BOUND RO-VIBRATIONAL STATES OF H_2...CN($X^2\Sigma^+$) VAN DER WAALS COMPLEX

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The abstraction reaction H_2+CN $\longrightarrow$ H+HCN proceeds via a collinear transition state. The entrance channel to this transition state may be examined through spectroscopic studies of the H_2-CN van der Waals complex. In addition, as the barrier to reaction is only 1200 cm^{-1}, it may be possible to initiate reaction within the cluster by vibrational excitation of the H_2 moiety. To learn more about the pre-reaction dynamics and identify states that sample the transition state geometry, we have examined the characteristics of bound states supported by the van der Waals well.

A previously reported 4-D interaction potential (with H_2 and CN bonds fixed) was used to calculate the bound states for **J**=0,1,..., ignoring spin. The ro-vibrational eigenstates are calculated in a body-fixed formalism, where the unsigned projection of **J** onto van der Waals bond (K) and its reflectional parity (ϵ) are nearly good quantum numbers. For the *para*-H_2 complex the lowest energy state is $K=0^+$ corresponding to the **J**=0 manifold. Its binding energy with respect to the H_2(j=0)+CN(j=0) asymptote is ~16 cm^{-1}. Similarly, the *ortho*-H_2 complex has a $K=0^+$ ground state deriving from **J**=0. It is bound by ~31 cm^{-1} relative to the H_2(j=1)+CN(j=0) asymptote. In both cases, the first excited state is only ~1 cm^{-1} above the zero point; it derives from **J**=1 and belongs to $K=0^-$ symmetry with some mixing from $K=1^-$ state. Potential and Coriolis coupling terms mix different K and ϵ states, rendering the eigenstate structure very complicated. Examination of probability density for the *ortho*-H_2 complex showed that some low-lying states sample the linear H-H...C-N geometry.