good yields, and secondary alcohols were not affected to this oxidation system. The advantage of this new oxidizing agent lies in its simplicity and avoidance of the reactive oxidants.

Acknowledgements. We thank the Korea Research Foundation through Non Directed Research Fund, 1992.

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Overtone Transition Intensities for NH by *Ab Initio* Effective Valence Shell Hamiltonian

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Received May 2, 1994

Recently the effective valence shell Hamiltonian method (H^v) has been extended to calculate one-electron molecular properties as well as valence state energies. The H^v method is an ab initio multireference state perturbation formalism for treating electron correlations, and is based on the quasidegenerate many-body perturbation theory (QDMBPT). In the H^v method, the effective operators act only in the space spanned by the set of valence orbitals, and the effective operators are defined in terms of perturbation sums over a complete set of complementary core and excited orbitals. In energy calculations, H^v is the effective operator of Hamiltonian (H), which has been applied to a number of atomic and molecular systems where the computations of valence state energies show that the method provides an accurate description of the electronic structure.[1-10]

As for molecular properties, an operator A, which represents a molecular property is transformed to the effective valence shell operator A^v. And the diagonal and off-diagonal matrix elements of a given A^v can be obtained simultaneously for all valence states of a molecule and its ions. The dipole moment and transition dipole moment functions of CH and OH have been calculated using A^v.[11-15] Also the dipole and transition moments of SiH, PH and SH at each molecule's equilibrium internuclear distance have been reported.[16] As another test case for understanding A^v, we have calculated the dipole moment functions of NH and NH^+.[17] NH in particular has been previously studied theoretically and experimentally.[18-38]

Now we calculate the overtone vibrational transition intensities of various electronic states of NH using the dipole moment functions computed with A^v method. This provides a more stringent test of the quality of the H^v effective valence wavefunction than that given by potential energy curves alone. The accuracy of dipole moment function much depends on the accuracy of the electronic wavefunction. And to study the vibrational transition, we, of course, have to calculate vibrational wavefunction which depends on the whole profile of potential energy curve. Therefore, the calcuation of overtone intensities is very meaningful to assess the quality of the new A^v method.

The brief summary of the effective valence shell Hamiltonian formalism is as follows. The molecular electronic Hamiltonian H can be divided into a zeroth order part H_0 and a perturbation V, *i.e.*, $H=H_0+V$. The full many-electron Hilbert space can be divided into a primary space with projector P and its orthogonal complement with projector $Q=1-P$, where the P space is supposedly taken to contain a set of many-electron basis functions which are quasidegenerate with respect to the zeroth order Hamiltonian H_0. Our choice for P takes it to span the valence space of all distinct configuration state functions involving a filled core and the remaining electrons distributed among the valence orbitals. Hence, the Q space contains all basis functions with at least one core hole and/or one occupied excited orbital.

QDMBPT transforms the full Schrödinger equation

$$H\Psi_\Lambda = E_\Lambda \Psi_\Lambda \tag{1}$$

into the P space effective valence shell Schrödinger equation,

$$H^v \Psi^v_\Lambda = E_\Lambda \Psi^v_\Lambda \tag{2}$$

for the projection $\Psi^v_\Lambda = P\Psi_\Lambda$ where the E_Λ are the exact eigenvalues of (1). Note that the energies E_Λ in (1) and (2) are identical. QDMBPT gives, in the second order approximation,

$$H^v = PHP + (1/2) \sum_{\lambda\lambda'} \{P(\lambda)VQ(E_\lambda - H_0)^{-1}QVP(\lambda') + h.c.\} \tag{3}$$

where *h.c.* designates the Hermitian conjugate of the preceding term and $P(\lambda)$ designates the projector onto the valence space basis function $|\lambda\rangle$. The detailed expressions for (3) are given elsewhere.[8,9] As described in (2), the Λ indicates a valence state. Therefore the state energy for the valence state Λ is $E_\Lambda = \langle \Psi^v_\Lambda | H^v | \Psi^v_\Lambda \rangle$.

From the characteristics of H^v, by one computation, we determine E_Λ for all the valence states of NH. When the calculation is repeated for various internuclear distances, we finally determine the potential energy curves for valence state Λ, *i.e.*, $\upsilon_\Lambda(R)$ and effective electronic wavefunction Ψ^v_Λ.

Now consider an operator A whose diagonal matrix elements between the normalized full space Ψ_Λ we desire. The matrix elements may be transformed into the matrix elements of an effective valence shell operator A^v between the orthonormal valence space eigenfunctions Ψ^v_Λ,

$$\langle \Psi_\Lambda | A | \Psi_\Lambda \rangle = \langle \Psi^v_\Lambda | A^v | \Psi^v_\Lambda \rangle. \tag{4}$$

The specification that A^v be Hermitian and independent of the state Ψ_Λ leads to the first order perturbative expansion,

$$A^v = PAP + \sum_{\lambda\lambda'} \{P(\lambda)VQ(E_\lambda - H_0)^{-1}QAP(\lambda') + h.c.\} \tag{5}$$

Thus, we may obtain the expectation values of A by first solving (3) and (5), and then by taking the corresponding matrix elements on the right hand side of (4). The detailed expressions for each effective operator in (7) are given elsewhere.[11,12]

In the present work, the vibrational transition is considered to occur through the change of dipole moment only. The dipole operator μ, in atomic units, is defined as

$$A = \mu = \sum_{\alpha} \boldsymbol{R}_\alpha Z_\alpha - \sum_{i} \mathbf{r}_i \tag{6}$$

where Z_α is the charge on the nucleus α at the position $\boldsymbol{R}_\alpha$, and $\boldsymbol{r}_i$ is the position operator for electron i, and summation is over for all electrons. The minus sign indicates a charge of electron. This dipole operator μ corresponds to an A operator in (4).

From the repeated A^v calcuations at the various internuclear distances, we obtain the dipole moment functions $D_\Lambda(R)$, *i.e.*, $D_\Lambda(R) = \langle \Psi^v{}_\Lambda | \mu^v | \Psi^v{}_\Lambda \rangle$. Here the integrals are over the coordinates of electrons. In the present work, we determine the effective wavefunctions $\Psi^v{}_\Lambda$ using the second order energy expressions of H^v. The μ^v is evaluated through the first order expansion of A^v in (5).

The dipole moment functions over the internuclear distances are used in the calculation of oscillator strengths. For each bound electronic states of NH, vibrational wavefunctions and vibrational state energies are numerically determined under the Born-Oppenheimer approximation. The total wavefunction $\Phi_{\Lambda v}(R, \boldsymbol{r})$ for the electronic Λ and vibrational v state is written as

$$\Phi_{\Lambda v}(R, \boldsymbol{r}) = \Psi_{\Lambda v}(R)\Psi_\Lambda(\boldsymbol{r}) \tag{7}$$

where $\Psi_{\Lambda v}(R)$ is a vibrational wavefunction and $\Psi_\Lambda(\boldsymbol{r})$ is an electronic wavefunction. After integrating over the electronic coordinates, we obtain the nuclear Schrödinger equation,

$$-\frac{1}{2mR^2}\frac{d^2\Psi_{\Lambda v}(R)}{dR^2} + \upsilon_\Lambda(R)\Psi_{\Lambda v}(R) + \frac{\Lambda(\Lambda+1)}{2mR^2}\Psi_{\Lambda v}(R) = E_{\Lambda v}\Psi_{\Lambda v}(R) \tag{8}$$

where m is the reduced mass of N and H, and $E_{\Lambda v}$ is a vibrational energy of v state associated with the electronic state Λ. Here the electronic orbiting angular momentum projected onto the molecular axis(Λ) is a good quantum number. The oscillator strength for the transition from the v'' to v' vibrational state in a particular Λ state is defined by

$$f_{\Lambda v' \Lambda v''} = (2/3)\Delta E |\langle \Psi_{\Lambda v'}(R) | D_\Lambda(R) | \Psi_{\Lambda v''}(R) \rangle|^2 \tag{9}$$

where the integral is over the nuclear coordinate R and ΔE is an energy difference between v'' and v' vibrational state. The oscillator strengths are identified as vibrational transition intensities.

The H^v calculated potential energy curves, $\upsilon_\Lambda(R)$ and spectroscopic constants for NH may be found in Reference 10. Reference 17 explains the nature of the dipole moment functions of NH in detail.

Table 1. Vibrational Levels (cm^{-1}) for $X^3\Sigma^-$, $a^1\Delta$, $b^1\Sigma^+$, and $A^3\Pi$ states of NH

v	$X^3\Sigma^-$	$a^1\Delta$	$b^1\Sigma^+$	$A^3\Pi$
0	0	0	0	0
1	3132	3184	3229	3081
	3131[a]*	3183[b]*	3206[e]*	2977[a]*
		3180[c]*		3010[c]*
				3034[f]*
2	6133	6236	6358	5981
		6219[d]*	6293[e]*	5918[f]*
3	8995	9169	9377	8672
		9112[d]*		
4	11710	11978	12231	11119
5	14280	14660	14945	13282
6	16700	17219	17557	
7	18951	19642	20037	
8	21022	21928	22374	
9	22893	24068	24568	
10	24530	26052	26611	
11		27872	28494	
12		29523	30210	
13			31770	

*Experimental values. [a] Ref. 30. [b] Ref. 33. [c] Ref. 32. [d] Ref. 36. [e] Ref. 35. [f] Ref. 31.

From the H^v calculations we have found the five lowest bound valence states, *e.g.*, $X^3\Sigma^-$, $a^1\Delta$, $b^1\Sigma^+$, $A^3\Pi$, and $c^1\Pi$ states for NH. For the $c^1\Pi$ state, our H^v potential energy curve shows a rather shallow minimum and a maximum(barrier).[10] We could only find one vibrational level in the potential well. Therefore the state is not of interest in the present work.

The vibrational energy $E_{\Lambda v}$ and vibrational wavefunction $\Psi_{\Lambda v}(R)$ are numerically evaluated by solving (8) for various Λ states listed below. The vibrational levels considered in oscillator strength calculations are $v = 0 \sim 10$ for $X^3\Sigma^-$, $v = 0 \sim 12$ for $a^1\Delta$, $v = 0 \sim 13$ for $b^1\Sigma^+$, and $v = 0 \sim 5$ for $A^3\Pi$. The calculated vibrational level energies ($E_{\Lambda v}$) are listed in Table 1.

As shown in Table 1, the vibrational energy spacing is not constant meaning that the vibrational motion is anharmonic. From the comparison of our theoretical values with experimental ones which are also listed in Table 1, we see that our theoretical energy levels are in good agreement with experimental data.

With $\Psi_{\Lambda v}(R)$ and $D_\Lambda(R)$, the overtone intensities (*i.e.*, oscillator strengths) are calculated using (9). In Table 2, some of fundamental and overtone transition intensities are listed for $X^3\Sigma^-$, $a^1\Delta$, $b^1\Sigma^+$, and $A^3\Pi$ states.

The fundamental transitions ($\Delta v = 1$) exhibit larger intensities than overtone transitions ($\Delta v > 1$). When Δv increases, the intensities generally decrease. This general feature of vibrational absorption spectrum is clearly shown in Table 2.

Experimentally it is not easy to measure the intensities of vibrational overtone intensities because many vibrational peaks are mixed with rotational transition peaks. Tipping

Table 2. Overtone Transition Intensities for NH. 7.87(−6) should read 7.87×10^{-6}

$v''\rightarrow v'$	$X^3\Sigma^-$	$a^1\Delta$	$b^1\Sigma^+$	$A^3\Pi$
0→1	7.87(−6) 8.26(−6)[a]	5.47(−6)	3.01(−6)	4.45(−5)
0→2	2.50(−9)	2.51(−10)	1.45(−8)	2.82(−6)
0→3	2.01(−9)	1.49(−9)	3.14(−9)	1.78(−8)
0→4	8.24(−10)	2.44(−10)	3.42(−9)	4.02(−9)
0→5	9.89(−11)	4.13(−11)	2.39(−9)	8.93(−9)
1→2	1.68(−5) 3.46(−5)[a]	1.17(−5)	6.87(−6)	7.17(−5)
1→3	2.28(−8)	5.01(−9)	1.76(−9)	9.94(−6)
1→4	5.62(−10)	4.31(−9)	3.04(−8)	1.21(−7)
1→5	1.88(−9)	7.63(−10)	6.28(−9)	1.71(−8)
2→3	2.69(−5) 1.08(−4)[a]	1.88(−5)	1.06(−5)	7.70(−5)
2→4	2.05(−9)	3.35(−8)	1.44(−9)	2.34(−5)
2→5	1.18(−8)	8.19(−9)	3.28(−9)	7.31(−7)
3→4	5.09(−5) 2.13(−4)[a]	2.66(−5)	1.60(−5)	5.89(−5)
3→5	2.87(−7)	1.08(−7)	8.44(−9)	4.40(−5)
4→5	1.27(−4) 3.20(−4)[a]	3.50(−5)	2.17(−5)	2.42(−5)

[a] Ref. 38. See the text.

and Ogilvie[37] suggested a simple semiempirical formula determining the integral of $\langle\Psi_{\Lambda v}'(R)|D_\Lambda(R)|\Psi_{\Lambda v}''(R)\rangle$. The formula is expressed in terms of some parameters (Herman-Wallis factors) and spectroscopic constants. Chackerian et al. used experimental data to fit the parameters (for the $X^3\Sigma^-$ state only) required in Tipping and Ogilvie's formula.[38] Using Chackerian *et al.*'s parameters we have calculated the fundamental transition intensities for the $X_3\Sigma^-$ state. Those values, which can be essentially considered as experimental ones are also listed in Table 2. From the Table 2, we see that our theoretical value of 7.87×10^{-6} for the $v''=0$ to $v'=1$ transition is very similar to the experimental value of 8.26×10^{-6}. For other fundamental transitions ($v''=1$ to $v'=2$, etc.) our values are consistently smaller than experimental ones. Since the dipole moment of the $v=0$ state of $X^3\Sigma^-$ was accurately measured, the experimental value of 8.26×10^{-6} is very reliabe. And as discussed above, our value is in very good agreement with it. Other experimental values are believed to be the upper limit.[38] It indirectly explains why our values are consistently smaller than experimental ones. There should be more experimental data available to compare with, but we can say, at this stage, that our theoretical values are not far from the exact ones.

The effective valence shell Hamiltonian formalism has been extended to treat operators for properties other than the effective Hamiltonian for the valence state energies. The lowest order correlation corrections for the effective operators are shown for dipole moments corresponding to one-electron operators, and explicit computations are presented for the overtone transition intensities for several low lying electronic states of NH. Our computed intensities are in reasonable agreement with experimental values available and this comparison supports the utility of the effective Hamiltonian method for evaluating molecular properties.

Acknowledgments. This work has been supported by the Korea Science and Engineering Foundation through the Center for Molecular Science.

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