

THEORETICAL STUDY OF BOUND STATES SUPPORTED BY
THE $I^1\Pi_g$ OUTER POTENTIAL WELL IN HD

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Abstract. The bound states of HD close to the $n=2$ dissociation limit are strongly affected by non-adiabatic coupling which breaks the gerade-ungerade (g-u) symmetry in HD. The coupled-states formalism is used to describe loosely bound rovibrational states in the $I^1\Pi_g$ outer potential well. For f -parity states it was sufficient to take into account the constant asymptotic g-u coupling with $C^1\Pi_u$ state. In the case of e -parity states, besides the g-u coupling, the asymptotically strongest rotational coupling with $GK^1\Sigma_g^+$ was also taken into account. The calculated binding energies are in excellent agreement with data obtained in XUV+IR multistep laser experiments.

1. INTRODUCTION

The states close to the $n = 2$ dissociation limit of HD are particularly interesting because they are markedly different from their homonuclear analogues. There are actually two different dissociation limits corresponding to $H(n = 1)+D^*(n = 2)$ and $H^*(n = 2)+D(n = 1)$, separated by an energy gap of 22.38 cm^{-1} . One of the Born-Oppenheimer (BO) potentials from the $n = 2$ manifold is the $\Pi^1\Pi_g$ double well potential. Recently, very precise and systematic measurements of the rovibrational states corresponding to the outer well ($I^1\Pi_g$) have been reported as results of XUV+IR multistep laser experiments (De Lange et al. 2000, Pielage et al., 2002). In order to interpret their results the authors have constructed a semi-empirical potential (De Lange et al., 2000) which incorporates the effects of the nonadiabatic g-u coupling with the nearby lying $C^1\Pi_u$ state. The aim of the present work is to go beyond the notion of a single effective potential by considering the minimal sets of coupled BO states necessary to accurately describe bound states of the $I^1\Pi_g$ potential well.

Atomic units are used throughout, except when explicitly stated.

2. HAMILTONIAN AND COUPLED EQUATIONS

We neglect the spin-orbit and hyperfine interactions as they are much smaller than g-u coupling, concentrate on singlet 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 $\{R, \theta, \phi\}$ 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, 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 and H_{gu} , the g-u coupling (cross derivative) term are

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

H_{mp} , the mass polarization term and H_e , the (BO) electronic Hamiltonian

$$H_{mp} = -\frac{1}{8\mu} \left(\sum_{j=1,2} \nabla_j \right)^2, \quad H_e = -\frac{1}{2} \sum_{i=1,2} \nabla_i^2 + V(\vec{R}, \vec{r}_1, \vec{r}_2). \quad (3)$$

In the equations (2-3), 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 $\mu_a = m_D m_H / (m_D - m_H) = 3674.1340$.

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 so called e -parity states and $\tilde{p} = 1$ to f -parity states.

The total molecular wavefunction can then be expanded as :

$$\Psi^{\tilde{p}JM}(R, \theta, \phi, \vec{r}_1, \vec{r}_2) = \frac{1}{R} \sum_{\alpha} \chi_{\alpha}(R) \Phi_{\alpha}^{\tilde{p}JM}(\theta, \phi, \vec{r}_1, \vec{r}_2; R), \quad (4)$$

where the basis functions $\Phi_{\alpha}^{\tilde{p}JM}(\theta, \phi, \vec{r}_1, \vec{r}_2; R)$ are symmetrized products of Wigner rotational functions and BO electronic eigenfunctions (the eigenfunctions of (3) in body-fixed coordinate framwe which parametrically depend on R), (for details see Grozdanov et al., 2008).

Restricting our basis to electronic BO states which correlate to $n=2$ dissociation limit, we find that there are two f -symmetry basis functions related to $\Pi^1\Pi_g$ and $C^1\Pi_u$ BO states and six e -parity basis states related to $B^1\Sigma_u^+$, $\Pi^1\Pi_g$, $EF^1\Sigma_g^+$, $B^1\Sigma_u^+$, $C^1\Pi_u$ and $GK^1\Sigma_g^+$ BO states. The label α used above corresponds to set of quantum numbers: $\alpha = \{s, l, \Lambda\}$ where $s = g, u$ is related to gerade-ungerade symmetry, $l = 1, 0$ is the asymptotic atomic orbital angular momentum quantum number of the excited ($n=2$) electron and $\Lambda = 0, 1$ is the modulus of the projection of the orbital electronic angular momentum onto the internuclear axis.

Table 1: Energies (in cm^{-1}) of the $I^1\Pi_g$ e -parity levels relative to the $X^1\Sigma_g^+(v = 0, J = 0)$ ground state. E_{calc}^a - present results, E_{calc}^b - results obtained by using a semi-empirical potential. E_{obs} - experimental data.

J	E_{obs}	E_{calc}^a	E_{calc}^b	$E_{obs} - E_{calc}^a$	$E_{obs} - E_{calc}^b$
$v = 0$					
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
4	630.38	630.13	630.50	0.24	-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

The calculation of the molecular spectrum is then reduced to set of coupled equations for vibrational wavefunctions:

$$\left(-\frac{1}{2\mu}\frac{\partial^2}{\partial R^2} + \frac{J(J+1)}{2\mu R^2} + V_{\alpha\alpha}(R) - E\right)\chi_{\alpha}(R) + \sum_{\beta \neq \alpha} V_{\alpha\beta}(R)\chi_{\beta}(R) = 0. \quad (5)$$

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

$$V_{\alpha\alpha}(R) = V_{\alpha}^{BO}(R) + V_{\alpha}^{ad}(R), \quad (6)$$

$$V_{\alpha}^{ad}(R) = \langle \psi_{\alpha} | -\frac{1}{2\mu}\frac{\partial^2}{\partial R^2} + \frac{L_x^2 + L_y^2 - L_z^2}{2\mu R^2} + H_{mp} | \psi_{\alpha} \rangle \quad (7)$$

where $\psi_{\alpha}(\vec{r}_1, \vec{r}_2; R)$ are the BO electronic wavefunctions and $L_i, i = x, y, z$ are body-fixed components of the electronic orbital angular momentum. The off diagonal coupling terms (operators $V_{\alpha\beta}(R)$) are defined by

$$V_{\alpha\beta}(R)\chi_{\beta} = \langle \Phi_{\alpha}^{\tilde{p}JM} | RH \frac{1}{R} \Phi_{\beta}^{\tilde{p}JM} \chi_{\beta} \rangle. \quad (8)$$

3. RESULTS AND DISCUSSION

The binding energies of f -parity rovibrational states localized in the outer well of the $\Pi^1\Pi_g$ potential have been calculated by solving two coupled equations (5) 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 $\Pi^1\Pi_g$ 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). While for the BO potentials and adiabatic corrections there are *ab initio* (Dressler et al. 1984, Wolniewicz et al. 2003) and asymptotic (Stephens et al. 1974) results in the literature, this is not the case for the coupling matrix element (8) 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 their (constant) asymptotic values at $R \rightarrow \infty$ (Grozdanov et al. 2008):

$$V_{12}(R) = V_{21}(R) \asymp V_{12}(\infty) = \frac{3}{16\mu_a} = 11.20 \text{ cm}^{-1}, \quad (9)$$

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. This includes, beside the constant g-u coupling (9) with $C^1\Pi_u$ e -parity state, 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 (see Grozdanov et al, 2008) and are therefore neglected. The third basis function is labeled by index "3" identified with quantum numbers $3 \equiv \{g, l = 1, \Lambda = 0\}$ (corresponding to the $GK^1\Sigma_g^+$ potential). The $V_{33}(R)$ potential was constructed using the *ab initio* data from (Wolniewicz et al. 1994) and asymptotic multipole expansions taken from (Stephens et al. 1974). The $GK^1\Sigma_g^+$ - $\Pi^1\Pi_g$ rotational coupling is given by

$$V_{13}(R) = V_{31}(R) = -[2J(J+1)]^{\frac{1}{2}} \frac{S(R)}{2\mu R^2}, \quad (10)$$

with $S(R) = \langle \psi_1 | L_+ | \psi_3 \rangle$ taken from *ab initio* data (Dressler et al. 1984). We have set $V_{23}(R) = V_{32}(R) = 0$ since this interaction actually falls off like R^{-4} .

Table 1 shows results of calculated term values for the e -parity states, with the assumed dissociation energy $D=118664.80 \text{ cm}^{-1}$. It can be seen that the agreement with experiments (De Lange et al. 2000, Pielage et al. 2002) is excellent and that the close-coupling method is superior to calculations using a single semiempirical potential (De Lange et al. 2000).

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