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Sudden Approximation Mass Validity Criteria Values for Accurate Transition Probabilities in Two-Mode Collinear Collisions

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By comparing approximate and exact transition probabilities for several new collision systems, we have established lower, less restrictive, values for validity criteria for use in predicting which collinear atom−triatom or diatom−diatom collision systems could be reliably treated in the vibrational sudden approximation. The specific lower bounds for the atom−triatom (A + 1−2−1) validity criterion, $2m_1(2m_1 + m_2 + m_A)/[m_A(2m_1 + m_2)]$, and the diatom−diatom ($A_2 + B_2$) validity criterion, $m_B/3m_A$, are 14 and 6, respectively.

1. Introduction

The vibrational sudden approximation (VSA) was first introduced by Bowman[1] and shown to be accurate for vibrational energy transfer in collinear light atom−heavy diatomic molecule systems. Several years later the VSA was derived in a manner analogous to the previous sudden approximations used in scattering theory,[2] and reliable accuracy was demonstrated for vibrational energy transfer in collinear atom−diatom,[3] atom−triatom,[4] and diatom−diatom[5] collisions and for vibrational and rotational energy transfer in three-dimensional atom−diatom[6] collisions. In the atom−diatom cases, the VSA was made upon the single vibrational mode present, but in the cases of the two-mode collinear atom−triatom and diatom−diatom systems, the VSA was made upon only the lowest frequency vibrational mode. In the remainder of this report, we will consider collinear geometries exclusively in order to focus upon the VSA and to simplify the scattering equations to be solved so that not only the approximate but also the exact solutions may be obtained in a convenient amount of time.

In testing and developing any new approximate method, the choice of systems to study is critical since some scattering partners and collision conditions may not satisfy the assumptions inherent in the approximation. The choice of systems can be guided by validity criteria, most often given in terms of the masses of the atoms involved in the collision. There are other factors that effect the accuracy of the VSA such as the collision energy and the potential energy surface, but we will concentrate upon the simple mass validity criteria. These criteria have been reported in the VSA work[1,3−5] and can be generated from previous studies.[7] The validity criteria for a collinear atom−triatom collision (A + 1−2−1) can be written as[4]

$$\frac{2m_1 m_{\text{total}}}{m_A m_{\text{triatom}}} = \frac{2m_1(2m_1 + m_2 + m_A)}{m_A(2m_1 + m_2)} \gg 1 \tag{1}$$

Another version can be derived from eq 1 to give

$$\frac{2m_1(2m_1 + m_2)}{m_A m_2} \gg 1 \tag{2}$$

These equations show that as the mass of the end atom in the triatom increases or the mass of the colliding atom decreases or the mass of the central atom in the triatom decreases, the validity of the VSA increases. The validity criterion for collinear diatom−diatom ($A_2 + B_2$) collisions is[5]

$$m_B/3m_A \gg 1 \tag{3}$$

where the second diatom, B_2, is treated under the VSA. Equation 3 shows that as the mass of the molecule treated in the VSA increases and the mass of the colliding atom decreases, the VSA becomes more valid.

Table 1 gives the values of eqs 1−3 for the previously studied systems. The atom−triatom work established that values of the validity criteria in eqs 1 and 2 could be as low as 40 and 750, respectively, and give acceptable results but could not be as small as 9 and 30 to be reliable. This information is useful, but the large range of possible values between, for example, 40 and 9 has not been explored; therefore, picking a lower bound on these equations of 40 may be too restrictive. Similarly, in the diatom−diatom case, the lowest value of the validity criteria in eq 3 for which the VSA was reasonably accurate was found to be 12, but the only other value used was 0.74. Again, the range between 12 and 0.74 is sufficiently large to question whether the lower bound of 12 is too restrictive. Being inequalities, eqs 1−3 cannot predict precise values below which the VSA becomes inappropriate; nevertheless, less stringent values of the lower bounds could be established. In the present work, we study the agreement between the VSA and exact probabilities for other systems which also are listed in Table 1, all of which have intermediate values of the validity criteria, in order to determine less confining lower bounds.

2. Theory

The VSA equations for both atom−triatom and diatom−diatom collinear collisions have been given before.[4,5] Here we

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TABLE 1: List of Two-Mode Systems Studied Using the VSA and the Corresponding Values of the Validity Criteria

system	eq 1	eq 2	eq 3
$He + CO_2$[a]	9	30	
$Ne + BeBr_2$[b]	9	150	
$Ne + BeI_2$[b]	14	370	
$He + BeCl_2$[b]	19	160	
$He + BeBr_2$[a]	40	750	
$He + BeI_2$[a]	64	1900	
$He + HI_2$[a]	64	16000	
$O_2 + Cl_2$[c]			0.74
$N_2 + I_2$[b]			3.0
$H_2 + F_2$[b]			6.3
$H_2 + Cl_2$[c]			12

[a] Systems studied in ref 4. [b] Systems studied here. [c] Systems studied in ref 5.

present only the background necessary to provide the notation for further discussions and to define the parameters used in the current work. Assuming that the VSA is made upon the symmetric vibrational mode of the triatom or the vibrational mode of the heavier diatom (in both cases, the VSA mode is labeled with a subscript 2), the transition probabilities can be calculated using

$$P(n_1n_2 \rightarrow n_1'n_2') = |\langle n_2|S(n_1n_1';Q_2;\bar{n}_2)|n_2'\rangle|^2 \qquad (4)$$

where $\langle ... \rangle$ denotes in eq 4 an integral over the harmonic oscillator wave functions for the approximated modes. The n's are the vibrational quantum numbers, S is the VSA **S**-matrix, Q_2 is the normal coordinate for the approximated mode in the triatom or a mass-weighted internuclear distance for the heavier diatom, and $\bar{n}_2$ is the arbitrary, quantum-number-like parameter introduced in the VSA.

The potential energy function commonly employed in these collinear studies is used here and is given by

$$V(r,Q_1,Q_2) = A \exp[-\alpha(r - \gamma_1Q_1 - \gamma_2Q_2)] \qquad (5)$$

Here Q_1 is the normal mode or internuclear distance for the non-VSA mode. The values for the potential parameter, α, in eq 5 are, for the triatomic systems, based upon He−Ar, Ne−Kr, and Ne−Xe interactions[8] and become $1.8686b^{-1}$ ($He + BeCl_2$, $1\ b^{-1} = 5.29177 \times 10^{-11}$ m), $2.1927b^{-1}$ ($Ne + BeBr_2$), and $2.0301b^{-1}$ ($Ne + BeI_2$). For all of the diatom−diatom cases, $\alpha = 0.26459b^{-1}$. The values for γ_1 and γ_2 are given by $(2m_1)^{-1/2}$ and $(m_2/2m_1m_{\text{triatom}})^{-1/2}$, respectively.[9] For the diatomic cases, the γ's are both 0.5 for the homonuclear species considered here.[10] The solution to eq 4 is independent of A for sufficiently large values of A. The vibrational frequencies (in cm^{-1}, $1\ cm^{-1} = 1.986 \times 10^{-23}$ J) are required in the solution process. For the asymmetric and symmetric stretches in the triatom, these values are 1135 and 390 for $BeCl_2$, 1010 and 230 for $BeBr_2$, and 873 and 160 for BeI_2.[11] For the diatomic molecules, the vibrational frequencies are 4401.213 for H_2, 916.64 for F_2, 2358.57 for N_2, and 214.502 for I_2.[12]

On the basis of previous work,[3−5] we have chosen $\bar{n}_2 = n_2'$. The scattering equations were solved with appropriate numerical accuracy to give three reliable digits in the probabilities. All results reported herein are for a collision energy of 1.0 eV (1 eV = 1.6022×10^{-19} J) and for P(00→01). Similar results, though in some situations with less quantitative agreement, are seen with larger vibrational quantum number changes, transfer from nonzero initial vibrational states, excitations of the non-VSA vibrational mode, and other energies.

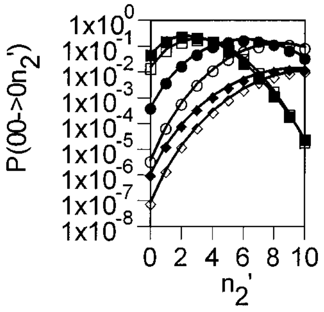

Figure 1. Comparison of the exact and VSA transition probabilities as a function of n_2' for three atom−triatom systems for a 00 → $0n_2'$ transition at 1.0 eV. Legend: $He + BeCl_2$ exact (■) and VSA (□); $Ne + BeBr_2$ exact (●) and VSA (○); $Ne + BeI_2$ exact/10 (◆) and VSA/10 (◇).

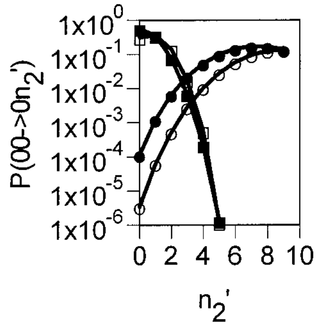

Figure 2. Comparison of the exact and VSA transition probabilities as a function of n_2' for two diatom−diatom systems for a 00 → $0n_2'$ transition at 1.0 eV. Legend: $H_2 + F_2$ exact (■) and VSA (□); $N_2 + I_2$ exact (●) and VSA (○).

3. Results and Discussion

Figure 1 shows the transition probabilities for the three atom−triatom systems with validity criteria values between those values that gave acceptable and unacceptable probabilities in previous work.[4] Note that the $Ne + BeI_2$ probabilities have been decreased by 1 order of magnitude for purposes of visualization. The implications of Figure 1 can be summarized as follows. Clearly, the VSA for $He + BeCl_2$ with criteria values for eq 1 (eq 2) of 19 (160) is qualitatively and quantitatively accurate, while for $Ne + BeBr_2$ with criteria values of 9 (150), the VSA does not reasonably reproduce the exact results. The VSA for the remaining system, $Ne + BeI_2$, shows errors of at most a factor of 10 and nearly qualitative agreement with the exact results. Taken together, these results lead to two suggestions. First, the validity criterion of eq 1 is the strongest and could be used exclusively, since the performance of the VSA is correlated with the value of this criterion. Table 1 has been organized from top to bottom with regard to eq 1, and the agreement of the VSA and exact probabilities increases monotonically with this value. There is no such smooth dependence of the degree of agreement of the VSA and the validity criteria of eq 2 as seen by the $He + BeCl_2$ results with the eq 2 value of 160 being substantially more correct than the $Ne + BeI_2$ results with the eq 2 value of 370. Second, the minimum value of the eq 1 validity criterion should be no less than 14 for decent VSA performance. Table 1 indicates that this value is significantly lower than the previous lowest value of 40.[4]

Figure 2 shows the present diatom−diatom results for systems with intermediate values of the validity criterion of eq 3. Here one can see that a value of 6.3 for the validity criterion ($H_2 + F_2$) gives very good agreement between the VSA and the exact probabilities, whereas a value of 3.0 for $N_2 + I_2$ gives poor agreement. Consequently, we suggest that a lower limit of 6 for the validity criterion of eq 3 be taken for acceptable performance of the VSA in collinear diatom−diatom collisions. Once again, Table 1 shows that this value of the validity criterion significantly decreases the lower limit for expecting reasonable VSA performance.

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