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Photodissociation and nuclear dynamics of H_2He^+ in intense laser fields
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Introduction. The dynamics of H_2^+ molecules in intense laser fields have been an attractive research topic both experimentally and theoretically. The nuclear motion is commonly treated as that on the two lowest potential energy curves, which are coupled by the interaction between the transition dipole moment and the electromagnetic field. Through these studies, it has been found that a variety of nonlinear optical processes are induced by a laser field, and these discoveries on the simplest molecular system, H_2^+ , have afforded the basis for understanding intense-laser induced phenomena of more complex molecular systems. Therefore, it is of great interest to investigate how the photo-induced dynamics of H_2^+ is affected by the presence of additional atoms nearby. This may lead to valuable insight into how specific photochemical processes can be induced or controlled by the formation of molecular complexes such as van der Waals clusters and hydrogen-bonded complexes. The simplest molecular complex to be investigated may be a weakly bound atom-diatom type complex formed by He and H_2^+ .

Bound states and adiabatic alignment. In order to have a better understanding of the nuclear dynamics of the H_2He^+ system, all bound rovibrational eigenstates were determined for the field free H_2He^+ , utilizing an accurate electronic ground state potential energy surface (PES)¹ and full-dimensional variational computations² for the nuclear dynamics. It was found, that since the system is so weakly bound ($D_0 = 1780 \text{ cm}^{-1}$), the ground state PES supports only 16 vibrational states with 411 rovibrational levels up to the first dissociation limit. The highest rotational excitation below the threshold for the rotational predissociation has a rotational quantum number of $N = 20$. For all bound levels, the H_2^+ moiety is in its vibrational ground state, as the energy required for a single excitation in the H-H stretching mode would exceed the small dissociation energy of the complex. By taking into account time-averaged polarization interaction with an oscillating external field, and by expanding the adiabatically-aligned³ states of the “molecule + aligning field” system in terms of the bound rovibrational levels of the field-free H_2He^+ , it was found that a linear two-dimensional model is feasible to investigate the photodissociation dynamics of a spatially aligned H_2He^+ exposed to a femtosecond intense laser pulse.

Wavepacket dynamics due to femtosecond laser pulse. To investigate the time-dependent nuclear dynamics of H_2He^+ exposed to a femtosecond intense laser pulse, a reduced

dimensional model was adopted, in which the molecular complex has a linear H-H-He structure whose axis is aligned parallel to the laser polarization direction, with the H-H and H-He stretching being active. Extensive *ab initio* electronic structure calculations were carried out to construct the PESs and transition dipole moment surfaces (DMS) for the model molecular complex. The theoretical calculations revealed that the presence of He creates a third PES which allows for the charge transfer reaction, $\text{H}_2^+ + \text{He} \rightarrow \text{H}_2 + \text{He}^+$, to occur (see Fig. 1). With the PESs and DMSs at hand, the linear, spatially aligned H_2He^+ exposed to a femtosecond laser pulse was investigated by time-dependent quantum wave packet propagations, and very rich photodissociation dynamics were revealed: 1) Both excited PESs are involved in the laser-matter interaction, and a variety of photofragments are produced, such as HeH , HeH^+ , H_2 , H_2^+ , H , H^+ , He and He^+ . 2) H_2He^+ seems to dissociate to much lesser extent than H_2^+ in the same laser field conditions. 3) After fast initial dissociation processes, a slow dissociation process is observed on the ground state PES along the H-He coordinate via vibrational energy redistribution from the vibrationally excited states in the H-H stretching mode. 4) The kinetic coupling among the vibrational degrees of freedom greatly affects the wavepacket dynamics, and consequently, the dissociation product yields. 5) Vibrationally highly excited states of H_2He^+ are produced.

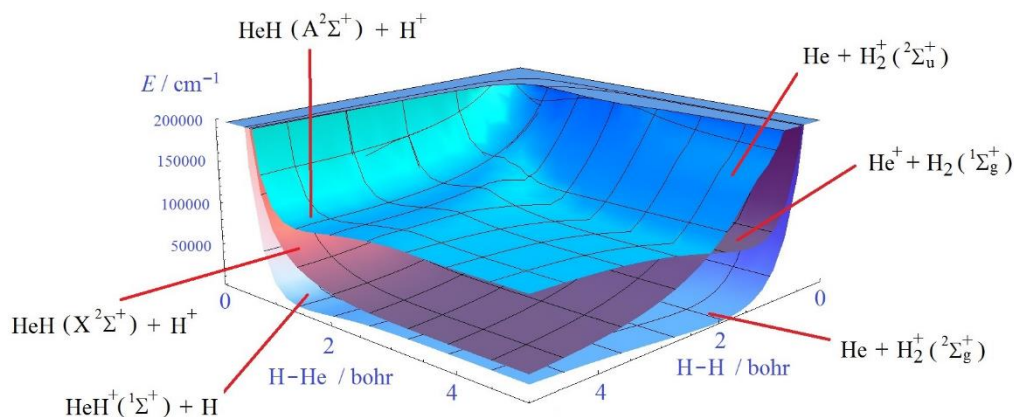


Figure 1. Potential energy surfaces of the linear $(\text{H-H-He})^+$ molecule as a function of the H-H and H-He internuclear distances. Correlated dissociation pathways are also indicated with the fragments at the asymptotic regions.

References

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