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Morphing *ab initio* potential energy curve of beryllium monohydride

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ABSTRACT

Effective (mass-dependent) potential energy curves of the ground electronic states of ^{9}BeH, ^{9}BeD, and ^{9}BeT are constructed by morphing a very accurate MR-ACPF *ab initio* potential of Koput (2011) within the framework of the reduced potential energy curve approach of Jenč (1983). The morphing is performed by fitting the RPC parameters to available experimental ro-vibrational data. The resulting potential energy curves provide a fairly quantitative reproduction of the fitted data. This allows for a reliable prediction of the so-far unobserved molecular states in terms of only a small number of fitting parameters.

1. Introduction

A quantitatively correct description of ro-vibrational states of a given molecule in a given electronic state requires accurate knowledge of a potential energy function defined over a wide range of positions of the molecular atoms. In principle, such a function can be evaluated from first principles using advanced quantum-chemical approaches (see e.g. Ref. [1]). Alternatively, one can employ a straightforward RKR inversion of experimental data (see e.g. Ref. [2]). However, both these approaches can have serious drawbacks. The RKR inverting of experimental data is not only approximate but also strongly limited by a notorious scarcity of required data. As a result, the theoretical potential energy functions will rarely meet the accuracy requirements imposed by spectroscopic applications. To overcome these problems it becomes more and more popular to use the so called "direct potential fit" (DPT) methodology (see Ref. [3] and references therein), in which the sought potential energy functions (potentials) are determined by fitting their mathematical approximants to experimental data within the framework of adequate ro-vibrational Hamiltonians. The actual approximants are expressed in terms of suitable elementary mathematical functions so that they are to be (see Ref. [4]) (i) flexible - able to represent all available data within the experimental uncertainties; (ii) "well-behaved" - continuous and differentiable to all orders at all atomic positions; (iii) robust - able to provide physically reasonable extrapolations outside the region over which the data used to determine the potential are sensitive; (iv) compact - defined by a minimum number of free (empirical) parameters; and (v) exhibit the correct theoretically known long-range behaviour.

The choice of a suitable approximant is not a simple task; the shapes of the genuine potentials are *a priori* unknown and cannot be derived from theory. Thus, despite a vast variety of their variants available in the literature (see e.g. Ref. [5]), it may easily happen that they provide representations which are too awkward to allow for 'smooth' fittings of available experimental data (for instance see [6] where to describe quantitatively an *ab initio* potential of the helium dimer, which supports only one bound state, it was necessary to use 45 fitting parameters). To overcome this problem there are two strategies to use. Either to design more flexible approximants of the genuine potentials (the strategy advocated especially by Le Roy [3,4,7–9]), or to rely on the homotopic morphing of topologically correct *ab initio* potentials (see e.g. [10]). In the case of diatomic molecules the morphing procedure appears to be especially suitable when it is combined with the reduced potential curve (RPC) method of Jenč [11] or its generalizations [12,13]. For instance, this procedure has revealed the existence of the 'elusive' twelfth vibrational state of the beryllium dimer and its two rotational states [14] and allowed for a correct assignment of the FTS spectra of highly excited, bound vibrational states of the lowest KRb triplet solely on the basis of experimental scattering lengths [15]. The purpose of this study is to probe the morphing

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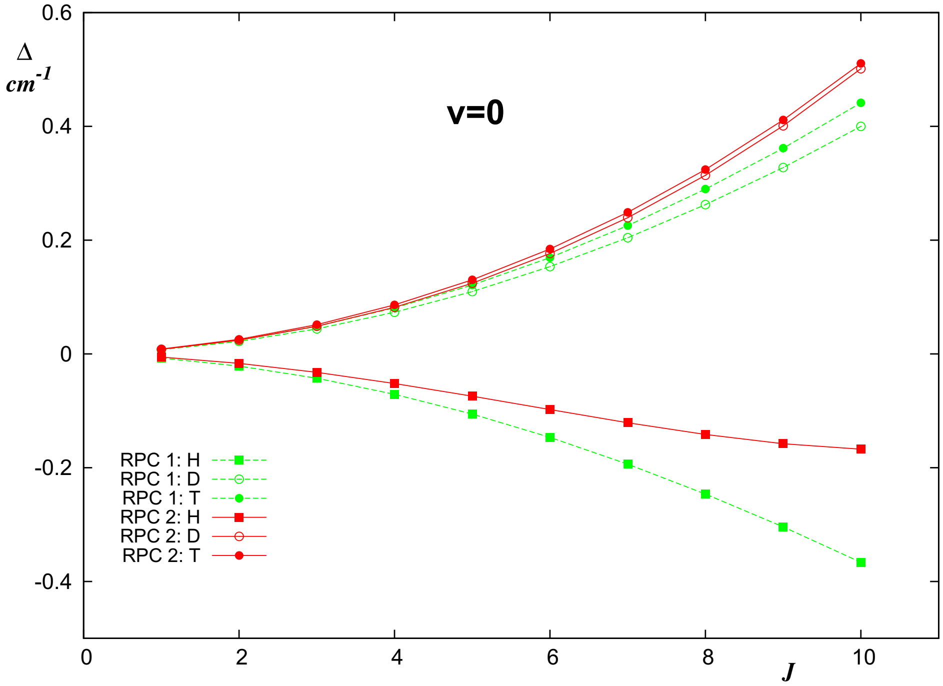

Fig. 1. Reproduction of experimental rotational energies (E_{exp}) of the beryllium isotopomers in their vibrational ground states by a dereduced potential fitted simultaneously to the ^{9}BeH, ^{9}BeD and ^{9}BeT data. $\Delta = E_{exp}(J) - E_{calc}(J)$, J is the rotational quantum number.

procedure as a tool for studying the breakdown of the Born-Oppenheimer approximation. The actual probing is performed for the benchmark BeH molecule and its isotopologues BeD and BeT.

2. Theory

Although the ground electronic state of beryllium monohydride is the $X^2\Sigma^+$ state, there is no spin-splitting observed in the measured spectra. Therefore, the probed ro-vibrational states can be rationalized within the framework of the following effective ro-vibrational Hamiltonian for an isolated $^1\Sigma^+$ state [16]

$$H_{\rm eff} = -\frac{\hbar^2}{2\mu}\frac{\mathrm{d}}{\mathrm{d}R}(1+g_v(R))\frac{\mathrm{d}}{\mathrm{d}R} + \frac{\hbar^2}{2\mu R^2}(1+g_r(R))J(J+1) + V_{BO}(R) + V'(R), \tag{1}$$

where μ is the appropriate atomic reduced mass, R is the internuclear distance, V_{BO} is the 'mass-independent' part of the molecular potential energy curve (assumed to include the Born-Oppenheimer and relativistic terms) and the terms $V'(R)$, $g_r(R)$ and $g_v(R)$ account for QED, residual retardation, adiabatic, and nonadiabatic effects. $V_{eff} = V_{ad}(R) + V'(R)$ is assumed to be determinable by fitting to the available experimental data. The function $g_r(R)$ is assumed to possess the form $g_r(R) = g(R-R_e)^2/R^2$, where g is an additional fitting parameter, and the vibrational g-factor is neglected (a preliminary model calculation has revealed its negligible role in the present study).

The actual determination of the sought effective potential energy functions V_{eff} is achieved within the framework of the reduced potential curve (RPC) method of Jenč (see Refs. [11–13]) and is performed in two steps. First, a given (reference) *ab initio* potential energy function $V^{ref}(R)$ is used to generate its reduced form $u(\rho)$, which is defined as follows

$$u(\rho) = V^{ref}(R)/D_{\rm e}^{ref}, \tag{2}$$

where $D_{\rm e}^{ref}$ is the depth of $V^{ref}(R)$, and the reduced variable ρ is related to R via the expression

$$\rho(R) = \frac{R - \rho_{ij}\left[1-\exp\left(-R/\rho_{ij}\right)\right]}{R_{\rm e}^{ref} - \rho_{ij}\left[1-\exp\left(-R/\rho_{ij}\right)\right]}. \tag{3}$$

$R_{\rm e}^{ref}$ is the distance for which $V^{ref}(R)$ acquires its minimum, ρ_{ij} satisfies the transcendental equation

$$\rho_{ij} = \frac{R_{\rm e}^{ref} - \sqrt{\kappa D_{\rm e}^{ref}/k_{\rm e}}}{1-\exp\left(-R_{\rm e}^{ref}/\rho_{ij}\right)}, \tag{4}$$

where

$$k_{\rm e} = (\mathrm{d}^2V^{ref}/\mathrm{d}R^2)_{R=R_{\rm e}^{ref}}, \tag{5}$$

and finally, the 'universal' reduced force constant κ is assumed to acquire its recommended value of 3.96 (see Ref. [11]).

In the second step, the reducing procedure is reverted by expressing $V(R)$ as the function of $u(\rho)$, namely

$$V(R) = D_{\rm e}u(\rho), \tag{6}$$

with ρ defined by

$$\rho(R) = \frac{R - \rho_{ij}\left[1-\alpha\exp\left(-\beta(1+\gamma R)R/\rho_{ij}\right)\right]}{R_{\rm e} - \rho_{ij}\left[1-\alpha\exp\left(-\beta(1+\gamma R)R/\rho_{ij}\right)\right]}, \tag{7}$$

and involving *a priori* unknown parameters $D_{\rm e}$, $R_{\rm e}$, ρ_{ij}, α, β, and γ, which are to be determined by fitting the available experimental data (in the standard RPC scheme, $\alpha = \beta = 1$ and $\gamma = 0$).