

## GERADE-UNGERADE SYMMETRY BREAKING IN HD: STATES CLOSE TO N=2 DISSOCIATION LIMIT

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**Abstract.** *We review the consequences of the gerade-ungerade symmetry breaking in HD molecule. A particular attention is devoted to electronic states close to  $n=2$  dissociation limit. The effects of the breakdown of the Born-Oppenheimer approximation are discussed. For the description of the molecular dynamics the formulation of the coupled-states method is given. The method is applied to calculations of loosely bound states in the outer well of the  $\Pi^1\Pi_g$  potential. The results are in excellent agreement with experimental data and calculations based on a semi-empirical potential.*

**Keywords:** *HD molecule, gerade-ungerade symmetry breaking, coupled equations*

### INTRODUCTION

The main differences in the spectral characteristics of the isotopomers  $H_2$ ,  $D_2$  and HD stem from differences of their reduced nuclear masses. However, in the case of HD molecule an additional and important fact is the breakdown of the molecular gerade-ungerade ( $g-u$ ) symmetry (i.e. symmetry related to the inversion of the electronic coordinates with respect to the midpoint of the internuclear separation). One of the well known consequences is the appearance of the electric dipole moment in the ground electronic state [1] and the observation of the infra red, i.e. vibrational [2] and pure rotational spectrum in the far infra red domain [3]. As for the electronic transitions in HD, the  $g-u$  symmetry breaking is here responsible for the occurrence of the otherwise dipole forbidden  $g \leftrightarrow g$  or  $u \leftrightarrow u$  transitions. These transitions have been observed in  $EF^1\Sigma_g^+ - X^1\Sigma_g^+$  [4,5],  $GK^1\Sigma_g^+ - X^1\Sigma_g^+$  and  $I^1\Pi_g - X^1\Sigma_g^+$  [4] systems. More recently, strong  $g-u$  coupling was studied between the rovibrational  $\tilde{H}^1\Sigma_g^+$  and  $\tilde{B}^1\Sigma_u^+$  states [6]. More details on the above issues can be found in a recent review [7].

In suitably chosen coordinates, the  $g-u$  symmetry breaking term in the Hamiltonian describing the HD molecule is proportional to the mass difference of the isotopes and leads to non-adiabatic corrections which go beyond the Born-Oppenheimer (BO) approximation.

The states close to the  $n=2$  dissociation limit of HD are particularly interesting because they are markedly different from their homonuclear analogues. The proper account of the  $g-u$  nonadiabatic coupling reveals that there are actually two different dissociation limits corresponding to  $H^*(n=2)+D(n=1)$  and  $H(n=1)+D^*(n=2)$ , separated by an energy gap of  $22.38 \text{ cm}^{-1}$  related to the atomic isotope shift. One of the BO potentials from the  $n=2$  manifold is the  $\Pi^1\Pi_g$  double well potential. Recently, very precise and systematic measurements [8,9] of the rovibrational states corresponding to the outer well ( $\Gamma^1\Pi_g$ ) have been reported. In order to interpret their results the authors have constructed a semi-empirical potential [8] that incorporates the effects of the  $g-u$  coupling.

In the following sections we shall describe a theoretical approach based on the coupled-states method that goes beyond the notion of a single effective potential. After an analysis of the asymptotic forms of all relevant nonadiabatic couplings a minimal sets of coupled BO states are determined for description of both  $e$ -parity and  $f$ -parity rovibrational states in the  $\Gamma^1\Pi_g$  potential well. The calculated energy levels are in very good agreement with experimental data.

Atomic units ( $m_e=e=\hbar=1$ ) are used throughout, except when explicitly stated.

#### HAMILTONIAN AND COUPLED EQUATIONS

We neglect the spin-orbit and hyperfine interactions as they are much smaller than  $g-u$  coupling, concentrate on singlet (total electronic spin  $S=0$ ) states of HD and therefore ignore the spin variables. After the separation of the center-of-mass motion, introduction of the internuclear vector  $\vec{R} = \vec{R}_D - \vec{R}_H$  with spherical polar coordinates  $\{R, \theta, \varphi\}$  and using the relative position vectors  $\vec{r}_1$  and  $\vec{r}_2$  of the electrons with respect to the geometric center between the nuclei (see Fig.1), the non-relativistic Hamiltonian of HD molecule is :

$$H = T_R + H_{gu} + H_{mp} + H_e, \quad (1)$$

where  $T_R$ , the nuclear kinetic energy term is

$$T_R = - \frac{1}{2\mu} \nabla_R^2, \quad (2)$$

$H_{gu}$ , the  $g-u$  coupling (cross derivative) term is

$$H_{gu} = - \frac{1}{2\mu_a} \nabla_R \cdot \sum_{j=1,2} \nabla_j, \quad (3)$$

$H_{mp}$ , the mass polarization term is

$$H_{mp} = - \frac{1}{8\mu} \left( \sum_{j=1,2} \nabla_j \right)^2, \quad (4)$$

and  $H_e$ , the (BO) electronic Hamiltonian is

$$H_e = - \frac{1}{2} \sum_{j=1,2} \nabla_j^2 + V(\vec{R}, \vec{r}_1, \vec{r}_2). \quad (5)$$

In equations (1)-(5), the reduced mass of the nuclei is given by  $\mu = m_D m_H / (m_D + m_H) = 1223.8988$  and the mass asymmetry is defined by  $\mu_a = m_D m_H / (m_D - m_H) = 3674.1340$ . All the above operators are invariant with respect to transformation  $\vec{r}_j \rightarrow -\vec{r}_j$  except the  $g-u$  coupling term which transforms like  $H_{gu} \rightarrow -H_{gu}$ .

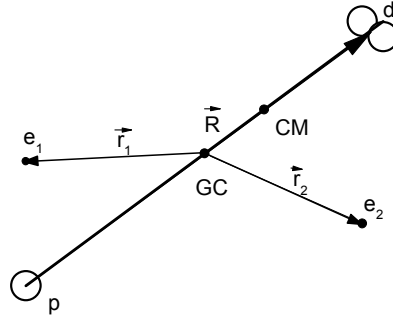


Fig. 1. Relative position vectors used in description of HD molecule

The exact integrals of motion, commuting with the Hamiltonian (1) are the square of the total angular momentum  $\vec{J}^2$ , its projection  $J_Z$  onto the space-fixed Z-axis and the parity operator  $i$  corresponding to inversion of all (nuclear and electronic) space-fixed coordinates. So, we can consider the subspaces with the corresponding fixed angular momentum quantum numbers  $J, M$  and parity  $(-1)^{J+\tilde{p}} = \pm 1$ , where  $\tilde{p}=0$  corresponds to the so called  $e$ -parity states and  $\tilde{p}=1$  to  $f$ -parity states.

The total molecular wave function can be expanded as:

$$\Psi^{\tilde{p}JM}(R, \theta, \varphi, \vec{r}_1, \vec{r}_2) = \frac{1}{R} \sum_{\gamma \Lambda} \chi_{\gamma \Lambda}(R) \Phi_{\gamma \Lambda}^{\tilde{p}JM}(\theta, \varphi, \vec{r}_1, \vec{r}_2) \quad (6)$$

$$\begin{aligned} \Phi_{\gamma \Lambda}^{\tilde{p}JM}(\theta, \varphi, \vec{r}_1, \vec{r}_2) = & \frac{1}{\sqrt{2(1+\delta_{\Lambda 0})}} [\tilde{D}_{M\Lambda}^J(\varphi, \theta) \psi_{\gamma\Lambda}(\vec{r}_1, \vec{r}_2; R) \\ & + (-1)^{\tilde{p}+\sigma} \tilde{D}_{M-\Lambda}^J(\varphi, \theta) \psi_{\gamma-\Lambda}(\vec{r}_1, \vec{r}_2; R)] \end{aligned} \quad (7)$$

where

$$\tilde{D}_{M\pm\Lambda}^J(\varphi, \theta) = \sqrt{\frac{2J+1}{4\pi}} D_{M\pm\Lambda}^J(\varphi, \theta, 0) \quad (8)$$

and  $D_{M\pm\Lambda}^J(\varphi, \theta, \psi)$  are the Wigner rotational functions. The BO electronic wave functions in a molecular (body-fixed) coordinate frame with the z-axis along the internuclear vector,  $\psi_{\gamma\pm\Lambda}(\vec{r}_1, \vec{r}_2; R)$ , are eigenfunctions of the electronic Hamiltonian (5)

corresponding to BO potential energy curves  $V_{\gamma\Lambda}^{BO}(R)$ . They parametrically depend on  $R$  and are labeled by  $\pm\Lambda$  -the eigenvalue of the projection of the electronic orbital angular momentum  $L_z$  onto the internuclear axis and by an additional set of quantum numbers  $\gamma$ . Parameter  $\sigma=1$  in the case of  $\Sigma^-$  BO states and  $\sigma=0$  in all other cases.

Using the expansion (6) for solving the eigenvalue problem for the total Hamiltonian (1), one can derive a set of coupled equations for the radial functions  $\chi_{\gamma\Lambda}(R)$ :

$$\sum_{\gamma'\Lambda'} \left\langle \Phi_{\gamma\Lambda}^{\tilde{p}JM} \left| RH \frac{1}{R} \Phi_{\gamma'\Lambda'}^{\tilde{p}JM} \chi_{\gamma'\Lambda'} \right. \right\rangle = E \chi_{\gamma\Lambda} \quad (9)$$

### N=2 dissociation limit

We now focus our attention to states correlating to the n=2 dissociation limit of HD. Solving for the eigenvalues of the electronic Hamiltonian (5) one finds 6 singlet BO potentials:  $B^1\Sigma_u^+$ ,  $\Pi^1\Pi_g$ ,  $EF^1\Sigma_g^+$ ,  $B'^1\Sigma_u^+$ ,  $C^1\Pi_u$ ,  $GK^1\Sigma_g^+$ , (see Fig.2).

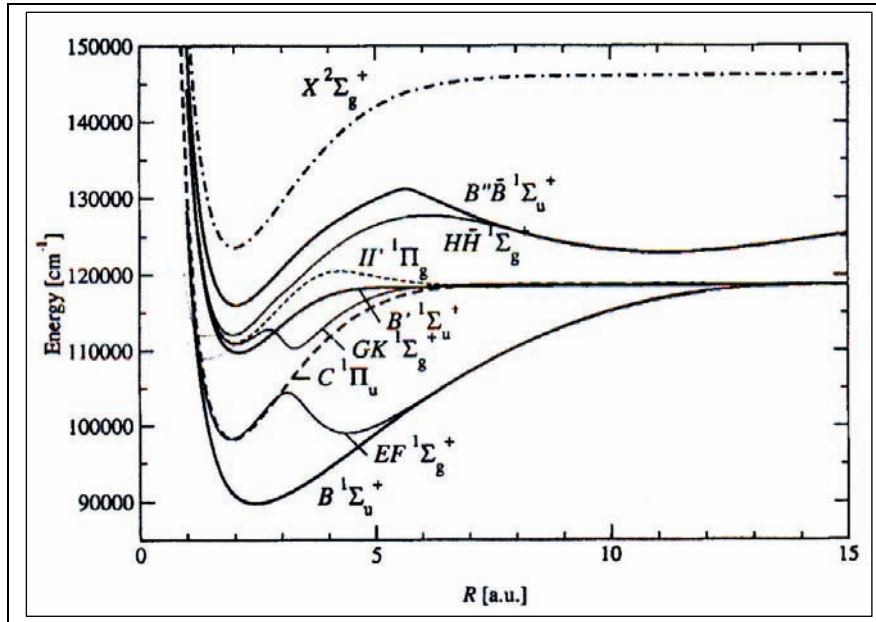


Fig. 2. BO potential curves in hydrogen. Three dissociation limits correspond to  $H(1s)+H(n)$  with  $n=2$ ,  $n=3$  and  $n=\infty$ . The uppermost curve is the ground state of the  $H_2^+$  ion. From [7].

Instead of the spectroscopic labels: B,  $\Pi'$ , EF, B', C and GK one can respectively use the values of the additional quantum number  $l=1,1,0,0,1$  and 1, corresponding to the asymptotic atomic electronic orbital angular momentum quantum number of the excited ( $n=2$ ) electron. So we can introduce a set of quantum numbers:  $\alpha \equiv \gamma\Lambda \equiv s\ l\ \Lambda$ , where  $s=g,u$ . With these BO states, according to (7), one can form 2  $f$ -parity basis functions involving

only  $\Pi$  - states and 6  $e$ -parity basis functions involving 4  $\Sigma$  -states and 2  $\Pi$  - states. For either parity, coupled equations (9) take the form:

$$\left( -\frac{1}{2\mu} \frac{\partial^2}{\partial R^2} + \frac{J(J+1)}{2\mu R^2} + V_\alpha^{BO}(R) + V_\alpha^{ad}(R) - E \right) \chi_\alpha(R) + \sum_{\beta \neq \alpha} V_{\alpha\beta}(R) \chi_\beta(R) = 0. \quad (10)$$

The diagonal potentials are sums of the BO potentials and the so called adiabatic corrections:

$$V_\alpha^{ad}(R) = \left\langle \psi_\alpha \left| -\frac{1}{2\mu} \frac{\partial^2}{\partial R^2} + \frac{L_x^2 + L_y^2 - L_z^2}{2\mu R^2} + H_{mp} \right| \psi_\alpha \right\rangle, \quad (11)$$

and the off diagonal coupling terms are defined by

$$V_{\alpha\beta}(R) \chi_\beta(R) = \left\langle \Phi_\alpha^{\tilde{p}JM} \left| RH \frac{1}{R} \Phi_\beta^{\tilde{p}JM} \chi_\beta \right. \right\rangle \quad (12)$$

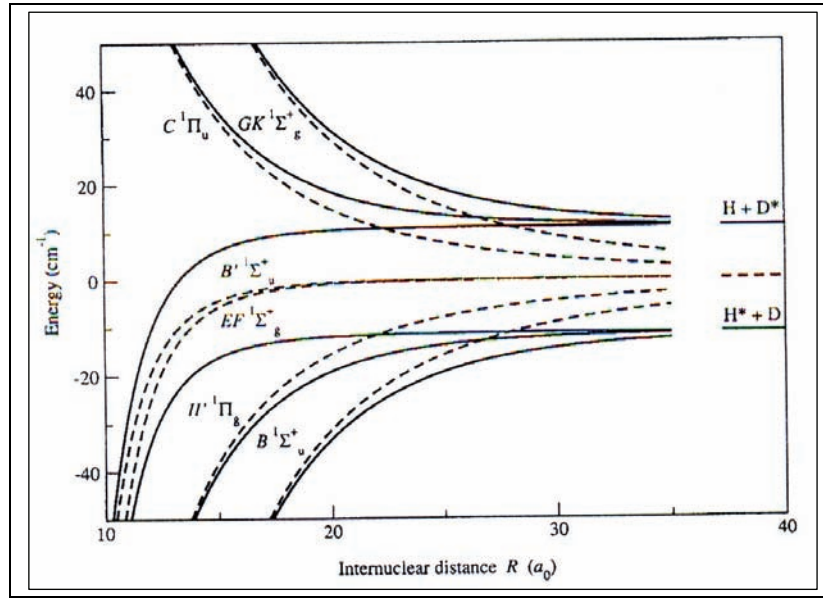


Fig. 3. Dashed curves are unperturbed adiabatic potentials. Full lines are 'effective adiabatic potentials' as defined in (14). From [7].

In the asymptotic region, when  $R \rightarrow \infty$  we find [10] for diagonal potentials:

$$V_\alpha^{BO}(\infty) = -\frac{1}{2} - \frac{1}{8} \text{ a.u. and } V_\alpha^{ad}(\infty) = \frac{5}{16\mu} = 56.039 \text{ cm}^{-1}, \text{ for all states. At the same time,}$$

all couplings are zero except the  $g$ - $u$  couplings  $V_{\alpha\beta}(\infty) = \frac{3}{16\mu_a} = 11.20 \text{ cm}^{-1}$  between

$\Pi^1\Pi_g - C^1\Pi_u$  states (of both,  $e$ - and  $f$ - parities) and between  $B^1\Sigma_u^+ - GK^1\Sigma_g^+$  and  $B^1\Sigma_u^+ - EF^1\Sigma_g^+$  states (of  $e$ -parity). One can eliminate these constant couplings at infinity by diagonalizing the  $2 \times 2$  potential energy matrices:

$$\begin{bmatrix} V_g(R) & V_{gu} \\ V_{gu} & V_u(R) \end{bmatrix} \psi(R) = V(R) \psi(R) \quad (13)$$

and defining new "effective adiabatic potentials":

$$V_{\pm}(R) = \frac{V_g + V_u}{2} \pm \sqrt{\left(\frac{V_g - V_u}{2}\right)^2 + V_{gu}^2} \quad (14)$$

These potentials are shown in Fig.3 together with the unperturbed potentials. It is seen that the main effect is the appearance of two dissociation limits corresponding to  $H^*(n=2)+D(n=1)$  and  $H(n=1)+D^*(n=2)$ . Note that at smaller internuclear separations effective potentials approach unperturbed values indicating the approximate validity of the  $g$ - $u$  symmetry.

### Bound States in outer $\Pi^1\Pi_g$ potential

The bound states of HD localized in the outer well of the  $\Pi^1\Pi_g$  potential have been studied in XUV+IR multi-step laser excitation experiments [8,9]. The excitation scheme is shown in Fig.4.

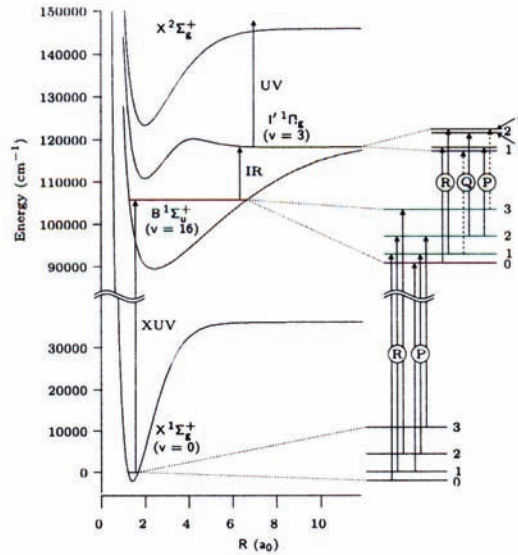


Fig. 4. Excitation scheme in multi-step laser excitation experiment. From [9].

A XUV laser excites HD from the  $X^1\Sigma_g^+$  ground state potential to intermediate  $B^1\Sigma_u^+$  state, and the IR laser populates states in  $I^1\Pi_g$  potential. A third pulsed UV laser excites the HD molecules from the  $I'$  state into the dissociation continuum of  $HD^+$  forming either  $H^+$  or  $D^+$ . The ions are mass selected and detected by an electron multiplier.

A typical spectrum obtained by changing the frequency of the second laser is shown in Fig.5. Note that the continuum onset in the upper trace corresponds to the  $H^*+D$  dissociation limit, whereas the onset in the second trace corresponds to the  $H+D^*$  dissociation limit, in accord with Fig.3. Various peaks correspond to bound states as indicated at the top of the figure. In particular, in this way most of the bound states from the  $I'$  potential, of both,  $e-$  and  $f-$  symmetry have been determined. The authors have also constructed a single semi-empirical potential in order to theoretically interpret their results [7,8].

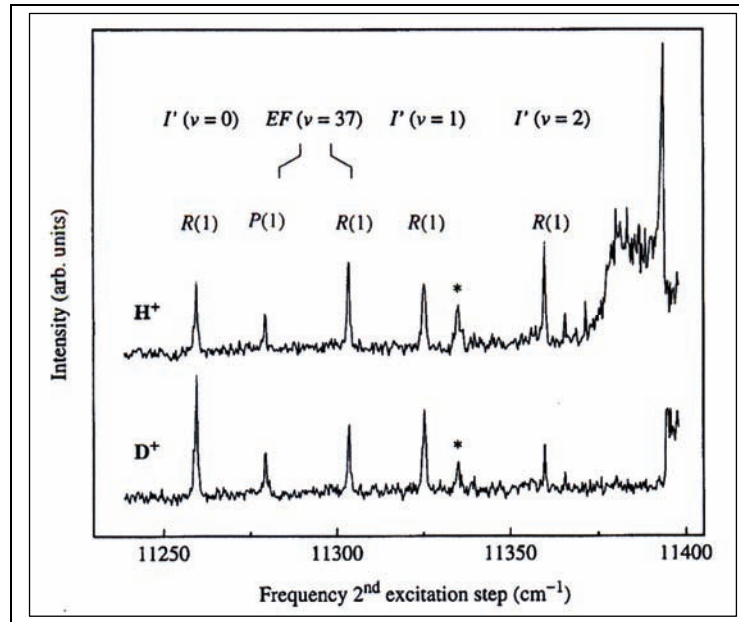


Fig. 5.  $H^+$  and  $D^+$  ion signals obtained after the UV ionization pulse. The XUV laser is tuned to the  $B^1\Sigma_u^+-X^1\Sigma_g^+$  (18,0)  $R(0)$  transition and the frequency of the IR laser is varied. From [8].

Recently, we have solved the coupled equations (10) in order to go beyond the single-effective potential description [10]. The binding energies of  $f$ -parity rovibrational states have been calculated by solving two coupled equations (10) with  $\alpha, \beta=1, 2$ . The index "1" is identified with the set of quantum numbers  $1 \equiv \{s=g, l=1, \Lambda=1\}$  (that is with the  $I^1\Pi_g$  potential) and index "2" with the set of quantum numbers  $2 \equiv \{s=u, l=1, \Lambda=1\}$  (that is with the  $C^1\Pi_u$  potential).

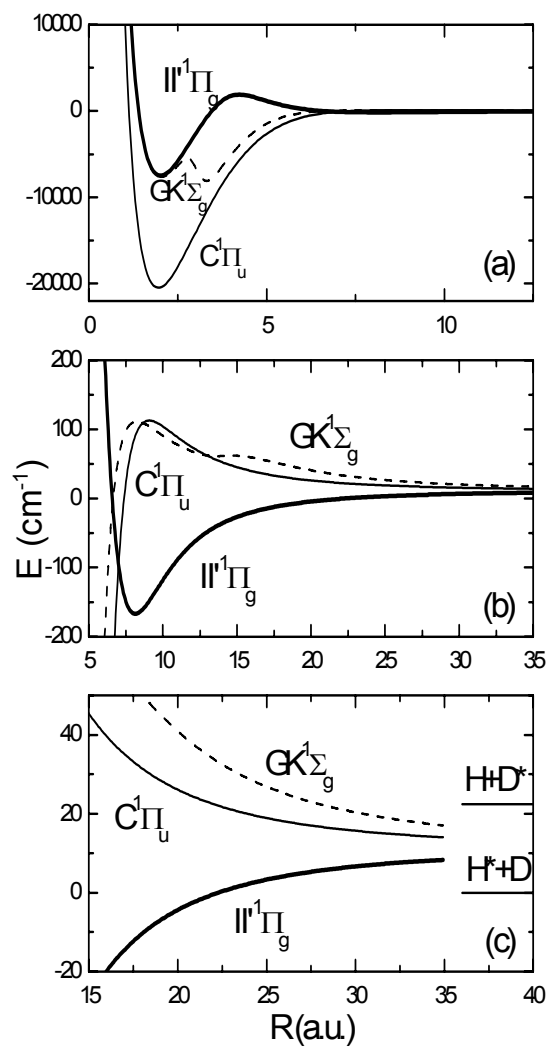


Fig. 6. Adiabatic potentials (BO potentials plus adiabatic corrections) as functions of the internuclear separation. (a) At small to intermediate separations. (b) At large separations showing the outer shallow well of the  $I'$  potential. (c) At large separations and close to dissociation limits. The zero of energy is chosen to correspond to the lower ( $H^*(n=2)+D(1s)$ ) limit so that the upper ( $H(1s)+D^*(n=2)$ ) limit is located at  $2V_{12}(\infty)=22.4 \text{ cm}^{-1}$ .



While for the BO potentials and adiabatic corrections there are *ab initio* [11,12] and asymptotic [13] results in the literature, this is not the case for the coupling matrix element (12) which in this case involves only  $H_{gu}$ . Since we are interested here in the states localized in the outer well of the  $\Pi^1\Pi_g$  potential, that is, at large internuclear distances, we shall replace  $V_{12}(R)$  with its (constant) asymptotic value at  $R \rightarrow \infty$  [10]:

$$V_{12}(R) = V_{21}(R) \approx V_{12}(\infty) = \frac{3}{16\mu_a} = 11.20 \text{ cm}^{-1} \quad (15)$$

Table 1. Energies (in  $\text{cm}^{-1}$ ) of the  $\Gamma^1\Pi_g$   $f$ -parity states relative to the  $X^1\Sigma_g^+$  ( $v=0, J=0$ ) ground state.  $E_{\text{obs}}$  – experiment data [8,9]  $E_{\text{calc}}^a$  – coupled states calculations [10],  $E_{\text{calc}}^b$  – semi-empirical potential [8],  $\Delta_{\text{oc}}^i = E_{\text{obs}} - E_{\text{calc}}^i$ ,  $i = a, b$

J	$E_{\text{obs}}$	$E_{\text{calc}}^a$	$E_{\text{calc}}^b$	$\Delta_{\text{oc}}^a$	$\Delta_{\text{oc}}^b$
v=0					
1		118548.18	118548.33		
2	118552.95	552.99	553.11	-0.04	-0.16
3	560.03	560.14	560.20	-0.11	-0.17
4		569.53	569.55		
v=1					
1	118614.17	118614.23	118615.36	-0.06	-1.19
2	618.43	618.44	618.81	0.01	-0.38
3	623.75	623.71	623.89	0.04	-0.14
4	630.38	630.13	630.50	0.25	-0.12
v=2					
1	118650.51	118650.34	118650.13	0.17	0.38
2	652.89	652.71	652.26	0.18	0.63
3	655.15	655.08	655.31	0.07	-0.16
4	659.26	659.07	659.14	0.19	0.12
v=3					
1	118663.650	118663.493	118663.42	0.157	0.230
2	664.544	664.359	664.29	0.185	0.254

To solve the coupled equations (10) we used the particle-in-the-box discrete variable representation (DVR) of Colbert and Miller [14]. The converged results were obtained by using  $N_{\text{DVR}}=600$  equidistant grid points spanning the interval from  $R_{\text{min}}=0.5$  to  $R_{\text{max}}=75$ .

Tab. 1 shows the results of the calculated term values for the  $f$ -parity states, with the assumed dissociation energy  $D=118664.80 \text{ cm}^{-1}$ . It can be seen that the agreement with experiments [8,9] is excellent and that the close-coupling method [10] is superior to calculations using a single semi-empirical potential [8].

Similarly, when treating  $e$ -parity states we include only the dominant direct couplings of the  $\Pi^1\Pi_g$   $e$ -parity state at large internuclear separations. Besides the constant  $g-u$

coupling (15) with  $C^1\Pi_u$   $e$ -parity state, this includes the rotational coupling with the  $GK^1\Sigma_g^+$  state, which has an  $R^{-2}$  dependence. All other couplings fall off more rapidly, like  $R^{-4}$  and faster [10], and are therefore neglected. The third basis function is labeled by index "3" identified with quantum numbers  $3\equiv\{s=g, l=1, \Lambda=0\}$  (corresponding to the  $GK^1\Sigma_g^+$  potential). The  $V_{33}(R)$  potential was constructed using the *ab initio* data from [15] and asymptotic multipole expansions taken from [13]. The  $GK^1\Sigma_g^+ - \Pi^1\Pi_g$  rotational coupling is given by

$$V_{13}(R) = V_{31}(R) = \sqrt{2J(J+1)} \frac{S(R)}{2\mu R^2} \quad (16)$$

with  $S(R) = \langle \Psi_1 | L_+ | \Psi_3 \rangle$  taken from *ab initio* data [11]. We have set  $V_{23}(R) = V_{32}(R) = 0$  since this interaction actually falls off like  $R^{-4}$ .

Table 2. Energies (in  $\text{cm}^{-1}$ ) of the  $\Pi^1\Pi_g$   $e$ -parity states relative to the  $X^1\Sigma_g^+$  ( $v=0, J=0$ ) ground state.  $E_{\text{obs}}$  – experiment data [8,9]  $E_{\text{calc}}^a$  – coupled states calculations [10],  $E_{\text{calc}}^b$  – semi-empirical potential [8],  $\Delta_{\text{oc}}^i = E_{\text{obs}} - E_{\text{calc}}^i$ ,  $i = a, b$

J	$E_{\text{obs}}$	$E_{\text{calc}}^a$	$E_{\text{calc}}^b$	$\Delta_{\text{oc}}^a$	$\Delta_{\text{oc}}^b$
v=0					
1	118548.14	118548.18	118548.33	-0.04	-0.19
2	552.92	552.88	553.11	0.04	-0.19
3	560.05	560.00	560.20	0.05	-0.15
4	569.30	569.32	569.55	-0.02	-0.25
v=1					
1	118614.17	118614.23	118615.36	-0.06	-1.19
2	618.43	618.44	618.81	0.01	-0.38
3	623.75	623.71	623.89	0.04	-0.14
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2	664.544	664.359	664.29	0.185	0.254

The calculated term values for  $e$ -parity states are shown in Table 2. It is obvious that the results obtained by solving coupled equations are superior to those obtained by using single semi-empirical potential. In particular, in the case of the state ( $v=1, J=1$ ), we see

the largest deviation ( $-1.19 \text{ cm}^{-1}$ ) of the semi-empirical value from the experimental result. The reason for this is that this state has an inherent two-channel character due to the quasi-resonance with an energy level in the  $C^1\Pi_u$  potential [10] and therefore can be precisely described only by the coupled-state method.

## CONCLUSION

We have emphasized that the  $g$ - $u$  symmetry breaking in HD is a non-adiabatic effect. Therefore, the proper theoretical framework for description of this phenomenon is the method of coupled state equations. A specific property of the  $g$ - $u$  coupling is that it does not vanish at infinite internuclear separations. This, however, leads to proper description of two dissociation limits:  $H^*(n=2)+D(n=1)$  and  $H(n=1)+D^*(n=2)$ . For bound states located in the outer well of the  $\Pi^1\Pi_g$  potential the asymptotic description works well. For incorporating the  $g$ - $u$  symmetry breaking effects for other states, new *ab initio* calculations providing the  $R$ -dependence of non-adiabatic couplings are necessary.

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## **NARUŠENJE GERADE – UNGERADE SIMETRIJE U HD: STANJA BLISKA N=2 DISOCIJATIVNOM LIMITU**

**Tasko Grozdanov**

*Dat je pregled posledica narušenja gerade-ungerade simetrije u HD molekulu. Posebna pažnja je posvećena elektronskim stanjima bliskim  $n=2$  disocijativnom limitu. Diskutovani su efekti vezani za narušenje Born-Oppenheimer-ove aproksimacije. Za opisivanje dinamike molekula formulisan je metod spregnutih stanja. Metod je primenjen za izračunavanje slabo vezanih stanja u spoljašnjoj jami  $\Pi^1\Pi_g$  potencijala. Rezultati se odlično slažu sa eksperimentom i izračunavanjima baziranim na semiempirijskom potencijalu.*