

Nonadiabaticity in ion-molecule reactions: Coupling of proton and charge transfer in the H_2^+ and D_2^+ + Ar system

F. A. Houle,^{a)} S. L. Anderson,^{b)} D. Gerlich,^{c)} T. Turner,^{d)} and Y. T. Lee^{e)}

Department of Chemistry, University of California, Berkeley, California 94720
and Materials and Molecular Science Division, Lawrence Berkeley Laboratory, Berkeley, California 94720
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An experimental study of proton and charge transfer in $H_2^+ + Ar$ and $D_2^+ + Ar$ has been carried out as a function of kinetic and vibrational energy. The data show that charge transfer is predominantly long range, having a weak translational, but strong vibrational dependence. The existence of near-resonant energy levels is very important in determining the magnitude of the cross sections, while favorable Franck-Condon factors between the states is found to be less critical. Undulations in the charge transfer cross sections for both H_2^+ and $D_2^+(\nu = 0)$ as a function of kinetic energy have been observed for the first time. As kinetic energy increases, the resemblance between the vibrational dependences of the proton and charge transfer channels becomes quite pronounced. This indicates that the two channels are closely coupled, especially above ~ 3 eV.

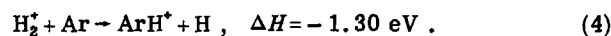
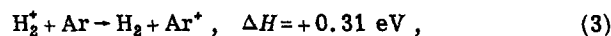
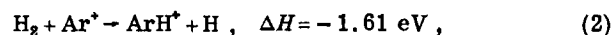
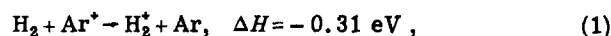
INTRODUCTION

In any positive ion-molecule reaction, at least two potential energy surfaces must be involved, corresponding to the two charge states of the reagents: $A^+ + B$ and $A + B^+$. A particularly interesting situation arises when the two charge states of the system are close in energy.¹ Interaction between the surfaces is strong and transitions between these states have a high probability and are often a sensitive function of reagent internal energy. Accessibility of both surfaces to the reagents leads to an intimate coupling between charge transfer and other processes such as reaction and collision-induced dissociation. If low-lying electronically excited states of one or both reagents are present, interactions of their potential energy surfaces with those of the ground state will serve to complicate the reaction dynamics even further. Measurements of reaction cross sections as a function of kinetic and vibrational energy of the reagents can provide a great deal of information on the role of multiple potential energy surfaces in ion-molecule reactions, especially concerning the involvement of particular regions of the surfaces over various energy ranges. A recent investigation in this laboratory² of the reactions of isotopic $H_2^+ + H_2$ is an example of a situation where near-resonant and resonant charge transfer are always possible and where the same chemical products arise from either initial charge state of the reagents. The vibrational effects on the reaction cross sections at various collision energies were sufficiently distinctive to allow reaction mechanisms to be identified.

In this paper, results for a somewhat different type of system $H_2^+ + Ar$, are described.³ In this system, near resonance occurs between only a few of the energy levels

of the reagent charge states and, since the system is asymmetric, the mechanism of product formation depends on the initial charge state of the reagents. Isotopic substitution of D_2^+ for H_2^+ , together with variations of kinetic and internal energy, allows probing of the potential energy surfaces involved in the reaction dynamics.

The channels open above 0.31 eV in $(H_2 + Ar)^+$, excluding collisional dissociation, are



Theoretical investigations of $(H_2 + Ar)^+$ have provided a clear picture of some aspects of the dynamics of channels (1)–(4).^{4–7} Mahan⁴ has shown that for high symmetry collisions, the initial charge state $Ar^+ + H_2$ does not correlate to ground state ArH^+ , but $H_2^+ + Ar$ does. This implies that charge transfer must take place prior to proton transfer in order for Reaction (2) to occur. Calculations of diatomics-in-molecules (DIM) potential surfaces,⁵ and trajectory studies⁶ of (1) and (2) on them confirm this mechanism.

There is an avoided crossing between the surfaces corresponding to the $H_2^+ + Ar$ and $Ar^+ + H_2$ charge states of the reagents, which allows mixing (CT) to occur. The crossing seam lies parallel to the reaction coordinate and only vibration carries the system through the seam. At large reagent separation, the mixing is weak; but as the reagents approach, charge transfer begins to become probable as the system vibrates. A trajectory study of Reaction (2) by Chapman and Preston⁶ confirms that for the $Ar^+ + H_2$ reagent charge state, charge transfer precedes reaction. This type of behavior was observed in the $H_2^+ + H_2$ system,³ and can occur for those polyatomic ion-molecule systems whose potential energy surfaces have an avoided crossing.^{1,8} A further result of the surface⁵ and trajectory⁶ studies is that Reactions (1)–(4) are predicted to be direct; a long-lived ArH_2^+ intermediate is not likely to be involved.

^{a)} IBM Postdoctoral Fellow, 1979–1980. Present address: IBM Research Laboratory, 5600 Cottle Road, San Jose, California 95193.

^{b)} NSF Graduate Fellow. Present address: Department of Chemistry, Stanford University, Stanford, California 94305.

^{c)} Present address: Fakultät für Physik der Universität, Freiburg, West Germany.

^{d)} Fannie and John Hertz Foundation Fellow.

^{e)} Miller Professorship, 1981–82.

A recent set of exact and approximate one-dimensional scattering calculations for Reactions (1)–(4) using DIM surfaces has focused on the role of vibration in proton transfer.⁷ The total energy range used was 0.5–0.8 eV. It was found that proton transfer to Ar can occur on a single surface for $H_2^+(v=0, 1)$ and no potential barriers are involved. Avoided crossings make barriers to reaction for $H_2^+(v>1)$ and all states of $Ar^+ + H_2(v)$. The primary effect of these barriers is on the shape of the reaction cross section function at very low kinetic energies. Also, evidence for formation of quasibound states at about 0.1 eV was found. It was suggested that these states were likely to be formed in the turning region rather than in one of the wells formed at an avoided crossing. Although these one-dimensional theoretical calculations provide some insight on the reaction dynamics, they are not expected to have a significant relation to what one observes in experiments.

Experimental work using mass spectroscopy, crossed molecular beams, and photoionization have served to confirm the general aspects of the theoretical understanding.^{9–16} Owing to the difficulty of producing H_2 and H_2^+ in known vibrational states, much of the published work has been restricted to reactions of electronically state-selected $Ar^+(^2P_{3/2}, ^2P_{1/2})$ with ground state H_2 . Recently, several studies of Reactions (3) and (4) using crossed molecular beams have appeared.^{10–12} In those experiments, beams of H_2^+ , presumably in a Franck–Condon distribution of vibrational states, were produced by electron impact. The proton transfer reactions were found to be direct, but the dynamics were more complex than a simple stripping process. Arguments were made that formation of ArH^+ with high rotational excitation allowed product internal energy to be well above the dissociation limit.¹¹ In a separate experiment, the H_2^+ beam was partially state-selected, leaving ions of $v=0–2$. It was found that, at fixed collision energy, the change in reagent vibrational state beyond $v=2$ had little or no effect on the reaction.¹²

The crossed beam work suggests that charge transfer between H_2^+ and Ar occurs by two mechanisms¹⁰: a long-range process involving grazing collisions at all energies and an intimate collision process at low energy (< 1 eV). Both mechanisms were translationally endothermic, i.e., relative translation was converted to produce internal excitation at all energies, in spite of the fact that charge transfer to Ar is only endoergic for $H_2^+(v=0, 1)$. The observation of two mechanisms was also made in crossed beam studies of the other reagent charge state $H_2 + Ar^+$.¹³ However, in that work little or no translational energy was transferred during the long range charge transfer collisions. The intimate collisions were found to involve a small conversion of translation to vibration in the products. The probability for long range charge transfer was found to depend strongly on the existence of resonant or near-resonant states of the products. This effect was masked in the $H_2^+ + Ar$ work because of the distribution of reagent vibrational states.

Three studies have appeared in which photoionization has been used to select the initial H_2^+ vibrational

state.^{14–16} Data were obtained for kinetic energies of ≤ 1 and ~ 20 eV. As found in the beam experiments at low relative translational energies (≤ 1 eV), the vibrational energy has little or no effect on the proton transfer reaction.^{14,15} The charge transfer reaction, on the other hand, has a very strong vibrational dependence which follows a model in which charge transfer is most probable between two states that are near-resonant in energy and have favorable Franck–Condon factors for the transition.^{15–18} This is consistent with the observation of a long-range mechanism in crossed beam experiments. The smaller contributions of the intimate collision mechanism observed in the differential scattering experiments cannot be detected in the integral cross section measurements because of the strong weighting of the large impact parameter collisions.

Several of the experimental studies have addressed the question of competition between proton and charge transfer as a function of kinetic energy. Using crossed beams and nonstate-selected reagents, it was found that the two processes are about equally probable at low kinetic energy, while charge transfer becomes increasingly more important as kinetic energy increases.¹⁰ This is in agreement with photoion–photoelectron coincidence experiments at ≤ 1 eV, if the strong variation in charge transfer cross section with vibrational state is taken into account.¹⁵ A very interesting observation was made in that work of a resonant enhancement of charge transfer at the expense of proton transfer at very low kinetic energy. With the exception of this result, the two channels do not appear to be linked, in any general way, at low energies, as evidence by the great difference between their vibrational dependence.

The data presented in this paper confirm the general conclusions reached in earlier studies. The range of kinetic energies used, 0–10 eV, bridges those of previous photoionization experiments, providing new information on the interaction of proton and charge transfer in this system. Isotopic substitution allows examination of the relative importance of resonance and Franck–Condon factors in determining the vibrational dependence of charge transfer cross sections. Finally, oscillatory structure in the kinetic energy dependence of charge transfer involving ground vibrational state ions has been observed for the first time.

EXPERIMENTAL

The cross sections reported here were obtained under conditions similar to those used for studies of $(H_2 + D_2)^+$. The apparatus and data analysis have also been described in detail elsewhere.² Briefly, the experiment involves formation of ions in a known vibrational state distribution by photoionization, accelerating the resulting ion beam to the desired kinetic energy, and passing it through a target gas cell. Reagent and product ions are then mass analyzed and counted. Use of radiofrequency ion guides¹⁷ ensures that a narrow beam kinetic energy distribution is maintained and that all ions are collected. It is possible, therefore, to obtain absolute integral reaction cross sections as a function of wavelength and kinetic energy for various reaction channels. Vibrational state distributions at each wavelength are then

used to extract cross sections as a function of vibrational and kinetic energy.

Sources of error in the absolute cross sections reported in this paper have been discussed previously.² It has been noted that back diffusion of gas from the scattering cell into the ionization region introduces a background signal that is difficult to correct for into the charge transfer cross sections. This problem has been alleviated by changing the location of a differential wall in the instrument, but could not be eliminated completely. In the case of H_2^+ and D_2^+ charge transfer with Ar, the nature of the error is as follows. The photoionization efficiency curve for Ar is not constant over the wavelength range used because of the formation of two spin-orbit states of the ion.¹⁸ If it were constant, the Ar back-diffusion signal would be constant, introducing a uniform error into the CT cross sections. Instead, no Ar^+ is formed at the wavelengths used for H_2^+ and D_2^+ ($v=0, 1$), small amounts are present for H_2^+ ($v=2, 3$) and D_2^+ ($v=2-4$), and a larger quantity is formed with H_2^+ ($v=4$). Control experiments have allowed the following error limits to be placed on the charge transfer data: $\pm 5\%$ for H_2^+ and D_2^+ ($v=0, 1$), $\pm 7\%$ for H_2^+ ($v=2, 3$) and D_2^+ ($v=2-4$), and $\pm 15\%$ for H_2^+ ($v=4$). The appropriate error limits for the proton transfer cross sections are $\pm 5\%$.

RESULTS

Absolute cross sections for proton and charge transfer of H_2^+ and D_2^+ with Ar have been obtained as a function of both collision energy and vibrational energy. Figures 1 and 2 show the collision energy dependence of the proton transfer and charge transfer reactions for several initial H_2^+ states. Figure 3 shows the oscillations observed in the collision energy dependence of H_2^+ (D_2^+) $v=0$ charge transfer with Ar. In Figs. 4 and 5, data are plotted to emphasize the vibrational effects. Shown are the cross sections as a function of ion vibrational state for several collision energies. In Figs. 1-3, the raw data are presented, while in Figs. 4 and 5, the data have been corrected for the vibrational

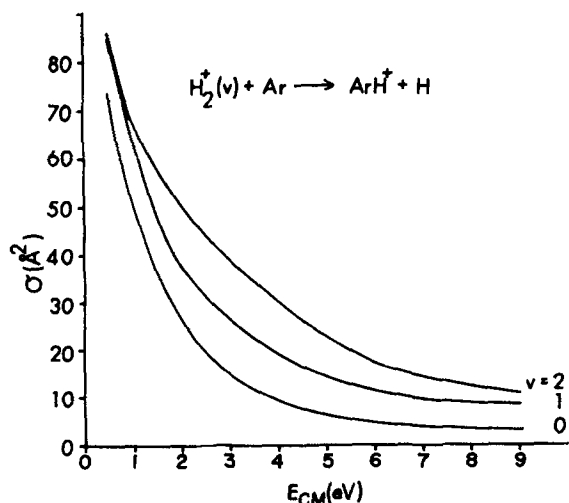


FIG. 1. Kinetic energy dependence of cross sections for proton transfer in the $H_2^+(v) + Ar$ system.

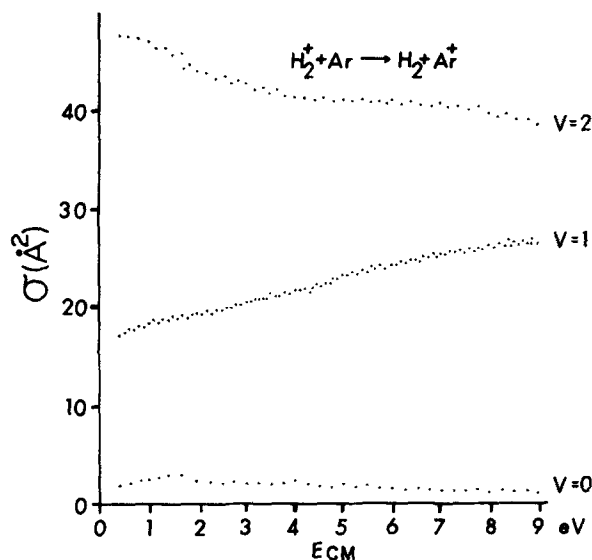


FIG. 2. Kinetic energy dependence of cross sections for CT of $H_2^+ + Ar$.

distribution present in the ion beam.² Both the raw and corrected data are given in Table I.

Charge transfer

Cross sections for the two isotopic systems are similar in magnitude. For each vibrational state, the kinetic energy dependences of the two isotopes are quite similar. At each kinetic energy, the vibrational dependence is also similar, peaking at $v=2$. In the D_2^+ system, however, the enhancement of $v=1$ relative to $v=0$ is not as strong and the decrease from $v=2$ to $v=3$ is not as great.

In general, the kinetic energy dependence of charge transfer for a single vibrational state is found to be quite smooth and relatively flat. This is not the case for the $v=0$ state of both H_2^+ and D_2^+ , as can be seen in Fig. 3. Clear, reproducible structure is seen in the cross section functions. To our knowledge, this observation has not been reported previously.

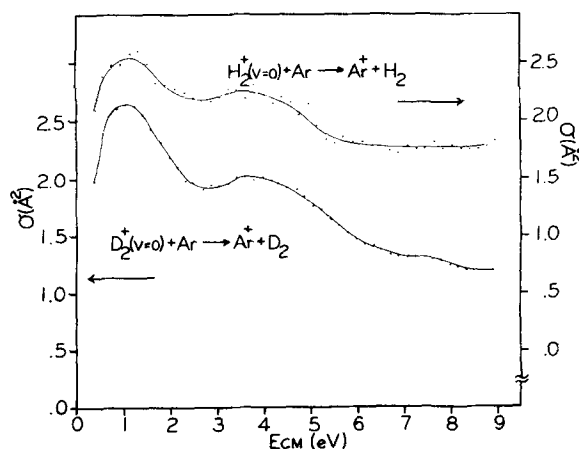


FIG. 3. Absolute cross sections for charge transfer from H_2^+ and D_2^+ ($v=0$).

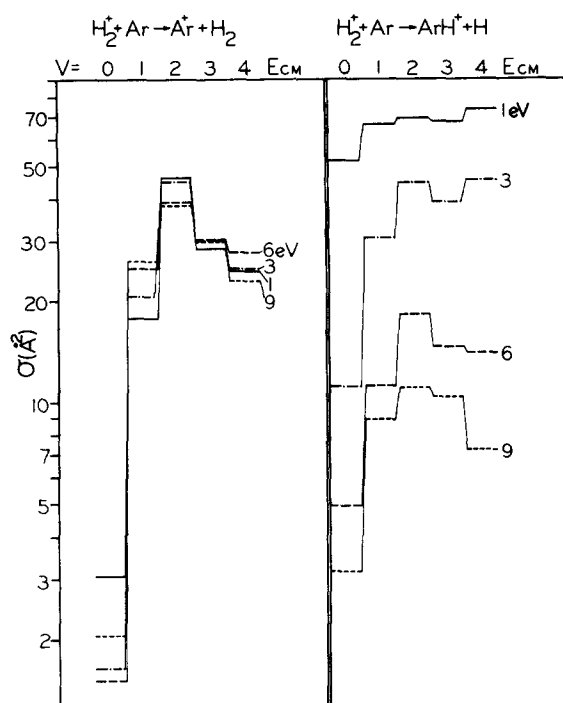


FIG. 4. Absolute reaction cross sections for charge transfer and proton transfer in the $\text{H}_2^+ + \text{Ar}$ system as a function of kinetic and vibrational energy.

Our results can be compared with previous photoionization studies of $\text{H}_2^+ + \text{Ar}$ at two energies. At low kinetic energy, ≤ 1 eV, Tanaka and co-workers¹⁵ have found the vibrational dependence to be qualitatively similar to that shown in Fig. 4 (see comparison of data normalized to $v=2$ presented in Table II). The cross section has a maximum at $v=2$, but the magnitude of the cross section for $v=1$ relative to $v=2$ is somewhat smaller than that found in the present work. This disagreement is at the limit of experimental error. Relative cross sections for charge transfer from H_2^+ ($v=4$) are also in

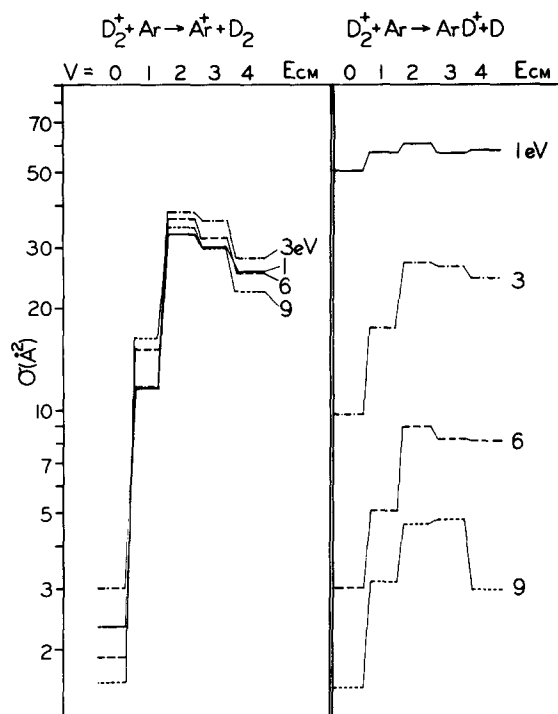


FIG. 5. Absolute reaction on cross sections for charge transfer and proton transfer in the $\text{D}_2^+ + \text{Ar}$ system as a function of kinetic and vibrational energy.

disagreement; however, this may be attributed to errors in the estimated vibrational state distribution generated at that wavelength. While the relative data are in agreement with experimental error, the exceptions having been noted, the absolute values are in poor agreement. For $v=2$, we obtain $\sigma=50 \text{ \AA}^2$, while their value is about 25 \AA^2 . Although we did not obtain charge transfer data at 20 eV, trends apparent in the data at 9 eV can be compared to results of Tanaka¹⁵ and Campbell.¹⁶ Peaking of the cross section at $v=2$ is maintained, in agreement with Tanaka, but not with Camp-

TABLE I. Raw and vibrationally corrected cross sections for charge and proton transfer of H_2^+ and D_2^+ with Ar.

| Reaction | E_{cm} | Corrected | | | | | Raw | | | | |
|---------------------------------|----------|-----------|------|------|------|------|-------|------|------|-------|------|
| | | $v=0$ | 1 | 2 | 3 | 4 | $v=0$ | 1 | 2 | 3 | 4 |
| $\text{H}_2^+ + \text{Ar}$, CT | 1 | 3.06 | 17.7 | 47.2 | 28.4 | 24.4 | 3.06 | 16.1 | 38.9 | 28.1 | 26.2 |
| | 3 | 1.64 | 20.6 | 44.9 | 30.0 | 24.4 | 1.64 | 18.5 | 37.5 | 29.0 | 26.4 |
| | 6 | 1.51 | 24.8 | 38.9 | 30.1 | 27.8 | 1.51 | 22.2 | 33.6 | 28.6 | 27.7 |
| | 9 | 2.06 | 26.3 | 38.3 | 29.9 | 22.8 | 2.06 | 23.6 | 33.5 | 28.6 | 25.4 |
| $\text{H}_2^+ + \text{Ar}$, PT | 1 | 51.8 | 66.1 | 69.1 | 67.7 | 73.4 | 51.8 | 64.5 | 67.2 | 66.4 | 69.3 |
| | 3 | 12.3 | 30.4 | 44.6 | 38.9 | 45.3 | 12.3 | 28.4 | 39.7 | 36.4 | 39.8 |
| | 6 | 4.95 | 12.5 | 18.2 | 14.6 | 14.0 | 4.95 | 11.7 | 16.2 | 14.2 | 13.9 |
| | 9 | 3.17 | 8.9 | 12.1 | 10.8 | 7.24 | 3.17 | 8.27 | 10.9 | 10.1 | 8.5 |
| $\text{D}_2^+ + \text{Ar}$, CT | 1 | 2.32 | 13.3 | 32.8 | 30.0 | 25.5 | 2.32 | 12.2 | 28.2 | 26.7 | 25.4 |
| | 3 | 3.0 | 13.3 | 38.0 | 35.9 | 27.9 | 3.0 | 12.3 | 32.4 | 31.4 | 28.5 |
| | 6 | 1.89 | 15.1 | 36.5 | 32.0 | 25.4 | 1.89 | 13.8 | 31.4 | 28.9 | 26.4 |
| | 9 | 1.59 | 16.3 | 34.3 | 29.9 | 22.2 | 1.59 | 14.8 | 29.8 | 27.3 | 24.1 |
| $\text{D}_2^+ + \text{Ar}$, PT | 1 | 50.7 | 57.2 | 60.8 | 57.1 | 58.1 | 50.7 | 56.5 | 59.7 | 57.49 | 56.5 |
| | 3 | 9.74 | 17.5 | 27.1 | 26.5 | 24.4 | 9.74 | 10.7 | 24.7 | 24.4 | 23.7 |
| | 6 | 3.03 | 5.1 | 9.0 | 8.24 | 8.2 | 3.03 | 4.89 | 8.8 | 7.67 | 7.77 |
| | 9 | 1.55 | 3.15 | 4.64 | 4.8 | 3.0 | 1.55 | 2.99 | 4.25 | 4.36 | 3.48 |

TABLE II. Comparison of vibrational effects of this work and those of Tanaka *et al.* (Ref. 11).

| V | Charge transfer | | | |
|---|--|------------------------------|-----------------------------------|--------------|
| | A | B | C ^a | D |
| | Tanaka <i>et al.</i> (Ref. 11) 1.24 eV | Present work 1 eV | Tanaka scaled to $v=2=47.7$ | Ratio B/C |
| 0 | $2.0 \pm 3.5 \text{ \AA}^2$ | $3.06 \pm 0.3 \text{ \AA}^2$ | 3.3 ± 5.8 | 0.93 |
| 1 | 6.8 ± 3.5 | 17.7 ± 0.9 | 11.2 ± 5.8 | 1.6 |
| 2 | 29.0 ± 3.5 | 47.7 ± 2 | 47.7 ± 5.8 | 1.0 |
| 3 | 16.8 ± 3.5 | 28.4 ± 1.6 | 27.6 ± 5.8 | 1.02 |
| 4 | 9.45 ± 3.5 | 24.4 ± 2.2 | 15.5 ± 5.8 | 1.5 |

| V | Proton transfer | | | |
|---|--|---------------------------|-----------------------------------|--------------|
| | A | B | C ^a | D |
| | Tanaka <i>et al.</i> (Ref. 11) 1.24 eV | Present work 1.0 eV | Tanaka scaled to $v=2=69.1$ | Ratio B/C |
| 0 | 21.5 ± 5.4 | 51.8 ± 2 | 57.1 ± 14 | 0.91 |
| 1 | 23.6 ± 5.4 | 66.1 ± 2.2 | 62.7 ± 14 | 0.94 |
| 2 | 26.0 ± 5.4 | 69.1 ± 2.3 | 69.1 ± 14 | 1.00 |
| 3 | 31.8 ± 5.4 | 67.7 ± 2.4 | 84.5 ± 14 | 0.80 |
| 4 | 25.4 ± 5.4 | 73.4 ± 3.0 | 67.5 ± 14 | 0.92 |

^aScaling factor for CT=1.64. Scaling factor for PT=2.66.

bell, who observed a maximum at $v=1$. An increase in the relative magnitude of the $v=1$ cross section with increasing kinetic energy is evident in our data, as is also observed by Tanaka. Both Tanaka and Campbell obtain absolute cross sections of about 5 \AA^2 at 20 eV. This reflects a strong dropoff in cross section with kinetic energy. As shown in both Figs. 3 and 4, only a relatively weak decrease with energy is observed in our data up to 9 eV. A possible reason for the discrepancy is that our use of rf ion guides guarantees nearly unit product collection efficiency, even for cases where the product has very low laboratory energy.

Proton transfer

As is found in the charge transfer data, the magnitudes of the proton transfer cross sections for the two isotopes are similar, although in the D_2^+ system, the cross sections fall off much more sharply with kinetic energy. The vibrational dependences are similar in shape, those of the D_2^+ system being much weaker, in general, than those of the H_2^+ system. In both systems, the cross sections rise gently with increasing vibrational energy at 1 eV. As the kinetic energy increases, however, the vibrational enhancement for $v=0-2$ becomes much more pronounced and the dependence bears a strong resemblance to that observed for the charge transfer channel. The proton transfer cross section is much larger than that for charge transfer at low kinetic energy (1 eV). As the relative energy increases to 3 eV the cross sections become nearly equal for the two channels. Above this point, charge transfer clearly dominates.

These data can only be compared to previous experiments on $H_2^+ + Ar$ at 1 eV, as shown in Table II. Within

experimental error, the vibrational dependence found by Tanaka¹⁵ is in good agreement with ours, showing a weak increase with vibrational state. Chupka¹⁴ also reported that proton transfer has little or no vibrational dependence at thermal energies. The absolute cross sections in Fig. 2 are in disagreement with those of Tanaka, ours being about a factor of 2 to 3 higher.

DISCUSSION

The present results are in qualitative agreement with previous work. However, measurement of reaction cross sections over a wide energy range as a function of vibrational and kinetic energy has provided important new information concerning the interplay of charge transfer and proton transfer in $H_2^+ + Ar$ and, hence, on the role of the potential energy surfaces in the reaction.

Long-range charge transfer involves motion of the system through an avoided crossing region. When the system reaches the crossing seam, it can either remain adiabatically on the original surface, undergoing charge transfer, or hop to the other surface, remaining in the initial charge state. In general, vibrational motion, rather than relative translation, is effective in carrying the system through the seam, thus playing a crucial role in determining whether or not charge transfer occurs.¹ Other factors are also important. When vibronic levels belonging to the two charge states of the system are close in energy, they will interact strongly and their crossing will be more avoided than if their energies were not so close. The Franck-Condon overlap between the initial and final charge states also affects the probability of electron transfer at the avoided crossing. Thus, vibrational motion, resonance between energy levels, and favorable Franck-Condon factors are all expected to play a role in determining the magnitude of long-range charge transfer cross sections. Translational energy is not likely to be critical.

Schematics of the energy levels for Reaction (3) are presented in Figs. 6 and 7. The reason for the low H_2^+ , $D_2^+(v=0)$ cross sections is evident from these diagrams. Reactions of these states is endoergic and only translational energy conversion will enable it to occur. Such transfer is inefficient except at short range, and thus

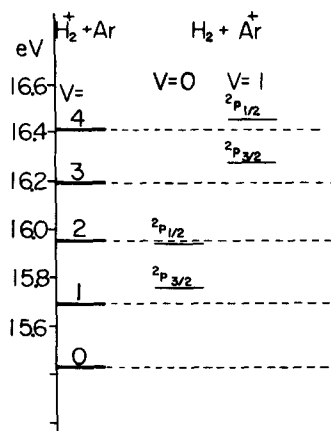


FIG. 6. Schematic of $(H_2 + Ar)^+$ energy levels.

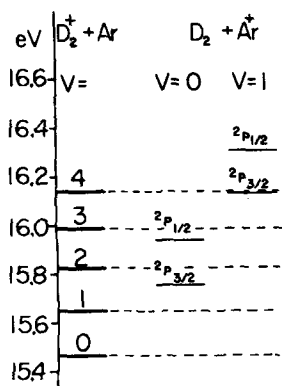


FIG. 7. Schematic of $(D_2 + Ar)^+$ energy levels.

the cross sections are low. The endoergicity of charge transfer for H_2^+ and D_2^+ ($v=1$) is smaller than for $v=0$. This is likely to be a major reason for the enhanced reaction cross sections of these states compared to those of $v=0$. The ordering $\sigma(H_2^+, v=1) > \sigma(D_2^+, v=1)$ may be due to the fact that the reaction of D_2^+ is more endoergic. For $v=2$ in both systems, exoergic charge transfer to near-resonant energy levels is possible and the cross sections are high. While near-resonant levels also exist for $v=3$ and $v=4$, they are endothermic for H_2^+ and exothermic for D_2^+ . The cross sections, while remaining high, are seen to drop off much more rapidly for H_2^+ above $v=2$ than for D_2^+ .

The kinetic energy dependence of the cross sections is consistent with these trends. For $v=0$, the charge transfer cross sections exhibit structure in the translational energy dependences. For H_2^+ and D_2^+ ($v=1$), the cross sections are observed to increase with kinetic energy. This is consistent with the fact that translational energy is required in order to overcome a rather modest endothermicity. For $v \geq 2$, the kinetic energy dependences are found to be rather flat, dropping slowly with increasing energy.

Massey¹⁹ proposed an adiabatic model to predict the location of maxima in the kinetic energy dependence of long-range nonresonant charge transfer cross sections. These maxima are expected to occur when the following relation is satisfied:

$$\frac{\Delta E a}{h V_{rel}} \approx 1,$$

where ΔE is the asymptotic energy difference between the two charge states of the system, a is a parameter which is related to the relative distance at which charge transfer occurs, and V_{rel} is the relative velocity of the ion and neutral. The maxima will be pronounced for systems having only two accessible charge states that are not near resonant in energy. This implies that structure would not be observable in the charge transfer cross sections of the systems having many vibronic levels that are closely spaced in energy. A theory like that proposed by Bates,²⁰ which explicitly takes contributions from all possible transitions into account in calculating charge transfer cross sections, is more appropriate for such systems. In general, charge transfer involving more than two atoms falls into the latter category—indeed, the kinetic energy dependence of charge transfer for H_2^+ and D_2^+ ($v > 0$) shows the data

to be quite smooth. H_2^+ and D_2^+ ($v=0$) can be considered to be a system amenable to the Massey hypothesis, however. Table III shows a comparison between the positions of the peaks observed in the charge transfer function for H_2^+ and D_2^+ ($v=0$) in Fig. 3 and those calculated by fitting one peak to obtain the a parameter. [$a(H_2^+) = 1.56 \text{ \AA}$, $a(D_2^+) = 1.24 \text{ \AA}$. The significance of the difference is unclear.] The parameter depends slightly on the energy of the peak used, which is reasonable in light of its physical significance. The fact that this simple model can be used to fit the peaks in the cross sections suggests that a velocity scaling law may be valid to describe charge transfer in this system. However, it should be noted that the peaks for H_2^+ and D_2^+ fall at the same collision energy leading to the possibility that these peaks in the cross sections scale with collision energy rather than relative velocity.

As noted above, overlaps of the nuclear wave functions should also be considered in a discussion of the vibrational effects. Franck-Condon factors for H_2 and D_2 are obtained from exact calculations.²¹ They show that the maximum transition probability between neutral and ion is for $v=0-2$ and $0-3$ in H_2 and D_2 , respectively. If overlaps of wave functions between the charge states were the overriding factors determining the magnitude of the cross sections, the data in Figs. 4 and 5 would show maxima at $v=2$ for H_2^+ and $v=3$ for D_2^+ . Instead, both peak at $v=2$ and the cross sections for D_2^+ ($v=3$) are slightly less at all energies. The peaking for D_2^+ ($v=2$) may result in part from the statistical weight of the Ar ($^2P_{3/2}$) state reached compared to that of the $^2P_{1/2}$ state accessible from D_2^+ ($v=3$). If the H_2^+ ($v=0-2$) + Ar charge transfer data were considered alone, the relative importance of near resonance and Franck-Condon effects could not be determined since the vibrational dependence mirrors trends in both. Isotopic substitution, however, allows the conclusion to be drawn that Franck-Condon effects do not influence the dependence as strongly as energy resonance and statistical effects in this particular system. In our recent studies on vibrational energy dependent of charge transfer processes in the collision of for H_2^+ (D_2^+) with N_2 , CO, O_2 , and Ar,²² it is shown that Franck-Condon effects, while not as important as energy resonance, play a substantial role in determining the probability of a given charge transfer channel even under our low collision energy conditions.

Crossed molecular beam experiments have shown that

TABLE III. Maxima in H_2^+ and D_2^+ ($v=0$) charge transfer cross sections.

| Transition | $E(\sigma_{max})$ Observed (eV) | $E(\sigma_{max})$ Calculated (eV) |
|--|------------------------------------|--------------------------------------|
| $\rightarrow H_2(v=0) + Ar(^2P_{3/2})$ | 1.2 | 1.55 |
| $\rightarrow H_2(v=0) + Ar(^2P_{1/2})^a$ | 3.65 | 3.65 |
| $\rightarrow D_2(v=0) + Ar(^2P_{3/2})$ | 1.1 | 1.46 |
| $\rightarrow D_2(v=0) + Ar(^2P_{1/2})^a$ | 3.77 | 3.77 |
| $\rightarrow D_2(v=1) + Ar(^2P_{3/2})$ | 7.6 | 7.50 |

^aTransition used to obtain the a parameter (see the text).

charge transfer between H_2^+ and Ar is predominately long range, but that at low collision energies, a fraction of the collisions are intimate in nature.¹⁰ Kinetic energy analysis of the scattered products indicated that the reaction was translationally endothermic at all relative energies. This is surprising in view of the fact that the ion beam used was internally excited, since all vibrational levels greater than zero can undergo near-resonant charge transfer and the corresponding energy defects are only on the order of a few meV. The large transfer of kinetic energy implies that charge transfer occurs largely via nonresonant, endoergic channels even when near-resonant channels are available. If this is the case, one would expect charge transfer to be dependent on collision energy, since the energy transfer necessary is dependent on the reagent relative velocity. This is not what we observe (Fig. 2). The weak dependence of the charge transfer cross sections on kinetic energy found in our experiments is incompatible with substantial energy conversion during the collision. Rather, we conclude that charge transfer in these systems is mainly long range in nature and involves states that are very close in energy. One possible explanation for the inconsistency of the two sets of data is that the beam used by Farrar is substantially lower in internal energy than is assumed. However, this does not account for the translational endothermicity quantitatively.

Proton transfer to Ar is a direct, exoergic process and the reaction cross sections in Figs. 1, 4, and 5 have a typical kinetic energy dependence. The falloff for proton transfer compared to deuteron transfer is slower, however. Simple kinematic considerations account for the direction of the effect, but cannot account for the magnitude of the falloff. The origin of the difference in kinetic energy dependence of the two isotopic systems is not clear.

One-dimensional calculations by Baer and Beswick⁷ predict the existence of a barrier to proton transfer of 0.7 eV for H_2^+ ($v=2$). As can be seen in Fig. 1, there is no downturn of the cross section at low kinetic energy and thus no evidence for a barrier high enough to influence the reaction.

The vibrational dependence of the proton transfer process is particularly interesting. The data show that at all kinetic energies the reaction cross section for ground state ions is smaller than that for vibrationally excited ions, with relatively little variation for $v \geq 2$. This is why Farrar *et al.*¹² saw little effect of quenching the high vibrational state ions from their beams. This is the opposite of what would be expected on the basis of the vibronic potential surfaces alone. Proton transfer from H_2^+ ($v=0$) is the only reaction that takes place on a surface too far away from those of other charge states to interact with them significantly. Lack of competition from charge transfer would therefore be expected to enhance the probability of proton transfer in the $v=0$ state with respect to higher states where charge transfer cross sections are large. The fact that the observed trends are counter to these simple ideas indicates that the reaction dynamics of this system are quite complicated. The proton and charge transfer channels cannot be considered to be independent.

Evidence for this can be found in comparing the vibrational dependence of the cross sections for proton and charge transfer. Although the trends are evident at all energies, the similarity in the dependences is particularly strong at higher kinetic energy. This implies that, regardless of the outcome of the collision, proton and charge transfer both involve a common region of the available potential surfaces. Moreover, the major part of the vibrational dependence of either channel appears to be determined in this region, which is most likely to be that of the avoided crossings in the entrance channel. The structure of the intersection region is quite complicated for H_2^+ ($v > 0$) since vibronic surfaces for all accessible states of the system (corresponding to the asymptotic energy levels in Figs. 6 and 7) each generate their own set of avoided crossings. This enables the system to undergo multiple hops between the surfaces, emerging either as the charge transfer product or in its original charge state.

One possible way in which multiple charge hopping in the collision entrance channel could increase the subsequent proton transfer probability is that, in the process of crossing back and forth between the two diabatic potential surfaces, the system may become vibrationally excited. This vibrational excitation may in itself promote proton transfer and certainly the concomitant reduction in reagent relative velocity will have this effect (Fig. 1). We would expect this mechanism to be less important at low collision energy partly because the proton transfer probability is inherently large (large cross section) and also because less kinetic energy is available for conversion to vibrational energy. Of course this mechanism is speculative and determining the actual mechanism which couples charge transfer and proton transfer would be an interesting theoretical problem.

In summary, cross sections for proton and charge transfer in the H_2^+ and D_2^+ + Ar system have been measured as a function of vibrational and kinetic energy. The data are in qualitative agreement with previous work. Charge transfer proceeds mainly by a long-range mechanism. The existence of near-resonant energy levels accounts for the major features of the vibrational dependence. Franck-Condon overlaps appear to play a less important role. Comparison of the vibrational dependences of the two reaction channels indicates that proton and charge transfer are closely linked in this system. This is very similar to the situation found for $\text{H}_2^+ + \text{H}_2$,² however, in that case, the vibrational dependence of the two channels did not appear to be determined in a single potential region.

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