AN ANALYTIC THREE-DIMENSIONAL POTENTIAL ENERGY SURFACE FOR CO_2-He, AND ITS PREDICTED INFRARED SPECTRUM

HUI LI and ROBERT J. LE ROY, *Guelph-Waterloo Centre for Graduate Work in Chemistry and Biochemistry, University of Waterloo, Waterloo, Ontario N2L 3G1, Canada*.

A three-dimensional, analytic potential energy surface for CO_2-He that explicitly incorporates its dependence on the Q_3 asymmetric-stretch normal-mode coordinate of the CO_2 monomer, has been obtained by least-squares fitting new *ab initio* interaction energies to a new potential form. The potential energy values were obtained from a supermolecule calculation performed at the CCSD(T) level using an aug-cc-pVQZ basis set supplemented with bond functions, and the full counterpoise correction was applied. These points were fitted to a 3-dimensional generalization of the "Morse/Long-Range" potential function form[a] which incorporates theoretically known angle-dependent long-range inverse-power dispersion coefficients. The three-dimensional discrete-variable representation method was employed to calculate the rovibrational eigenvalues, without separating the inter- and intramolecular nuclear motions, and our simulated infrared spectra in ν_3 region of CO_2 is compared with experiment.[b] This three-dimensional surface will be used to predict the IR vibrational frequency shifts which have been observed for CO_2-$(He)_N$ clusters with N up to 20.[c]

[a] R.J. Le Roy and R.D.E. Henderson, *Mol. Phys.* (2007, in press).
[b] M.J. Weida, J.M. Sperhac and D.J. Nesbitt, *J. Chem. Phys.* **101**, 8351 (1994).
[c] J. Tang and A. R. W. McKellar, *J. Chem. Phys.* **121**, 181 (2004).