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Limit of the vibrational sudden approximation for $H^+ + H_2$ collisions

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Vibronic close-coupling calculations of charge transfer and H_2 vibrational excitation total cross sections in $H^+ + H_2(^1\Sigma_g^+, \nu=0)$ collisions are presented and compared with experimental data in the energy range $50\ \text{eV} < E < 2\ \text{keV}$. It is shown that the sudden approximation for vibration is inappropriate for this system at low velocities, where the dominant mechanism involves transitions between quasidegenerate vibronic levels.

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Ion-diatom collisions have been studied using two different approaches depending on the energy range of interest. At sufficiently high velocities, one can use a similar treatment to that of ion-atom collisions [1], which employs rectilinear trajectories for the ion-molecule relative motion and some kind of sudden approximation for target rotation and vibration (see Refs. [2,3]). The basis of the former approximation is explained in detail, e.g., in Ref. [4], and its accuracy has been checked for ion-atom collisions [5]: by comparing with quantal transition probabilities, it was shown that trajectory effects are in general unimportant for impact velocities $v > 0.03$ a.u. ($E > 225$ eV/amu), and that straight lines can be employed at lower velocities when only total cross sections are required (see also Ref. [6]). In addition, high v calculations are often based on the Franck-Condon (FC) approximation, whose accuracy has been analyzed in detail in Refs. [7] by comparison with the more general vibrational sudden approach (SEIKON) [8]. In this SEIKON method, one uses rectilinear trajectories and the rovibrational component of the collision wave function is taken to be identical to the initial one; the electronic part is expanded in terms of a set of wave functions of the triatomic system, leading to the electronic transition amplitudes, which are then employed to evaluate vibrationally resolved orientation averaged transition probabilities and cross sections.

On the other hand, at low v a different approach is often employed, based on the so-called infinite order sudden approximation (IOSA); this method (see [9] and references therein) employs a quantal treatment with both energy and centrifugal sudden approximations, so that the rotational motion of the diatom is frozen and the rotational couplings are eliminated. A semiclassical treatment with the ion-diatomic motion treated classically, and the sudden approximation for the diatomic rotation has been compared with IOSA in Refs. [10–12] for $H^+ + O_2$ collisions. The trajectory surface hopping method (TSH) [13], has also been used at low v, where the nuclei follow classical trajectories, defined by the potential energy surfaces, and nonadiabatic transitions take place when a trajectory reaches an avoided intersection region between the energy surfaces, with a probability defined by the Landau-Zener [14] model.

The present article focuses on the benchmark system of $H^+ + H_2$ collisions to determine the low v limit of SEIKON and FC approaches, by carrying out a vibronic close-coupling calculation based on *ab initio* molecular data. In doing so, we shall show a change of mechanism as v decreases, which explains the success of different approximations in describing these reactions.

Previous work on $H^+ + H_2$ collisions include TSH calculations of charge transfer cross sections at low velocities ($E \leqslant 30$ eV) [15,16]. Baer *et al.* [17] have employed the IOSA method, with diatomic in molecules (DIM) wave functions [18], to study charge transfer and H_2 vibrational excitation, and have compared their results with experimental differential cross sections [15]. The electron-nuclear dynamics approach has been employed in [19] for $E = 30$ eV. These calculations [15,17,19] and experiments [15] yielded partial cross sections for population of H_2^+ vibrational states with a remarkable deviation with respect to the FC distribution. Besides, it was suggested [15] that the charge transfer process takes place through a resonant mechanism. At higher energies, Kimura [20] carried out an approximate vibronic close-coupling calculation of total charge transfer cross section; this work employed DIM electronic wave functions, and used the FC approximation to evaluate the coupling matrix elements in the vibronic basis. Shingal and Lin [21] evaluated charge-transfer transition probabilities from an unitarized coherent sum of transition amplitudes for two independent H^+-H processes, obtained using a two-center atomic basis. Elizaga *et al.* [22] carried out a FC treatment of charge transfer with a model potential description of the H_2 electronic structure, and the independent particle model to calculate two-electron transition probabilities; this work reported results of molecular and one-center atomic (including pseudostates) calculations. Similar model potential and FC approximations have been employed in classical calculations [23] of charge transfer and ionization total cross sections.

A more refined calculation [25] referred to the state-to-state reaction

$$H^+ + H_2(^1\Sigma_g^+, \nu=0) \rightarrow H(1s) + H_2^+(^2\Sigma_g^+, \nu') \qquad (1)$$

and the isotopically modified species D_2, DT, T_2. This work used the SEIKON treatment in the energy range $50\ \text{eV} \leqslant E$

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$\leqslant 6.25$ keV, and *ab initio* techniques [26] to evaluate the molecular data. The vibronic part of the collisional wave function was of the form:

$$\Psi = \psi(\boldsymbol{r}_1, \boldsymbol{r}_2, \boldsymbol{\rho}, t)\chi_{10}(\rho), \tag{2}$$

where $\boldsymbol{r}_1, \boldsymbol{r}_2$ are the electronic coordinates, $\boldsymbol{\rho}$ the H-H internuclear vector, and $\chi_{10}(\rho)$ is the wave function of the H_2 vibrational ground state. We found that, at the highest energies in this interval ($E \geqslant 2$ keV), total and partial vibrational cross sections agree with the FC ones. The SEIKON total charge-transfer cross section agrees with experiment [24] down to $E \simeq 200$ eV and, at lower energies ($50 \text{ eV} < E < 200$ eV), there are significant deviations between experiment and theory. To analyze the reason for this disagreement, the first question is which of the two basic approximations employed in the SEIKON treatment (the use of linear trajectories or of the sudden approach) is too poor. We checked in Ref. [25] that the former is unlikely by comparing between quantal and semiclassical cross sections at the FC level. In Ref. [25] we also showed that the total cross section for charge transfer from H_2 in its first excited vibrational state ($\nu = 1$) is, at low energies ($\simeq 50$ eV), one order of magnitude larger than that from the ground state ($\nu = 0$), which led to a tentative explanation of the disagreement with the experiment in terms of a previous formation of H_2 ($\nu = 1$) during the collision. Another result of Ref. [25] is the large total cross section for the H_2 vibrational excitation reaction:

$$H^+ + H_2(^1\Sigma_g^+, \nu = 0) \rightarrow H^+ + H_2(^1\Sigma_g^+, \nu \neq 0), \tag{3}$$

for which there is no experimental counterpart. As pointed out in [27], this result suggests the inadequacy of the collisional wave function employed in the vibrational sudden approximation [see Eq. (2)], whose vibrational component is identical to χ_{10}.

In the present work, we have employed, instead of the wave function of Eq. (2), a close-coupling vibronic expansion of the form

$$\Psi = D(\boldsymbol{r}_1, \boldsymbol{r}_2, t)\left(\phi_1 \sum_{\nu} a_{1\nu}(t)\chi_{1\nu} \exp\left[\int_0^t H_{1\nu} \mathrm{d}t'\right] + \phi_2 \sum_{\nu'} a_{2\nu'}(t)\chi_{2\nu'} \exp\left[\int_0^t H_{2\nu'} \mathrm{d}t'\right]\right), \tag{4}$$

where $D(\boldsymbol{r}, t)$ is a common translation factor [28] of the form proposed in Ref. [29]; $\phi_{1,2}$, the lowest two adiabatic electronic states of H_3^+, and $\chi_{1\nu}$, $\chi_{2\nu'}$ are, respectively, H_2 and H_2^+ vibrational functions; $H_{i\nu}$ are the expectation values for the vibronic functions $\phi_i \chi_{i\nu}$, of the Hamiltonian excluding the kinetic energy term for the ion-diatomic internuclear vector. In practice, we have obtained $\phi_{1,2}$ by employing a full configuration-interaction procedure with a Gaussian basis set, whose accuracy was checked by comparing the asymptotic energies with the experimental values, and the ground-state electronic energy with the accurate potential surface of Ref. [30] (differences are smaller than 10^{-3} a.u.). The dynamical coupling matrix elements were calculated numerically as explained in Ref. [26]. We have included in expansion (4) 14 vibrational states for each electronic state.

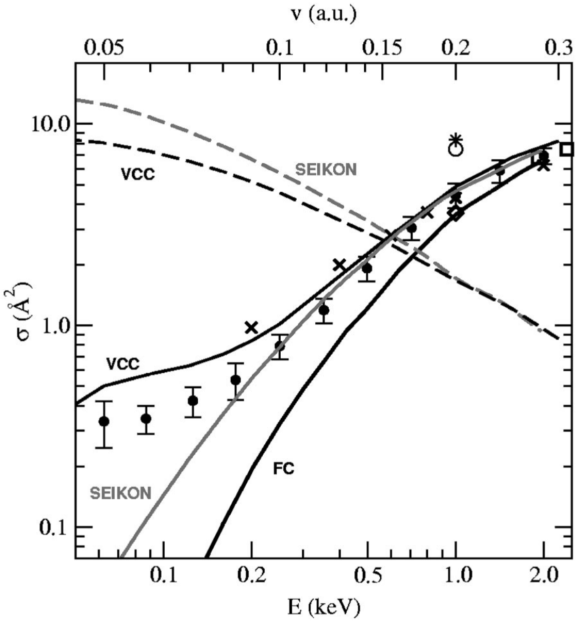

FIG. 1. Cross sections for $H^+ + H_2$ collisions. Lines, present results (VCC, vibronic close-coupling; SEIKON: vibrational sudden; FC, Franck-Condon). Solid lines and symbols: charge transfer [Eq. (1)]; dashed lines: vibrational excitation [Eq. (3)]. ×, [20] multiplied by 2 following the author's suggestion. Experiments: ●, [24]; ◇, [31]; ○, [32]; ⋆, [33].

Our total cross sections for charge transfer and excitation are plotted in Fig. 1 and show a good agreement with the experimental values for charge transfer of Ref. [24], and a corresponding discrepancy with respect to the SEIKON ones for $E < 200$ eV. A smaller difference between calculated cross sections is obtained for reaction (3). These results point out to a limitation of the sudden vibrational approximation for this system and confirms the accuracy of the experimental measurements, without invoking a contamination of the primary beam with $H_2(\nu = 1)$.

To further analyze the results of Fig. 1, we have studied the mechanism of the charge transfer process. In this respect, in the semiclassical treatment one can follow the population of the vibronic states during the trajectory, as illustrated in Fig. 2, where we have plotted the time evolution of the populations $|a_{1,2\nu}|^2$ (the "history" of the collision) for a representative trajectory with impact parameter $b = 2.0$ a.u. at two velocities: $v = 0.05$ a.u. ($E = 62.5$ eV) and $v = 0.2$ a.u. ($E = 1$ keV). The mechanism at low v [Fig. 2(a)] involves excitation to channels $\phi_1 \chi_{1\nu}$, followed by transitions in the outgoing part of the collision from these excited states (mainly from χ_{14}) to $\phi_2 \chi_{20}$. The populations of states $\phi_2 \chi_{2\nu'}$ ($\nu' > 0$) are very small and are not included in the figure. In fact, this mechanism is essentially that suggested by Niedner *et al.* [15] to explain the experimental results at $E = 30$ eV, where the charge transfer process takes place through a (quasi)resonant process involving states $\phi_1 \chi_{14}$ and $\phi_2 \chi_{20}$, which are quasidegenerate for $R \geqslant 6.0$ a.u. (see Fig. 3). It is important to note that the failure of the SEIKON

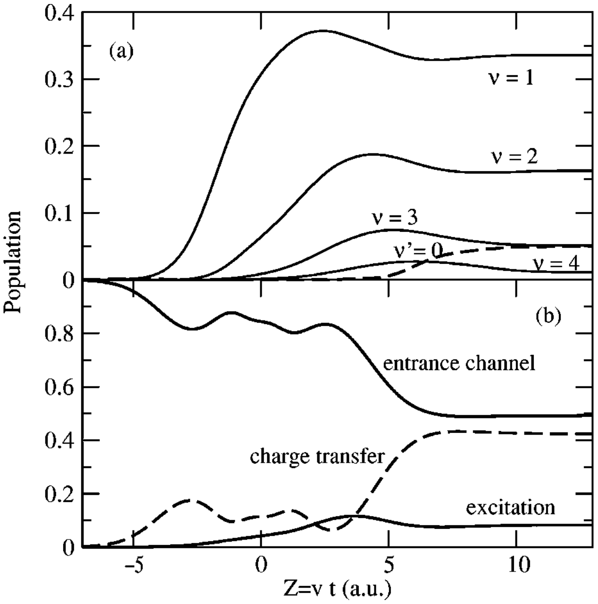

FIG. 2. (a) Time evolution of the populations of the vibronic states for a trajectory with $b=2.0$ a.u and $v=0.05$ a.u. ($E=62.5$ eV). (b) Time evolution of the populations of the vibronic states for a trajectory with $b=2.0$ a.u and $v=0.20$ a.u. ($E=1$ keV).

treatment at low v is a consequence of its inability to describe the above-mentioned resonant mechanism for charge transfer. More explicitly, in the SEIKON approach the populations of the vibrational levels are obtained by projecting the sudden wave function $\psi(\boldsymbol{r}_1,\boldsymbol{r}_2,\boldsymbol{\rho},t)\chi_{10}(\rho)$ of Eq. (2) onto the exit channels $\phi_2(\boldsymbol{r}_1,\boldsymbol{r}_2,\boldsymbol{\rho})\chi_{2\nu}$, and the relative energies of the vibronic levels do not play any role in this procedure. Moreover, a modification of the sudden approximation of Eq. (2), where χ_0 is substituted by a linear combination of H_2 vibrational functions $\chi_{1\nu}$, improves the description of H_2 vibrational excitation, but is not able to describe the resonant mechanism of the charge transfer.

A completely different mechanism takes place at high energies, as illustrated in Fig. 2(b) for $E=1$ keV, where we have plotted the sum of populations of the exit channels of reactions (1) and (3) to simplify the figure. The main difference with respect to the low-v case is that charge-transfer states are now populated directly from the entrance channel, with transitions at $Z\simeq 5.0$ a.u. This means that transitions occur when the system is well described by the initial state vibrational wave function, which explains the good agreement, at this energy range, between the SEIKON calculation and experiment.

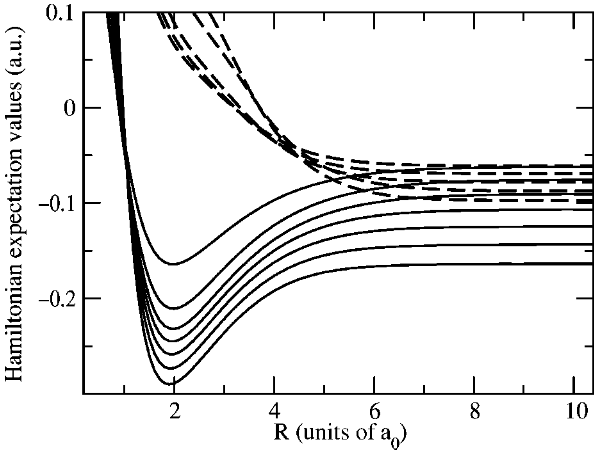

FIG. 3. Hamiltonian expectation values $H_{n\nu}$ [see Eq. (4)]. Full lines, $H_{1\nu}$; dashed lines, $H_{2\nu}$.

To sum up, this contribution to the understanding of the low-v limit of the vibrational sudden approximation has focused on the benchmark case of $H^+ + H_2$ collisions, using *ab initio* molecular data. For this case, we have found that, for $v>0.1$ a.u, the sudden vibrational approximation holds; and for $v>0.3$ a.u., the FC treatment gives reasonable results. Furthermore, we have shown that these conclusions are closely related to the collisional mechanism: at low v, a resonant process is at work through transitions at a crossing between a vibronic state of the entrance electronic channel and a transfer state, whereas at higher v, the vibrational distribution of the capture channels can be obtained through a sudden treatment after the capture process. As far as we know, this is the first explicit study of the low-v limit of the sudden vibrational approach, which is far simpler than close-coupling treatments. Accordingly, similar analysis for other systems would be useful.

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