MICROWAVE AND $AB\ INITIO$ STUDIES OF THE XE-CH_4 VAN DER WAALS COMPLEX

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We previously reported on experimental and theoretical studies of the Xe-N_2 complex as a test case to investigate Xe-molecule interaction potentials.[a] Here, we present our work on the Xe-CH_4 complex, which is another appealing test case because of the high symmetry of methane monomer and its anticipated near free internal rotation. As a starting point, an $ab\ initio$ potential energy surface was constructed at the CCSD(T) level of theory. The recently developed aug-cc-pVQZ-PP basis set was used for the xenon atom and the aug-cc-pVTZ basis set for the other atoms. The basis sets were supplemented with bond functions. Dipole moments were also calculated at various configurations. The reliability of the $ab\ initio$ calculations was tested against the experimental rotational transition frequencies. Rotational transitions were measured using a pulsed-nozzle Fourier transform microwave spectrometer. Transitions within three internal rotation states, namely the j=0, K=0; j=1, K=0; and j=2, K=1 states, were measured and assigned. Nuclear quadrupole hyperfine structures due to the presence of ^{131}Xe (I=3/2) were detected and analyzed. It was found that the j=1, K=0 state is perturbed by a Coriolis interaction with a nearby j=1, K=1 state. For isotopomers containing CH_3D and CHD_3, the j=2 states are no longer metastable and could not be observed. The spectroscopic results were used to derive information about the molecular structure and intermolecular dynamics of the Xe-CH_4 complex.

[a] Q. Wen and W. Jäger, **paper WH09**, 59th $International\ Symposium\ on\ Molecular\ Spectroscopy, Ohio\ State\ University, Columbus, Ohio, USA, June\ 21-25, 2004.$