HIGH RESOLUTION INFRARED SPECTRA OF CARBON DIOXIDE SOLVATED WITH HELIUM ATOMS

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Infrared spectra of He_N-CO_2 clusters with N up to about 20 have been studied in the region of the CO_2 ν_3 fundamental band (2350 cm^{-1})
using a tunable diode laser spectrometer and pulsed supersonic jet source with cooled (> -150 C) pinhole or slit nozzles and high backing pressures (< 40 atm). Compared to previous studies of He_N-OCS [1] and -N_2O [2] clusters, the higher symmetry of CO_2 results in simpler spectra but less information content. The binary complex, He-CO_2, was studied previously by Weida et al. [3]. With increasing cluster size, N = 2 to 17, we observe discrete rotation-vibration transitions ($R(0), P(2), R(2)$) whose analysis yields the variation of the band origin and B rotational constant over this size range. The vibrational origin variation is very similar to He_N-OCS, with an initial blue shift up to N = 5, followed by a monotonic red shift, consistent with a model where the first 5 He atoms fill a ring around the equator of the molecule, forcing subsequent He atom density to locate closer to the ends. The B value initially drops as expected for a normal molecule, reaching a minimum for N = 5. Its subsequent rise for N = 6 to 11 can be interpreted as the transition from a normal (though floppy) molecule to a quantum solvation regime, where the CO_2 molecule starts to rotate separately from
the He atoms. For $N > 13$, the B value is approximately constant with a value about 17% larger than that measured in much larger helium nanodroplets [4]. Very recent quantum Monte Carlo simulations by Mezzacapo and Moroni are in excellent agreement with these experimental results [5].

References

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