Ab initio Valence-Bond Calculations of H$_2$O

II. Valence State Energies

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A new technique for the determination of atomic valence states and their energies has been developed and applied to the water molecule and hydroxyl radical. This method is applicable to valence-bond studies involving a large number of resonance structures rather than simply a one structure perfect pairing approach. The original basis of resonance structures is transformed into a basis of approximate composite functions which are orthogonal and non-interacting for the separated atoms. The equilibrium molecular eigenfunction is analyzed in terms of the composite functions by means of structure projections. A description of the valence states and the promotional energies of each of the component atoms in H$_2$O and OH is obtained.

1. Introduction

In any theory of molecular structure it is of interest to consider the change in state of an isolated atom as it becomes an "atom" within a molecular environment. Information about such a change in state would be useful in describing the formation of chemical bonds between separated atoms. The state of an atom as it exists within a molecule has been called the "valence state" by Van Vleck [1]. Van Vleck described the valence state as the "chemically active condition" of an atom necessary for molecular formation but attained prior to the onset of interatomic bonding. The valence state of an atom is, in general, a non-stationary state and therefore it is a hypothetical concept. Nevertheless, the idea has proven valuable in interpretations of molecular properties such as bond energies, bond dissociation energies, excitation energies, and electronegativities [1–4].

The important valence state discussion by Moffitt [2] employed a single non-hybridized perfect pairing valence bond structure as the molecular wavefunction. Later work by Öpik [5] and Anno [6] emphasized the calculation of energies of hybridized valence states. Limited configuration interaction between valence bond structures has been used in valence state discussions by Hurley [4] and by Craig and Thirunamachandran [7]. The present paper outlines a different method of determining the valence state description and promotional energy of

atoms in molecules. The method is then applied to the results of a previous configuration interaction valence bond study of H_2O and OH [8].

2. Method

In the present paper the expression "valence state of an atom" refers to a non-stationary state of an isolated atom in which the electronic structure approximates, as closely as possible, the electronic structure associated with the atom as it exists within the environment of the other atoms of a molecule. Another description of the valence state would be that state of each component atom of a molecule such that if isolated atoms were prepared in these states and then non-adiabatically brought to their equilibrium molecular positions, the superposition of the electronic structures of the atoms would duplicate the molecular electronic structure. These ideas will be made clearer by the descriptions given later in this section of the various steps in the determination of the valence states of the oxygen and hydrogen atoms in the H_2O and OH molecules.

Valence bond theory is a chemically appealing approach to molecular structure, in part because it describes the electronic distribution in a given molecule by the interaction of various "structures", each of which is an instantaneous picture of a plausible distribution of the electrons in the bond regions and on the various nuclear centers. Using the criterion of maximum overlap between bonding atoms and electronegativity arguments, various covalent and ionic structures may be quickly conceived which should be major contributors in a superposition method for developing the molecular electronic structure. A previous paper [8] reported the use of forty-nine structures chosen by the above intuitive process in describing the H_2O and OH molecules. The usual secular equations were solved for the energies and the accompanying wavefunctions are then linear combinations of contributions from the forty-nine basis structures.

One possible approach to a valence state description would be to express the contribution of each basis structure to the wavefunction by means of a structure projection, v_n, with

$$v_n = a_n \sum_m a_m S_{mn} , \tag{1}$$

where a_i is the coefficient of structure i in the wavefunction, and where S_{ij} is the overlap integral between structures i and j. The wavefunction is normalized such that

$$\sum_n v_n = 1 . \tag{2}$$

The v_n represent the relative weights of each of the basis structures in the molecular wavefunction and account in the manner shown by Eq. (1) for the non-orthogonality of the basis structures at the equilibrium molecular geometry. Next, each of the basis structures can be interpreted by means of the procedure of Companion and Ellison [9] as representing, for the infinitely separated atoms, each of the component atoms in a particular valence state. This valence state description is generally a linear combination of spectroscopic states for which energies are available from experiment [10] or from approximate calculations (e.g. Table 2). Finally, the valence state of an atom in the molecule could be

represented by the sum over all the basis structures of the product of the v_n for a structure times the spectroscopic state description for that structure. In a similar manner the valence state energy of an atom would be obtained by multiplying the v_n for each structure times the valence state energy of an atom in that structure and summing these products over all the structures in the wavefunction.

The difficulty with the above straightforward determination of the valence state and its energy lies in the fact that the basis structures interact and are non-orthogonal even at the geometry of infinitely separated atoms. In order to analyze the molecular wavefunction by the method of Companion and Ellison [9], a non-adiabatic dissociation of the molecule is hypothetically carried out such that the coefficients of the wavefunction at the equilibrium geometry are maintained constant at all internuclear distances. The Slater determinants in the wavefunction can now be separated into simple products of determinants, where each smaller determinant represents an intra-atomic wavefunction. These intra-atomic wavefunctions can then be expressed as a linear combination of spectroscopic states, where each of the spectroscopic states is represented by an orbital approximation. The above determination of the valence state carries out this procedure for each of the basis structures in the molecular wavefunction and then sums the result over each structure. However, since the basis structures interact at the geometry at which the spectroscopic state analysis is carried out, it is improper to calculate the valence state for the molecular wavefunction by simply summing over the individual contributions from each basis structure.

An alternate procedure has been used in the present paper. When the forty-nine original structures are used as a basis at the separated atoms geometry, the resultant eigenvectors are orbital approximations to specific spectroscopic states. That is, an analysis of each eigenvector indicated that the intra-atomic determinants comprising the eigenvector were, in general, characteristic of only one spectroscopic state. This is in contrast to the original structures whose intra-atomic determinants were in general characteristic of linear combinations of spectroscopic states. In Table 1 are listed the forty-nine eigenvectors and in columns 3 and 4 are listed the appropriate spectroscopic states for oxygen and hydrogen characterizing each structure. Each eigenvector of this set was orthogonal to all other eigenvectors. In particular, functions representing neutral atomic states were orthogonal to functions representing ionic states, and functions corresponding to the same spectroscopic states were orthogonal to each other. The eigenvalues of the secular determinant are thus orbital approximations to the energies of the spectroscopic states. These calculated energies are listed for each state in Table 2.

The set of orthogonal functions was then used as a new basis for a calculation of the H_2O molecule at its equilibrium geometry. Each basis function may be written as

$$\psi_i = \mathscr{A}'(\Phi_i^O \Phi_i^{H_1} \Phi_i^{H_2}), \tag{3}$$

where Φ_i^A is an orbital approximation to the i-th spectroscopic state of atom A, and $\mathscr{A}'$ is a partial antisymmetrizer operator which performs only the identity permutation and those permutations in which electrons are interchanged between different state functions Φ_i^A, Φ_i^B, etc. These ψ_i would be the "approximate composite functions" of Moffitt [2]. At the equilibrium geometry the molecular

C. Peterson and G. V. Pfeiffer

Table 1. Structure projections and promotional energies using 49 orthogonal VB structures for the equilibrium geometry of H_2O[1]

Structure	Projection	O State	H State	Promotional Energy[2] O State	H State	Promotional Energy of Each Structure from O State	H State
1	0.19926	$O(^3P)$	$2H(^2S)$	0	0.1600	0.0000	0.0319
2	0.00000	$O(^1D)$	$2H(^2S)$	0.0805	0.1600	0.0000	0.0000
3	0.03530	$O(^1D)$	$2H(^2S)$	0.0805	0.1600	0.0028	0.0056
4	0.03009	$O(^1D)$	$2H(^2S)$	0.0805	0.1600	0.0024	0.0048
5	0.00800	a $O(^1S)$ + b $O(^1S\ast)$	$2H(^2S)$	0.2544	0.1600	0.0020	0.0013
6	0.01700	$O(^3P\ast)$	$2H(^2S)$	0.6282	0.1600	0.0107	0.0027
7	0.08044	$O(^3P\ast)$	$2H(^2S)$	0.6282	0.1600	0.0505	0.0129
8	0.00674	$O-(^2P)$	$H(^2S)+H^+$	0.1594	0.5798	0.0010	0.0039
9	0.19950	$O-(^2P)$	$H(^2S)+H^+$	0.1594	0.5798	0.0318	0.1157
10	0.14212	$O-(^2P)$	$H(^2S)+H^+$	0.1594	0.5798	0.0227	0.0824
11	0.06412	$O-(^2P)$	$H(^2S)+H^+$	0.1594	0.5798	0.0102	0.0372
12	0.00877	$O(^1D)$	$H-(^1S)+H^+$	0.0805	1.0350	0.0007	0.0091
13	0.00877	$O(^1D)$	$H-(^1S)+H^+$	0.0805	1.0350	0.0007	0.0091
14	0.00073	$O(^1D)$	$H-(^1S)+H^+$	0.0805	1.0350	0.0001	0.0008
15	0.00073	$O(^1D)$	$H-(^1S)+H^+$	0.0805	1.0350	0.0001	0.0008
16	0.00429	$O(^1D)$	$H-(^1S)+H^+$	0.0805	1.0350	0.0003	0.0044
17	0.00429	$O(^1D)$	$H-(^1S)+H^+$	0.0805	1.0350	0.0003	0.0044
18	0.00326	a $O(^1S)$ + b $O(^1S\ast)$	$H-(^1S)+H^+$	0.2544	1.350	0.0008	0.0034
19	0.00326	a $O(^1S)$ + b $O(^1S\ast)$	$H-(^1S)+H^+$	0.2544	1.0350	0.0008	0.0034
20	0.00105	$O^+(^2P)$	$H-(^1S)+H(^2S)$	0.6501	0.6152	0.0007	0.0006
21	0.00085	$O^+(^2P)$	$H-(^1S)+H(^2S)$	0.6501	0.6152	0.0005	0.0005
22	0.00105	$O^+(^2P)$	$H-(^1S)+H(^2S)$	0.6501	0.6152	0.0007	0.0006
23	0.00084	$O^+(^2P)$	$H-(^1S)+H(^2S)$	0.6501	0.6152	0.0005	0.0005
24	-0.00005	$O^+(^2D)$	$H-(^1S)+H(^2S)$	0.7306	0.6152	-0.0000	-0.0000
25	-0.00150	$O^+(^2D)$	$H-(^1S)+H(^2S)$	0.7306	0.6152	-0.0010	-0.0009
26	-0.00005	$O^+(^2D)$	$H^-(^1S)+H(^2S)$	0.7306	0.6152	-0.0000	-0.0000

Table 1 (continued)

Structure	Projection	O State	H State	Promotional Energy O State	Promotional Energy H State	Promotional Energy of Each Structure from O State	Promotional Energy of Each Structure from H State
27	−0.00150	$O^+(^2D)$	$H^-(^1S)+H(^2S)$	0.7306	0.6152	−0.0010	−0.0009
28	0.00454	$O(^1P)$	$2H(^2S)$	0.9441	0.1600	0.0043	0.0007
29	0.00033	$O(^1P)$	$2H(^2S)$	0.9441	0.1600	0.0003	0.0000
30	0.04109	$O^-(^2S)$	$H(^2S)+H^+$	0.8596	0.5798	0.0353	0.0238
31	0.04107	$O^-(^2S)$	$H(^2S)+H^+$	0.8596	0.5798	0.0353	0.0238
32	0.00066	$O^+(^2D\star)$	$H^-(^1S)+H(^2S)$	1.3240	0.6152	0.0009	0.0004
33	−0.00041	$O^+(^2D\star)$	$H^-(^1S)+H(^2S)$	1.3240	0.6152	−0.0005	−0.0002
34	0.00071	$O^+(^2D\star)$	$H^-(^1S)+H(^2S)$	1.3240	0.6152	0.0009	0.0004
35	−0.00046	$O^+(^2D\star)$	$H^-(^1S)+H(^2S)$	1.3240	0.6152	−0.0006	−0.0003
36	0.00270	$O^+(^2D\star)$	$H^-(^1S)+H(^2S)$	1.3240	0.6152	0.0036	0.0017
37	0.00213	$O^+(^2D\star)$	$H^-(^1S)+H(^2S)$	1.3240	0.6152	0.0028	0.0013
38	0.00029	a $O(^1S)$ + b $O(^1S\star)$	$2H(^2S)$	1.4992	0.1600	0.0004	0.0000
39	0.00564	$O(^1P)$	$H^-(^1S)+H^+$	0.9441	1.0350	0.0053	0.0058
40	0.00749	$O(^1P)$	$H^-(^1S)+H^+$	0.9441	1.0350	0.0071	0.0077
41	−0.00128	$O(^1P)$	$H^-(^1S)+H^+$	0.9441	1.0350	−0.0012	−0.0013
42	−0.00128	$O(^1P)$	$H^-(^1S)+H^+$	0.9441	1.0350	−0.0012	−0.0013
43	−0.00087	$O^+(^2S)$	$H^-(^1S)+H(^2S)$	1.4447	0.6152	−0.0012	−0.0005
44	−0.00087	$O^+(^2S)$	$H^-(^1S)+H(^2S)$	1.4447	0.6152	−0.0012	−0.0005
45	−0.00217	$O^+(^2P\star)$	$H^-(^1S)+H(^2S)$	1.5591	0.6152	−0.0034	−0.0013
46	−0.00217	$O^+(^2P\star)$	$H^-(^1S)+H(^2S)$	1.5591	0.6152	−0.0034	−0.0013
47	0.09074	$O^=(^1S)$	$2H^+$	1.0072	0.9996	0.0914	0.0907
48	−0.00263	b $O(^1S)$ + a $O(^1S\star)$	$H^-(^1S)+H^+$	1.4992	1.0350	−0.0039	−0.0027
49	−0.00263	b $O(^1S)$ + a $O(^1S\star)$	$H^-(^1S)+H^+$	1.4992	1.0350	−0.0039	−0.0027
		(including (−) terms) →				0.3055	0.4784
						0.7839	

[1] Each Hydrogen atom is scaled by $(1.4)^2$; $a = 0.9612453$; $b = 0.03875480$.

[2] Relative to the calculated $O(^3P)$ energy and relative to the calculated $H(^2S)$ unscaled energy.

Table 2. Atomic energies (Hartrees)

$1s^2 2s^2 2p^4$		$1s^2 2s^2 2p^4$	
$O(^3P)$	$= -74.7919$	$O^+(^2S)$	$= -73.3472$
$O(^1D)$	$= -74.7114$	$O^+(^2D)$	$= -73.4679$
$O(^1S)$	$= -74.5881$	$O^+(^2P)$	$= -73.2328$
$1s^2 2s 2p^5$		$1s^2 2p^5$	
$O(^3P)$	$= -74.1637$	$O^+(^2P)$	$= -72.7397$
$O(^1P)$	$= -73.8478$		
$1s^2 2p^6$		$1s$	
$O(^1S)$	$= -73.2824$	$H(^2S)$	$= 0.4998^c$
			$= -0.4198^d$
$1s^2 2s^2 2p^5$		$1s^2$	
$O^-(^2P) = -74.6325^a$		$H^-(^1S)$	$= -0.3746^c$
			$= 0.0354^d$
$1s^2 2s 2p^6$			
$O^-(^2S) = -73.9323$			
$1s^2 2s^2 p^6$			
$O^=(^1S) = -73.7847$			
$1s^2 2s^2 p^3$			
$O^+(^2P) = -74.1418$ $\Big\}$ b			
$O^+(^2D) = -74.0613$			

[a] Note that the electron affinity is quite wrong.
[b] Note wrong order (Hund's rule).
[c] Hydrogen atom unscaled.
[d] Hydrogen atom scaled by $(1.4)^2$.

wavefunction is

$$\Psi = \sum_i a_i \psi_i, \tag{4}$$

and the energy is given by

$$E = \frac{\sum_i \sum_{i'} a_i a_{i'} \int \psi_i \mathscr{H} \psi_{i'} \, d\tau}{\sum_i \sum_{i'} a_i a_{i'} S_{ii'}}, \tag{5}$$

where Ψ is normalized such that

$$\sum_i \sum_{i'} a_i a_{i'} S_{ii'} = 1 .$$ (6)

In Eqs. (5) and (6) the $S_{ii'}$ are overlap integrals between basis functions ψ_i and $\psi_{i'}$. If the molecule is now hypothetically dissociated in a nonadiabatic manner, the expansion coefficients, a_i, of each of the basis functions remain unchanged and Eq. (5) becomes

$$E_\infty = \frac{\sum_i \sum_{i'} a_i a_{i'} \int (\Phi_i^O \Phi_i^{H_1} \Phi_i^{H_2})(\mathscr{H}^O + \mathscr{H}^{H_1} + \mathscr{H}^{H_2})(\Phi_{i'}^O \Phi_{i'}^{H_1} \Phi_{i'}^{H_2}) d\tau}{\sum_i \sum_{i'} a_i a_{i'} S_{ii'}} ,$$ (7)

where $\mathscr{H}^A$ is the atomic Hamiltonian operator for atom A, and the wavefunctions ψ_i and $\psi_{i'}$ become simple products of atomic state functions. Since the basis is orthonormal and non-interacting for the infinitely separated atoms, Eq. (7) becomes

$$E_\infty = \frac{\sum_i a_i^2 (E_i^O + E_i^{H_1} + E_i^{H_2})}{\sum_i a_i^2} .$$ (8)

The E_i^A in Eq. (8) are the calculated energies for state i of atom A. The valence state of atom A may now be defined as

$$E_A = \frac{\sum_i a_i^2 E_i^A}{\sum_i a_i^2} .$$ (9)

However, the ψ_i are non-orthogonal at the molecular equilibrium geometry and the weighting factor $a_i^2 / \sum_i a_i^2$ doesn't properly take into account this non-orthogonality. Instead, following Hurley [4], the weight of each basis function at the equilibrium position which should appear in Eq. (9) is taken to be the structure projection, v_i, defined in Eq. (2). The valence state energy of atom A then becomes

$$E_A = \sum_i v_i E_i^A .$$ (10)

The v_i calculated for each ψ_i at the molecular equilibrium geometry of H_2O are given in column 2 of Table 1. The energy of each spectroscopic state is usually taken to be the promotional energy which is the difference between the calculated energy values for the given spectroscopic state and the ground ^3P state for oxygen or the ground ^2S state for hydrogen. These values are given in columns 5 and 6 of Table 1.

The last step in the method is simply to sum the product of v_i times the promotional energy of ψ_i for each of the basis functions to give the total promotional energies for each of the component atoms. These products for each structure are given in the final two columns of Table 1. Since these basis functions are orthogonal and non-interacting for the infinitely separated atoms, it is now correct to obtain the overall promotional energy by summing over the individual contributions from each structure.

C. Peterson and G. V. Pfeiffer

3. Results and Discussion

The total promotional energies for the oxygen and two hydrogen atoms in the ground state wavefunction for H_2O are given in Table 1 as 0.3055 Hartrees and 0.4784 Hartrees respectively. An entirely similar analysis employing the same orthogonal basis set was used for the OH radical (the second hydrogen was infinitely separated from the radical) and the results are given in Table 3. The promotional energies for the oxygen atom and hydrogen atom are 0.1321 Hartrees and 0.2392 Hartrees respectively. The minus signs of some of the structure projections are apparently artifacts of the calculations, but they have been included in the Tables and in the summation processes in order to present the complete results. In the following the oxygen atom as it appears in H_2O will be represented by O** and the oxygen atom as it appears in OH will be represented by O*.

From the structure projections it is apparent that the higher promotional energy associated with O** compared to O* is due to the decrease in the contribution of the ψ_1 function in going from OH to H_2O. The ψ_1 function represents the oxygen atom in the ^3P state. Concurrent with the decrease in ^3P character, there is an increase in the ionic contributions such as $O^-(^2P)$, $O^-(^2S)$, and $O^=(^1S)$ in the H_2O wavefunction. This is somewhat unfortunate since the O^- states are poorly represented by the minimal orbital basis used in these calculations. Because of the unrealistically high energies for these species reported in Table 2, the promotional energy calculated for O** and O* are undoubtedly too high. Additional calculations using an extended basis orbital set are being planned to correct for the intra-atomic correlation deficiencies of the present orbital set.

Table 3. Structure projections and promotional energies using 49 orthogonal VB structures[a]

Structure	Projection	O State	H State	Promotional Energy[b] O State	H State	Promotional Energy of Each Structure from O State	H State
1	0.42966	$O(^3P)$	$H(^2S)$	0	0.0800	0.0	0.03437
2	0.00942	$O(^1D)$	$H(^2S)$	0.0805	0.0800	0.00076	0.00075
3	0.07397	$O(^1D)$	$H(^2S)$	0.0805	0.0800	0.00595	0.00592
4	0.03184	$O(^1D)$	$H(^2S)$	0.0805	0.0800	0.00256	0.00255
5	-0.00003	$+$ a $O(^1S)$ b $O(^1S*)$	$H(^2S)$	0.2544	0.0800	0.0	0.0
6	0.01539	$O(^3P*)$	$H(^2S)$	0.6282	0.0800	0.00967	0.00123
7	0.05192	$O(^3P*)$	$H(^2S)$	0.6282	0.0800	0.03262	0.00415
8	0.00000	$O^-(^2P)$	H^+	0.1594	0.4998	0.0	0.0
9	0.00000	$O^-(^2P)$	H^+	0.1594	0.4998	0.0	0.0
10	0.12941	$O^-(^2P)$	H^+	0.1594	0.4998	0.02063	0.06468

Table 3 (continued)

Structure	Projection	O State	H State	Promotional Energy		Promotional Energy of Each Structure from	
				O State	H State	O State	H State
11	0.23261	$O^-(^2P)$	H^+	0.1594	0.4998	0.03708	0.11626
20	0.0	$O^+(^2P)$	$H^-(^1S)$	0.6501	0.5352	0.0	0.0
21	0.0	$O^+(^2P)$	$H^{\sim}(^1S)$	0.6501	0.5352	0.0	0.0
22	0.00647	$O^+(^2P)$	$H^{\sim}(^1S)$	0.6501	0.5352	0.00421	0.00346
23	0.00374	$O^+(^2P)$	$H^-(^1S)$	0.6501	0.5352	0.00243	0.00200
24	0.0	$O^+(^2D)$	$H^-(^1S)$	0.7306	0.5352	0.0	0.0
25	0.0	$O^+(^2D)$	$H^-(^1S)$	0.7306	0.5352	0.0	0.0
26	0.00114	$O^+(^2D)$	$H^-(^1S)$	0.7306	0.5352	0.00083	0.00061
27	0.00054	$O^+(^2D)$	$H^-(^1S)$	0.7306	0.5352	0.00039	0.00029
28	0.00379	$O(^1P)$	$H(^2S)$	0.9441	0.0800	0.00358	0.00030
29	0.00602	$O(^1P)$	$H(^2S)$	0.9441	0.0800	0.00568	0.00048
30	0.0	$O^-(^2S)$	$H^+(^1S)$	0.8596	0.4998	0.0	0.0
31	0.0	$O^-(^2S)$	$H^+(^1S)$	0.8596	0.4998	0.0	0.0
32	0.0	$O^+(^2D*)$	$H^-(^1S)$	1.3240	0.5352	0.0	0.0
33	0.0	$O^+(^2D*)$	$H^-(^1S)$	1.3240	0.5352	0.0	0.0
34	0.00268	$O^+(^2D*)$	$H^-(^1S)$	1.3240	0.5352	0.00355	0.00143
35	0.00019	$O^+(^2D*)$	$H^-(^1S)$	1.3240	0.5352	0.00025	0.00010
36	0.0	$O^+(^2D*)$	$H^-(^1S)$	1.3240	0.5352	0.0	0.0
37	0.0	$O^+(^2D*)$	$H^-(^1S)$	1.3240	0.5352	0.0	0.0
38	0.0	$b\ O(^1S)$ $+\ a\ O(^1S*)$	$H(^2S)$	1.4992	0.0800	0.0	0.0
43	0.0	$O^+(^2S)$	$H^-(^1S)$	1.4447	0.5352	0.0	0.0
44	0.00025	$O^+(^2S)$	$H^-(^1S)$	1.4447	0.5352	0.00036	0.00013
45	0.0	$O^+(^2P*)$	$H^-(^1S)$	1.5591	0.5352	0.0	0.0
46	0.00097	$O^+(^2P*)$	$H^-(^1S)$	1.5591	0.5352	0.00151	0.00052
						0.13206	0.23923
						0.37129	

[a] The H atom in OH has been scaled by $(1.4)^2$ while the free H is unscaled.

[b] Relative to the calculated $O(^3P)$ energy and relative to the calculated $H(^2S)$ unscaled energy.

Moffitt [2] estimated the valence state energies of oxygen to be the same in both H_2O and OH. This analysis was based on a perfect pairing model. From the results presented here it is apparent that Moffitt's analysis must be modified when a large amount of configuration interaction is permitted. This modification will disturb Moffitt's interpretation of the difference in the bond dissociation energies of H_2O as being due simply to a relaxation of the O atom, following complete dissociation, from its valence state energy to the energy of the ground state ^3P term. The present paper indicates that there must be another relaxation process at work. The OH radical originally produced (via a non-adiabatic dissociation) with the oxygen atom in the valence state O** must relax to an OH radical with an oxygen atom in the valence state O*.

Van Vleck [1] defined gross bonding energy as the sum of the experimental bond dissociation energy and the promotional energy prorated per bond of the "atoms" within the molecule. From the previous H_2O results [8] the difference in energy of H_2O and the free ground state atoms was 0.2289 Hartrees. Adding to this the promotional energy of the oxygen and hydrogen atoms in H_2O of 0.7839 Hartrees and dividing by two yields the gross bond energy in H_2O as 0.5065 Hartrees. The same type of analysis for the OH radical gives 0.0957 Hartrees plus 0.3713 Hartrees promotional energy or a gross bond energy of 0.4670 Hartrees. The difference in these gross bond energies would reflect the difference in the experimentally observed bond dissociation energies if the two relaxation processes mentioned earlier were similar in energy. The relaxation of the products from the OH dissociation is, of course, 0.3713 Hartrees. The energy of the relaxation of the products (H + OH) of the first dissociation of H_2O must be similar. Since the relaxation of the H atom from its valence state to the ^2S ground state is 0.2392 Hartrees, the remaining relaxation must amount to about 0.13 Hartrees. This would be the change in energy accompanying the change in the OH radical as the O atom changes from O** to O*. (It is interesting that the valence state of the H atom remains unchanged during this relaxation.) The only other indication of the magnitude of the relaxation in OH is the difference in the promotional energies of O** and O*, which is 0.1734 Hartrees.

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