THEORETICAL STUDIES OF THE $\tilde{B} \leftarrow \tilde{X}$ TRANSITIONS IN He·ICl AND He·Br_2

ANNE B. McCOY, *Department of Chemistry, The Ohio State University, Columbus, OH 43210*; JOHN M. HERBERT, *Department of Chemistry, University of California, Berkeley, CA 94720*; JOSHUA P. DARR, DAVID S. BOUCHER, DAVID B. STRASFELD and RICHARD A. LOOMIS, *Department of Chemistry, Washington University, Saint Louis, MO 63130*.

The electronic ($\tilde{B} \leftarrow \tilde{X}$) transitions of He·$Br_2$ and He·ICl have been investigated. In these studies literature potentials are used for all but the X-state of He·Br_2.[a,b] In that case, we calculated the potential at the CCSD(T)level of theory using the SDD+G($3df$) basis for Br, the aug- cc-pVQZ basis for He and a $3s3p2d2f1g$ set of bond functions, optimized for rare-gas molecule interactions,[c] centered at the midpoint between He and the Br_2 center of mass. The potential was fit it to an expansion in Legendre polynomials and radial functions that had the proper short- and long-range behaviors. Using these potentials, the energies and wave functions of the bound states of the complexes are generated for $J \leq 8$ and from these the vibronic spectra are computed over a range of temperatures from 0.1 to 2.5 K. Excellent agreement with the reported spectra is obtained. Based on these results we compare the temperature dependencies of the experimental and calculated spectra to obtain insights into the relative binding energies of the linear and T stereo isomers of both of these complexes.

[a] A. B. McCoy, J. P. Darr, D. S. Boucher, P. R. Winter, M. D. Bradke, and R. A. Loomis, J. Chem. Phys. 120, 2677 (2004) and references therein.
[b] M. P. de Lara-Castells, A. A. Buchachenko, G. Delgado-Barrio, and P. Villarreal, J. Chem. Phys. 120, 2182 (2004).
[c] S. M. Cybulski and R. R. Toczylowski, J. Chem. Phys. 111, 10520 (1999).