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RESEARCH PAPER

Structures and Potential Energy Functions of PdN and PdN2 Molecules

Yu Zhu, Gang Jiang*, Fang Fang, Guifeng Yu, Zhenghe Zhu

Institute of Atomic and Molecular Physics, Sichuan University, Chengdu 610065, P.R. China

Abstract: Based on the relativistic effective core potential (RECP/SDD) for Pd atom and AUG-cc-pVTZ basis function for N atom, the structures of PdN and PdN_2 have been optimized using B3LYP method. The results show that the ground state of PdN is $^4\Sigma^-$ and the ground state of PdN_2 is $C_{\infty V}$ symmetry and $^1\Sigma^+$ state. The Murrell-Sorbie potential energy function of PdN molecule has been fitted through the least square fitting, and the potential energy function of PdN_2 is based on many-body expansion theory. The potential energy curves describe the structure character of PdN and PdN_2 ground state molecules correctly, and detail the inner transfer process of Pd. There is a saddle point in C_{2V} structure (R_{NN} = 0.11700 nm, R_{PdN} = 0.22088 nm). The energy barrier of inner transfer is 0.5197 eV, which is close to the calculated value 0.4560 eV

Key Words: PdN; PdN_2; Density functional method; Relativistic effective core potential (RECP); Many-body expansion potential energy function

Using the palladium alloys for hydrogen diffusion membrane method has its unique superiority in pick-up, separation and purification of hydrogen isotopes. But the disadvantage of using Pd alloys membrane is that impurity of gases can poison it through adsorption, dissociation and occupancy course on the membrane surface thus changing its structure. There was a preliminary study of impurity gases poisoning palladium alloys membrane[1,2]. In this article, the structural characters of possible resultants such as PdN and PdN_2 of Pd and N_2 are calculated, and the potential energy functions are given. These are very important to understand the molecule reaction dynamics and micro-mechanism occurring during membrane poison of palladium alloys.

1 Calculation method

Pd is a heavy transition element. Its relativistic effect is very evident because of *d* orbit interaction. Whereas the character of atom is decided mostly by valence electron, Pd can be dealt using RECP (Relativistic Effective Core Potential). The results have been given using RECP [3, 4].

The structures of PdN and PdN_2 are optimized using B3LYP (the hybrid density functional theory (DFT) of Becke's three parameter exchange function and Lee-Yang-Parr correlation function)[5] method, RECP/SDD basis function for Pd and AUG-cc-pVTZ basis function for N. The Murrell-Sorbie potential energy function of PdN molecule has been fitted through the least square fitting, and the potential energy function of PdN_2 is given by many-body expansion theory.

2 Result and discussion

2.1 Structures of PdN and PdN2 molecules

The *ab initio* calculation shows that ground state of PdN is $^4\Sigma^-$, equilibrium nuclear distance R_e = 0.18158 nm, dissociation energy D_e = 2.1437 eV. The ground state of PdN_2 is $C_{\infty V}$ symmetry and $^1\Sigma^+$ state, equilibrium nuclear distance R_{NN} = 0.11026 nm, R_{PdN} = 0.19537 nm, dissociation energy D_e = 10.7047 eV. Then harmonic vibration frequencies of the ground state PdN_2 ($C_{\infty V}$) are given: symmetry stretched vibration frequency v_1 = 356.9753 cm^{-1}, bend vibration frequency v_2 = 180.9400 cm^{-1} and antisymmetry stretched vibration frequency v_3 = 2318.1252 cm^{-1}.

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*Corresponding author. Email: gjiang@scu.edu.cn; Tel: +86028-85408810).

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2.2 Dissociation limit of PdN and PdN₂ molecules

The ground state of PdN is $X^4\Sigma^-$, and its orbit arrangement is shown below:

α electron: $\sigma\,\sigma\,\sigma\,\pi\,\pi\,\sigma\,\sigma\,\pi\,\pi\,\delta\,\delta\,\pi\,\pi\,\sigma$

β electron: $\sigma\,\sigma\,\sigma\,\pi\,\pi\,\sigma\,\sigma\,\pi\,\pi\,\delta\,\delta$

According to the theory of atomic and molecular reaction statics[6], dissociation limit of the ground state $\mathrm{PdN}(X^4\Sigma^-)$ molecule is shown as follows:

$$\mathrm{PdN}(X^4\Sigma^-)\rightarrow\mathrm{Pd}(^1S_g)+\mathrm{N}(^4S_u)$$

The ground state of $\mathrm{PdN_2}$ is $X^1\Sigma^+$, $C_{\infty V}$ group and its orbit arrangement is shown below:

α electron: $\sigma\,\sigma\,\sigma\,\sigma\,\pi\,\pi\,\sigma\,\sigma\,\pi\,\pi\,\sigma\,\pi\,\pi\,\delta\,\delta\,\sigma$

β electron: $\sigma\,\sigma\,\sigma\,\sigma\,\pi\,\pi\,\sigma\,\sigma\,\pi\,\pi\,\sigma\,\pi\,\pi\,\delta\,\delta\,\sigma$

Dissociation channels of the ground state $\mathrm{PdN_2}(X^1\Sigma^+)$ molecule are shown as follows:

$$\mathrm{PdN_2}(X^1\Sigma^+)\rightarrow\begin{cases}\mathrm{Pd}(^1S_g)+\mathrm{N_2}(X^1\Sigma_g^+) & \text{(a)}\\ \mathrm{PdN}(X^4\Sigma^-)+\mathrm{N}(^4S_u) & \text{(b)}\\ \mathrm{N}(^4S_u)+\mathrm{N}(^4S_u)+\mathrm{Pd}(^1S_g) & \text{(c)}\end{cases}\qquad(1)$$

As for channel (a), ^1S_g can be resolved into $^1A_1$ of $C_{\infty V}$ group, and $^1\Sigma_g^+$ into $^1A_1$ of $C_{\infty V}$ group. According to the direct product of the $C_{\infty V}$ group representation: $^1A_1\otimes{}^1A_1={}^1A_1$. This is the ground state of $\mathrm{PdN_2}$ molecule.

For channel (b), $^4\Sigma^-$ can be resolved into $^4A_1$ of $C_{\infty V}$ group, and ^4S_u into $^4A_1$ of $C_{\infty V}$ group. According to the direct product of the $C_{\infty V}$ group representation: $^4A_1\otimes{}^4A_1=(^1A_1\otimes{}^3A_1\otimes{}^5A_1\otimes{}^7A_1)$. It also includes component of $^1A_1$.

For channel (c), according to dissociation channel of the ground state $\mathrm{PdN}(X^4\Sigma^-)$ and the microscopic process transitive principle, it is possible.

2.3 The potential energy function and spectral data of PdN molecule

After the structure of PdN has been optimized using B3LYP method, the single point energy (SP) of the ground state $\mathrm{PdN}(X^4\Sigma^-)$ is calculated, the bond length is maintained from 0.10 to 0.58 nm and step length is 0.01 nm. Then the form of Murrell-Sorbie (M-S) potential energy function[7] is fitted through the least square fitting.

$$V=-D_e(1+a_1\rho+a_2\rho^2+a_3\rho^3)\exp(-a_1\rho)\qquad(2)$$

Where, $\rho=R-R_e$, R and R_e are the nuclear distance and equilibrium nuclear distance, respectively. D_e, a_1, a_2 and a_3 are fitting parameters. The fitting results are shown in Table 1.

Table 1 M-S potential energy functions for PdN and N_2 molecules

State	D_e/eV	R_e/nm	a_1/nm^{-1}	a_2/nm^{-2}	a_3/nm^{-3}
$\mathrm{PdN}(X^4\Sigma^-)$	2.1437	0.18158	35.413	186.38	705.01
$\mathrm{N_2}(X^1\Sigma^+)$	9.905	0.10977	53.96	732.8	4985

As can be seen in Fig.1, the fitting curve (solid line) shows good agreement with *ab initio* calculation values of $\mathrm{PdN}(X^4\Sigma^-)$. By using the Murrell-Sorbie potential energy function (2), harmonic force constants and spectral data of $\mathrm{PdN}(X^4\Sigma^-)$ are calculated according to the formulas[7] about parameters D_e, a_1, a_2 and a_3 with harmonic force constants and spectral data. The results are shown in Table 2.

2.4 The many-body expansion potential energy function of PdN₂ molecule

The reference structure of C_{2V} is chosen in this article ($\mathrm{PdN_2}$: $R_1^0=R_{\mathrm{NN}}$, $R_2^0=R_3^0=(R_{\mathrm{NN}}+R_{\mathrm{PdN}}+R_{\mathrm{PdN}})/2$ are reference coordinates) to study the potential energy function of $\mathrm{PdN_2}$ molecule. The internal coordinates are written as $\rho_i=R_i-R_i^0$ (i=1,2,3), then the corresponding symmetric internal coordinates are given as follows:

$$\begin{bmatrix}S_1\\S_2\\S_3\end{bmatrix}=\begin{bmatrix}1&0&0\\0&1/\sqrt{2}&1/\sqrt{2}\\0&1/\sqrt{2}&-1/\sqrt{2}\end{bmatrix}\begin{bmatrix}\rho_1\\\rho_2\\\rho_3\end{bmatrix}$$

The many-body expansion potential energy function of $\mathrm{PdN_2}$ molecule is as follows:

$$V(R_1,R_2,R_3)=V_{\mathrm{NN}}^{(2)}(R_1)+V_{\mathrm{PdN}}^{(2)}(R_2)+V_{\mathrm{PdN}}^{(2)}(R_3)+V_{\mathrm{NNPd}}^{(3)}(R_1,R_2,R_3)\qquad(3)$$

Where, $V_{\mathrm{NN}}^{(2)}(R_1)$, $V_{\mathrm{PdN}}^{(2)}(R_2)$ and $V_{\mathrm{PdN}}^{(2)}(R_3)$ are two-body terms, and use form of Murrell-Sorbie potential energy function (2), which parameters are shown in Table1, the pa-

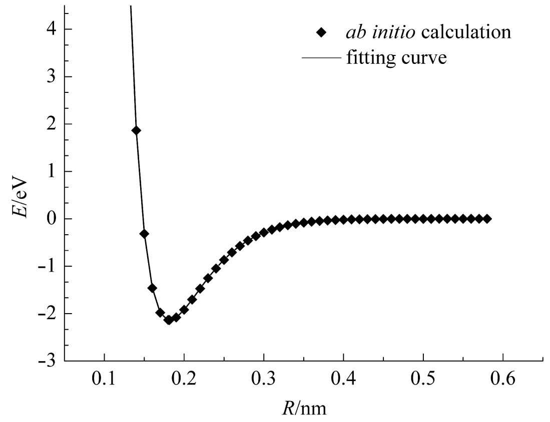

Fig.1 The potential curve of $\mathrm{PdN}(X^4\Sigma^-)$

Table 2 Harmonic force constants and spectral data of $\mathrm{PdN}(X^4\Sigma^-)$

State	$10^{-2}f_2$/aJ·nm^{-2}	$10^{-3}f_3$/aJ·nm^{-3}	$10^{-4}f_4$/aJ·nm^{-4}	ω_e/cm^{-1}	$\omega_e\chi_e$/cm^{-1}	B_e/cm^{-1}	α_e/cm^{-1}
$X^4\Sigma^-$	3.0270	−18.3581	86.2961	6.4427×10^3	558.2997	0.4131	5.6743×10^{-3}