

Ab Initio Potential Energy Surface and Vibrational–Rotational Energy Levels of $X^2\Sigma^+$ CaOH

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The equilibrium structure and potential energy surface of calcium monohydroxide in its ground doublet state, $X^2\Sigma^+$ CaOH, have been determined from large-scale ab initio calculations using the spin-restricted coupled-cluster method, RCCSD(T), with basis sets of quadruple- and quintuple- ζ quality. The vibrational–rotational energy levels of the CaOH and CaOD isotopomers were calculated using the variational method. The spectroscopic constants determined are found to be in remarkably good agreement with experimental data.

1. Introduction

In the series of alkaline earth monohydroxides, MOH (M = Be, Mg, Ca), calcium monohydroxide is considered to be the most ionic compound, with a charge distribution closely resembling Ca^+OH^- . Therefore, its equilibrium structure can be expected to be linear. The observed electronic–vibrational–rotational spectra of the CaOH and CaOD species^{1–17} are indeed consistent with this structure and a nearly harmonic CaOH bending potential energy function. In particular, the dependence of the effective rotational constant B_v on the quantum number v_2 of the CaOH bending mode was found to be nearly linear,^{11–14} thus indicating low anharmonicity of the CaOH bending vibration. The harmonic force field and two cubic stretch–bend interaction force constants were determined by Li and Coxon.^{11,14} A comparison of the reported results indicates, however, that uncertainties in the determined force constants are quite large. To our knowledge, this is the only experimental anharmonic force field of calcium monohydroxide available in the literature.

In contrast to a large body of experimental data, the theoretical ab initio studies on calcium monohydroxide are rather sparse.^{18–23} Bauschlicher et al.^{18–20} studied properties of the CaOH radical at various levels of theory. Using an extended one-particle basis set of spdf quality, the equilibrium structure of calcium monohydroxide was found to be linear, with the CaOH bending potential energy function being dominated by the quadratic term. Kong and Boyd^{21,22} studied the 1,2 migration of hydrogen and predicted the HCao isomer to be linear, with the total energy being higher than that of the CaOH isomer by about 0.11 hartrees (69 kcal/mol). The harmonic frequencies for the CaOH radical were also calculated at the CASSCF/TZ2P²² and MP2/6-311++G**²³ levels of theory. A theoretical ab initio anharmonic force field of calcium monohydroxide has not been reported so far in the literature.

In this study, we present a detailed and accurate characterization of the potential energy surface and vibrational–rotational

energy levels of calcium monohydroxide. The molecular parameters are determined here by the ab initio approach using highly correlated wave functions calculated with large correlation-consistent spdfgh basis sets and taking into account core-electron correlation effects.

2. Method of Calculation

The molecular parameters of calcium monohydroxide were calculated using the spin-restricted coupled-cluster method including single and double excitations and a perturbational correction due to connected triple excitations, RCCSD(T),^{24–26} based on spin-restricted Hartree–Fock (RHF) molecular orbitals as a reference wave function. The one-particle basis sets employed for oxygen and hydrogen were the correlation-consistent polarized valence basis sets, cc-pVnZ.²⁷ For calcium, the corresponding cc-pVnZ basis sets were developed. As pointed out by Bauschlicher et al.¹⁹ and found by us in benchmark calculations,²⁸ a proper treatment of a calcium-containing molecule requires explicit consideration of the Ca valence 4s and “outer-core” 3sp electrons. Therefore, the new valence basis sets for calcium were augmented with sets of tight functions. The resulting core-valence basis sets, cc-pCVnZ, were designed to describe both the valence and outer-core spaces of the calcium atom. The details of the basis sets for calcium and results of the supporting benchmark calculations will be reported elsewhere. In this study, one-particle basis sets of quadruple- ($n = Q$) and quintuple- ζ ($n = 5$) quality were employed. Thus, the largest basis set consists of an (8s4p3d2f1g)/[5s4p3d2f1g] set for hydrogen, a (14s8p4d3f2g1h)/[6s5p4d3f2g1h] set for oxygen, and a (26s18p12d6f4g2h)/[12s10p9d6f4g2h] set for calcium. The latter 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- and 1s-like core orbitals of the calcium and oxygen atoms, respectively, were excluded from the active space.

The calculations were performed using the MOLPRO-2000 package of ab initio programs.²⁹

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TABLE 1: Equilibrium Molecular Parameters of $X^2\Sigma^+$ CaOH Determined Using the RCCSD(T) Method^a

	$n = Q$	$n = 5$
$r(\text{CaO})$ (Å)	1.9776	1.9778
$r(\text{OH})$ (Å)	0.9519	0.9520
energy + 752 (hartrees)	-0.907268	-0.926220

^a cc-pCVnZ basis set for Ca, and the cc-pVnZ basis set for O and H.

The vibrational–rotational energy levels were calculated variationally using the 6D Hamiltonian of a triatomic molecule.^{30–33} The Hamiltonian, including the exact kinetic energy operator, was derived in terms of the internal valence coordinates. The initial vibrational basis set consisted of harmonic oscillator functions for the stretching coordinates and of associated Legendre functions for the bending coordinate. Expansion functions were constructed as contracted combinations of the initial basis set functions. For the stretching part, the 1D expansion functions were optimized to yield contracted 2D stretching functions. Vibrational basis set functions were then formed as products of the contracted 2D stretching functions and 1D bending functions. For each value of the total angular momentum quantum number $J = N \pm S$, where N and S are the rotational and spin quantum numbers, respectively, the secular matrix was constructed using the vibrational expansion functions and the rotational symmetric-top functions. The matrix elements were evaluated by numerical quadrature. The secular matrix was then diagonalized to obtain the vibrational–rotational-spin energy levels. The number of contracted 2D stretching functions was 40, and the number of contracted bending functions was 20, leading to a total of 800 vibrational basis functions. This size of the basis set ensured the convergence in the energy to within $\sim 10^{-6}$ cm⁻¹ for the vibrational–rotational energy levels of interest.

3. Results and Discussion

As in the previous theoretical studies,^{18–23} the CaOH radical was found to be linear at equilibrium in the ground electronic state, being of $^2\Sigma^+$ symmetry in the $C_{\infty v}$ point group. The equilibrium bond lengths and total energy computed here by the RCCSD(T) approach are listed in Table 1. Changes in the calculated bond lengths beyond the quintuple- ζ basis set ($r(\text{CaO}) = 1.9778$ Å and $r(\text{OH}) = 0.9520$ Å) can be expected to be negligibly small. Considering the effects of the limited one-particle basis set and of approximations inherent to the CCSD(T) approach, we estimate the uncertainty in the calculated bond lengths to be about ± 0.002 Å. In comparison, the equilibrium CaO bond length has been determined previously at various other levels of theory to be 1.988 Å at the CISD/TZ4P level,¹⁹ 2.027 Å at the CASSCF/TZ4P level,²² and 2.033 Å at the MP2/6-311++G** level.²³ The equilibrium OH bond length was predicted to be 0.956 Å at the CASSCF/TZ4P level²² and 0.954 Å at the MP2/6-311++G** level.²³ The experimental equilibrium (r_e) CaO and OH bond lengths were determined by Li and Coxon to be 1.9751 and 0.9536 Å¹¹ or 1.9746 and 0.9562 Å¹⁴, respectively. The ground-state effective (r_0) CaO and OH bond lengths were estimated by Nuccio et al.¹³ to be 1.985 and 0.922 Å, respectively. The equilibrium CaO bond length predicted in this work to be 1.978 Å is slightly longer than the two experimental values quoted above. However, the calculated equilibrium OH bond length of 0.952 Å is slightly shorter than the experimental estimates. Nevertheless, in comparison to the previous theoretical estimates,^{19,22,23} the equilibrium structure of calcium monohydroxide predicted here at the RCCSD(T)/

TABLE 2: Anharmonic Force Field of $X^2\Sigma^+$ CaOH

i	j	k	c_{ijk}^a	i	j	k	c_{ijk}^a
0	0	2	0.007394	1	3	0	-0.012247
2	0	0	1.246952	1	0	6	-0.003252
0	2	0	0.916985	0	1	6	-0.000609
0	0	4	-0.000025	3	1	0	0.155737
1	1	0	0.029228	3	0	2	0.111915
1	0	2	-0.077830	0	3	2	-0.007764
0	1	2	-0.011613	2	2	0	-0.284928
3	0	0	-1.159636	2	0	4	-0.011566
0	3	0	-0.188076	0	2	4	-0.003313
0	0	6	-0.000107	1	1	4	0.010251
1	2	0	0.034570	1	2	2	-0.054025
1	0	4	0.024325	2	1	2	0.066186
0	1	4	-0.000214	5	0	0	1.192319
2	1	0	-0.182842	0	5	0	-0.302574
2	0	2	0.003431	2	3	0	-0.247085
0	2	2	-0.011848	3	2	0	0.235053
1	1	2	-0.016157	3	1	2	-0.082455
4	0	0	-0.599040	1	2	4	0.026928
0	4	0	-0.352939	2	2	2	0.096663
0	0	8	0.000093				

^a The expansion coefficients are given in hartrees, the coordinates q_1 and q_2 are dimensionless, and q_3 is in radians.

spdfgh level of theory is in remarkably good agreement with the experimental data. The remaining discrepancy in the equilibrium bond lengths is most likely due to neglect of the core-valence correlation effects of the oxygen 1s and calcium 2sp electrons.

To determine the shape of the potential energy surface of calcium monohydroxide, the total energy was calculated at 129 points in the vicinity of the equilibrium configuration, with the energies ranging to approximately 12 000 cm⁻¹ above the minimum. The energies were determined at the RCCSD(T)/spdfgh level of theory with an accuracy better than 10^{-8} hartrees. The potential energy surface was then approximated by a 3D expansion along the internal valence coordinates. The internal coordinates for the CaO and OH stretching modes were chosen as Simons–Parr–Finlan coordinates,³⁴ $q = (r - r_e)/r$, where r and r_e are instantaneous and equilibrium bond lengths, respectively. For the CaOH bending mode, a curvilinear displacement coordinate was used,³⁵ which is defined as the supplement of the valence angle CaOH. The coordinates for the CaO and OH stretching modes are referred to hereafter as q_1 and q_2 , respectively, whereas that for the CaOH bending mode, as q_3 . Thus, the potential energy surface of calcium monohydroxide can be written as the polynomial expansion

$$V(q_1, q_2, q_3) = V_m + \sum_{ijk} c_{ijk} q_1^i q_2^j q_3^k \quad (1)$$

where V_m is the total energy at the minimum. The expansion coefficients c_{ijk} were determined from a least-squares fit of eq 1 to the computed total energies, and 40 coefficients appeared to be statistically significant. The optimized values of the expansion coefficients are listed in Table 2. Note that because of the symmetry of the CaOH molecule the exponent k (for the CaOH bending mode) takes only even values. The root-mean-square deviation of the fit was 2.2 μ hartrees (0.5 cm⁻¹).

A comparison of the calculated and observed vibrational–rotational term values for the two isotopic species, CaOH and CaOD, is presented in Table 3. The spin-doubling splittings are omitted, and the averaged vibrational–rotational term values are quoted. The energy levels are labeled with the quantum numbers v_1 and v_3 for the CaO and OH stretching modes, respectively, and with the quantum numbers v_2 and l_2 for the

TABLE 3: $N = l_2$ 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 $X^2\Sigma^+$ CaOH and CaOD

$(v_1, v_2^{l_2}, v_3)$	CaOH				CaOD			
	energy (calcd)	energy (obsd)	ΔB_v (calcd)	ΔB_v (obsd)	energy (calcd)	energy (obsd)	ΔB_v (calcd)	ΔB_v (obsd)
(0, 0 ⁰ , 0)	0.	0.	0.	0.	0.	0.	0.	0.
(0, 1 ¹ , 0)	351.9	352.93 ^a	−27.0	−26.332 ^d	266.0	266.84 ^a	3.0	2.166 ^e
(0, 2 ⁰ , 0)	687.5	688.67 ^b	−40.9	−40.245 ^d	517.6	519.15 ^b	10.8	10.385 ^e
(0, 2 ² , 0)	711.6	713.71 ^b	−54.7	−53.687 ^d	535.1	536.94 ^b	3.5	3.113 ^e
(0, 3 ¹ , 0)	1031.4		−56.5		774.4		18.0	
(0, 3 ³ , 0)	1080.9		−83.6		808.0		2.4	
(0, 4 ⁰ , 0)	1359.7		−61.1		1019.5		31.9	
(0, 4 ² , 0)	1385.2		−74.5		1036.4		23.9	
(0, 4 ⁴ , 0)	1462.1		−113.8		1085.7		−0.5	
(1, 0 ⁰ , 0)	608.1	609.02 ^b	−66.2	−66.725 ^d	604.5	604.90 ^b	−53.7	−55.707 ^e
(2, 0 ⁰ , 0)	1208.3	1210.15 ^b	−131.9	−132.0 ^b	1203.3	1204.16 ^b	−108.7	−114.2 ^b
(3, 0 ⁰ , 0)	1800.1	1803.05 ^b	−197.0	−198.9 ^b	1796.6	1797.61 ^b	−163.6	−167.0 ^b
(4, 0 ⁰ , 0)	2383.4	2387.27 ^b	−261.0	−256.7 ^b	2384.3		−218.4	
(0, 0 ⁰ , 1)	3792.7	3778 ^c	−16.7		2799.6	2790 ^c	−22.4	
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^a Reference 11. ^b Reference 7. ^c Reference 15. ^d Reference 12. ^e Reference 13. ^f The zero-point energy.

TABLE 4: Vibrational Constants ω^0 and x^0 (in cm^{-1}) of $X^2\Sigma^+$ CaOH and CaOD

	CaOH		CaOD	
	calcd	obsd	calcd	obsd
ω_1^0	612.1	610.4 ^a , 612.8 ^b	607.3	607.8 ^b
ω_2^0	347.6	350.0 ^a , 349.3 ^c	262.7	265.5 ^c
ω_3^0	3873.9		2843.0	
x_{11}^0	−4.0	−3.7 ^a , −3.7 ^b	−2.8	−2.9 ^b
x_{22}^0	−1.9	−0.8 ^a , −4.0 ^c	−2.0	−2.6 ^c
x_{33}^0	−81.3		−43.4	
x_{12}^0	−7.7	−7.1 ^a	−5.2	
x_{13}^0	−5.6		−0.9	
x_{23}^0	−15.0		−9.2	

^a Reference 15. ^b Reference 7. ^c Reference 14.

doubly degenerate CaOH bending mode. For both isotopic species, the experimental CaO stretching and CaOH/CaOD bending fundamental wavenumbers are reproduced to within 1 cm^{-1} . For the corresponding excited vibrational energy levels, differences between the calculated and observed term values are smaller than 4 cm^{-1} . The predicted OH/OD stretching fundamental wavenumbers overestimate the experimental values by 15 and 10 cm^{-1} for the CaOH and CaOD isotopomers, respectively. Following the experimental studies,^{10,11,14,15} the vibrational energy levels can further be characterized by the constants ω^0 and x^0 .³⁶ The calculated and observed constants are given in Table 4. The theoretical values were determined from the nine low-energy vibrational energy levels with $l_2 = 0$, including the fundamental, overtone, and combination levels. For both isotopomers, the predicted constants ω^0 agree with the experimental values to within 3 cm^{-1} . Note that because the Fermi resonance between the ν_1 and $2\nu_2$ energy levels^{8,14} is not explicitly considered here, the calculated vibrational constants should be compared with the experimental “perturbed” values. By using the predicted values of the constants ω^0 and x^0 , the harmonic wavenumbers are determined to be $\omega_1 = 626.5$, $\omega_2 = 362.7$, and $\omega_3 = 3973.0 \text{ cm}^{-1}$ for the CaOH isotopomer and $\omega_1 = 615.7$, $\omega_2 = 273.9$, and $\omega_3 = 2896.0 \text{ cm}^{-1}$ for the CaOD isotopomer. It is worth noting that the calculated harmonic wavenumber for the OH/OD stretching mode of CaOH/CaOD is substantially larger than that of 3738/2717 cm^{-1} assumed in the experimental study.¹⁴ The vibrational constant g_{22} for the $\nu_2 = 2$ state is predicted to be 5.9 and 4.2 cm^{-1} for the CaOH and CaOD isotopomers, respectively. The corre-

sponding experimental values were determined to be 6.087 and 4.303 cm^{-1} .¹⁴ The harmonic frequencies predicted for the main CaOH isotopomer can be compared with those determined at other levels of theory. At the CASSCF/TZ2P level,²² the harmonic wavenumbers ω_1 , ω_2 , and ω_3 were calculated to be 597, 407, and 3925 cm^{-1} , respectively. At the MP2/6-311++G** level,²³ the corresponding values were found to be 597, 506, and 4056 cm^{-1} . The harmonic frequencies determined in this work are the most accurate.

The calculated vibrational–rotational energy levels were used to determine the effective rotational constant B_v for each vibrational state. These values were obtained by fitting an odd-order power series in $(N + 1)$ to the calculated rotational transition frequencies. The effective rotational constant B_0 for the ground vibrational state of the CaOH and CaOD isotopomers is determined in this way to be 9994.9 and 9057.2 MHz, respectively. The predicted constants are in good agreement with the corresponding experimental values of 10 023.084¹² and 9083.151 MHz,¹³ being consistently underestimated merely by ~ 30 MHz. The observed and predicted changes in the rotational constant B_v due to excitation of the vibrational modes are also listed in Table 3. The experimentally observed changes ΔB_v are reproduced to high accuracy, with the root-mean-square deviation being 1.9 and 2.8 MHz for the CaOH and CaOD isotopomers, respectively. By using the experimentally determined dependence of the rotational constant B_v on the quantum numbers v_2 and l_2 , Fletcher et al.¹² predicted the B_v values for the $v_2^{l_2} = 3^1$ and 3^3 states of CaOH to be 9967.90 and 9941.02 MHz, respectively. The corresponding experimentally predicted changes ΔB_v are thus −55.18 and −82.06 MHz, and these values coincide to within 2 MHz with the theoretical estimates determined in this work (see Table 3). For the CaOH isotopomer, the l -type doubling constant q_v is calculated to be 21.6 and 20.2 MHz for the $v_2^{l_2} = 1^1$ and 3^1 states, respectively, as compared with the experimental value¹² of 21.649 MHz for the $v_2^{l_2} = 1^1$ state. For the CaOD isotopomer, the corresponding constants are predicted to be 22.9 and 24.2 MHz, as compared with the experimental value¹³ of 22.983 MHz for the $v_2^{l_2} = 1^1$ state. For both isotopomers, the predicted patterns of the rotational transitions in the excited vibrational states thus agree very favorably with the experimental data.

The changes ΔB_v can further be characterized by the rotational–vibrational interaction constants α_i . For the CaO and OH stretching modes, a conventional linear dependence with respect to the quantum numbers v_1 and v_3 can be assumed.

TABLE 5: Vibrational Dependence of the Effective Rotational Constant B_v (in MHz) for $X^2\Sigma^+$ CaOH and CaOD

	CaOH		CaOD	
	calcd	obsd	calcd	obsd
α_1	66.2	66.725 ^a	53.7	55.707 ^b
α_2	31.3	31.518 ^a	-1.0	-0.357 ^b
γ_{22}	2.7	2.849 ^a	1.2	1.209 ^b
γ_{11}	-3.3	-3.361 ^a	-2.0	-1.818 ^b
α_3	16.7		22.4	

^a Reference 12. ^b Reference 13.**TABLE 6: Harmonic and Selected Anharmonic Force Constants f (in aJ Å⁻ⁿ)^a of $X^2\Sigma^+$ CaOH**

	calcd	obsd
f_{11}	2.7796	3.064 ^b , 2.669 ^c
f_{22}	0.0645	0.242 ^b , 0.061 ^c
f_{33}	8.8223	7.413 ^b , 7.850 ^c
f_{13}	0.0677	1.837 ^b , 0.463 ^c
f_{122}	-0.1716	-0.181 ^b , -0.165 ^c
f_{223}	-0.0532	-0.133 ^b , 0.136 ^c

^a The coordinates Δr_1 and Δr_3 are in angstroms, and $\Delta\alpha$ is in radians.^b Reference 11. ^c Reference 14.

Following the experimental studies,^{10,12,13} a nonlinear dependence³⁷ of ΔB_v on the quantum numbers v_2 and l_2 was assumed for the CaOH/CaOD bending mode:

$$\Delta B_v = -\alpha_2(v_2 + 1) + \gamma_{22}(v_2 + 1)^2 + \gamma_{11}l_2^2 \quad (2)$$

The calculated and observed values of these constants are given in Table 5. For both isotopomers, the quadratic form of eq 2 reproduces all of the predicted changes ΔB_v that are due to the excitation of the v_2 mode with the root-mean-square deviation of about 0.3 MHz.

A slice through the ab initio potential energy surface of calcium monohydroxide $V(q_1, q_2, q_3)$ along the CaOH bending coordinate q_3 is determined to be (see Table 2)

$$V(q_1 = 0, q_2 = 0, q_3) = 1623q_3^2 - 5q_3^4 - 23q_3^6 + 20q_3^8 \quad (3)$$

where the energy and q_3 coordinate are given in wavenumbers and radians, respectively. This is essentially a harmonic potential energy function, as could have been expected from the overall pattern of the vibrational-rotational energy levels of calcium monohydroxide.

Finally, it is interesting to compare the anharmonic force field predicted in this work with that determined by Li and Coxon^{11,14} from the experimental data. The empirical force field was defined in terms of the curvilinear displacement coordinates $\Delta r = r - r_e$ and the force constants f :

$$V(\Delta r_1, \Delta\alpha, \Delta r_3) = \frac{1}{2}f_{11}(\Delta r_1)^2 + \frac{1}{2}f_{22}(\Delta\alpha)^2 + \frac{1}{2}f_{33}(\Delta r_3)^2 + f_{13}(\Delta r_1)(\Delta r_3) + f_{122}(\Delta r_1)(\Delta\alpha)^2 + f_{223}(\Delta\alpha)^2(\Delta r_3) + \dots \quad (4)$$

where Δr_1 and Δr_3 are the CaO and OH stretching coordinates, respectively, and $\Delta\alpha$ is the CaOH bending coordinate. Therefore, the anharmonic force field given by eq 1 must be transformed, and the force constants f can be calculated from the expansion coefficients c_{ijk} and the equilibrium CaO and OH bond lengths. Some of the force constants f calculated in this way and those determined experimentally^{11,14} are listed in Table 6. The two reported empirical force fields are quite different, with the force constants substantially deviating in magnitude or even in sign. The force constants reported in ref 14 are

considered by Li and Coxon to be “more reliably determined”, and these appear to be more consistent with the force constants predicted in this work at the RCCSD(T)/spdfgh level of theory. In this context, it is also instructive to compare the vibrational term values of the CaOH radical determined by the perturbational approach^{38,39} with those determined variationally. As is customary in the perturbational treatment, the anharmonic force field in the displacement coordinates was truncated at quartic order. Because a Fermi resonance of the type $2\omega_2 \approx \omega_1$ occurs, the corresponding anharmonic terms (with near-zero denominators) were removed from the perturbational equations, and the resonance interactions were treated explicitly by diagonalizing an appropriate energy-level matrix. The vibrational term values are determined to be 630, 320, and 3791 cm⁻¹ for the $(v_1, v_2^{1/2}, v_3) = (1, 0^0, 0)$, $(0, 1^1, 0)$, and $(0, 0^0, 1)$ states, respectively. These can be compared to the variational results of 608, 352, and 3793 cm⁻¹, respectively, shown in Table 3. The calculated term values for the v_1 and v_2 modes thus differ substantially from those calculated by the variational approach as well as those determined experimentally (see Table 3). Surprisingly though, the largest difference between the variational and perturbational approach occurs for the CaOH bending mode. This is likely the joint result of approximations inherent to the second-order perturbational equations, neglecting the vibrational dependence of the kinetic energy terms, and truncating of the anharmonic force field.

In light of the excellent agreement between the predicted and observed vibrational-rotational spectroscopic properties of calcium monohydroxide, it is reasonable to conclude that the equilibrium structure and potential energy surface of $X^2\Sigma^+$ CaOH predicted in this work represent the most accurate parameters available.

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