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Rotationally Resolved Threshold Photoionization of H_2S

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1. INTRODUCTION

Photoionization leading to a singly charged ion and free electron represents one the simplest molecular fragmentation processes and determination of the final states of the products (ion and photoelectron) provides a complete description of the photoejection dynamics. Quantum characterization of the molecular fragment requires resolution of the internal rovibronic state distribution which in turn reflects the exchanges of energy and angular momentum in the "scattering" of the photoexcited electron and the anisotropic molecular ion potential. With the recent development of zero kinetic energy threshold photoelectron spectroscopy (ZEKE-PES) by Müller-Dethlefs, Schlag and coworkers[1] it is now possible to take advantage of the high resolution capabilities of laser radiation and measure the rotational distributions of many small cations produced via photoionization.

We have used threshold photoelectron spectroscopy in conjunction with a VUV laser source to probe the rotational distributions of several molecular cations following one-photon VUV photoionization.[2-6] Spectra are obtained by the delayed, pulsed field ionization (PFI) method which is a variant of the ZEKE-PES technique as first demonstrated by Reiser, *et al.*[7] The PFI technique takes advantage of the similarity between the distribution of Rydberg levels populated 1–2 cm^{-1} below an ionization threshold and the partial wave distribution of the photoelectron with near zero kinetic energy. The narrowband ($\leq$1 cm^{-1}), tunable VUV radiation required for rotationally resolved photoionization measurements is produced by third harmonic or sum frequency generation of visible and/or near UV laser light in pulsed, free jet expansions of the rare gases (Ar, Kr, Xe) or the diatomic gases CO and N_2.[8,9]

In this paper, we report on the rotationally-resolved threshold photoelectron spectra of the non-linear triatomic H_2S. These measurements are an extension of our earlier study on H_2O which provided the first look at the symmetry properties of allowed rotational transitions in the photoionization of non-linear molecules.[5] For photoionization of asymmetric top systems, transitions between levels involving the rotational angular momentum projections (K_a, K_b, K_c) permit resolution of the photoelectron continua according to symmetry. For H_2O, both type A ($\Delta K_c = \pm 1, \Delta K_a = 0$) and type C ($\Delta K_c = 0, \Delta K_a = \pm 1$) rotational transitions were observed and these were shown to be associated with ka_2 and ka_1 photoelectron continua, respectively. The appearance of type A transitions with $\Delta K_a = 0$ is in variance with the predictions of a multichannel quantum defect theory (MQDT) analysis based on the symmetry properties of the initial state[10] in which the near atomic-like nature of the outermost $1b_1$ molecular orbital is invoked. The PFI results are also the subject of two very recent theoretical calculations which draw very different conclusions concerning the near-threshold photoionization dynamics for H_2O.[11,12] The new spectra reported here for the (000) and (010) states of H_2S^+ exhibit both type A and type C rotational photoionization transitions and coupled

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