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April 1984

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THE EFFECT OF COLLISION ENERGY AND VIBRATIONAL EXCITATION ON THE REACTION OF $\text{C}_2\text{H}_2^+ + \text{H}_2$

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THE EFFECT OF COLLISION ENERGY AND VIBRATIONAL EXCITATION
ON THE REACTION OF C₂H₂⁺ + H₂

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Abstract

The relative efficiencies between the excitation of C-C stretching vibration and collision energy on the promotion of the H atom transfer reaction of C₂H₂⁺ + H₂ → C₂H⁺ + H have been examined. At low collision energies the reaction is strongly vibrationally enhanced in agreement with previous thermal energy studies. Translational energy was found to be not as effective as exciting the C-C stretching vibration in promoting the reaction. The results indicate that the H atom transfer from H₂ to the C atom should have a late barrier, but the C-C stretching vibration of C₂H₂⁺ is apparently coupled to the reaction coordinate. Because the C-C bond in C₂H⁺ is expected to be longer than that of C₂H₂⁺, vibrational energy added to the C-C bond might reduce the barrier for H atom transfer from H₂ to a C atom in C₂H₂⁺.
Introduction

The effect of vibrational and translational energy on the reaction cross section for endothermic atom-diatom systems is fairly well understood with respect to the location of the barrier along the reaction coordinate on a potential energy surface (PES).\(^1\) Generally, translational energy is more effective than vibrational energy in driving the reaction if the barrier to the reaction is encountered early on the PES. If the barrier is found late in the exit channel, then vibrational energy is more effective than the same amount of energy present as translation in driving the reaction. The $\text{H}_2^+ + \text{He} \rightarrow \text{HeH}^+ + \text{H}$ reaction is characterized by this latter case.\(^2\)

For an endothermic reaction between two molecules, the effect of translational and vibrational excitation on the reaction cross section is somewhat more complicated. There are many ways of adding vibrational energy in polyatomic molecules and in contrast to atom-diatom systems, added vibrational energy is not necessarily coupled directly to the reaction coordinate. The trends seen for these larger systems may be expected to be qualitatively the same as those seen for the atom-diatom systems if the reaction is a simple atom transfer reaction and the vibrational energy is added to the bond being broken. But the effect vibrational energy has in promoting an endothermic reaction might not be appreciable if the excited vibrational degree of freedom is not coupled directly to the reaction coordinate.

Relatively few endothermic reactions involving polyatomic systems containing 4 or more atoms have been studied as a function collision and vibrational energy. Krajnovich, et. al. have carried out such a study on
the $\text{Br} + \text{CF}_3\text{I} \rightarrow \text{CF}_3 + \text{IBr}$ reaction by the crossed molecular beams method; highly vibrationally excited $\text{CF}_3\text{I}$ was prepared by the infrared multiphoton excitation process and a beam of hyperthermal Br atoms was produced by seeded supersonic expansion. Two trends could be related to generalizations obtained from the results of classical scattering calculations on endothermic atom transfer reactions. The amount of forward scattered IBr (with respect to the initial Br direction) increases with vibrationally hot $\text{CF}_3\text{I}$ as compared to vibrationally cold $\text{CF}_3\text{I}$ in accord with previous trajectory calculations. When the collision energy is comparable to the endoergic barrier height, vibration is substantially more effective than translation in promoting the reaction partially due to constraints imposed by the conservation of angular momentum of the system. However, when the collision energy is several times the barrier height, vibrational energy appears to be less effective than an equivalent amount of translational energy in driving the reaction suggesting that the PES has a gradual barrier with most of the barrier lying in the entrance channel. The comparison of vibrational to translational energy in this experiment was only qualitative as the extent of vibrational excitation of the $\text{CF}_3\text{I}$ could only be estimated for the multiphoton absorption process.

In a molecule-molecule reaction, a chemical bond which is not to be broken but is coupled to the reaction coordinate may be excited. Duncanson and Guillory reacted $\text{CH}(v=0,1)$ with $\text{N}_2$ presumably to form the products HCN and N. The HCN + N product channel is the least endothermic reaction channel for $v=0$ and becomes exothermic for $v=1$. The rate of disappearance of CH increased by a factor of 40 from $v=0$ to $v=1$ as determined from the
decay rate of CH monitored by LIF. Although the substantial increase of the disappearance rate of CH(v=1) over CH(v=0) could be due to the enhanced reactivity, neither the HCN product formation nor the increase of CH(v=0) due to vibrational relaxation of CH(v=1) was monitored directly; the relative contributions of reaction and vibrational relaxation to the decay rate of CH are not known.

Experiments have shown the \( \text{H}_2 + \text{D}_2 \rightarrow 2\text{HD} \) metathesis reaction to proceed with vibrational energy added to either \( \text{H}_2 \) or \( \text{D}_2 \).\textsuperscript{7,8} Ab initio studies, however, predict an activation barrier well above the \( \text{H}_2 \) bond energy for this reaction.\textsuperscript{9} The reaction of \( \text{NO} + \text{O}_3 \rightarrow \text{NO}_2 + \text{O}_2 \) has been shown to overcome its activation barrier with vibrational excitation in either of the reactants.\textsuperscript{10,11}

The excitation of the C-C stretching vibration in \( \text{C}_2\text{H}^+ \) in promoting the H atom transfer reaction of \( \text{C}_2\text{H}^+ + \text{H}_2 \rightarrow \text{C}_2\text{H}_3^+ + \text{H} \) has proven itself interesting. The reaction is endothermic for ground state reactants and becomes exothermic for \( \text{C}_2\text{H}^+ \) in its first excited vibrational state. Photoionization appearance potentials of reactants and products set the ground state reaction endothermicity close to 1 kcal/mole.\textsuperscript{12-17} Buttrill, et al. studied this reaction by both photoionization and ion cyclotron resonance (ICR) techniques.\textsuperscript{18} A photoionization mass spectrometer arrangement was used to examine the reaction cross sectional dependence on ion vibrational energy, however, only at thermal collision energies. The reaction was found to be strongly vibrationally enhanced for \( \nu=0-2 \) at this collision energy. The ICR experiment was used to measure an absolute rate for this reaction averaged
over all the vibrational states produced in the electron impact ionization of \( \text{C}_2\text{H}_2 \). A value of \( 6.3 \pm 1.8 \times 10^{-11} \text{ cm}^3 \text{ molecule}^{-1} \text{ sec}^{-1} \) was obtained. No evidence was found to support a long lived complex mechanism for this reaction. In a more recent study, Adams and Smith estimate a thermal reaction rate of \( 7.0 \times 10^{-11} \text{ cm}^3 \text{ molecule}^{-1} \text{ sec}^{-1} \) using their SIFT apparatus,\(^1\) in close agreement with Buttrill's experiment.

In this paper results obtained using our unique apparatus consisting of a photoionization ion source and octapole RF ion guide to study the \( \text{C}_2\text{H}_2^+(v) + \text{H}_2 \) system are described. The reaction cross section for this system was measured as a function of both ion vibrational and translational energy for the purpose of making a comparison between vibrational energy and translational energy in driving an endoergic reaction, especially for a larger polyatomic system where vibrational energy is added to a part of the molecular system which might be only weakly coupled to the reaction coordinate. When the H atom transfers from \( \text{H}_2 \) to \( \text{C}_2\text{H}_2^+ \), the H-H bond is ruptured and a new C-H bond is formed. Although the acetylene ion C-C bond appears to remain intact, the formation of the new C-H bond could reduce the bond order and lengthen the C-C bond and its stretching vibration could be a part of the reaction coordinate. The 50–750 meV center of mass (CM) kinetic energy range used here extends the knowledge derived from previous thermal studies.
Experiment

The experimental arrangement used in this study is similar to those of the \((H_2 + D_2)^+\) experiment which has been described in detail elsewhere. Briefly a beam of \(C_2H_2\), produced by expanding 250 torr of \(C_2H_2\) through a 70 micron nozzle at room temperature, is photoionized with a selected wavelength inside an RF octopole ion guide. \(C_2H_2\) was passed through a dry ice trap before entering the beam source to remove acetone in commercial grade acetylene. The \(C_2H_2^+\) photoions of known vibrational state distributions are formed into a beam, guided along the octopole axis, and are accelerated to a given kinetic energy before passing through a scattering cell surrounding a section of the octopole ion guide. Product ions are extracted from the octopole, mass analyzed, and counted using a liquid \(N_2\) cooled Li drifted Si detector. VUV light was produced by a standard capillary discharge hydrogen lamp. Particular ionizing wavelengths are selected using a McPherson model 225 monochromator set at 4 Å FWHM resolution. Near the ionization threshold of \(C_2H_2\) (1088 Å, 11.40 eV), the ion yield exhibits step structure when the \(v_2\) C-C vibrational mode of the ion, the \(<\mathrm{H}<\mathrm{C}-\mathrm{C}>\mathrm{H}>\) symmetric stretch, is being excited, with an average vibrational quanta of 227 meV. The relative step sizes for \(v=0\): 1: 2 are 1.00: 0.33: 0.11 which are exactly the calculated relative Franck-Condon factors for the transitions of \(C_2H_2(v=0)\) to those final ionic vibrational states. Assuming the relative step heights represent the relative vibrational populations at a given wavelength, Table I is derived giving the vibrational distribution for \(C_2H_2^+\). The following wavelengths were used: \(v=0\), 1076 Å; \(v=0\) and 1, 1056 Å; and \(v=0\), 1, and 2,
1034 Å. All ionizing wavelengths leave the $\text{C}_2\text{H}_2^+$ molecule predominantly in the $v=0$ state.

In a typical experiment, with a $\text{C}_2\text{H}_2^+(v=0-2)$ beam intensity of 0.5 KHz, the resulting product count rate was roughly 0.5 Hz. Wavelength scans at a particular energy commonly lasted over 2 days. The wavelength scans were repeated several times at each particular energy and the data herein is the time weighted average of these scans. The energy scan to which the wavelength scans are normalized (as described in the next section) represents over 1500 repeated energy scans; this data was accumulated for 6 days.
Results and Analysis

Figure 1 shows the raw relative reaction cross sections as a function of vibrational and kinetic energy. Because the scattering cell pressure was not accurately calibrated and measured, the total absolute cross section was not measured. However, the total absolute reaction cross section in its raw form is estimated from ion gauge pressure measurements near the scattering cell to be approximately 1 \( \text{Å}^2 \) at its maximum value. The cross section for \( v=0 \) is normalized to the thermal rate constant as measured by Adams and Smith. Their reported rate constant is \( 1.0 \times 10^{-11} \text{ cm}^3 \text{ molecule}^{-1} \text{ sec}^{-1} \) which corresponds to an average cross section of 0.54 Å to which the 50 meV, \( v=0 \) cross section of this experiment is normalized. Figure 2 shows the data of Figure 1 after the raw cross sections have been vibrationally deconvoluted. All collision energies are for the CM frame unless otherwise specified. At 50 meV collision energy the reaction is strongly vibrationally enhanced. The relative cross section increases from 1.00 to 5.72 at 50 meV, \( v=0-2 \). As the collision energy is increased, the vibrational enhancement becomes less pronounced. The \( v=0-1 \) step decreases monotonically from 50-750 meV; however the \( v=1-2 \) step decreases with energy until 250 meV when the \( v=1-2 \) step gradually increases.

Figure 3 is a plot of the raw relative reaction cross section as a function of collision energy for \( \text{C}_2\text{H}_2^+(v=0) \). The cross section shows a monotonic increase from 100-750 meV. Figure 4 is a plot of the raw relative reaction cross section as a function of collision energy for \( \text{C}_2\text{H}_2^+ \) produced at 1034 Å which consists of \( v=0-2 \) vibrational states. For the energy range covered in this experiment, the measured cross section
is highest at 50 meV and rapidly decreases thereafter. This rapid decline is real and reflects the strong vibrational enhancement of the cross section from v=0-2 at low collision energies. The cross section levels off from 100-400 meV at which time it slowly starts to climb. At 750 meV, the cross section is roughly 30 percent greater than its minimum value. The cross section basically shows slight translational dependence beyond 100 meV. The wavelength scans at different collision energies are all normalized to this energy scan. Table II gives the values of the cross section as a function of kinetic and vibrational energy for both the raw and vibrationally deconvoluted data normalized to the data found in Figure 4. Table III gives the values of the cross section as a function of vibrational energy only; the v=0 cross sections are normalized to 1.00 at each collision energy. This table also gives the vibrational step cross section ratio for v=2-1.

Upon vibrationally deconvoluting the data, cross sectional trends seen in the raw data can become enormously magnified because of the enormous contribution of v=0 at each selected wavelength. Small errors in the raw data can result in large errors upon deconvolution and can greatly influence interpretation and analysis of the deconvoluted data. For this reason both the raw and vibrationally deconvoluted data are reported.
Discussion

Although the uncertainty of the estimated heat of reaction of 
\[ \text{C}_2\text{H}_2^+ + \text{H}_2 \rightarrow \text{C}_2\text{H}_3^+ + \text{H} \] is larger than the estimated endothermicity, the experimental results of this reaction appears to be in agreement with what is expected for a slightly endothermic reaction. Combining the well defined ionization potential for \( \text{C}_2\text{H}_2 \) of 11.402 eV\(^{12} \) with the well known heat of formation of 
\[ \Delta H_{\text{f}298}^0(\text{C}_2\text{H}_2) = 2.350 \text{ eV}\] one calculates 
\[ \Delta H_{\text{f}298}^0(\text{C}_2\text{H}_2^+) = 13.752 \text{ eV}. \] The heat of formation of \( \text{C}_2\text{H}_3^+ \) is less well defined, however, as its appearance threshold from the dissociative photoionization of \( \text{C}_2\text{H}_4 \) is not well determined and is estimated by Chupka, et al. to be 13.25 ± 0.05 eV as an upper limit.\(^{23} \) Using \( \Delta H_{\text{f}298}^0(\text{C}_2\text{H}_4) = 0.544 \text{ eV}\) one may calculate 
\[ \Delta H_{\text{f}298}^0(\text{C}_2\text{H}_3) = 11.535 \text{ eV}. \] The above chemical reaction then simply has an upper limit to its endothermicity of 42 meV at 298°K. Taking Chupka's other possible appearance potential for \( \text{C}_2\text{H}_3^+ \) of 13.13 ± 0.02 eV,\(^{23} \) one arrives at a reaction exothermicity of -78 meV. This threshold is less well defined and is not consistent with our experimental observations.

The data presented here, at a relative collision energy of 50 meV shows an enhancement of the reaction cross section of over a factor of 5 for increasing C-C stretching vibration in \( \text{C}_2\text{H}_2^+ \) from \( v=0 \) to \( v=2 \). The substantial vibrational enhancement is in qualitative agreement with the previous study of Buttrill, et. al.\(^{18} \) However, as the collision energy is raised, the vibrational enhancement of the reaction cross section declines.
Energy partitioned into the translational degree of freedom between the reactants is seen to only slightly enhance the reaction compared to the vibrational enhancement; over the energy range covered, the cross section for $\text{C}_2\text{H}^+_2(v=0)$ increases only about a factor of two from its minimum to maximum values as seen in Figure 3.

Experimentally this $\text{C}_2\text{H}^+_2(v) + \text{H}_2$ reaction behaves in many ways similarly to the $\text{H}_2^+(v) + \text{He}$ reaction. In the $\text{H}_2^+(v) + \text{He}$ reaction, one is exciting the bond which is to be broken. Both $v=0$ reactions show little translational energy dependence. The $\text{H}_2^+(v=0)$ reaction probably proceeds through intimate, small impact parameter collisions. At low collision energies the $\text{H}_2^+ + \text{He}$ reaction is strongly vibrationally enhanced. Vibrational energy along the reaction coordinate strongly promoting the reaction over translational energy is indicative of a barrier found late in the exit channel of the PES. Collision energy being less effective than an equivalent amount of vibrational energy even up to several times the barrier height suggests that the barrier lies mostly in the exit channel of the PES. The failure of translational energy in promoting the reaction of $\text{C}_2\text{H}^+_2(v=0)$ efficiently clearly suggests that the potential energy barrier associated with the C-H bond formation and H-H bond rupture is late along the reaction coordinate, similar to the $\text{H}_2^+ + \text{He}$ reaction.

In an earlier study using the photoionization mass spectrometer technique, Buttrill, et al. found that the cross section is enhanced over an order of magnitude when the C-C stretching vibration is increased from $v=0-2$; the vibrationally corrected relative cross sections for $v=0$: $1:2$ are
Buttrill attributes the appreciable reactivity of the endothermic reaction of $\text{C}_2\text{H}_2^+(v=0)$ at thermal energies to the thermal excitation of the lower frequency bending modes. At room temperature it was estimated that 14 percent of the $\text{C}_2\text{H}_2$ molecules have one quanta of vibration in either of the doubly degenerate $\nu_4$ or $\nu_5$ bending modes (76 and 90 meV respectively). Assuming the energy of these modes remains the same for the ion as the neutral upon photoionization, this residual vibrational energy is above the calculated reaction endothermicity and would be able to drive the $v=0$ reaction. But whether only those $\text{C}_2\text{H}_2^+$ molecules with one quanta of bending excitation are responsible for the thermal energy reaction of $\text{C}_2\text{H}_2^+(v=0)$ is not clear. At 300°K, the average translational energy between collision pairs is 39 meV. A large fraction of molecules have enough relative collision energy to drive the reaction even without the thermal excitation of the bending vibrations or rotational degrees of freedom.

In our experiment $\text{C}_2\text{H}_2^+$ was produced by photoionization of a supersonic beam of $\text{C}_2\text{H}_2$ and the $\nu_4$ and $\nu_5$ vibrational modes of $\text{C}_2\text{H}_2^+$ (612 and 729 cm$^{-1}$ respectively) are expected to substantially relax during the isentropic expansion. McClelland, et. al. and Mariella, et. al. studied the effect of vibrational relaxation of diatomic molecules in seeded supersonic beams. They studied the relaxation processes for $\text{I}_2$ and LiF respectively. The $\text{I}_2$ vibrational energy spacing is 214 cm$^{-1}$ and that of LiF is 910 cm$^{-1}$. In both cases the molecules were substantially relaxed upon supersonic expansion with up to a 40 percent decrease in vibrational temperature. Consequently most of the
product seen from the v=0, C$_2$H$_2^+$ ions in this experiment is expected to be the actual reaction of v=0 ions.

Buttrill and co-workers further investigated the reaction of C$_2$H$_2^+$, formed with the electron impact of 15 eV electrons, with D$_2$ at thermal collision energies. Since no C$_2$D$_2^+$ ions were detected at low D$_2$ pressures, the conclusion was reached that the a long-lived intermediate C$_2$H$_2$D$_2^+$ complex does not play any role as a reaction mechanism. A rate constant of $6.3 \pm 1.8 \times 10^{-11}$ cm$^3$ molecule$^{-1}$ sec$^{-1}$ which represents an average over the distribution of vibrationally excited C$_2$H$_2^+$ molecules reacting with H$_2$ was measured. Adams and Smith report agreement with this rate constant using their SIFT apparatus at room temperature.$^{19}$ The thermalized C$_2$H$_2^+$ molecules are reacted with H$_2$ and a rate constant of $1.0 \times 10^{-11}$ cm$^3$ molecule$^{-1}$ sec$^{-1}$ was measured. Using Buttrill's argument they say 14 percent of the C$_2$H$_2^+$ molecules at room temperature have one vibrational quanta in either the v$_4$ or v$_5$ mode which are responsible for the formation of C$_2$H$_3^+$. The estimated rate coefficient for these excited state reactions is more like $7 \times 10^{-11}$ cm$^3$ molecule$^{-1}$ sec$^{-1}$ in agreement with the value of Buttrill, et al. In fact at a temperature of 300$^\circ$K and using a value of 76 and 90 meV for the doubly degenerate v$_4$ and v$_5$ modes respectively, one calculates that 8 percent of the total number of C$_2$H$_2^+$ molecules have one quanta in either of these two modes instead of 14 percent. Adams and Smith perform their experiment in a flow tube which guarantees all reactants to have a Boltzmann vibrational population distribution due to the collisional quenching of the higher vibrational
levels by the carrier gas before reactions can take place. Thus the measured rate is for \( C_2H_2^+(v=0) \) with some excitation in the \( v_4 \) and \( v_5 \) bending modes, but without those \( C_2H_2^+ \) which have one and two quanta in the C-C stretching vibration. The rate constants measured in each experiment are not the same and the reported closeness of their values is entirely based on the assumption that ground state \( C_2H_2^+ \) does not react at thermal energy which is not at all convincing.

The PES for this reaction has not been previously calculated. Electronically excited and charge transfer states are not expected to play a role in this reaction because the first electronic state of \( C_2H_2^+ \) above the \( X^2\pi_u \) ground state is 4.96 eV higher in energy. The difference in the ionization potentials (IP) between \( C_2H_2 \) and \( H_2 \) puts the charge exchanged system of reactants, \( C_2H_2 + H^+ \), 4.02 eV higher than ground state reactants. Based on the IP of \( C_2H_4 \) of 10.51 eV and \( \Delta H^0_{f298}(C_2H_4) = 0.544 \) eV, the potential well corresponding to the \( C_2H_4^+ \) complex is 2.698 eV below reactants. Apparently this potential well cannot be accessed from the ground states of \( C_2H_2^+ \) and \( H_2 \) under our experimental conditions. A large potential barrier must exist between \( C_2H_4^+ \) and \( C_2H_2^+ + H_2 \).

The electronic configuration of the \( X^2\pi_u \) ground state of \( C_2H_2^+ \) is \((1\sigma_g)^2(1\sigma_u)^2(2\sigma_g)^2(2\sigma_u)^2(3\sigma_g)^2(1\pi_u)^3\) where one lone electron is found in one of the degenerate \( 1\pi_u \) molecular orbitals. The \( 1\pi_u \) orbital is formed from a combination of \( 2p_x \) and \( 2p_y \) atomic orbitals of the C atoms with the \( 2p_z \) orbital defined as lying along the internuclear axis. This electron is shared equally between the two C
atoms. As H₂ approaches the C₂H₄⁺ molecule, the electron cloud along the C-C bond distorts and H atom addition to one C atom should localize the lone electron to that C atom and localize the positive charge on the other C atom unless the bridged structure with one H atom bridging the two C atoms is more stable. As one of the H atoms in the H₂ molecule continues to approach the extended C-C bond, the electron becomes more and more localized. The C-C bond of C₂H₃⁺ should resemble the double bond of C₂H₄. Since the bond order of C₂H₂⁺ is 2-1/2 as compared to 2 for C₂H₃⁺, one would expect the bond length of C₂H₃⁺ to be slightly longer than that of C₂H₂⁺. H atom addition to C₂H₂⁺ in its ground vibrational state v=0 will accompany a corresponding increase in the C-C bond distance and the C-C stretching vibration is indeed coupled directly to the reaction coordinate. With C₂H₂⁺ in an excited vibrational state, C-H bond formation would be facilitated by the extension of the C-C bond. Consequently vibrational energy would serve to effectively lower the barrier to reaction and one would see a vibrational enhancement to the reaction.

Apparently vibrational energy in the C-C bond is quite effective in driving the C₂H₂⁺ + H₂ reaction over its barrier, especially at low collision energies. Simplistically the C-C bond does not appear to play an important role in this reaction; the H₂ bond must be severed and a C-H bond must be formed. However, the reaction coordinate is apparently not so simple as for the H₂⁺ + He case. For the present reaction, as the H₂ bond is breaking and the new C-H bond is forming, the C-C bond must stretch to accommodate these changes. Thus the reaction coordinate involves the
concerted motion of the four H–H–C–C atoms. The stretching motion of the C–C bond seems to be as important as that of the H–H bond for the H atom transfer.
Acknowledgment

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References


Figure Captions

Figure 1. \( \text{C}_2\text{H}_2^+(v) + \text{H}_2 \rightarrow \text{C}_2\text{H}_3^+ + \text{H} \). Vibrational and translational energy dependence for \( \text{C}_2\text{H}_3^+ \) formation. Raw relative cross sections shown. The cross sections are normalized to 0.541 for \( v=0 \), 50 meV as described in the text.

Figure 2. \( \text{C}_2\text{H}_2^+(v) + \text{H}_2 \rightarrow \text{C}_2\text{H}_3^+ + \text{H} \). Vibrational and translational energy dependence for \( \text{C}_2\text{H}_3^+ \) formation. Relative cross sections shown are deconvoluted from the raw data of Figure 1 using the vibrational distribution of \( \text{C}_2\text{H}_2^+ \) given in Table I.

Figure 3. \( \text{C}_2\text{H}_2^+(v=0) + \text{H}_2 \rightarrow \text{C}_2\text{H}_3^+ + \text{H} \). Total cross section versus CM kinetic energy obtained at the wavelength chosen to produce \( v=0 \), raw cross sections shown.

Figure 4. \( \text{C}_2\text{H}_2^+(v=0-2) + \text{H}_2 \rightarrow \text{C}_2\text{H}_3^+ + \text{H} \). Total cross section versus CM kinetic energy obtained at the wavelength chosen to produce \( v=0-2 \), raw cross sections shown.
Table I. Estimated vibrational distribution for $\text{C}_2\text{H}_2^+$. 

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Table II. Raw and vibrationally corrected data for $\text{C}_2\text{H}_2^+(v) + \text{H}_2 \rightarrow \text{C}_2\text{H}_3^+ + \text{H}$. Cross sections are normalized relative to the v=0, 50 meV cross section as 0.541 as described in the text.

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<td>0.726</td>
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</tr>
</tbody>
</table>
Table III. Vibrationally corrected data for $\text{C}_2\text{H}_2^+(v) + \text{H}_2 \rightarrow \text{C}_2\text{H}_3^+ + \text{H}$ with all $v=0$ cross sections normalized to 1.00. Total cross sections and the cross section ratio for $v=2: v=1$ are given.

<table>
<thead>
<tr>
<th>$E_{\text{cm}}$ (meV)</th>
<th>$v=0$</th>
<th>1</th>
<th>2</th>
<th>$v=2:v=1$</th>
</tr>
</thead>
<tbody>
<tr>
<td>50</td>
<td>1.00</td>
<td>2.64</td>
<td>5.72</td>
<td>2.16</td>
</tr>
<tr>
<td>100</td>
<td>1.00</td>
<td>2.38</td>
<td>4.07</td>
<td>1.71</td>
</tr>
<tr>
<td>250</td>
<td>1.00</td>
<td>1.69</td>
<td>2.08</td>
<td>1.24</td>
</tr>
<tr>
<td>500</td>
<td>1.00</td>
<td>1.31</td>
<td>2.02</td>
<td>1.54</td>
</tr>
<tr>
<td>750</td>
<td>1.00</td>
<td>1.06</td>
<td>2.02</td>
<td>1.91</td>
</tr>
</tbody>
</table>
$C_2H_2^+(v) + H_2 \rightarrow C_2H_3^+ + H$

Figure 1
Figure 2

\[ C_2H^+ (v) + H_2 \rightarrow C_2H_3^+ + H \]
\[ \text{C}_2\text{H}_2^+ (v=0) + \text{H}_2 \rightarrow \text{C}_2\text{H}_3^+ + \text{H} \]

Figure 3
$C_2H_2^+(v=0-2) + H_2 \rightarrow C_2H_3^+ + H$

**Figure 4**
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