Base Properties of H_2CO in the Excited $^1n \rightarrow \pi^*$ State

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CCSD and EOM-CCSD calculations with the aug′-cc-pVDZ basis set have been carried out to investigate the structures, energies, and vibrational spectra of H_2CO, protonated H_2CO, and hydrogen-bonded $HF{:}H_2CO$ complexes in ground and excited $^1n \rightarrow \pi^*$ states. The computed structures, vibrational spectra, and excitation energies of H_2CO are in agreement with experimental data. In the $^1n \rightarrow \pi^*$ state two protonated isomers, H_2COH^+ and H_3CO^+, exist. These differ in stability by 14 kcal/mol, with H_2COH^+ being more stable. The proton affinity of excited H_2CO is 17 kcal/mol less than the ground-state proton affinity. Two hydrogen-bonded complexes $HF{:}H_2CO$ also exist in the excited $^1n \rightarrow \pi^*$ state. The more stable complex has hydrogen bond formation occurring at the oxygen and is approximately 2 kcal/mol less stable than the corresponding ground-state complex. The complex with hydrogen bonding at the carbon is only a weakly bound, Born−Oppenheimer minimum.

Introduction

The past two decades have witnessed dramatic progress in ab initio theoretical studies of molecules in ground electronic states. This progress has moved theory beyond the computing of equilibrium structures of isolated molecules, to the state of providing chemical reaction energies, reaction pathways, and spectral data. By comparison, ab initio studies of excited electronic states have lagged far behind. Excited-state calculations are inherently more difficult, are more demanding of computer resources, and require more sophisticated levels of theory in order to obtain reliable results. Fortunately, new approaches for studying electronic states have been developed and applied recently. These include SAC-CI (symmetry-adapted cluster configuration interaction),[1,2] CCLR (coupled cluster linear response),[3,4] CASPT2 (complete active space second-order perturbation theory),[5] MR-CCSD (multireference coupled-cluster theory with singles and doubles),[6−9] and EOM-CCSD (equation-of-motion coupled-cluster with single and double excitations).[10−12] EOM-CCSD and its extension EOM-CCSD(T)[13,14] have been used successfully to investigate the electronic absorption spectra of selected molecules and have produced vertical excitation energies that are in agreement with experimental values.[15−19]

In this paper, we will employ coupled-cluster methods to examine the structures, excitation energies, and vibrational spectra of H_2CO in ground and $^1n \rightarrow \pi^*$ states. We will then predict some base properties of excited H_2CO by determining the structures, binding energies, and vibrational spectra of complexes of excited $^1n \rightarrow \pi^*$ H_2CO with the acids H^+ and HF.

Method of Calculation

The ground-state structures of H_2CO, protonated H_2CO (H_2COH^+), and the hydrogen-bonded complex $HF{:}H_2CO$ were fully optimized with correlation using the method of coupled-clusters with single and double excitations (CCSD).[20−23] Harmonic vibrational frequencies were obtained to confirm that these structures are equilibrium structures and to evaluate zero-point vibrational energies. The equation-of-motion coupled-cluster method (EOM-CCSD)[10−12] was used to optimize structures in excited $^1n \rightarrow \pi^*$ states, employing newly developed gradient optimization techniques.[24−26] The excited-state species include H_2CO; two protonated isomers (H_2COH^+ and H_3CO^+) and the transition structure which connects them; and the hydrogen-bonded complexes $HF{:}H_2CO$ with hydrogen bonding occurring at either C or O, and the transition structure which connects these two isomers. Excited-state harmonic vibrational frequencies were computed to identify and distinguish equilibrium (local minima) and transition structures and to obtain zero-point vibrational energies.

Although ground-state coupled-cluster calculations are approximately invariant to orbital choice including proper reference, the CI-like nature of the excited state removes most of this invariance. Therefore, the choice of orbitals requires some attention in EOM-CC calculations, especially when the excited-state minimum is far from that of the ground state, and the Hartree−Fock reference is not appropriate. This situation arose in the current study for H_3CO^+, in which case the A″ excited-state open-shell singlet lies below the A′ closed-shell singlet at that geometry. In C_s symmetry this is not a problem, since the two states cannot mix. However, when the symmetry is lowered to C_1 for the calculation of nonsymmetric vibrational frequencies, the two states can mix, and this leads to relatively large T1 amplitudes and a vibrational frequency that is unreasonably large. To circumvent this problem, Brueckner orbital based EOM-CCSD calculations[27,28] were performed to obtain the excited-state structure and vibrational frequencies of H_3CO^+. For this calculation, the orbitals were chosen to make the T1 amplitudes zero. This approach yielded a structure very similar to that obtained previously, while overcoming the problem with the large vibrational frequency. The structure and frequencies of H_3CO^+ reported in this paper are those resulting from the Brueckner orbital based EOM-CCSD calculations.

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TABLE 1: H_2CO Ground- and Excited-State Structures and Vibrational Frequencies[a]

	ground state		excited $^1n \rightarrow \pi^*$ state	
	CCSD	exptl[b]	EOM-CCSD	exptl[c]
Structural Data				
r(C−O)	1.224	1.208	1.321	1.321
r(C−H)	1.099	1.116	1.105	1.097
∠H−C−H	116.6	116.5	116.3	118.6
∠H−C−O−H	180.0	180.0	147.4	148
Vibrational Frequencies[d]				
out-of-plane bend	1185	1167	600	683
CH_2 rock	1259	1249	912	898
C−O stretch	1787	1746	1269	1173
CH_2 scissor	1531	1500	1347	1290
sym. C−H stretch	2963	2782	3031	2847
asym. C−H stretch	3042	2843	3147	2968

[a] Distances in angstroms; angles in degrees; frequencies in cm^{-1}. [b] The ground-state structure is from ref 33. The vibrational frequencies are from ref 36. [c] The excited-state structure is from ref 34. The vibrational frequencies are from refs 37 and 38. [d] The description of each mode is that appropriate to the ground state of the C_{2v} structure. The corresponding mode in the excited state is given on the same line.

The correlation-consistent polarized valence double-split basis set of Dunning augmented with diffuse functions on nonhydrogen atoms (aug′-cc-pVDZ)[29−31] was used throughout this study. This basis contains two sets of s and p orbitals in the valence shell, a set of d orbitals in the first polarization space of C and O, and another set of diffuse s, p, and d orbitals. The hydrogen atom basis set includes two s orbitals and a set of p orbitals. This basis appears flexible enough to describe adequately the structures and energies of H_2CO, protonated H_2CO, and HF:H_2CO complexes in both ground and excited $^1n \rightarrow \pi^*$ states. All electrons were correlated in the CCSD and EOM-CCSD calculations. These calculations were carried out using the ACES-II[32] program on the Quantum Theory Project computing facilities at the University of Florida and the Cray Y-MP8E/128 computer at the Ohio Supercomputer Center.

Results and Discussion

H_2CO. The optimized CCSD/aug′-cc-pVDZ and EOM-CCSD/aug′-cc-pVDZ structures of H_2CO in ground and $^1n \rightarrow \pi^*$ states are reported in Table 1. In the ground state, H_2CO has C_{2v} symmetry, with computed C−O and C−H bond lengths of 1.224 and 1.099 Å. These values are in agreement with the experimental values of 1.208 and 1.116 Å, respectively.[33] There is also good agreement between the computed (116.6°) and experimental (116.5°) H−C−H angle.

Excitation to the lowest singlet excited state of H_2CO ($^1n \rightarrow \pi^*$) leads to significant electron redistribution and structural changes, as H_2CO assumes a pyramidal structure with C_s symmetry. The computed EOM-CCSD and experimental[34] C−O distances in the excited state are identical at 1.321 Å, showing a significant lengthening of the C−O bond relative to the ground state. This lengthening is easily understood in terms of the nature of the $n \rightarrow \pi^*$ excitation. The EOM-CCSD C−O distance is significantly improved relative to the computed CIS (configuration interaction with all single excitations) distance of 1.248 Å.[35] There is also good agreement between the computed EOM-CCSD and the experimental C−H distances. The EOM-CCSD H−C−H angle of 116.3° underestimates the experimental by 2.3°. The computed dihedral H−C−O−H angle of 147.4° is in agreement with the experimental angle of approximately 148°.[34] Experimental vibrational frequencies are available for H_2CO in both ground and excited $^1n \rightarrow \pi^*$ states.[36−38] These are given in Table 1, along with the computed frequencies. The CCSD harmonic frequencies for the four lowest vibrational modes in the ground state are similar to, but slight greater than, the experimental frequencies, overestimating these by less than 50 cm^{-1}. The largest differences between computed and experimental frequencies are found for the symmetric and asymmetric C−H stretching vibrations, which are overestimated at CCSD by about 200 cm^{-1}. In the excited state, the lowest energy vibrational band is found experimentally at 683 cm^{-1} and is underestimated by the computed EOM-CCSD frequency of 600 cm^{-1}. The computed frequencies of the next three absorption bands overestimate the experimental, but are within 100 cm^{-1} of the experimental values. The largest differences between computed and experimental frequencies are found for the C−H stretching vibrations, which are again overestimated by about 200 cm^{-1}. The computed EOM-CCSD frequencies for excited H_2CO are significantly improved relative to the CIS frequencies, especially for the C−O stretching mode.[35]

The large geometry change that occurs in H_2CO after excitation to the $^1n \rightarrow \pi^*$ state leads to a significant difference between vertical and adiabatic excitation energies. Experimentally, these excitation energies are 4.07[39] and 3.50 eV,[34] respectively. The EOM-CCSD vertical excitation energy of 3.98 eV underestimates the experimental energy by 0.09 eV, while the computed adiabatic excitation energy of 3.65 eV overestimates the experimental energy by 0.15 eV. Again, EOM-CCSD vertical and adiabatic excitation energies are significantly improved relative to the corresponding CIS and CIS-MP2 energies.[35]

The good agreement of computed CCSD and EOM-CCSD ground- and excited-state structures, vibrational frequencies, and vertical and adiabatic $n \rightarrow \pi^*$ excitation energies with experimental data demonstrates the robustness of the EOM-CCSD approach. These results for excited $^1n \rightarrow \pi^*$ H_2CO give confidence that the EOM-CCSD method can be used to obtain reliable information about the chemistry of H_2CO in the excited $^1n \rightarrow \pi^*$ state.

Protonated H_2CO in Ground and Excited States. In the ground electronic state, protonation of H_2CO occurs at the carbonyl oxygen, producing a planar ion with C_s symmetry. Protonation is accompanied by a lengthening of the C−O bond from 1.224 to 1.257 Å. The computed CCSD/aug′-cc-pVDZ electronic proton affinity is 177.9 kcal/mol. This leads to a standard proton affinity at 298 K of 170.5 kcal/mol, in excellent agreement with the experimental value of 171.7 kcal/mol.[40] Does H_2CO have an appreciable proton affinity in its excited $n \rightarrow \pi^*$ state?

It is well-known that excitation to the $^1n \rightarrow \pi^*$ state leads to a weakening of the C−O bond and a significant redistribution of electron density. As a result of excitation, the carbonyl carbon experiences an increase in total electron density, while the electron density of the carbonyl oxygen decreases. However, vertical $n \rightarrow \pi^*$ excitation leads to an increase in π electron density at both C and O, so that electrophilic attack at either of these atoms may be anticipated through the π system. In its relaxed $n \rightarrow \pi^*$ state, H_2CO has only C_s symmetry, and π is no longer an appropriate designation. Neverthess, the π system of ground-state H_2CO lies in the C_s symmetry plane of the relaxed excited molecule. The attack of H^+ in this plane at both C and O has been investigated.

A search of the potential energy surface of excited protonated H_2CO led to the identification of two equilibrium structures, H_2COH^+ and H_3CO^+, both having C_s symmetry. These

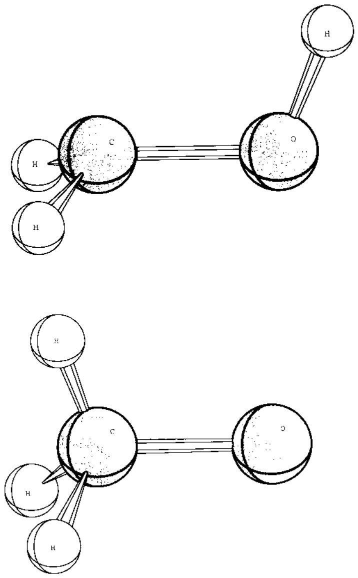

Figure 1. Equilibrium structures of protonated H_2COH^+ and H_3CO^+ in the excited $^1n \rightarrow \pi^*$ state.

TABLE 2: C−O and X−H Distances (Å) and Proton Affinities (kcal/mol) in Ground and Excited $^1n \rightarrow \pi^*$ States of H_2CO^a

	ground state at O	n→π* state at O	n→π* state at C
r(C−O)	1.257	1.365	1.282
r(X−H)	0.983	1.000	1.168
electronic PA	177.9	159.8	145.0
PA at 298 K	170.5	153.4	139.4

[a] X−H is the O−H distance for protonation at O and the nonequivalent C−H distance for protonation at C.

TABLE 3: Infrared Frequencies (ν, cm^{-1}) and Intensities (I, km/mol) for Protonated H_2CO in Ground and Excited $^1n \rightarrow \pi^*$ States

	ground state		n→π* state at O		n→π* state at C^a
	ν	I	ν	I	ν
ν_1	1034	108	592	70	683
ν_2	1122	60	815	8	773
ν_3	1241	16	1023	11	973
ν_4	1410	123	1162	184	1166
ν_5	1477	40	1252	20	1374
ν_6	1663	44	1591	47	1804
ν_7	3129	5	2879	273	2418
ν_8	3280	24	3026	117	2747
ν_9	3625	287	3400	255	3348

[a] Intensities are not available for the Bruckner-orbital-based calculation.

TABLE 4: Intermolecular Coordinates, Binding Energies, and F−H Vibrational Frequency Shifts in HF:H_2CO Complexes in Ground and Excited $^1n \rightarrow \pi^*$ States^{a,b}

	ground state at O	n→π* state at O	n→π* state at C
r(F−X)	2.667	2.764	3.159
∠H−F-X	9.	7.	5.
ΔE	−8.2	−5.8	−3.0
$\Delta H°$	−5.6	−3.7	−1.4
$\delta\nu$	−354	−239	−174

[a] Distances in angstroms; angles in degrees; energies in kcal/mol; frequencies in cm^{-1}. [b] F−X is the intermolecular distance to the hydrogen-bonding site; ∠H−F−X is a measure of the nonlinearity of the hydrogen bond.

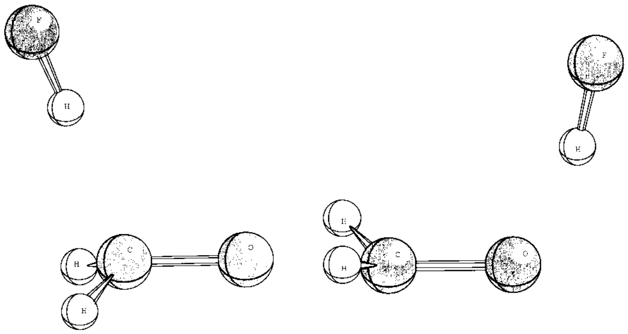

Figure 2. Equilibrium structures of the hydrogen-bonded complexes of HF with H_2CO in the excited $^1n \rightarrow \pi^*$ state.

structures are shown in Figure 1, and selected structural parameters are given in Table 2. In both protonated forms, the proton adds trans to the CH_2 group. Excited-state protonation at O leads to a large increase of 0.108 Å in the C−O distance, while protonation at C leads to a small increase of 0.025 Å. The electronic proton affinities are 159.8 kcal/mol for O protonation and 145.0 kcal/mol for protonation at C. The standard proton affinities at 298 K are 153.4 and 139.4 kcal/mol for the O- and C-protonated species, respectively. Thus, H_2CO is a weaker base in the excited $^1n \rightarrow \pi^*$ state than in the ground state, although the difference between O protonation in these two states is only about 17 kcal/mol. Gas-phase experimental proton affinities are not available for comparison.

The computed barrier to proton transfer from C to O in the excited $^1n \rightarrow \pi^*$ state is 27 kcal/mol, which suggests that both H_2COH^+ and H_3CO^+ are stable excited-state species. Despite the short lifetime of the $^1n \rightarrow \pi^*$ state, it should be possible to detect the protonated species using modern spectroscopic methods. To assist in this effort, Table 3 reports vibrational data for both protonated isomers. The strongest bands in the spectrum of H_2COH^+ in the excited state are predicted at 1162, 2879, 3026, and 3400 cm^{-1}. The band at 1162 cm^{-1} arises from the C−O−H bending mode, while the band at 3026 cm^{-1} is the O−H stretching vibration. The bands at 2879 and 3400 are the symmetric and asymmetric C−H stretches.

H_2CO Complexes with HF in Ground and Excited States. In the ground state of H_2CO, hydrogen bond formation occurs at the carbonyl oxygen, leading to a planar complex with C_s symmetry. In this complex, the computed CCSD intermolecular F−O distance is 2.667 Å, and the hydrogen bond deviates from linearity by 9°. The electronic binding energy of this complex is −8.2 kcal/mol. With the zero-point energies included, $\Delta H°$ is −5.6 kcal/mol. The computed red shift of the F−H stretching frequency in HF:H_2CO is 354 cm^{-1}. Selected data for HF:H_2CO complexes in ground and excited states are summarized in Table 4.

Vertical excitation of the HF:H_2CO complex to the $^1n \rightarrow \pi^*$ state of H_2CO requires 4.26 eV, compared to 3.98 eV in the monomer. This increase is consistent with the well-known blue shift of the n→π* band of carbonyl compounds in hydrogen-bonding solvents.[41] The computed blue shift of 0.28 eV may be compared with the ground-state hydrogen bond energy of 0.35 eV. These data are consistent with the interpretation that the blue shift of the n→π* band reflects primarily the additional energy required to break or severely weaken the hydrogen bond in the excited n→π* state.[41,42]

Two hydrogen-bonded complexes between HF and H_2CO in its relaxed $^1n \rightarrow \pi^*$ state have been found on the intermolecular surface, with hydrogen bond formation occurring at C and O. These two complexes are shown in Figure 2, and selected energetic, structural, and vibrational data are reported in Table

4. In both complexes hydrogen bond formation occurs in the C_s symmetry plane, and structural similarities between the protonated and hydrogen-bonded structures are evident. The more stable HF:H_2CO complex is that in which hydrogen bonding occurs at the oxygen. In this complex the F−O distance is about 0.1 Å longer than in the ground state, and the hydrogen bond again deviates slightly from linearity. Unlike the proton in H_2COH^+, the HF molecule is cis to the CH_2 group with respect to the C−O bond. This may be due to a long-range favorable interaction between the fluorine and the hydrogens of H_2CO, but this interaction must be weak. The HF:H_2CO complex with hydrogen bonding at the oxygen has an electronic binding energy of −5.8 kcal/mol. Inclusion of zero-point energies leads to a $\Delta H°$ value of −3.7 kcal/mol. Hence, the excited-state complex is about 2 kcal/mol less stable than the ground-state complex. The smaller red shift of the F−H stretching band in the excited complex (239 cm^{-1}) relative to the ground state (354 cm^{-1}) is also indicative of a weaker F−H···O hydrogen bond.

The less stable HF:H_2CO complex formed in the excited state of H_2CO is that with hydrogen bond formation at the carbon. The electronic binding energy is only −3.0 kcal/mol, which leads to a $\Delta H°$ value of −1.4 kcal/mol. In this complex, the HF molecule is trans to the CH_2 group relative to the C−O bond. The F−C distance of 3.159 Å is significantly longer than the intermolecular F−O distances in the ground- and excited-state complexes, and once again, the hydrogen bond is slightly nonlinear. The weakness of the hydrogen bond is also reflected in the small red shift of 174 cm^{-1} of the F−H stretching frequency.

In the excited state, the electronic energy barrier to HF transfer from the carbon to the oxygen is only 0.2 kcal/mol. Thus, although there are two hydrogen-bonded complexes that are local minima on the intermolecular surface, it is the complex with hydrogen bonding at the oxygen that is the stable excited-state complex.

Conclusions

CCSD and EOM-CCSD calculations have been carried out to investigate the structures, energies, and vibrational spectra of H_2CO, protonated H_2CO, and hydrogen-bonded HF:H_2CO complexes in ground and excited $^1n{\rightarrow}\pi^*$ states of H_2CO. The following statements are supported by the results of these calculations.

1. The computed structures and vibrational spectra of H_2CO in ground and $^1n{\rightarrow}\pi^*$ excited states are in agreement with experimental data. The computed vertical excitation energy is 0.09 eV less than the experimental energy, and the computed adiabatic excitation energy is 0.15 eV greater than experiment.

2. Protonation of excited H_2CO can occur at either the carbon or the oxygen. The more stable isomer is the oxygen-protonated form. The proton affinity of excited H_2CO is 17 kcal/mol less than the ground-state proton affinity. Since the barrier to proton transfer from C to O in the excited state is 27 kcal/mol, both excited-state isomers should exist.

3. Two hydrogen-bonded complexes HF:H_2CO are found in the excited $^1n{\rightarrow}\pi^*$ state. The more stable complex has hydrogen bond formation occurring at the oxygen. This complex is approximately 2 kcal/mol less stable than the corresponding ground-state complex. Although the complex with hydrogen bonding at the carbon is a local minimum on the surface, it is a weakly bound, Born−Oppenheimer minimum.

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References and Notes

(1) Nakatsuji, H.; Hirao, K. *J. Chem. Phys.* **1978**, *68*, 2053.

(2) Nakatsuji, H.; Ohta, K.; Hirao, K. *J. Chem. Phys*. **1986**, *75*, 409.

(3) Monkhorst, H. J. *Int. J. Quantum Chem. Quantum Chem. Symp*. **1977**, *11*, 421.

(4) Koch, H.; Jensen, H. J. Aa.; Jo/rgensen, P.; Helgaker, T. *J. Chem. Phys.* **1990**, *93*, 3345.

(5) Roos, B. O.; Andersson, K.; Fulscher, M. *Chem. Phys. Lett.* **1992**, *192*, 5.

(6) Mukherjee, D.; Pal, S. *Adv. Quantum Chem.* **1989**, *20*, 292.

(7) Kaldor, U. *Theor. Chim. Acta* **1991**, *80*, 427.

(8) Pal, S.; Rittby, M.; Bartlett, R. J.; Dinha, D.; Mukherjee, D. *J. Chem. Phys.* **1988**, *88*, 4357.

(9) Rittby, C. M. L.; Bartlett, R. J. *Theor. Chim. Acta* **1991**, *80*, 469.

(10) Geertsen, J.; Rittby, C. M. L.; Bartlett, R. J. *Chem. Phys. Lett.* **1989**, *164*, 57.

(11) Comeau, D. C.; Bartlett, R. J. *Chem. Phys. Lett.* **1993**, *207*, 414.

(12) Stanton, J. F.; Bartlett, R. J. *J. Chem. Phys.* **1993**, *98*, 7029.

(13) Watts, J. D.; Bartlett, R. J. *Chem. Phys. Lett.* **1995**, *233*, 81.

(14) Watts, J. D.; Bartlett, R. J. *Chem. Phys. Lett*. **1996**, *258*, 581.

(15) Stanton, J. F.; Bartlett, R. J. *J. Chem. Phys.* **1993**, *98*, 9335.

(16) Del Bene, J. E.; Watts, J. D.; Bartlett, R. J. *Chem. Phys. Lett.* **1995**, *246*, 541.

(17) Gwaltney, S. R., Bartlett, R. J. *Chem. Phys. Lett.* **1995**, *241*, 26.

(18) Watts. J. D.; Gwaltney, S. R.; Bartlett, R. J. *J. Chem. Phys.* **1996**, *105*, 6979.

(19) Del Bene, J. E.; Watts, J. D.; Bartlett, R. J. *J. Chem. Phys*. **1997**, *106*, 6051.

(20) Cizek, J. *Adv. Chem. Phys.* **1969**, *14*, 35.

(21) Paldus, J.; Cizek, J.; Shavitt, I. *Phys. Rev. A* **1972**, *5*, 50.

(22) Bartlett, R. J.; Purvis, G. D., III. *Int. J. Quantum Chem.* **1978**, *14*, 561.

(23) Purvis, G. D., III.; Bartlett, R. J. *J. Chem. Phys.* **1982**, *76*, 1910. Lee, Y. S.; Kucharski, S. A.; Bartlett, R. J. *J. Chem. Phys.* **1984**, *81*, 5906.

(24) Stanton, J. F. *J. Chem. Phys.* **1993**, *99*, 8840.

(25) Stanton, J. F.; Gauss, J. *J. Chem. Phys.* **1994**, *100*, 4695.

(26) Stanton, J. F.; Gauss, J. *Theor. Chim. Acta* **1995**, *91*, 267.

(27) Stanton, J. F.; Gauss, J.; Bartlett, R. J. *J. Chem. Phys*. **1992**, *97*, 5554.

(28) Watts, J. D.; Bartlett, R. J. *Int. J. Quantum Chem. Quantum Chem., Symp.* **1994**, *28*, 195.

(29) Dunning, T. H., Jr. *J. Chem. Phys.* **1989**, *90*, 1007.

(30) Kendall, R. A.; Dunning, T. H., Jr.; Harrison, R. J. *J. Chem. Phys.* **1992**, *96*, 6796.

(31) Woon, D. E.; Dunning, T. J., Jr. *J. Chem. Phys.* **1993**, *98*, 1358.

(32) ACES-II is a program product of the Quantum Theory Project, University of Florida. Authors: Stanton, J. F.; Gauss, J.; Watts, J. D.; Nooijen, M.; Oliphant, N.; Perera, S. A.; Szalay, P. G.; Lauderdale, W. J.; Gwaltney, S. R.; Beck, S.; Balkova, A.; Bernholdt, D. E.; Baeck, K.-K.; Rozyczko, P.; Sekino, H.; Huber, C.; Bartlett, R. J. Integral packages included are VMOL (Almlöf, J.; Taylor, P. R.); VPROPS (Taylor, P. R.); ABACUS (Helgaker, T.; Jensen, H. J. Aa.; Jorgensen, P.; Olsen, J.; Taylor, P. R.).

(33) Takagi, K.; Oka, T. *J. Phys. Soc. Jpn.* **1963**, *18*, 1174.

(34) Shah, A. K.; Moule, D. C. *Spectrochim. Acta* **1978**, *34A*, 749. Jensen, P.; Bunker, P. R. *J. Mol. Spectrosc.* **1982**, *94*, 114.

(35) Hadad, C. M.; Foresman, J. B.; Wiberg, K. B. *J. Phys. Chem.* **1993**, *97*, 4293.

(36) Naganaka, T.; Kondo, S.; Saeki, S. *J. Chem. Phys.* **1982**, *76*, 3860.

(37) Job, V. A.; Sethuraman, V.; Innes, K. K. *J. Mol. Spectrosc*. **1969**, *30*, 365.

(38) Moule, D. C.; Walsh, A. D. *Chem. Rev.* **1975**, *75*, 67.

(39) Robin, M. B. *Higher Excited States of Polyatomic Molecules*; Academic Press: New York, 1985; Vol. III.

(40) Lias, S. G.; Bartmess, J. E.; Liebman, J. F.; Holmes, J. L.; Levin, R. D.; Mallard, W. G. *J. Phys. Chem. Ref. Data, Suppl*. **1988**, 17 (Suppl. 1).

(41) Mataga, N.; Kubota, T. *Molecular Interactions and Electronic Spectra*; Marcel Dekker: New York, 1970. Vinogradov, S. N.; Linnell, R. H. *Hydrogen Bonding*; Van Nostrand-Reinhold: New York, 1971.

(42) Del Bene, J. E. *J. Am. Chem. Soc.* **1973**, *95*, 6517.