LBL-17729
Preprint c.2

Lawrence Berkeley Laboratory
UNIVERSITY OF CALIFORNIA

Materials & Molecular Research Division

RECEIVED
LAWRENCE
BERKELEY LABORATORY

JUN 12 1984

LIBRARY AND
DOCUMENTS SECTION

Submitted to the Journal of Chemical Physics

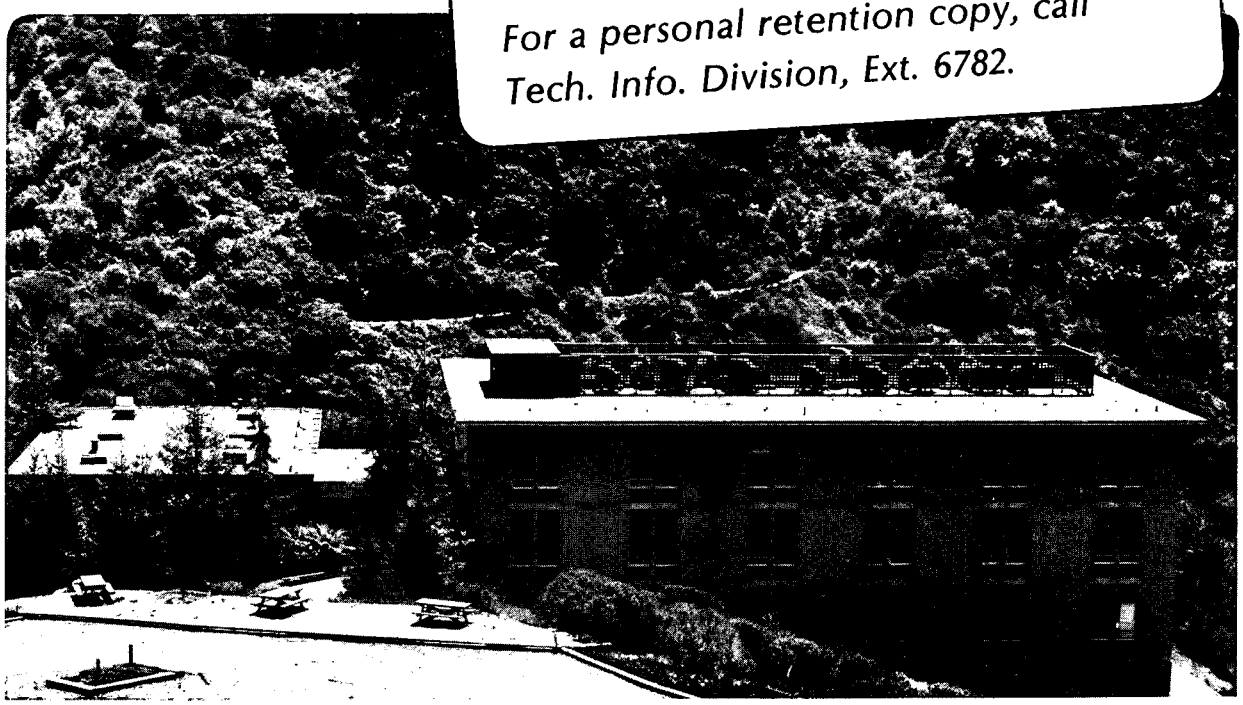
THE EFFECTS OF COLLISION ENERGY AND VIBRATIONAL EXCITATION ON H_2^+, HD^+ + He REACTIONS

T. Turner, O. Dutuit, and Y.T. Lee

April 1984

TWO-WEEK LOAN COPY

This is a Library Circulating Copy which may be borrowed for two weeks. For a personal retention copy, call Tech. Info. Division, Ext. 6782.



Prepared for the U.S. Department of Energy under Contract DE-AC03-76SF00098

LBL-17729 c.2

DISCLAIMER

This document was prepared as an account of work sponsored by the United States Government. While this document is believed to contain correct information, neither the United States Government nor any agency thereof, nor the Regents of the University of California, nor any of their employees, makes any warranty, express or implied, or assumes any legal responsibility for the accuracy, completeness, or usefulness of any information, apparatus, product, or process disclosed, or represents that its use would not infringe privately owned rights. Reference herein to any specific commercial product, process, or service by its trade name, trademark, manufacturer, or otherwise, does not necessarily constitute or imply its endorsement, recommendation, or favoring by the United States Government or any agency thereof, or the Regents of the University of California. The views and opinions of authors expressed herein do not necessarily state or reflect those of the United States Government or any agency thereof or the Regents of the University of California.

THE EFFECTS OF COLLISION ENERGY AND VIBRATIONAL EXCITATION ON H_2^+, HD^+ + He REACTIONS

T. Turner,[a] O. Dutuit,[b] and Y. T. Lee

Materials and Molecular Research Division
Lawrence Berkeley Laboratory and
Department of Chemistry, University of California
Berkeley, California 94720 USA

ABSTRACT

An experimental study of proton and deuteron transfer in H_2^+ + He and HD^+ + He has been carried out as a function of kinetic and vibrational energy. The data gives evidence that at lower kinetic energies, the spectator stripping mechanism indeed plays an important role when H_2^+ or HD^+ is vibrationally excited. The $H_2^+(v=0)$ reaction has a much smaller cross section than the v=1-4 reactions and seems to go through intimate, small impact parameter collisions involving all the atoms. Investigation of the competition between both the proton and deuteron transfer channels for the HD^+ case, shows that vibrational enhancement towards forming the HeD^+ product falls off sooner with increasing kinetic energy than does the HeH^+ product again in accordance with the spectator stripping model. The higher yield for HeH^+ production at both higher vibrational levels of HD^+ and at lower kinetic energy and the behavior of translational energy dependence of HeH^+ seems to indicate the importance of the induced orientation of HD^+ during the collision with He. Because of the displacement of the center of mass from the center of charge in HD^+, the charge induced dipole interaction between He and HD^+ tends to swing the H atom more towards He during the approach of He and HD^+.

a) Fannie and John Hertz Foundation Fellow.
b) permanent address: Laboratoire de Resonance Electronique et Ionique, Bat. 350, Centre Universitaire d'Orsay, 91405 Orsay, FRANCE.

INTRODUCTION

The reaction between H_2^+ and He forming HeH^+ has been extensively investigated in the past. This reaction is endothermic by 0.8eV and was the first experimental example, as shown by Chupka, et. al., that vibrational energy strongly promotes product formation over kinetic energy.[1,2] Aside from these photoionization studies which prepared H_2^+ in a specific vibrational state, most past experimental work, including crossed beam,[3-5] mass spectrometric,[6,7] merged beam,[8] and ion beam-gas cell[9] techniques, used H_2^+ produced by electron impact ionization of H_2; thus a broad range of H_2^+ vibrational states participated in the reaction with He. These studies all give evidence to a direct reaction with a maximum cross section for HeH^+ production of approximately 5Å^2 at a collision energy of 1eV in the center of mass (CM) coordinate system. The cross section decreases sharply with the increase of collision energy beyond 1eV. The crossed beams studies of Herman, et. al.[4,5] have shown the reaction to proceed mainly via the spectator stripping (SS) mechanism when the collision energy is between 0.5 and 4.0eV. However, when H_2^+ was specially prepared to be in lower vibrational states, the intensity of products which can be ascribed to the SS mechanism is substantially smaller.

This system is one of the simplest ion-molecule reactions for which potential energy surfaces can be rigorously calculated. Because of the large difference between the ionization potentials of He and H_2, the excited and charge transfered states of this triatomic system lie appreciably above the ground state[10,11] and the reaction between H_2^+ and He, at low collision energies, is expected to take place on a single

potential energy surface. Brown and Hayes have calculated an ab initio surface for the linear $H_2^+ + He \rightarrow HeH^+ + H$ reaction.[12] Their surface shows a barrier late in the exit channel and the existence of a small well (0.15eV below reactants) cooresponding to a weak HeH_2^+ complex. The linear complex has been shown to be the most stable geometry. Kuntz then fit this surface to a surface generated by the diatomics-in-molecules (DIM) method;[13] however, quantum mechanical (QM) scattering calculations using this surface does not give the experimentally observed enhancement in the reaction cross section with an increase of H_2^+ vibrational energy.[14,15] The reaction probability as a function of collision energy shows sharp resonance structure above the reaction threshold with resonance widths ranging anywhere from 0.002 to 0.04eV. The qualitative disagreement between experimental and calculated results may not be entirely due to the limitation of using the 1D collinear potential energy surface. Kuntz and Whitton have run classical trajectories on a revised DIM surface with good, qualitative experimental agreement.[16,17] Raff and his coworkers have also generated a spline fitted ab initio (SAI) surface which gives vibrational enhancement to the reaction probability in a collinear calculation using both QM and quasiclassical trajectory (QCT) methods.[18] They have also found that the difference in the shape of the inner repulsive wall between the SAI and DIM surfaces accounts for their dynamical differences,[19] whereas including or excluding the potential well on a spline fitted DIM surface was shown by Sathyamurthy to have little effect.[20]

More recently McLaughlin and Thompson have calculated the four lowest electronic energies for HeH_2^+ in C_s symmetry; 596 ab initio points are reported for a total of 7 different bond angles.[21] Trajectory studies of both Hartree-Fock (HF) and the configuration interaction (CI) collinear versions of the surface give vibrational enhancement for reaction from v=0 to v=1, but the more accurate CI surface gives a decreasing reaction probability as vibration is increased.[22]

Although collinear QM scattering calculations on the original Kuntz DIM surface does not give the desired vibrational dependence, the three dimensional QCT results of Schneider, et. al.[23] were in satisfactory agreement with their experimental differential cross sections,[4,5] and, except for low translational energies and low vibrational states, they are in good agreement with the data of Chupka, et. al.[1,2]

Truhlar, et. al. extended the earlier application by Light and Lin[24] of statistical phase space theory to the H_2^+ + He reaction using an ion-induced dipole potential.[25,26] Although vibrational enhancement of the reaction is obtained, the cross section varies too slowly with energy, being too large for low vibrational levels and too small for higher levels. Apparently the full statistical assumption is not valid for this system.

In this paper results obtained using our unique apparatus consisting of a photoionization ion source and octapole RF ion guide for the investigation of the reactions of $H_2^+(v)$ + He and $HD^+(v)$ + He are described. The 0-10eV center of mass kinetic energy range used here extends as well as improves the knowledge of the translational energy dependence derived from previous photoionization studies. The previous studies of the translational

energy dependence were derived from the repeller voltage dependence of the reaction taking place in the ion source. The substantially better kinetic energy definition between reactants in this experiment allows the direct determination of the microscopic cross section as a function of kinetic energies. New information on the HD^+ system, especially its cross section and branching ratio as a function of vibrational and kinetic energy of reaction provides additional information on the dynamical aspects of this reaction.

Part of the original motivation for carrying out the detailed investigation of the translational energy dependence of the reaction cross section for various vibrational states of H_2^+ was the possibility of experimentally observing the sharp resonances shown in the collinear QM calculations of the reaction probability as a function of collision energy.[14,15] No evidence of these resonances was detected in this experiment.

EXPERIMENTAL

The experimental arrangement used in this study is similar to those of the $(H_2 + D_2)^+$ experiment which has been described in detail.[27] Briefly, a beam of H_2 is photoionized with wavelength selected VUV photons inside an RF octapole ion guide. Owing to the domination of autoionization processes near the ionization threshold, depending on the selection of the wavelength, the H_2^+ ions produced are in fairly pure and well characterized vibrational states. The ions are formed into a beam, guided along the octapole axis, and are accelerated to a given kinetic energy before passing through a scattering cell. The scattering cell which surrounds a section of the octapole ion guide and contains a measured pressure of He gas. Product ions are then extracted from the octapole, mass analyzed by a quadrupole mass spectrometer, and counted using a liquid N_2 cooled Li drifted Si detector with a detection efficiency of nearly 100 percent.

Because the reaction cross section of this system is very small, the original scintillator and PMT of the Daly detector were replaced with this Li drifted Si detector in order to decrease the counting background as much as possible. This detector has extremely high energy resolution, thus a clean separation of low energy background pulses from high energy ion pulses can be made. Using the octapole ion guides ensures 100 percent collection efficiency of all ions involved.

The HD was produced by reacting $LiAlH_4$ with D_2O.[28] The purity of HD was better than 95 percent. The ionization wavelengths for producing specific vibrational states of HD^+ were chosen based on the energy levels of the vibrational states of HD^+ [29] and on the HD photoionization

efficiency spectrum obtained with this experimental arrangement. For each vibrational state, the wavelength was chosen to cover clusters of autoionizing peaks which are as far away from adjacent vibrational levels as possible. Exact state distributions for each wavelength are estimated from the high resolution HD photoionization efficiency curve, measured recently by Dehmer and Chupka,[30] which contains well resolved autoionization structure. The autoionization and direct ionization contributions were estimated by integrating the autoionization peaks and direct ionization background of Dehmer and Chupka's spectrum. The autoionization process was assumed to leave HD^+ in its highest possible vibrational state. Franck-Condon factors obtained by Berkowitz and Spohr are used to provide an estimate of the vibrational state distributions of HD^+ ions produced by direct ionization.[31] The following wavelengths were used at a FWHM resolution of 4Å: v=0, 797Å; v=1, 782Å; v=2, 772Å; v=3, 763Å; and v=4, 754Å. Table I gives the estimated vibrational population distributions for both H_2^+ and HD^+.

For some of the HD^+ experiments, especially for the investigation of the HeH^+ channel, an improved ion source was required because the small amounts of D_2H^+ produced by the reaction of HD^+ with HD in the ion source interferes with the product HeH^+ which has the same mass. A new electroformed skimmer and an increased nozzle-skimmer distance were used in the later experiment to have a better defined HD beam in the ion source. A cleaner HD beam produced less background HD gas with which the HD^+ could react.

RESULTS AND ANALYSIS

$H_2^+ + He$

Figure 1 shows the raw data of the collision energy dependence of the reaction cross section for HeH^+ formation from state selected H_2^+. The wavelengths were chosen to produce the various $H_2^+(v)$ states shown. In all the cases except for v=0, the cross section rises sharply below 1eV (all kinetic energies are CM kinetic energies unless otherwise specified), peaks at 1-2eV, then decreases sharply until about 4eV. At 4eV and above, the cross section decreases at a visibly slower rate. For the v=0 state, the cross section rises much more slowly, peaks broadly with a value of about $0.15Å^2$ around 3eV, and decreases very slowly thereafter. Although the state selection is not pure, contamination of lower vibrational states for the chosen state tend to deemphasize the vibrational dependence, yet the vibrational enhancement of the cross sections can be clearly seen in these raw data. Figure 2 gives the cross section, deconvoluted for the vibrational state distribution of H_2^+, as a function of ion vibrational energy for a given kinetic energy. The reaction is substantially vibrationally enhanced at the lower translational energies. At 1eV, the reaction probability is increased well over an order of magnitude for v=0 to 4, from 0.0569 to $1.67Å^2$. At 2eV, near the cross section maximum, the cross section varies from 0.129 to $0.964Å^2$ for v=0 to 4. Above 5eV, little vibrational dependence is seen. Table II gives the values of the cross section as a function of kinetic and vibrational energy for both the raw data and the deconvoluted results.

$HD^+ + He$

Figure 3 shows raw data plots of HeD^+ production as a function of kinetic energy. The reaction is again strongly vibrationally enhanced at low kinetic energy and the cross section at maximum is roughly the same as that for HeH^+ production from H_2^+. Owing to the limited supply of HD available, only one extensive energy scan of the HeH^+ channel was made and is shown in Figure 4. The cross section of the HeH^+ channel drops more sharply with collision energy than for the HeD^+ channel. Data shown in Figure 4 are the results using the improved ion source, which substantially decreased the time needed to obtain the HeH^+ signal with reasonable statistical errors. The cross sections of the HeH^+ channel were normalized to the data shown in Figure 4.

Figure 5 shows the dependence of the reaction cross section on HD^+ vibration at various kinetic energies for both the HeH^+ and HeD^+ channels. These data are deconvoluted from the raw data based on the estimated HD^+ vibrational state distributions given in Table I. For HeH^+ formation at 1eV, the reaction is strongly vibrationally enhanced, increasing one order of magnitude for v=0 to 4, from 0.099 to 2.25Å^2. Vibrational enhancement is seen up to 4eV. By 8eV, the cross section shows only a slight vibrational enhancement. In contrast the HeD^+ channel shows little vibrational dependence at 4eV even though at 1-2eV both channels behave similarly. By 8eV, the HeD^+ channel shows a noticeable vibrational inhibition. The branching ratio for the formation of HeH^+ to HeD^+ is 1.79:1 for HD^+(v=4) at 1eV. Table III gives the values of the cross sections for both reaction channels as a function of kinetic and vibrational energy for both the raw and deconvoluted data.

DISCUSSION

Herman, et. al. have studied the reaction of H_2^+, formed by electron impact, with He in the 0.5-4.0eV range using the crossed beams method and have found most of the product HeH^+ peaked at spectator stripping (SS) velocities.[4] The data presented here indeed contain some features which support the significant involvement of the SS mechanism for this reaction when H_2^+ is vibrationally excited.

The role played by the SS mechanism can be seen in Figure 1. For v=1-4, above 3eV, the cross section decreases rapidly for vibrationally excited H_2^+, but around 4eV the rate of decrease becomes markedly slower as if a sudden disappearence of a reaction mechanism occurs leaving a second reaction mechanism which does not strongly depend on collision energy. The range of collision energies in which the breaks in the cross sections occur for various H_2^+ vibrational states is exactly the range of critical energies for the SS mechanism.

The range of kinetic energies over which product formation by SS is stable is calculated in a sraightforward manner. In the CM frame, the SS model implies that the He atom abstracts the proton without imparting any momentum to the remaining H atom of the original H_2^+ molecule. If HeH^+ is to be formed, the two body kinetic energy between He and H^+ must be larger than the reaction endothermicity, but no more than the binding energy of H_2^+. Below the threshold energy, the product formation is energetically impossible and above the critical energy, HeH^+ formed will contain too much internal energy to be bound. Table IV lists the kinetic energy range for each ion vibrational level for which SS is stable. The

energy range for the formation of stable products via the SS model shifts for each vibrational level of H_2^+ by that vibrational energy in the 2 body (H^+ + He) CM frame. The 3 body (H_2^+ + He) CM kinetic energy

$$E_{cm} = \frac{m_{He} \; m_{H_2^+} \; v_{rel}^2}{2m_{He+H_2^+}}$$

is related to the 2 body CM kinetic energy

$$E_{He,H^+} = \frac{m_{He} \; m_{H^+} \; v_{rel}^2}{2m_{He+H^+}}$$

by a factor of

$$\frac{m_{He+H^+} \; m_{H_2^+}}{m_{He+H_2^+} \; m_{H^+}} = \frac{5}{3}$$

that is

$$E_{cm}=(5/3)E_{He,H^+}.$$

Vibrational energy dependence of the reaction cross sections at various collision energies shown in Figure 2 also reveal the important role played by the SS mechanism. For example at 4eV the cross section decreases from v=2-4. Referring to Table IV reveals that HeH^+ cannot be formed via a SS mechanism for these vibrational levels at this collision energy. At 8eV, the strong vibrational enhancement is completely absent and energetically, product cannot be formed by SS. The breaks in the collision energy

dependence of the reaction cross section shown in Figure 1 are dependent on the vibrational state of H_2^+. For v=3, this break occurs at 3.4eV, close to the calculated critical energy for SS. For v=2, the break moves up with energy to 4eV as expected. The fact that a visible break does occur near the SS critical energy supports the presence of the SS mechanism for this reaction.

The role played by the SS reactions is seen to become more and more important as the vibrational energy in H_2^+ is increased. For v=0, the cross sectional dependence as a function of kinetic energy shows a broad peak which decays slowly with energy. Here one must assume that SS does not play as important a role as in the case of vibrationally excited H_2^+. The small magnitude of the cross section (under 0.15Å^2) and the slow variation of the cross section with kinetic energy indicate that this v=0 reaction probably proceeds mostly via intimate, small impact parameter collisions which involve all three atoms. The increase of vibrational energy not only reduces the dissociation energy, but also extends the average H_2^+ bond distance which facilitates the capture of H^+ in H_2^+ by He as a two body collision, leaving the H atom as a spectator. Pacak, et. al. have looked at HeH^+ formation using a v=0,1 enhanced H_2^+ beam.[5] The contour maps of product angular and velocity distributions at 3.58eV reveals a substantial amount of product which is backscattered with respect to the He direction; this backscattered peak is approximately 2/3 the intensity of the forward peaked product. Using a nonselected H_2^+ beam (produced by electron bombardment ionization) at a similar collision energy, the forward peak is 5 times the backscattered

peak,[4] that is, H_2^+ in higher vibrational levels reacts to form product mainly in the forward direction.

Above the critical energy for the SS mechanism, the formation of HeH^+ is only possible when the H atom ceases to be a spectator and the extra energy is carried away as the relative motion between the H atom and HeH^+ molecule. The reaction mechanism must remain direct and is most likely a sequential impulse type of mechanism[17,32] which forms the product at predominently small impact parameters. Energetically the collision induced dissociation (CID) channel opens up at the bond energy of H_2^+, 2.65eV. But, for vibrationally excited H_2^+, CID only becomes important beyond the critical energy for the SS mechanism. Chupka, et. al. have indeed found CID to be vibrationally enhanced.[2] Their data shows that for v=0 the cross section is small, comparable to that of proton transfer and for v=3 the cross section rises slowly and peaks at 6eV total energy. All these results indicate a clear relation between SS and CID at collision energies beyond the critical energy of the SS mechanism; at translational energies above 4eV, vibrational inhibition exists as a result of CID competition against proton transfer. The trajectory studies of Whitton and Kuntz also indicate that CID is vibrationally enhanced.[17]

The CID mechanism using SS as an intermediate step can be viewed in two ways. Either the H atom or the proton may be left after the reaction as the spectator. With the proton as the spectator, its velocity would simply be the same as the initial H_2^+ velocity. The He atom strips the H atom which subsequently falls apart, leaving behind the proton to be detected in the direction of initial H_2^+ velocity. Havemann, et. al. do find a

peaking of proton intensity occuring in the direction of the original H_2^+ motion close to the initial H_2^+ velocity.[33] If the H atom is the spectator, the He atom will strip the proton from the H_2^+ molecule to form HeH^+ which subsequently falls apart. H^+ is detected in the direction of the initial He atom (backward with respect to the initial H_2^+ motion). Because of the experimental difficulty in detecting these low laboratory energy, backward scattered protons in crossed beams experiments, the failure to observe backward scattered H^+ in the CID work of Havemann, et. al. might not imply a preference of H^+ to be the spectator over H in the CID of H_2^+ with He.

The qualitative agreement between this work and that of Chupka is satisfying. The proton transfer reaction for v=0 is in qualitative agreement, but for v=3 our cross sectional dependence differs somewhat from that of Chupka. Their data is found to peak sharply at 0.2eV with a cross section of 5.2Å^2 and it falls off sharply afterwards. In our data shown in Figure 1, the cross section rises sharply, but peaks at 1.7eV with a value of 1.16Å^2. After peaking the cross section also falls off sharply through 4eV. The discrepencies in magnitude and where the maximum occurs may be due in part to the experimental method.[1] In these pioneering studies of Chupka, et. al., the reaction took place in a single photoionization chamber where the ion kinetic energy was varied by changing the repeller voltage and a mass spectrometer sampled products from that chamber. Due to the presence of the electric field over which the H_2 molecules were photoionized and reacted, the ions reacted with He over a range of kinetic energies. Consequently, phenomenological cross sections

were measured; microscopic cross sections were derived by use of a deconvolution method given by Light.[34] In the present experiment, the kinetic energy between H_2^+ and He is very well defined and the microscopic cross sections are measured directly.

Using HD^+ as the reactant ion, it is possible to verify many dynamical features of the HeH_2^+ system in greater detail. Both channels forming HeH^+ and HeD^+ exhibit the same qualitative features as for HeH^+ formation from H_2^+. At lower kinetic energy strong vibrational enhancement is seen which turns into vibrational inhibition as the collision energy is raised. The SS mechanism can again explain the cross sectional behavior. Here, $E_{cm}=(15/7)E_{He,H^+}$ for HeH^+ and $E_{cm}=(9/7)E_{He,D^+}$ for HeD^+ as SS formed products. As seen on Figures 3 and 4, the cross sections decrease similarly with collision energy over the energy range studied. The plot, however, does not show a sudden shift in this rate of decay as in Figure 1 for the HeH_2^+ system. Near 1eV, the maximum cross section is 0.66 and 0.51Å^2 for HeH^+ and HeD^+ respectively from HD^+, v=2 compared to 0.74Å^2 for HeH^+ from H_2^+, v=2.

Different kinematic relations may be seen between the proton and deuteron transfer channels HeH^+ and HeD^+. Both channels exhibit similar vibrational enhancement at 1 and 2eV. However, at 8eV, the HeH^+ channel is slightly vibrationally enhanced for v=0-3 while HeD^+ is vibrationally inhibited for the same vibrational levels. The energy range for HeD^+ formation by the SS mechanism is lower than for HeH^+ as shown in Table IV. As the collision energy is raised, SS is closed to stable HeD^+ formation first. At 4eV all vibrational levels except v=4 are open to SS

for HeH^+, but no $HD^+(v)$ levels are open for HeD^+ SS formation. SS also manifests itself near its threshold at 1eV. The cross section increases at an even rate of roughly 0.3Å^2 with each vibrational level v=1-4 for the HeD^+ channel. All these vibrational levels are open to SS. But for HeH^+, only v=2-4 is accessible via SS. The v=0-1 increase is only 0.15Å^2 while those for v=1-4 are each on the order of 0.4Å^2 or greater. The larger cross section jumps correlate with the onset of SS channels.

The HeH^+:HeD^+ branching ratio is 1.79:1 for the reaction of $HD^+(v=4)$ with He at 1eV relative translational energy. The cross section for $HD^+(v=2)$ + He -> HeH^+ + D shown in Figure 4 drops considerably faster than for $HD^+(v=2)$ + He -> HeD^+ + H in Figure 3. Possible charge induced orientation effects where the H atom points more towards the He atom during collision may account for a sharper rise of cross section at lower collision energies. At low energies a charge induced dipole interaction between HD^+ and He will govern the reaction dynamics of vibrationally excited HD^+. For HD^+ the charge is centered between the two atoms and is shifted from the CM, which lies closer to the D atom. The charge induced dipole interaction, being much larger than the HD^+ rotational energy, may rotate the HD^+ about its CM preferentially pointing the positive charge and therefore the H atom towards the He atom. The He atom then abstracts the H^+ leaving the neutral D atom behind. Therefore the HeH^+ cross section would be enhanced over HeD^+. At higher energies when the charge induced dipole interaction becomes less important, the induced orientation effect disappears and the expected sharp cross sectional drop off can be seen as in Figure 4.

The potential energy surface for the HeH_2^+ system has its barrier, which is approximately the reaction endothermicity, late in its exit channel. Based on this feature, one may expect that vibrational rather than translational energy is more efficient towards making the proton transfer reaction proceed.[35] At low kinetic energies above the reaction threshold, this enhancement is indeed seen. Trajectory calculations using the DIM surface generated by Whitton and Kuntz have clearly demonstrated the reaction to be strongly vibrationally enhanced.[17] Potential energy contours of extended $H_2^+(v)$ molecules with respect to an incoming He atom show an attractive well which lies further from the center of H_2^+ (or is localized on one H atom) as v is increased. This effect becomes important from v=3-5 and illustrates how HeH^+ is forming as the H_2^+ bond is partially broken.

Their trajectory studies show good agreement with the present experiment. The v=0 total cross sectional dependence rises slowly, peaks at 3eV total energy (almost 0.5Å^2), and then decays slowly in similar fashion to these results. The maxima for v=2 and v=3 are found at 1.3 and 1.4eV respectively compared to 1.6 and 1.7eV in this experiment. Also in agreement is v=3,4 where the cross sections decline rapidly until 4eV where all the cross sections (v=0-4) decrease slowly and little vibrational dependence is seen in the cross section as function of total energy thereafter. In comparison with the results of our experiments, three major differences are noted: a) the v=0-1 enhancement is absent with v=1 nearly identical to v=0, b) v=2 does not rise and fall as steeply as it should, c) the magnitude of the total cross section is roughly a factor of 2 too

large. They attribute the drop in reactive cross section at high translational energy (2-5eV) to two reasons: a) as translational energy is increased, the maximum impact parameter decreases for which capture of He by H_2^+ is possible and b) compared to the ion vibrational period, as translational energy is increased, collision time becomes too short to allow the rearrangement to proceed.

In the same work Whitton and Kuntz have also calculated approximate 3D reactive cross sections for HD^+ + He. Both channels show strong vibrational enhancement. The v=3 HeD^+ curve falls too slowly and the cross sections are again too large, but the agreement is qualitatively assuring. The discrepencies between their calculations and this work may be due to their use of collinear points to generate 3D surfaces.

Classical trajectory calculations on some of the potential energy surfaces have reproduced many of the important features of this reaction. A 3D quantum scattering calculation on a more accurate ab initio potential energy surface would be very useful for a better theoretical understanding of many of the fine details of the reaction dynamics.

The failure to observe resonances in the energy dependence of the total reaction cross section is not entirely surprising. Redmon and Wyatt have shown that for the 3D quantum calculations of F + H_2 reactions, since the reactants with different orbital angular momenta form quasibound states at different translational energies, the sharp resonances observed in the collinear quantum mechanical calculation of the energy dependence of reaction probability is likely to be smoothed out in a 3D reactive scattering calculation, especially when a substantial number of partial

waves are involved in the scattering.[36] The experimental observation of reactive resonances for this system might only be possible with the measurement of vibrational state resolved product angular distributions at appropriate collision energies.[37]

CONCLUSION

In summary, total cross sections for the proton transfer reactions of H_2^+, HD^+ + He have been measured as a function of ion vibrational and collisional energy. The data are in qualitative agreement with previous work in the energy range where comparison can be made. Where energetically possible the v=1-4 reaction proceeds via a SS mechanism. The v=0 reaction most likely proceeds via a more intimate 3 body collision. Evidence shows that at high collision energies where SS is not allowed, the reaction competes with CID. New data is presented on the state selected $HD^+(v)$ reactions; the vibrational enhancement of the cross section for the HeD^+ channel falls off before that of HeH^+, in accordance with SS energetics. The larger cross sections for HeH^+ formation at low translational and higher vibrational energies seems to indicate the importance of the induced orientation of HD^+ due to the charge induced dipole interaction during the approach between HD^+ and He.

ACKNOWLEDGMENTS

We wish to acknowledge the assistance of Prof. S. L. Anderson with this experiment and we wish to thank Mike Valentine for producing the HD. This work was supported by the Director, Office of Energy Research, Office of Basic Energy Sciences, Chemical Sciences Division of the U.S. Department of Energy under Contract DE-AC03-76SF00098.

REFERENCES

1. W. A. Chupka and M. E. Russell, J. Chem. Phys. 49, 5426 (1968)
2. W. A. Chupka, J. Berkowitz, and M. E. Russell, Sixth International Conference on the Physics of Electronic and Atomic Collisions, Abstracts of Papers, M. I. T. Press, Cambridge, 1969, pg. 71
3. J. A. Rutherford and D. A. Vroom, J. Chem. Phys. 58, 4076 (1973)
4. F. Schneider, U. Havemann, L. Zulicke, V. Pacak, K. Birkinshaw, and Z. Herman, Chem. Phys. Lett. 37, 323 (1976)
5. V. Pacak, U. Havemann, Z. Herman, F. Schneider, and L. Zulicke, Chem. Phys. Lett. 49, 273 (1977)
6. H. von Koch and L. Friedman, J. Chem. Phys. 38, 1115 (1963)
7. C. F. Giese and W. B. Maier II, J. Chem Phys. 39, 739 (1963)
8. R. H. Naynaber and G. D. Magnuson, J. Chem. Phys. 59, 825 (1973)
9. J. J. Leventhal, J. Chem. Phys. 54, 3279 (1971)
10. B. H. Mahan, J. Chem. Phys. 55, 1436 (1971)
11. F. Schneider and L. Zulicke, Chem. Phys. Lett. 67, 491 (1979)
12. P. J. Brown and E. F. Hayes, J. Chem. Phys. 55, 922 (1971)
13. P. J. Kuntz, Chem. Phys. Lett. 16, 581 (1972)
14. D. J. Kouri and M. Baer, Chem Phys. Lett. 24, 37 (1974)
15. J. T. Adams, Chem. Phys. Lett. 33, 275 (1975)
16. P. J. Kuntz and W. N. Whitton, Chem. Phys. Lett. 34, 340 (1975)
17. W. N. Whitton and P. J. Kuntz, J. Chem. Phys. 64, 3624 (1976)
18. C. Stroud, N. Sathyamurthy, R. Rangarajan, and L. M. Raff, Chem Phys. Lett. 48, 350 (1977)

19. N. Sathymurthy, J. W. Duff, C. Stroud, and L. M. Raff, J. Chem. Phys. 67, 3563 (1977)

20. N. Sathyamurthy, Chem. Phys. Lett. 59, 95 (1978)

21. D. R. McLaughlin and D. L. Thompson, J. Chem. Phys. 70, 2748 (1979)

22. N. Sathymurthy, Chem. Phys. 62, 1 (1981)

23. F. Schneider, U. Havemann, L. Zulicke, and Z. Herman, Chem. Phys. Lett. 48, 439 (1977)

24. J. C. Light and J. Lin, J. Chem. Phys. 43, 3209 (1965)

25. D. G. Truhlar, J. Chem. Phys. 56, 1481 (1972)

26. A. F. Wagner and D. G. Truhlar, J. Chem. Phys. 57, 4063 (1972)

27. S. L. Anderson, F. A. Houle, D. Gerlich, and Y. T. Lee, J. Chem. Phys. 75, 2153 (1981)

28. I. Wender, R. A. Friedel, and M. Orchin, J. Am. Chem. Soc. 71, 1140 (1949)

29. K. P. Huber and G. Herzberg, Molecular Spectra and Molecular Structure IV. Constants of Diatomic Molecules, Van Nostrand Reinhold Co., N. Y., 1979, pg. 272

30. P. M. Dehmer and W. A. Chupka, J. Chem. Phys. 79, 1569 (1983)

31. J. Berkowitz and R. Spohr, J. Electron. Spectrosc. Relat. Phenom. 2, 143 (1973)

32. K. T. Gillen, B. H. Mahan, and J. S. Winn, J. Chem. Phys. 59, 6380 (1973)

33. U. Havemann, V. Pacak, Z. Herman, F. Schneider, Ch. Zuhrt, and L. Zulicke, Chem. Phys. 28, 147 (1978)

34. J. C. Light, J. Chem. Phys. 41, 586 (1964)

35. J. C. Polanyi and W. H. Wong, J. Chem. Phys. 51, 1439 (1969)

36. M. J. Redmon and R. E. Wyatt, Chem. Phys. Lett. 63, 209 (1979)

37. D. M. Neumark, A. M. Wodtke, G. N. Robinson, C. C. Hayden, and Y. T. Lee, submitted to Phys. Rev. Lett. (1984)

TABLE I. Estimated vibrational state distributions for H_2^+ and HD^+.

	H_2^+ v nominal					HD^+ v nominal				
	0	1	2	3	4	0	1	2	3	4
v = 0	1.000	0.107	0.078	0.085	0.070	1.000	0.139	0.108	0.083	0.077
1		0.893	0.161	0.174	0.145		0.861	0.220	0.168	0.156
2			0.761	0.188	0.157			0.672	0.206	0.191
3				0.553	0.152				0.543	0.184
4					0.476					0.392

TABLE II. Raw and vibrationally corrected data for $H_2^+(v)$ + He -- HeH^+ + H. Cross sections given are *10-1Å2.

	Raw				Deconvoluted			
Ecm/eV	1	2	4	8	1	2	4	8
v = 0	0.569	1.29	1.45	1.24	0.569	1.29	1.45	1.24
1	3.62	4.10	1.84	1.36	3.99	4.44	1.89	1.38
2	7.30	6.04	2.46	1.24	8.70	6.86	2.69	1.21
3	9.70	7.17	2.26	1.24	13.2	9.03	2.35	1.21
4	12.0	7.77	2.20	0.957	16.7	9.64	2.20	0.624

TABLE III. Raw and vibrationally corrected data for the HD^+ + He -> HeH^+,HeD^+ + D,H reactions. Cross sections given are *$10^{-1}Å^2$.

		HeH^+				HeD^+			
	Ecm/eV	1	2	4	8	1	2	4	8
	v = 0	0.989	0.340	0.627	0.464	1.01	1.16	1.27	0.698
	1	2.26	1.19	1.03	0.531	3.10	2.44	1.75	0.574
Raw	2	4.93	2.05	0.893	0.639	4.97	3.56	1.85	0.437
	3	8.55	3.57	1.10	0.819	6.81	4.45	1.94	0.335
	4	12.8	5.41	1.23	0.537	8.38	5.18	1.87	0.368

	Ecm/eV	1	2	4	8	1	2	4	8
	v = 0	0.989	0.340	0.627	0.464	1.01	1.16	1.27	0.698
	1	2.47	1.33	1.09	0.542	3.44	2.65	1.83	0.554
Deconvoluted	2	6.36	2.56	0.870	0.699	6.11	4.24	1.94	0.357
	3	12.4	5.13	1.26	1.00	9.01	5.60	2.08	0.203
	4	22.5	9.55	1.56	0.250	12.6	7.25	1.86	0.313

TABLE IV. Energies for which the proton transfer reaction is allowed via spectator stripping.

$v(H_2^+)$	HeH^+	$v(HD^+)$	HeH^+	HeD^+
0	1.33-4.42eV	0	1.76-5.72eV	1.05-3.43eV
1	0.88-3.97	1	1.24-5.21	0.75-3.12
2	0.45-3.53	2	0.75-4.71	0.45-2.83
3	0.05-3.13	3	0.24-4.20	0.14-2.52
4	0.00-2.77	4	0.00-3.69	0.00-2.21

FIGURE CAPTIONS

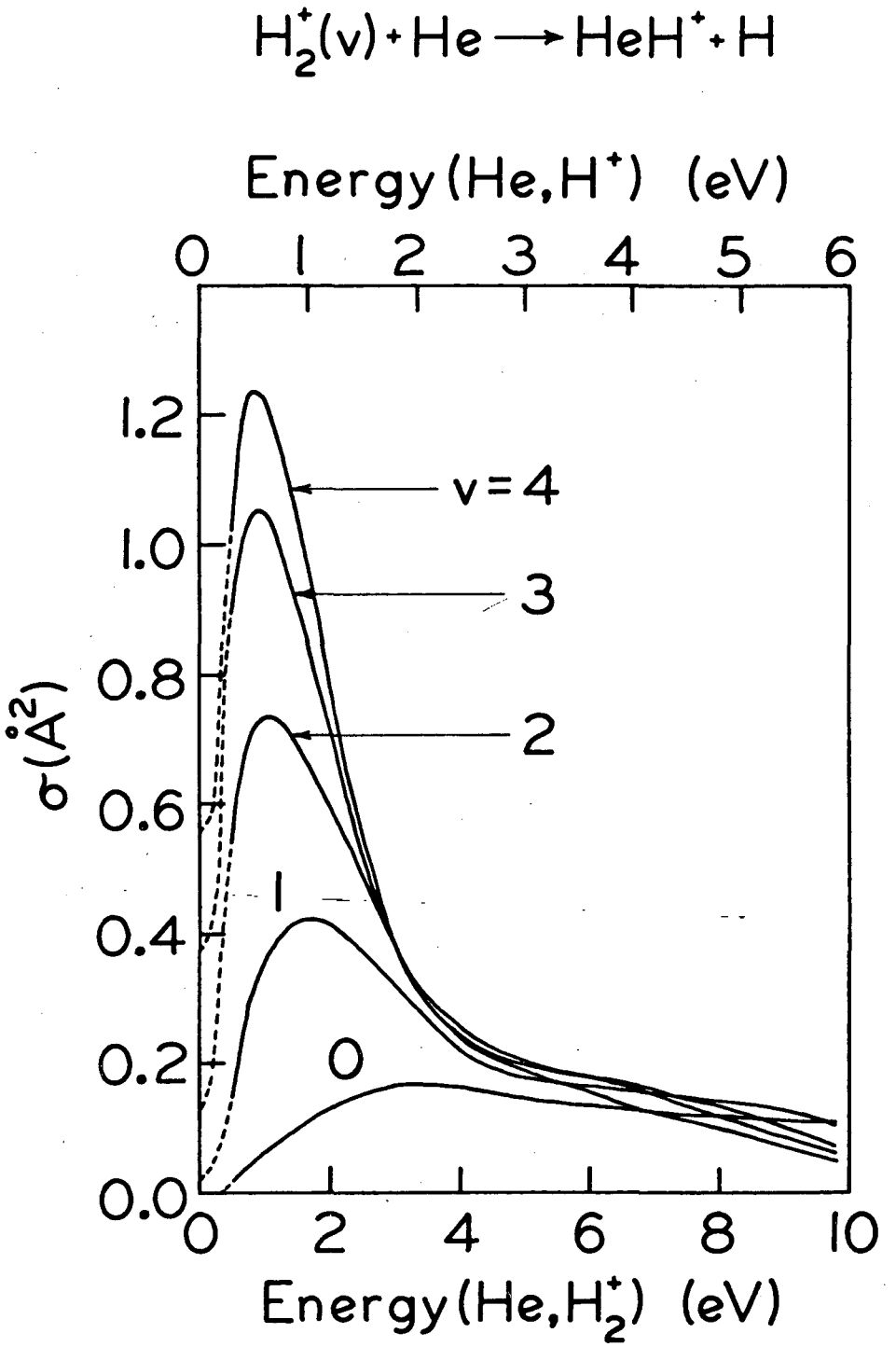
FIG. 1. $H_2^+(v) + He \rightarrow HeH^+ + H$. Total cross section versus CM kinetic energy obtained at the wavelengths chosen to produce v=0-4, raw cross sections shown.

FIG. 2. $H_2^+(v) + He \rightarrow HeH^+ + H$. Vibrational and translational energy dependence for HeH^+ formation. Cross sections shown are deconvoluted from the raw data using the vibrational distributions of H_2^+ shown in Table I.

FIG. 3. $HD^+(v) + He \rightarrow HeD^+ + H$. Total cross section versus CM kinetic energy obtained at the wavelengths chosen to produce v=0-4, raw cross sections shown.

FIG. 4. $HD^+(v=2) + He \rightarrow HeH^+ + D$. Total cross section versus CM kinetic energy obtained at the wavelength chosen to produce v=2, raw cross sections shown.

FIG. 5. Vibrational and translational energy dependence for the competition reactions of $HD^+ + He$ to form both HeH^+ and HeD^+. Cross sections shown are deconvoluted from the raw data using the vibrational state distributions of HD^+ shown in Table I.



XBL 834-9164

Fig. 1

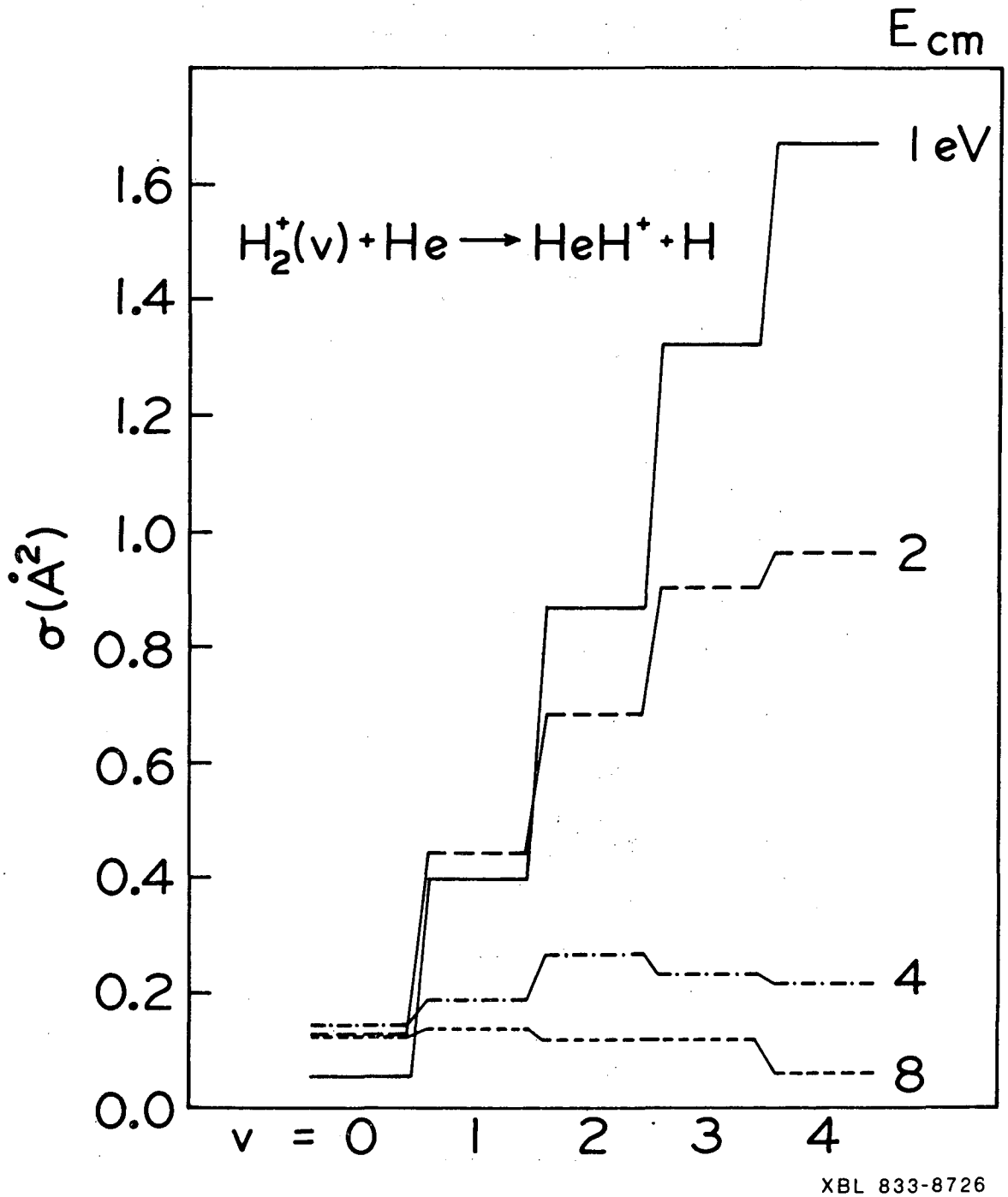
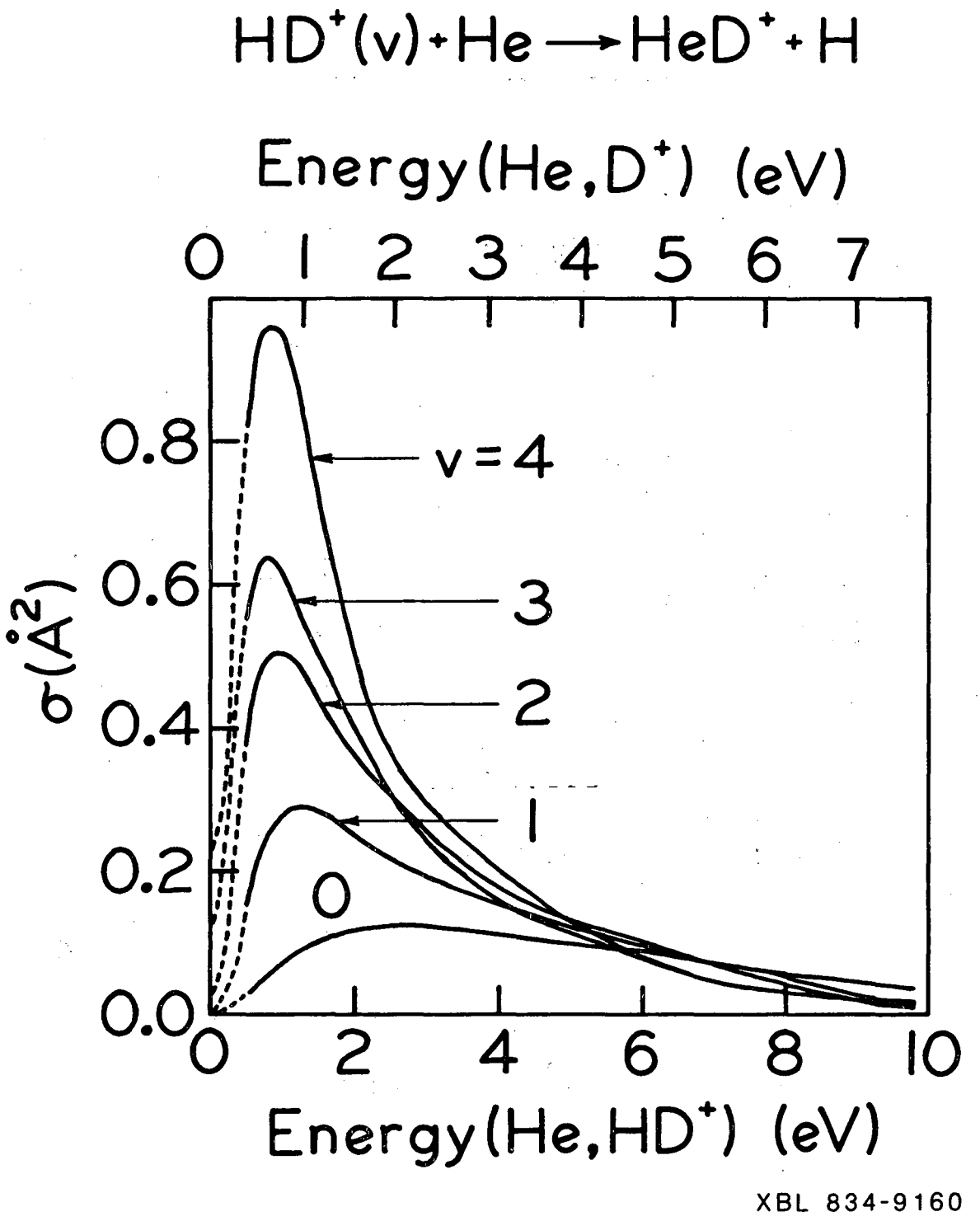
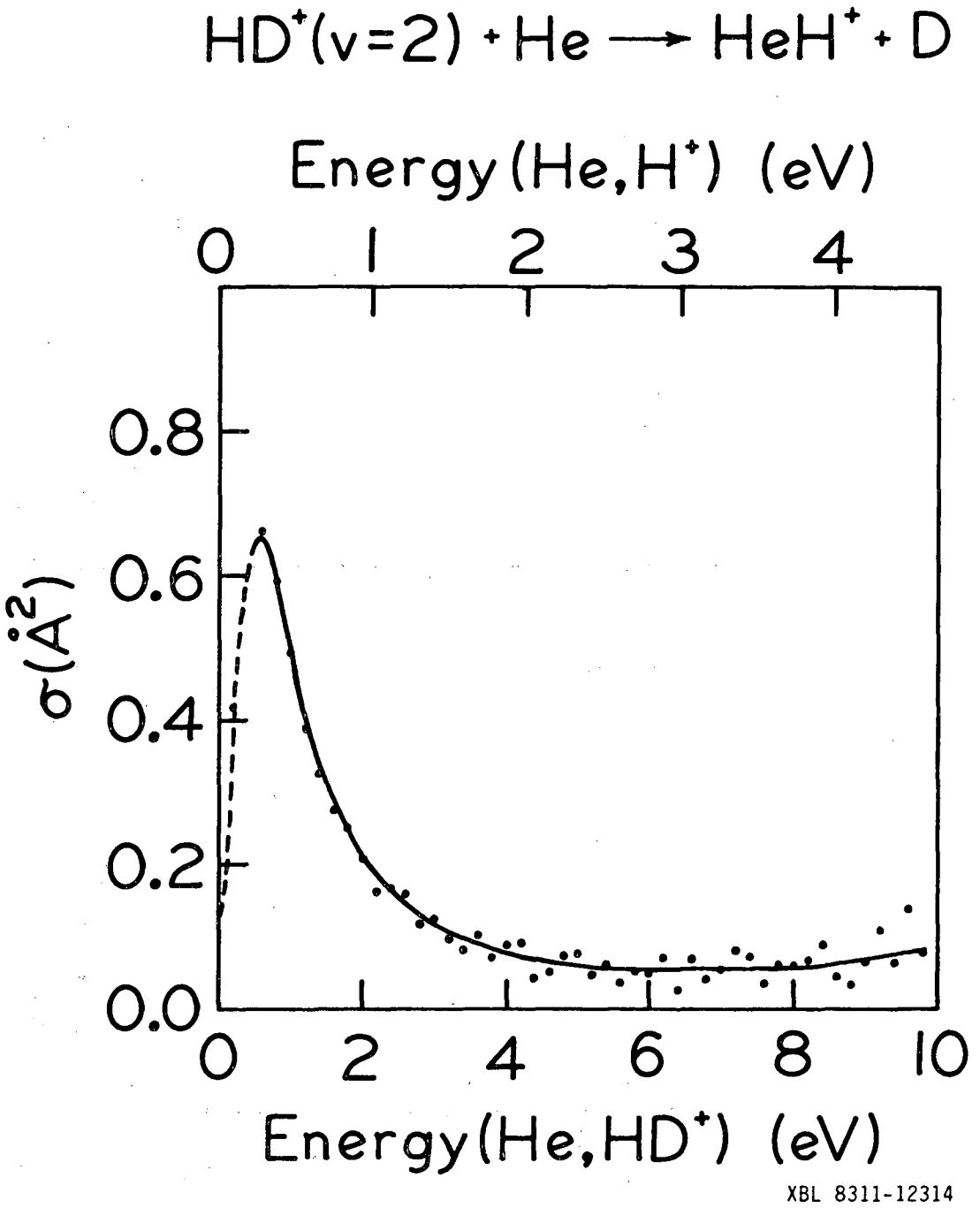

E cm
1 eV
2
4
8
$H_2^+(v) + He \rightarrow HeH^+ + H$
1.6
1.4
1.2
1.0
0.8
0.6
0.4
0.2
0.0
σ(Å²)
v = 0
1
2
3
4
XBL 833-8726

Fig. 2



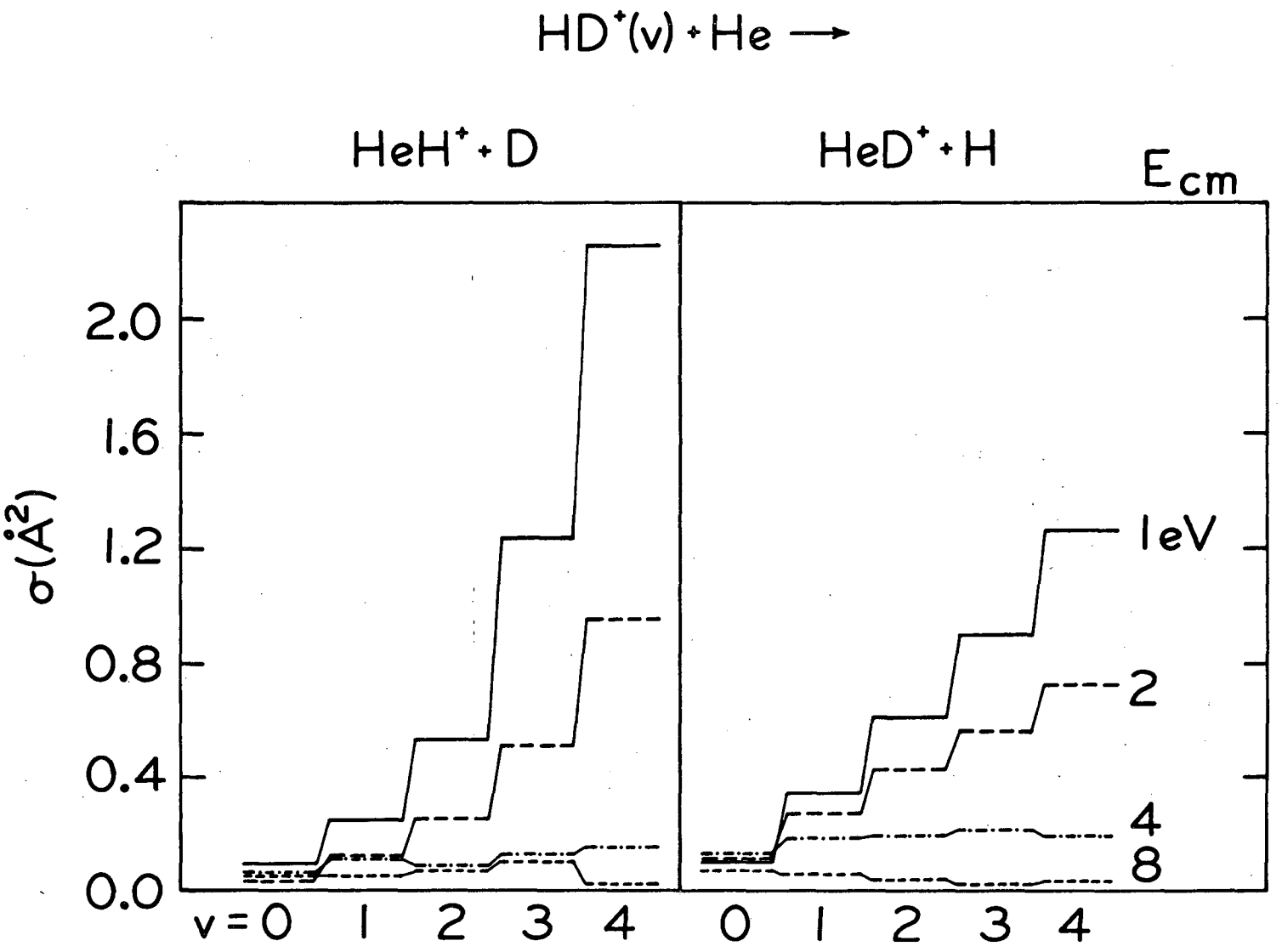
XBL 834-9160

Fig. 3



XBL 8311-12314

Fig. 4



XBL 842-736

Fig. 5

This report was done with support from the Department of Energy. Any conclusions or opinions expressed in this report represent solely those of the author(s) and not necessarily those of The Regents of the University of California, the Lawrence Berkeley Laboratory or the Department of Energy.

Reference to a company or product name does not imply approval or recommendation of the product by the University of California or the U.S. Department of Energy to the exclusion of others that may be suitable.

TECHNICAL INFORMATION DEPARTMENT
LAWRENCE BERKELEY LABORATORY
UNIVERSITY OF CALIFORNIA
BERKELEY, CALIFORNIA 94720