

MICROWAVE AND *AB INITIO* STUDIES OF THE Xe-CH₄ VAN DER WAALS COMPLEX

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We previously reported on experimental and theoretical studies of the Xe-N₂ complex as a test case to investigate Xe-molecule interaction potentials.^a Here, we present our work on the Xe-CH₄ 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 ¹³¹Xe ($I=3/2$) 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 CH₃D and CHD₃, 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-CH₄ complex.

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