

Spectroscopy and reaction dynamics of triatomic systems

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The rovibrational spectra of H_3^+ and its isotopomers have been investigated for low ro-vibrational excitations in a very detailed way [1-4]. Using gaussian geminals [2] an absolute accuracy of the Born-Oppenheimer potential energy surface (PES) by $\sim 0.02 \text{ cm}^{-1}$ was reached. Of similar quality are calculations of relativistic effects and diagonal adiabatic contributions. For the calculated ro-vibrational transition frequencies we can show that by taking into account that non-adiabatic couplings can be simulated by using atomic masses for vibrational motion and nuclear masses for rotational motion the deviation to experiment can be reduced to a few hundredths of a wavenumber.

A recently derived analytical potential based on 69 points has been extended to give a highly reliable form of the topology of the surface far beyond the barrier to linearity. New result for higher, ro-vibrationally excited states will be presented.

Investigations of charge exchange processes $\text{H}^+ + \text{H}_2 \rightarrow \text{H}_2^+ + \text{H}$ need an extension of this work to electronically excited states for getting global surfaces for energies, adiabatic and non-adiabatic couplings. We would like to perform accurate quantum mechanical calculations of the reaction probabilities for these atom/ion -molecule collisions using time-dependent wavepacket propagation techniques.

One of our test examples for ion-molecule collisions is the reaction $\text{H}^- + \text{H}_2$ and its different isotopomers [5, 6]. In the case of $\text{H}^- + \text{D}_2 \leftrightarrow \text{HD} + \text{D}^-$ the calculated state-to-state reaction probabilities using product-Jacobi-coordinates are compared with (a) energy resolved reaction probabilities calculated with the flux-operator using reactant-Jacobi-coordinates and (b) with time-independent calculations. The shallow potential well of ca. -0.05 eV leads to some resonances in the reaction probabilities [5, 6]. New results for integral cross sections will be compared with different experiments and will reveal clearly the quality of the potential energy surface. Work for partial and differential cross sections is in progress.

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