13. Minoura, Y. In *Structure and Mechanism in Vinyl Polymerization*; Tsuruta, T.; O'Driscoll, K. F., Eds.; Marcel Dekker, Inc.: New York, 1969; p 190.
14. Tawney, P. O.; Snyder, R. H.; Conger, R. P.; Leibbrand, K. A.; Stiteler, C. H.; Williams, A. R. *J. Org. Chem.* **1961**, *26*, 15.
15. Paesschen, G. V.; Timmerman, D. *Makromol. Chem.* **1964**, *78*, 112.
16. Vanderbilt, D. P.; Butler, G. B. *J. Macromol. Sci. Chem.* **1986**, *A23*, 541.
17. Turner, S. R.; Anderson, C. C.; Kolterman, K. M. *J. Polym. Sci., Polym. Lett.* **1989**, *27*, 253.
18. Barrales-Rienda, J. M.; De La Campa, J. I. G.; Lamos, J. G. *J. Macromol. Sci.-Chem.* **1977**, *A11*, 267.

A Theoretical Treatment of the Resonances in the Predissociation of Lower Rovibrational Levels of the $A^2\Sigma^+$ State of OH

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An exact quantum mechanical theory is employed to treat predissociation process of the $A^2\Sigma^+$ state of OH. The widths and positions of the lower ($v=2$ and $v=3$) rovibrational levels are calculated. Energy shifts of the resonances from the zeroth order (pure Hund's case (b)) positions are shown to be small for $N\leq 10$, indicating that the $A^2\Sigma^+$ state can be described as case (b) very well for low N. Due to the differential interactions of the $A^2\Sigma^+_{1/2}$ and $A^2\Sigma^+_{-1/2}$ states with $X^2\Pi$ and $2^2\Pi$ states, small splittings between the F_1 and F_2 levels are predicted. Calculated lifetimes of the resonances agree with experimental results reasonably well.

Introduction

The hydroxyl radical (OH) is an important constituent of combustion gas and cometary gas. Many *ab initio* studies have been done on the potential energy curves[1~5] and also on the spin-orbit interactions[2] and transition dipole moments [1~5] between the low-lying electronic states of OH. Photodissociation processes of OH have also been of interest in a number of investigations, because of the astrophysical importance of the molecule. Dalgarno and coworkers,[1,3,5] for example, have done extensive studies on the direct photodissociation processes of the low-lying states of OH. The A-X band system of OH has been studied for a long time[6~8] especially because of the potential use in detecting OH fragments by laser induced fluorescence technique.

Predissociation is one of the dynamic processes[9,10] that result from the breakdown of the Born-Oppenheimer approximation. It is now well known that interactions between the binding and dissociating states basically determine the widths and positions of the resonances (or quasi-bound states) observed in the photodissociation spectra. There have been numerous studies where the relationships between these interactions and the characteristics of the resonances have been investigated. In these works, the widths and shifts of the resonances have been expressed in terms of the matrix elements of the interactions between the wave functions of the binding states and the continuum wave functions of the dissociating states. Continuum wave functions are usually obtained by using methods based on scattering theory. Various levels of approximations have been employed in these methods, the consequences of which are that some of the interactions, which are expected to play a significant role in the dynamic processes, are not considered. In Yarkony's recent calculations,[2] for example, case (b) limit has been *assumed* for the $X^2\Pi$ and $^4\Pi$ states of OH. In most situations, molecular electronic states do not belong to the pure Hund's cases. These assumptions had to be made because *not* all of the couplings have been included in the formalism. Particular Hund's coupling cases need not be assumed for these states as long as all the nonadiabatic interactions between these states and other states correlating with the dissociation products are included to evaluate the total Hamiltonian. These deficiencies are also evident in Sink *et al.*'s work,[11,12] where asymptotic couplings among the dissociative states have not been included. Many interesting observables such as the population ratios of the photofragments internal states and anisotropy parameters cannot be calculated by employing these approximation methods.

Intensities and line shapes are also very important characteristics of the resonances that cannot be properly calculated by employing approximate schemes where some of the interactions are not incorporated. It is well known[13] that the resonances can exhibit a variety of asymmetric profiles when the continuum states, interacting with discrete states, are optically coupled with the initial states. These asymmetric resonances have recently been observed for the predissociation processes of Cs_2[14,15] and FNO.[16] Theoretical analyses of the photodissociation spectra of these molecules have provided detailed informations on the underlying mechanisms. The quantum interferences between the discrete states and the continuum states, which give rise to these very interesting non-Lorentzian absorption line shapes, can only be pro-

perly incorporated by employing exact photodissociation formalism. Recently we have developed[17] such an *exact* theory to treat diatomic photodissociation processes to atomic fine structure states where several atomic term limits are involved. We have demonstrated that both the continuum-continuum interactions between states dissociating to the *same* atomic term and the interactions in the Franck-Condon region between states correlating to *different* atomic terms can significantly affect the shapes of the resonances in the total cross sections as well as in the partial cross sections to each of the atomic fine structure components in a very complicated way. It has also been shown that the resulting branching ratios of the fine structure states can be dramatically altered by these interactions. Implications of these findings have been discussed in the spirit of coherent control of electronically excited states and selective production of photofragments.

In this paper we briefly describe the exact theory we have recently developed. We employ the methods to perform exact quantum mechanical calculations for OH photodissociation processes at energies between the dissociation thresholds to triplet oxygen ($O(^3P)$) and singlet oxygen ($O(^1D)$) terms. We investigate whether the $A^2\Sigma^+$ state can be approximated as Hund's case (b) by computing the positions of the resonances and by comparing them with those of pure Hund's case (b) rotational levels. We also evaluate the widths of the resonances corresponding to the lower ($v=2$ and 3) rovibrational levels of the $A^2\Sigma^+$ state of OH, and compare them with the experimental results.

Theory and Computational Methods

Hamiltonian and Basis Functions. The total Hamiltonian for the dissociating molecule in the Adiabatic Born-Oppenheimer (ABO) electronic basis can be written as

$$H_{tot}(r)=H_{elec}(r)+T(r)+H_{rel}(r), \tag{1}$$

where $H_{elec}(r)$ is a diagonal matrix of ABO potential energy curves, $T(r)$ is the nuclear kinetic operator and $H_{rel}(r)$ represents the relativistic Hamiltonian. Only spin-orbit interactions are included in the present work. Since $H_{elec}(r)$ is diagonal in Hund's case (a) basis, $H_{tot}(r)$ is expanded in good parity Hund's case (a) basis function $|JMc\Lambda S\Sigma p>$,

$$|JMc\Lambda S\Sigma p>=(2-\delta_{\Lambda 0,\Sigma 0})^{-1/2}\ [(2J+1)/8\pi^2]^{1/2}\ [D^{J}_{M\Omega}(\alpha\beta\gamma)|\Lambda S\Sigma>$$
$$+(1-\delta_{\Lambda 0,\Sigma 0})\ (-1)^{p+J-S+\sigma}\ D^{J}_{M\Omega}(\alpha\beta\gamma)|-\Lambda S-\Sigma>], \tag{2}$$

where p is the parity, J is the total angular momentum quantum number, M is its component along the space-fixed z axis, S is the total spin, Λ and Σ are the components of J and S along the molecular axis, respectively, and c denotes any other electronic state labels. σ is 1 for Σ^- states, and 0 for other states. Hund's case (a) basis functions are coupled by spin-orbit Hamiltonian and by Coriolis couplings due to the rotational part of $T(r)$.

The total Hamiltonian can also be separated into two parts, $H^{(0)}$ that describes internal motion of the fragments and relative motion, and interactions $V(r)$ that vanish at large interfragment separations,

$$H_{tot}(r)=H^{(0)}+V(r), \tag{3a}$$

$$H^{(0)}=T(r)+H_{int}. \tag{3b}$$

The final states of the dissociating system must be expanded in eigenstates of $H^{(0)}$ in order to properly define transition rates to individual fragment atomic fine structure levels. Since the ABO electronic eigenstates do not dissociate in this fashion (it yields a linear combination), it is necessary to adopt a molecular basis which at large interfragment separations asymptotically becomes a product of atomic fine structure states $|c_O j_O m_O j_H m_H>$ and a sperical harmonics $Y_{l\mu}(\hat{r})$ describing the rotation of the diatomic about its center of mass. Here $j_O(j_H)$ and $m_O(m_H)$ are the total electronic angular momentum of the oxygen (hydrogen) fragment and its space-fixed projection, respectively, and $\hat{r}$ is a unit vector along the internuclear axis. c_O denotes extra quantum numbers needed to describe oxygen fine structure states (that is, spin and orbital angular momentum quantum numbers). The asymptotic degeneracy of these product atomic states makes it convenient to couple these asymptotic states to produce states with definite total angular momentum J and its projection M,

$$|JMjlc_O j_O j_H>=\sum_{m\mu}|jmc_O j_O j_H m_H>\ Y_{l\mu}\ <JM|jlm\mu>, \tag{4}$$

where

$$|jmc_O j_O j_H>=\sum_{m_O m_H}|c_O j_O m_O>|j_H m_H>\ <jm|j_O m_O j_H m_H>. \tag{5}$$

Here $j=j_O+j_H$, $J=j+l$, and $<JM|jlm\mu>$ and $<jm|j_O m_O j_H m_H>$ are Clebsch-Gordan coefficients. Thus we introduce "atomic limit" molecular basis functions which asymptotically become simple $|JMjlc_O j_O j_H>$ states of good parity and which diagonalize the Hamiltonian at large r. These two bases are related to each other by an r-independent transformation matrix

$$<jlc_a j_a c_b j_b|c\Lambda S\Sigma p>_J=1/(2-\delta_{\Lambda 0,\Sigma 0})^{1/2}\ \{[<l0|jJ-\Omega\Omega>\ (-1)^{j-J-\Omega}$$
$$\times\sum_{\Lambda_a\Lambda_b}<j\Omega j_a j_b|\Lambda_a\Lambda_b S\Sigma><\Lambda_a\Lambda_b|c\Lambda>]+[(1-\delta_{\Lambda 0,\Sigma 0})(-1)^{p+J-S+\sigma}$$
$$\times(-1)^{j+\Omega-J}<l0|jJ\Omega-\Omega>\ \sum_{\Lambda_a\Lambda_b}<j-\Omega j_a j_b|-\Lambda_a-\Lambda_b S-\Sigma>$$
$$\times<-\Lambda_a-\Lambda_b|c-\Lambda> \tag{6}$$

When there occurs explicit curve crossing in the Franck-Condon region, at least two atomic term limits are involved in the dissociation process. The nonadiabatic interactions between states correlating to different atomic term limits do not vanish at large internuclear distances in general, and this requires special treatments. Because of these nonvanishing interactions, atomic limit basis functions that result in only one of the atomic term limit do not diagonalize $H^{(0)}$ and, consequently, two atomic term limits must be explicitly considered and all the ABO states correlating with these atomic terms should be properly incorporated as well. This means that *two* transformation matrices must be constructed, each of which describes correlation to the corresponding atomic term. This situation is in direct contrast with direct dissociating systems, where all the ABO states involved dissociate to the same atomic term limit. In OH predissociation the spin-orbit interactions between the $A^2\Sigma^+$ and $^2\Sigma^-$, $^4\Sigma^-$, $^4\Pi$ states do not vanish at large internuclear distances. Hence, a transformation matrix describes the correlation be-

tween O(^{3}P) and $X^2\Pi$, $^2\Sigma^-$, $^4\Sigma^-$, $^4\Pi$ states while another one connects O(^{1}D) to $A^2\Sigma^+$, $^2\Delta$ and $2^2\Pi$ states.

Evaluation of the Hamiltonian is performed by using these transformation matrices. Each term in the Hamiltonian is evaluated in the basis which is most convenient. The electronic Hamiltonian is calculated in terms of the ABO molecular basis, since it is diagonal in this basis. Hund's case (a) basis functions are employed to expand the electronic Hamiltonian. Other basis functions can also be used to give identical results, as long as all the interactions are included in the calculations. Spin-orbit Hamiltonian and rotational term are calculated in "atomic limit" basis, and are transformed to ABO basis by transformation matrices. These two parts are diagonal in "atomic limit" basis.

Scattering Equations and Photodissociation Cross Sections. We solve the close- coupled equations for the scattering wave function $|k,j_O m_O j_H m_H^{(-)}\rangle$ of energy E.

$$(H_{tot}-E)|k,c_O j_O m_O j_H m_H^{(-)}\rangle = 0. \quad (7)$$

The scattering wave function $|k,c_O j_O m_O j_H m_H^{(-)}\rangle$ is expanded in terms of the continuum wave functions with definite total angular momentum,

$$|k,c_O j_O m_O j_H m_H^{(-)}\rangle = \sum_{jlm\mu} |EJjlc_O j_O j_H^{(-)}\rangle \langle JM|jlm\mu\rangle \times \langle jm|j_O j_H m_O m_H\rangle i^l Y_{l\mu}(k) \quad (8)$$

Transition matrix elements to a specific fine structure component of the oxygen atom is given by the Golden rule expression,

$$T(k,c_O j_O m_O j_H m_H|\Psi_i) = \sum_{jlm\mu} \langle EJjlc_O j_O j_H^{(-)}|H_I|\Psi_i\rangle \times \langle JM|jlm\mu\rangle \langle jm|j_O m_O j_H m_H\rangle i^l\ Y_{l\mu}(k). \quad (9)$$

Applying the Wigner-Eckart theorem to the matrix element $\langle EJjlc_O j_O j_H^{(-)}|H_I|\Psi_i\rangle$, the transition amplitudes become

$$\langle EJjlc_O j_O j_H^{(-)}|H_I|\Psi_i\rangle = \sum_q \varepsilon q \langle JM|1J_i q M_i\rangle\ \tau(Jjlc_O j_O j_H|J_i\nu_i). \quad (10)$$

Here ε denotes the radiation polarization vector and $\tau(Jjlc_O j_O j_H|J_i\nu_i)$ represents the transition amplitude to a specific fine structure component of the oxygen atom, which is expressed by

$$\tau(Jjlc_O j_O j_H|J_i\nu_i) = \langle EJjlc_O j_O j_H^{(-)}|\mu(r)|J_i\nu_i\rangle \quad (11)$$

where $\mu(r)$ is the electronic transition dipole moment. The cross sections for the dissociation to oxygen fine structure state with j_O are calculated by

$$\sigma(c_O j_O|J_i\nu_i) = \Sigma(2J+1)|\tau(Jjlc_O j_O j_H|J_i\nu_i)|^2, \quad (12)$$

where $|J_i\nu_i\rangle$ is the wave function of the initial state. Branching ratio to each of the oxygen fine structure state is defined as the ratio of $\sigma(c_O j_O|J_i\nu_i)$ to the total dissociation cross section at the given energy.

Scattering wave functions are propagated by using the Renormalized Numerov method[18] and Cooley's algorithm[19] is employed to obtain the vibrational wave function of the ground state. RKR potentials obtained by Fallon *et al.*[20] and by Horsley *et al.*[21] are employed for the $X^2\Pi$ and $A^2\Sigma^+$ states, respectively. The $^2\Sigma^-$, $^4\Sigma^-$, and $^4\Pi$ states are represented by potential curves of Yarkony.[2] The $^2\Delta$ and $2^2\Pi$ states are described by using the *ab initio* potentials of van Dishoeck and Dalgarno.[1] Transition dipole moments from the $X^2\Pi$ to $A^2\Sigma^+$ and to $^2\Sigma^-$ states are taken from the work of Yarkony[2] and van Dishoek *et al.*,[3] respectively. The $^2\Delta - X^2\Pi$ and $2^2\Pi - X^2\Pi$ transitions are described by *ab initio* results of van Dishoeck and Dalgarno.[1] The r-dependent spin-orbit interactions between $A^2\Sigma^+$ and $^2\Sigma^-$, $^4\Sigma^-$, $^4\Pi$ states are taken from the work of Yarkony.[2]

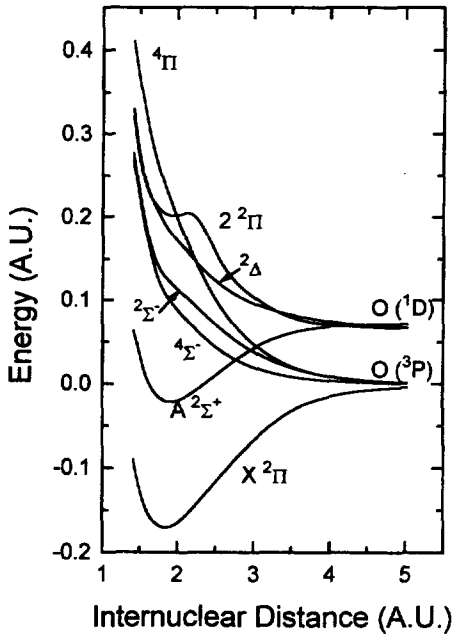

Figure 1. Potential energy curves of OH.

Results and Discussions

Figure 1 depicts the potential curves of the electronic states included in the present calculations. Between the thresholds to O(^{3}P) and O(^{1}D), $A^2\Sigma^+$ and $^2\Sigma^-$ states are optically coupled with the ground $X^2\Pi$ state. Since the $A^2\Sigma^+$ and $^2\Sigma^-$ states interact by spin-orbit couplings, and since the $^2\Sigma^-$ state is repulsive, photoabsorption to this energy regime may result in asymmetric line shapes. We have shown in a series of papers[17] that for higher ($v \geq 7$) rovibrational levels of the $A^2\Sigma^+$ state, resonances indeed exhibit non-Lorentzian absorption profiles. For lower levels ($v=2$ and $v=3$) considered here, however, the Franck-Condon overlap between the $X^2\Pi$ and $^2\Sigma^-$ states is very small, and the resonances are predicted to be essentially Lorentzian.

The Σ states with nonzero spin angular momentum quantum number are known[22] to be described as Hund's case (b) very well. It can be shown[23] that the Hund's case (a) basis functions $^2\Sigma_{1/2}$ and $^2\Sigma_{-1/2}$ states interact with each other by the S-uncoupling operator. Subsequent diagonalization leads to case (b) basis, whose rotational levels can be described in terms of the quantum number N as $N(N+1)B$, where $N=J-S$ and B is the rotational constant. Hence the F_1 ($J=N+1/2$) and F_2 ($J=N-1/2$) components of the pure case (b) rotational levels have the same energy. In OH molecule investigated here, however, the case (a) basis $A^2\Sigma_{1/2}$ and $A^2\Sigma_{-1/2}$ states can also interact with other states, and this may result in the splitting of the F_1 and F_2 levels. Dif-

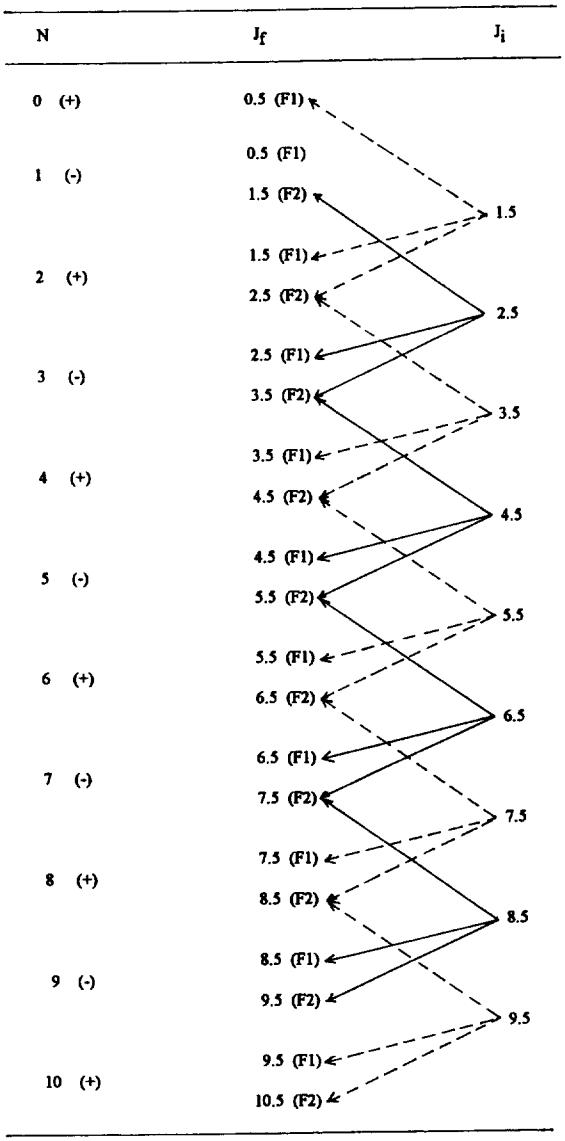

Figure 2. Electronic transitions from the *e*-components of the $X^2\Pi_{3/2}$. Solid lines: transitions from the $X^2\Pi^+{}_{3/2}$ states. Dashed lines: transitions from the $X^2\Pi^-{}_{3/2}$ states.

ferential interactions of the $^2\Sigma_{1/2}$ and $^2\Sigma_{-1/2}$ states with the two $^2\Pi$ states ($X^2\Pi$ and $2^2\Pi$) by the spin-electronic and L-uncoupling operators are known to result in such splittings.[23] In order to elucidate the degree of the deviations of the $A^2\Sigma^+$ state from the pure Hund's case (b), we perform the close coupled calculations for photodissociation processes resulting from photoexcitation of the $X^2\Pi_{3/2}$ states. Parity blocks are set up so that the photoabsorptions of the *e*-components of the $X^2\Pi_{3/2}$ state are only considered. Photoexcitations from the *f*-components of the $X^2\Pi_{3/2}$ state can be treated simply by exchanging the parity blocks. The angular momentum quantum numbers of the final state, J and N, which can be accessed from the $X^2\Pi_{3/2}$ state with a given initial angular momentum quantum number J_i, are described in Figure 2. Since the parity of the initial and the final states must be different for dipole transitions, $X^2\Pi^+{}_{3/2}$ ($X^2\Pi^-{}_{3/2}$) states connect to states with odd (even) N. The calculated positions of the F_1 resonances are depicted in Figure 3. It

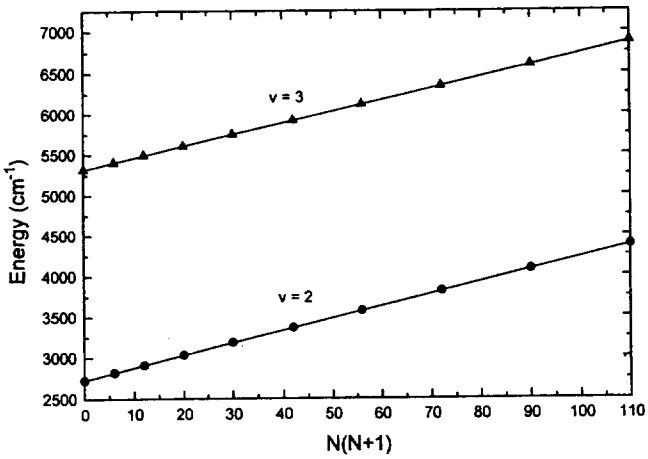

Figure 3. Positions of the F_1 resonances. Solid lines: pure case (b) positions.

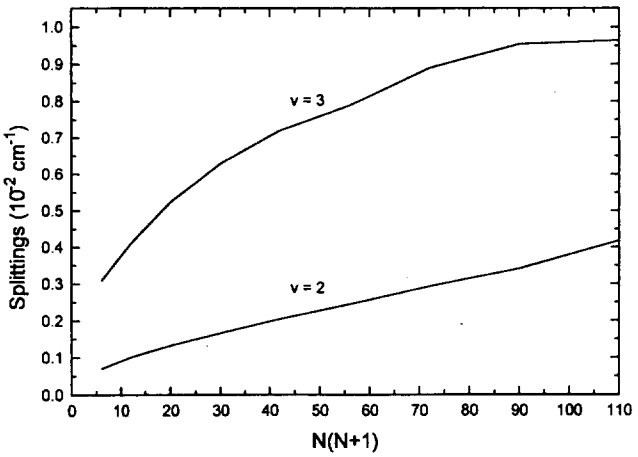

Figure 4. Splittings between the F_1 and F_2 resonances.

can be seen that the positions of the F_1 components vary nearly as linear functions of $N(N+1)$, indicating that the $A^2\Sigma^+$ state can be approximated as case (b) very well, at least for these lower levels. The positions of the F_2 components exhibit essentially identical behavior. We have also evaluated the zeroth-order (pure basis (b)) rovibrational levels of the $A^2\Sigma$ state by using Cooley's procedure.[19] The energy differences between these pure basis (b) levels and the computed resonance positions are found to be small (usually less that 2 cm^{-1}), again confirming the validity of describing the $A^2\Sigma^+$ state as case (b). The F_1 levels lie slightly higher than the F_2 levels for all N and v. The splittings between the F_1 and F_2 levels are found to be very small (Figure 4), although they tend to increase monotonically with N. Thus, deviations of the $A^2\Sigma^+$ state from the pure Hund's case (b) are expected to be significant for larger N.

The widths (or lifetimes) of the resonances are very important observables because they manifest the interactions between the binding and dissociating states. Total (radiative plus nonradiative) lifetimes of the rovibrational levels of the $A^2\Sigma^+$ state of OH have been measured in several studies[6,7,24] from the emission spectra. Since the computed lifetimes in the present work are for the nonradiative (that is, predisso-

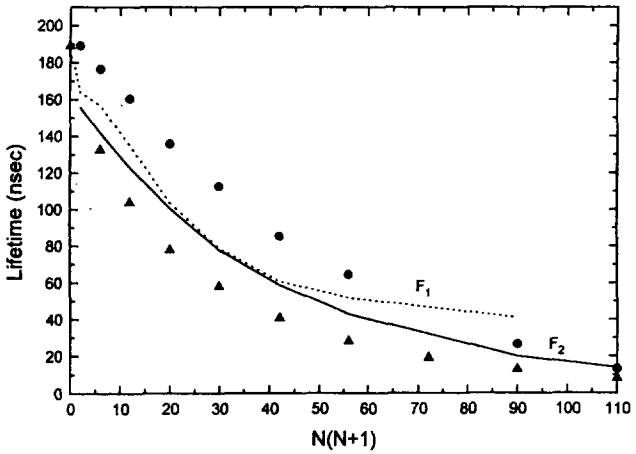

Figure 5. Nonradiative lifetimes for the $v=2$ resonances. Solid line: experimental, F_2 levels. Dotted line: experimental, F_1 levels. Circles: calculated, F_2 levels. Triangles: calculated, F_1 levels.

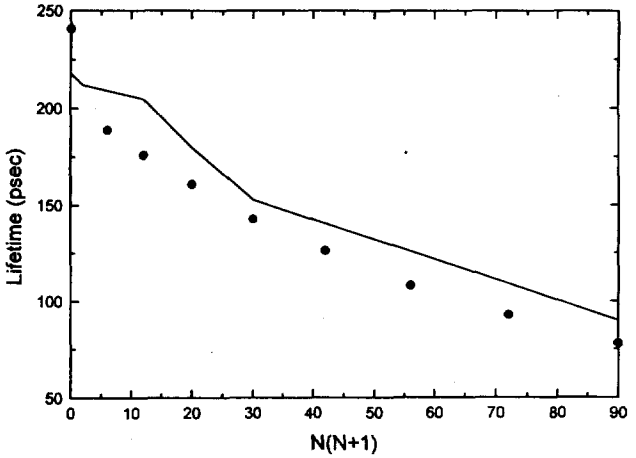

Figure 6. Nonradiative lifetimes for the F_1 components of the $v=3$ resonances. Solid line: experimental. Circles: calculated.

ciation) processes, contributions of the radiative lifetimes must be subtracted from the experimentally measured lifetimes for direct comparisons with the present calculations. Radiative lifetimes of the $v=2$ and $v=3$ levels of the $A^2\Sigma^+$ state are taken from the calculations of Yarkony,[2] and the total lifetimes are the results of Brzozowski[24] *et al.* The results are presented in Figure 5 and Figure 6. Although the experimental results are fragmentary, our computed results agree reasonably well with the measured lifetimes of the rovibrational levels of the $A^2\Sigma^+$ state. It should also be noted that the agreements between the present calculations and the experimental results will depend on the accuracy of the reported radiative lifetimes. The predissociation of the lower rovibrational levels considered in this work proceeds mainly through spin-orbit interactions between the $A^2\Sigma^+$ and $^4\Sigma^-$ states.[25-27] The spin-orbit interactions $<A^2\Sigma^+\ J\ N_b|H_{so}|^4\Sigma^-\ J\ N_c>$ between these states are such that the F_1 levels are coupled more strongly with $N_c=N_b-1$, while the F_2 levels interact more strongly with $N_c=N_b+1$.[25] Since the nuclear wave functions of the $^4\Sigma^-$ state with larger N_c have the classical turning points at larger internuclear distances, interactions between the $A^2\Sigma^+$ and $^4\Sigma^-$ states decrease with increasing N_c. Thus lifetimes (widths) of the F_2 levels are longer (smaller) than those of the F_1 levels as shown in Figure 5 and Figure 6.

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References

1. van Dishoeck, E. F.; Dalgarno, A. *J. Chem. Phys.* **1981**, *79*, 873.
2. Yarkony, D. R. *J. Chem. Phys.* **1992**, *97*, 1838.
3. van Dishoeck, E. F.; van Hemert, M. C.; Allison, A. C.; Dalgarno, A. *J. Chem. Phys.* **1984**, *81*, 5709.
4. Langhoff, S. R.; van Dishoeck, E. F.; Wetmore, R.; Dalgarno, A. *J. Chem. Phys.* **1982**, *77*, 1379.
5. van Dishoeck, E. F.; Langhoff, S. R.; Dalgarno, A. *J. Chem. Phys.* **1983**, *78*, 4552.
6. Gray, J. A.; Farrow, R. L. *J. Chem. Phys.* **1991**, *95*, 7054.
7. Heard, D. E.; Crosley, D. R.; Jeffries, J. B.; Smith, G. P.; Hirano, A. *J. Chem. Phys.* **1992**, *96*, 4366.
8. Bauslicher, C. W.; Langhoff, S. R. *J. Chem. Phys.* **1987**, *87*, 4665.
9. Iwai, M.; Lee, S.; Nakamura, H. *Phys. Rev. A*, **1993**, *47*, 2686.
10. Lee, S.; Iwai, M.; Nakamura, H. in *Molecules in Laser Fields*; Marcel Dekker: New York, 1994.
11. Sink, M. L.; Bandrauk, A. *Chem. Phys. Lett.* **1979**, *65*, 246.
12. Sink, M. L.; Bandrauk, A. *J. Chem. Phys.* **1980**, *73*, 4451.
13. Fano, U. *Phys. Rev.* **1961**, *124*, 1866.
14. Kim, B.; Yoshihara, K. *J. Chem. Phys.* **1993**, *99*, 1433.
15. Kim, B.; Yoshihara, K.; Lee, S. *Phys. Rev. Lett.* **1994**, *73*, 424.
16. Brandon, J. T.; Reid, S. A.; Robie, D. C.; Reisler, H. *J. Chem. Phys.* **1992**, *97*, 5246.
17. (a) Lee, S. *Bull. Chem. Soc.* **1995**, *16*, 387. (b) Lee, S. *Chem. Phys. Lett.* (in press). (c) Lee, S. *J. Chem. Phys.* (in press). (d) Lee, S. (submitted for publication).
18. Johnson, B. R. *J. Chem. Phys.* **1977**, *67*, 4086.
19. Cooley, J. W. *Math. Comp.* **1961**, *383*, 15.
20. Fallon, K. J.; Tobias, J.; Vanderslice, J. T. *J. Chem. Phys.* **1961**, *34*, 167.
21. Horsley, J. A.; Richards, W. G. *J. Chim. Phys.* **1969**, *66*, 41.
22. Herzberg, G. *Spectra of Diatomic Molecules*; Van Nostrand Reinhold: New York, 1950.
23. Lefebvre-Brion, H.; Field, R. W. *Perturbations in the Spectra of Diatomic Molecules*; Academic: New York, 1986.
24. Brzozowski, T.; Erman, P.; Lyyra, M. *Phys. Scr.* **1978**, *17*, 507.
25. Bergeman, T.; Erman, P.; Haratym, Z.; Larsson, M. *Phys. Scr.* **1981**, *23*, 45.
26. Lee, S.; Williams, C. J.; Freed, K. F. *Chem. Phys. Lett.* **1986**, *130*, 271.
27. Lee, S.; Freed, K. F. *J. Chem. Phys.* **1987**, *87*, 5752.