vibrational levels of the Rydberg states of the neutral molecule[5], some of which lie above the $v = 0$ level of the H_2^+ ion (figure 1). These states decay via crossing to the $^1\Sigma_g^+$ state followed by dissociation in the normal manner. Thus the process is represented by:-

$$e + H_2^+ (v) \quad H_2^R > H_2^{**} ({}^1\Sigma_g^+)$$

$$> H(1s) + H(n\ell) \qquad -- 1$$

Recently some very elegant theoretical studies of the role of indirect dissociative recombination have been published. Giusti-Suzor et al[6] and Nakashima et al[7] have predicted that the indirect process will destructively interfere with the direct process thus giving rise to resonant dips in the cross section. Hickman[8], using a configuration interaction approach has predicted that the indirect process will enhance the recombination.

Measurements of the total cross section for the dissociative recombination of H_2^+ have been performed using both inclined[9] and merged beam techniques[10].*

One of the major problems with H_2^+ however is the fact that when formed from energetic electron or photon impact, all 19 available vibrational states are populated since the minima of the ground states of H_2 and H_2^+ are displaced from each other. Since H_2^+ does not have a dipole moment these states have very long lifetimes (~10^6 seconds) and so do not decay.

* Plasma techniques are inappropriate since H_2^+ ions are quickly converted to H_3^+ via the reaction: -

$$H_2^+ + H_2 > H_3^+ + H.$$

It is possible, however to reactively remove excited vibrational states by allowing the H_2^+ ions to react with helium or neon gases. The reactions: -

$$H_2^+ (v) + He > HeH^+ + H \qquad -- 2$$

$$H_2^+ (v) + Ne > NeH^+ + H \qquad -- 3$$

are exothermic only for $v > 2$ and $v > 1$ respectively. By using helium or neon buffer gases in the ion source it is possible in principle to react away these states and so produce H_2^+ ions with only $v = 0, 1, 2$ or $v = 0, 1$ respectively.

This was attempted by McGowan et al (11) at The University of Western Ontario and indeed it was found that the use of a helium buffer reduced the recombination cross section by about a factor of two. Of particular significance however at the time was the appearance of resonant structures in the cross section which indicated the contribution of the indirect process.

Subsequent studies using the merged beam apparatus at U.W.O. failed to reproduce these resonances[12]. Theoretical analysis of the residence time of ions in the rf ion source used in the experiment indicated that incomplete quenching would occur and that vibrational states up to $v = 6$ could be populated in the beam.

With this in mind, a new source was constructed based upon an earlier design by Teloy & Gerlich[13]. In this source, ions formed by electron impact are confined by an rf field for up to several milliseconds before being extracted. This allows sufficient collisions to occur for complete elimination of excited vibrational states. Preliminary studies of collision induced dissociation of low energy H_2^+ ions on He have shown that indeed ions with only v = 0, 1, 2 or v = 0, 1 populated could be produced[14].

This paper describes new measurements for the dissociative recombination of H_2^+ ions formed using this ion source.

EXPERIMENTAL TECHNIQUE

The rf trap ion source has been installed in the terminal of a 400 KeV Van de Graaff accelerator which is used as the injector into the merged electron ion beam apparatus, MEIBE I[10]. The accelerated ions are mass analyzed and the beam is double deflected electrostatically to remove neutrals before entering the interaction region which is maintained at ultra high vacuum, 10^{-9} torr. An electron beam is formed from an indirectly heated barium oxide cathode, inside the merged beam chamber. Initially parallel to the ion beam, it is shifted laterally to overlap the ion beam using a trochoidal analyzer. The beams interact over a distance of 8.6 cms after which the electron beam is demerged using a second trochoidal analyzer whereupon it is collected and measured in a Faraday cup. The ion beam is electrostatically analyzed and deflected into a second Faraday cup. Undeflected neutrals, formed as a result of electron-ion and background gas collisions are detected using a surface barrier detector. The electron beam is modulated and counting is performed in and out of phase with the modulation so that the background gas collision rate can be identified and eliminated.

RESULTS AND DISCUSSION

The ion source was operated at a pressure of 10m torr with a 2:4:1 hydrogen/helium/argon gas mixture. Dissociative recombination cross sections were measured as a function of center of mass energy for H_2^+ ions produced under these source conditions. The results are shown in figure 2.

It can be seen that large resonant dips are apparent in the cross section. These are very narrow in width and were reproduced in several separate measurements. The positions of the measured structures do in fact correspond to those for the resonances calculated by Nakashima et al for $v = 0$ and 1.

The cross section rises very steeply on either side of the resonant dips and a study of the shape will involve scanning the energy in many small steps over the resonance. This will be performed at a later date at which time the higher energy resonances will be characterized in detail.

The deep resonance at 0.1 eV was examined in more detail than the others and it can be seen that it has a measured width of approximately 20 meV. This must mean that the energy resolution of the apparatus is better than this. A discussion of the ability of the merged beam technique to yield a high energy resolution in the center of mass frame has been given elsewhere[10] but this is the first direct evidence which shows this capability.

Cross sections for the dissociative excitation process

$$e + H_2^+ (1s\sigma_g) > H_2^+(2p\sigma_u) > H + H^+ \qquad - - 4$$

were also measured and these are shown in figure 3. Since the neutral detector is energy sensitive it can distinguish between H atom pairs arising from reaction 1, depositing the full beam energy (i.e. 400 KeV) and single H atoms from reaction 4 which deposit only half the energy (i.e. 200 KeV). The measured threshold for this process suggests that ions in the v = 2 state may be present in the beam. The appearance of the deep structure at 0.1 eV however argues against the v = 2 state being a major component since Nakashima et al found that H_2^+ (v = 2) displays a peak at that energy and this would mask the appearance of the resonance. Theoretical calculations for dissociative excitation have been made by Peek[15] using the Born Approximation but are only expected to be accurate at elevated energies. Accurate theoretical calculations for reaction 4 in the vicinity of thresholds for individual vibrational states would allow us to make a more definite statement regarding the population of these states.

It would appear therefore that for the first time we have clear unambiguous experimental evidence for the effects of the indirect mechanism in dissociative recombination. This is made possible by the ability to produce molecular H_2^+ ions with only two vibrational states populated.

A detailed comparison of these results with the theoretical calculations is premature and will require a much more extensive examination of the resonance shapes and positions. The absolute values of the cross section are closer however to the calculations of Nakashima et al and Giusti-Suzor et al. Hickman estimated that the recombination cross sections for H_2^+ (v = 0) and H_2^+ (v = 1) were of roughly the same magnitude with a value of about $10^{-14}cm^2$ at 0.01 eV. Nakashima et al and Giusti-Suzor et al each calculated a value for H_2^+ (v = 0) about an order of magnitude less than this, the v = 1 cross section being similar to Hickman's. Our results indicate a value of σ (0.01 eV) of 3.5 x $10^{-15}cm^2$ which given the mixture of v = 0 and 1 states in the beam would favour the lower value for σ (v = 0).

ACKNOWLEDGEMENTS

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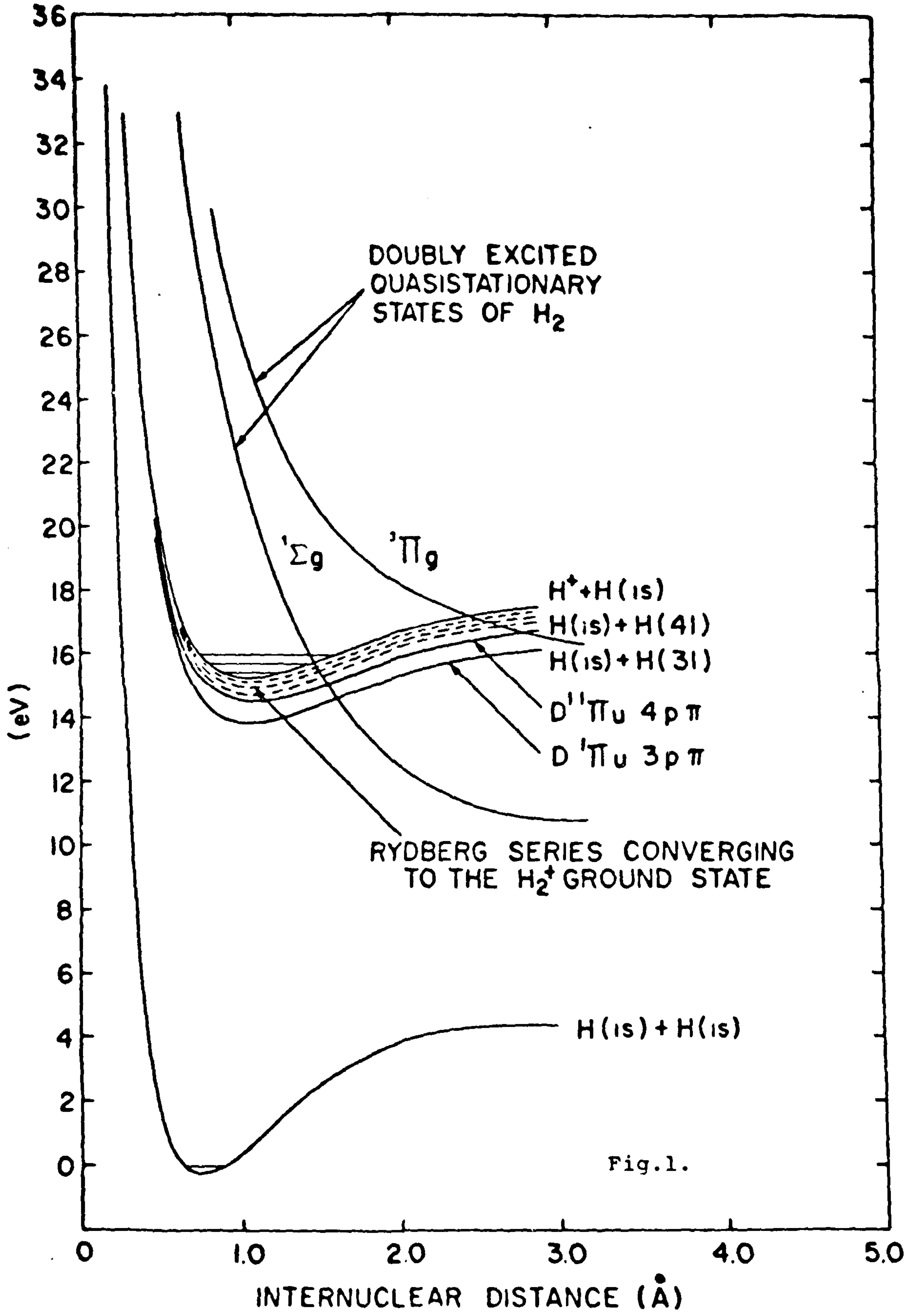
FIGURE CAPTIONS

1. The potential energy curves of H_2 and H_2^+.

2. Cross sections for the dissociative recombination of H_2^+. Points shown without error bars have values $<10^{-18}cm^2$.

3. Cross sections for the dissociative excitation process H_2^+ ($1s\sigma_g \rightarrow 1p\sigma_u$). The arrows indicate the thresholds for excitation from the indicated vibrational states of H_2^+.



36
34
32
30
28
26
24
22
20
18
16
14
12
10
8
6
4
2
0
(eV)
0
1.0
2.0
3.0
4.0
5.0
INTERNUCLEAR DISTANCE (Å)
DOUBLY EXCITED QUASISTATIONARY STATES OF H_2
$^1\Sigma_g$
$^3\Pi_g$
$H^+ + H(1s)$
$H(1s) + H(4l)$
$H(1s) + H(3l)$
$D'\,^1\Pi_u$ 4pπ
$D\,^1\Pi_u$ 3pπ
RYDBERG SERIES CONVERGING TO THE H_2^+ GROUND STATE
$H(1s) + H(1s)$

Fig.1.

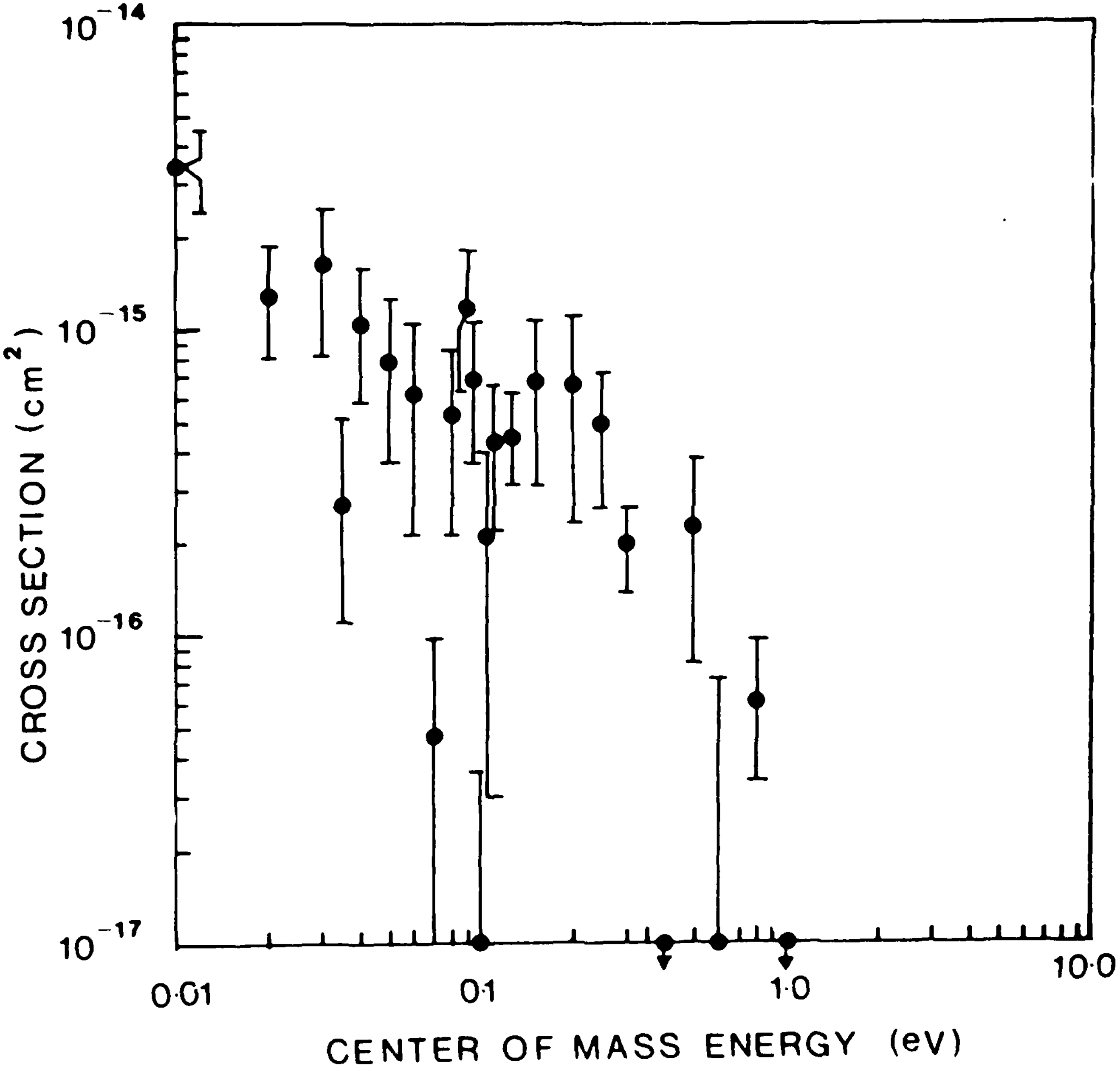

10^{-14}
10^{-15}
10^{-16}
10^{-17}
CROSS SECTION (cm^2)
0·01
0·1
1·0
10·0
CENTER OF MASS ENERGY (eV)

Fig.2.

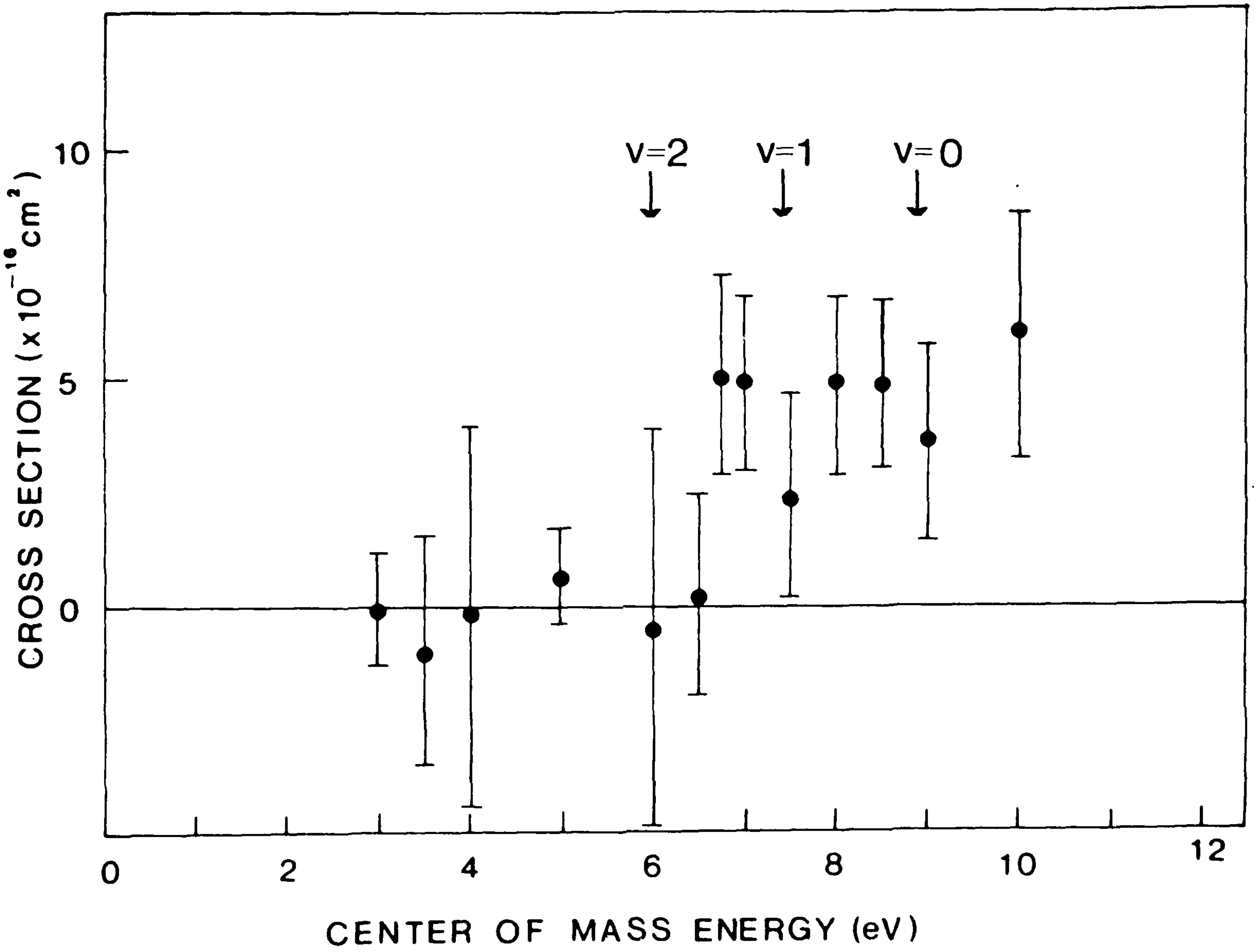

CROSS SECTION ($\times 10^{-16}$cm^2)
10
5
0
v=2
v=1
v=0
0
2
4
6
8
10
12
CENTER OF MASS ENERGY (eV)

Fig.3.