POTENTIAL ENERGY SURFACES AND VIBRATIONAL EIGENSTATE CALCULATIONS FOR THE $c^1\Pi$, $a^1\Delta$, $A^3\Pi$ AND $X^3\Sigma^-$ STATES OF NH-Ne

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We have recently recorded rotationally resolved spectra for the *c*-*a* and *A*-*X* transitions of the NH-Ne Van der Waals complex. The spectra show complex patterns of vibronic bands that cannot be reliably interpreted using conventional spectroscopic analysis techniques. In order to interpret these data we have simulated the spectra using high-level theoretical methods. Calculations for the singlet states are near completion, while those for the triplet states are in progress.

Potential energy surfaces were calculated for the singlet states derived from the π^2 configuration ($a^1\Delta$, $b^1\Sigma^+$ and $c^1\Pi$). *Ab initio* calculations were performed at the CASPT2 level of theory (CAS(4,4)), using Dunning′s basis set from avdz to av6z.

Potential surfaces for the *a*, *b* and *c* states are similar in their topology. The global minimum for all of these surfaces corresponded to the linear, hydrogen-bonded configuration. Secondary minima are found for collinear Ne-NH. The orbital degeneracies of the $a^1\Delta$ and $c^1\Pi$ states are lifted by side-on approach of the Ne atom, but this splitting is a minor perturbation, consistent with the fact that the states arise from the π^2 configuration.

In agreement with the experimental data, the depth of the Van der Waals interaction increases on *c*-*a* excitation, and the equilibrium bond length contracts. Bound state calculations predicted dissociation energies (D_0) and bond lengths ($<R>$) of 16.6 cm^{-1} and 4.01 for the *a* state, and 24.5 cm^{-1} and 3.70 for the *c* state. The predictions for the *a* state are reasonable, while the average bond length for the *c* state is too long. It was noted that the zero-point energy in the *c* state (71.8 cm^{-1}) takes up 75% of the binding energy, causing underestimation of the D_0 value and the monomer to complex red-shift.