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THEORETICAL DESCRIPTION OF THE $He(2^3S)$–H_2 AUTOIONISING COLLISION SYSTEM

J. VOJTÍK

J. Heyrovský Institute of Physical Chemsitry and Electrochemistry, Czechoslovak Academy of Sciences, 182 23 Prague 8, Czechoslovakia

The ionization event in the $He(2^3S)$–H_2 collision system at the collision energy of 80 meV is described by a modified version of the trajectory surface leaking method. The approach is found to yield an improved picture of the event which is consistent with Penning electron spectra measurements.

KEY WORDS: Autoionization, Penning ionization, Penning electron spectra, atom-diatom collisional ionization.

He^*–H_2 is the simplest molecular autoionizing collision system, yielding $H_2^+ + He$, $HeH^+ + H$, HeH_2^+ and $H^+ + H + He$ products along with Penning electrons. At thermal energy collisions, the autoionization process is best viewed as proceeding in two microscopic steps[1]

$$He^* + H_2 \rightarrow [He \ldots H_2^+] + e^- \quad (1)$$

$$[He \ldots H_2^+] \rightarrow \text{products} \quad (2)$$

For low collision energies, a theoretical description of a polyatomic autoionizing collision system can be based on the Born-Opppenheimer approximation[2,3] and thereby divided into two steps. The first one consists of the determination of the static characteristics of the system, namely the resonant surface $V^*(R)$, the width of the resonant state with respect to autoionization $\Gamma(R)$, and the ionic surface $V^+(R)$ which governs the motion of the system after ionization. The second step involves a treatment of the motion of the nuclei subject to the potentials and the width surface $\Gamma(R)$. Of the approaches used in dynamical calculations,[4–6] only the trajectory surface leaking (TSL) method[4] appears at present to be capable of furnishing a picture of the dynamics of polyatomic autoionizing collision systems which includes all degrees of freedom of the motion.

The TSL picture is obtained by means of Monte Carlo averages over a large number of classical trajectories. A trajectory starts on the resonant surface $V^*(R)$. At each numerical integration time step (denoted i) in the trajectory, the probability $P(R_i)$ of leaking of the system into the continuum is computed and compared with a pseudorandom number ξ_i to decide whether the trajectory continues on $V^*(R)$ or the system ejects an electron and starts evolving on the ionic surface $V^+(R)$. The sample calculations[7] revealed that the TSL approach leads to probabilities $P(v')$ for

population of $H_2^+(v')(\ldots He)$ which are markedly different from experimental ones.

In the modified approach, the decision about whether or not the transition $V^*(R) \rightarrow V^+(R)$ will take place in the A*–BC system is made at the end of each vibration period of the (perturbed) BC collision partner. In the case of ionization, the system undergoes the $V^*(R) \rightarrow V^+(R)$ (vertical) transition at one of the integration time steps of the vibrational period under question. The choice of this step is based on an extra pseudorandom number and the Franck–Condon factors for the transitions between $BC(v'' = 0)(\ldots A^*)$ and $BC^+(v')$ $(\ldots A)$ calculated numerically for the A–BC distance and A–BC orientation which corresponds to the (approximate) centre of the pertinent vibrational period of BC $(\ldots A^*)$.

The new version of the TSL approach is applied to the $He(2^3S)$–H_2 autoionizing system at the collision energy of 80 meV and with H_2 being intially in the $v'' = 0, J = 1$ state. The necessary information about the $V^*(R)$ and $\Gamma(R)$ surfaces is generated by use of our semiemperical DIM model for polyatomic autoionizing systems.[8,9] The ionic surface $V^+(R)$ is a Sorbie–Murrell type analytical representation of a CI *ab initio* potential.[10] The Franck–Condon factors were calculated numerically, the necessary radial rovibrational wavefunctions for $H_2(v'' = 0)(\ldots He^*)$ and $H_2^+(v')(\ldots He)$ were obtained by solving the corresponding Schrödinger equations with the potentials taken as appropriate one-dimensional cuts through the $V^*(R)$ and $V^+(R)$ surfaces.

Ionization step (1) was investigated with 270,000 trajectories. Of these, 5978 (2.21%) trajectories led to ionization of the system. The corresponding total ionization cross section is 6.96 a_0^2 which is in a very good agreement with both the TSL

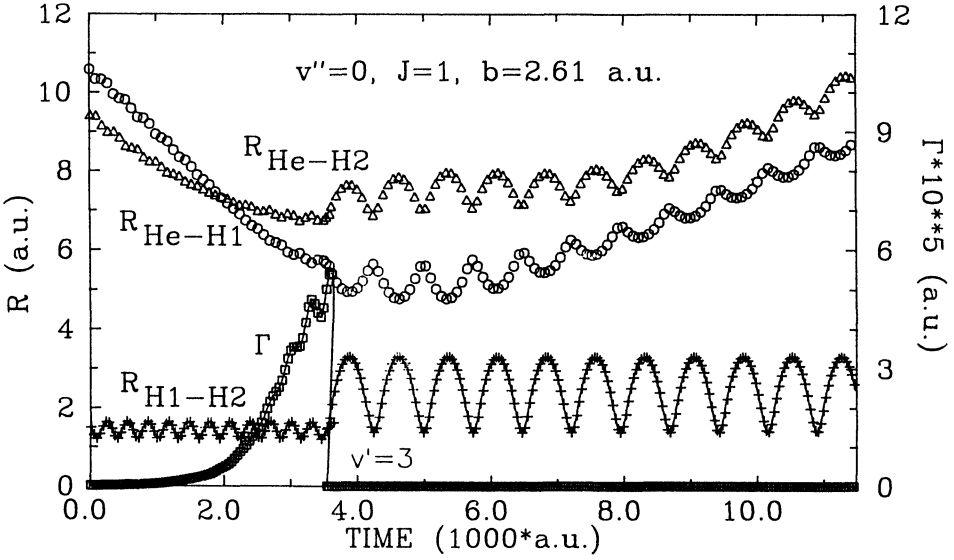

Figure 1 $He(2^3S)$–H_2 trajectory contributing to the Penning branch ($H_2^+ + He + e^-$) of the ionization process. Γ is the width of the state with respect to autoionization.

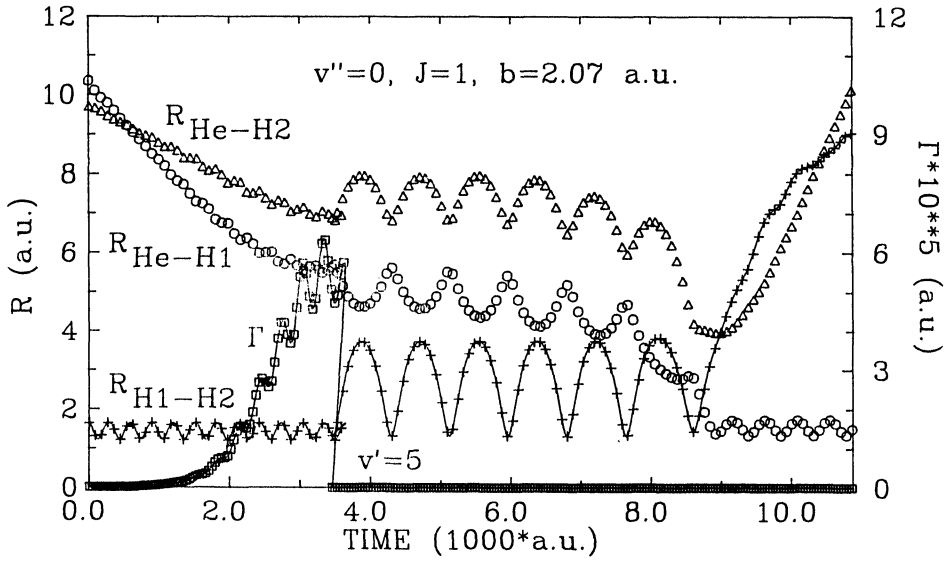

Figure 2 He(2^3S)–H_2 trajectory contributiing to the rearrangement branch ($HeH^+ + He + e^-$) of the ionization process. Γ is the width of the state with respect to autoionization.

value[4] and the results of model quantum calculations.[5,6] Examples of the He(2^3S)–H_2 trajectories which were found to ionize are shown in Figures 1 and 2.

The values of the vibrational population factors in Penning ionization of $H_2(v'' = 0, J = 1)$ by He(2^3S) are given in *Table 1*, together with the results of our sample TSL calculations[7] and the experimental values of Bregel *et al.*[11] The vib-

Table 1 Vibrational population factors (normalized to 100 at $v' = 2$) in Penning ionization of $H_2(v'' = 0)$ by He(2^3S)

v'	This work	Sample TSL calculations[a]	Experiment[b]
0	49.9	140.0	55.0 ± 1.5
1	88.8	165.5	94.7 ± 1.0
2	100	100	100
3	85.5	80.0	85.6 ± 1.0
4	64.0	76.4	65.5 ± 1.0
5	46.9	68.2	47.4 ± 1.0
6	33.8	45.5	32.4 ± 1.0
7	23.1	85.5	21.8 ± 0.8
8	29.3	125.5	14.5 ± 0.8
9	—	—	9.8 ± 0.8
10	—	—	6.5 ± 0.8
11	—	—	4.4 ± 0.8
12	—	—	2.9 ± 0.6
13	—	—	1.9 ± 0.5
14	—	—	1.3 ± 0.4
15	—	—	0.9 ± 0.3

[a]Ref. 7.
[b]Ref. 11.

rational levels $v' > 8$ of $H_2^+(\ldots He)$ are not populated, their absence being compensated, in a way, by an enhancement of the $P(v' = 8)$ population factor. This is a direct consequence of that the initial and final states of the ionization event are described classically, and that the $V^*(R) \rightarrow V^+(R)$ transition is vertical. The experimental populations of *Table 1* correspond to the $He(2^3S)$–H_2 collision energy ranging from 10 to 150 meV, with an average of ~51 meV. Taking into account that the present results correspond to $E_{rel} = 80$ meV, the degree of agreement between the two populations can be considered to be very satisfactory. It can be also inferred from *Table 1* that the present populations are physically much more relevant than those corresponding to the strictly classical description of the ionization event of the type used in the TSL approach.

The total energy and angular momentum of the system are conserved during each trajectory and the procedure retains a Monte Carlo character of the original TSL scheme. This, together with the present results indicates that the modified TSL approach could become useful in theoretical description of the dynamics of atom-diatom collision system exhibiting autoionization.

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