Ab Initio Prediction of the Potential Energy Surface and Vibrational−Rotational Energy Levels of Calcium Dihydride, CaH_2

Jacek Koput*

Department of Chemistry, Adam Mickiewicz University, Grunwaldzka 6, 60-780 Poznań, Poland

Received: March 10, 2005; In Final Form: March 30, 2005

The equilibrium structure and potential energy surface of calcium dihydride, CaH_2, have been determined from large-scale ab initio calculations using the coupled-cluster method, CCSD(T), in conjunction with basis sets of quadruple- and quintuple-ζ quality. The CaH_2 molecule was found to be quasilinear. The HCaH bending potential function was predicted to be extraordinarily flat near the minimum, located at the HCaH angle of 164°. The barrier to linearity was calculated to be just 6 cm^{-1}. The vibrational−rotational energy levels of various isotopomers were predicted using the variational method. The calculated vibrational fundamental frequencies are in good agreement with the results of matrix-isolation studies, and the other predicted spectroscopic constants can assist in the future detection of calcium dihydride in the gas phase.

1. Introduction

The alkaline-earth-metal dihydrides have attracted considerable interest because of their unusual equilibrium structure. Although the bonding in these molecules is almost entirely ionic, $H^-M^{2+}H^-$, similar to that in the alkaline-earth-metal dihalides,[1,2] the BeH_2 and MgH_2 molecules were found both experimentally and theoretically to be linear at equilibrium, whereas the SrH_2 and BaH_2 molecules were found to be definitely bent.[3−18] The CaH_2 molecule was found to represent an intermediate case; a molecule which is slightly bent at equilibrium, however, with a low potential energy barrier to the linear configuration.

The infrared spectra of the CaH_2, CaD_2, and CaHD isotopomers of calcium dihydride were investigated by Xiao et al.[3] and by Wang and Andrews[10] using the matrix-isolation technique. The infrared absorption bands due to the antisymmetric and symmetric CaH stretching modes ν_3 and ν_1, respectively, were observed in solid krypton and xenon[3] and in solid neon, argon, and hydrogen.[10] Absorption bands due to the HCaH bending mode ν_2 were not observed. The large matrix shifts of these bands were noticed, indicating substantial interaction of the calcium dihydride molecules with the matrix environment. The CaH_2 molecule was concluded in these studies to be nonlinear, and the equilibrium HCaH angle was determined from the ν_3/ν_1 band intensity ratio to be 168° (ref 3) and 166° (ref 10), with an error limit of about ±5°. In contrast to beryllium and magnesium dihydrides, an attempt[9] to measure the infrared spectrum of calcium dihydride in the gas phase was unsuccessful.

The results of theoretical studies are not definitive concerning the equilibrium structure of the CaH_2 molecule. In calculations at the Hartree−Fock level of theory,[11,12] it was shown that the predicted structure changes from bent to linear, with the equilibrium HCaH angle ranging from 127 to 180°, depending on the size and quality of a one-particle basis set. Using large all-electron basis sets or effective core potentials, Kaupp et al.[12] predicted the CaH_2 molecule to be linear at equilibrium, with a flat HCaH bending potential function. The electron correlation effects, accounted for by the single-reference configuration interaction method (CISD+Q), were found[12] to be small and insignificant concerning the equilibrium structure. Fujii and Iwata[15] predicted the similar shape of the potential energy surface of calcium dihydride by applying the complete-active-space self-consistent field (CASSCF) method. Using the second-order Møller−Plesset (MP2) approach, Bytheway et al.[14] found the CaH_2 molecule to be bent, with the equilibrium HCaH angle of 157° and the barrier to linearity of 0.5 kcal/mol, whereas Kaupp et al.[13] and Wang and Andrews[10] found it to be linear. Using the density functional theory (DFT) approach, Wang and Andrews[10] predicted the CaH_2 molecule to be bent, with the equilibrium HCaH angle of 142.7°. The results of the previous studies show clearly indeed that the reliable prediction of the equilibrium structure of calcium dihydride can only be obtained using both extensively correlated wave functions, beyond the MP2 level of theory, and large one-particle basis sets. The vibrational harmonic force field and frequencies for the three isotopomers mentioned above were calculated by Wang and Andrews[10] at the MP2 and DFT levels of theory. To our knowledge, neither an experimental nor a theoretical anharmonic force field of calcium dihydride was reported so far in the literature.

In this study, we present an accurate characterization of the three-dimensional potential energy surface and vibrational−rotational energy levels of calcium dihydride. The molecular parameters are determined here by the ab initio approach using extensively correlated wave functions calculated with large correlation-consistent spdfgh basis sets and taking into account the "outer-core" correlation effects of the calcium atom.

2. Method of Calculation

The molecular parameters of calcium dihydride were calculated using the coupled-cluster method including single and double excitations and a perturbational correction due to connected triple excitations, CCSD(T).[19−22] The one-particle basis sets employed were the correlation-consistent polarized valence basis sets of quadruple- and quintuple-ζ quality, cc-pVQZ and cc-pV5Z.[23,24] Because a proper treatment of a calcium-containing molecule requires explicit consideration of

---

* E-mail: koput amu.edu.pl.

10.1021/jp051240+ CCC: $30.25

TABLE 1: Molecular Parameters of CaH_2, Determined Using the CCSD(T) Method and Various cc-pV*n*Z Basis Sets

	CVQZ/VQZ[a]	CV5Z/V5Z
Equilibrium Configuration		
r(CaH) (Å)	2.0475	2.0452
∠(HCaH) (deg)	167.07	164.37
energy + 678 (hartree)	−0.256967	−0.267131
Linear Configuration		
r(CaH) (Å)	2.0502	2.0493
barrier (cm^{-1})	3	6

[a] The cc-pV*n*Z basis sets for the Ca/H atoms, respectively.

the Ca valence 4s and “outer-core” 3sp electrons, the valence basis sets for calcium were augmented with sets of tight functions.[24] The resulting core-valence basis sets, cc-pCV*n* Z, were designed to describe both valence and “outer-core” spaces of the calcium atom. The largest one-particle basis set applied in this study consists of a (26s18p12d6f4g2h)/[12s10p9d6f4g2h] set for calcium and a (8s4p3d2f1g)/[5s4p3d2f1g] set for hydrogen. The former basis set includes a (4s4p4d3f2g1h) set of tight functions. Only the spherical harmonic components of the d through h polarization functions were used. In the correlation treatment, the 1s2sp-like core orbitals of the calcium atom were excluded from the active space. The calculations were performed using the MOLPRO-2002 package of ab initio programs.[25]

The vibrational−rotational energy levels were calculated variationally using the six-dimensional Hamiltonian of a triatomic molecule developed by Carter and Handy.[26−28] The Hamiltonian consists of an exact representation of the kinetic energy operator and a representation of the potential energy operator, both expressed in terms of valence curvilinear coordinates. The method of solving the corresponding Schrödinger equation is described in detail in our previous work on calcium difluoride.[29]

3. Results and Discussion

The equilibrium structural parameters and total energy computed for the ground electronic state of calcium dihydride are listed in Table 1. The CaH_2 molecule is predicted to be slightly bent at equilibrium and the barrier to linearity is calculated to be just 6 cm^{-1}. The HCaH bending potential energy function is determined to be extraordinarily flat in the vicinity of a minimum. For the minimum-energy path along the HCaH angle, the CCSD(T) total energy changes by less than ±6 cm^{-1} upon varying the HCaH angle from 180 to 155° (see Figure 1 below). Considering convergence of the computed values with the one-particle basis set size, the effects of approximations inherent to the CCSD(T) approach, and the neglect of the Ca “inner-core” electron correlation, an uncertainty in the predicted equilibrium CaH bond length can be estimated to be ±0.002 Å. Because of extraordinary flatness of the HCaH bending potential energy function, it is difficult to reliably assign uncertainties to the predicted equilibrium HCaH angle and barrier height. The calculated values are believed to be accurate to about ±3° and ±5 cm^{-1}, respectively. The predicted equilibrium HCaH angle of 164° coincides with the experimental values of 168° (ref 3) and 166° (ref 10) to within their error bars. However, the agreement may be quite fortuitous because the experimental data quoted refer to the CaH_2 molecules isolated in various rare-gas matrices at very low temperatures and the matrix effects were shown to be significant.[3,10]

To determine the shape of the potential energy surface of calcium dihydride, the CCSD(T) total energies were calculated with the cc-pCV5Z/cc-pV5Z basis set at 198 points in the vicinity of the equilibrium configuration. The computed energies ranged to approximately 10000 cm^{-1} above the minimum. A slice through the potential energy surface is shown in Figure 1. The potential energy surface was then approximated by a three-dimensional expansion along the internal valence coordinates. The internal coordinates for the CaH stretching modes q_1 and q_2 were chosen as Simons−Parr−Finlan coordinates.[30] The HCaH bending mode coordinate θ was defined as the supplement of the valence HCaH angle measured from a linear reference configuration. Thus, the potential energy surface of calcium dihydride can be written as the polynomial expansion

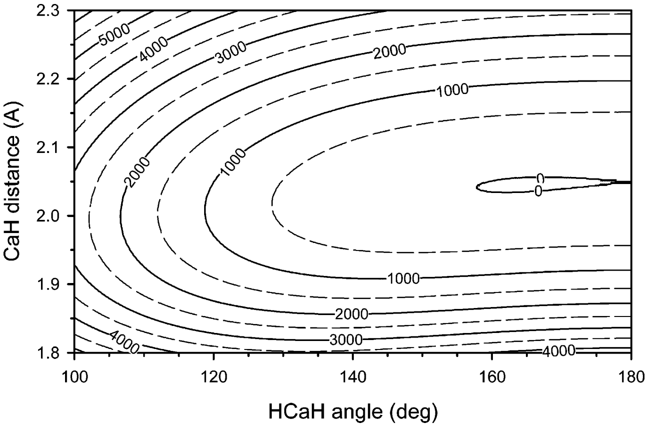

Figure 1. Contour diagram showing the CCSD(T) total energy of calcium dihydride as a function of the CaH internuclear distance and the HCaH angle, determined using the cc-pCV5Z/cc-pV5Z basis set for the configurations of C_{2v} symmetry. The energy contours (in cm^{-1}) are plotted relative to the total energy for the linear configuration. The total energy for the equilibrium configuration, at the CaH distance of 2.0452 Å and the HCaH angle of 164.37°, is −6 cm^{-1}.

$$V(q_1, q_2,\theta) = V_{\mathrm{lin}} + \sum_{ijk} c_{ijk} q_1^i q_2^j \theta^k \qquad (1)$$

where V_{lin} is the total energy at the linear configuration of the CaH_2 molecule and the index *k* takes only even values. The expansion coefficients c_{ijk} were determined from a least-squares fit of eq 1 to the computed total energies, and 28 coefficients appeared to be statistically significant. The optimized values of the expansion coefficients are listed in Table 2. The root-mean-square deviation of the fit was 2.5 μhartree (0.5 cm^{-1}).

The anharmonic force field was used to calculate variationally the vibrational−rotational energy levels of the four isotopic species, $^{40}CaH_2$, $^{40}CaD_2$, $^{44}CaH_2$, and $^{40}CaHD$. The predicted values of the vibrational fundamental wavenumbers are given Table 3. The calculated ν_1 and ν_3 values can be compared with the experimental data obtained in the matrix-isolation studies.[3,10] For the main $^{40}CaH_2$ isotopomer, the ν_3 fundamental was observed at 1203.1, 1216.3, 1192.0, and 1163.8 cm^{-1} in solid neon, argon, krypton, and xenon, respectively. The ν_1 fundamental was observed at 1289.7, 1267.0, and 1239.8 cm^{-1} in solid argon, krypton, and xenon, respectively. Note that the ν_1 fundamental band was not observed in solid neon[10] and that a “blue” matrix shift of the ν_3 fundamental upon going from solid neon to argon is rather unusual.[31] The vibrational frequencies of stretching modes for molecules trapped in an argon matrix tend to be somewhat lower than those in the gas phase.[31] Indeed, the predicted fundamental wavenumbers of the CaH stretching modes of 1298.5 and 1223.0 cm^{-1} are higher by 8.8 and 6.7 cm^{-1}, respectively, than those observed in solid argon.[10] For the $^{40}CaD_2$ isotopomer, the H−D isotopic frequency shifts of

TABLE 2: Anharmonic Force Field[a] of CaH_2

i	j	k	c_{ijk}
0	0	2	−0.000735
2	0	0	0.464237
0	0	4	0.005769
1	1	0	0.083912
1	0	2	0.027246
3	0	0	−0.052234
0	0	6	−0.001575
1	2	0	0.004828
1	0	4	−0.013008
2	0	2	−0.028400
1	1	2	−0.058729
4	0	0	−0.219616
0	0	8	0.000398
1	3	0	−0.045657
1	0	6	0.003701
3	0	2	−0.013162
2	2	0	−0.056897
2	0	4	0.007439
1	1	4	0.028777
1	2	2	0.033159
5	0	0	−0.150597
0	0	10	−0.000054
1	0	8	−0.000459
2	0	6	−0.001983
1	1	6	−0.005037
1	2	4	−0.010772
6	0	0	−0.176665
0	0	12	0.000003

[a] Expansion coefficients c_{ijk} of eq 1, in hartrees. The coordinates q_1 and q_2 are dimensionless; θ is in radians.

TABLE 3: Predicted Vibrational Fundamental Wavenumbers (in cm^{-1}) of $^{40}CaH_2$, $^{40}CaD_2$, $^{44}CaH_2$, and $^{40}CaHD$

	$^{40}CaH_2$	$^{40}CaD_2$	$^{44}CaH_2$	$^{40}CaHD$
ν_1	1298.5	926.3	1298.4	1262.0
ν_2	116.1	73.1	115.7	95.6
ν_3	1223.0	890.5	1220.5	907.2
ZPE[a]	1365	971	1363	1169

[a] The zero-point energy (with respect to a minimum of the potential energy surface).

TABLE 4: Harmonic Wavenumbers ω_i and Anharmonic Constants x_{ij} (in cm^{-1}) of $^{40}CaH_2$ and $^{40}CaD_2$

$^{40}CaH_2$				$^{40}CaD_2$			
ω_1	1330.0	x_{11}	−7.2	ω_1	941.5	x_{11}	−3.6
ω_2	96.4	x_{22}	9.7	ω_2	60.4	x_{22}	6.6
ω_3	1253.0	x_{33}	−7.7	ω_3	906.1	x_{33}	−4.2
		x_{12}	0.0			x_{12}	0.6
		x_{13}	−34.2			x_{13}	−17.4
		x_{23}	2.5			x_{23}	1.4

TABLE 5: Predicted $J = l_2$ Vibrational−Rotational Term Values (in cm^{-1}) and Changes in the Effective Rotational Constant B_v (in MHz) for the Low-Lying Energy Levels of $^{40}CaH_2$ and $^{40}CaD_2$

	$^{40}CaH_2$		$^{40}CaD_2$	
$(v_1, v_2^{l_2}, v_3)$	energy	ΔB_v	energy	ΔB_v
$(0, 0^0, 0)$	0.	0	0.	0
$(0, 1^1, 0)$	116.1	1043	73.1	441
$(0, 2^2, 0)$	254.9	1886	161.4	800
$(0, 2^0, 0)$	273.0	1558	175.3	649
$(0, 3^3, 0)$	411.3	2628	261.3	1115
$(0, 3^1, 0)$	438.9	2257	282.2	945
$(0, 4^4, 0)$	582.3	3295	370.9	1400
$(0, 4^2, 0)$	614.6	2903	395.5	1226
$(0, 4^0, 0)$	623.6	2774	403.1	1162
$(1, 0^0, 0)$	1298.5	−628	926.3	−228
$(0, 0^0, 1)$	1223.0	−662	890.5	−249

the ν_1 and ν_3 fundamentals are calculated to be −372.2 and −332.5 cm^{-1}, respectively. The ν_1 mode shift was found experimentally[3,10] to be −374.8, −367.9, and −354.6 cm^{-1} in solid argon, krypton, and xenon, respectively. The ν_3 mode shift was found experimentally[3,10] to be −329.4, −331.4, −325.2, and −316.0 cm^{-1} in solid neon, argon, krypton, and xenon, respectively. The predicted frequency shifts are close, to within about ±2 cm^{-1}, to those observed in solid argon.[10] For the $^{40}CaHD$ isotopomer, the CaH stretching mode was observed[3,10] at 1234.4, 1253.0, 1228.4, and 1201.7 cm^{-1} in solid neon, argon, krypton, and xenon, respectively. The CaD stretching mode was observed at 890.1, 899.9, 882.3, and 864.0 cm^{-1}, respectively. The predicted fundamental wavenumbers of the CaH and CaD stretching modes are higher by 9.0 and 7.3 cm^{-1}, respectively, than those observed in solid argon.[10] Thus, the ab initio predicted gas-phase values consistently overestimate, by about 8 cm^{-1}, the fundamental wavenumbers observed in solid argon for all three isotopomers discussed above. As could be expected for a nearly-linear triatomic molecule, the $^{40}Ca-^{44}Ca$ isotopic frequency shifts are predicted to be small, with the largest shift amounting to only 2.5 cm^{-1} for the ν_3 mode. Because the barrier to linearity of the CaH_2 molecule was found to be very low, calcium dihydride can be considered as a nonrigid linear molecule undergoing highly anharmonic HCaH bending motion. Therefore, the linear-molecule notation can be legitimately applied to describe the HCaH bending energy levels. The ν_2 fundamental wavenumbers quoted in Table 3 correspond to the $v_2^{l_2} = 1^1$ energy levels, where v_2 and l_2 are the quantum numbers for the doubly degenerate bending mode of a linear molecule. For the main $^{40}CaH_2$ isotopomer, the ν_2 fundamental is predicted to be 116.1 cm^{-1}, far below the infrared region covered in the experimental studies.[3,10] By solving the one-dimensional Schrödinger equation with the potential energy function $V(q_1 = 0, q_2 = 0, \theta)$ (see eq 1), the ground HCaH bending state was calculated to lie 77 cm^{-1} above the top of the barrier to linearity.

The vibrational energy levels of calcium dihydride can be further characterized by the harmonic frequencies ω_i and anharmonicity constants x_{ij}. The values predicted for the $^{40}CaH_2$ and $^{40}CaD_2$ isotopomers are given in Table 4. These were determined from the nine low-energy vibrational levels with $l_2 = 0$, including the fundamental, overtone, and combination levels (v_1, v_3 = 1, 2 and v_2 = 2, 4). The harmonic frequencies predicted in this study are consistently smaller, by about 10−20 cm^{-1}, than those calculated by Wang and Andrews[10] at the MP2/6-311++G(3df,3pd) level of theory. The vibrational constant g_{22} for the $v_2 = 2$ state is predicted to be −5.6 cm^{-1}.

For each vibrational energy level, the effective rotational constant B_v was determined by fitting an odd-order power series in the rotational quantum number J to the calculated rotational transition energies. The effective rotational constant B_0 for the ground vibrational state of the $^{40}CaH_2$, $^{40}CaD_2$, $^{44}CaH_2$, and $^{40}CaHD$ isotopomers is determined in this way to be 60678, 30333, 60674, and 40733 MHz, respectively. Simultaneously, the effective quartic centrifugal distortion constant D_0 is found to be 1.00, 0.25, 1.00, and 0.45 MHz, respectively. For the main isotopomer, varying the predicted equilibrium CaH bond length and HCaH angle within their estimated error bars (±0.002 Å and ±3°) results in changes of the B_0 value of about ∓120 and ∓230 MHz, respectively. The predicted changes in the effective rotational constant B_v due to excitation of the vibrational modes for the $^{40}CaH_2$ and $^{40}CaD_2$ isotopomers are listed in Table 5. The changes due to excitation of the CaH stretching modes, ν_1 and ν_3, are consistent with what is usually expected for smallamplitude stretching modes. The changes due to excitation of the HCaH bending mode ν_2 are much larger and clearly do not follow a conventional linear dependence with respect to the quantum number v_2. These changes also do not have a quadratic dependence[32] of ΔB_v on the quantum numbers v_2 and l_2. In the least-squares fit with this quadratic formula, the deviations between the predicted (quoted in Table 5) and fitted ΔB_v values were calculated to be as large as 100 MHz. For the $^{40}CaH_2$ isotopomer, the l-type doubling constant q_v is calculated to be 1964 and 1608 MHz for the $v_2^{l_2} = 1^1$ and 3^1 states, respectively. For the $^{40}CaD_2$ isotopomer, the corresponding constants q_v are determined to be 755 and 602 MHz.

From the methodological point of view, it was interesting to apply the second-order perturbational approach[33,34] to describe the vibrational−rotational energy levels of calcium dihydride. The internal coordinates for the stretching and bending modes were chosen as the displacement coordinates.[34] The potential energy surface of calcium dihydride was approximated by a three-dimensional expansion analogous to that given by eq 1, and as is customary, the anharmonic force field thus determined was truncated at the quartic order. In the zeroth-order approximation, the bent equilibrium structure of calcium dihydride was adopted as a reference configuration. In contrast to the variational approach, a linear reference configuration could not be employed, because the HCaH bending quadratic force constant is negative (see Table 2), thus resulting in an imaginary harmonic frequency. For the main $^{40}CaH_2$ isotopomer, the harmonic frequencies ω_1, ω_2, and ω_3 were calculated to be 1330.9, 103.3, and 1251.6 cm^{-1}, respectively. The anharmonic constants related to the CaH stretching modes were determined to be $x_{11} = -8.1$, $x_{33} = -7.9$, and $x_{13} = -35.6$ cm^{-1}. The fundamental wavenumbers of the ν_1 and ν_3 modes were then calculated to be 1297.1 and 1205.1 cm^{-1}, respectively. All these values are close to those determined by the variational approach. However, the HCaH bending anharmonic constant x_{22} was determined to be as large as -194.6 cm^{-1}, thus resulting in the negative fundamental wavenumber of the ν_2 mode of -298.7 cm^{-1}! The vibrational−rotational constants related to rotation about the molecule-fixed a axis were found to be meaningless, leading to an absurd pattern of the rotational energy levels. For example, the ground-state effective rotational constant A_0 was predicted to be 890 cm^{-1}. The second-order perturbational approach appeared thus to be inadequate for describing the vibrational−rotational dynamics of calcium dihydride. The variational treatment in conjunction with the rigorous vibration−rotation Hamiltonian is necessary for calculating the energy levels from this highly anharmonic potential energy surface.

In connection to experimental studies in the gas phase,[9] the heat of formation for the CaH_2 molecule was calculated using the CCSD(T) method. The vibrationless total atomization energy $\sum D_e$ of calcium dihydride was determined to be 99.8, 102.7, and 103.5 kcal/mol with the CVTZ/VTZ, CVQZ/VQZ, and CV5Z/V5Z basis sets, respectively. The calculated values are much larger than the atomization energy of 84.2 kcal/mol determined by Fujii and Iwata[15] using the CASSCF method. To assess the accuracy achievable at the level of theory applied in this study, the vibrationless dissociation energy D_e of the CaH radical was calculated using the RCCSD(T) approach.[35,36] The dissociation energy of calcium monohydride in its $^2\Sigma^+$ ground electronic state was determined to be 40.8 and 41.3 kcal/mol with the CVQZ/VQZ and CV5Z/V5Z basis sets, respectively. The later value is in remarkably good agreement with the experimental estimate[37] of 41.25 kcal/mol, thus lending plausibility to the predicted atomization energy of calcium dihydride. The best estimate for the vibrationless total atomization energy $\sum D_e$ of calcium dihydride can be obtained by extrapolating the computed values to the limit of an infinite one-particle basis set. Using the exponential/Gaussian formula,[38] the complete-basis-set (CBS) limit of $\sum D_e$ we calculated to be 104.0 kcal/mol, with a conservative error estimate of ±1 kcal/mol. Including the calculated zero-point vibrational energy, the total atomization energy $\sum D_0$ of the CaH_2 molecule is predicted at the CCSD(T)/CBS level of theory to be 100.1 kcal/mol. This value can be combined with the experimental heats of formation at 0 K for the gaseous Ca and H atoms,[39] leading to the heat of formation for the CaH_2 molecule $\Delta_f H°(0\ K)$ of 45.5 kcal/mol.

Considering the shape of the HCaH bending potential energy function, irregular spacing of the energy levels, and nonlinear dependence of the effective rotational constants upon excitation of the bending mode ν_2, calcium dihydride can be concluded to be an another prominent example of a quasilinear molecule. The parameter γ_0, that can be used to quantify the quasilinearity,[40] is calculated here to be -0.70, as compared with that of 0.23 for the CaF_2 molecule.[29]

Acknowledgment. I thank Dr. Peter F. Bernath for critically reading and commenting on the manuscript, and Dr. Stuart Carter for providing a copy of the RVIB3 program.

References and Notes

(1) Hargittai, M. *Chem. Rev.* **2000**, *100*, 2233.
(2) Kaupp, M. *Angew. Chem., Int. Ed.* **2001**, *40*, 3534.
(3) Xiao, Z. L.; Hauge, R. H.; Margrave, J. L. *High Temp. Sci.* **1991**, *31*, 59.
(4) Tague, T. J., Jr.; Andrews, L. *J. Am. Chem. Soc.* **1993**, *115*, 12111.
(5) Tague, T. J., Jr.; Andrews, L. *J. Phys. Chem.* **1994**, *98*, 8611.
(6) Bernath, P. F.; Shayesteh, A.; Tereszchuk, K.; Colin, R. *Science* **2002**, *297*, 1323.
(7) Shayesteh, A.; Tereszchuk, K.; Bernath, P. F.; Colin, R. *J. Chem. Phys.* **2003**, *118*, 3622.
(8) Shayesteh, A.; Appadoo, D. R. T.; Gordon, I.; Bernath, P. F. *J. Chem. Phys.* **2003**, *119*, 7785.
(9) Shayesteh, A.; Walker, K. A.; Gordon, I.; Appadoo, D. R. T.; Bernath, P. F. *J. Mol. Struct.* **2004**, *695*−*696*, 23.
(10) Wang, X.; Andrews, L. *J. Phys. Chem. A* **2004**, *108*, 11500.
(11) DeKock, R. L.; Peterson, M. A.; Timmer, L. K.; Baerends, E. J.; Vernooijs, P. *Polyhedron* **1990**, *9*, 1919.
(12) Kaupp, M.; Schleyer, P. v. R.; Stoll, H.; Preuss, H. *J. Chem. Phys.* **1991**, *94*, 1360.
(13) Kaupp, M.; Schleyer, P. v. R.; Stoll, H. *J. Phys. Chem.* **1992**, *96*, 9801.
(14) Bytheway, I.; Gillespie, R. J.; Tang, T.-H.; Bader, R. F. W. *Inorg. Chem.* **1995**, *34*, 2407.
(15) Fujii, T. S.; Iwata, S. *Chem. Phys. Lett.* **1996**, *251*, 150.
(16) Tschumper, G. S.; Schaefer, H. F. *J. Chem. Phys.* **1998**, *108*, 7511.
(17) von Szentpály, L. *J. Phys. Chem. A* **2002**, *106*, 11945.
(18) Li, H.; Xiea, D.; Guo, H. *J. Chem. Phys.* **2004**, *121*, 4156.
(19) Čižek, J. *J. Chem. Phys.* **1966**, *45*, 4256.
(20) Purvis, G. D., III; Bartlett, R. J. *J. Chem. Phys.* **1982**, *76*, 1910.
(21) Raghavachari, K.; Trucks, G. W.; Pople, J. A.; Head-Gordon, M. *Chem. Phys. Lett.* **1989**, *157*, 479.
(22) Scuseria, G. E.; Lee, T. J. *J. Chem. Phys.* **1990**, *93*, 5851.
(23) Dunning Jr., T. H. *J. Chem. Phys.* **1989**, *90*, 1007.
(24) Koput, J.; Peterson, K. A. *J. Phys. Chem. A* **2002**, *106*, 9595.
(25) MOLPRO-2002 is a package of ab initio programs designed by Werner, H.-J.; Knowles, P. J. with contributions from Amos, R. D.; Bernhardsson, A.; Berning, A.; Celani, P.; Cooper, D. L.; Deegan, M. J. O.; Dobbyn, A. J.; Eckert, F.; Hampel, C.; Hetzer, G.; Korona, T.; Lindh, R.; Lloyd, A. W.; McNicholas, S. J.; Manby, F. R.; Meyer, W.; Mura, M. E.; Nicklass, A.; Palmieri, P.; Peterson, K. A.; Pitzer, R.; Rauhut, G.; Schütz, M.; Schumann, U.; Stoll, H.; Stone, A. J.; Tarroni, R.; Thorsteinsson, T.
(26) Carter, S.; Handy, N. C. *Mol. Phys.* **1986**, *57*, 175.
(27) Carter, S.; Handy, N. C. *Comput. Phys. Rep.* **1986**, *5*, 117.
(28) Handy, N. C. *Mol. Phys.* **1987**, *61*, 207.
(29) Koput, J.; Roszczak, A. *J. Phys. Chem. A* **2004**, *108*, 9267.
(30) Simons, G.; Parr, R. G.; Finlan, J. M. *J. Chem. Phys.* **1973**, *59*, 3229.

(31) Jacox, M. E. *Chem. Phys.* **1994**, *189*, 149.
(32) Lide, D. R.; Matsumura, C. *J. Chem. Phys.* **1969**, *50*, 3080.
(33) Papoušek, D.; Aliev, M. R. *Molecular Vibrational Rotational Spectra*; Academia: Prague, 1982.
(34) Gaw, J. F.; Willetts, A.; Green, W. H.; Handy, N. C. In *Advances in Molecular Vibrations and Collision Dynamics*; Bowman, J. M., Ed.; JAI Press: Greenwich, CT, 1990.
(35) Knowles, P. J.; Hampel, C.; Werner, H.-J. *J. Chem. Phys.* **1994**, *99*, 5219.
(36) Knowles, P. J.; Hampel, C.; Werner, H.-J. *J. Chem. Phys.* **2000**, *112*, 3106.
(37) Martin, H. *J. Chem. Phys.* **1988**, *88*, 1797.
(38) Peterson, K. A.; Woon, D. E.; Dunning, T. H. Jr. *J. Chem. Phys.* **1994**, *100*, 7410.
(39) Chase, M. W. Jr., Ed. NIST-JANAF Thermochemical Tables, 4th ed., *J. Phys. Chem. Ref. Data Monogr.* **1988** (no. 9).
(40) Yamada, K.; Winnewisser, M. *Z. Naturforsch. A* **1976**, *31*, 139.