BOUND RO-VIBRATIONAL STATES OF H₂...CN(X²Σ⁺) VAN DER WAALS COMPLEX

ALEXEY L. KALEDIN, MICHAEL C. HEAVEN, JOEL M. BOWMAN, Cherry L. Emerson Center for Scientific Computation and Department of Chemistry, Emory University, Atlanta, GA 30322.

The abstraction reaction \( H_2+CN \rightarrow H+HCN \) 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 (\( e \)) are nearly good quantum numbers. For the \textit{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 \( \sim 16 \text{ cm}^{-1} \). Similarly, the \textit{ortho}-\( H_2 \) complex has a \( K=0^+ \) ground state deriving from \( J=0 \). It is bound by \( \sim 31 \text{ cm}^{-1} \) relative to the \( H_2(j=1)+CN(j=0) \) asymptote. In both cases, the first excited state is only \( \sim 1 \text{ cm}^{-1} \) 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 \( e \) states, rendering the eigenstate structure very complicated. Examination of probability density for the \textit{ortho}-\( H_2 \) complex showed that some low-lying states sample the linear \( H-H...C-N \) geometry.