

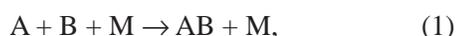
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Theoretical Chemistry & Molecular Physics

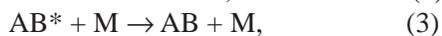
Mechanisms of Recombination and Collision-Induced Dissociation

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The chemical equation for recombination is



where A and B are any atoms, molecules, or radicals for which AB has bound states, and M is any species that can carry away the excess energy. In all the textbooks Reaction (1) is assumed to proceed only via sequences of two-body collisions, i.e., the Lindemann energy transfer mechanism,



where AB^* represents metastable intermediates, or by the similar bound complex mechanism (not shown).

Question: Can Reaction (1) also occur directly in one step via a three-body collision? Consider collision-induced dissociation,



the reverse of Reaction (1). The time-reversal invariance of quantum mechanics requires that Reactions (1) and (4) have exactly the same scattering matrix and mechanism. Hence, if recombination proceeds only via two-body collisions, then collision-induced dissociation must do likewise; that seems unlikely.

Actually, the two-body mechanisms give the wrong pressure dependence when A and B are atoms or diatomic molecules. Also, in H atom recombination they predict an ortho-para ratio in clear disagreement with experiment. Furthermore, if A and B are atoms, the standard energy transfer theory identifies the AB^* as quasibound states formed in (2) by tunneling through an angular momentum barrier. However classical mechanics, which

excludes tunneling and thus can only give recombination by true three-body collisions, gives rates in good agreement with experiment!

To get a definite answer we are doing the first 3D quantum calculations of these processes; they include all possible mechanisms at once. The first reaction we are studying is



This very simple reaction contains good physics and chemistry. Because NeH has no bound or quasibound states, the bound complex mechanism cannot contribute. However, because Ne_2 has 8 bound and 8 resonant rotational and vibrational states, both the energy transfer and true three-body mechanisms are possible, and we can clearly distinguish them.

Programming of exact three-body quantum scattering calculations on this reaction is underway. However, to quickly get answers to our questions, we have used the Vibrational Rotational Infinite Order Sudden approximation. It is expected to give semiquantitative accuracy for this problem. In it, one calculates phase shifts for the scattering of an H atom by a Ne_2 with fixed bond lengths and angles, forms a simple scattering matrix, and then calculates matrix elements of that to get the physical scattering matrix. This approximation has the nice property that it gives an exactly unitary scattering matrix for any complete set of diatomic wavefunctions, bound or continuum. Accurate numerical Ne_2 wavefunctions are used. The continuum wavefunctions are normalized to a Dirac delta function on the wavenumber k . Then, the usual formulas give the integral cross sections σ for transitions between bound states and $d\sigma/dk$ for transitions involving continuum states,

for which σ is then determined by integration over k . Two checks of numerical accuracy show our calculations have converged: (1) The completeness relation gives total integral cross sections in excellent agreement with the sum of individual integral cross sections over all possible processes. (2) For very narrow quasibound states, integration over k gives the same σ as does treating them as normalizable bound states.

As an example, we consider the collision of H with Ne₂ with an incident relative energy of only 0.0035 eV. For it, Figure 1 shows the $d\sigma/dk$ connecting all the bound states of Ne₂ to its continuum states with $j_f = 2$. This broad peak is not due to any resonances but is a direct three-body contribution! Other low j_f states behave similarly.

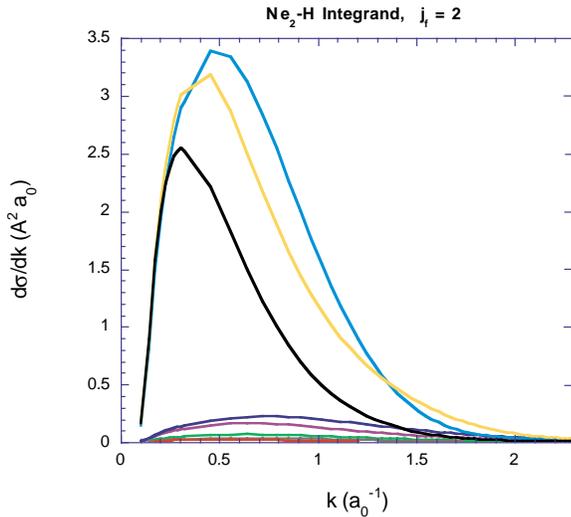


Figure 1: $d\sigma/dk$ versus k for transitions from all the bound states of Ne₂ to its continuum states with $j_f = 2$. The largest peaks are from the excited vibrational states

For the higher j_f states of Ne₂ the contributions tend to be resonance dominated. Figure 2 shows the $d\sigma/dk$ from all the bound Ne₂ states to its continuum states with $j_f = 10$. The sharp spike in this figure, which peaks at a value of 10^7 , is due to a narrow quasibound state. However, additional important broad contributions are also seen. They are due to a broad, above-barrier Ne₂ resonance of a type often omitted from energy transfer theories.

Our results show that the more deeply bound states of Ne₂ have only small cross sections to the continuum,

and their populations will be controlled by vibrational relaxation. However, its higher states have large cross sections to the continuum. At an energy of 0.0035 eV the average integral cross section from the three highest bound states to all quasibound states is 11.5, to all broad above-barrier resonances is 8.0, and to all nonresonant three-body continuum states is 5.8 square Angstroms.

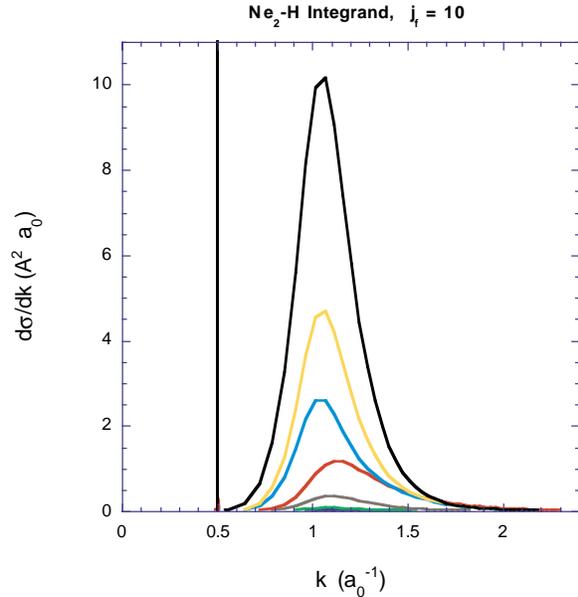


Figure 2: $d\sigma/dk$ versus k for transitions from all the bound states of Ne₂ to its continuum states with $j_f = 10$. The largest peaks are from the excited vibrational states

Hence, we conclude that three mechanisms all contribute at the same order of magnitude to the recombination and collision-induced dissociation of simple atoms; namely, the quasibound states of the energy transfer mechanism, broad above-barrier resonances usually omitted from energy transfer calculations, and direct three-body collisions! None are negligible, and the usual energy transfer calculations get less than half the total. These are the first results to show the relative contributions. Calculation of rate constants and detailed treatment of the kinetics are in process. They will provide more details yet.