The Theoretical Calculation of Potential Energy Functions and Thermodynamic Functions for the Ground State of PuN

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Abstract The potential energy function force constant and spectroscopic data for the ground state X⁶Σ⁺ of PuN have been derived by the Gaussian 98 program with the B3LYP method based on the approximation of relativistic effective core potential for Pu atom and all-electron 6-311G* basis set for N atom. The separated atomic group method is used to derive the possible electronic states for PuN. The ground states for Pu and N are ^4S_1 respectively which are the components of irreducible representation of the S^[(n)] group. PuN belongs to the C₆₉ group. The irreducible representations of the S^[(n)] group can be resolved into those of the C₆₉ group. That is the possible electronic states of PuN are given. P[(6^4S_1),] and N[(4^4S_1),] are resolved into the direct sum of C₆₉. Their direct product and its reduction are the possible electronic states of PuN. Dissociation limit is derived by atomic and molecular reaction statics. The potential energy function of the ground state for PuN molecule is derived by ab initio with the B3LYP method based on the approximation of relativistic effective core potential for Pu atom and all-electron 6-311G* basis set for N atom and fitting the Murrell-Sorbie M-S function. In addition the thermodynamic function ΔH₀, ΔS₀, and ΔG₀ of PuN in the standard state are also calculated which are -487.239 kJ/mol 95.345 J/mol K and -515.6661 kJ/mol respectively.

Key words PuN Potential energy function Thermodynamic Function B3LYP
论计算

已有研究方法对处理电子相关问题，在量子化学计算中，

本工作用镧系和锕系元素化合物分子的核外电子数多，

近似下，分子的基态势能函数与光谱常数的计算

分子的电子状态与离解极限(B, M)

方法处理镧系和锕系化合物分

序数，当二者生成

可得到

密度泛函

学

物理

计算出力常数与光谱数据

其中，

通过计算优化出平衡核间距，然后用最小二乘法拟合出

数据的关系

势能曲线，由图

及不同

为离解能

表

的

Table 1 Parameters of the potential function of PuN

<table>
<thead>
<tr>
<th>State</th>
<th>(R_e/\text{nm})</th>
<th>(D_r/\text{eV})</th>
<th>(a_1/\text{nm}^{-1})</th>
<th>(a_2/\text{nm}^{-2})</th>
<th>(a_3/\text{nm}^{-3})</th>
</tr>
</thead>
<tbody>
<tr>
<td>PuN (X^6\Sigma^+)</td>
<td>0.1937</td>
<td>3.4328</td>
<td>22.0291</td>
<td>95.5571</td>
<td>601.2379</td>
</tr>
</tbody>
</table>

Table 2 Derived force constants and spectroscopic data

<table>
<thead>
<tr>
<th>State</th>
<th>(f_2/\text{eV/\AA^2})</th>
<th>(f_3/\text{eV/\AA^4})</th>
<th>(f_4/\text{eV/\AA^6})</th>
<th>(\omega_e/\text{cm}^{-1})</th>
<th>(\omega_e\chi_e/\text{cm}^{-1})</th>
<th>(B_e/\text{cm}^{-1})</th>
<th>(\alpha_e/\text{cm}^{-1})</th>
</tr>
</thead>
<tbody>
<tr>
<td>PuN (X^6\Sigma^+)</td>
<td>0.1618</td>
<td>-6.7967</td>
<td>257.3428</td>
<td>455.5567</td>
<td>2.1511</td>
<td>0.3395</td>
<td>0.0026</td>
</tr>
</tbody>
</table>
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The application of the same method was used to calculate the heat of formation $\Delta H$, the heat capacity $C_p$, and the entropy $S$ of molecules $(+) \text{ and } (+)$ in the ground state $\text{PuN}$.

Quantum chemistry calculations of single atoms or molecules were considered as ideal gases, where the energy $E$ was obtained from functions $H$.

Under standard conditions, for calculating the reaction $H \text{PuN} \rightarrow H \text{Pu} + C_p$, the heat of formation $\Delta H$ is calculated as

$$\Delta H_n = H_{\text{PuN}} - H_{\text{Pu}} - \frac{1}{2}H_{\text{N}_2}$$

The standard thermodynamic functions for $H\text{PuN}$ and $H\text{Pu}$ are shown in Table 3.

<table>
<thead>
<tr>
<th>$H_{\text{PuN}}$ (kJ/mol)</th>
<th>$S_{\text{PuN}}$ (J/mol K)</th>
<th>$C_p$ (J/mol K)</th>
</tr>
</thead>
<tbody>
<tr>
<td>12.65012</td>
<td>245.446</td>
<td>33.4849</td>
</tr>
<tr>
<td>23.31905</td>
<td>191.418</td>
<td>29.1085</td>
</tr>
<tr>
<td>5.1779</td>
<td>54.392</td>
<td>26.2476</td>
</tr>
</tbody>
</table>

The electronic contribution to the heat of formation $\Delta H_e$ is calculated as

$$\Delta H_e = \Delta_{\text{sub}} H_{\text{PuN}} + \frac{1}{2}D_{e\text{N}_2} - D_{e\text{PuN}}$$

$\Delta_{\text{sub}} H_{\text{PuN}}$ is calculated from $H_{\text{PuN}}$ and $H_{\text{Pu}}$.

$D_{e\text{N}_2}$ and $D_{e\text{PuN}}$ are single bond dissociation energies.

The calculation was performed at the temperature $T = 298$ K, yielding $\Delta H_e = -483.0557$ kJ/mol.
运动和电子运动的贡献,可以得到反应式(1)的总焓变为
$$
\Delta f H^0 = \Delta H_a + \Delta H_e
$$
$$
\Delta S^0 = S_{fB} - S_{B} - \frac{1}{2} S_{N_2}
$$
$$
\Delta f G^0 = \Delta f H^0 + T \Delta S^0
$$

表1中的熵已包含上述两部分的贡献,这样反应式(1)的标准自由能变化可以由下式计算
$$
\Delta f G^0 = -487.239 \text{ kJ/mol} \Delta f S^0 = 95.345 \text{ J/mol K} \Delta f G^0 = -515.6661 \text{ kJ/mol}.
$$

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参

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