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LETTERS

Three-Dimensional Quantum Mechanical Treatment of the Reaction Ne + H_2^+ → NeH^+ + H

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In this Letter are presented three-dimensional quantum mechanical cross sections for the title reaction, as calculated for the *ab initio* potential energy surface of Urban, Jaquet, and Staemmler. The calculations were done within the coupled-states approximation. It is shown that not only are the $J = 0$ probabilities affected by numerous sharp resonances but even the energy-dependent cross sections, for which such resonances are expected to be smoothed out, are characterized by a rich resonance structure. This is the first time that such oscillatory integral cross sections have been obtained for a chemical exchange process. From comparison with quasi-classical-trajectory results, it is shown that the reaction is dominated by quantum effects to the extent that the quasi-classical-trajectory calculations sometimes become irrelevant.

The ($X + H_2^+$), X = He, Ne, systems were studied in numerous high-quality experiments which yielded data that ranged from temperature-dependent rate constants to differential cross sections.[1−7] Moreover, there are available potential energy surfaces (PES)[8,9] that can be used to compare the different theoretical approaches and experiments cited above. However, the feature which makes these systems particularly interesting is (according to quantum mechanical reduced dimensionality treatments) that they, more than other known reactive systems, are dominated by strong quantum effects.[10,11] Already in the first quantum mechanical (QM) treatment, carried out by Kouri and Baer,[10a] it was established that the (He,H_2^+) reactive interaction produces numerous sharp resonances—probably even sharp enough to affect total cross sections. A few years later Baer et al.[10e] obtained QM reduced dimensionality (reactive infinite order sudden approximation, IOSA) integral cross sections and found them to be significantly larger than the quasi-classical-trajectory (QCT) ones.[12] To our knowledge, no three-mathematical-dimensional (3MD) QM cross sections had been reported for these two systems, and therefore it was not clear to what extent reactive cross sections are affected by the resonances or eventually by other nonclassical processes (e.g. tunneling). In this paper are presented, for the first time, 3MD-QM energy-dependent cross sections for the reactions

$$\mathrm{Ne} + \mathrm{H_2}^+ (v_i, j_i = 0) \rightarrow \mathrm{NeH}^+ + \mathrm{H}; \quad v_i = 0, 1, 2 \qquad \mathrm{(I)}$$

as calculated within the coupled-states approximation (CSA).[13] The results were compared with QCT cross sections. The two types of calculations were done employing the Urban, Jaquet, and Staemmler *ab initio* PES[9a] as fitted by Pendergast et al.[9c] using an analytic form of Aguado and Paniagua.[9d]

The QM calculations follow from a time-independent approach which was introduced a few years ago.[14] It is based on

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solving the perturbative-type Schroedinger equation (SE) in the reagents (i.e., Ne + H_2^+) arrangement channel (AC). In order to be able to solve this equation, arrangement decoupling negative imaginary potentials (NIP)[15] were added to the Hamiltonian to form absorbing boundary conditions at the exits to the various products ACs. As was mentioned above, the SE was solved within the CSA known to be a reliable approximation not only for energy transfer processes[13] but also, as we found recently, for reactive systems.[16]

The aim of the calculation was to obtain the following (reactive) **S**-matrix elements

$$\mathbf{S}(t_\nu|t_{0\lambda}) = \frac{m}{i\hbar^2}\langle\psi_{t\nu}|V_{t\nu}|\Psi_{t0\lambda}\rangle \exp(i\varphi_{t\nu}) \qquad (1)$$

where $\Psi_{t0\lambda}$ is the total wave function as calculated in the reagents AC for a given initial state labeled by $t_{0\lambda}$, $\psi_{t\nu}$ is the unperturbed wave function in the products AC, $V_{t\nu}$ is the (t_ν-dependent) perturbation, $\varphi_{t\nu}$ is the corresponding (elastic) phase shift related to $\psi_{t\nu}$, and $t_{0\lambda}$ and t_ν stand for a set of relevant quantum numbers, namely:

$$t_\alpha = (v_\alpha j_\alpha \Omega_\alpha J); \quad \alpha = \lambda, \nu \qquad (2)$$

Here the letters v and j label vibrational and rotational quantum numbers, respectively, J is the total angular momentum quantum number, and Ω is the corresponding projection along the body-fixed axis. The indices λ and ν designate arrangement channels: λ for the reagents and ν for the products.

The matrix elements in eq 1, once derived as a function of various initial conditions, are used to calculate the reactive state-to-state integral cross sections according to the following formula:

$$\sigma(v_\nu j_\nu \leftarrow v_{0\lambda} j_{0\lambda}) = \frac{\pi}{k^2(v_{0\lambda} j_{0\lambda})(2j_{0\lambda}+1)} \times \sum_J (2J+1) \sum_{|\Omega_{0\lambda}|\le\tau_{0\lambda}} \sum_{|\Omega_\nu|\le\tau_\nu} |\mathbf{S}(t_\nu|t_{0\lambda})|^2 \qquad (3)$$

Here $k(v_{0\lambda} j_{0\lambda})$ is the reagents wave vector and the τ's stand for the following expressions:

$$\tau = \mathrm{Min}(J,j) \qquad (4)$$

To calculate the required **S**-matrix elements, the perturbed part of the total wave function, $\Psi_{t0\lambda}$, was expanded in terms of L^2 functions (in all coordinates). Those chosen for the present calculations are localized functions along the translational axis R_λ ($\equiv R_{\mathrm{Ne-H_2}}$) and an adiabatic basis set related to the internal coordinates (r_λ,γ_λ). In order to keep the number of L^2 functions as small as possible, the R_λ axis was divided into sectors and to each sector was attached one translational (Gaussian) function and a set of the relevant adiabatic (internal) basis functions. The size of the adiabatic set of functions in each sector was controlled by an energy parameter E_c[14c] which was chosen to be $E_c = 1.8$ eV. The numerical effort concentrated (for each E_{tot} and J) on solving ~6200 complex equations by the LU decomposition method. The unusually large number of equations was dictated by the ionic character of the surface. We found that in order to obtain converged results the range of the translational coordinate R_λ had to be extended to 8 Å (~15 au) and so the number of sectors had to be increased to ~80. The cross sections were calculated employing J values in the range $0 \le J \le J_{\mathrm{max}}$, where J_{max} is in the range (28,40) depending on E_{tot}. Due to the oscillatory nature of the J-dependent probability functions, the cross sections had to be calculated for each J, i.e. $\Delta J = 1$.

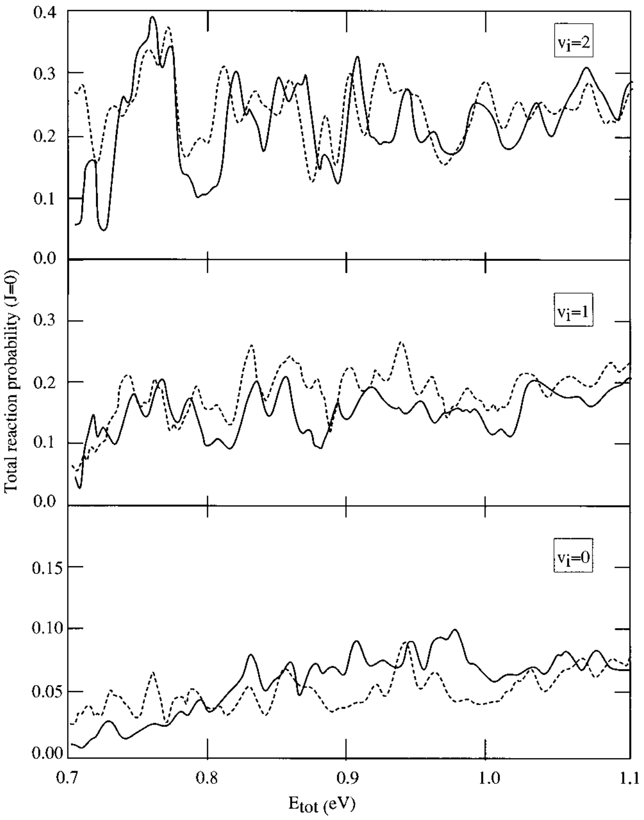

Figure 1. Energy-dependent transition probabilities for the following reactions, Ne + H_2^+ ($v_i, j_i = 0$) → NeH^+ + H; $v_i = 0, 1, 2$, as calculated for $J = 0$. — Present calculations. - - - Results from ref 11.

The first task within the numerical treatment was the calculation of $J = 0$ energy-dependent reactive transition probabilities for three initial vibrational states, namely, $v_i = 0$, 1, 2, in order to compare them with available results. Since the energy dependent probabilities were so strongly oscillatory and in order to get the overall shape of the probability functions, the calculations were done for ~300 energies and then smoothed by a five-point progressing average (along the energy axis) process. (It is important to emphasize that each of our numerical results are accurate and well converged, and the smoothing process was carried out just for the sake of the above mentioned reason.) A similar process was done for the original probabilities of Kress, Walker, Hayes, and Pendergast (KWHP).[11a] We got from KWHP their actual results as calculated for 600 energies[11b] and smoothed them to the same extent; namely, because they have results for twice as many energies, we used a 10-point progressing average process. The two types of results are presented in Figure 1. As is noticed, a qualitative fit is obtained, although quite frequently the fit becomes even quantitative. In our opinion the discrepancy could be attributed, mainly, to the relative short range assumed for the hyperspherical radius ρ ($\le$14 au) in the KWHP calculations.[11]

In Figure 2 are presented the full 3MD reactive cross sections as calculated from eq 3 using the **S**-matrix elements of eq 1. The cross section curves are seen to be oscillatory but less so than the corresponding probability curves (although sharp spikes were sometimes encountered). The QCT excitation functions are also shown, and they are, for all practical purposes, smooth. As is noticed the QCT curves deviate rather significantly from

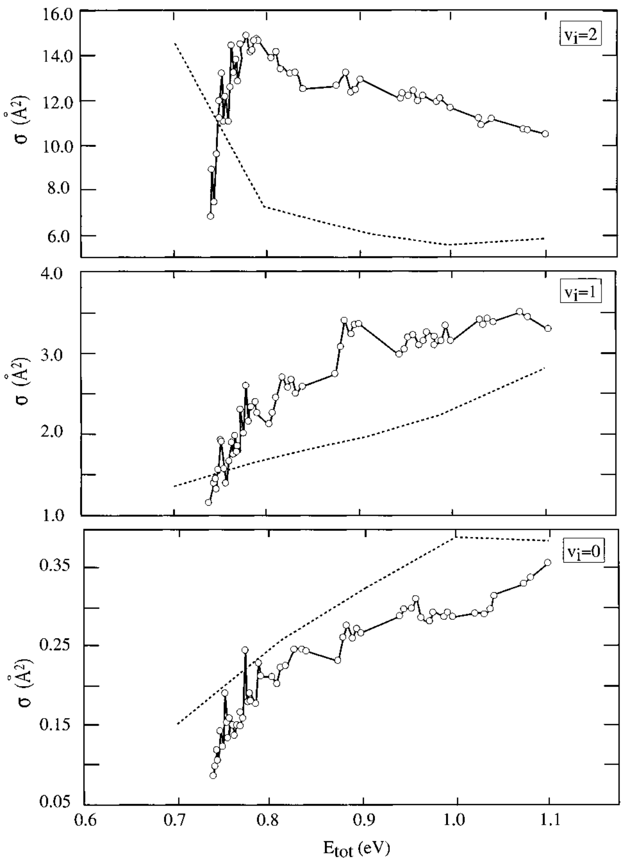

Figure 2. Energy dependent cross sections for the following reactions, Ne + H_2^+ (v_i, j_i = 0) → NeH^+ + H; v_i = 0, 1, 2. — Quantum mechanical results. - - - Quasi-classical-trajectory results.

the QM curves; the deviations are manageable for $v_i = 0$, but they increase to about 30% for $v_i = 1$ and then to 50% for $v_i = 2$.

The results presented here require a detailed analysis as they are unique in several ways. Resonances for reactive processes were encountered before and analyzed in great detail, but this is the first time that a full 3MD-QM calculation yields resonances that are observed in integral cross sections. Usually the resonances in such situations are Feshbach type resonances, and it seems to us that the present ones are of the same kind. In fact, Sathyamourthy et al.[10h,m] analyzed such resonances for the collinear configuration and found them to result from the quasi-bound states supported by the vibrationally adiabatic potential energy curves of the system. In our forthcoming full publication these 3MD resonances will be analyzed in detail. The second unique feature revealed in this study is the inadequacy of the QCT approach to reproduce correctly the QM results. Such large discrepancies between QM and QCT cross sections were not observed before in triatom systems although they seem to be quite common for tetraatom systems.[17] Again a detailed analysis will be given elsewhere. Here we will just say that the unusually large QCT cross sections at the threshold are mainly because of the inability of classical mechanics to handle correctly the zero-point energy of the products and the smaller QCT cross sections at higher energies are due to a combination of tunneling processes and the existence of the resonances.

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