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Detailed Energy Dependences of Cross Sections and Rotational Distributions for the Ne + H_2^+ → NeH^+ + H Reaction[†]

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Detailed energy dependences of state-to-state and state-to-all integral cross sections have been studied by means of exact three-dimensional hyperspherical calculations, for the complex-forming Ne + H_2^+ → NeH^+ + H reaction. Integral cross sections show an outstandingly marked structure as a function of energy. This structure has been characterized analyzing the state-to-state contributions, on one hand, and the partial cross section cumulative sums as a function of the total angular momentum quantum number *J*, on the other. As expected, the key fact is that strongly bound metastable states lead to peaks in the above quantities narrow enough to avoid an effective quenching of the resulting structure, when summing either over *J* or over final product states. This feature, which has already been found for other complex-forming reactions, indicates that quantum effects can be more relevant than expected, so as to require their explicit consideration when accurately characterizing a reactive event. Additionally, the implications of the observed behavior for the *J*-shifting approximation have been analyzed. In particular, it is shown how a clear *J*-shifting behavior is found for low *J*, $\Omega = 0$. However, it is lost as higher *J* values are considered (for $\Omega = 0$) or, as it is well-known, higher Ω projections are included in the calculation. A rationale for this behavior is presented.

1. Introduction

Intense work has been recently devoted to the exact calculation of moderately involved three-atom system dynamics, mainly due to the availability of quantum reactive scattering methods capable of handling the associated computational requirements.[1] Besides representing a harder challenge from both the computational and methodological points of view, the exact calculation of involved systems dynamics has evidenced the quantum mechanical nature of several dynamical features, in such an intense way that new intrinsic information has been generated. Perhaps the most relevant feature may be the dominant role played by metastable states and its influence on potentially measurable dynamical quantities.[2,3] These metastable states can originate on a purely dynamical basis or, alternatively, may be formed by means of a mixed contribution, from a minimum in the strong interaction region of the potential energy surface (PES) and a dynamical trapping owing to the existence of effective potential barriers. Several recent examples have appeared in the literature, demonstrating that the latter case leads to a dense spectrum of rather long-lived metastable states.[4,5] These states, as is well-known, may appear as sharp peaks, minima, or shoulders in the state-to-state, fixed *J* reactive probability as a function of total energy. However, the fingerprints of the resonance pattern do rarely survive when adequately summing up and averaging the reaction probabilities over product states and partial waves, so that they are easily smoothed out.[6] This is not case, though, for the title system, where the structured behavior of the reaction probability is not completely quenched. Actually, in some cases, the angular momentum quantum number summation leads to several, wider peaks which are amplified. Moreover, the large density of metastable states causes the effect of raising the whole integral cross section profile to larger values than expected on the basis of a purely direct collision mechanism. This has caused, for this system, a large disagreement between quantum and classical calculations, even in the high energy limit.[7−9] This is a most remarkable effect.

The above effects were preliminarily accounted for, by some of the authors,[7,8] as a part of a comprehensive quantum dynamical study on the title reaction. A centrifugal sudden-negative imaginary potential (CS-NIP)[8] method was used to calculate the state-to-all integral cross section over a fine energy grid. Results showed that (a) a dense spectrum of resonance peaks was found to dominate the reactivity over the whole energy range and (b) important discrepancies were detected between the quantum method and the results of equivalent quasiclassical (QCT) calculations. In particular, the QCT reactivity was found to be only about half the CS-NIP quantum at 1.1 eV, the highest total energy considered. Another meaningful disagreement was found at the threshold region, for the initial reactant vibrational level $v = 2$. This latter effect was attributed to the inability of the QCT method to handle correctly the zero-point energy (ZPE) at threshold energies.

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Such discrepancies suggested the application of an accurate method in order to confirm the above results, because the reaction is dominated by complex collisions, which may impose severe limitations on the applicability of the centrifugal sudden approximation. A first stage consisted in generating exact cross sections over a coarse grid, covering the complete energy range chosen for the previous studies, in order to establish the global performance of the CS approach versus the exact one.[9] These results were encouraging, since little discrepancy was found. Consequently, it was argued that the importance of metastable states was not an artifact of the centrifugal approximation (usually, approximate methods lead to stronger resonance behaviors than more accurate ones), but could actually correspond to a true dynamical effect.

The above results motivated the present work. This has consisted of a fine energy grid study of the $Ne + H_2^+$ system, using the same PES as in previous studies, focusing mainly on state-to-state and state-to-all integral cross sections as well as product rotational distributions (PRD). The effect of the summation over partial waves, which accounts for the influence of angular momentum, is analyzed here evaluating the partial cumulative cross section sums, for each value of the total angular momentum quantum number J, since it provides a natural link between the state-to-state reaction probability and a typical quantity measured in experiments, the integral cross section. Special attention is paid to the possibility of actually detecting the fingerprints of resonance reactivity. Among those quantities experimentally measurable, we focus here on product rotational distributions and their variation with energy, since they are relative quantities which can lead to precise measurements. For direct reactions, PRDs usually evolve smoothly with energy. However, for the present case we expect to find, instead, more drastic variations with small changes in energy which, although being based on a relative measure, should be important enough. This might provide an additional way of detecting the influence of reactive scattering resonances, which is based on a relative rather than on an absolute measure of the total particle flux emerging in a given state. This prognosis is based on equivalent effects actually measured in product rotational distributions of unimolecular decomposition processes.[10] Moreover, Schatz et al.[2] have discussed an example where a reactive scattering resonance influences the product vibrational distribution (PVD). Although the energies explored in the present study do not allow analyzing the PVD, the effects evidenced in ref 2 point toward the adequacy of looking at these quantities for a clear record of the resonance reactivity.

In this work, the relevance of the present results for the so-called J-shifting approximation is analyzed. This analysis is motivated by the nevertheless large overload which still represents performing a complete reactive scattering calculation at the cross section level. The J-shifting approximation simplifies the whole work to a single probability calculation. Although being a rather crude approximation, such an enormous saving makes worthwhile investing some effort in establishing its actual potentiality. In particular, it will be shown how a centrifugal barrier-type effective potential naturally emerges from the hyperspherical reactive scattering approach used here. This effective potential provides an adequate framework for discussing the accuracy of the J-shifting approximation. As a final result, it will be shown that the distortion of the effective potential, when the total angular momentum J is increased, leads to a clear departure from the pure J-shifting behavior.

The remainder of the paper is organized as follows. A brief discussion of the details of the calculation, in section 2, is followed by the results and their discussion in section 3. Discussion focuses on the components of the total integral cross section, in terms of total angular momentum partial waves (section 3.1) and product states (section 3.2). The implications of the present results for the J-shifting approximation are discussed in section 3.3. Finally, section 4 concludes.

2. Outline of the Calculations

The method employed in the present work is the close-coupling hyperspherical method as developed by Launay and LeDourneuf, which has been described with detail elsewhere[11−13] and successfully applied to a number of triatomic systems.[9,12−14] For this reason, only details concerning the present calculations will be given here.

Calculations have been performed on the 0.50 eV endoergic $^2A'$ PES of the system, as fitted to ab initio points by Pendergast, Heck, Hayes, and Jaquet in their third fit.[15] This PES shows a barrierless collinear minimum energy path with a 0.51 eV well in the entrance channel. The reactant zero-point energy (ZPE) is 0.14 eV, while the product ZPE is 0.18 eV. Thus, the endoergicity considering the ZPE is 0.54 eV. Departure from the collinear geometry leads to shallower wells and the appearance of a gradually higher barrier to reaction (see refs 7−9 for a more detailed description of the PES).

Optimal numerical parameters have been taken to be the same as in the previous exact calculation,[9] where a comprehensive convergence study was performed (including a careful check of the asymptotic matching distance), for both probabilities and cross sections. Nevertheless, they were rechecked at some of the energies, those showing prominent cross section peaks. Results remained unchanged in these cases. Calculations have been performed on a dense energy grid, essentially divided in two intervals. The first one corresponds to low energies, where most of the present work focuses, with a total of 110 equally spaced points in the 0.698−0.800 eV range, while the second ranges from 0.8 to 1.1 eV, with a cross section calculation every 0.025 eV. As will be seen in the next section, interesting effects may still be observed beyond 1.1 eV. However, calculations by means of time-independent close-coupling techniques require a larger effort, the higher the total energy, so that 1.1 eV turned out to be the highest value for which the calculations that resulted were reasonably affordable. For all energy values, converged integral cross sections have been computed. This meant including all relevant total angular momentum partial waves. Depending on the energy range, the number of partial waves was, approximately, 25, 35, 50, and 60 for 0.75, 0.80, 0.90, and 1.1 eV, respectively. For each partial wave, it has been seen, in agreement with previous calculations using the same method, that not all the projections of the total angular momentum (denoted as Ω) onto the quantization axis had to be included. This possibility relies on the fact that most of the reactive collisions take place in the collinear or near collinear configurations. In this case, it can be easily shown that the total angular momentum is essentially perpendicular to the interatomic axis and thus its projection onto this axis is small. In the present case, all Ω's have been taken for $J < 7$ but $\Omega_{max} = \pm 6$ has been kept for $J \geq 7$. This parameter was checked taking $\Omega_{max} = \pm 10$ in several reactive probability calculations, and discrepancies were smaller than 1%. More recently, a further check with $\Omega_{max} = \pm 22$ showed again no relevant change in reactive probabilities, although they are necessary to converge differential cross sections.[16]

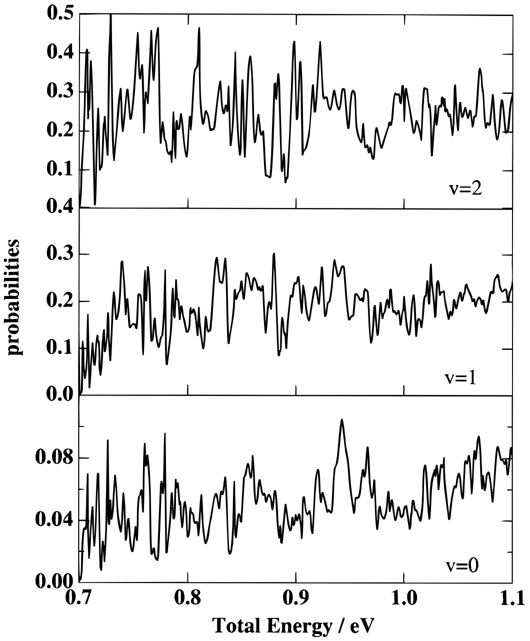

Figure 1. State-to-all $J = 0$ reaction probability as a function of total energy, for the first three reactant (v, $j = 0$) states.

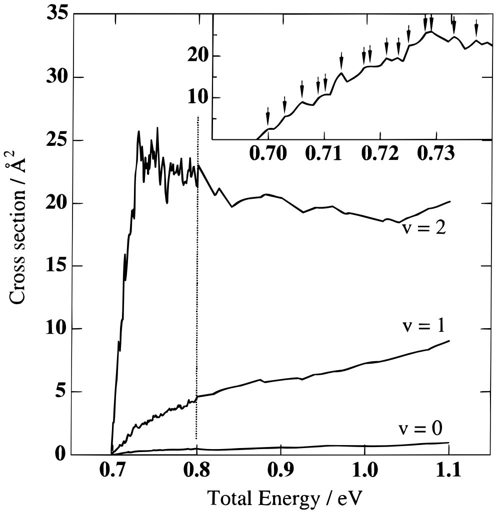

Figure 2. State-to-all integral cross section as a function of total energy, for the first three reactant vibrational levels. All cases correspond to initial $j = 0$. The inset shows an enlargement of the threshold region for the $v = 2$ case, where the arrows show the progression of maxima in the cross section. The vertical dashed line at $E = 0.8$ eV separates the fine and coarse regions in the energy scanning (see text).

3. Results and Discussion

The strongly structured behavior of the dynamics for the title reaction, as a function of the total energy, was previously anticipated when computing the $J = 0$ reaction probability. Figure 1 reproduces these results for the sake of completeness. From the average width of the probability peaks, a lifetime of roughly 1 ps can be inferred for several of them, being in addition much more dense than for the related He + H_2^+ system.[17,18]

Our main scope has been to ascertain whether the prominent structure found for $J = 0$ might survive the angular momentum summation, since different starting conditions (overlapping resonances, departure from the J-shifting behavior) seem to apply in the present work, when compared to previous studies.[2] Figure 2 shows the results corresponding to the integral, state-to-all cross sections as a function of total energy. It can be clearly seen that, in some of the cases, especially for the initial rovibrational level ($v = 2$, $j = 0$) in the finely scanned energy range (from threshold to 0.8 eV), the structure is actually kept or even amplified, rather than being quenched, when summing over J. It is remarkable that its oscillations around 0.75 eV are about 5 Å^2, intense enough to consider it detectable with the high-resolution molecular beam apparatus currently available.[19] Cross sections for ($v = 0$, $j = 0$) and ($v = 1$, $j = 0$) also show a comparable structure, but since it is relative to the absolute value of the cross section, it appears much smoother as a consequence of the y-axis scale.

3.1. Partial Wave Analysis. The fact that the resonant structure survives the angular momentum quantum number summation is not frequent in the available quantum reactive scattering calculations for triatomic systems. Previous calculations of integral cross sections for systems such as H + H_2, F + H_2, and Cl + H_2 and their isotopic variants[18] showed just the opposite behavior (see, however, ref 6), i.e., the complete quenching of the $J = 0$ structure, which was actually much less prominent. In another case, the Cl + HCl system, the reactive integral cross section showed a smooth steplike behavior.[2] A first indication of the possibility of observing a more intense surviving structure was given by Launay and LeDourneuf in their detailed calculations on the He + H_2^+ system,[18] which showed how the existence of a minimum in the PES leads to strongly bounded metastable states, so that the resulting peaks are narrow enough to avoid quenching when summing over J. An additional proof for such a behavior has been recently provided by Russell and Manolopoulos,[4] with their time-dependent wave packet calculations for the N^+ + H_2 system. However, for this latter case the authors use the adiabatic rotational approximation to compute the integral cross sections. Thus, in this case the conclusions should not be strictly definitive, although they point again toward the survival of the resonant structure.

The present system appears to be dominated by a dense pattern of (in some cases) overlapping resonances. The cross section profile versus energy thus depends on how this pattern changes as one sums over the final states and over J. This is an incoherent (since we are summing probabilities) summation which leads to a pattern, still reflecting resonances, but strongly affected by how the reaction probability changes with (v', j'), the product states, and J. It is thus difficult to rationalize on the final result without having, previously, a description of the main features resulting in the final, integral cross section quantity. This is what comes next.

A detailed image of the angular momentum summation "process" can be obtained by computing the partial cumulative summations over J, i.e., an ensemble of curves each one containing the partial wave summation of the cross section up to the J value labeling the curve. The specific expression being used is thus

$$\bar{\sigma}^J(E) = \sum_{J'=0}^{J} \sigma^{J'}(E) \tag{1}$$

The resulting graph is shown in Figure 3 for the initial rovibrational level ($v = 2$, $j = 0$), i.e., the case showing the most prominent structure. For the sake of clarity, the partial summations are shown in steps of 5, except for the $J = 40$, 50, and 60 traces. Most interesting is the finer scanned energy range, since it shows several important features.

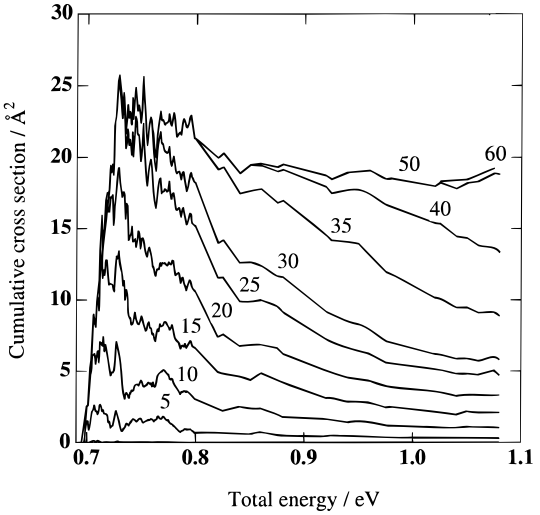

Figure 3. Cumulative cross section dependence as a function of total energy (expresion 1 in the text), for several values of the total angular momentum quantum number and initial reactant state (v, j) = (2, 0). Each trace is labeled by the maximum total angular momentum quantum number value included in the partial cross section summation.

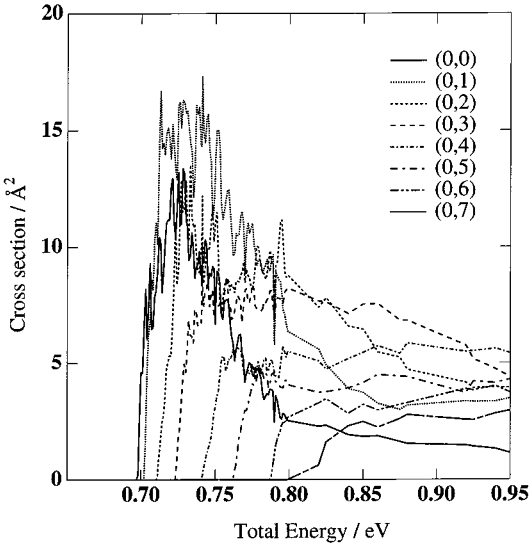

Figure 4. State-to-state integral cross sections, for several (v', j') states, for the initial state (v, j) = (2, 0), as a function of total energy.

First, it is important to notice that the $2J + 1$ factor, premultiplying the reaction probability in the cross section expression, leads to a magnification of the contribution from the highest angular momenta. A large portion of the structure surviving the complete summation actually originates in the high-J contributions. This case corresponds to the structure around 0.75 eV.

A second case we distinguish corresponds to the peaks which are found in the entire J range, as is seen approximately at 0.73 eV. This peak is found to exist even for $J = 0$ (that reaching a probability of 0.5 in the ($v = 2, j = 0$) case of Figure 1), being subsequently amplified as larger J values are considered. It is remarkable that the peak position slightly shifts toward larger energy values as larger J's are considered. This fact is a clear indicator of an energy shift owing to an increase in the effective potential barrier, as a consequence of a larger centrifugal term, in agreement with the analysis in ref 2. Perhaps a key feature would be that the shift caused by increasing J is small in this case, thanks to a relatively small rotational constant, which is in turn a consequence of the Ne heavy mass (this is especially true when comparing to the He + H_2^+ case). Nevertheless, the survival conditions undoubtedly originate from the especially intense resonant peak found in the $J = 0$ probability profile, indicating a rather strongly bound metastable state.

A third feature we wish to stress is the approximate regularity in the shoulders (rather than peaks) appearing in the low energy regime, superimposed on the rapid increase of the integral cross section. A total of 15 “bumps” can be identified in the integral cross section profile (shown by the arrows in Figure 2), both in Figures 2 and 3, among which the first seven are, excepting one (the fourth counting from the lowest in energy), almost equally spaced. Those corresponding to larger energies show their corresponding component at smaller J's, as seen in Figure 3 (so that they belong to the second case).

An opposite case, concerning the survival after J summation, is found for the three intense peaks appearing in the $J = 0$ probability, between 0.75 and 0.77 eV. The corresponding analysis for larger J's shows that they are clearly already quenched at the very first partial waves. It is seen however that those peaks, although being intense, are much broader than the intense, sharp peak analyzed in the second case. These are clearly the conditions for an effective quenching on averaging with J, and in addition, a larger contribution of direct reactivity could be found also in this case.

3.2. Product Rotational Distributions. Another interesting issue to be analyzed is the possible influence of complex formation in those quantities referring to product states, such as product energy distributions. This would lead to additional possibilities as far as the experimental detection of resonance features is concerned.[10] For the present case, only product rotational distributions are relevant, since only one (and two in the high energy regime) product vibrational state remains open at the energies explored in this study and, in particular, at the range scanned in detail. The consideration of product rotational distributions leads us to the state-to-state quantities. State-to-state integral cross sections as a function of total energy are shown in Figure 4, again for ($v = 2, j = 0$). Inspection of this figure allows easy identification of the successive product rotational thresholds. Once each product rotational channel is open, its state-to-state cross section shows a rather irregular behavior. In particular, most of the rotational levels show an initial cross section increase, followed by a smooth decrease. Superimposed on it a prominent structure is seen, reflecting the influence of the resonance states. Some of the resonant structure appears correlated between several product rotational levels, in the sense that a peak in one particular rotational level appears at the same position as a dip associated with another rotational level.

Given the structured behavior observed in the state-to-state integral cross section, one would expect strong variations to be observed in the product rotational distributions, with small changes in the total energy. This behavior is in strong contrast with that obtained for direct reactions, for which a smooth evolution for the PRD pattern is expected as a function of energy. An illustration for this is displayed in Figure 5, where the product rotational distributions are shown at four, closely spaced energies. In particular, the two first distributions, at 0.748 and 0.749 eV, differ by only 1 meV but change the maximum in the distribution from $j' = 2$ to $j' = 1$, respectively. Given the small amount of increase in energy, we think this behavior to be a rather remarkable one. The third and fourth cases, corresponding to energies of 0.755 and 0.757 eV, show a very similar behavior, although the distribution highest in energy is slightly hotter than the lower. The decrease in population for

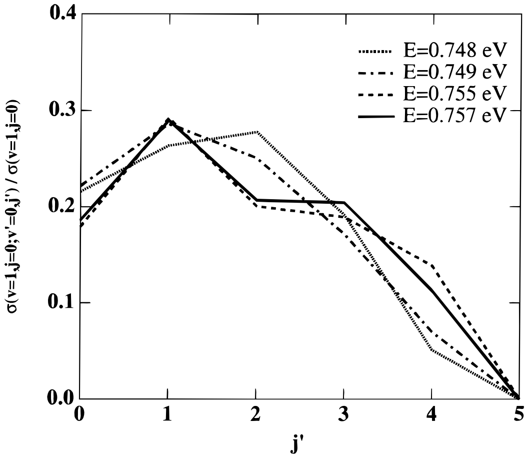

Figure 5. Product rotational distribution, at four selected total energies, for initial (v, j) = (1, 0). All distributions have been normalized to its corresponding sum.

the $j' = 2$ level is however more important, between the first and second group of transitions, since the overall energy difference is only 9 meV. A similar observation can be made for the decrease in the $j' = 0$ population, although it is not as intense as in the former case.

3.3. Implications for the *J*-Shifting Approach. The availability of exact results at the cross section level, i.e., accurate probabilities for all relevant values of the total angular momentum quantum number *J*, provides a unique benchmark for testing approximate theories aimed at simplifying the well-known angular momentum "problem". Among the approximate methods available, the *J*-shifting approach (JSA)[20] has received some attention recently.[21−23,25] The JSA, as originally formulated, assumes that rotational motion is separable from the other degrees of freedom and, furthermore, that this rotational motion corresponds to that of a rigid rotor. In spite of its apparent crudeness, its main advantage relies on its simplicity; i.e., the cross section calculation essentially amounts to a single probability calculation. It is precisely its inexpensive cost that makes worthwhile a comprehensive test, once accurate cross section results become available on systems showing more complex reaction dynamics, as in the present case.

The JSA accuracy has been tested several times,[21−25] although some of the tests were based on approximate calculations of the reaction cross section. Results show, overall, reasonably good agreement between JSA and more accurate results, when the reaction proceeds through a direct collision mechanism and a barrier to reaction shows up. In all cases some effort is devoted to ascertain which is the best reference geometry for the calculation of the rigid rotor shifting constant. It appears that choosing it to coincide with the transition state geometry leads to the best results, even for complex-forming reactions such as H+O_2[21] (although the description of HCO resonances by the JSA was shown to work better choosing the HCO minimum as the reference geometry[26]).

In the present work we focus, though, on a way of expliciting the applicability conditions for the JSA, given the complex-forming nature of the title reaction, for which a nonsimple behavior, concerning the angular momentum coupling, is expected. These conditions are analyzed, on the one hand, by means of the exact calculations presently available and, on the other, by a formal development. The latter naturally comes from the specific hyperspherical approach used here, under the proper restrictions corresponding to a collinearly dominated system.

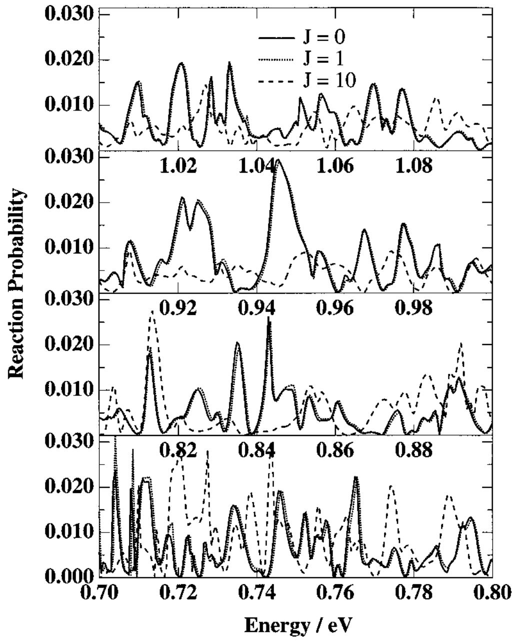

Figure 6. State-to-state reaction probabilities as a function of total energy, for $J = 0$, 1, and 10, and $\Omega = 0$, for the (v, j) = (0, 0) → (v', j') = (0, 0) transition.

It is well-known that the reaction probability as a function of collision energy, for total angular momentum $J = 1$, should evidence differences between its $\Omega = 0$ and ± 1 projections. A complete set of energy points have been inspected, in order to ensure a strict analysis in terms of energy range and resolution. Results appear to show a nice *J*-shifting behavior when comparing $J = 0$ with ($J = 1$, $\Omega = 0$) results. However, as expected, the shifting is clearly, although not extensively, broken when a second Ω component is added; i.e., one computes the ($J = 1$, $\Omega = 1$) reaction probabilities. This somewhat illustrates what was expected from previous analysis of the *J*-shifting accuracy.[21−25]

Figure 6 considers an additional case, which is the influence of *J* on a purely Ω-decoupled basis. It shows again reaction probabilities for $J = 0$, 1, and 10, with $\Omega = 0$. The *J*-shifting behavior is clearly seen in the figure for the $J = 0$ and 1 cases. However, the remarkable result is that the *J*-shifting behavior is clearly abandoned, this time extensively, for the $J = 10$, $\Omega = 0$ case. This means that even the simple increase of the total angular momentum, without Ω-coupling, is sufficient to destroy the applicability conditions for the JSA. Owing to this fact, it turns out that the *J*-shifting description of the integral cross section, for the title reaction, is poor.

A rather simple explanation for this latter behavior has been worked out. It is based on the construction of *J*-dependent surface function plots, under the specific case of collinearly dominated reactions. To see this, one begins with the expression for the angular part of the Hamiltonian, as obtained in Smith−Whitten symmetric hyperspherical coordinates[11]

$$\Lambda^2 = \Lambda_0^{\,2} + \frac{4\mathbf{J}_z^{\,2}}{\sin^2(\theta)} + \mathbf{R} \qquad (2)$$

where the first term in the rhs corresponds to the $J = 0$ angular Hamiltonian and the last terms describe the rotational and Coriolis couplings[11] (see ref 11 for a detailed description of the coordinate system and, in particular, for the meaning of the

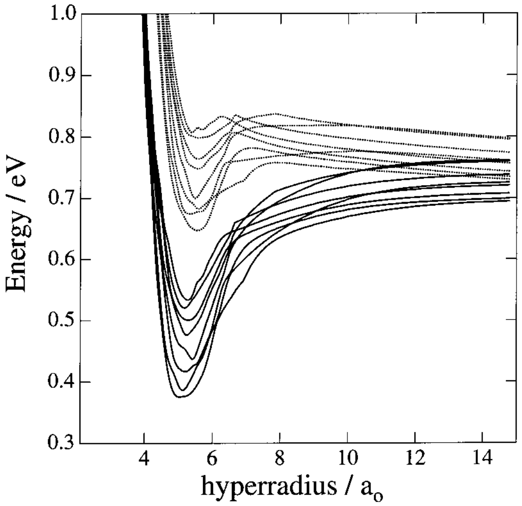

Figure 7. Selected $J = 0$, $\Omega = 0$ surface function eigenvalues as a function of the hyperradius (continuous lines). The whole set has been modified according to the last expression in section 3.3, leading to the *J*-dependent upper curve set (dotted lines). The case here shown corresponds to a moderately high *J* value. Since the transformation is homogeneous, the relative ordering for each curve is preserved.

θ and Φ hyperspherical angles). The explicit expression for it is

$$\mathbf{R} = \frac{\mathbf{J}_x^{\,2} - \mathbf{J}_z^{\,2}}{\cos^2(^1/_2\theta)} + \frac{\mathbf{J}_y^{\,2}}{\cos^2(\theta)} - \frac{2i\sin(\theta)}{\cos^2(\theta)}\mathbf{J}_y\frac{\partial}{\partial\Phi} \qquad (3)$$

Since, in the present case, we only consider $\Omega = 0$, we simply drop $\mathbf{J}_z$ from $\mathbf{R}$, resulting in

$$\mathbf{R} = \frac{\mathbf{J}_x^{\,2}}{\cos^2(^1/_2\theta)} + \frac{\mathbf{J}_y^{\,2}}{\cos^2(\theta)} - \frac{2i\sin(\theta)}{\cos^2(\theta)}\mathbf{J}_y\frac{\partial}{\partial\Phi} \qquad (4)$$

However, since θ ranges from 0 to π, where $\theta = 0$ corresponds to linear configurations, we assume that θ is close to zero and then

$$\mathbf{R} = \mathbf{J}_x^{\,2} + \mathbf{J}_y^{\,2} = \mathbf{J}^2 \qquad (5)$$

Consequently, the **R**-matrix elements in the close-coupling equations[11] lead to the simple expression

$$\mathbf{R}^J = J(J + 1) \qquad (6)$$

(in atomic units). Then we can obtain a *J*-dependent correction to each surface function eigenvalue, labeled with a generic index *k*, for each sector, according to

$$\epsilon_k^{\mathrm{corr}}(\rho) = \epsilon_k(\rho) + \frac{\pi}{2\mu\rho^2}J(J + 1) \qquad (7)$$

which ends our derivation. The last equation tells that, under the assumptions of the present model, the *J*-dependence of the surface function eigenvalues can be traced back to a simple effective centrifugal distortion barrier, although it is superimposed to a complicated bare potential. Figure 7 shows the actual change in the surface function curves, when the correction due to a given (and sufficiently large) *J* value is added. As is easily seen, the distortion in the adiabatic curves is strong enough to explain why the reactivity pattern is so distorted when considering a large *J* value, even in the case of no Ω-coupling. This is especially true when looking at the distortions, as a function of *J*, in the regions of closest approach between adiabatic curves. Therefore, the pattern of non-adiabatic couplings (i.e., reaction) might be strongly altered as *J* is increased.

A clear conclusion is that the formation of a long-lived complex complicates the applicability conditions for the *J*-shifting approximation. This is intuitive since, during the complex existence, time is given for the energy flow to break the basic separability assumption between the rotational and the remaining degrees of freedom. Despite that, the crude *J*-shifting approach has been shown to work pretty well for a variety of systems. Since it bypasses the tremendous effort of accounting for the complete effect of angular momentum on reactions, we think it deserves further attention. Further work is in progress on this subject, mainly centered at improving its applicability under complex-forming conditions.

4. Conclusions

A detailed exploration of the energy dependence of integral state-to-state and state-to-all cross sections and product rotational distributions has been performed for the $\mathrm{Ne} + \mathrm{H}_2^+ \rightarrow \mathrm{NeH}^+ + \mathrm{H}$ reaction, on the same potential energy surface as previous studies.

The most remarkable feature is the strongly structured behavior of all cross sections, and especially that corresponding to initial $v = 2$, reflecting the influence of metastable states. These states, originating from a mixed contribution of an electronic minimum and centrifugal barrier effective potentials, are bounded enough to show large lifetimes. The corresponding sharp probability peaks are found to survive the angular momentum summation.

However, the final structure which is present in the cross section stems from, basically, two kinds of behaviors. On the one hand, most of the structure originates with the high angular momenta; i.e., it is magnified by the $2J + 1$ term appearing in the cross section expression. On the other hand, some peaks really survive the whole angular momentum summation since they manifest along the whole angular momentum range. This is the case of only especially intense and sharp peaks for $J = 0$. In this case it is clear also how the centrifugal barrier shifts to higher energy values the peak position, as one considers higher angular momentum quantum numbers. The relatively small value of the rotational constant, owing to the heavy Ne mass, helps in avoiding the effective quenching of the peak, since it is little shifted.

Some of the structure, in particular that peaking between 0.73 and 0.77 eV, approximately, for $v = 2$, is prominent enough to be amenable for experimental detection in high-resolution molecular beam machines.[18] The possibility of experimental detection through relative, as opposed to absolute, measurements has also been explored by computing the state-to-state integral cross sections and the related product rotational distributions. Relevant variations in the latter quantity are found with very small increases in total energy. This important variation could be used as an additional indicator of the presence of reaction complexes during the collision. Of course, the final word has to be said once experimental data and improved estimations of the potential energy surface become available.

Given the availability of exact results, corresponding to reaction probabilities and integral cross sections, for a complex-forming reaction, it has been considered valuable to test the well-known *J*-shifting approximation and, in particular, its applicability conditions for the present involved system. Results show that not only the Ω-coupling is responsible for an erroneous behavior of the JSA, but even large J values with $\Omega = 0$ lead to important deviations. This latter feature has been interpreted in terms of the important distortion of the J-dependent effective potential curves, clearly demonstrated from a simple model arising from the symmetric hyperspherical coordinate angular part of the triatomic Hamiltonian.

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