Vibrational Excitation Effects on Charge-Transfer Processes Involving H_2^+ and D_2^+ Between 70 and 1000 eV*

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Charge-transfer cross sections have been measured for H_2^+ in H_2, D_2, and Ar, and for D_2^+ in H_2 as a function of both incident ion energy and ion-source electron energy. The ion energy range was 70 – 1000 eV for the $H_2^+ + H_2$ case and 250 – 1000 eV for the processes $H_2^+ + D_2$, $H_2^+ + Ar$, and $D_2^+ + H_2$. Ionizing electron energy was varied from 16 to 21 eV. The primary H_2^+ ions were magnetically separated from other beam constituents. Charge-transfer cross sections were deduced from slow-ion currents measured in a charge-transfer cell employing a cylindrical slow-ion energy analyzer. Measured cross sections for H_2^+ in H_2 decreased 5 to 10% as the electron energy was increased over the 5-eV interval. The minimum in the $H_2^+ + H_2$ cross-section–versus–energy curve observed by other investigators was found to persist at low electron energies, thus ruling out the possibility of contributing exothermic effects by highly excited incident ions. The lack of agreement between experimental results and theory is discussed. Sizable differences were observed at low electron energies between the $D_2^+ + H_2$ and the $H_2^+ + D_2$ cross sections. Both results fell below those for the symmetric $H_2^+ + H_2$ case. At higher electron energies, these differences were smaller. An overall change of 20% in the $H_2^+ + Ar$ cross section was observed over the given electron-energy interval with 700-eV ions.

I. INTRODUCTION

The theory of charge-transfer processes involving molecules is still in a rather rudimentary state, and comparisons of cross sections obtained in different laboratories are difficult because of unknown effects of varying ion-source conditions. A dramatic example is that of charge transfer between low energy O_2^+ and N_2 when the O_2^+ ions are formed by electron-impact energies above 20 eV.[1,2] In that case, it has been shown that an electronically excited metastable ion accounts for practically all the charge-transfer cross section

By varying the ionizing electron energy used in forming N_2^+ and O_2^+ ions, it has also been found that changes of 10 to 15% could be observed in the symmetric charge-transfer cross sections for these ions in their parent gases.[1,3] However, in that work it was not established with certainty whether the effective N_2^+ ion excitation was electronic or vibrational. Subsequent studies[4] of the near-resonant process: $N_2^+ + Ar \rightarrow N_2 + Ar^+$ suggested that the cross section for that process depended upon the relative population of the vibrationally excited states of the N_2^+ ions. That work implies that for the N_2^+ beam used by Amme and Utterback[1] the excited states were vibrational.

In 1963, McClure,[5] using 10-keV H_2^+ ions incident on H_2 gas, found that the cross section for H^+ production (and, to a lesser degree, for single-electron transfer) was sensitive to the pressure of his discharge ion source. In H_2^+ the excited electronic states are generally repulsive, so that the interpretation in this case is probably restricted to excited vibrational levels. McGowan and Kerwin,[6] utilizing an electron-impact ion source, subsequently showed that for H_2^+ colliding with H_2 the cross section for collision-induced dissociation is indeed a function of the vibrational-level populations.

Hydrogen is particularly suitable for investigating vibrational excitation effects, because the vibrational spacings are large and the populations formed by electron impact are broadly distributed.[7] Moreover, the existence of D_2, with nearly the same ionization potential but different vibrational-level spacings, permits the examination of two related near-resonant non-symmetric cross sections. The purpose of the present investigation was primarily to study the symmetric charge-transfer cross section for molecular hydrogen, both as a function of incident ion energy and of the ionizing electron energy. The energy interval chosen for study was 70–1000 eV. In this region it was possible to obtain a usable H_2^+ beam with electron energies down to 16 eV, which is sufficient to populate only the first two or three vibrational states (electron-energy spread was about 0.5 eV). Although a narrower electron-energy spread would be desirable, the accompanying decrease in ion-beam current would yield greater uncertainties in the measured cross sections.

Also studied were the processes:

$$H_2^+ + Ar \rightarrow H_2 + Ar^+ \qquad (1)$$

and

$$H_2^+ + D_2 \rightarrow H_2 + D_2^+ \qquad (2)$$

over the energy interval of 250–1000 eV. Then a D_2^+ beam was employed to measure the charge-transfer cross section for the inverse of process (2), again as a function of ionizing electron energy.

II. APPARATUS

The ion source is similar to that used in earlier work.[1] However, since in the present study the ion current from the source contained varying amounts of H^+ and H_3^+ as impurities, a separating magnet was employed after the second lens. A deflection of 30° was sufficient to separate the H_2^+ from the protons and the H_3^+. A ceramic sheath was used around the filament, so that only the central portion was exposed. The filament was formed from wire consisting of 88% tungsten, 10% rhenium, and 2% thoria. Some additional improvements were made in the beam-focusing elements.

The charge-transfer cell, of the same type as described previously,[1,8] is shown in Fig. 1. A cylindrical grid, maintained at ground potential, is surrounded by a concentric, cylindrical cup whose potential may be varied from −3 to +45 V relative to the grid. Slow ions formed from

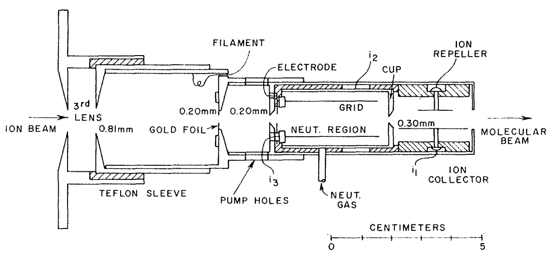

FIG. 1. Charge-transfer cell and slow-ion energy analyzer.

charge transfer are collected on the grid with a cup potential of a few volts and measured by an electrometer as i_3. Ions scattered with sufficient energy are collected on the cup as i_2. The fast ions which do not become scattered or undergo charge transfer pass through the 0.12-in exit aperture and are measured on an ion collector as i_1. Secondary electrons emitted from the collector toward the repeller were returned to the collector, as described previously, and were thus not counted as i_1. The incident ion-beam intensity, $i_1+i_2+i_3$, varied from about 10^{-11} to 10^{-9} A.

As a preliminary check, the resonant charge-transfer cross section for $He^+ + He$ was measured and compared with earlier results obtained using the older apparatus. Good agreement was found after making a 25% correction for secondary-electron ejection at the grid, as discussed by Hayden and Utterback.[9]

III. RESULTS

By varying the cup potential and noting the rise in grid current i_3, an approximate energy analysis of the slow ions may be performed. In Fig. 2 are plotted values of β/P versus cup potential, where $\beta = i_3/(i_1+i_2+i_3)$, and P is the pressure of the neutralizing gas. Results for four different beam energies are shown, all obtained using 17-eV ionizing electron energy. By extrapolating the linear portion of the curve back to zero cup potential, we obtain the values of β/P corresponding to essentially zero-energy ions. The cross sections for charge transfer (slow-ion

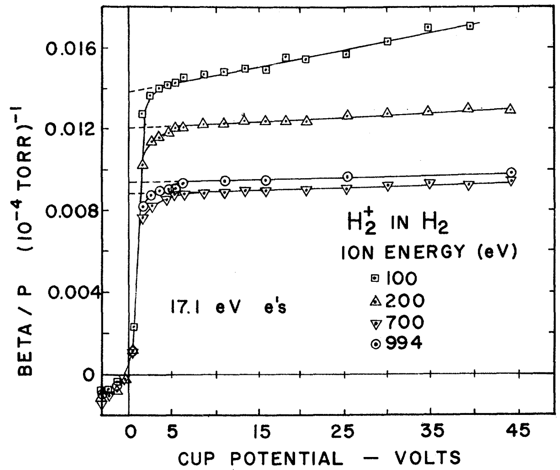

FIG. 2. β/P versus cup potential for H_2^+ in H_2.

formation) we obtain from the equation:

$$\sigma = 763(\beta/P)(1+\tfrac{1}{2}\beta) \ (\text{Å}^2), \quad (3)$$

using extrapolated β/P values. The numerical constant involves the temperature of the target gas and the length of the cell, which is 4 cm. The pressure, measured with a McLeod gauge,[10] is in units of 10^{-4} Torr. The correction term $\frac{1}{2}\beta$, usually 5–10%, results from attenuation of the beam as it passes through the cell. In Fig. 3 we have plotted the calculated cross sections as a function of the ion energy, along with results obtained by several other investigators.[11–16] The agreement between our results and those of Gilbody and Hasted,[15] who used high-energy electrons, is very good. The uncertainty in our measurements due to systematic errors is approximately 15%.

From the β/P curves of Fig. 2, one sees that a cup potential of 5 V is sufficient to collect most of the slow current, and that the value of β/P at

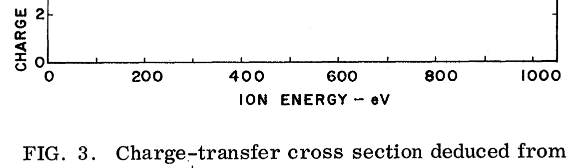

FIG. 3. Charge-transfer cross section deduced from β/P curves for H_2^+ in H_2 using 16-eV ionizing electron energy. Results of other investigators are shown for comparison. V&B: Vance and Bailey, Ref. 12. The cross section calculated by Gurnee and Magee appears at the top.

this potential is rather close to the intercept value. By holding the cup constant at 4.5 V and varying the ionizing electron energy, we have determined the sensitivity of the charge-transfer cross section to this parameter. Results for four different beam energies are shown in Fig. 4. Increasing the electron energy from 16 eV to 21 eV reduces the cross section by about 10% in all these cases.

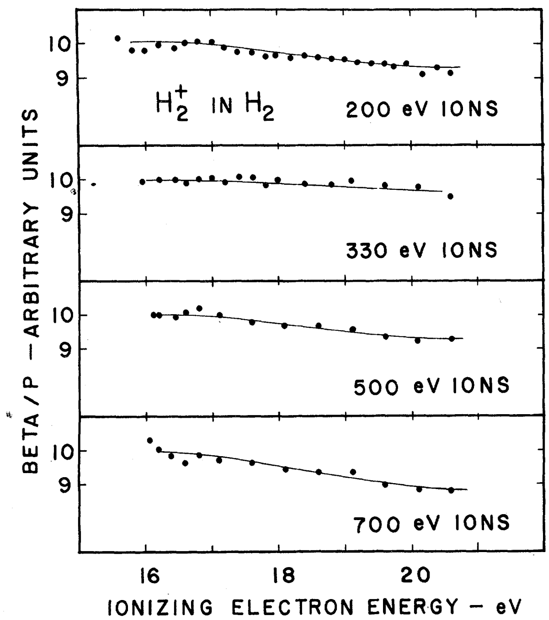

FIG. 4. Effect of varying ionizing electron energy on slow-ion current formed from H_2^+ on H_2. Cup potential was set at 4.5 V.

To investigate possible effects of ion-source pressure on the vibrational excitation of the extracted ions, the ratio of β at 17-eV electron energy to that at 21-eV electron energy was determined (at constant target pressure) for 700-eV ions as a function of this parameter. A Pirani gauge, calibrated for H_2, was used to measure ion-source pressure over the interval 14–70 μ. No significant variations were observed.

Because relatively little change in the cross sections was found in the interval 16–17 eV electron energy, argon was substituted as the neutralizing gas, and the electron energy was varied at an H_2^+ ion-beam energy of 700 eV. Results are shown in Fig. 5. It is seen that in this instance a 6-eV increase in the ionizing electron energy reduces the cross section for slow-ion production by nearly 20%. The curves of β/P versus cup potential for this case (not shown) exhibit the same rapid rise at low cup potentials as seen with hydrogen in the cell. Values of β/P with a 5-V cup are again within a few percent of those obtained at 45 V. The dependence of the cross section on incident ion energy is shown in Fig. 6 for 17.1- and 20.6-eV ionizing electrons. The data of Koopman[10] and of Stedeford and Hasted[14] are shown for comparison. No evidence is seen, at these energies, of the

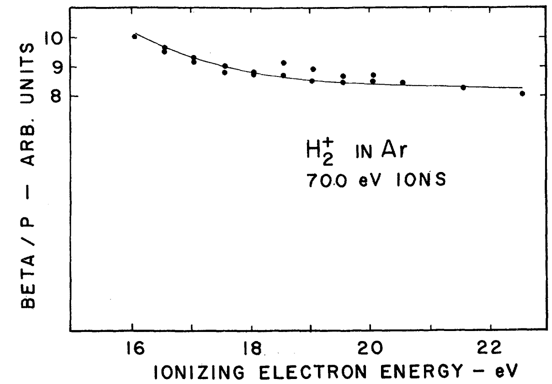

FIG. 5. Effect of varying ionizing electron energy on slow-ion current formed from H_2^+ on Ar. Cup potential was set at 4.5 V.

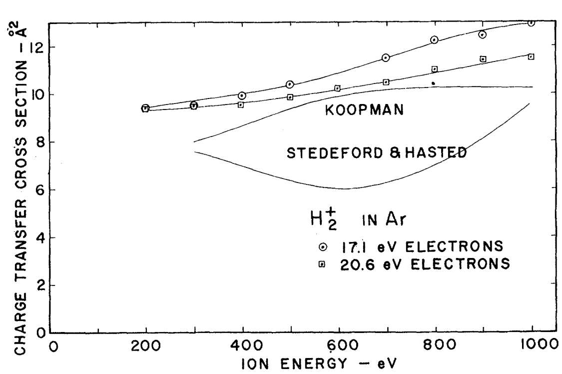

FIG. 6. Charge-transfer cross section deduced from β/P curves for H_2^+ in Ar at two different electron energies. Results of other investigators are also shown.

oscillatory behavior reported for this cross section below 135 eV by Menendez, Thomas, and Bailey.[17] Extrapolation of our data to 135 eV gives a charge-transfer cross section of 9 Å^2, which is 60% of their value.

Cross sections for the production of slow ions from collisions of H_2^+ with D_2 and of D_2^+ with H_2 are presented in Fig. 7 as a function of the incident ion velocity. Cross sections for $H_2^+ + H_2$ are shown for comparison. With 16-eV ionizing electrons, a sizable difference seems to appear between the two nonsymmetric cases. Since the ionization potentials of H_2 and D_2 differ[18,19] by only 0.037 eV, both cross sections would be expected to appear near-resonant in the absence of vibrational effects. However, the $H_2^+ + D_2$ cross section generally increases with increasing incident ion velocity. On the other hand, at higher electron energy, one sees a close similarity in the functional dependence of all three cross sections on the incident velocity.

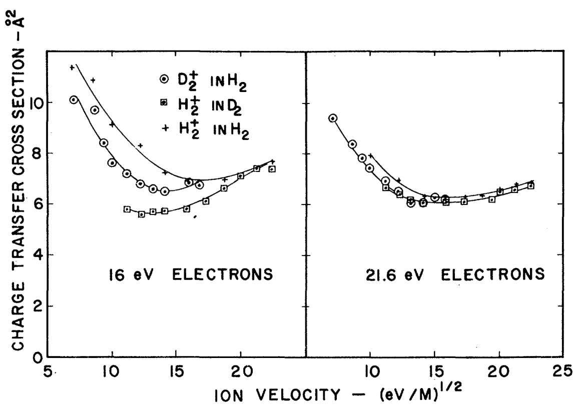

FIG. 7. Charge-transfer cross sections for H_2^+ in H_2, D_2; and D_2^+ in H_2 at two different electron energies shown as functions of ion velocity. M is the molecular weight of the incident ion.

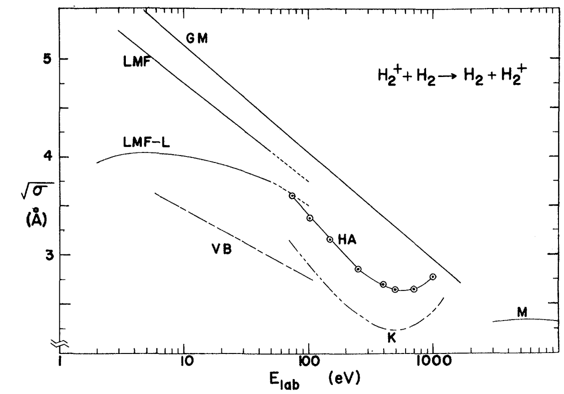

FIG. 8. Plot of $\sqrt{\sigma}$ versus logarithm of ion energy. GM: Gurnee and Magee Calculation, Ref. 21; LMF: Leventhal, Moran and Friedman, Ref. 22; LMF-L: LMF Calculation corrected for Langevin orbiting cross section (see Ref. 22); HA: present experimental result; VB: Vance and Bailey, Ref. 12; K: Koopman experimental result, Ref. 16; M: McClure experimental result, Ref. 5.

IV. DISCUSSION

Ions Collected

Because of the low dissociation energies of H_2^+ and D_2^+ ions, the interpretation of experiments in which no mass analysis of the products is performed may be questioned. The degree of uncertainty in charge-transfer cross-section measurements could be influenced by the relative magnitudes of the cross sections for H^+ and H_3^+ production, etc., through the processes of Collision-induced dissociation (CID):

$$\underline{H}_2^+ + H_2 \rightarrow \underline{H}^+ + \underline{H} + H_2; \tag{4}$$

Dissociative charge transfer (DCT):

$$\underline{H}_2^+ + H_2 \rightarrow \underline{H}_2 + H^+ + H; \tag{5}$$

Ion-molecule reaction:

$$\underline{H}_2^+ + H_2 \rightarrow H_3^+ + H, \tag{6}$$

and similarly for processes involving D_2 and D_2^+.

Protons formed by CID are expected to possess an energy approximately equal to half the incident H_2^+ energy.[5,12] In our work, therefore, these protons should be forward-scattered to the collector. Since the exit aperture of the cup is 0.12 in, energetic ions scattered from the center of the cup at angles greater than 5° will be collected on the cup. Thus, protons from CID should not reach the grid. The shape of the β/P curves indicates that essentially all of the ions counted in the charge-transfer current have an energy not exceeding 5 eV. These facts could be an important consideration if the cross section for CID is comparable to that for charge transfer. At 3 keV, McClure[5] finds that the CID cross section is 2.2 Å² and is decreasing with decreasing beam energy. Vance and Bailey[12] report a cross section of 4.5 Å² from 40 to 100 eV, which is more than half of their measured charge-transfer cross section (See Fig. 8). It may be noted that the ion source utilized by Vance and Bailey employs an electron energy of 50 eV. High vibrational excitation might then give rise to a greater cross section for CID as a competitive channel to that of charge transfer. However, according to McGowan and Kerwin, one would not expect the vibrational state populations to change appreciably for electron energies above 24 eV.

The ion-molecule reaction cross section leading to H_3^+ formation is small[12] at the energies involved in this study and may be neglected.

Protons resulting from the reaction shown in Eq. (5), i.e., through dissociation of the target molecule subsequent to electron transfer, may be sufficiently slow that a significant fraction might reach the grid. The energy defect for a charge-transferring collision which leaves the target in the repulsive $2p\sigma_u$ state will be quite large if Franck-Condon transitions prevail. If, on the other hand, the target molecule becomes highly excited vibrationally so that a transition may occur at large internuclear separation, the energy defect can be very small, depending also on the vibrational level of the incident ion. In such a case, the time required for the collision would be expected to be comparable to or greater than the vibrational period of the excited $\underline{H}_2$ target. This condition does obtain, for a 7-Å interaction distance, at incident ion energies below 100 eV. The resulting proton would have a kinetic energy of only about 1 eV. In any case, the cross section for slow H^+ production may be quite small. Gustafsson and Lindholm[20] found a cross section of 0.07 Å² for H^+ production at 50 eV. In our work, we can only state that if slow protons are formed from DCT, they will probably be collected (See below).

$H_2^+ + H_2$ Case

From Fig. 3, two important results emerge.

The first is that practically none of the experimental cross sections is as high, or has the same energy dependence, as the semiclassical calculation by Gurnee and Magee. This lack of agreement is readily understood, since H_2^+ ions, formed either in an electron-bombardment ion source or in a discharge, possess a broad distribution of vibrational states. The Gurnee-Magee calculation pertains to the single resonant process:

$$H_2^+(v=0)+H_2(v=0)\rightarrow H_2(v=0)+H_2^+(v=0).$$

The second important consideration seen from Fig. 3 is that, without exception, all experimental cross sections appear to *increase* with increasing energy over the interval 600–1000 eV. This behavior is just as pronounced in our data, for which 16-eV electrons were used, as in the recent work of Koopman,[16] who used a discharge-type ion source.

The only attempt to take the vibrational states of the incident ions into account in a quantitative way is the calculation by Leventhal, Moran, and Friedman,[22] (LMF), who consider the ions to have a Franck-Condon distribution of vibrational levels. Again, their calculation assumes that all cross sections are resonant, i.e., that each resulting slow ion has the same vibrational energy as the incident ion to which the electron was transferred. The resonant nature of these theoretical cross sections is evidenced by the plots in Fig. 8, in which the square root of the calculated value is plotted against the logarithm of the incident energy. The behavior is seen to be closely linear, just as in any resonant atomic case. It is especially interesting to note that the recent measurements by Vance and Bailey[12] at low energies also exhibit resonant character, although they fall considerably below the theoretical values. LMF also performed a crude united-atom calculation to establish an approximate lower limit for the charge-transfer cross sections as a function of energy. These values were shown to be in close agreement with Vance and Bailey's measurements.

In Fig. 8 we have also included a corrected charge-transfer cross section obtained by LMF extended to 100 eV. This consists of the impact-parameter calculation, described above, less the Langevin orbiting cross section (See their Table I). At the lowest energy, our present experimental values are in close agreement with this calculation. Up to ion energies of about 300 eV, our measurements also show a resonant behavior.

The effect of varying the ionizing electron energy, Fig. 4, appears to be insufficient to explain the minimum observed in the cross section near 600 eV. This suggests that some process is involved which does not require a high vibrational excitation of the incident H_2^+. If the increase is real, it would mean that nonresonant processes are beginning to contribute significantly to the total charge-transfer cross section, which could occur when the slow ion is frequently left in a high vibrational state differing from that of the incident ion. Such endothermic contributions are not included in existing theories. One sees from Fig. 8 that the increasing cross sections will not fit smoothly onto the higher-energy results by McClure.[23] Since no mass analysis of the product ions has been performed in absolute measurements conducted at 500- to 1000-eV energies, the production of slow protons from dissociative charge transfer may be the explanation. However, Fite, Brackmann and Snow,[24] making relative measurements, also found a minimum in the $H_2^+ + H_2$ charge-transfer cross section. They placed an upper limit of about 5% on the H^+/H_2^+ ratio for the slow secondary ions with 600-eV incident H_2^+ energy. Furthermore, a DCT cross section of about 2 Å^2 would be required at 1 keV to permit a fairly smooth joining of our data to those of McClure. This is a value which is much larger than the CID cross section at that energy. Hasted's data,[15] which are in excellent agreement with our own from 100 to 1 keV, show a leveling off at about 2 keV, with a cross section for slow-ion production of 10 Å^2.

H_2^+ + Ar Case

Fig. 5 shows that for the case of H_2^+ charge transferring in argon, the cross section is relatively more sensitive to ionizing electron energy than for a hydrogen target. A decrease is immediately apparent when the electron energy is increased from 16 to 17 eV, indicating that the vibrational-state populations of the extracted ions are, in fact, changing over this interval. The relative insensitivity of the cross section for $H_2^+ + H_2$ over the same one-volt interval, Fig. 4, suggests that ions in the lower vibrational levels do not differ greatly in their charge-transferring efficiencies in H_2.

Because of the split ground state of Ar^+, many near-resonant reactions are possible. These are described in greater detail by Amme and McIlwain,[8] who have reported cross sections for the inverse process. In that work, a maximum was observed at about 180 eV, while in Fig. 6 for the present case, the cross section is still rising at 1 keV. This is not surprising in view of the larger average energy defect resulting from the population of H_2^+ vibrational states.

Cases Involving D_2

Since the vibrational-energy-level spacings are closer in D_2 and D_2^+ than in H_2 and H_2^+, respectively, some differences in the cross sections for H_2^+ in D_2 and D_2^+ in H_2 are to be expected. However, the energy defects for the two processes are generally small. For example, if the neutral products are unexcited,

$$H_2^+(v'=1)+D_2(v=0)\rightarrow H_2(v=0)+D_2^+(v'=1) \quad +0.037\text{ eV}$$

$$H_2^+(v'=2)+D_2(v=0)\rightarrow H_2(v=0)+D_2^+(v'=3) \quad -0.076\text{ eV}.$$

The adiabatic criterion would suggest a maximum in the cross section below 4 eV for processes of the above type. The Franck-Condon factors[7] indicate that at high ionizing electron energies, the $v=2$ level of H_2^+ and the $v=3$ level of D_2^+ will be the most highly populated in the incident beams. An increasing cross section with decreasing beam energy is clearly established for 22-eV electrons (Fig. 7), for both nonsymmetric cases. The observed difference between the two cases for low electron energies and at lower incident velocities is perhaps greater than expected and requires further study.

The possible influence of ionizing collisions should also be discussed. Stripping of the fast H_2^+ will merely produce two fast protons, but ionization of the target H_2 could produce some H_2^+ ions slow enough to be collected on the grid. The free electron would travel to the positive cup. The total ionization cross section (stripping and target ionization) is probably of the order of 1 $Å^2$ at a c. m. energy of 500 eV. Most of these ions will probably possess more than 4 to 5 eV of kinetic energy, and thus should not be collected as charge-transfer current. If the upturn in the cross section at high energies were, in fact, due to ionization, one would expect to see a greater cross section at a given beam energy for the $H_2^+ + D_2$ case than for $H_2^+ + H_2$ or $D_2^+ + H_2$, since the c. m. energies are significantly greater. Hence, the data shown in Fig. 7 support the conclusion that ionization is not responsible for the observed minimum. It could, however, be of significance in the case of $H_2^+ + Ar$, both in our results and in those of other investigators.

V. CONCLUSIONS

We have shown that the cross sections for slow-ion production in collisions of $H_2^+ + H_2$, and D_2, and of $D_2^+ + H_2$, all possess relative minima in the vicinity of 600-eV ion energy and therefore are of a nonresonant nature. This result was found to persist even with very low ionizing electron energies, where only one or two vibrational levels are excited in the incident ions. Energy analyses show that nearly all the collected slow ions have less than 4–5-eV energy, which tends to rule out contributions from competing processes. Relative cross sections obtained by Fite *et al.*, appear to rule out also the process of slow-proton production. We conclude that at higher beam energies, endothermic processes, probably vibrational excitation of the products, are involved. Over the intervals studied, the ionizing electron energy was found to affect the observed charge-transfer cross sections by at most 10–20%, depending on the particular process. For H_2^+ charge transferring in argon, changes in the populations of the lower vibrational states of H_2^+ appear to influence the cross section more than they do for the H_2^+ in H_2 cross section.

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