$He + H_2^+$ ion-molecule reaction: A comparison between experimental and quantum-mechanical results

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In this work a comparison between new experimental and quantum-mechanical results is performed for the reactions $He+H_2^{+}(v_i) \rightarrow HeH^{+}(\sum v_f)+H$; $v_i=0-4$ in the energy range 1 $eV \leq E_{tot} \leq 2 eV$, 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.¹ 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 $v_i \ge 2$, for instance, show maxima in the energy range 1.3 eV $\leq E_{tot} \leq 2$ 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]² 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;³ 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,⁴⁻⁶ 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 calculations⁷ 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 Whitton and Kuntz,⁴ which was constructed to fit best the *ab initio* points of Brown and Hayes.⁸ 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,² 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_i) are produced in an ionization chamber by photoionization of the parent molecule H₂ 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 steradiancy 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

34 1748

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_i state, ions produced are $H_2^+(v_i)$, $H_2^+(v_i-1)$, $H_2^+(v_i-2)$, ..., $H_2^+(0)$, out of which only $H_2^+(v_i)$ give threshold electrons. Thus, although all of the above ions react with He to produce HeH⁺, we can selectively observe the reactions of $H_2^+(v_i)$ 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 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_{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



FIG. 1. Relative cross section as a function of total energy E_{tot} . Solid lines connect the data points of the same center-of-mass (c.m.) translational energy. Dashed lines connect those of the same vibrational quantum number. E_{th} is the threshold energy.

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 $(\geq 4 \text{ eV})$. 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 as³

$$\sigma(v_f \mid v_i) = \frac{\pi}{2k_{v_i}^2} \sum_{l_i} (2l_i + 1) \int_{-1}^{+1} d(\cos\gamma_i) |S_{l_i v_i}^{v_f}(\gamma_i; B)|^2 ,$$
(1)

TABLE I. Relative cross sections for the reaction $H_2^+(v) + He \rightarrow HeH^+ + H$ at fixed total energies.

		Total energy, E_{tot} (eV)		
v	E_v (eV)	1.5	2.6	3.5
0	0.14	1	1	1
1	0.41	9.0	4.0	3.2
2	0.67	44	7.2	3.7
3	0.91	92	16.8	5.3
4	1.13	107	34	11

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 quantum number in the initial channel, γ_i is the IOSA angle defined as $\gamma_i = \cos^{-1}(\mathbf{R}_i, \mathbf{r}_i)$, where \mathbf{R}_i and \mathbf{r}_i are the translational and vibrational vectors and $S_{l_i v_i}^{v_f}(\gamma_i; B)$ is the reactive state-to-state S-matrix element calculated for a fixed value of γ_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 γ_i in the initial arrangement channel to a single value of γ_f in the final arrangement channel.

In general, keeping γ_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 γ_i and γ_f :

$$\gamma_f = \pi - \gamma_i \ . \tag{2}$$

In the present case B was found to be 0.8 and consequently the relation between γ_i and γ_f is much more complicated, namely

$$\cos\gamma_{f} = -\frac{\cos\gamma_{i} + (1 - B^{2})\cot\phi \cot\beta}{B[1 + (1 - B^{2})\cot^{2}\phi]^{1/2}},$$
(3)

where

$$\cot\phi = \frac{\sin\beta}{B^2 - \cos^2\beta} \left[\cos\beta\cos\gamma_i + (B^2 - \sin^2\gamma_i\cos^2\beta)^{1/2}\right]$$
(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 β is the skewing angle, a characteristic angle for the three-particle reactive system.

The calculations were done for three energies, namely, $E_{\rm tot} = 1.3$, 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 $0 \le \gamma_i \le \pi/2$ due to the symmetry, and the final results are multiplied by 2. The number of γ_i grid points was 10,

with $\Delta \gamma = 10^{\circ}$. As for the l_i range, it was strongly dependent on E_{tot} and γ_i . The smaller γ_i and the higher E_{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 γ_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 γ_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

$$\mathbf{H}_{2}^{+}(v_{i}) + \mathbf{H}\mathbf{e} \rightarrow \mathbf{H}\mathbf{e}\mathbf{H}^{+} \left[\sum v_{f} \right] + \mathbf{H}, \quad v_{i} = 0, 1, 2, 3, 4, 5.$$

In addition to the RIOSA results, we show those due to the QCT treatment of Whitton and Kuntz⁴ and another set of quantum-mechanical results which, unlike the RIOSA, are based only on the *collinear* arrangement $(\gamma_i = 0)$, i.e.,

$$\sigma(v_f \mid v_i) = \frac{\pi}{k_{v_i}^2} \sum_{l_i} (2l_i + 1) |S_{l_i v_i}^{v_f}(\gamma_i = 0)|^2 .$$
(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 $E_{tot}=1.5$ eV on the initial vibrational quantum number v_i . ——: RIOSA [Eq. (1)]; — ——: quasiclassical trajectory calculation (Ref. 4); · · · ·: quasicollinear approximation [Eq. (6)].

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 $E_{tot} \leq 2$ eV, only because the RIOSA study was carried out for three energy values below 2 eV. All the results are normalized to those for $v_i = 4$ and $E_{tot} = 1.55$ eV. The results for $v_i = 5$ 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 $v_i (\geq 2)$, decrease with the energy in the range $1.3 \leq E_{\text{tot}} \leq 2$ eV and the maxima appear at lower energies.⁴ Our experimental results, however, indicate that all the cross sections for $v_i = 2, 3, 4$ seem to have maxima in the above energy range. The quantum-mechanical results reproduce this tendency better than the QCT results, although the agreement with the experimental results is not quantitatively very satisfactory. The cross sections for the lower vibrational states $v_i = 0, 1$ are quite small and show very weak energy dependence in the range.

As for the quantum-mechanical calculations, it should be mentioned that the He + H₂⁺ system is the first system, 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 $He + H_2^+$ 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_{tot} . Figures attached to each line are the initial vibrational quantum numbers. ——: present experimental result; - - -: present theoretical result (RIO-SA); $\cdot \cdot \cdot$: 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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