

Ab Initio Study of Stretch-Bend Coupling in HOOH

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Ab initio calculations are used to investigate the dependence of the OOH bend force constants on the OO and OH bond lengths in HOOH. The calculations were performed using second-order Møller-Plesset perturbation theory with a split-valence triple- ζ basis set augmented with multiple polarization functions on both the oxygen and hydrogen atoms [6-311G(3d,2p)]. Analytical functions describing the variation of the bending force constants with the bond lengths are obtained by fitting the ab initio data and are found to be significantly different from the switching functions previously used in trajectory studies of HOOH.

I. Introduction

There has been considerable experimental¹ and theoretical² interest in the vibrational overtone induced decomposition of polyatomic molecules. The possibility of inducing unimolecular dissociation in state-specific fashion has provided the stimulus for many of the studies. Hydrogen peroxide is an attractive polyatomic molecule for study of overtone-induced unimolecular dissociation.³⁻⁸ The O-H bonds are good local modes and provide well-defined sites for overtone excitation; classical trajectory simulations⁹⁻¹⁵ are feasible, and the relatively small size (four atoms) makes it possible to perform ab initio calculations with large basis sets.¹⁶⁻²⁵

Early work on the spectroscopy of HOOH established the nonplanar geometry and the existence of a hindered internal rotational mode.²⁶⁻³⁰ Some of the earlier studies indicated the importance of torsion-vibration interactions and the dependence of the torsional potential on the degree of excitation of the OH stretch.³⁰⁻³² Several valence force fields were proposed which gave reasonable fits to the experimental data,^{16,33} and some ab initio calculations¹⁶⁻¹⁹ were also performed.

More recently, several experimental studies of the vibrational overtone initiated decomposition of HOOH have been reported.³⁻⁸ The vibrationally mediated photodissociation of HOOH and HOOD³⁴ and UV-induced photodissociation of hydrogen peroxide³⁵ have also been investigated.

On the theoretical side, both ab initio and semiempirical quantum mechanical potential surface calculations^{12,16,24,25} and classical trajectory calculations of the OH overtone induced dissociation⁹⁻¹⁵ have been carried out. We briefly discuss some of the more recent studies below.

The equilibrium structure of hydrogen peroxide has been the subject of controversy for several years.^{30,31,36-42} Although it is known that the equilibrium dihedral angle is between 110° and 120°, the exact value has not been well established until very recently.³⁸ Khachkuruzov and Przhevalskii³⁷ reported a dihedral angle of 119.1° obtained by fitting rotational constants from microwave studies, while Hunt and co-workers³¹ obtained a value of 111.5° by fitting torsional frequencies. Koput³⁸ determined a value of 111.83° by solving the torsional Schrödinger equation for a fixed OH bond distance of 0.965 Å and then fitting the solution to the experimental data. Koput argues that the value reported by Khachkuruzov and Przhevalskii corresponds to an average dihedral angle for the torsional ground state and that 111.83° is the correct equilibrium dihedral angle. More recently, experimental studies^{41,42} also indicate that the dihedral angle in HOOH is near the value reported by Koput.

There is a long history of ab initio calculations on the structure and torsional barriers of HOOH. A comprehensive account of the ab initio studies of HOOH before 1978 can be found in refs 18 and 19, while more recent work is discussed in refs 22 and 23.

The ab initio studies of Dunning and Winter¹⁸ provided a reasonable account of the torsional barriers and equilibrium

- (1) Crim, F. F. *Annu. Rev. Phys. Chem.* **1984**, *35*, 657.
- (2) Uzer, T. *Adv. At. Mol. Phys.* **1988**, *25*, 417.
- (3) Rizzo, T. R.; Hayden, C. C.; Crim, F. F. *Faraday Discuss. Chem. Soc.* **1983**, *75*, 112; *J. Chem. Phys.* **1984**, *81*, 4501.
- (4) Butler, L. J.; Tiejch, T. M.; Likar, M. D.; Crim, F. F. *J. Chem. Phys.* **1986**, *85*, 2331.
- (5) Scherer, N. F.; Doany, F. E.; Zewail, A. H.; Perry, J. W. *J. Chem. Phys.* **1986**, *84*, 1932. Scherer, N. F.; Zewail, A. H. *J. Chem. Phys.* **1987**, *87*, 97.
- (6) Luo, X.; Rieger, P. T.; Perry, D. S.; Rizzo, T. R. *J. Chem. Phys.* **1988**, *89*, 4448.
- (7) Dübäl, H.-R.; Crim, F. F. *J. Chem. Phys.* **1985**, *83*, 3863.
- (8) Tiejch, T. M.; Likar, D. M.; Dübäl, H.-R.; Butler, L. J.; Crim, F. F. *J. Chem. Phys.* **1987**, *87*, 5820. Likar, M. D.; Baggot, J. E.; Sinha, A.; Tiejch, T. M.; Vander Wal, R. L.; Crim, F. F. *J. Chem. Soc., Faraday Trans. 2* **1988**, *84*, 1483. Likar, M. D.; Sinha, A.; Tiejch, T. M.; Vander Wal, R. L.; Crim, F. F. *Ber. Bunsen-Ges. Phys. Chem.* **1988**, *92*, 289.
- (9) Uzer, T.; Hynes, J. T.; Reinhardt, W. P. *Chem. Phys. Lett.* **1985**, *117*, 600; *J. Chem. Phys.* **1986**, *85*, 5791.
- (10) Uzer, T.; MacDonald, B. D.; Guan, Y.; Thompson, D. L. *Chem. Phys. Lett.* **1988**, *152*, 405.
- (11) Sumpter, B. G.; Thompson, D. L. *J. Chem. Phys.* **1985**, *82*, 4557; *J. Chem. Phys.* **1987**, *86*, 2805; *Chem. Phys. Lett.* **1988**, *153*, 243.
- (12) Sumpter, B. G. Ph.D. Thesis, Oklahoma State University, 1986.
- (13) Getino, C.; Sumpter, B. G.; Santamaria, J.; Ezra, G. S. In *Synergetics, Order and Chaos*; Velarde, M. G., Ed.; World Scientific: Singapore, 1987; p 499.
- (14) Getino, C.; Sumpter, B. G.; Santamaria, J.; Ezra, G. S. *J. Phys. Chem.* **1989**, *93*, 3877.
- (15) Getino, C.; Sumpter, B. G.; Santamaria, J.; Ezra, G. S. To be submitted for publication.
- (16) Botschwina, P.; Meyer, W.; Semkow, A. M. *Chem. Phys.* **1976**, *15*, 25.
- (17) Veillard, A. *Theor. Chim. Acta* **1970**, *18*, 21; *Chem. Phys. Lett.* **1969**, *4*, 51.
- (18) Dunning, T. H.; Winter, N. W. *Chem. Phys. Lett.* **1971**, *11*, 194; *J. Chem. Phys.* **1975**, *63*, 1847.
- (19) Cremer, D. *J. Chem. Phys.* **1978**, *69*, 4440.
- (20) Rogers, J. D.; Hillman, J. J. *J. Chem. Phys.* **1981**, *75*, 1085; **1982**, *76*, 4046. Rogers, J. D. *J. Phys. Chem.* **1984**, *88*, 526.
- (21) Bair, R. A.; Goddard, W. A., III *J. Am. Chem. Soc.* **1982**, *104*, 2719.
- (22) Block, R.; Jansen, L. *J. Chem. Phys.* **1985**, *82*, 3322.
- (23) Carpenter, J. E.; Weinhold, F. J. *J. Phys. Chem.* **1986**, *90*, 6405; **1988**, *92*, 4295, 4306.
- (24) Willetts, A.; Gaw, J. F.; Handy, N. C. *J. Mol. Spectrosc.* **1989**, *135*, 370.
- (25) Harding, L. B. *J. Phys. Chem.* **1989**, *93*, 8004.
- (26) Zumwalt, L. R.; Giguère, P. A. *J. Chem. Phys.* **1941**, *9*, 458. Giguère, P. A. *J. Chem. Phys.* **1950**, *18*, 88.
- (27) Giguère, P. A.; Bain, O. J. *J. Phys. Chem.* **1952**, *56*, 340. Bain, O.; Giguère, P. A. *Can. J. Chem.* **1955**, *33*, 527. Chin, D.; Giguère, P. A. *J. Chem. Phys.* **1961**, *34*, 690.
- (28) Giguère, P. A.; Srinivasan, T. K. K. *J. Raman Spectrosc.* **1974**, *2*, 125; *J. Mol. Spectrosc.* **1977**, *66*, 168.
- (29) Helminger, P.; Bowman, W. C.; De Lucia, F. C. *J. Mol. Spectrosc.* **1981**, *85*, 120. Bowman, W. C.; De Lucia, F. C.; Helminger, P. *J. Mol. Spectrosc.* **1981**, *87*, 571. Hillman, J. J. *J. Mol. Spectrosc.* **1982**, *95*, 236.
- (30) Redington, R. L.; Olson, W. B.; Cross, P. C. *J. Chem. Phys.* **1962**, *36*, 1311.
- (31) Hunt, R. H.; Leacock, R. A.; Peters, C. W.; Hecht, K. T. *J. Chem. Phys.* **1965**, *42*, 1931. Hunt, R. H.; Leacock, R. A. *J. Chem. Phys.* **1966**, *45*, 3141.
- (32) Hirota, E. *J. Chem. Phys.* **1958**, *28*, 839.
- (33) Przhevalskii, I. N.; Krachkuruzov, G. A. *Opt. Spectrosc.* **1974**, *36*, 175. Krachkuruzov, G. A.; Przhevalskii, I. N. *Opt. Spectrosc.* **1972**, *33*, 127, 434; **1973**, *35*, 216; **1976**, *41*, 323.

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structure of HOOH. They employed the Hartree-Fock approximation using a [4s3p1d/2s1p] basis set and showed the necessity of using geometry optimization and polarization functions in order to obtain good geometries and torsional barrier heights.

Cremer¹⁹ undertook a systematic study of the dependence of the torsional barriers and molecular geometry on the basis set and level of theory and made a critical comparison of theory and experimental results. He concluded that 2p polarization functions at the H are important to accurately describe the cis configuration, and inclusion of correlation is necessary to obtain good agreement with the experimental geometry.

Bair and Goddard²¹ calculated the equilibrium geometry for HOOH using the generalized valence bond (GVB) plus CI method. They obtained a geometry in good agreement with that reported by Cremer¹⁹ and stressed the importance of inclusion of electron correlation in obtaining the correct equilibrium geometry.

Botschwina, Meyer, and Semkow (BMS)¹⁶ derived the first ab initio quadratic force field for HOOH using a small basis set and then scaled the diagonal **F** matrix to obtain estimated vibrational frequencies. The BMS semiempirical global surface was subsequently used in modified form in classical trajectory studies by Uzer et al.^{9,10}

Carpenter and Weinhold²³ have carried out high-level ab initio calculations to characterize the OH overtone vibration-torsion potential coupling on the ground-state potential surface. They have provided a detailed analysis of the effect of the level of theory and basis set on the equilibrium structure and torsional barrier heights, and their results support the conclusions presented by Koput. Carpenter and Weinhold find that the trans torsional barrier increases with each OH stretch quantum of excitation, in good agreement with the experimental measurements of Dübal and Crim,⁷ and provide an explanation for this trend.

Willets et al.²⁴ have carried out ab initio calculations using the double- and triple- ζ DZP, DZ2P, and TZ2P+f basis sets to characterize the quartic force field (Dunham form) for HOOH. MP2 perturbation theory was used to estimate electron correlation. A six-dimensional variational calculation using the quartic force field was carried out to determine the vibrational energy levels, and good agreement with experiment was obtained for levels up to 6000 cm⁻¹.

Harding²⁵ has carried out the most extensive ab initio calculations on the ground-state potential energy surface of hydrogen peroxide to date, employing a (4s3p2d1f/2s7p) basis set and using GVB+1+2 calculations with a correction for quadruple excitations. From a fit to the 480 calculated ab initio energies as a function of internal coordinates, Harding carried out a normal-coordinate analysis and reexpanded the potential in terms of normal coordinates.⁴³ The calculated normal-mode frequencies were in very good agreement with the experimental values. The geometric parameters obtained from the ab initio calculations were also in good agreement with experiment. A reaction path analysis of the

torsional mode was also performed, and quantitatively accurate torsional energy levels were obtained.

There have been several classical trajectory calculations of the overtone-induced decomposition of hydrogen peroxide.⁹⁻¹⁵ These studies have shown the importance of the bending degrees of freedom in the flow of energy out of the initially excited OH stretch overtone and also provided some evidence for incomplete redistribution of energy on the time scale for dissociation.⁹

Uzer et al.^{9,10} have carried out several classical trajectory studies of the unimolecular decomposition of HOOH, using a potential energy surface that incorporated spectroscopic and thermodynamic data. The OH and OO bond stretches were modeled as Morse oscillators and the OOH bends as harmonic oscillators. Potential coupling between the various modes was taken into account by off-diagonal **F** matrix elements (linear coupling) and by switching functions describing the attenuation of the OOH bend force constants by the OO and OH stretches (nonlinear coupling). The torsional motion was found to play an insignificant role in the intramolecular dynamics of nonrotating hydrogen peroxide. The unimolecular decay rate calculated by Uzer et al. for an overtone excitation of $\nu_{\text{OH}} = 6$ was consistent with statistical calculations,⁵⁷ although vibrational energy redistribution was not complete in the time scale for dissociation. In particular, the initially unexcited OH bond remains unexcited and does not receive a statistical proportion of the total energy prior to reaction.

While the classical trajectories of Uzer et al. indicate that the torsional mode plays an insignificant role in the $\nu_{\text{OH}} = 6$ overtone-induced dissociation of rotationless HOOH molecules, the work of Sumpter and Thompson¹¹ has shown that internal rotation becomes more important for higher excitation energies. The importance of coupling of internal rotation to stretching and bending modes has also been stressed by Spears and Hutchinson.⁴⁴ Moreover, overall molecular rotation has been shown to induce both rotation-vibration and vibration-vibration coupling,⁴⁵ suggesting the possibility of increased dynamical activity of the torsional mode at higher total angular momenta.

We have recently studied the classical dynamics of HOOH for various potential energy surfaces and initial excitations ($\nu_{\text{OH}} = 4, 5, 6, 7$).¹³⁻¹⁵ Unimolecular decay lifetimes of HOOH were found to be sensitive to details of the potential energy surfaces. In the case of CH overtone relaxation in benzene, it is known that it is important to include switching functions in the potential to attenuate the CCH bending force constants as a function of the CH bond length.⁴⁶ Such attenuation induces a potential coupling which leads to increased localization of energy in the CH bond by an effective cancellation of the kinetic and potential couplings.⁴⁷ Similarly, we have found that the overtone-induced unimolecular decay lifetime of HOOH is strongly dependent on the rate at which the HOO bend force constant is attenuated by OO stretching.¹³⁻¹⁵ It is therefore important to determine an accurate switching

(44) Spears, L. G.; Hutchinson, J. S. *J. Chem. Phys.* **1988**, *88*, 250.

(45) Bunker, D. L. *J. Chem. Phys.* **1967**, *91*, 6106. Hung, N. C.; Wilson, D. J. *J. Chem. Phys.* **1963**, *38*, 828. Hung, N. C. *J. Chem. Phys.* **1972**, *57*, 332. Parr, C. A.; Kupperman, A.; Porter, R. N. *J. Chem. Phys.* **1977**, *66*, 2914. Rolfe, T. J.; Rice, S. A. *J. Chem. Phys.* **1983**, *79*, 4863. Clodius, W. B.; Shirts, R. B. *J. Chem. Phys.* **1984**, *81*, 6244. Shirts, R. B. *J. Chem. Phys.* **1986**, *85*, 4949. Shirts, R. B. *Int. J. Quantum Chem.* **1987**, *31*, 199. Combs, J. A.; Hoover, W. G. *J. Chem. Phys.* **1984**, *80*, 2243. Uzer, T.; Natanson, G. A.; Hynes, J. T. *J. Chem. Phys. Lett.* **1985**, *122*, 12. Stace, A. *J. Ber. Bunsen-Ges. Phys. Chem.* **1977**, *81*, 200. Quack, M.; Troe, J. *Ber. Bunsen-Ges. Phys. Chem.* **1974**, *78*, 240. Schlier, Ch. G. *Mol. Phys.* **1987**, *62*, 1009. Wolf, R. J.; Hase, W. L. *J. Chem. Phys.* **1980**, *73*, 3779; **1981**, *75*, 3809. Hovingh, W. J.; Parson, R. *J. Chem. Phys. Lett.* **1989**, *158*, 222. Frederick, J. H.; McClelland, G. M.; Brumer, P. *J. Chem. Phys.* **1985**, *83*, 190. Frederick, J. H.; McClelland, G. M. *J. Chem. Phys.* **1986**, *84*, 4347. McClelland, G. M.; Nathanson, G. M.; Frederick, J. H.; Farley, F. W. In *Excited States*; Lim, E. C., Innes, K. K., Eds.; Academic: London, 1987; Vol. 7. Ezra, G. S. *J. Chem. Phys. Lett.* **1986**, *127*, 492. Sumpter, B. G.; Martens, C. C.; Ezra, G. S. *J. Phys. Chem.* **1988**, *92*, 7193. Sumpter, B. G.; Ezra, G. S. *J. Chem. Phys. Lett.* **1987**, *144*, 144. To be submitted. Nathanson, G. M.; McClelland, G. M. *J. Chem. Phys.* **1986**, *85*, 4311; **1984**, *81*, 629; **1986**, *84*, 3170; *J. Chem. Phys. Lett.* **1985**, *114*, 441; **1985**, *118*, 228. Farley, F. W.; Novakoski, L. V.; Dubey, M.; Nathanson, G. M.; McClelland, G. M. *J. Chem. Phys.* **1988**, *88*, 1460.

(46) Lu, D.-H.; Hase, W. L. *J. Phys. Chem.* **1988**, *92*, 3217.

(47) Garcia-Ayllon, A.; Santamaria, J.; Ezra, G. S. *J. Chem. Phys.* **1988**, *89*, 801.

(34) Brouard, M.; Martinez, M. T.; O'Mahoney, J.; Simons, J. P. *Chem. Phys. Lett.* **1988**, *150*, 6; *J. Chem. Soc., Faraday Trans. 2*, in press.

(35) Docker, M. P.; Hodgson, A.; Simons, J. P. *Chem. Phys. Lett.* **1986**, *128*, 264; *Faraday Discuss. Chem. Soc.* **1986**, *82*, 25. Jacobs, A.; Wahl, M.; Weller, R.; Wolfgram, J. *Appl. Phys. B* **1987**, *42*, 173. Gericke, K.-H.; Kice, S.; Comes, F. J.; Dixon, R. N. *J. Chem. Phys.* **1986**, *85*, 4463. Comes, F. J.; Gericke, K.-H.; Grunewald, A. U.; Klee, S. *Ber. Bunsen-Ges. Phys. Chem.* **1988**, *92*, 273. Klee, S.; Gericke, K.-H.; Comes, F. J. *Ber. Bunsen-Ges. Phys. Chem.* **1988**, *92*, 429.

(36) Oelfke, W. C.; Gordy, W. *J. Chem. Phys.* **1969**, *51*, 5336.

(37) Khachkuruzov, G. A.; Przhevalskii, I. N. *Opt. Spectrosc.* **1974**, *36*, 172; **1989**, *46*, 586; **1988**, *63*, 685.

(38) Koput, J. *J. Mol. Spectrosc.* **1986**, *115*, 438.

(39) Cremer, D.; Cristen, D. *J. Mol. Spectrosc.* **1979**, *74*, 480.

(40) Hillman, J. J.; Jennings, D. F.; Olson, W. B.; Goldman, A. *J. Mol. Spectrosc.* **1986**, *117*, 46.

(41) Olson, W. B.; Hunt, R. H.; Young, B. W.; Maki, A. G.; Brault, J. W. *J. Mol. Spectrosc.* **1988**, *127*, 12.

(42) Flaud, J.-M.; Camy-Peyret, C.; Johns, J. W. C.; Carli, B. *J. Chem. Phys.* **1989**, *91*, 1504.

(43) Harding, L. B.; Ermler, W. C. *J. Comput. Chem.* **1985**, *6*, 13. Ermler, W. C.; Hsiuchin, C. H.; Harding, L. B. *Comput. Phys. Commun.* **1988**, *51*, 257.

TABLE I: Comparison of Energies, Geometric Parameters, and Torsional Barrier Heights of HOOH for Various Basis Sets and Levels of Theory^a

method basis	energy	r_{OO}	r_{OH}	θ	ϕ	V_{trans}	V_{cis}
HF/6-31G**	-150.776965	1.3958	0.9457	102.32	116.23	0.72	8.60
HF/6-311G(2d,p)	-150.824671	1.3891	0.9432	102.57	112.13	1.21	8.15
HF/6-311G(3d,2p)	-150.828338	1.3847	0.9409	102.83	109.21	1.43	7.77
MP2/6-31G*	-151.134914	1.4680	0.9760	98.77	119.38	0.60	9.43
MP2/6-31G**	-151.157088	1.4666	0.9681	98.62	119.39	0.60	8.78
MP2/6-311G	-151.071746	1.5518	0.9798	97.27	179.94		
MP2/6-311G(2d,p)	-151.307980	1.4550	0.9650	99.07	116.03	0.89	8.38
MP2/6-311G(3d,2p)	-151.323161	1.4499	0.9615	99.50	111.08	1.28	7.87
MP2/6-311G(3df,2pd)	-151.369671	1.4388	0.9602	99.51	113.21	1.12	7.76
MP2/6-311G(3df,3pd)	-151.374431	1.4396	0.9612	99.88	111.61	1.31	7.63
MP3/6-31G**	-151.158422	1.4512	0.9630	99.85	118.31		
RHF/[4s2p1d/2s1p] ^a	-150.81766	1.393	0.946	102.5	113.7	1.10	8.35
RHF/(1s6p2d/6s2p) ^b	-150.84548	1.390	0.943	102.9	111.2	1.44	7.69
RS-MP/[4s3p1d/2s1p] ^b	-151.28031	1.451	0.967	99.3	119.3	0.94	8.13
GVB+CI/SV-DZP ^c	-151.0216	1.464	0.967	99.9	119.10		
GVB+1+2/(4s3p2d1f/3s2p) ^d	-151.312607	1.456	0.956	99.9	115.0	0.94	7.46
GVB+1+2+QC/(4s3p2d1f/3s2p) ^d	-151.352673	1.462	0.964	99.6	113.4	1.06	7.38
MP2/TZ2P+F ^e	-151.38316	1.454	0.967	99.5	114.5	0.98	7.67
experiment ^f		1.464	0.965	99.6	111.8	1.11 ^g	7.32 ^g

^a Reference 18. ^b Reference 19. ^c Reference 21. ^d Reference 25. ^e Reference 24. ^f Reference 38. ^g Reference 42. ^h Energies are given in hartrees, bond lengths in angstroms, angles in degrees, and barrier heights in kcal/mol.

function for the attenuation of the bending force constant as a function of the OO bond length. Appropriate switching functions can be obtained by ab initio calculations, and this method has previously been used to obtain switching functions for methane,⁴⁸ propylene,⁴⁹ methanol,⁴⁹ benzene,⁴⁹ and the hydroperoxyl radical.^{49,50}

The purpose of the present paper is to determine the dependence of the HOO bending force constants on the OO and OH bond lengths for the ground-state potential surface of HOOH. In particular, we obtain analytical switching functions describing the stretch-bend couplings in HOOH. The switching function approach⁴⁶⁻⁵⁰ combined with ab initio calculations yields global potential energy functions which describe both the low- and high-energy regimes, in which mode-mode potential couplings are included in a reasonable fashion. In particular, potential couplings decrease to zero as the molecule dissociates^{14,15} in a physically reasonable way. The details of the ab initio calculations are given in section II, and results on the switching functions are presented in section III. Conclusions are given in section IV.

II. Ab Initio Calculations: Basis Set Selection

We have carried out several calculations at different levels of theory and for various sizes of basis set to determine an appropriate method and basis set for studying the dependence of the bending force constants on the OO and OH bond lengths. We require that the method used should provide both torsional barrier heights and equilibrium geometries in good agreement with experiment.

The equilibrium geometries and torsional barrier heights (energies of the fully optimized cis or trans configurations relative to the equilibrium energy) obtained for basis sets ranging from 6-31G* to 6-311G(3df,3pd) for HF and MP2 levels of theory are given in Table I along with some of those discussed in section I. All of the calculations reported here were carried out using the GAUSSIAN suite of programs.⁵¹

In order to obtain reasonable torsional barrier heights, it is necessary to include multiple polarization functions on all the atoms and to fully optimize the geometry. Inclusion of electron correlation is very important in obtaining an accurate equilibrium

geometry for a given basis set. These points have also been stressed in previous ab initio studies of HOOH.¹⁷⁻¹⁹ Inclusion of f orbitals on the oxygen atoms and d orbitals on the hydrogen atoms leads to an important stabilization of the equilibrium cis and trans configurations, compared to the results for smaller basis sets (see Table I). The torsional barrier heights obtained for MP2/6-311G(3df,2pd) are in very good agreement with experiment. On the other hand, smaller basis sets at the MP2 level of theory yield equilibrium geometries in better accord with the experimental results. The MP2/6-311G(3d,2p) calculation gives both reasonable barrier heights and geometry and was chosen as a suitable compromise for the study of the dependence of the OOH bending force constant on the OH and OO bond lengths.

The quadratic internal coordinate force constants, the harmonic normal-mode frequencies, and the rotational constants obtained in the present work for the different basis sets and levels of theory are summarized in Table II, together with those obtained by Harding.²⁵ The MP2/6-311G(3d,2p) calculation gives force constants and vibrational frequencies that are in reasonable agreement with Harding's calculations. Whereas the force constants for the MP2/6-311G(2d,p) calculation appear to be in even better agreement, the smaller basis set yields a relatively poor description of the equilibrium geometry and barrier heights for the torsion (see Table I). The largest deviations for the MP2/6-311G(3d,2p) force constant matrix are for the O-O bond stretch force constant (F_{RR}) and for the coupling between the OH and adjacent OOH bend (F_{ra}). Although the calculations of Harding give a negative sign on the coupling constant F_{ra} , our constant is positive. F_{ra} is in fact the only coupling constant for which the sign changes as a function of the basis set and level of calculation, and its magnitude is small. We therefore do not consider the discrepancy with Harding's calculation to be significant.

The experimentally determined fundamental frequencies^{30,40} are ν_1 (symmetric OH stretch) = 3614 cm⁻¹, ν_2 (symmetric bend) = 1393 cm⁻¹, ν_3 (OO stretch) = 863 cm⁻¹, ν_5 (asymmetric OH stretch) = 3615 cm⁻¹, and ν_6 (asymmetric bend) = 1269 cm⁻¹. As is well-known,⁵² harmonic frequencies (ω) obtained by ab initio calculations give a poor description of the experimental normal-mode frequencies and need to be corrected for anharmonicity. Using the correction for anharmonicity ($\omega - \nu$) obtained by Harding²⁵ (for GVB+1+2+QD), we obtain for the MP2/6-311G(3d,2p) calculation the following fundamental normal-mode frequencies: $\nu_1 = 3638$ cm⁻¹, $\nu_2 = 1418$ cm⁻¹, $\nu_3 = 893$ cm⁻¹, $\nu_5 = 3632$ cm⁻¹, and $\nu_6 = 1300$ cm⁻¹. The largest deviation from experiment is 3.5% and is for the OO stretch. A reason for this could be the underestimation of the electron correlation energy⁵³

(48) Duchovic, R.; Hase, W. L.; Schlegel, B. H. *J. Chem. Phys.* **1984**, *88*, 1339.

(49) Wolf, R. J.; Bhatia, D. S.; Hase, W. L. *Chem. Phys. Lett.* **1986**, *132*, 493; private communication.

(50) Lemon, W. J.; Hase, W. L. *J. Phys. Chem.* **1987**, *91*, 1596.

(51) Frisch, M. J.; Binkley, J. S.; Schlegel, H. B.; Raghavachari, K.; Melius, C. F.; Martin, R. L.; Stewart, J. J. P.; Bobrowicz, F. W.; Rohlfing, C. M.; Kahn, L. R.; Defrees, D. J.; Seeger, R.; Whiteside, R. A.; Fox, D. J.; Fluder, E. M.; Topeol, S.; Pople, J. A. This work (GAUSSIAN 86 system of programs) is based on the GAUSSIAN 82 system, which is copyright 1983 by Carnegie-Mellon University.

(52) Herzberg, G. *Infrared and Raman Spectra of Polyatomic Molecules*; Van Nostrand: Princeton, NJ, 1945.

TABLE II: Harmonic Force Constants, Calculated Harmonic Normal-Mode Frequencies, and Rotational Constants for Hydrogen Peroxide^a

	HF/II	HF/IV	HF/V	MP2/I	MP2/III	MP2/IV	MP2/V	GVB+QC ^b
F_{rr}	9.626	9.587	9.659	7.777	7.273	8.183	8.224	8.133
F_{RR}	6.912	7.059	7.128	4.764	3.543	4.869	4.808	4.347
$F_{\alpha\alpha}$	1.149	1.165	1.177	1.002	0.901	0.965	0.988	0.957
$F_{\phi\phi}$	0.0389	0.0453	0.048	0.0353	0.0048	0.0391	0.0427	0.039
$F_{rr'}$	-0.0085	-0.0027	-0.0038	-0.0133	-0.0241	-0.0018	-0.0051	-0.014
F_{rR}	-0.0704	-0.0601	-0.0440	-0.1354	-0.2143	-0.1515	-0.1494	-0.092
$F_{r\alpha}$	-0.0112	-0.0178	-0.0116	-0.0124	0.1032	-0.0037	0.0043	-0.028
$F_{r\alpha'}$	0.0083	0.0083	0.0050	0.0100	0.0215	0.0121	0.0050	0.003
$F_{R\alpha}$	0.654	0.659	0.669	0.625	0.574	0.633	0.650	0.575
$F_{\alpha\alpha'}$	0.104	0.094	0.088	0.096	0.199	0.085	0.075	0.076
$F_{R\phi}$	-0.024	-0.018	-0.010	-0.018	-0.00001	-0.013	-0.005	-0.0012
$F_{r\phi}$	0.015	0.016	0.016	0.015	0.00002	0.016	0.016	0.020
$F_{\alpha\phi}$	0.041	0.041	0.038	0.039	0.00004	0.036	0.031	0.026
ω_1 (sym OH st)	4152	4145	4160	3731	3602	3830	3839	3816
ω_2 (sym bend)	1615	1619	1625	1462	1466	1442	1455	1429
ω_3 (OO stretch)	1149	1162	1166	928	786	932	921	887
ω_4 (torsion)	387	423	440	357	136	371	404	383
ω_5 (asym OH st)	4153	4144	4160	3734	3614	3828	3838	3820
ω_6 (asym bend)	1474	1500	1518	1328	1143	1322	1357	1328
A	10.7615	10.8289	10.8968	9.7903	9.6786	10.0273	10.1181	
B	0.9476	0.9532	0.9566	0.8698	0.8007	0.8852	0.8852	
C	0.9135	0.9242	0.9314	0.8344	0.7241	0.8593	0.8593	

^a Units of force are mdyne, units of length angstroms, angles radians, frequencies and rotational constants wavenumbers. The basis sets used are as follows: I, 6-31G*; II, 6-31G**; III, 6-311G; IV, 6-311G(2d,p); V, 6-311G(3d,2p). ^b Reference 25.

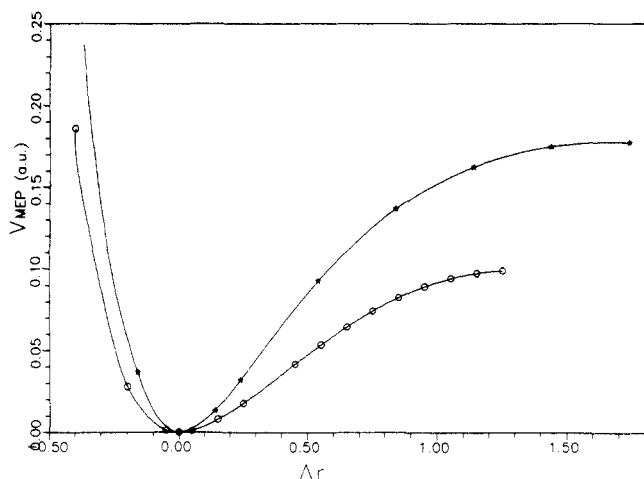


Figure 1. Minimum-energy paths along OO (circles) and OH (stars) bond stretch coordinates. Potential energy is calculated at the MP2/6-311G(3d,2p) level with full optimization of all geometric parameters for fixed OO or OH bond lengths. Energies are in hartrees and bond displacements in angstroms.

as calculated by second-order Møller–Plesset perturbation theory, which also leads to an OO equilibrium bond length which is too short (see Table I).

III. Switching Functions

Figure 1 shows the MP2/6-311G(3d,2p) potential energy along the minimum-energy paths (MEP's) for dissociation along the OO (circles) and OH (stars) bond stretch coordinates, obtained by full optimization of *all* of the geometric parameters for fixed OO or OH bond lengths, respectively. The OO MEP is energetically more favorable and is the reaction coordinate pathway for overtone-induced unimolecular dissociation of HOOH;³ we are interested in accurately describing the potential couplings along this coordinate. The OH stretch–bend potential coupling is also important in determining overtone decay dynamics,¹⁴ and the OH stretch–OOH bend coupling is therefore also of interest.

The OOH bending potential is determined from energies calculated by varying one of the bend angles over 20° about the

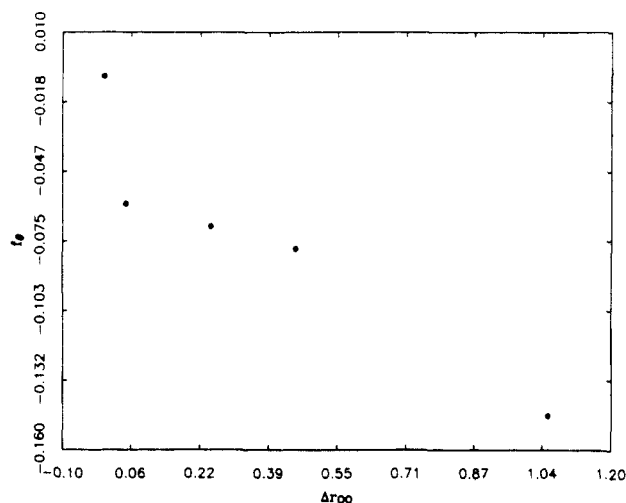


Figure 2. Quartic bending force constant as a function of the OO bond length. Force constants are in hartree/rad.⁴

equilibrium angle for fixed values of the OO or OH bond lengths along the MEP's. (The remaining geometric parameters are fully optimized.) The energies obtained are fit by using the nonlinear least-squares method to a quadratic

$$V_{\theta} = 0.5K_{\theta}(\theta - \theta^0)^2 \quad (1a)$$

or a quadratic–quartic function

$$V_{\theta} = 0.5K_{\theta}(\theta - \theta^0)^2 + f_{\theta}(\theta - \theta^0)^4 \quad (1b)$$

The force constants calculated as a function of the bond lengths are then fit to a suitable functional form. Figure 2 shows the quartic force constant (f_{θ}) dependence on the OO bond length. Quadratic force constants (K_{θ}) obtained from both fits (eqs 1a and 1b) are very similar, and the small magnitude of the quartic correction suggests that deviations from harmonicity are small for the bending angle displacements studied here.

Figure 3 shows the calculated switching function (a) for the OO bond compared to that used in previous dynamics calculations of HOOH.^{9–15} In this figure, the circles are the ab initio data (K/K_0 , where K_0 is the force constant at equilibrium) and the solid line is the fit given by

$$S(r_{OO}) = \exp[-1.468\Delta r_{OO}] \quad (2)$$

(53) Wahl, A. C. *J. Chem. Phys.* **1964**, *41*, 2600. Nesbet, R. K. *J. Chem. Phys.* **1962**, *36*, 1518.

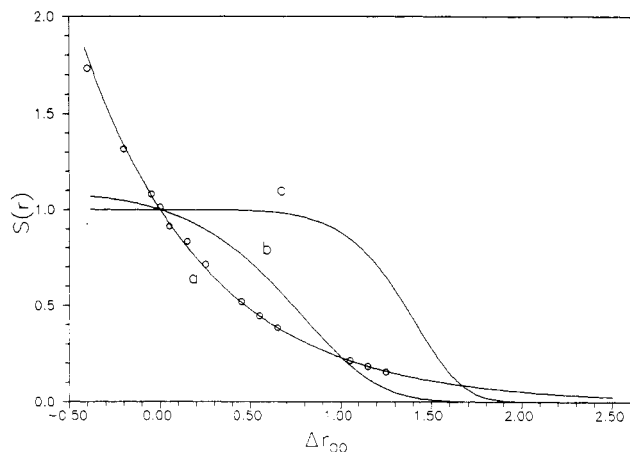


Figure 3. Switching functions describing variation of HOO bend force constant with the OO bond length: (a) MP2/6-311G(3d,2p) ab initio results (this paper; the circles are the ab initio points, and the solid line is the fit given by eq 2); (b) function describing HCH attenuation in CH_4 ; (c) ab initio results at HF/6-31G** level.¹²

The second switching function (b) describes the HCH bend attenuation for methane⁴⁸ and corresponds to

$$S(r_{\text{OO}}) = 1 - \tanh [1.531 \times 10^{-7} \Delta r_{\text{OO}} (r_{\text{OO}} + 4.67)^8] \quad (3)$$

This function has been used by Uzer et al. in classical trajectory studies of HOOH.^{9,10} The third switching function (c) was obtained by ab initio calculations at the Hartree-Fock level for a 6-31G** basis¹²

$$S(r_{\text{OO}}) = 1 - \tanh [0.1205 \Delta r_{\text{OO}}^5] \quad (4)$$

We have previously used this function in a study of the dissociation dynamics of HOOH.¹³⁻¹⁵

There are substantial differences between the various switching functions. The switching function (Figure 3a) calculated in the present paper shows very strong stretch-bend coupling in the region of small bond displacements ($-0.5 < \Delta r < 0.5$) as compared to the other functions but decreases relatively slowly at large distances. On the other hand, curve c of Figure 3 shows very weak coupling for moderate bond displacements and abruptly decreases to zero at larger displacements. The stretch-bend coupling described by Figure 3b is of a type intermediate between the other two; this function was, however, derived for the HCH bend of methane and not for HOOH. The transferability of switching functions from one molecule to another has been seriously questioned by several authors.¹¹⁻¹⁵ As the intramolecular dynamics of HOOH and other polyatomic molecules^{14,15,47} is sensitive to changes in the rate of attenuation of bending force constants as described by switching functions of the type shown in Figure 3, it is clearly important to use functions that correctly describe this type of stretch-bend coupling.

Figure 4 illustrates the switching function for the OH bond stretch. Curve a is the best fit to the ab initio points (stars) and corresponds to a function of the form

$$S(r_{\text{OH}}) = 0.076[1 - \tanh [5.752 \Delta r_{\text{OH}} - 0.450]] + 0.892 \exp(-0.364 \Delta r_{\text{OH}}^3) \quad (5a)$$

although a simpler function

$$S(r_{\text{OH}}) = 1 - \tanh [0.00823 \Delta r_{\text{OH}} (r_{\text{OH}} + 1.757)^3] \quad (5b)$$

was found to give a reasonable fit. The switching function used by Uzer et al.⁴⁸ (curve b)

$$S(r_{\text{OH}}) = 1 - \tanh [1.531 \times 10^{-7} \Delta r_{\text{OH}} (r_{\text{OH}} + 4.67)^8] \quad (6)$$

and one appropriate for the hydroperoxyl radical^{49,50} (curve c)

$$S(r_{\text{OH}}) = 1 - \tanh [1.0279 \Delta r_{\text{OH}} (r_{\text{OH}} - 0.797)^2] \quad (7)$$

are also shown in Figure 4. The parameters in eqs 2-7 are appropriate for distances measured in angstroms.

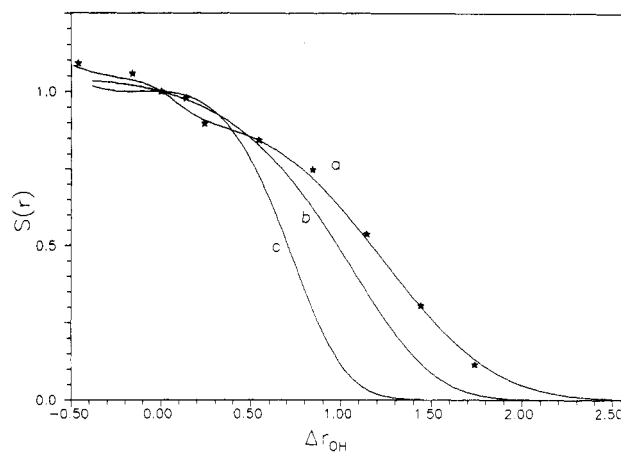


Figure 4. Switching functions describing variation of HOO bend force constant with the OH bond length: (a) MP2/6-311G(3d,2p) ab initio results (this paper; the stars are the ab initio points, and the solid line is the fit given by eq 5a); (b) function describing HCH attenuation in CH_4 ; (c) function appropriate for HOO radical.^{49,50}

The differences between these switching functions are not as striking as for the OO bond coordinate. The rate of attenuation of curve a (Figure 4) is slower for the large bond displacements than either curve b or c.

In the simplest statistical adiabatic channel (SAC) approach⁵⁴ to unimolecular bond fission and the reverse association reaction, the shape of the potential surface governing dissociation depends on two parameters. The first parameter, β , is the usual Morse parameter describing the radial interaction potential, while the second parameter, α , determines the function used to interpolate the adiabatic channel eigenvalues between their equilibrium and asymptotic eigenvalues.⁵⁵ In fact, α is directly related to the radial dependence of the bending force constant⁵⁵

$$K(r) = K_e \exp[-2\alpha \Delta r] \quad (8)$$

(cf. eq 2; note the factor of 2).

Application of SAC theory to a large number of neutral radical reactions⁵⁶ leads to an approximately constant value of the ratio α/β close to 0.5, implying a correlation between the range of the radial interaction potential and the switching function (8). Wolf et al.⁴⁹ have recently pointed out such a correlation for the HO bond rupture in the hydroperoxyl radical. The short range of the switching function (Figure 4c) correlates with the short-range interaction of the H + O_2 association potential, where the latter can be understood by noting that the double bond in O_2 must be broken to form the OH bond. The bending switching function for HOOH (Figure 4a) has a longer range than the function (c), which is consistent with the longer range radial interaction expected for the association of H and HO_2 radicals to form hydrogen peroxide.

From the switching function exponent $2\alpha = 1.4683 \text{ \AA}^{-1}$ (cf. eq 2) and a fit of the MEP for OO dissociation to a Morse function with $\beta = 2.005 \text{ \AA}^{-1}$, we obtain a ratio $\alpha/\beta = 0.37$. This number should be compared with the value (0.44) used in the SAC calculation of the HOOH dissociation rate of ref 57.

IV. Conclusions

We have reported ab initio calculations of the OO and OH bond length dependence of HOO bending force constants in HOOH at the MP2/6-311G(3d,2p) level and have determined switching functions describing the stretch-bend potential couplings. The switching functions differ markedly from those used previously in classical trajectory calculations of HOOH dissociation.⁹⁻¹⁵ In particular, the attenuation of the bending force constant by OO

(54) Troe, J. J. *Chem. Phys.* **1981**, *75*, 226.

(55) Troe, J. J. *Phys. Chem.* **1986**, *90*, 3485.

(56) Cobos, C. J.; Troe, J. J. *Chem. Phys.* **1985**, *83*, 1010; *Chem. Phys. Lett.* **1985**, *113*, 419.

(57) Brouwer, L.; Cobos, C. J.; Troe, J.; Dübal, H.-R.; Crim, F. F. *J. Chem. Phys.* **1987**, *86*, 6171.

bond stretching is of BEBO form⁵⁸ and is more rapid than for the functions previously used.

We believe that the present ab initio results give an accurate description of the stretch-bend coupling in HOOH. As the HOOH dissociation rate is strongly dependent on the rate of attenuation of the bending force constants,¹⁴ it will be important to study the unimolecular reaction dynamics using the switching functions determined here. Preliminary classical trajectory calculations for rotationless HOOH, using the switching functions of the present paper in the potential surface of refs 14 and 15, give a lifetime for $\nu_{\text{OH}} = 6$ of around 8 ps. Further details of both

the ab initio potential surface and the classical trajectory calculations will be given elsewhere.

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Registry No. H₂O₂, 7722-84-1.

(58) Johnston, H. S. *Gas Phase Reaction Rate Theory*; Ronald Press: New York, 1966.

Dipolar-Chemical Shift NMR Spectra of the Carbon-Nitrogen Linkage in Benzylideneaniline. Carbon and Nitrogen Chemical Shielding Anisotropies

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The magnitudes and orientations of the principal components of the carbon and nitrogen chemical shift tensors for the "localized" imine moiety of the Schiff base benzylideneaniline have been determined by the analysis of dipolar-chemical shift NMR spectra. The carbon chemical shift anisotropy was determined to be 156 ± 2 ppm with $\eta = 0.88 \pm 0.02$ whereas the nitrogen shift anisotropy was found to be 545 ± 2 ppm with $\eta = 0.92 \pm 0.01$. The most shielded component of both the carbon and nitrogen shift tensors is approximately perpendicular to the imine fragment. For the imine carbon the intermediate component of the shift tensor is approximately along the C=N axis. The corresponding component of the nitrogen chemical shift tensor is oriented along the direction of the nitrogen lone pair. These results are compared to those available in the literature for related molecules. For the ¹³C,¹⁴N spin pair, the ¹³C dipolar-chemical shift NMR spectrum cannot be accurately simulated if the high-field approximation for the ¹⁴N nucleus is assumed. To circumvent this problem, a general equation is described that can be used to calculate the dipolar-chemical shift NMR spectrum of a spin 1/2 nucleus dipole coupled to a spin 1 nucleus where the high-field approximation is not invoked.

Introduction

In the past 10-15 years information about the anisotropic nature of chemical shielding has become available for carbon nuclei¹⁻⁶ and to a lesser extent for nitrogen nuclei^{1,2,6,7} in a variety of molecular environments. Generally the principal components of the chemical shift tensor for any given functional group are reasonably constant or typical for the particular functional group under consideration.^{1,2,8,9} For example, in a series of 10 relatively unstrained molecules containing olefinic carbons, Orendt et al.^{8c} found that the most shielded component of the ¹³C chemical shift tensor, δ_{33} , varied between 5 and 51 ppm; similarly, the intermediate component, δ_{22} , varied between 85 and 152 ppm and the least shielded component, δ_{11} , varied between 214 and 288 ppm. In this same series of molecules the isotropic chemical shift, $\delta_{\text{iso}} = (\delta_{11} + \delta_{22} + \delta_{33})/3$, has a smaller range, 116-149 ppm. Potentially much more information about the mechanism or origin of magnetic chemical shielding at a nuclear site is available from the principal components of the shift tensor than from the isotropic chemical shift, particularly if the orientation of the principal axis system of the tensor in the molecular framework is known. One of the simplest experimental techniques available for obtaining information about the orientation of the chemical shift tensor is dipolar-chemical shift NMR spectroscopy.^{10,11} The technique involves measuring the static NMR powder pattern for a spin which is dipolar coupled to a neighboring spin.

In order to characterize the carbon and nitrogen chemical shift tensors of the imine fragment, we have analyzed the ¹³C and ¹⁵N dipolar-chemical shift NMR powder spectra of the ¹³C=¹⁴N and ¹³C=¹⁵N spin pairs in benzylideneaniline (1). This compound was chosen since it is easy to prepare with selective enrichment at either the imine carbon or nitrogen or both simultaneously. Also, the availability of X-ray diffraction data greatly facilitates

(1) Mehring, M. *High Resolution NMR in Solids*, 2nd ed.; Springer-Verlag: Berlin, 1983.

(2) Spiess, H. W. In *NMR Basic Principles and Progress*; Diehl, P., Fluck, E., Kosfeld, R., Eds.; Springer-Verlag: New York, 1978; Vol. 15, p 55.

(3) Veeman, W. S. *Prog. Nucl. Magn. Reson. Spectrosc.* **1984**, *16*, 193.

(4) Duncan, T. M. *J. Phys. Chem. Ref. Data* **1987**, *16*, 125.

(5) Facelli, J. C.; Grant, D. M.; Michl, J. *Acc. Chem. Res.* **1987**, *20*, 152.

(6) Jameson, C. J. In *Specialist Periodic Report—NMR Spectroscopy*; Webb, G. A., Ed.; The Chemical Society: London, 1989; Vol. 18 and previous volumes of this annual review.

(7) Mason, J. In *Multinuclear NMR*; Mason, J., Ed.; Plenum Press: New York, 1987; pp 337-340.

(8) (a) Beeler, A. J.; Orendt, A. M.; Grant, D. M.; Cutts, P. W.; Michl, J.; Zilm, K. W.; Downing, J. W.; Facelli, J. C.; Schindler, M. S.; Kutzelnigg, W. *J. Am. Chem. Soc.* **1984**, *106*, 7672. (b) Facelli, J. C.; Orendt, A. M.; Beeler, A. J.; Solum, M. S.; Depke, G.; Malsch, K. D.; Downing, J. W.; Murthy, P. S.; Grant, D. M.; Michl, J. *J. Am. Chem. Soc.* **1985**, *107*, 6749.

(c) Facelli, J. C.; Orendt, A. M.; Solum, M. S.; Depke, G.; Grant, D. M.; Michl, J. *J. Am. Chem. Soc.* **1986**, *108*, 4268. (d) Solum, M. S.; Facelli, J. C.; Michl, J.; Grant, D. M. *J. Am. Chem. Soc.* **1986**, *108*, 6464. (e) Orendt, A. M.; Facelli, J. C.; Beeler, A. J.; Reuter, K.; Horton, W. J.; Cutts, P.; Grant, D. M.; Michl, J. *J. Am. Chem. Soc.* **1988**, *110*, 3386.

(9) Sardashti, M.; Maciel, G. E. *J. Phys. Chem.* **1988**, *92*, 4620.

(10) VanderHart, D. L.; Gutowsky, H. S. *J. Chem. Phys.* **1968**, *49*, 261.

(11) Zilm, K. W.; Grant, D. M. *J. Am. Chem. Soc.* **1981**, *103*, 2913.

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