

Variational calculations of HBN energy levels in the $X^2\Pi$ and $A^2\Sigma^+$ states

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Rok wydania

2003

Czasopismo

Journal of Chemical Physics

Numer woluminu

119

Strony

4197-4203

DOI

10.1063/1.1594174

Kolekcja

Naukowa

Język

Angielski

Typ publikacji

Artykuł

Streszczenie

A theoretical study of the HBN radical in the $X^2\Pi$ and $A^2\Sigma^+$ states, taking into account vibronic coupling effects, is reported. The lowest ($1^2A'$, $1^2A''$, $2^2A'$) potential energy surfaces (PES) of the HBN–BNH system have been studied to identify all stationary points. The HBN minimum was found to be 20.0 kcal/mol above BNH, with an isomerization barrier of $\approx 11\,000\text{ cm}^{-1}$ on the $1^2A'$ surface. For the HBN isomer, accurate near-equilibrium three-dimensional diabatic PESs for the ground $X^2\Pi$ ($1^2A'$, $1^2A''$) and first excited $A^2\Sigma^+$ ($2^2A'$) electronic states have been calculated at the multireference configuration interaction level of theory, with extended basis set. A vibronic coupling between bend and BN stretch, analogous to that found in the isoelectronic C_2H and HCN^+ radicals, has been found to take place due to the crossing of the $X^2\Pi$ and $A^2\Sigma^+$ states at energies close to $11\,000\text{ cm}^{-1}$. Vibronic energy levels of HBN and DBN have been calculated variationally using a previously developed method [Carter et al., Mol. Phys. 98, 1967 (2000)] suitable for three-atomic molecules showing three-state vibronic interactions. Energy levels of Σ and Π symmetry up to $10\,000\text{ cm}^{-1}$ for HBN, and 8800 cm^{-1} for DBN, are reported. It is shown that due to the high-energy surface crossing, the vibronic interaction becomes non-negligible only for levels above 8500 cm^{-1} . For all levels, Renner–Teller effects and Fermi resonances are analyzed.

Adres publiczny

<http://dx.doi.org/10.1063/1.1594174>

Strona internetowa wydawcy

<https://www.aip.org/>