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# Gegenbauer polynomials in a theoretical study of the vibrational structure of the $\text{Ca}^+-\text{H}_2$ system

Received: 5 August 2005 / Accepted: 16 September 2005 / Published online: 2 December 2005  
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**Abstract** This work presents an application of Gegenbauer polynomials in vibrational calculations. We illustrated that by example calculations of vibrational structure of the  $\text{Ca}^+-\text{H}_2$  exciplex, in the state correlated with 3D calcium ion state. For this case Gegenbauer polynomials are used for formation of a basis set for a bending mode. We showed that this basis set leads to a faster convergence of results than a basis set formed from Legendre polynomials. Additionally we compared vibrational structure obtained in this manner with results of discrete variable representation-distributed Gaussian basis (DVR–DGB) method.

**Keywords** Vibrational structure · Gegenbauer polynomials · Exciplex

## 1 Introduction

The calcium ion has an interesting energy level scheme. The lowest excited states  $D_{3/2,5/2}$  of the singly charged ion with alkali-like electronic structure are metastable states. The radiative lifetimes of the  $D_{3/2,5/2}$  states range from 50–300 ms for  $\text{Sr}^+$ ,  $\text{Yb}^+$  and  $\text{Hg}^+$ , nearly 1 s for  $\text{Ca}^+$ , up to 20–40 s for  $\text{Ba}^+$  [2–4]. Such long lifetimes suggest that these ions are very attractive candidates for optical (D–S) transition and long infrared ( $D_{3/2}-D_{5/2}$ ) transition frequency standards. However, some results [5–8] have shown that the quenching rates of these states (even in ion trap conditions) caused by inelastic

collisions with rare gas (RG) atoms are high. With small gas molecules quenching is even two orders of magnitude more efficient. Therefore, the knowledge of quenching processes is essential for establishing frequency standards.

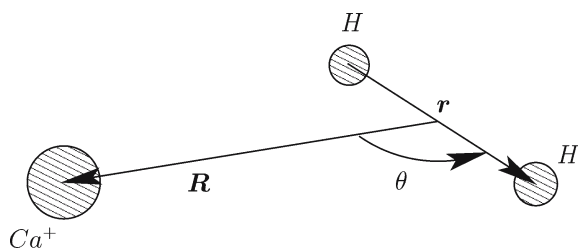
For collisions of small molecules with ions, a high quenching rate means that the potential energy surface (PES) for the excited (D) state of the complex intersects with the PES of the ground (S) state, leading to an radiationless excitation energy transfer from the ion to the molecule during the collision. There is also an other possibility. Due to the successive collisions of such complexes with other molecules, or the interaction with an electromagnetic field, an exciplex can be formed. Experimental [9] and theoretical [10] investigations of the  $\text{Ca}^+-\text{N}_2$  system has proven that it has a linear geometry, both in the ground and excited states, and it can be stabilized in the ground state.

The calculations of the electronic structure are described elsewhere [1]. We summarize only the most important results. Potential energy surfaces for the ground and a few excited states were obtained using the multireference configuration interaction (MRCI) method. The calculated PES exhibits strong anharmonicity and anisotropy. The calculations have shown also that contrary to the  $\text{Ca}^+-\text{N}_2$  case the T-shaped configuration of the nuclei ( $C_{2v}$  geometry) is energetically the most favorable one for both ground and excited states. The ground state PES has a very shallow minimum ( $24.2\text{ cm}^{-1}$ ) located at  $R = 7.02$  au and  $r = 1.40$  au, where  $R, r, \theta$  are the standard Jacobi coordinates (Fig. 1) of the system. Our calculations have shown that for this PES only two bound vibrational states are possible. It is evident that such a molecule cannot exist in normal conditions.

However, the electronic energy of the  $(3d) \ ^2D^2B_2$  state has a global minimum of  $5510\text{ cm}^{-1}$ , located at  $R = 3.72$ ,  $r = 1.54$  au and  $\theta = \pi/2$  (see Figure 3a). Intuition suggests that in this case the existence of many bound states is possible. Therefore the main goal of the further part of this work is the theoretical calculation of the vibrational structure of the exciplex  $\text{Ca}^+-\text{H}_2$  in the state correlating with the  $(3d) \ ^2D \text{ Ca}^+$  level. There is not yet experimental evidence that the exciplex  $\text{Ca}^+-\text{H}_2$  exists. Therefore,

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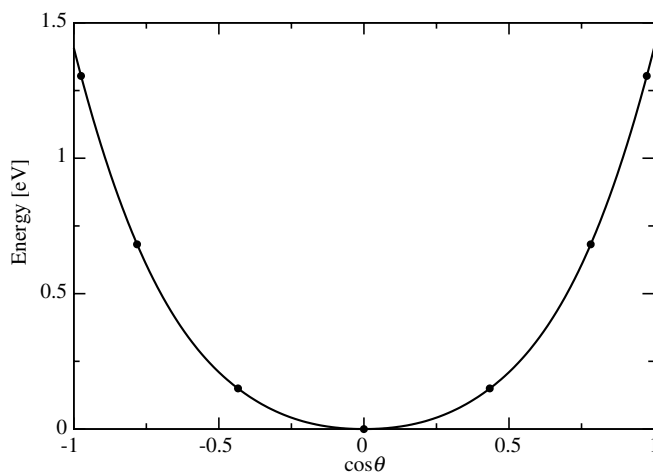
**Fig. 1** Jacobi coordinates for  $\text{Ca}^+-\text{H}_2$  complex

calculations were limited to the vibrational spectrum while the rotational structure was neglected ( $J=0$ ).

It seems that such a structure could be verified by coherent anti-stokes Raman scattering (CARS), in a similar way as it was done for the  $\text{Na}(3p^2\text{P})\text{H}_2$  complex [11], or by analyzing the discrete infrared absorption spectra. The existence of a stabilized  $\text{Na}(3p^2\text{P})\text{H}_2$  exciplex was proven experimentally. Stabilization was possible by two successive collisions of the Na atom with two  $\text{H}_2$  molecules. The same way should lead to formation of a  $\text{Ca}^+-\text{H}_2$  exciplex. The other possibility is a radiative collision, in which the  $\text{Ca}^+$  ion in the ground state collides with the  $\text{H}_2$  molecule in the presence of a laser beam with proper frequency  $\omega$ .

The vibrational energetic structure of triatomic molecules can be calculated by the commonly accepted DVR–DGB method [12–15], but the method based on coupled normal modes approach (secular determinant method) is still attractive due to the simple physical picture of the normal oscillations. For atom–diatom complexes with a strong anisotropy of the PES, three types of basis functions are necessary to describe the system properly, two for stretching modes and one for the bending mode. Usually Lagrange polynomials are used for the construction of the angular basis. However, this basis is related to the free rotations of the  $\text{H}_2$  bound in the complex. Application of such basis functions in the case of a strongly anisotropic potential as in the case of the  $\text{Ca}^+-\text{H}_2$  complex (see Figs. 2 and 3) results in slow convergence of the calculations.

The strong anisotropy does not allow for free rotation of the  $\text{H}_2$  molecule. Thus, it is reasonable to use an angular basis which better describes the physical nature of restricted rotations. In our opinion, a suitable basis can be formed from Gegenbauer polynomials, because the Gegenbauer polynomials form exact analytic solutions for the angular motion on a model potential, which is similar to the computed potential as shown in Fig. 2 (see also Appendix A, Eq. (14)). This potential restricts the rotation of the  $\text{H}_2$  molecule to the range from  $0^\circ$  to  $180^\circ$ . This potential can have a similar role in case of bending motions as the harmonic oscillator potential for vibrational motion. Such an angular basis formed from Gegenbauer polynomials can be applied only to complexes for which the bending potential has a minimum near  $\theta = 90^\circ$  and has repulsive branches at angles of  $\theta = 0^\circ$  and  $\theta = 180^\circ$ . The quality of the angular basis formed from Gegenbauer polynomials is discussed further in Appendix B,



**Fig. 2** Angular dependence of the potential energy curve for the first excited state correlated to the  $(3d)^2\text{D Ca}^+$  term for equilibrium values of  $r, R$

where results obtained in calculations based on Gegenbauer and Legendre basis sets are compared.

## 2 Details of vibrational calculations

The calculations of the pure vibrational spectrum ( $J = 0$ ) for the  $\text{Ca}^+-\text{H}_2$  exciplex in the Born–Oppenheimer approximation are reduced to the solution of an eigenvalue problem, which in the body fixed frame [16] and Jacobi coordinates has the form

$$\left[ \hat{K}_V + V(r, R, \theta) \right] \psi(r, R, \theta) = E \psi(r, R, \theta). \quad (1)$$

The operator  $K_V$  represents the kinetic energy of the three normal vibrations: the  $\text{Ca}^+-\text{H}_2$  and  $\text{H}-\text{H}$  stretching modes as well the bending mode

$$\hat{K}_V = -\frac{\hbar^2}{2\mu R^2} \frac{\partial}{\partial R} \left( R^2 \frac{\partial}{\partial R} \right) - \frac{\hbar^2}{2\mu_m r^2} \frac{\partial}{\partial r} \left( r^2 \frac{\partial}{\partial r} \right) - \frac{\hbar^2}{2I \sin \theta} \frac{\partial}{\partial \theta} \left( \sin \theta \frac{\partial}{\partial \theta} \right), \quad (2)$$

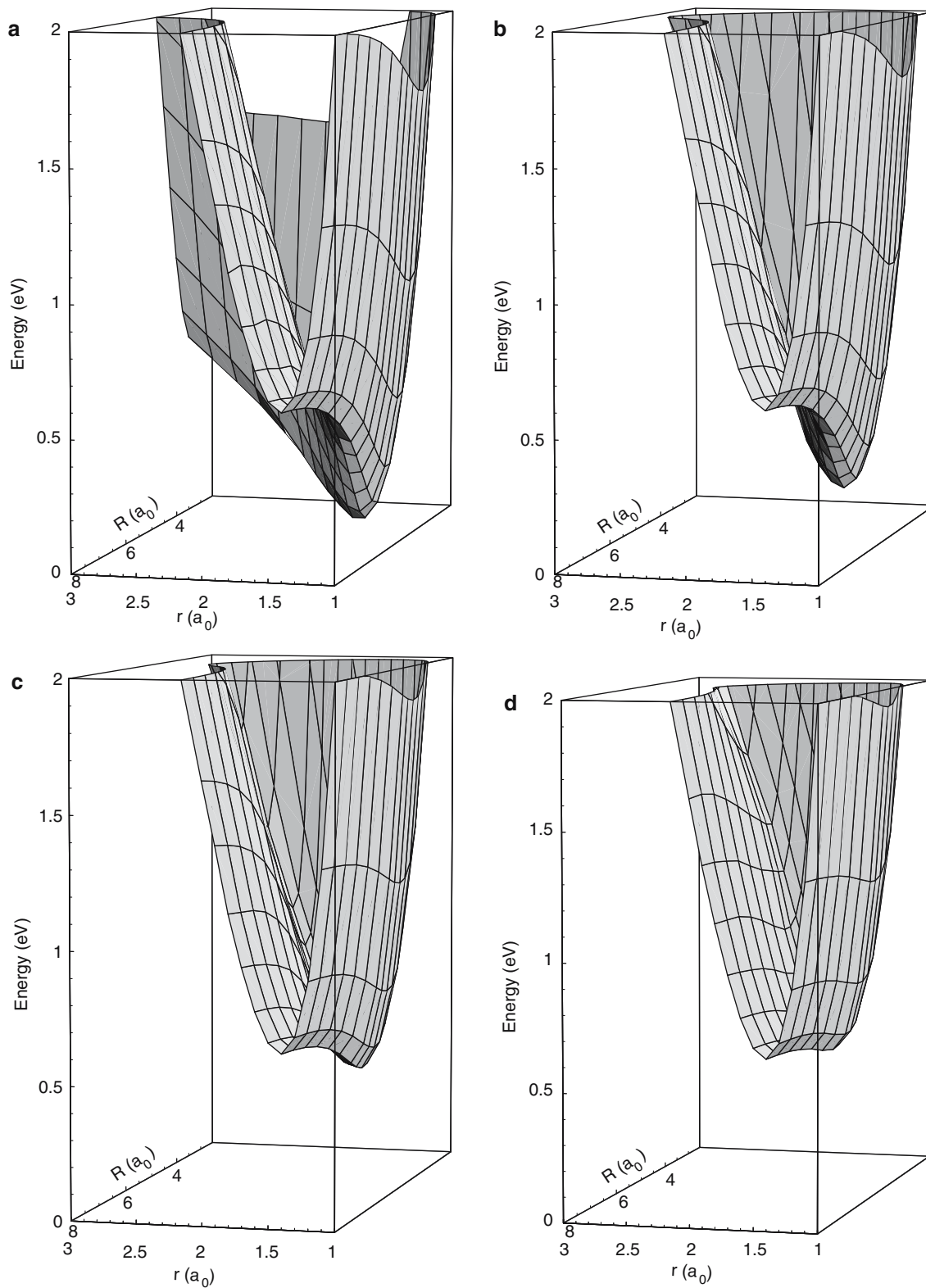
where  $\mu$  denotes the reduced mass of the  $\text{Ca}^+-\text{H}_2$  system, and  $\mu_m$  stands for the reduced mass of  $\text{H}_2$ . The momentum of inertia  $I$  is defined as

$$\frac{1}{I} = \frac{1}{\mu R^2} + \frac{1}{\mu_m r^2}. \quad (3)$$

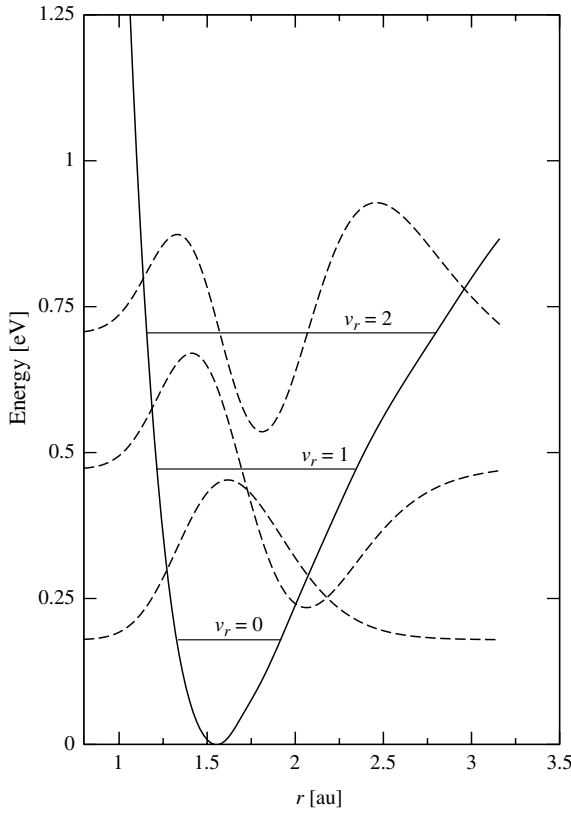
$V(r, R, \theta)$  is the ab initio potential energy surface in Jacobi coordinates. Figure 3 shows the PES for the first excited state correlating to the  $(3d)^2\text{D Ca}^+$  term close to its minimum.

The eigenfunctions  $\Psi_v(r, R, \theta)$  of the Eq. (1) are expanded in a three dimensional orthogonal basis

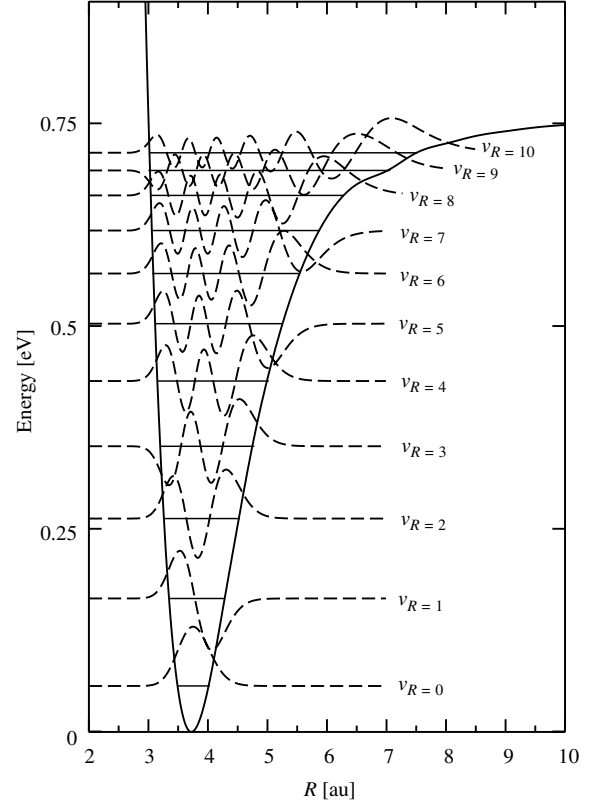
$$\Psi_v(r, R, \theta) = \sum_{i=1}^n \sum_{j=1}^m \sum_{k=1}^l c_{ijk}^{(v)} \frac{\phi_i(r)}{r} \frac{\chi_j(R)}{R} \xi_k(\cos \theta). \quad (4)$$



**Fig. 3** Potential energy surfaces for the first excited state correlating to the  $(3d)^2D Ca^+$  term for different angles. **a**  $\theta = \frac{\pi}{2}$ . **b**  $\theta = \frac{5\pi}{14}$ . **c**  $\theta = \frac{3\pi}{14}$ . **d**  $\theta = \frac{\pi}{14}$ , as a function of  $r$  and  $R$



**Fig. 4** Potential curve  $V_{R_e}(r)$  for state  $(1)^2B_2$ .  $v_r$  denotes the quantum number for oscillation H–H



**Fig. 5** Potential curve  $V_{r_e}(R)$  for state  $(1)^2B_2$ .  $v_R$  denote the quantum number for oscillation  $\text{Ca}^+-\text{H}_2$

The basis functions  $\phi_i(r)$  and  $\chi_j(R)$  are eigenfunctions of equations for the stretching modes of

$$\begin{aligned} \text{H-H} \left[ -\frac{\hbar^2}{2\mu_m} \frac{d^2}{dr^2} + V_{R_e}(r) \right] \phi_i(r) \\ = E_i^{(r)} \phi_i(r), \quad i = 1, \dots, n \end{aligned} \quad (5)$$

and

$$\begin{aligned} \text{Ca}^+-\text{H}_2 \left[ -\frac{\hbar^2}{2\mu} \frac{d^2}{dR^2} + V_{r_e}(R) \right] \chi_j(R) \\ = E_j^{(R)} \chi_j(R), \quad j = 1, \dots, m, \end{aligned} \quad (6)$$

respectively.

The basis functions  $\phi_i(r)$  and  $\chi_j(R)$  were found numerically. Equations (5) and (6) were solved using the Numerov–Cooley method. The related one dimensional potential energies  $V_{R_e}(r) = V(r, R_e, \frac{\pi}{2})$  and  $V_{r_e}(R) = V(r_e, R, \frac{\pi}{2})$ , are displayed in Figs. 4 and 5. Appropriate eigenvalues and eigenfunctions of Eqs. (5) and (6) are also presented in these figures.

The quantities  $R_e$  and  $r_e$  are the equilibrium values of  $R$  and  $r$ , respectively. One dimensional vibrational calculations yield 3 eigenstates for the H–H stretching mode with eigenvalues (1446, 3806, 5687  $\text{cm}^{-1}$ ),<sup>1</sup> and 13 states in case of

the  $\text{Ca}^+-\text{H}_2$  stretching mode (453, 1323, 2118, 2837, 3486, 4056, 4555, 4983, 5332, 5580, 5756, 5906, 6002  $\text{cm}^{-1}$ ).

The basis functions  $\xi_k(\cos \theta)$  used to describe the bending mode correspond to analytic eigenfunctions of the non free rigid rotator, whose motion is restricted by forces related to the model potential  $V_{\text{mod}}(\theta)$  (see Appendix A). As was mentioned earlier, such an approach is used because the angular dependence of the PES is strongly anisotropic. Thus, the  $\text{H}_2$  bond cannot rotate freely in the complex. Therefore, the angular basis formed from Gegenbauer polynomials reflects the physics of the problem. Normalized  $\xi_k(\cos \theta)$  functions have the form

$$\begin{aligned} \xi_k(\theta) = 2^{2\sigma} |\Gamma(2\sigma + 1/2)| \left[ \frac{k!(2\sigma + 1/2 + k)}{\pi \Gamma(k + 4\sigma + 1)} \right]^{1/2} \\ \times (1 - z^2)^\sigma C_k^{2\sigma+1/2}(\cos \theta). \end{aligned} \quad (7)$$

These functions correspond to the eigenvalues

$$\lambda_{k,\sigma} = \frac{\hbar^2}{2I_e} [k^2 + (4\sigma + 1)k + 2\sigma(2\sigma + 1)] + V_u. \quad (8)$$

Here  $C_k^{2\sigma+1/2}(\cos \theta)$  denotes the Gegenbauer polynomial of the  $k$ -order,  $\sigma = \sqrt{\frac{I_e V_0}{2\hbar^2}}$  and  $\Gamma$  is the  $\Gamma$ -function. For details see Appendix A. Constant values  $V_u$  and  $V_0$  are chosen in such a way that one obtains the best fit of (14) to the ab initio values of  $V(r_e, R_e, \theta)$ .

<sup>1</sup> Here and in other points of this article vibrational energies are referred to the minimum of the  $(3d)^2B_2$  potential energy surface

One can rewrite Eq. (1) in the form of a secular equation. First one has to substitute function (4) into Eq. (1), then add and subtract the one dimensional potentials  $V_{R_e}(r)$ ,  $V_{r_e}(R)$  and  $V_{\text{mod}}(z = \cos \theta)$  from the resultant equation. Then, after grouping appropriate terms, one can use the properties of the eigenequations for the stretching [Eqs. 5 and 6] and bending [Eq. 13] modes. Ultimately, multiplication of the result by  $\phi_{i'}^*(r)\chi_{j'}^*(R)\xi_{k'}^*(z)$  and integration over all coordinates leads to the following secular equations

$$\sum_{i=1}^n \sum_{j=1}^m \sum_{k=1}^l \left[ \Delta V_{i'j'k',ijk} - \left( E - E_i^{(r)} - E_j^{(R)} \right) \times \delta_{i'i} \delta_{j'j} \delta_{k'k} + I_e \left( \left\langle \frac{1}{\mu_m r^2} \right\rangle_{i'i} \delta_{j'j} + \left\langle \frac{1}{\mu R^2} \right\rangle_{j'j} \delta_{i'i} \right) \lambda_k \delta_{k'k} \right] c_{ijk}^{(v)} = 0, \quad (9)$$

where the matrix elements  $\Delta V_{i'j'k',ijk}$  are defined by

$$\begin{aligned} \Delta V_{i'j'k',ijk} = & \int dr dR dz \phi_{i'}^*(r) \chi_{j'}^*(R) \xi_{k'}^*(z) \\ & \times V(r, R, z) \phi_i(r) \chi_j(R) \xi_k(z) \\ & - \int dr \phi_{i'}^*(r) V_{R_0}(r) \phi_i(r) \delta_{j'j} \delta_{k'k} \\ & - \int dR \chi_{j'}^*(R) V_{r_0}(R) \chi_j(R) \delta_{i'i} \delta_{k'k} \\ & - I_e \left( \left\langle \frac{1}{\mu_m r^2} \right\rangle_{i'i} \delta_{j'j} + \left\langle \frac{1}{\mu R^2} \right\rangle_{j'j} \delta_{i'i} \right) \\ & \times \int dz \xi_{k'}^*(z) V_{\text{mod}}(z) \xi_k(z). \end{aligned} \quad (10)$$

In order to find the vibrational structure of the  $\text{Ca}^+\text{-H}_2$  exciplex numerically, the PES should be known in each point of  $r$ ,  $R$  and  $\theta$ . To reach that goal the ab initio data were interpolated for each value of  $\theta$  by a two dimensional cubic spline of  $r$  and  $R$ . Next we factorized the  $\theta$  dependence of  $V(r, R, \theta)$  by expanding the potential in a series of Legendre polynomials and truncating it after the sixth term

$$V(r, R, \theta) = \sum_{l=0}^6 V_l(r, R) P_l(\cos \theta). \quad (11)$$

This potential can be written in the equivalent form

$$V(r, R, \theta) = a_0(r, R) + a_2(r, R) \cos^2 \theta + a_4(r, R) \cos^4 \theta + a_6(r, R) \cos^6 \theta. \quad (12)$$

The absence of odd terms reflects the symmetry of  $V(r, R, \theta)$  (see [1] and Fig. 2). Equation (12) may be interpreted as the Lagrange interpolation of  $V(r, R, \theta)$ . To minimize the error of the interpolation we choose values of  $\theta$  at  $\frac{\pi}{14}$ ,  $\frac{3\pi}{14}$ ,  $\frac{5\pi}{14}$ ,  $\frac{\pi}{2}$ . These points are the nodes of the Chebyshev polynomial of the seventh order. The coefficients  $a_i(r, R)$  are obtained by the solution of the linear set of equations formed by insertion of the calculated potential energy values into Eq. (12). The

angular potential matrix elements are evaluated analytically, but they could also be obtained numerically. Application of the Gauss–Chebyshev quadrature gives precise results.

### 3 Results of vibrational calculations

The secular set of equations (9) was solved numerically. The stabilized results were obtained for the basis formed from sets of  $n = 3$ ,  $m = 10$ ,  $l = 12$  basis functions. The results of the vibrational calculations are presented in Table 1. The calculations showed the existence of ten bound levels in the excited  $^2B_2$  state of the  $\text{Ca}^+\text{-H}_2$  complex. These states were denoted by  $v$ . The indices  $\nu_r$ ,  $\nu_R$ ,  $\nu_\theta$  stand for the vibrational quantum numbers of the  $\text{H}_2$  and the  $\text{Ca}^+\text{-H}_2$  stretching modes and the bending mode, respectively. The third column of Table 1 presents the probability that a state of the exciplex is the state with the quantum numbers  $\nu_r$ ,  $\nu_R$ ,  $\nu_\theta$ . In the next column the energy levels are shown. As we mentioned earlier the energy values are referring to the global minimum of the  $(1)^2B_2$  potential energy surface. The last column stands for the difference between energies of successive vibrational energy levels. The fundamental state is denoted by  $v = 0$ . The first excited state can be considered as the pure  $\text{Ca}^+\text{-H}_2$  bond vibration. The second one corresponds to the pure bending mode vibration. The next state is the second excited state of the stretching mode of the  $\text{Ca}^+\text{-H}_2$ . The state with  $v = 4$  is the first one in which combined vibrations of the  $\text{Ca}^+\text{-H}_2$  stretching mode and the bending mode appear. The states with  $v = 6$  and  $v = 9$  can also be regarded as almost pure ones. The remaining states present combinations of different modes with a stronger coupling between the  $\text{Ca}^+\text{-H}_2$  stretching mode and the bending mode. The only state where the first excited state of the  $\text{H}_2$  ( $\nu_r = 1$ ) introduces a more important contribution lies very high, close to the dissociation limit.

The mean values of  $r$  and  $R$  in the fundamental mode are  $\langle r \rangle_{v=0} = 1.67$  au and  $\langle R \rangle_{v=0} = 3.76$  au, while the equilibrium values are  $r_e = 1.54$  au and  $R_e = 3.72$  au. The  $\text{H}_2$  bond length in comparison to the free molecule is increased by about 0.29 au.

To estimate the accuracy of the results obtained in our approach we repeated the calculations applying the DVR–DGB method. We used Tennyson's et al. [17] DVR3DRJ

**Table 1** Vibrational structure of the  $\text{Ca}^+\text{-H}_2$  complex in the first excited state correlating to the  $(3d)^2D \text{Ca}^+$  term

$v$	$\nu_r \nu_R \nu_\theta$	$ c_{ijk}^{(v)} ^2$	$E$ (cm $^{-1}$ )	$\Delta E$ (cm $^{-1}$ )
0	000	0.98	2495	
1	010	0.94	3322	827
2	001	0.88	3638	316
3	020	0.90	4085	447
4	011	0.68	4401	316
5	002	0.70	4636	235
6	030	0.86	4770	134
7	021	0.48	5095	325
8	100	0.49	5142	47
9	040	0.81	5383	241

**Table 2** Comparison of results obtained with the DVR–DGB method and the secular approach with assumption  $I = I_e(r_e, R_e)$  for the Ca<sup>+</sup>-H<sub>2</sub> complex for the first excited state correlating to the (3d)<sup>2</sup>D Ca<sup>+</sup> term

$\nu$	DVR–DGB method		Secular method $I = I_e(r_e, R_e)$	
	E (cm <sup>-1</sup> )	$\Delta E$ (cm <sup>-1</sup> )	E (cm <sup>-1</sup> )	$\Delta E$ (cm <sup>-1</sup> )
0	2514		2513	
1	3340	826	3340	827
2	3670	330	3647	307
3	4103	433	4103	456
4	4419	316	4406	303
5	4667	248	4693	287
6	4792	125	4788	95
7	5109	317	5095	307
8	5156	47	5267	172
9	5470	314	5401	134

code. In this code the angular basis functions are associated Legendre polynomials. The radial basis functions are either the Morse oscillator-like functions [16] or the spherical oscillator functions [18]. Forming a radial basis set, we chose Morse oscillator-like functions. In DVR3DRJ code available for us, one uses for these basis functions DVR quadrature approximation for the integrals of the  $r^{-2}$  matrix, and this makes its transformation diagonal [17]. So, to compare the results of our approach with DVR ones on the same footing, we have replaced  $I$  (3) in the Hamiltonian (2) by the constant value  $I = I(r_e, R_e)$ . The vibrational energies obtained in this manner from the secular method and the results of the DVR–DGB method are presented in Table 2. One can see from this table, that both methods give very similar results.

#### 4 Conclusions

Calculations of the vibrational energy structure for the first electronic excited state correlating with (3d)<sup>2</sup>D Ca<sup>+</sup> term were performed. For this purpose the secular determinant and the DVR–DGB methods were used.

The basis set for the secular method was formed from the product of functions determined numerically for the Ca<sup>+</sup>-H<sub>2</sub> and the H<sub>2</sub> stretching modes and an analytic one for the bending mode. According to our calculations ten bound vibrational states exist for this exciplex. Some of these states can be interpreted as pure Ca<sup>+</sup>-H<sub>2</sub> stretching and bending modes. The remaining states are combinations of modes. Only one state corresponds to a significant coupling of the excited H<sub>2</sub> vibrational mode with other modes. The existence of the Ca<sup>+</sup>-H<sub>2</sub> exciplex is not experimentally confirmed yet. However, one can suppose that the stabilization of this complex is possible by different physical mechanisms. For example, this exciplex could be stabilized in an experiment in which a mixture of Ca<sup>+</sup> and H<sub>2</sub> gases is illuminated by a laser light adjusted to the energy difference between the ground state and one of the vibrational states of the exciplex. For the equilibrium values of the (3d)<sup>2</sup>D<sup>2</sup>B<sub>2</sub> PES the laser energy should be in the range 6250–9138 cm<sup>-1</sup>.

We have shown that Gegenbauer polynomial are much better basis functions than Legendre polynomials for the bending motion of systems with a minimum around  $\theta = \frac{\pi}{2}$  and a strong anisotropy. The Gegenbauer polynomials lead to much faster basis set convergence. Due to our knowledge this is the first attempt to apply Gegenbauer polynomials in vibrational calculations.

**Acknowledgement** This work was supported by the KBN grant No. 5 P03B 038 20.

#### Appendix A. The bending motion

For describing the bending motion we have used analytic functions which are eigenfunctions of the equation

$$\left[ -\frac{\hbar^2}{2I_e} \left( \frac{1}{\sin\theta} \frac{\partial}{\partial\theta} \sin\theta \frac{\partial}{\partial\theta} + \frac{1}{\sin^2\theta} \frac{\partial^2}{\partial\varphi^2} \right) + V_{\text{mod}}(\theta) \right] \Phi(\theta, \varphi) = \lambda \Phi(\theta, \varphi), \quad (13)$$

where

$$V_{\text{mod}}(\theta) = V_u + \frac{V_0}{\sin^2\theta}. \quad (14)$$

The momentum of inertia  $I_e$  is defined as

$$\frac{1}{I_e} = \frac{1}{\mu R_e^2} + \frac{1}{\mu_m r_e^2}. \quad (15)$$

Equation (13) describes a rigid rotator which motion is restricted by the potential  $V_{\text{mod}}(\theta)$ . Its eigenfunctions have the form

$$\Phi(\theta, \varphi) = Y(\theta) \frac{1}{\sqrt{2\pi}} e^{\pm im\varphi}, \quad (16)$$

where  $m = 0, \pm 1, \pm 2, \pm 3, \dots$ . Defining

$$\gamma = \frac{2I_e(\lambda - V_u)}{\hbar^2}, \quad \kappa^2 = \frac{2I_e V_0}{\hbar^2} \quad \text{and} \quad z = \cos\theta, \quad (17)$$

and inserting (16) into (13) we can rewrite Eq. (13) in the form

$$\left[ \frac{\partial}{\partial z} (1 - z^2) \frac{\partial}{\partial z} - \frac{m^2 + \kappa^2}{1 - z^2} + \gamma \right] Y(z) = 0. \quad (18)$$

To get rid of the singularity we postulate the solution as

$$Y(z) = (1 - z^2)^\sigma K(z). \quad (19)$$

Therefore, Eq. (18) can be rewritten in the form

$$(1 - z^2) K''(z) - 2z(2\sigma + 1) K' + [\gamma - 4\sigma^2 - 2\sigma] K(z) = 0, \quad (20)$$

where the condition  $\sigma = +\frac{1}{2}\sqrt{m^2 + \kappa^2}$  leads to a proper behavior of the  $Y^\sigma(z)$  when  $z$  tends to  $\pm 1$ . We can find a solution of this equation by expanding  $K(z)$  in a series  $K(z) =$

**Table 3** Comparison of convergence rates for the lowest energies of the bending mode in a basis formed from Legendre Polynomials ( $E_{Leg}$ ), and a basis formed from Gegenbauer polynomials ( $E_{Geg}$ )

N	$\nu = 0$ $E_d = 520.2016 \text{ cm}^{-1}$		$\nu = 1$ $E_d = 1648.0515 \text{ cm}^{-1}$		$\nu = 2$ $E_d = 2828.9413 \text{ cm}^{-1}$	
	$E_{Geg} [\text{cm}^{-1}]$	$E_{Leg} [\text{cm}^{-1}]$	$E_{Geg} [\text{cm}^{-1}]$	$E_{Leg} [\text{cm}^{-1}]$	$E_{Geg} [\text{cm}^{-1}]$	$E_{Leg} [\text{cm}^{-1}]$
1	521.4851	2975.9357				
2	521.4851	2975.9357	1650.0601	5879.1468		
	520.2960	920.2566	1650.0601	5879.1468	2833.6101	7740.6373
3	520.2960	920.2566	1648.9771	2643.8516	2833.6101	7740.6373
	520.2340	578.5943	1648.9771	2643.8516	2833.6093	4331.2711
4	520.2340	578.5943	1648.3372	1829.1914	2833.6093	4331.2711
	520.2101	524.5147	1648.3372	1829.1914	2830.5328	3153.0073
5	520.2101	524.5147	1648.1440	1665.1440	2830.5328	3153.0073
	520.2073	520.2864	1648.1440	1665.1440	2829.5347	2864.8431
	520.2073	520.2864	1648.1055	1648.5341	2829.5347	2864.8431

$E_d$  denotes the accurate value,  $N$  stands for the number of symmetric (antisymmetric) basis functions. We have used parameters ( $V_0 = 0.02$ ,  $V_u = -0.02$ ) for the model potential.

$\sum_{k=0}^{\infty} a_k z^k$ . Substituting  $K(z)$  into (20) we can find a recursive relation for the  $a_k$  coefficients

$$\frac{a_{k+2}}{a_k} = \frac{k(k-1) + (4\sigma+2)k + 4\sigma^2 + 2\sigma - n(n+1)}{(k+2)(k+1)}. \quad (21)$$

Finally, by cutting  $K(z)$  on the  $n$ th term one gets a condition for the eigenvalues.

Equation (20) can be also reduced to the hypergeometric equation by the substitution  $t = (1-z)/2$ . A simple calculations yields

$$\left[ \frac{d^2}{dt^2} + \frac{2(1+2\sigma)t - (1+2\sigma)}{t(t-1)} \frac{d}{dt} + \frac{4\sigma^2 + 2\sigma - \gamma}{t(t-1)} \right] K(t) = 0. \quad (22)$$

Following the standard procedure of comparing coefficients we get the solution

$$K_n^\sigma(z) = F\left(-n, 1+4\sigma+n, 1+2\sigma; \frac{1-z}{2}\right), \quad (23)$$

expressed by the hypergeometric function  $F$ . Both methods lead to the eigenvalues

$$\lambda_{n,\sigma} = \frac{\hbar^2}{2I_e} [n^2 + (4\sigma+1)n + 2\sigma(2\sigma+1)] + V_u. \quad (24)$$

The full function  $Y_n^\sigma(z)$  can be written in terms of Gegenbauer polynomials  $C_n^{2\sigma+1/2}(z) = NK_n^\sigma(z)$  (for definition see [19, 20]). The normalized functions  $Y_n^\sigma(z)$  have the form

$$Y_n^\sigma(z) = 2^{2\sigma} |\Gamma(2\sigma+1/2)| \left[ \frac{n!(2\sigma+1/2+n)}{\pi\Gamma(n+4\sigma+1)} \right]^{1/2} \times (1-z^2)^\sigma C_n^{2\sigma+1/2}(z). \quad (25)$$

For the case where quantity  $\sigma = 0$ , the Gegenbauer polynomials  $C_n^{2\sigma+1/2}(z)$  reduce to the associated Legendre polynomials  $P_n^{|m|}(\cos\theta)$ . This is obvious, because in this case in the model potential  $V_0$  is 0 and Equation (13) reduces to the rigid rotor equation.

The eigenfunctions  $Y_n^\sigma(z)$  (25) for  $m = 0$  are denoted  $\xi_n^\sigma(\theta)$  and are used for spanning a basis set for the bending mode (see formula (7)).

## Appendix B. Comparison of the basis sets

We solved numerically the eigenvalue problem

$$\left[ -\frac{\hbar^2}{2I_e} \left( \frac{1}{\sin\theta} \frac{\partial}{\partial\theta} \sin\theta \frac{\partial}{\partial\theta} \right) + V(r_e, R_e, \theta) \right] \chi(\theta, \varphi) = E \chi(\theta, \varphi), \quad (26)$$

in order to compare convergence rates of calculations performed in basis sets formed from Gegenbauer and Legendre polynomials, respectively.  $V(r_e, R_e, \theta)$  stands for the ab initio potential energy curve of the bending mode (see Fig. 2) of the  $\text{Ca}^+ - \text{H}_2$  system.

First of all Eq. (26) was solved numerically using the finite differences method. The eigenenergies obtained by this method are regarded as the most precise, and they are treated as the reference energies for other calculations, and they are denoted by  $E_d$ .

Next, we solved Eq. (26) using the secular method with two different basis sets.

Once the function  $\chi(\theta)$  was expanded in terms of Gegenbauer polynomials. We chose parameters  $V_0 = 0.02 \text{ au}$  and  $V_u = -0.02 \text{ au}$  for the potential  $V_{\text{mod}}(\theta)$ . In this calculations the resultant eigenvalues are denoted by  $E_{Geg}$ .

Finally, the secular equations are obtained by expanding the  $\chi(\theta)$  in the basis formed from Legendre polynomials. In this case  $E_{Leg}$  stands for the eigenvalue.

The Hamiltonian (26) is invariant to the interchange of H nuclei in the  $\text{H}_2$  moiety. Therefore, the wavefunctions are either symmetric or antisymmetric in respect of this interchange. Thus, only the proper symmetry basis functions have influence on a wavefunction. The results concerning low lying levels are presented in Table 3. We can see from Table 3 that the convergence rate for the basis formed from Gegenbauer polynomials is high.

The  $V(r_e, R_e, \theta)$  potential energy curve is rather shallow so for excited states the convergence is worse then for low lying states, but still it is better for Gegenbauer than for Legendre polynomials. It seems that the basis formed from

Gegenbauer polynomials will work even better if the real potential energy is deeper.

We have also carried out a comparison of these two angular basis sets in a three dimensional case. For this purpose vibrational energies were calculated in a basis obtained by replacing the angular basis functions  $\xi_k(\cos\theta)$  in expansion (4) by Legendre polynomials. We observed a similar behavior of the convergence rates as in the one dimensional example.

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