A QUANTUM-MECHANICAL STUDY OF CHARGE TRANSFER STERIC FACTORS FOR THE THREE ISOTOPIC SYSTEMS: H⁺+H₂, D₂, HD

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The steric effect on charge transfer has been studied theoretically for three isotopic systems H⁺+H₂, D₂, HD at a center of mass collision energy, Ecm, = 20 eV. The orientational-dependent cross sections were calculated quantum mechanically employing the recently introduced infinite order sudden approximation (IOSA). Of all three, the H⁺+HD system exhibits an unusually large steric factor which was found to be related to the orientational-dependent inelastic vibrational excitation.

1. Introduction

The state resolved differential cross sections for inelastic scattering and charge transfer scattering of H⁺+H₂ have recently been studied experimentally and theoretically [1-3] at Ecm, = 20 eV. A comparison between the experimental results and classical trajectory surface hopping and quantum-mechanical infinite order sudden approximation (IOSA) [4] calculations suggests that the latter provides a better overall description of the data. Especially encouraging agreement was obtained with integral observables such as the inelastic and the charge transfer state-to-state vibrational transition probabilities using the IOSA. The same applies to the vibrational state resolved differential cross sections except that the predicted rainbow position is shifted to larger angles by 1.5°. A similar shift was observed for the semiclassical trajectory surface hopping (TSH) treatment [1]. This discrepancy was attributed to the deficiencies of the diatomic-in-molecules (DIM) potential surfaces used in both calculations [5].

The IOSA affords an opportunity to study steric effects, namely the dependence of various calculated magnitudes on the orientation angle γ since these appear in an intermediate step in the calculations. It was hoped that by comparing the steric factors for the inelastic and the charge transfer processes more insight would be gained into the charge transfer process. However, due to the spherical symmetry of the scattering potential no conclusive statements could be made for H⁺+H₂.

Here the study of the steric factor was extended to two additional isotopic systems namely H⁺+HD and H⁺+D₂. These systems, although described by the same potential, have a dynamic anisotropy introduced by the displacement of the molecular centers of mass. In this communication a few of the more interesting findings are presented.

2. Details of the calculations

The inelastic (in) and charge transfer (ct) channels considered are respectively

\[
\text{H}^+ + \text{M}(u_i = 0) \rightarrow \text{H}^+ + \text{M}(u_f) \quad (1)
\]

and

\[
\text{H}^+ + \text{M}(u_i = 0) \rightarrow \text{H} + \text{M}^+(u_f) , \quad (2)
\]

where M=H₂, D₂, HD.

To obtain the various transition probabilities the two coupled Schrödinger equations were solved [3,4]:

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\[
\left[ -\frac{\hbar^2}{2\mu} \left( \frac{\partial^2}{\partial R^2} + \frac{\partial^2}{\partial \gamma^2} \right) + W_1 + \frac{\hbar^2}{2\mu} \frac{l(l+1)}{R^2} - E \right] \times \psi_1(R, r, \gamma) + w_{12} \psi_2(R, r, \gamma) = 0, \tag{3a}
\]
\[
\left[ -\frac{\hbar^2}{2\mu} \left( \frac{\partial^2}{\partial R^2} + \frac{\partial^2}{\partial \gamma^2} \right) + W_2 + \frac{\hbar^2}{2\mu} \frac{l(l+1)}{R^2} - E \right] \times \psi_2(R, r, \gamma) + w_{12} \psi_1(R, r, \gamma) = 0. \tag{3b}
\]

Here \(l\) is the orbital angular quantum number, \(\mu\) is the reduced mass of the system, \(E\) is the total energy, \(w_1\) and \(w_2\) are the two diabatic surfaces and \(w_{12}\) is the diabatic coupling term. The three diabatic potential terms follow from the adiabatic-diabatic transformation as applied to the adiabatic surfaces and the nonadiabatic coupling terms. The two coupled equations are solved for nineteen equally spaced \(\gamma\) values \(0^\circ \leq \gamma \leq 180^\circ\) where \(\Delta \gamma = 10^\circ\) and 25 \(l\) values. In the case of \(H_2\) and \(D_2\), this number is only ten due to symmetry as used in the previous calculations [3]. All calculations were carried out for a collision energy of \(E_{\text{c.m.}} = 20\) eV. Solution of the two coupled Schrödinger equations yields \(\gamma\)- and \(l\)-dependent \(S^\gamma\) matrix elements i.e. \(S^\gamma(\gamma, l|v_i, v_f)\); here \(v_i\) and \(v_f\) are the initial and final vibrational states, respectively, and the superscript \(q\) designates either the inelastic \((q=\text{in})\) or the charge transfer \((q=\text{ct})\) channel.

The \(\gamma\)-dependent integral cross sections which provide the steric effects are defined as
\[
\sigma^\gamma(v_i, v_f) = \frac{\pi}{k_{vn}^2} \sum_{l=1}^{L} (2l+1) |S^\gamma(\gamma, l|v_i, v_f)|^2, \tag{4}
\]
where \(k_{vn}\) is the initial wave vector. The corresponding integral cross section is obtained by integrating over \(\gamma\):
\[
\sigma^\gamma(v_i, v_f) = \int_{-1}^{1} d(\cos \gamma) \sigma^\gamma(\gamma|v_i, v_f). \tag{5}
\]

Another source of information for the steric effects is the \(\gamma\)-dependent average energy transfer:
\[
\Delta E^\gamma(v_i) = \frac{\sum_{v_f} \sigma^\gamma(\gamma|v_i, v_f) (E_{v_i} - E_{v_f} - \Delta E_0^\gamma)}{\sum_{v_f} \sigma^\gamma(\gamma|v_i, v_f)}, \tag{6}
\]
where \(\Delta E_0^\gamma\) is the endothermicity. It is zero in the case of the vibrational inelastic process and has the following slightly differing values for the three charge transfer scattering calculations:

- \(H_2: \Delta E_0^\gamma = 1.827\) eV,
- \(HD: \Delta E_0^\gamma = 1.846\) eV,
- \(D_2: \Delta E_0^\gamma = 1.868\) eV.

To solve the two coupled Schrödinger equations, the \(\psi_i(R, r, \gamma); i=1, 2\) functions are expanded in terms of adiabatic \(R\)-dependent vibrational basis-set functions. In the case of \(H_2\) 14 functions were included for the lower surface and 11 for the upper surface; for \(D_2\) we used 21 and 18, and for HD 23 and 17 functions, respectively.

The calculations of \(\Delta E^\gamma(v_i)\) in eq. (6) were based on 7 vibrational states for \(q=\text{in}\) and on 4 vibrational states for \(q=\text{ct}\) in the case of \(H_2\); on 10 and 9 vibrational states, respectively, for \(D_2\) and on 12 and 9 vibrational states, respectively, for HD.

3. Results

The integral \(\gamma\)-dependent charge transfer cross section \(\sigma^\gamma(\gamma|v_i)\) is defined as
\[
\sigma^\gamma(\gamma|v_i) = \sum_{v_f} \sigma^\gamma(\gamma|v_i, v_f). \tag{7}
\]

Results for all three charge transfer systems are presented in fig. 1. At the bottom of the figure the meaning of the orientation angle \(\gamma\) for HD is illustrated. Thus for \(0^\circ \leq \gamma < \pi/2\) the proton approaches the HD molecule from the H side and for \(\pi/2 < \gamma \leq \pi\) from the D side.

The main findings to be noted are: (a) The relatively small and isotropic cross sections for \(H_2\) and \(D_2\). The cross sections for \(H_2\) are seen to be about 20% larger than those for \(D_2\). (b) The relatively strong dependence of the integral cross section for HD on \(\gamma\) with largest cross sections for collinear approach from the H side.

The average \(\gamma\)-dependent vibrational energy transfer for the inelastic and charge transfer channels are

\footnote{The results for \(H_2\) were increased by 10% to account for the error introduced by including only 4 vibrational states. From previous work at least 6 or 7 would have been required to avoid this error (see ref. [3]). The calculations for the other systems are converged.}
Fig. 1. Orientational-dependent integral cross sections for charge transfer.

Fig. 2. Orientational-dependent average vibrational energy transfer for vibrationally inelastic collisions.

Fig. 3. The same as in fig. 2 but for charge transfer collisions.

presented in figs. 2 and 3, respectively. In general a pronounced steric factor for this magnitude is obtained. As expected the largest effect is obtained for HD but an unexpectedly large steric effect is obtained also for D2. The curves for H2 for both cross sections are seen to be only weakly dependent on y. The greatest probability is at y=0° and 180° in agreement with an earlier classical study [8]. The most striking feature to be noticed is the similarity between the two kinds of curves; whenever one encounters a larger energy transfer in the inelastic process a relatively large energy transfer is also obtained for the charge transfer process. The opposite is also true, namely, whenever the average energy transfer for the inelastic process is small, the same applies for the charge transfer process as well. These observations indicate a strong linkage between the two processes of vibrational inelastic and charge transfer scattering.

We have discussed this connection several times in the past [1,3,9]. The present results, based for the first time on different mass combinations, explicitly support these findings. In order to explain the large isotopic effects as obtained in figs. 2 and 3 it is important to remember that the effect of the masses enters in three different ways (recalling that H+ is always the projectile): (a) As collision partners of H+, the equal mass H atoms are expected to be more efficient in transforming translational energy into vibrational energy. (b) The vibrational energy-transfer process is expected to be more efficient the greater the mass of the atom on the far side of the colliding molecule. (c) The vibrational energy transfer is expected to be more efficient for molecules with the smallest vibrational energy level spacing, since the number of quantum states will then be greatest.

From figs. 2 and 3, we conclude that the mechanisms (b) and (c) are responsible for the small en-
ergy transfer in the case of H₂. In general one would expect the large vibrational level spacing in H₂ to be the biggest inhibiting factor, but the results for HD (γ < π/2) indicate that this may not be so. In HD the vibrational spacing is relatively large (0.455 eV versus 0.521 eV in H₂) but still large energy transfers are obtained. Apparently it is favored by the large mass of the far side D atom in HD, which is twice as heavy as the corresponding atom in H₂. The effect of the D atom, in this case, is like a solid wall so that when the hydrogen atom is pressed against the deuterium it bounces sharply back and the HD molecule becomes highly excited. If the deuterium is replaced by a hydrogen atom, its resistance to the pressure is much smaller and consequently the H₂ molecule will be less excited. The D₂ case appears to be an intermediate case. Here mechanisms (b) and (c) are responsible for promoting energy transfer but then mechanism (a) is unfavorable. A very interesting case is HD when γ > π/2 (impact at D end). Here all three mechanisms are acting in the same direction to reduce the energy transfer and the result shows the smallest energy transfer. Thus the large steric effect in HD is consistent with these mechanisms. Another possible explanation for the HD steric factor is the shift of the center of mass of HD, which is twice as close to D than to H. However, if this were the main reason for the observed steric factor then the cross sections for γ = 0 and γ = π would have to be at least five times smaller than the actually calculated ones. In fact the range of impact parameters for charge transfer for the γ = 0 orientation extends out to 3.5 Å and therefore the relative small shift (≈0.12 Å) in the position of the center of mass can hardly be an important factor.

This last observation is very important for assessing the validity of the IOSA for this anisotropic system. If the main source for the observed steric factor in HD had been the shift in the center of mass position, which is related to the greater potential anisotropy, then the observed differences might be due to different errors introduced by the IOSA which can depend on the potential anisotropy. Since, however, the steric factor appears to depend on differences of the dynamics with collision angle γ, which should be correctly treated within the IOSA, results for the H⁺ + HD system should be nearly as reliable as the ones for both the H⁺ + H₂ and H⁺ + D₂ systems.

4. Conclusions

In this work we studied steric effects for charge transfer in the three isotopic systems H⁺ + H₂, D₂, HD at the energy $E_{c.m.} = 20$ eV. Hardly any steric effects were encountered for H⁺ + H₂, significant steric effects were seen for H⁺ + D₂, and unusually large steric effects were found for H⁺ + HD. We have shown that the extent of charge transfer is directly related to the ability of the ion–diatom system to transform translational energy into vibrational energy. Due to favorable mass conditions in the H⁺ + HD system for γ = 0, it has nearly twice as large an integral charge transfer cross sections (≈1.8 Å versus ≈1.0 Å) compared to the other systems and also exhibits an interesting steric dependence.

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References