He + H$_2^+$ ion-molecule reaction: A comparison between experimental and quantum-mechanical results

M. Baer, S. Suzuki, K. Tanaka, I. Koyano, H. Nakamura, and Z. Herman

Institute for Molecular Science, Myodaiji, Okazaki 444, Japan

D. J. Kouri

Department of Chemistry and Department of Physics, University of Houston, Houston, Texas 77004

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In this work a comparison between new experimental and quantum-mechanical results is performed for the reactions He + H$_2^+$(v$_j$)→HeH$^+$(Σ v$_j$)+H; v$_j$=0→4 in the energy range 1 eV ≤ E$_{tot}$ ≤ 2 eV, where E$_{tot}$ is the total (vibrational plus relative translational) energy including the zero-point energy. It was found that the two features which characterize this system, namely, the strong enhancement of the reaction rate with initial vibrational energy (at fixed total energy) and the relatively weak dependence of the cross sections on translational energy, are moderately well reproduced by the quantum-mechanical infinite-order sudden approximation.

I. INTRODUCTION

The systems H$^+$ + H$_2$, He + H$_2^+$, and H + H$_2$, and their isotopic analogues (two- or three-electron systems) constitute the simplest available reactive systems. Moreover, the latter two reactions are expected to proceed adiabatically up to total energies of about 10 eV. The He + H$_2^+$ system is therefore one of the apt prototype cases for comparing theory and experiment. There are, however, other features which make this system interesting. One is its endothermicity, due to which the energy stored in the vibrational mode is much more efficient in promoting the reaction than the translational energy. Although in general not unforeseeable, this feature is intriguing. Another interesting feature is the typical energy dependence of the reactive cross sections of the system. The cross sections for the higher initial vibrational states v$_j$ ≥ 2, for instance, show maxima in the energy range 1.3 eV ≤ E$_{tot}$ ≤ 2 eV, while the quasiclassical trajectory calculations give only monotonically decreasing cross sections in this range.

Considering the above three reasons, we decided to carry out a joint study which would differ from other studies in two main ways.

(i) In contrast to other experimental techniques, the one we used [the threshold-electron—secondary-ion coincidence (TESICO) technique] made it possible for us to measure the reaction in the most straightforward way. This in turn enabled us to carry out a detailed study of the (relative) cross sections as a function of both the initial vibrational state and the translational energy. Special emphasis was put on the low-energy region (1–2 eV) for which the comparison with theory is feasible.

(ii) The theoretical part of the study was carried out employing the quantum-mechanical reactive infinite-order sudden approximation (RIOSA) which has been found to be both reliable and predictive; namely, with a given potential, the state-to-state cross sections can be obtained. It should be mentioned that this reaction has been exposed to several quasiclassical-trajectory (QCT) treatments, but it is not obvious whether using classical mechanics is fully justified. This is not only owing to the fact that relatively light atoms are involved in the exchange process, but also because it is known from collinear quantum-mechanical calculations that this system is vulnerable to strong resonances which can profoundly affect the dynamics and are not detectable by the QCT.

Because of the importance of this system and because it is a three-electron system, several attempts were made to calculate the potential-energy surface governing the motion of the three particles. The best-known model is the diatomics-in-molecules (DIM) potential of Whitten and Kuntz, which was constructed to fit best the ab initio points of Brown and Hayes. Since most of the available calculations were done with this surface, we too use it for our present treatment.

II. EXPERIMENTAL METHOD AND RESULTS

The experiments were carried out using the TESICO technique, which allows direct measurements of reactions of state-selected molecular ions as a function of collision energy. The reactant ions H$_2^+$ in a specified vibrational state of interest (v$_j$) are produced in an ionization chamber by photoionization of the parent molecule H$_2$ at the threshold wavelength for the state, the source of the monochromatic light being the helium Hopfield continuum emission dispersed by a 1-m Seya-Namioka vacuum monochromator. Under almost collision-free conditions the ions and photoelectrons produced are repelled out of the chamber into the directions perpendicular to the incident photon beam and opposite each other. An electrostatic electron-energy analyzer, together with a straight section which serves as a steradiance analyzer, selects threshold electrons from a mixture of photoelectrons having various kinetic energies and lets them pass to a channel multiplier. The ions, on the other hand, are formed
into a beam of desired velocity by a lens system and focused into a reaction chamber, where they react with neutral He. Product ions HeH\(^{+}\) as well as unreacted primary ions are again extracted from the reaction chamber in the same direction as the primary ion beam, mass analyzed by a quadrupole mass spectrometer, and detected by another channel multiplier. These ion signals are then counted in coincidence with the threshold-electron signals using a standard technique involving a time-to-pulse height converter and a multichannel analyzer.

When the wavelength of incident photons corresponds to the threshold energy for the \(v\) state, ions produced are \(\text{H}_2^+(v), \text{H}_2^+(v-1), \text{H}_2^+(v-2), \ldots, \text{H}_2^+(0)\), out of which only \(\text{H}_2^+(v)\) give threshold electrons. Thus, although all of the above ions react with He to produce HeH\(^{+}\), we can selectively observe the reactions of \(\text{H}_2^+(v)\) by measuring HeH\(^{+}\) in coincidence with the threshold electrons. The relative cross sections are determined from the ratio of the coincidence count rates for HeH\(^{+}\) and \(\text{H}_2^+\) (obtained after sufficiently long signal accumulation time) at a fixed pressure of He in the reaction chamber. The collision energy is determined by the difference of the potentials at the point of primary ion production and at the reaction chamber.

The experimental results are summarized in Fig. 1, where relative cross sections are plotted against total available energy \(E_{\text{tot}}\). Solid lines connect data points of the same center-of-mass collision energy and the dashed lines connect those of the same vibrational quantum number, as indicated in the figure. From Fig. 1, several important features of this reaction are clearly seen. First of all, remarkable vibrational enhancement of the reaction is immediately evident from the solid lines. The slopes of these lines are sharper for lower collision energies, indicating that the vibrational energy enhances the reaction more effectively at lower collision energies than at higher collision energies. On the other hand, collision energy is seen to be quite ineffective in promoting this endoergic reaction, as evidenced from the \(v=0\) and \(v=1\) curves; with these low vibrational states, the cross sections are quite small even when the total energy exceeds the endoergicity considerably.

In order to compare the relative effectiveness of the two forms of energy quantitatively, we give in Table I the relative cross sections for five vibrational states numerically at three fixed total energies of 1.5, 2.6, and 3.5 eV. The cross section for \(v=0\) is normalized to 1 within each column corresponding to a fixed total energy. It can be seen that the replacement of a fixed amount of translational energy by the same amount of vibrational energy enhances the reaction considerably and that this effect is larger for smaller total energies than for larger total energies. For instance, the replacement of 0.99 eV of translational energy by the same amount of vibrational energy (corresponding to the energy difference between \(v=0\) and \(v=4\)) enhances the reaction by a factor of 107 at 1.5 eV of total energy, while the enhancement is only by a factor of 11 at 3.5 eV of the total energy.

When the cross section for each vibrational state is viewed as a function of collision energy, it is found that, in all the cases except for \(v=0\), the cross section first rises sharply at an energy that exceeds the threshold by a certain amount, passes through a maximum, and then decreases. The maximum position is shifted to smaller energies as the vibrational quantum number is increased. The cross sections for all vibrational states seem to reach a certain common finite value at higher collision energies (\(\geq 4\) eV). This may indicate that there is another mechanism different from that corresponding to the vibrationally enhanced part of the cross sections. The cross section for \(v=0\) rises much more slowly and its maximum is hardly discernible.

### III. THEORY AND NUMERICAL TREATMENT

A state-to-state integral reactive cross section within the framework of the RIOSA is written as

\[
\sigma(v_f | v_i) = \frac{\pi}{2k_{\text{v}}} \sum_{l_i} (2l_i + 1) \int_{-1}^{1} d(\cos \gamma_i) \left| S^{v_f}_{\gamma_i}(\gamma_i;B) \right|^2,
\]

where

<table>
<thead>
<tr>
<th>(E_{\text{tot}}) (eV)</th>
<th>1.5</th>
<th>2.6</th>
<th>3.5</th>
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<tr>
<td>(v)</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>0</td>
<td>1.42</td>
<td>1.00</td>
<td>0.98</td>
</tr>
<tr>
<td>1</td>
<td>1.58</td>
<td>1.05</td>
<td>0.98</td>
</tr>
<tr>
<td>2</td>
<td>1.95</td>
<td>1.06</td>
<td>0.97</td>
</tr>
<tr>
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<td>2.30</td>
<td>1.09</td>
<td>0.97</td>
</tr>
<tr>
<td>4</td>
<td>2.53</td>
<td>1.10</td>
<td>0.96</td>
</tr>
</tbody>
</table>

### TABLE I. Relative cross sections for the reaction \(\text{H}_2^+(v) + \text{He} \rightarrow \text{HeH}^+ + \text{H}\) at fixed total energies.
where $v_i$ and $v_f$ are the initial and final vibrational states ($i$ stands for “initial” and $f$ for “final”; each refers to a different arrangement channel), $k_{v_i}$ is the initial wave number, $l_i$ is the orbital angular momentum number in the initial channel, $\gamma_i$ is the IOSA angle defined as $\gamma_i = \cos^{-1}(R_i r_i)$, where $R_i$ and $r_i$ are the translational and vibrational vectors and $S_{i|v_i}^{v_f}(\gamma_i; B)$ is the reactive state-to-state S-matrix element calculated for a fixed value of $\gamma_i$ and $l_i$. As can be noted, the S-matrix element also depends on a parameter, the RIOSA $B$ constant, which permits transformation from a given value of $\gamma_i$ in the initial arrangement channel to a single value of $\gamma_f$ in the final arrangement channel.

In general, keeping $\gamma_i$ constant means forcing the three-particle system to move on one single plane defined by $\gamma_i = \text{const}$ in the three-dimensional (3D) coordinate space. Within the RIOSA the three-particle system moves on one plane in the initial arrangement and on the other defined by $\gamma_f = \text{const}$ in the final arrangement. The two planes intersect along a straight line that goes through the origin ($r=R=0$). The parameter $B$ determines the tangent of this line. Thus, assigning a value to $B$ means fixing the line that separates the reagent channel from the product channel. This line has to follow the ridge of the potential-energy surface that governs the motion of the three particles in the two arrangement channels. In a symmetric case such as $H + H_2$, the value of $B$ is 1, and this yields the following relation between $\gamma_i$ and $\gamma_f$:

$$\gamma_f = \pi - \gamma_i.$$  

(2)

In the present case $B$ was found to be 0.8 and consequently the relation between $\gamma_i$ and $\gamma_f$ is much more complicated, namely

$$\cos \gamma_f = \frac{\cos \gamma_i + \left(1 - B^2\right) \cot \phi \cot \beta}{B \left[1 + \left(1 - B^2\right) \cot^2 \phi\right]^{1/2}},$$  

(3)

where

$$\cot \phi = \frac{\sin \beta}{B^2 - \cos^2 \beta} \left[\cos \phi \cos \gamma_i + \left(B^2 - \sin^2 \gamma_i \cos^2 \beta\right)^{1/2}\right]$$

(4)

and

$$\cos \beta = \left[\frac{m_A m_C}{(m_A + m_C)(m_B + m_C)}\right]^{1/2},$$

$$\sin \beta = (1 - \cos^2 \beta)^{1/2}.$$  

(5)

Here, $m_B$ and $m_C$ are the masses of the two hydrogen atoms and $m_A$ the mass of helium. The angle $\beta$ is the skewing angle, a characteristic angle for the three-particle reactive system.

The calculations were done for three energies, namely, $E_{\text{tot}} = 1.3, 1.5$, and $1.8$ eV. For the highest energy value, eight open vibrational states in the reagent channel and three in the product channel are encountered. The calculations have to be carried out only for the range $0 \leq \gamma_i \leq \pi/2$ due to the symmetry, and the final results are multiplied by 2. The number of $\gamma_i$ grid points was 10, with $\Delta \gamma = 10^\circ$. As for the $l_i$ range, it was strongly dependent on $E_{\text{tot}}$ and $\gamma_i$. The smaller $\gamma_i$ and the higher $E_{\text{tot}}$, the larger the range for $l_i$. The largest encountered value was $l_i = 56$.

In order to obtain reliable results we had to include closed channels. The number of these had to be increased until convergence was obtained. The rate of convergence depended not only on the energy (a fact well known from collinear studies), but also on $\gamma_i$ and $l_i$. The total number of vibrational states included in the calculation was between 15 and 30; a particularly large number of states had to be included when both $\gamma_i$ and $l_i$ were small.

Figure 2 shows the integral cross sections [Eq. (1)] for $E_{\text{tot}} = 1.5$ eV as a function of $v_i$ for the reaction

$$H_2^+(v_i) + He \rightarrow HeH^+ \sum v_f \rightarrow H, \quad v_i = 0, 1, 2, 3, 4, 5.$$

In addition to the RIOSA results, we show those due to the QCT treatment of Whitten and Kuntz and another set of quantum-mechanical results which, unlike the RIOSA, are based only on the collinear arrangement ($\gamma_i = 0$), i.e.,

$$\sigma(v_f | v_i) = \frac{\pi}{k_{v_i}^2} \sum_{l_i} (2l_i + 1) |S_{i|v_i}^{v_f}(\gamma_i = 0)|^2.$$  

(6)

The main observations from the figure are the following.

(i) The RIOSA and QCT approaches yield the vibrational propensity rule, namely, enhancement of reaction rate with vibrational energy (total energy fixed). However, it is also seen that the collinear results due to Eq. (6) fail to do so, since a larger cross section is encountered for $v_i = 3$ than for $v_i = 4$. This fact actually indicates that the system is not collinear dominated.

(ii) A reasonably good fit is obtained between the RIOSA and QCT cross sections, except for $v_i = 2$ where the RIOSA result is almost 3 times larger. This

![FIG. 2. Dependence of the theoretical cross sections for $E_{\text{tot}} = 1.5$ eV on the initial vibrational quantum number $v_i$. ———: RIOSA [Eq. (1)]; ———: quasiclassical trajectory calculation (Ref. 4); · · · ·: quasicollinear approximation [Eq. (6)].](image-url)
discrepancy is not yet well understood.
More results are shown in Sec. IV below, and a more
detailed study will be given in a forthcoming publication.

IV. COMPARISON BETWEEN THEORY
AND EXPERIMENT

The comparison between experiment and theory is
presented in Fig. 3, which shows normalized cross
sections for different initial vibrational states as a function
of total energy. The comparison with the RIOSA is given in
Fig. 3(a) and with QCT in Fig. 3(b). We show results for
\( E_{\text{tot}} \leq 2 \) eV, only because the RIOSA study was carried
out for three energy values below 2 eV. All the results are
normalized to those for \( v_j = 4 \) and \( E_{\text{tot}} = 1.55 \) eV. The
results for \( v_j = 5 \) are not shown because the data were not
collected due to experimental limitations.

As for Fig. 3(a), note the following two main points.
(i) The vibrational propensity rule applies to both the
experimental and the RIOSA results along the whole
studied energy range.
(ii) The cross sections are relatively weakly dependent
on the total energy.

As is seen from Fig. 3(b), the QCT calculations yield
cross sections which, for a given initial vibrational state
\( v_j \geq 2 \), decrease with the energy in the range
1.3 \( \leq E_{\text{tot}} \leq 2 \) eV and the maxima appear at lower ener-
gies. Our experimental results, however, indicate that all
the cross sections for \( v_j = 2, 3, 4 \) seem to have maxima in
the above energy range. The quantum-mechanical results
reproduce this tendency better than the QCT results, al-
though the agreement with the experimental results is not
quantitatively very satisfactory. The cross sections for the
lower vibrational states \( v_j = 0, 1 \) are quite small and show
very weak energy dependence in the range.

As for the quantum-mechanical calculations, it should
be mentioned that the \( \text{He} + \text{H}_2^+ \) system is the first sys-
tem, so far, to be treated by the RIOSA and to yield cross
sections which are so weakly dependent on the energy.

In conclusion, the system \( \text{He} + \text{H}_2^+ \) is intriguing in its
dependency on the initial vibrational energy (for a given
total energy) and on translational energy. It is gratifying
to find out that this dynamic behavior is moderately well
reproduced by the RIOSA.

FIG. 3. Comparison between theory and experiment for the
cross sections as a function of \( E_{\text{tot}} \). Figures attached to each
line are the initial vibrational quantum numbers. ——: present
experimental result; ——: present theoretical result (RIOSA);
———: quasiclassical trajectory calculation (Ref. 4). (a)
Comparison between experimental and quantum mechanical
(RIOSA) results. (b) Comparison between experimental and
quasiclassical (QCT) results.

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*Permanent address: Soreq Nuclear Research Center, Yavne,
Israel.
†Permanent address: J. Heyrovsky Institute of Physical Chem-
istry and Electrochemistry, Czechoslovak Academy of Sci-
ences, 12138 Prague 2, CSSR.
(1968); W. A. Chupka, in I on-Molecule Reactions, edited by
3M. Baer, Adv. Chem. Phys. 49, 191 (1982); J. Jellinek and D. J.
Kouri, in The Theory of Chemical Reaction Dynamics, edited by
M. Baer (CRC, Boca Raton, Florida, 1985).
4W. N. Whitton and P. J. Kuntz, J. Chem. Phys. 64, 3624
(1976).
5F. Schneider, U. Havemann, L. Zülicke, and Z. Hermann,
6T. Joseph and N. Sathyamurthy, J. Chem. Phys. 80, 5332