Accurate 3 dimensional quantum dynamical study of the Ne+H$_2^+$→NeH$^+$+H reaction

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In this work a comprehensive, fully converged coupled states (CS) quantum mechanical (QM) study of the endothermic Ne+H$_2^+$ ion-molecule reaction is presented. The computed dynamical properties are compared with quasi-classical trajectory (QCT) and with the available experimental data. To this end, the analytical potential energy surface of Pendergast, Heck, Hayes, and Jacquet was employed. The two main features of the dynamical behavior for this system are: (1) the rich structure present in the state-selected integral cross section energy-dependent curves, which may be attributed to resonances surviving the partial wave summation; and (2) the large differences between the quantum and the QCT cross sections which are caused by the inability of classical mechanics to conserve the zero point energy. Also noteworthy are the strong enhancement of the reactivity due to higher vibrational states and the effect of the activated complex, formed during the reaction process, on the angular and the rotational distributions. © 1999 American Institute of Physics.

I. INTRODUCTION

Determining the most general rules connecting the dynamics of elementary chemical reactions and the topology of the potential energy surface (PES) has long been a challenge for chemical kineticists. To achieve that purpose, accurate state-to-state single-collision experiments were designed and performed, and new theoretical methods showing better performance, thanks to novel algebraic and numerical ideas, were recently introduced.

Theoretical and experimental data are available for the title atom–diatomic (ion) reaction:

$$\text{Ne} + \text{H}_2^+ \rightarrow \text{NeH}^+ + \text{H}, \quad \Delta H_0 = 0.54 \text{ eV},$$  \hspace{1cm} (I)

which has been a studied in different experiments, yielding results that ranged from energy-dependent cross sections to differential cross sections.\textsuperscript{1–7} This reaction is also of significant importance for practical purposes, mainly for plasmas physics.\textsuperscript{8} It was found that adding Ne atoms to plasma systems cools the high temperature plasma close to the walls, since the Ne atoms efficiently eliminate the highly excited H$_2^+$ ions, thus preventing the conversion of their internal energy into heat.

Scattering experiments for the title reaction have been performed for more than 30 years. Moran and Friedman\textsuperscript{1} studied the formation of NeH$^+$ by electron bombardment of a Ne–H$_2$ mixture, concluding that NeH$^+$ was mainly produced by H$_2^+$ in the second or higher vibrational states, namely $v_\lambda \geq 2$ (here, and in what follows, $\lambda$ designates the reagents, $v$ the products, and $v_\lambda$ stands for the vibrational state of the reactant molecule H$_2^+$). Chupka and Russell\textsuperscript{2} studied several hydrogen–rare gas (He, Ne, and Ar) mixtures by photoionization mass spectrometry and determined that NeH$^+$ was produced by vibrationally excited states with a reaction threshold lying close to the $v_\lambda = 2$ state of H$_2^+$. Ryan and Graham\textsuperscript{3} observed the formation of NeH$^+$ in weakly ionized mixtures of Ne and H$_2$. Using a photoelectron secondary-ion coincidence method, Van Pijkeren et al.\textsuperscript{4} determined the relative energy-dependent cross sections for reaction (I), which was also studied in a crossed molecular beam apparatus by Bilotta and Farrar\textsuperscript{5} in the 0.87–4.05 eV relative translational energy range. The angular distributions and flux contour maps in these experiments showed that the majority of reactive collisions lead to products in the direction of the incoming Ne atoms (forward scattering) for all energies considered. Relative total cross sections for selected vibrational levels $v_\lambda$ from 0 to 4 of the H$_2^+$ molecular ion were measured as a function of the translational energy in a beam scattering experiment performed by Herman and Koyano.\textsuperscript{6} Finally, the most recent experiments on the title reaction were performed by Brunetti et al.,\textsuperscript{7} who measured the intramolecular isotope branching ratio from chemionization of HD by metastable Ne atoms in a molecular beam apparatus.

The first accurate potential energy surface (PES) for this system was produced by McLaughlin and Thompson.\textsuperscript{9} It was subsequently fitted by Joseph and Sathyamurthy, who also used it in their quasi-classical trajectory (QCT) calculations.\textsuperscript{10} Recently, new fits of fairly accurate \textit{ab initio} PES calculations became available\textsuperscript{11–13} and were used in dynamical calculations\textsuperscript{14,15} for the title reaction. The main features of the PES used in the present calculations\textsuperscript{13} will be described below.

Stroud and Raff\textsuperscript{16} performed the first scattering calcula-
tions, running quasi-classical trajectories on several collinear PESs, including the approximate diatomics-in-molecules (DIM) surface of Hayes et al.\textsuperscript{17} Urban et al.\textsuperscript{11} reported on collinear quantum dynamical calculations applied to their collinear surface. In addition, they also performed QCT calculations on the 3D version of their surface.\textsuperscript{12} Kress\textsuperscript{14} carried out exact 3D quantum mechanical calculations for $J = 0$ using the DIM surface of Hayes et al.,\textsuperscript{17} reporting vibrational state-to-state and cumulative reaction probabilities. More recently, Kress et al.\textsuperscript{14d} reported approximate quantum cross sections, using the bending-corrected rotating linear model (BCRLM), observing numerous long-lived scattering resonances.

The title reaction and its isotopic variants were also treated by some of the present authors.\textsuperscript{15} They performed QCT and quantum reactive infinite order sudden (R-IOS) computations for Ne$^+$H$_2$ and Ne$^+$HD$^+$ in the 0.02–0.77 eV collision energy range. The goals were: (1) to study the dependence of the intramolecular isotope branching ratio in this reaction with respect to the translational energy and vibrational excitation of the molecular ion, using two different analytical PESs; and (2) to compare the results with the mass spectrometric experiments of Brunetti et al.\textsuperscript{7} Although the QCT and the R-IOS results agreed with the mass spectrometric experiments at high energies, these authors were unable to reproduce the experimental intramolecular isotope effect measured from chemionization of HD by metastable Ne atoms.

The atom molecular-ion Ne$^+$H$_2$ reaction is a moderately endoergic—$-0.54$ eV—reaction (see Fig. 1 for the arrangement of the asymptotic states of the Ne$^+$H$_2$ and the H+NeH$^+$ channels). The reaction takes place on the ground $^2A'$ PES of the NeH$_2^+$ system, which leads to Ne$^+$H$_2$ ($X^2\Sigma^+)$ at the reactants’ arrangement channel (AC) and to NeH$^+$($X^2\Sigma^+)$ at the products’ AC. Both asymptotes dissociate to the same ionic-atomic species Ne$^+$H$^+$+H. The analytical fit\textsuperscript{13} of the \textit{ab initio} calculations\textsuperscript{11} of the ground $^2A'$ PES reveals, for the collinear configuration in the entrance AC, a potential well of depth 0.51 eV below the reactants’ asymptotic potential. No other potentials’ wells or barriers (except for the endothermicity) were found for this configuration. For noncollinear configurations the fit revealed milder potential wells, but at the same time new potential barriers were exposed.

In this paper we report on a converged three-dimensional QM treatment of the

\[
\text{Ne}+\text{H}_2^+(v_\lambda,j_\lambda=0)\rightarrow\text{NeH}^++\text{H}, \quad v_\lambda=0,1,2, \quad (II)
\]

atom–diatom (ion) reaction as calculated within the coupled states approximation (CSA), employing negative imaginary potentials (NIP) to decouple the reactant and product ACs.\textsuperscript{18} A few results with this treatment have been published recently.\textsuperscript{19} This study was performed in the low (total) energy regime, which ranges from threshold, at about $E_{\text{tot}} = 0.68$ eV, to $E_{\text{tot}} = 1.10$ eV.

The paper is organized as follows: In Sec. II the theoretical approach is briefly described; in Sec. III the convergence test of the CS-NIP results is presented; the QM results are given in Sec. IV where they are, when possible, compared with QCT results; finally, concluding remarks are made in Sec. V.

II. COMPUTATIONAL METHOD

The theoretical approach employed in the present study was described in detail elsewhere,\textsuperscript{18} and therefore only a brief outline will be given here.

The main idea behind the present QM approach is the application of negative imaginary potentials (NIP) to decouple arrangement channels (AC). In this way the complicated multi-AC reactive problem reduces to a single-AC, inelastic, scattering calculation. The other main feature is the use of the perturbed Schroedinger equation (SE). Here the full wave function $\Psi_{i0}$, to be calculated in the reagents AC is assumed to be a sum of two functions: one, namely, $\psi_j$, is taken to be a solution of an unperturbed (elastic) Hamiltonian $H_{i0}$, and the other, namely, $\chi_{i\alpha}$, is still to be determined. In this way the homogeneous SE for $\Psi_{i0}$ becomes an inhomogeneous equation for $\chi_{i\alpha}$, which contains the correct boundary conditions. The solution of this equation yields the relevant $\chi_{i\alpha}$ function. The S-matrix element for the transition between a given set of quantum numbers $t_h$ related to the reagents and a set $t_s$ ($\lambda \neq \nu$) related to the products is given in the form

\[
S(t_v|t_h) = \frac{m}{i\hbar^2} \langle \psi_{t_v}|V_{t_s}|\Psi_{i0}\rangle \exp(i\varphi_{t_v}), \quad (1)
\]

Here, as before, $\Psi_{i0}$ is the total wave function, $\psi_{t_v}$ is the unperturbed (elastic) wave function in the products AC, $t_s = (v_\alpha,j_\alpha,\Omega_{\alpha},J)$, $\alpha = \lambda, \nu$ are the abovementioned sets of quantum numbers, $V_{t_s}$ is the $t_s$ dependent perturbation (namely, $V_{t_s} = H - H_{t_s}$, with $H_{t_s}$ being the Hamiltonian for the elastic scattering problem in the products $\nu$ AC), and $\varphi_{t_v}$ is the elastic phase shift related to $\psi_{t_v}$. In the present calculation, the ordinary, inelastic, CSA\textsuperscript{20} is employed. However, since each AC is treated separately, the CSA is applied twice (independently) — once in the reagents AC and once in the products AC. Substitution of a NIP in the asymptotic region of the reagents AC permits the conversion of the scattering problem into a variational bound-state problem, since it can be solved by expanding the unknown $\chi_{i\alpha}$ function in terms of
$L^2$ basis sets in all internal coordinates.\textsuperscript{18(c),e,21} To achieve that, equally spaced localized Gaussian functions are assumed along the reactants’ AC translational coordinate $R_{\lambda}$.\textsuperscript{22} For each sector, a set of adiabatic internal basis functions is calculated. To control the size of the adiabatic basis set, an overall energy parameter $E_{\text{cut}}$ is introduced, such that vibrational eigenfunctions with eigenvalues larger than $E_{\text{cut}}$ are no longer considered.

Following this approach, obtaining state-to-state S-matrix elements reduces to solving a set of linear complex algebraic equations. Then, the state-to-state reactive cross-matrix elements reduces to solving a set of linear complex differential eigenfunctions with eigenvalues larger than $E$.

It must be able to achieve total flux absorption.\textsuperscript{18} In actual use it is necessary to tune the position and parameters of the potential to obtain the correct probabilities. The NIP’s location must be compatible with the perturbing parameters of the potential to obtain the correct probabilities. The overall energy parameter must be taken to be at least as large as 8 Å, and $r_{\text{km}}$ had taken to be 4.5 Å (this is to be compared, for instance, with values of about 4 Å and 3 Å, respectively, in the case of F+H$_2$).

Another difficulty encountered was related to the number of Gaussians necessary to correctly represent the translational components of the wave function. The number of these was large for two reasons: first, simply because of the long range ionic nature of the interaction. We found that the four NIP parameters would be the most difficult to fix in this respect. However, what we found was that the NIP parameters were not as much of a problem as the translational asymptotic distance, $R_{\lambda,m}$, and the upper range of the vibrational coordinate $r_{\lambda}$ (designated as $r_{\lambda,m}$). This is mainly caused by the long range ionic nature of the interaction. We found that $R_{\lambda,m}$ had taken to be at least as large as 8 Å, and $r_{\lambda,m}$ had taken to be 4.5 Å.

FIG. 2. |$\Omega_{\lambda}$|-dependent state-selected reaction probabilities at several fixed $J$ values: (a) $E_{\text{tot}}=0.80$ eV; (b) $E_{\text{tot}}=1.10$ eV.
spected due to the presence of the potential well in the reactants channel. We found that this number should be about 80, as compared, for instance, to about 30 in the case for H+H₂.

Another parameter which has to be tuned is the value of $E_{\text{cut}}$. We found that a value of 1.6 eV yielded the required accuracy for the whole energy range.

One of the main advantages of the present approach is that approximations can be carried out at each AC independent of the others. This also applies to the CSA used here. As a result each S-matrix element is calculated for fixed values of $\Omega_v (\alpha=\lambda, \nu)$, According to Eq. (2), it is enough to consider $\Omega_0 = 0$, since all calculations are performed starting with $j_0 = 0$. For products, it is usually necessary to take into account all projections of $J$, namely $\Omega_v = \{- \tau_\nu, \tau_v\}$ where $\tau_v = \min(j_v, J)$. In practice, however, in many cases this number is much smaller and it is enough to include only a few values of $\Omega_v$ in order to obtain converged results. Such a case is shown in Fig. 2, in which $\Omega_\nu$-dependent reaction probabilities (summed over all $j_\nu$’s) for selected values of $J$, $v_\nu$ and $E_{\text{tot}}$ are presented. It is noticed that all results are usually converged when $|\Omega_\nu|=4$, but for the large $J$’s, i.e., those mostly contributing to the integral cross section, convergence is attained even for lower values of $|\Omega_\nu|$.

The convergence tests are presented in Tables I and II. In Table I the various sets of parameters tested in the calculations are listed. The fifth set in the table (p5) is the standard set for which all calculations were carried out. In Table II, the actual state-selected cross sections as calculated for $E_{\text{cut}} = 0.7$, 0.9 and 1.1 eV and for the eight different sets of parameters are presented. Notice that the range of the vibrational coordinate is shown to have a decisive influence in determining the convergence of results.

As is well known, in such calculations the main numerical effort focuses on solving a set of linear complex algebraic equations. In the present case, a system of about 6200 complex linear equations had to be solved, requiring about 1500 CPU seconds per energy per $J$ value, using a single R8000 processor SGI Power Challenge L Workstation. Thus, for instance, 50 $J$ values are required for a complete calculation of $E_{\text{tot}}=1.1$ eV and therefore such a calculation took about 75 000 CPU seconds, or 20 h.

IV. RESULTS AND DISCUSSION

A. State-selected cross sections and rate constants

The QM CSA state-selected cross sections $\sigma_{v_j=0 \rightarrow \text{all}}$ are presented in Figs. 3(a)–3(c), for $\nu_v = 0$, 1 and 2, respectively. The following is to be noted: (a) The most characteristic feature of the QM-CS results is the unusual oscillatory behavior of the cross section curve, particularly near threshold. It is important to emphasize that all the calculations of the cross sections were carried out with all $J$ values, namely for $\Delta J = 1$. It may not be obvious that this structure is caused by resonances but it is very likely so. (b) The reactive cross sections become larger as $v_\lambda$ increase. Thus, for instance, the ratio $\sigma_{v_j=2\rightarrow \text{all}}/\sigma_{v_j=0\rightarrow \text{all}}$ is usually much larger than 10 and at some energies it even approaches 100. In other words, the vibrational energy is much more effective in promoting the reaction process than is the translational energy. This can only happen when the endothermic barrier is lo-

<table>
<thead>
<tr>
<th>Parameter set</th>
<th>$E=0.70$ eV</th>
<th>$E=0.90$ eV</th>
<th>$E=1.10$ eV</th>
<th>$E=0.70$ eV</th>
<th>$E=0.90$ eV</th>
<th>$E=1.10$ eV</th>
<th>$E=0.70$ eV</th>
<th>$E=0.90$ eV</th>
<th>$E=1.10$ eV</th>
</tr>
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<td>p1</td>
<td>0.0226</td>
<td>0.134</td>
<td>0.177</td>
<td>0.0517</td>
<td>1.683</td>
<td>1.670</td>
<td>0.487</td>
<td>6.491</td>
<td>5.071</td>
</tr>
<tr>
<td>p2</td>
<td>0.0226</td>
<td>0.134</td>
<td>0.184</td>
<td>0.0518</td>
<td>1.647</td>
<td>1.695</td>
<td>0.489</td>
<td>6.480</td>
<td>5.284</td>
</tr>
<tr>
<td>p3</td>
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<td>0.180</td>
<td>0.0513</td>
<td>1.661</td>
<td>1.695</td>
<td>0.496</td>
<td>6.443</td>
<td>5.248</td>
</tr>
<tr>
<td>p4</td>
<td>0.0162</td>
<td>0.231</td>
<td>0.270</td>
<td>0.0502</td>
<td>3.097</td>
<td>3.096</td>
<td>0.497</td>
<td>8.086</td>
<td>7.030</td>
</tr>
<tr>
<td>p5</td>
<td>0.0197</td>
<td>0.243</td>
<td>0.289</td>
<td>0.0218</td>
<td>3.003</td>
<td>3.178</td>
<td>0.549</td>
<td>8.332</td>
<td>6.986</td>
</tr>
<tr>
<td>p6</td>
<td>0.0229</td>
<td>0.243</td>
<td>0.293</td>
<td>0.0284</td>
<td>2.951</td>
<td>3.162</td>
<td>0.462</td>
<td>8.130</td>
<td>6.950</td>
</tr>
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<td>p7</td>
<td>0.0232</td>
<td>0.251</td>
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<td>0.0300</td>
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<td>3.161</td>
<td>0.522</td>
<td>8.171</td>
<td>6.879</td>
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<td>0.0237</td>
<td>0.236</td>
<td>0.326</td>
<td>0.0560</td>
<td>2.899</td>
<td>3.105</td>
<td>0.674</td>
<td>8.052</td>
<td>6.876</td>
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cated in the products AC, according to the celebrated Polanyi rules. All cross sections display a clear and nice threshold behavior, as one would expect for an endothermic reaction. The QM threshold for this reaction is $E_{\text{thr}} = 0.68$ eV, which is identical to the height of the ground vibrational state of the products (see Fig. 1). The reaction from all three lowest vibrational states is endothermic, although for $v_l = 2$ it becomes almost thermoneutral, i.e., 0.66 eV versus 0.68 eV.

In Fig. 3 are also presented the energy-dependent QCT cross sections. In general, the QM and the QCT cross section curves differ significantly. The main reason for that is connected with the fact that the classical endothermicity is much smaller than the quantum one: the classical endothermicity is at $E_{\text{thr}} \sim 0.50$ eV, i.e., the height of the minimum potential well in the products’ asymptote, and the quantum one is, as mentioned earlier, at $E_{\text{thr}} \sim 0.68$ eV, i.e., the height of the $v_p = 0$ level (see Fig. 1). The only exception is the $v_l = 2$ case where the (classical) threshold is now at $E_{\text{thr}} \sim 0.66$ eV which is the height of this level itself. It is important to mention that, classically, the reaction from $v_l = 2$ is not anymore endothermic but exothermic, the exothermicity being $-0.16$ eV. This is the reason that, in this case only, the calculated cross section curve has a shape typical of a barrierless atom(ion)-ion(molecule) reaction curve, namely its maximum is at $E_{\text{thr}} \sim 0.0$ eV and from there on it becomes a decreasing function of energy.

One way to, eventually, correct for the differences between the classical and quantum results is to ignore all trajectories for which the product molecule (NeH)$^+$ has a final vibrational energy below its zero point energy (ZPE); in other words, those which do not conserve the ZPE. In Fig. 4, the comparison between the QM and the modified QCT cross sections is presented. It is seen that, whereas this modification shifts the classical threshold to the correct value, it also decreases the QCT cross sections to such small values so that, altogether, the QCT results now become even less relevant.

In Fig. 3 are also presented the R-IOS cross sections. These results are, to a certain extent, encouraging. The R-IOS method yields the correct threshold in all three cases and for $v_l = 0$ the fit is semiquantitative. However, significant deviations are observed for $v_l = 1, 2$ for which the CS cross sections are about 2–4 times larger than the R-IOS ones. The failure of the R-IOS at the higher vibrational states (and therefore at lower translational energies) and its success at the lowest one (and therefore at higher translational energies) is consistent with the relevance of this approximation. The R-IOS is an approximation that ignores rotational motions for both the reagents and the products. Obviously, such an approximation improves the higher the translational energy.
Quantum rate constants for \( j = 0 \) and \( v = 0,1,2 \) at several temperatures are presented in Table III. The large differences in the rate constants for the various initial vibrational states resemble the differences in the cross sections and are due to the different endothermicities, as discussed above.

**B. Differential cross sections**

The differential cross section for the total energies \( E_{\text{tot}} = 0.8 \) and 1.1 eV and for the three initial vibrational states \( v = 0,1,2 \) are presented in Figs. 5 and 6. In each figure, both QM and QCT cases are shown, which are, overall, rather coincident. However, significant differences are to be seen and they will be discussed below. The various curves can be divided into two categories: those that are nearly symmetric with respect to forward and backward scattering, and those which correspond mainly to forward scattering. Curves nearly symmetric are the QM for \( v = 0 \) and 1 and \( E_{\text{tot}} = 0.8 \) and 1.1 eV. The corresponding QCT curves may fit into the mainly forward category. The symmetrical feature, where the curves peak at both ends, is usually indicative of the existence of an activated complex; indeed one would expect an activated complex in these cases, particularly for low \( v \). The reason is as follows: in order to have a reaction in this case, the reagents starting in \( v = 0 \) and 1 must first direct part of their translational energy into the appropriate mode, essentially converting it from translational to vibrational, in order to overcome the endothermicity which is located in the products AC. Due to the low energy this will be a relatively long process and therefore, for it to be completed, the system must spend a long time in the close interaction region. In other words, only those collisions spending a sufficient time in the close interaction region allow for the

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**Table III. QM-CS state-specific total reactive rate constants for the Ne+H\(_2\) system at several temperatures in units of cm\(^3\) mol/s.**

<table>
<thead>
<tr>
<th>Initial state</th>
<th>( T = 300 ) K</th>
<th>( T = 500 ) K</th>
<th>( T = 700 ) K</th>
<th>( T = 900 ) K</th>
<th>( T = 1100 ) K</th>
</tr>
</thead>
<tbody>
<tr>
<td>( K_{v=0,j=0} )</td>
<td>( 1.493 \times 10^4 )</td>
<td>( 9.9216 \times 10^7 )</td>
<td>( 4.1428 \times 10^9 )</td>
<td>( 3.2012 \times 10^{10} )</td>
<td>( 1.1492 \times 10^{11} )</td>
</tr>
<tr>
<td>( K_{v=1,j=0} )</td>
<td>( 2.6964 \times 10^7 )</td>
<td>( 2.8552 \times 10^{11} )</td>
<td>( 2.0834 \times 10^{12} )</td>
<td>( 6.1958 \times 10^{12} )</td>
<td>( 1.2190 \times 10^{13} )</td>
</tr>
<tr>
<td>( K_{v=2,j=0} )</td>
<td>( 6.0050 \times 10^{13} )</td>
<td>( 1.2513 \times 10^{14} )</td>
<td>( 1.7192 \times 10^{14} )</td>
<td>( 2.0372 \times 10^{14} )</td>
<td>( 2.2398 \times 10^{14} )</td>
</tr>
</tbody>
</table>

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**Fig. 5.** Differential cross sections as calculated for \( E_{\text{tot}} = 0.80 \) eV and for the three initial vibrational states: (a) \( v = 0 \) state at \( E_{\text{tr}} = 0.66 \) eV; (b) \( v = 1 \) state at \( E_{\text{tr}} = 0.39 \) eV; (c) \( v = 2 \) state at \( E_{\text{tr}} = 0.14 \) eV. Continuous line: QM results; dotted line: QCT results.

**Fig. 6.** Differential cross sections as calculated for \( E_{\text{tot}} = 1.10 \) eV and for the three initial vibrational states: (a) \( v = 0 \) state at \( E_{\text{tr}} = 0.96 \) eV; (b) \( v = 1 \) state at \( E_{\text{tr}} = 0.69 \) eV; (c) \( v = 2 \) state at \( E_{\text{tr}} = 0.44 \) eV. Continuous line: QM results; dotted line: QCT results.
translational to vibrational energy transfer to take place, a situation which is more unlikely the higher the amount of energy transfer necessary to overcome the barrier, and this explains the low overall reactivity for \( v_1 = 0 \) and 1. However, it turns out that, due to the existence of a potential well (of a depth of 0.56 eV) in the close interaction region, the capture of portions of the interacting wave function (or wave packets in a broader sense, or trajectories within the QCT treatment) is possible. These portions (or trajectories), once they succeed in reaching the products AC, are expected to be scattered isotropically, as seen in the Fig. 5(a) for the QM case. The QCT curve is seen to be less isotropic, which means that the reactive trajectories spent less time in the interaction region before moving into the products AC. The main reason for this is that, classically, endothermicity is much lower (0.36 eV versus 0.54 eV; see Fig. 1). The angular distribution is less for \( v_\lambda = 2 \) [see Fig. 5(c)]. Here the reaction is only slightly endothermic (and classically it is, even, exothermic) and therefore only a short stay in the interaction region is required for the system to be able to react. The angular distributions become less isotropic as the translational energy increases (due to the shortening of the excitation times, accordingly). This is well noticed when one compares the corresponding curves in Fig. 5 with those in Fig. 6. Once symmetry starts to fade away the QM treatment yields the forward scattering distributions as expected for atom/ion-ion-molecule) reactions. The situation for the classical treatment is similar, but due to the lower exothermicity (as explained earlier) the corresponding reaction times are shorter and therefore the forward scattering starts sooner.

The forward type distribution as obtained in the QM treatment agrees to a certain extent with the experimental results of Bilotta and Farrar,\(^6\) which were done at \( E_{ul} = 0.8 \) eV (namely, within the range of our translational energies). In these experiments no separation with respect to the reagents vibrational states was done and therefore the experimental results apply to a linear combination of all \( \text{H}_2^+ \) states (probably a Franck–Condon distribution). Bilotta and Farrar’s experiments result in a strong forward distribution. Our results of rotational QM state-to-state cross sections, \( \sigma_{l,v} \), for the products’ ground vibrational state, i.e., \( v_v = 0 \), show a forward peaked distribution already for \( E_{ul} = 0.44 \) eV. (b) In the studied energy interval the reactive cross sections for \( v_\lambda = 2 \) are much larger than those of \( v_\lambda = 0 \) and therefore their contribution to the total differential cross sections is small (their Franck–Condon weights are not particularly large). (c) It is expected that the contribution of all higher vibrational states will also be in the forward direction, as they all lead to exothermic reactions.

**C. \( J \)-Dependent reactive probabilities (opacity functions)**

In Fig. 7 are presented the QM total opacity functions (namely the \( J \)-dependent reactive probabilities summed over all final states) for three different energies and for the three initial vibrational states. In Fig. 8 are presented the corresponding QCT opacity functions. As for the QM distributions they had to be smoothed because of the strong oscillatory behavior. The main findings for Fig. 7 are: (a) All opacity functions are oscillatory—a feature which seems to be typical for this system, also in other ways. However, it is also noted that for some reason the \( v_\lambda = 1 \) opacity functions are more oscillatory than the other two. (b) Whereas the opacity functions for \( v_\lambda = 0 \) are more or less evenly spread along the \( J \) axis, they are less so for the \( v_\lambda = 2 \) curves. In particularly the \( v_\lambda = 2 \) curve gets its main contribution from large \( J \) values. This behavior is uncommon for a tri-atom system and may be associated with a combination of two features, namely the relatively long range of the charged PES and the potential well in the interaction region. The corresponding QCT opacity functions have similar shapes but are still quite different. In general the QCT curves are seen to decrease as \( J \) increases, but on top of this general pattern they have, in particular for \( v_\lambda = 2 \) and to a lesser extent for \( v_\lambda = 1 \), an additional hump. The presence of this hump, which occurs at larger \( J \) values, renders the QCT opacity functions similar to the QM ones but the differences between them are still significant.

**D. Rotational distributions in products**

The results of rotational QM state-to-state cross sections, namely, \( J_1 \rightarrow J_v \), as calculated for three initial vibrational states and two total energies are shown in Fig. 9. It is important to emphasize that all of these distributions are obtained for the products’ ground vibrational state, i.e., \( v_v = 0 \).
imposed on those plots is the corresponding statistical distribution as derived from the rigid-rotor harmonic-oscillator (RRHO) model for this system.\textsuperscript{28} The statistical RRHO model, which in our case is essentially the RR model,\textsuperscript{28} is expected to be relevant in case the collision process is dominated by a long-lived complex, namely the NeH\textsubscript{2} complex, which enables the randomization of the total available energy between the different internal modes of the complex. In the previous sections it was claimed that at low energies the reactive NeH\textsubscript{2} process follows from an activated complex and therefore, in these cases, the rotational distributions are expected to be statistical. In Fig. 9(a) are presented the QM final rotational distributions as calculated at the low energy \(E_{\text{tot}} = 0.8\) eV. It is noticed that all three distributions are relatively close to being statistical but still, differences are observed. The rotational distribution closest to the RR distribution is the one for \(v_{\lambda} = 0\). In Sec. IV B it was explained in detail why we expect the reaction process to be dominated, in this case, by an activated complex. Both the differential cross sections and the rotational distributions support this finding. In Fig. 9(b) are presented the QM rotational distributions as calculated at the energy \(E_{\text{tot}} = 1.1\) eV. This is, in our terminology, the high energy case. In Sec. IV B it was argued, following the shape of the calculated differential cross section curves, that the reaction processes at this energy are less susceptible to the effect of the potential well and as a result they are more direct. The fact that all three rotational distributions deviate significantly from the RR distribution (not to mention the additional ripples) supports this finding.

In Fig. 10 are presented the rotational QCT state-to-state cross sections for the same cases shown in Fig. 9. The most striking feature is that the rotational classical distribution extends to larger \(J\) values. Thus the classical range for the lower energy is \([0,11]\) whereas the quantum range is \([0,7]\). In the same way, at the higher energy, the classical range is \([0,16]\) whereas the corresponding quantum range is \([0,14]\). The reason for these differences is, again, the nonconservation of the ZPE which results in a lower endothermicity thus permitting the excitation to higher \(J\) values. Also, the fact that the classical distribution is less statistical could be due to the same as explained earlier. As in the quantum case, here also the rotational distribution at the higher energy is less statistical than at the lower one.

E. The effects of resonances on the total cross sections

The state-selected cross sections for the title reactions were presented in Fig. 3. One of the most striking findings is the survival of strong resonances in the cross sections. The resonances are Feshbach-type resonances\textsuperscript{29} caused by the fact that the initial translational energy is converted to internal energy due to the existence of the potential well in the interaction region. In this section we shall analyze one of

\begin{figure}[h]
\centering
\includegraphics[width=0.4\textwidth]{fig8.png}
\caption{QCT reactive opacity functions (l-dependent state-selected probability functions) as calculated for: (a) \(E_{\text{tot}} = 0.8\) eV; (b) \(E_{\text{tot}} = 0.9\) eV; (c) \(E_{\text{tot}} = 1.1\) eV. Continuous line: \(v_{\lambda} = 2\); dotted line: \(v_{\lambda} = 1\); long dashed line: \(v_{\lambda} = 0\).}
\end{figure}

\begin{figure}[h]
\centering
\includegraphics[width=0.4\textwidth]{fig9.png}
\caption{QM final rotational distributions as calculated for (a) \(E_{\text{tot}} = 0.8\) eV and (b) \(E_{\text{tot}} = 1.1\) eV.}
\end{figure}
them, namely the one calculated for \( v_\lambda = 2 \) near the threshold in the vicinity of \( E_{\text{tot}} = 0.7 \) eV. For this we consider the energy range \( 0.69 < E_{\text{tot}} < 0.80 \) eV. In Fig. 11 are presented partial cross sections where the summation over \( J \) is done from \( J = 0 \) up to a given \( J \) value (specified in the figure). It is seen that this resonance is made up of eight curves corresponding to the eight lowest \( J \) values, some of them presenting a well-defined peak at the vicinity of \( E_{\text{tot}} = 0.70 \) eV. It is also noted that the various curves that contribute to this resonance do not just peak at one single point but each one of them has a characteristic structure in the short energy interval \( 0.695 < E_{\text{tot}} < 0.700 \) eV around the peak. As a result, not only does the summation over \( J \) not smooth out the peak structure but, on the contrary, it enhances it. It may be argued that, in the case of an exact treatment of the nuclear motion, this clearly defined resonance may still be present or not, since the CS calculations neglect the coupling between projections of the total angular momentum so that, for collisions undergoing a long-lived collision complex, the result of its influence may not be negligible. A first indicator on that may be given by the fact that exact quantum mechanical results are available for the related system \( \text{He} + \text{H}_2^+ \), which display a similar post-threshold resonance in the state-selected integral cross section. Nevertheless, this quantitative assessment of the relevance of resonances on the integral cross section is being pursued in our laboratory, by means of an exact quantum dynamics of the title reaction.

V. CONCLUDING REMARKS

A QM-CS study accompanied by a QCT treatment was carried out for the \( \text{Ne} + \text{H}_2^+ \) system. The results were presented in terms of integral and differential reactive cross sections. The study concentrated on revealing specific features of this system, as well as clarifying the relevance of the classical treatment for it. The study was carried out along the \([0.68, 1.1]\) eV total energy range. The calculations were done for three different initial states but only for the ground initial rotational state. The main findings are as follows:

The quantum treatment yields oscillatory energy-dependent cross section curves. This structure is characteristic for an exchange process dominated by resonances. The resonances are expected to be Feshbach-type resonances originating in the potential well in the interaction region, because the reaction is endothermic. Sometimes sharp peaks are observed in the cross section curve; they seem to survive the summation process of the opacity functions. In particular, a well-defined peak for \( v_\lambda = 2 \) is observed at the energy region near the threshold.

The reaction process is endothermic but the quantum and the classical endothermicities differ by 0.18 eV. This difference is large enough to make the classical treatment irrel-

![FIG. 10. QCT final rotational distributions (for the rest see Fig. 9).](image)

![FIG. 11. Partial state-selected cross sections for \( v_\lambda = 2 \) as a function of total energy. (The specified \( J \)'s are the upper limits in the summation over \( J \) in Eq. (2)). The figure is divided into five subfigures to emphasize the contributions of the individual \( J \)'s. Note the scale change when going from bottom to top panels.](image)
vant for various purposes. For instance the classical magnitude of the cross sections and the classical threshold for the reactions should be considered with special care.

Since the reaction is endothermic and a potential well exists in the close interaction region, the existence of activated complexes is allowed. The effect of these becomes important in the close interaction region, the existence of activated complexes is allowed. The effect of these becomes apparent in the (quantum) state-selected differential cross sections as well as in the final rotational distributions. At the low energy region the products tend to be scattered isotropically and the (quantum) rotational distribution tends to be statistical. As the energy is raised the differential cross sections become forward peaked and the rotational distribution is no longer statistical. Some of these features can be found in the QCT treatment but if found they are less pronounced.

The shape of the quantum opacity functions is strongly dependent on the initial vibrational states; the higher $v_l$ the larger are the contributions of the large $J$ values. The QCT cross sections behave differently; essentially, they decrease as $J$ increases with only a few exceptions.

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