

# The $\text{NH}^{2+}$ and $\text{Be}_2^{2+}$ Vibrational Spectroscopic Constants From use of the New Analytical Potential Energy Function

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## Introduction

Experimental and computational studies of charged molecules are the great interest in chemistry, physical and biological systems, and the description of their properties are essential for understanding of fundamental mechanism<sup>1-3</sup>. Diatomic dications are interesting ions because they can be generated as a long-lived molecule in the gas phase. The study of potential energy curves (PECs) for small dications has received growing attention in recently papers because these can provide several spectroscopic properties<sup>1,4,5</sup>, however, the behavior of the PEC is very different when compared with neutral and singly charged diatomic molecules: these kinds of molecules have some new features that the potential curves may have both potential minimum and maximum or singly repulsive branch (Figure 1).

## Methods

In previous paper Wang and co-authors<sup>6</sup> proposed a new analytical PEC including an ionic Coulomb repulsion term and the Varandas potential term, as follow,

$$V(R) = \left( \sum_{n=0}^3 a_n R^n \right) e^{-a_4 R} + \frac{C}{R}, \quad (1)$$

which can be used to describe the diatomic ions with both potential minimum and maximum or without any stationary point.

In this work we propose a new analytical PEC for doubly charged diatomic ions. These functions are based on the deformed exponential function (d-Exponential), defined as:

$$e_d^{-x} = [1 - dx]^{\frac{1}{d}}. \quad (2)$$

In this way, we proposed a new analytical PEC, as follow:

$$V_d(R) = \left( \sum_{n=0}^3 a_n R^n \right) e_d^{-a_4 R} + \frac{C}{R}. \quad (3)$$

The new function, eq. 3 is most flexible to build up the PEC due to the inclusion of an additional parameter (parameter). The d-Exponential function has been applied successfully to a variety of problems in electronic structure<sup>7-10</sup>, where  $a_n$  and  $d$  are adjustable parameters. All coefficients were optimized using a hybrid procedure based on the global optimization method known as Generalized Simulated Annealing (GSA)<sup>11,12</sup>, the simplex

gradient and Levenberg-Marquardt 13 methods.

We evaluated the spectroscopic constants using the Dunham's method<sup>14</sup>, which is obtained by comparing Eq.(4) and the PEC written with a Taylor expansion around the equilibrium distances. The Dunham's method needs force constants at minimum. From the new function (equation 3) it is easy to derive quadratic, cubic and quadratic terms, as follows:

$$f_2 = \sum_{n=0}^3 a_n n(n-1)R^{n-2} [e_d^{-a_4 R}] + \sum_{n=0}^3 a_n (-2a_4 n R^{n-1} + a_4^2 d R^n) [e_d^{-a_4 R}] + 2C/R^3 \quad (4)$$

$$f_3 = \sum_{n=0}^3 a_n n(n-1)(n-2)R^{n-3} [e_d^{-a_4 R}] + \sum_{n=0}^3 a_n (-3a_4 n(n-1)R^{n-2} + 3a_4^2 d n R^{n-1} - a_4^3 d^2 R^n) [e_d^{-a_4 R}] - 6C/R^4, \quad (5)$$

and

$$f_4 = \sum_{n=0}^3 a_n n(n-1)(n-2)(n-3)R^{n-4} [e_d^{-a_4 R}] + \sum_{n=0}^3 a_n \left( \begin{array}{l} -4a_4 n(n-1)(n-2)R^{n-3} + 6a_4^2 d n(n-1)R^{n-2} \\ -4a_4^3 d^2 n R^{n-1} + a_4^4 d^3 R^n \end{array} \right) [e_d^{-a_4 R}] + 24C/R^5. \quad (6)$$

## Results and Discussions

In this section we present results of dynamics properties of the and  $\text{NH}_2^+$  system using the new analytical PECs proposed in this work. The PECs for are shown in Figure 1, and for  $\text{NH}_2^+$  are shown in Figure 2, where, in both cases, the red solid line represent the fitted line and the black circles re the ab initio calculated values.

The results of the maximum (minimum) deviation and the error found between values for the ab initio and fitted energies were:  $1.21 \times 10^{-3}$  ( $1.30 \times 10^{-5}$ ) and  $1.19 \times 10^{-6}$  and  $8.28 \times 10^{-4}$  ( $2.52 \times 10^{-5}$ ) and  $1.12 \times 10^{-5}$ , for the deformed PEC and the usual one, respectively. From these results we can see close agreement between the ab initio and fitted energies. It is important to point out that the success of the fitting procedure is, in part, due to the d-Exponential function's flexibility.

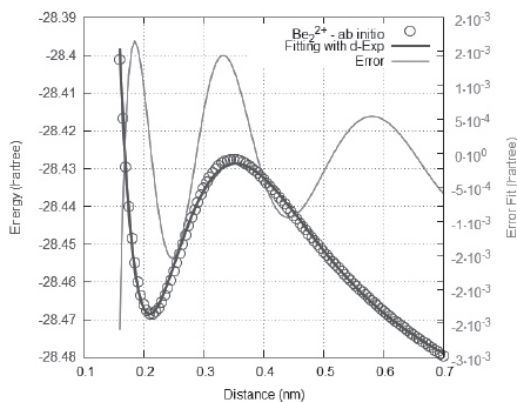


Figure 1 - The fitted potential energy curves for  $\text{Be}^{2+}(\text{X}1 \Sigma_g^+)$

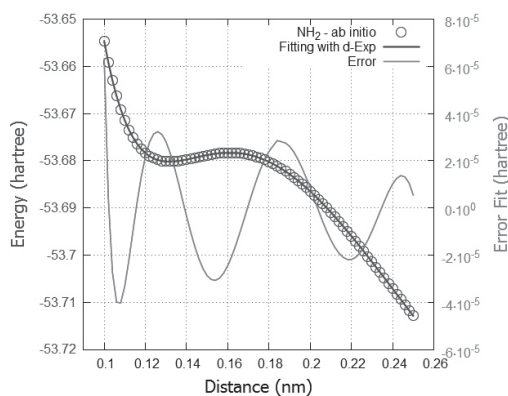


Figure 2 - The fitted potential energy curves for  $\text{NH}_2^+(\text{X}1 \Sigma_g^+)$

The results of calculated spectroscopic constants for  $\text{Be}_2^{2+}$  molecular system are show in the Table 1. From this Table we can see a good agreement with reference 6.

All values of  $\omega_e$ ,  $\omega_e x_e$  and  $B_e$  are in excellent agreement with experimental data <sup>6</sup>.

**Table 1:** The calculated potential minima and maxima for the ground state of  $\text{Be}_2^{2+}$ ,  $\text{BH}^{2+}$ ,  $\text{CH}^{2+}$ ,  $\text{NH}^{2+}$  molecules.

Molecules	Rmin(nm)	Rmax(nm)	$\Delta E(\text{Hartree})$
Be22+	0.215	0.350	0.0453
NH2+	0.132	0.163	0.0012

**Table 2:** The parameters of the analytic potential function for  $\text{Be}_2^{2+}$ .

Molecules	Be22+(X1 $\Sigma_g^+$ )	
	PEC	qPEC
a0 (eV)	165.987	-166.063
a1 (eV)	351.774	351.681
a2 (eV)	-588.099	-587.7244
a3 (eV)	-7200.8517	-7205.404
a4 (eV)	260.0921	260.078
C	6.0118	6.015
q	-	-5.92450E-012
X <sup>2</sup>	4.524E-010	3.37282E-010

**Table 3:** The derived force constant for  $\text{Be}_2^{2+}$  and  $\text{NH}^{2+}$  molecules.

		Be22+(X <sup>1</sup> $\Sigma_g^+$ ) → 2Be <sup>+</sup> ( <sup>2</sup> $S_g$ )
$f_2(\text{eV nm-2})$	PEC	4080.8
	d-PEC	4079.97
$f_3(\text{eV nm-3})$	PEC	-56941.8
	d-PEC	-56929.9
$f_4(\text{eV nm-4})$	PEC	1059383.0
	d-PEC	1059161.2
		NH2+(X <sup>2</sup> $\Sigma^+$ ) → H <sup>+</sup> ( <sup>1</sup> $S_g$ ) + N <sup>+</sup> ( <sup>1</sup> $D_g$ )
$f_2(\text{eV nm-2})$	PEC	5227.7
	d-PEC	5229.0
$f_3(\text{eV nm-3})$	PEC	-118812.6
	d-PEC	-118841.5
$f_4(\text{eV nm-4})$	PEC	3600384.4
	d-PEC	3601258.1

**Table 4:** The derived spectroscopic constants for  $\text{Be}_2^{2+}$  and  $\text{NH}^{2+}$  molecules.

		Be22+(X <sup>1</sup> $\Sigma_g^+$ )	NH2+(X <sup>2</sup> $\Sigma^+$ )
$B_e$	PEC	0.809	10.29
	d-PEC	0.809	10.29
$\omega_e$	PEC	1569.2	3888.8
	d-PEC	1568.7	3889.1
$\omega_e x_e$	PEC	0.3034	3.8594
	d-PEC	0.3034	3.8594
$\alpha_e$	PEC	-7.3732E-016	-3.9251E-012
	d-PEC	-1.2356E-020	3.34854E-016

## Conclusions

In this paper we have proposed a new alternative analytical function aiming to better describe the potential energies curves of the doubly charged diatomic molecules. To this end, we used the new PEC obtained by included the deformed exponential function (d-Exponential function). To test the new function, we also calculated the force constant, spectroscopic constants and the rovibrational spectra for the  $\text{Be}_2^{2+}$ . The calculated values of equilibrium vibrational frequency ( $\omega_e$ ), anharmonic constant ( $\omega_e x_e$ ) and rotational constant ( $B_e$ ) are very close to experimental data available in the literature. This fact suggests that the results of other spectroscopic constants and rovibrational energies presented in this work have the same accuracy. The results presented in this work show that the new PEC is sufficiently better when compared with the usual analytical.

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