

# Ro-Vibrational States of Triplet $\text{H}_2\text{D}^{+\dagger}$

Alexander Alijah\* and António J. C. Varandas\*

Departamento de Química, Universidade de Coimbra, 3004-535 Coimbra, Portugal

Received: November 14, 2005; In Final Form: December 22, 2005

We present rotational term values for  $J \leq 3$  of the vibrational states with up to twofold excitation of  $\text{H}_2\text{D}^+$  in the lowest electronic triplet state ( $a^3\Sigma_u^+$ ). The calculations were performed using the method of hyperspherical harmonics and our recent accurate double many-body expansion potential energy surface.

## 1. Introduction

$\text{H}_3^+$ , the simplest triatomic molecule, keeps challenging astronomers, experimental spectroscopists, and theoreticians. As far as the ro-vibrational states in excited electronic triplet state  $1^3E'$  are concerned, direct spectroscopic observations have not yet been reported, but considerable progress has been made in their theoretical description in recent years. Published data include ro-vibrational<sup>1–4</sup> states of  $\text{H}_3^+$  and vibrational states of  $\text{H}_3^{+5,6}$  and  $\text{D}_3^{+6}$  on the lower sheet,  $a^3\Sigma_u^+$ , of the double-valued  $1^3E'$  surface as well as Slonczewski resonance states<sup>7,8</sup> of  $\text{H}_3^+$  on the upper sheet. In the present paper, we extend our analysis of the ro-vibrational states on the lower sheet to the isotopomer  $\text{H}_2\text{D}^+$ . This can be formed from  $\text{H}_3^+$  by a single H/D substitution, which makes it the most important of the deuterated isotopomers. It is hoped that the combined theoretical data on  $\text{H}_3^+$ ,  $\text{D}_3^+$ , and  $\text{H}_2\text{D}^+$  will lead to the assignment of some of the lines not accounted for in hydrogen plasmas; see refs 9 and 10 and references therein.

## 2. Computation of Ro-Vibronic States and Their Symmetry Properties

**2.1. General.** In our computation of the ro-vibronic states of  $\text{H}_2\text{D}^+$ , we use the method of hyperspherical harmonics.<sup>11</sup> In this method, the wave function is expanded in terms of symmetrized hyperspherical harmonics,  $\Theta_{N,\Gamma,i}(\Omega)$

$$\Psi_{N,\Gamma}(\rho, \Omega) = \sum_i \Theta_{N,\Gamma,i}(\Omega) R_i(\rho) \quad (1)$$

Here,  $N$  denotes the quantum number of the angular momentum without electronic spin, which is neglected, that is,  $\bar{N} = \bar{J} - \bar{S}$ , and  $\Gamma$  is a symmetry index to be explained below. The coordinates used are the hyperradius,  $\rho$ , and five angles, which include the three Euler angles, denoted by  $\Omega$ . The hyperradial functions,  $R_i(\rho)$ , are then determined by numerical integration, according to the matrix Numerov method,<sup>12</sup> of the system of coupled equations that result from the expansion eq 1. The parameters of the computational method are identical to those used for  $\text{H}_3^+$  in ref 3, and the reader is referred to that article for details. The hyperspherical harmonics expansion is known to be slowly convergent. The large bases required demand the use of supercomputers. The numerical data obtained here, based

on our most accurate potential energy surface<sup>4</sup> and calculated with nuclear masses, are converged to about  $0.1 \text{ cm}^{-1}$  for the lowest states and to better than  $0.7 \text{ cm}^{-1}$  for the higher excited ones. In contrast, the absolute accuracy of the ab initio points produced at the Full CI level with the large cc-V5Z basis set has been estimated<sup>2</sup> to be  $100 \pm 30 \text{ cm}^{-1}$ , while the accuracy of their analytical DMBE-representation varies between  $1.3$  and  $2.8 \text{ cm}^{-1}$  in the energy region of interest for the present work. The frequencies derived from our data should be quite precise because of cancellation of errors. Inclusion of the diagonal adiabatic corrections, which are unavailable for the title system, are not expected to affect the results by more than a fraction of a wavenumber.

The hyperspherical method makes use of the exact symmetry properties of a molecule, which are those with respect to permutation of identical nuclei and inversion of the spatial coordinate system. In the present case,  $\text{H}_2\text{D}^+$ , the calculated states are readily classified in terms of the angular momentum,  $N$ , and the irreducible representation,  $\Gamma$ , of the two-particle permutation and inversion group,  $S_2 \times I$ . This group is isomorphic with the molecular symmetry group  $C_{2v}(M)$ .<sup>13</sup> The four irreducible representations ( $A_1, A_2, B_1, B_2$ ) are interpreted as follows:  $A$  and  $B$  denote states that are symmetric or antisymmetric with respect to the permutation operator (12), while the indices 1 and 2 distinguish states of different symmetry with respect to the operator (12)\* = (12)  $\times$   $E^*$ , where  $E^*$  denotes the inversion operator.

Although such a classification, based on fundamental symmetry properties, is exact, it is not necessarily the most useful one, and often the traditional classification in terms of spectroscopic quantum numbers is preferred even though those quantum numbers do hold only approximately. In the following, we will elaborate the alternative, spectroscopic representation of the ro-vibronic states, and provide a link between the two sets of quantum numbers.

The ro-vibronic states to be considered here are those on the lower sheet of the triplet potential energy surface. Because of the Jahn Teller effect, there are three equivalent minima at symmetric linear configurations of the nuclei, related by permutation of the nuclei, see ref 1. Any molecular state can thus be considered a superposition of localized linear molecule states as described in terms of the usual spectroscopic quantum numbers. For  $\text{H}_3^+$ , these superpositions lead to a triplication of states such that each linear molecule ro-vibronic state has one component of  $A$  symmetry and one of  $E$  symmetry. For  $\text{H}_2\text{D}^+$ , the situation is different, because two isomers exist,  $\text{HDH}^+$  and

<sup>†</sup> Part of the special issue "John C. Light Festschrift".

\* Corresponding authors. E-mail: alijah@ci.uc.pt; varandas@qtvsl.iqui.uc.pt.

**TABLE 1: Symmetry Classification of the Ro-Vibronic States of HDH<sup>+</sup> in  $D_{\infty h}(M)$  and  $C_{2v}(M)$** 

$v_2$	$v_3$	$s$	$\Gamma_{\text{rve}}[D_{\infty h}(M)]$		$\Gamma_{\text{rve}}[C_{2v}(M)]$		case
			$N$ even	$N$ odd	$N$ even	$N$ odd	
even	even	+	$\Sigma_u^+$	$\Sigma_u^-$	$B_2(3)$	$A_2(1)$	I
		-	$\Sigma_u^-$	$\Sigma_u^+$	$A_2(1)$	$B_2(3)$	III
	odd	+	$\Sigma_g^+$	$\Sigma_g^-$	$A_1(1)$	$B_1(3)$	II
		-	$\Sigma_g^-$	$\Sigma_g^+$	$B_1(3)$	$A_1(1)$	IV
odd	even	+	$\Sigma_g^-$	$\Sigma_g^+$	$B_1(3)$	$A_1(1)$	IV
		-	$\Sigma_g^+$	$\Sigma_g^-$	$A_1(1)$	$B_1(3)$	II
	odd	+	$\Sigma_u^-$	$\Sigma_u^+$	$A_2(1)$	$B_2(3)$	III
		-	$\Sigma_u^+$	$\Sigma_u^-$	$B_2(3)$	$A_2(1)$	I

HHD<sup>+</sup>. Of the latter, there are the two equivalent forms  $H_{[1]}H_{[2]}D^+$  and  $H_{[2]}H_{[1]}D^+$ , each corresponding to one of the minima of the potential energy surface, while the third minimum corresponds to HDH<sup>+</sup>.

Symmetrization of the two equivalent HHD<sup>+</sup> forms lead to superpositions that are symmetric or antisymmetric with respect to the permutation operator (12). Because these superpositions have well-defined and identical parity, the pairs formed are ( $A_1$ ,  $B_2$ ) or ( $A_2$ ,  $B_1$ ), which have positive or negative parity, respectively.

Our calculated states, which are readily classified in terms of their exact quantum numbers, do not distinguish the two isomers HDH<sup>+</sup> and HHD<sup>+</sup>. The remaining task is then to assign them to either of the two isomers and to attribute conventional linear molecule quantum numbers. To this end, we will elaborate, beginning with HDH<sup>+</sup>, the quantum numbers and symmetry properties of the two isomers.

**2.2. Spectroscopic Representation of the HDH<sup>+</sup> Ro-Vibronic States.** Isolated HDH<sup>+</sup> belongs to the molecular symmetry group  $D_{\infty h}(M)$ . The fundamental vibrational modes are the symmetric stretch  $\nu_1$  ( $\sigma_g^+$ ), the bending  $\nu_2$  ( $\pi_u$ ), and the antisymmetric stretch  $\nu_3$  ( $\sigma_u^+$ ). In terms of corresponding quantum numbers, the ro-vibrational eigen state can be written as

$$|\Psi^\pm\rangle = \frac{1}{\sqrt{2}}|\nu_1\nu_2^{|l|}\nu_3\rangle (|Nlm\rangle \pm |N, -lm\rangle) \quad (2)$$

for  $l \neq 0$  and

$$|\Psi\rangle = \frac{1}{\sqrt{2}}|\Psi^+\rangle \quad (3)$$

for  $l = 0$ . Here,  $l$  is the quantum number of the vibrational angular momentum, which takes the values  $l = -v_2, v_2 + 2, \dots, v_2$ , and  $N$  is the rotational quantum number defined above. Its internal projection is identical to  $l$ .  $m$  denotes the external projection. The  $\pm$  superscript is related to parity by

$$E^*|\Psi^\pm\rangle = \pm(-1)^{N+l}|\Psi^\pm\rangle \quad (4)$$

Quantum numbers and their meaning are thus identical to those of  $H_3^+$ , and we can use some of the results obtained in refs 1 and 3 directly. Following this work, the ro-vibronic symmetry of states,  $\Gamma_{\text{rve}}[D_{\infty h}(M)]$ , which is the direct product of the vibrational symmetry,  $\Gamma_{\text{rv}}[D_{\infty h}(M)]$ , and the electronic symmetry  $\Sigma_u^\pm$ , can be classified according to  $v_2$ ,  $v_3$ ,  $s$ , and  $N$ , where  $s = \pm$  denotes the sign of  $|\Psi^\pm\rangle$  in eq 2. The result, which is derived from Table 1 of ref 3, is shown in Table 1. Note that the  $\pm$  superscript of the symmetry labels in  $D_{\infty h}(M)$  indicates parity, while the  $g/u$  classification is according to the operator

**TABLE 2: Symmetry Classification of the Ro-Vibronic States of HHD<sup>+</sup> in  $C_{\infty v}(M)$  and  $C_{2v}(M)$** 

$v_2$	$s$	$\Gamma_{\text{rve}}[D_{\infty h}(M)]$		$\Gamma_{\text{rve}}[C_{2v}(M)]$		case
		$N$ even	$N$ odd	$N$ even	$N$ odd	
even	+	$\Sigma^+$	$\Sigma^-$	$A_1(1); B_2(3)$	$A_2(1); B_1(3)$	I
	-	$\Sigma^-$	$\Sigma^+$	$A_2(1); B_1(3)$	$A_1(1); B_2(3)$	III
odd	+	$\Sigma^-$	$\Sigma^+$	$A_2(1); B_1(3)$	$A_1(1); B_2(3)$	III
	-	$\Sigma^+$	$\Sigma^-$	$A_1(1); B_2(3)$	$A_2(1); B_1(3)$	I

(12)\*. With the analysis presented in the preceding subsection, the classification of states in  $C_{2v}(M)$  is straightforward. This classification is also shown in Table 1. Because of their distinct symmetry properties, the ro-vibronic states can be divided into four groups.

The statistical weight of a ro-vibronic state depends on the degeneracy of the nuclear spin state with which it is multiplied. The two protons can be coupled to yield an antisymmetric singlet function of symmetry  $B_2$  or a symmetric triplet function of symmetry  $A_1$ . Because the total function is required to be antisymmetric, the ro-vibronic functions of  $B$  symmetry must be combined with the triplet function, while those of  $A$  symmetry must be combined with the singlet function. The statistical weights are thus 3 and 1, respectively. They are given in Table 1 in parentheses.

**2.3. Spectroscopic Representation of the HHD<sup>+</sup> Ro-Vibronic States.** We will now work out the symmetry properties of the HHD<sup>+</sup> isomer. It belongs to the molecular symmetry group  $C_{\infty v}(M)$  and has as fundamental modes the HD stretch,  $\nu_1$  ( $\sigma^+$ ), the bending,  $\nu_2$  ( $\pi$ ), and the HH stretch,  $\nu_3$  ( $\sigma^+$ ). The ro-vibronic states are represented by the kets  $|\Psi^\pm\rangle$  as defined in eq 2 for HDH<sup>+</sup>, but with the modified meaning of  $v_1$  and  $v_3$ . Because  $C_{\infty v}(M)$  is a subgroup of  $D_{\infty h}(M)$ ,  $D_{\infty h}(M) = C_{\infty v}(M) \times C_i$ , the symmetry properties of HHD<sup>+</sup> can be derived from those presented for HDH<sup>+</sup> in Table 1 by simply omitting the  $g/u$  subscripts because these are due to operator  $C_i$ . Thus, cases I and II become equivalent as do III and IV, and hence we only retain cases I and III. Furthermore,  $\nu_3$  is no longer antisymmetric so that the  $\nu_3$  (odd) lines of that table do not appear here. The irreducible representations  $\Sigma^+$  and  $\Sigma^-$  in  $C_{\infty v}(M)$  correspond to  $A_1$  and  $A_2$  in the  $C_{2v}(M)$  molecular symmetry group, or to  $A_1/B_2$  and  $A_2/B_1$  if we add the second component of the delocalized state, which is antisymmetric with respect to the permutation operator (12), as discussed in section 2.1. The results are presented in Table 2.

### 3. Assignments of Calculated Ro-Vibronic States

In ref 14, a method for a semiautomatic assignment of the calculated ‘‘hyperspherical’’ states has been developed, which has been applied since to  $H_3^+$  and its isotopomers in the electronic ground state and to  $H_3^+$  in the triplet state.<sup>3</sup> The latter version of this code has been adapted to analyze the molecule under consideration here. The basis for the assignment is the exact symmetry of the ro-vibronic states in their spectroscopic representation and the requirement of sensible rotational progression within a band. No wave functions are needed. The input simply is a list of band origins, ordered with increasing energy. The computer program first attempts to assign the ro-vibronic states of HHD<sup>+</sup>, making use of the additional requirement that the two components, which arise from symmetric and antisymmetric superposition of localized structures, be within a certain energy interval, for example, within 0.5 cm<sup>-1</sup>. The hyperspherical states that remain unassigned at this stage must belong to the HDH<sup>+</sup> isomer. They are analyzed in the second phase of the program.

TABLE 3: Ro-Vibronic Term Values of the HHD<sup>+</sup> States of Group I<sup>a</sup>

$(v_1, v_2^l, v_3)$	$N$	$\Gamma_{\text{rve}}^{(1)}$	$n^{(1)}$	$\Gamma_{\text{rve}}^{(2)}$	$n^{(2)}$	$E^{(1)}$	$E^{(2)}$	$E_{\text{rel}}^{(1)}$	$E_{\text{rel}}^{(2)}$	$\Delta$
(0, 0 <sup>0</sup> , 0)	0	B <sub>2</sub>	1	A <sub>1</sub>	0	73.72	73.72	0.00	0.00	0.00
	1	A <sub>2</sub>	1	B <sub>1</sub>	0	80.67	80.67	6.95	6.95	0.00
	2	B <sub>2</sub>	1	A <sub>1</sub>	0	94.56	94.56	20.84	20.84	0.00
	3	A <sub>2</sub>	1	B <sub>1</sub>	0	115.39	115.39	41.67	41.67	0.00
(0, 1 <sup>1</sup> , 0) <sup>-</sup>	1	A <sub>2</sub>	2	B <sub>1</sub>	3	711.95	711.95	0.00	0.00	0.00
	2	B <sub>2</sub>	2	A <sub>1</sub>	3	724.09	724.09	12.15	12.15	0.00
	3	A <sub>2</sub>	2	B <sub>1</sub>	3	742.36	742.36	30.41	30.41	0.00
(0, 0 <sup>0</sup> , 1)	0	B <sub>2</sub>	2	A <sub>1</sub>	2	778.63	778.63	0.00	0.00	0.00
	1	A <sub>2</sub>	3	B <sub>1</sub>	4	785.85	785.85	7.22	7.22	0.00
	2	B <sub>2</sub>	3	A <sub>1</sub>	4	800.28	800.28	21.65	21.65	0.00
	3	A <sub>2</sub>	3	B <sub>1</sub>	4	821.87	821.87	43.24	43.24	0.00
(1, 0 <sup>0</sup> , 0)	0	B <sub>2</sub>	4	A <sub>1</sub>	3	946.81	946.81	0.00	0.00	0.00
	1	A <sub>2</sub>	4	B <sub>1</sub>	5	953.36	953.36	6.55	6.55	0.00
	2	B <sub>2</sub>	4	A <sub>1</sub>	5	966.46	966.46	19.65	19.65	0.00
	3	A <sub>2</sub>	4	B <sub>1</sub>	5	986.12	986.11	39.31	39.30	0.00
(0, 2 <sup>0</sup> , 0)	0	B <sub>2</sub>	6	A <sub>1</sub>	4	1293.23	1293.24	0.00	0.01	-0.01
	1	A <sub>2</sub>	8	B <sub>1</sub>	6	1298.34	1298.34	5.11	5.11	0.00
	2	B <sub>2</sub>	9	A <sub>1</sub>	6	1307.62	1307.62	14.40	14.39	0.01
	3	A <sub>2</sub>	9	B <sub>1</sub>	6	1321.90	1321.90	28.67	28.67	-0.01
(0, 1 <sup>1</sup> , 1) <sup>-</sup>	1	A <sub>2</sub>	9	B <sub>1</sub>	7	1303.46	1303.46	0.00	0.00	0.00
	2	B <sub>2</sub>	10	A <sub>1</sub>	7	1316.17	1316.17	12.70	12.71	0.00
	3	A <sub>2</sub>	10	B <sub>1</sub>	7	1336.17	1336.16	32.71	32.70	0.01
(0, 2 <sup>2</sup> , 0) <sup>+</sup>	2	B <sub>2</sub>	11	A <sub>1</sub>	8	1356.46	1356.46	0.00	0.00	0.00
	3	A <sub>2</sub>	11	B <sub>1</sub>	8	1381.39	1381.39	24.93	24.93	0.00
(0, 0 <sup>0</sup> , 2)	0	B <sub>2</sub>	7	A <sub>1</sub>	6	1437.31	1437.32	0.00	0.01	-0.01
	1	A <sub>2</sub>	10	B <sub>1</sub>	10	1442.78	1442.77	5.47	5.46	0.01
	2	B <sub>2</sub>	12	A <sub>1</sub>	11	1453.75	1453.74	16.44	16.44	0.00
	3	A <sub>2</sub>	12	B <sub>1</sub>	10	1470.55	1470.50	33.24	33.19	0.05
(1, 1 <sup>1</sup> , 0) <sup>-</sup>	1	A <sub>2</sub>	12	B <sub>1</sub>	11	1512.49	1512.51	0.00	0.02	-0.02
	2	B <sub>2</sub>	14	A <sub>1</sub>	12	1525.38	1525.36	12.89	12.86	0.03
	3	A <sub>2</sub>	14	B <sub>1</sub>	12	1544.66	1544.66	32.17	32.17	0.00
(1, 0 <sup>0</sup> , 1)	0	B <sub>2</sub>	9	A <sub>1</sub>	8	1561.41	1561.42	0.00	0.00	0.00
	1	A <sub>2</sub>	13	B <sub>1</sub>	13	1567.96	1567.96	6.55	6.54	0.00
	2	B <sub>2</sub>	15	A <sub>1</sub>	15	1581.08	1581.07	19.66	19.65	0.01
	3	A <sub>2</sub>	15	B <sub>1</sub>	14	1600.67	1600.65	39.26	39.24	0.02
(2, 0 <sup>0</sup> , 0)	0	B <sub>2</sub>	11	A <sub>1</sub>	9	1749.21	1749.53	0.00	0.32	-0.32
	1	A <sub>2</sub>	16	B <sub>1</sub>	15	1755.27	1754.96	6.06	5.75	0.31
	2	B <sub>2</sub>	17	A <sub>1</sub>	17	1766.50	1766.80	17.28	17.58	-0.30
	3	A <sub>2</sub>	17	B <sub>1</sub>	16	1784.41	1784.05	35.19	34.83	0.36
(0, 3 <sup>1</sup> , 0) <sup>-</sup>	1	A <sub>2</sub>	18	B <sub>1</sub>	16	1813.30	1813.67	0.00	0.37	-0.37
	2	B <sub>2</sub>	19	A <sub>1</sub>	18	1813.46	1813.53	0.15	0.22	-0.07
	3	A <sub>2</sub>	19	B <sub>1</sub>	19	1829.50	1829.47	16.20	16.16	0.03
(0, 3 <sup>3</sup> , 0) <sup>-</sup>	3	A <sub>2</sub>	20	B <sub>1</sub>	20	1848.01	1848.24	0.00	0.22	-0.22

<sup>a</sup> The energies  $E^{(1)}$  and  $E^{(2)}$  are with respect to the zero point energy, while the energies  $E_{\text{rel}}^{(1)}$  and  $E_{\text{rel}}^{(2)}$  are with respect to the band head of the first component.  $\Delta$  is the energy difference between the two components. All energies are in units of cm<sup>-1</sup>.  $\Gamma^{(1)}$  and  $\Gamma^{(2)}$  indicate the ro-vibronic symmetry of the states, while  $n^{(1)}$  and  $n^{(2)}$  are indices counting states with the same symmetry and angular momentum,  $N$ .

In Tables 3–8, we present term values, for  $N \leq 3$ , of all vibrational states  $(v_1, v_2^l, v_3)$  up to twofold excitation, plus  $(0, 3^1, 0)$  and  $(0, 3^3, 0)$ , because for the HDH<sup>+</sup> isomer their energies are below that of  $(2, 0, 0)$ . In these tables, the zero point energy is that of the lowest vibrational state  $(0, 0^0, 0)$  of HDH<sup>+</sup>. This energy is  $E_{\text{ZPE}} = -1.109100 E_{\text{H}}$ , and hence the corresponding state lies 1527.76 cm<sup>-1</sup> above the minimum of the potential energy surface. The isomerization barriers are at  $E = 1070$  cm<sup>-1</sup> above ZPE (all energies reported heretofore refer to this reference), while the HD<sup>+</sup> + H dissociation energy is at  $E = 2464$  cm<sup>-1</sup>. Vibrational states with more than single excitation are already located above the isomerization barriers.

The assignment of the HHD<sup>+</sup> states was straightforward, and all of the vibrational states show a quite regular energy progression in their rotational manifolds. Furthermore, the splitting between the symmetric and antisymmetric components is very small. Having identified the HHD<sup>+</sup> states in our database

of calculated eigenvalues, the assignment of the relatively few remaining eigenvalues to ro-vibronic states of HDH<sup>+</sup> is greatly facilitated. Looking at the tables of the HDH<sup>+</sup> states, we find some interesting irregular features. Such irregularities could cause problems in the automatic assignments, but because now we have to divide the calculated eigenvalues over four groups of states with different transformation properties, defined in Table 1, the assignments are quite certain. The irregularities in the energy region around 1100 cm<sup>-1</sup>, just above the barriers of the potential, can be explained in terms of Fermi resonances between members of the vibrational states  $(0, 2^0, 0)$ ,  $(0, 1^1, 1)$ , and  $(0, 2^2, 0)$ , see Figure 1. In this Figure, the three states on the left interact, as do the two states on the right. The interaction patterns of the two groups of states are quite different. For example, the  $N = 1$  member of  $(0, 2^0, 0)$  is pushed down by interaction with  $N = 1$ ,  $(0, 1^1, 1)$ <sup>-</sup>. Corresponding displacement of the latter manifests itself in the large energy splitting of almost

**TABLE 4: Ro-Vibronic Term Values of the HHD<sup>+</sup> States of Group III<sup>a</sup>**

$(v_1, v_2^l, v_3)$	$N$	$\Gamma_{\text{rve}}^{(1)}$	$n^{(1)}$	$\Gamma_{\text{rve}}^{(2)}$	$n^{(2)}$	$E^{(1)}$	$E^{(2)}$	$E_{\text{rel}}^{(1)}$	$E_{\text{el}}^{(2)}$	$\Delta$
(0, 1 <sup>1</sup> , 0)+	1	$B_2$	0	$A_1$	1	712.92	712.92	0.00	0.00	0.00
	2	$A_2$	0	$B_1$	1	727.00	727.00	14.08	14.08	0.00
	3	$B_2$	0	$A_1$	1	748.11	748.11	35.19	35.19	0.00
(0, 1 <sup>1</sup> , 1)+	1	$B_2$	2	$A_1$	2	1302.28	1302.27	0.00	-0.01	0.01
	2	$A_2$	3	$B_1$	2	1311.57	1311.58	9.29	9.30	-0.01
	3	$B_2$	3	$A_1$	2	1326.64	1326.63	24.36	24.35	0.01
(0, 2 <sup>2</sup> , 0)-	2	$A_2$	4	$B_1$	3	1356.57	1356.56	0.00	0.00	0.00
	3	$B_2$	4	$A_1$	3	1381.77	1381.77	25.20	25.20	0.00
(1, 1 <sup>1</sup> , 0)+	1	$B_2$	3	$A_1$	4	1512.46	1512.45	0.00	-0.02	0.02
	2	$A_2$	5	$B_1$	5	1525.23	1525.25	12.77	12.79	-0.02
	3	$B_2$	5	$A_1$	5	1544.40	1544.38	31.94	31.92	0.01
(0, 3 <sup>1</sup> , 0)+	1	$B_2$	5	$A_1$	6	1813.49	1813.11	0.00	-0.37	0.37
	2	$A_2$	7	$B_1$	8	1813.50	1813.43	0.01	-0.05	0.07
	3	$B_2$	7	$A_1$	9	1829.31	1829.34	15.83	15.85	-0.02
(0, 3 <sup>3</sup> , 0)+	3	$B_2$	8	$A_1$	10	1847.43	1847.15	0.00	-0.28	0.28

<sup>a</sup> Entries as in Table 3.**TABLE 5: Ro-Vibronic Term Values of the HDH<sup>+</sup> States of Group I<sup>a</sup>**

$(v_1, v_2^l, v_3)$	$N$	$\Gamma_{\text{rve}}$	$n$	$E$	$E_{\text{rel}}$
(0, 0 <sup>0</sup> , 0)	0	$B_2$	0	0.00	0.00
	1	$A_2$	0	9.55	9.55
	2	$B_2$	0	31.36	31.36
	3	$A_2$	0	60.04	60.04
(1, 0 <sup>0</sup> , 0)	0	$B_2$	3	946.77	0.00
	1	$A_2$	5	954.75	7.98
	2	$B_2$	5	976.91	30.13
	3	$A_2$	5	1001.68	54.91
(0, 2 <sup>0</sup> , 0)	0	$B_2$	5	1075.90	0.00
	1	$A_2$	6	1076.44	0.54
	2	$B_2$	6	1085.50	9.60
	3	$A_2$	6	1143.34	67.44
(0, 1 <sup>1</sup> , 1)-	1	$A_2$	7	1092.82	0.00
	2	$B_2$	7	1113.84	21.02
	3	$A_2$	7	1221.62	128.80
(0, 2 <sup>2</sup> , 0)+	2	$B_2$	8	1132.24	0.00
	3	$A_2$	8	1249.83	117.59
(0, 0 <sup>0</sup> , 2)	0	$B_2$	8	1438.90	0.00
	1	$A_2$	11	1447.77	8.87
	2	$B_2$	13	1470.42	31.53
	3	$A_2$	13	1504.12	65.22
(2, 0 <sup>0</sup> , 0)	0	$B_2$	10	1731.74	0.00
	1	$A_2$	15	1746.17	14.43
	2	$B_2$	18	1777.60	45.85
	3	$A_2$	18	1813.70	81.96

<sup>a</sup>  $E$  is with respect to the zero point energy, while  $E_{\text{rel}}$  is with respect to the band head. All energies are in units of  $\text{cm}^{-1}$ .  $\Gamma$  indicates the ro-vibronic symmetry of the states, while  $n$  is an index counting states with the same symmetry and angular momentum,  $N$ .

$10 \text{ cm}^{-1}$  with respect to the other component of the  $l$ -type doublet, (0, 1<sup>1</sup>, 1)+, which is unperturbed. In comparison, the splitting of the components of the (0, 1<sup>1</sup>, 0)  $l$ -type doublet is only about  $2 \text{ cm}^{-1}$ .

To obtain the selection rules for dipole transitions, we note that the dipole operator is antisymmetric with respect to inversion of the coordinate system and symmetric with respect to permutation of the two protons; thus, it transforms as  $A_2$  in  $C_{2v}(M)$ . Consequently, the selection rules are

$$A_1 \leftrightarrow A_2, B_1 \leftrightarrow B_2 \quad (5)$$

In addition, the usual selection rule  $\Delta J = 0, \pm 1$  applies. For convenience, we list in Table 9 the lowest frequencies of (far)

**TABLE 6: Ro-Vibronic Term Values of the HDH<sup>+</sup> States of Group II<sup>a</sup>**

$(v_1, v_2^l, v_3)$	$N$	$\Gamma_{\text{rve}}$	$n$	$E$	$E_{\text{rel}}$
(0, 1 <sup>1</sup> , 0)-	1	$B_1$	1	551.46	0.00
	2	$A_1$	1	570.73	19.26
	3	$B_1$	1	646.43	94.97
(0, 0 <sup>0</sup> , 1)	0	$A_1$	1	617.52	0.00
	1	$B_1$	2	628.32	10.80
	2	$A_1$	2	650.98	33.47
	3	$B_1$	2	710.57	93.05
(1, 0 <sup>0</sup> , 1)	0	$A_1$	5	1358.05	0.00
	1	$B_1$	8	1362.45	4.40
	2	$A_1$	9	1375.45	17.40
	3	$B_1$	9	1421.87	63.82
(1, 1 <sup>1</sup> , 0)-	1	$B_1$	9	1405.86	0.00
	2	$A_1$	10	1430.96	25.11
	3	$B_1$	11	1488.50	82.64
(0, 3 <sup>1</sup> , 0)-	1	$B_1$	12	1518.77	0.00
	2	$A_1$	13	1536.50	17.73
	3	$B_1$	13	1599.96	81.19
(0, 3 <sup>3</sup> , 0)-	3	$B_1$	15	1602.64	0.00

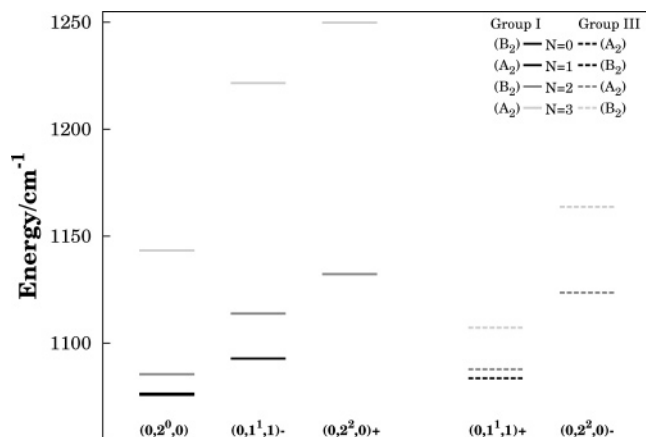
<sup>a</sup> Entries as in Table 5.**TABLE 7: Ro-Vibronic Term Values of the HDH<sup>+</sup> States of Group III<sup>a</sup>**

$(v_1, v_2^l, v_3)$	$N$	$\Gamma_{\text{rve}}$	$n$	$E$	$E_{\text{rel}}$
(0, 1 <sup>1</sup> , 1)+	1	$B_2$	1	1083.63	0.00
	2	$A_2$	1	1087.80	4.17
	3	$B_2$	1	1107.27	23.64
(0, 2 <sup>2</sup> , 0)-	2	$A_2$	2	1123.66	0.00
	3	$B_2$	2	1163.70	40.04

<sup>a</sup> Entries as in Table 5.**TABLE 8: Ro-Vibronic Term Values of the HDH<sup>+</sup> States of Group IV<sup>a</sup>**

$(v_1, v_2^l, v_3)$	$N$	$\Gamma_{\text{rve}}$	$n$	$E$	$E_{\text{rel}}$
(0, 1 <sup>1</sup> , 0)+	1	$A_1$	0	553.51	0.00
	2	$B_1$	0	572.84	19.33
	3	$A_1$	0	602.49	48.98
(1, 1 <sup>1</sup> , 0)+	1	$A_1$	3	1403.23	0.00
	2	$B_1$	4	1418.53	15.29
	3	$A_1$	4	1442.88	39.64
(0, 3 <sup>1</sup> , 0)+	1	$A_1$	5	1601.87	0.00
	2	$B_1$	7	1621.72	19.85
	3	$A_1$	7	1654.98	53.11
(0, 3 <sup>3</sup> , 0)+	3	$A_1$	8	1679.89	0.00

<sup>a</sup> Entries as in Table 5.



**Figure 1.** Ro-vibronic states of HDH<sup>+</sup> in the 1100 cm<sup>-1</sup> region, see the text. The lowest two (0, 2<sup>0</sup>, 0) levels are nearly indistinguishable within the scale of the Figure and appear as a slightly broader line.

**TABLE 9: Frequencies, in Wavenumbers, of the First Low-Energy IR Transitions Originating from the Vibrational Ground States of HDH<sup>+</sup> and HHD<sup>+</sup>**

isomer	initial state	$\Gamma_{\text{rve}}$ (weight)	final state	$\Gamma_{\text{rve}}$ (weight)	$\Delta E$
HDH <sup>+</sup>	$N = 0, (0, 0^0, 0)$	$B_2(3)$	$N = 1, (0, 1^1, 0)-$	$B_1(3)$	551.46
HDH <sup>+</sup>	$N = 0, (0, 0^0, 0)$	$B_2(3)$	$N = 1, (0, 0^0, 1)$	$B_1(3)$	628.32
HHD <sup>+</sup>	$N = 0, (0, 0^0, 0)$	$A_1(1)$	$N = 1, (0, 1^1, 0)-$	$A_2(1)$	638.23
HHD <sup>+</sup>	$N = 0, (0, 0^0, 0)$	$B_2(3)$	$N = 1, (0, 1^1, 0)-$	$B_1(3)$	638.23
HHD <sup>+</sup>	$N = 0, (0, 0^0, 0)$	$A_1(1)$	$N = 1, (0, 0^0, 1)$	$A_2(1)$	712.13
HHD <sup>+</sup>	$N = 0, (0, 0^0, 0)$	$B_2(3)$	$N = 1, (0, 0^0, 1)$	$B_1(3)$	712.13

IR transitions originating from the vibrational ground states of HDH<sup>+</sup> and HHD<sup>+</sup>.

#### 4. Conclusions

With the present work, the first data on ro-vibronic energies of H<sub>2</sub>D<sup>+</sup> in the electronic triplet state have become available. Because the hyperspherical harmonics expansion of the ro-

vibrational wave function is only slowly convergent for the title system, our present analysis has been restricted to states with up to moderate vibrational or rotational excitation. To make the method more efficient, we are exploring the concept of energy selected bases, as presented by Lee and Light,<sup>15</sup> within the hyperspherical harmonics contraction scheme. With such an optimized method, even higher excited states should become accessible. In the meantime, we hope that the data presented here may prove useful in an analysis of yet unassigned lines in hydrogen plasmas.

**Acknowledgment.** This work has the support of the Fundação para a Ciência e a Tecnologia, Portugal. We are also grateful to the John von Neumann Institut für Computing, Jülich, for the provision of supercomputer time on the IBM Regatta p690+ (Project EPG00).

#### References and Notes

- (1) Friedrich, O.; Aljiah, A.; Xu, Z. R.; Varandas, A. J. C. *Phys. Rev. Lett.* **2001**, *86*, 1183.
- (2) Cernei, M.; Aljiah, A.; Varandas, A. J. C. *J. Chem. Phys.* **2003**, *118*, 2637.
- (3) Aljiah, A.; Viegas, L. P.; Cernei, M.; Varandas, A. J. C. *J. Mol. Spectrosc.* **2003**, *221*, 163.
- (4) Varandas, A. J. C.; Aljiah, A.; Cernei, M. *Chem. Phys.* **2005**, *308*, 285.
- (5) Sanz, C.; Roncero, O.; Tablero, C.; Aguado, A.; Paniagua, M. *J. Chem. Phys.* **2001**, *114*, 2182.
- (6) Cuervo-Reyes, E.; Rubayo-Soneira, J.; Aguado, A.; Paniagua, M.; Tablero, C.; Sanz, C.; Roncero, O. *Phys. Chem. Chem. Phys.* **2002**, *4*, 6012.
- (7) Viegas, L. P.; Cernei, M.; Aljiah, A.; Varandas, A. J. C. *J. Chem. Phys.* **2004**, *120*, 253.
- (8) Viegas, L. P.; Aljiah, A.; Varandas, A. J. C. *J. Phys. Chem. A* **2005**, *109*, 3307.
- (9) Tennyson, J. *Rep. Prog. Phys.* **1995**, *57*, 421.
- (10) McNab, I. *Adv. Chem. Phys.* **1995**, *89*.
- (11) Wolniewicz, L. *J. Chem. Phys.* **1988**, *90*, 371.
- (12) Johnson, B. R. *J. Chem. Phys.* **1978**, *69*, 4678.
- (13) Bunker, P. R.; Jensen, P. *Molecular Symmetry and Spectroscopy*, 2nd ed.; NRC Press: Ottawa, Ontario, Canada, 1998.
- (14) Aljiah, A. Habilitation thesis, University of Bielefeld, Germany, 1996.
- (15) Lee, H.-S.; Light, J. C. *J. Chem. Phys.* **2003**, *118*, 3458.