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Ab Initio Prediction of the Potential Energy Surface and Vibration−Rotation Energy Levels of $CaCl_2$

Jacek Koput

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

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The equilibrium structure and potential energy surface of calcium dichloride ($CaCl_2$) have been determined from accurate ab initio calculations using the coupled-cluster method, CCSD(T), in conjunction with basis sets of quadruple- and quintuple-ζ quality. The $CaCl_2$ molecule was found to be linear at equilibrium. The vibration−rotation energy levels of various $CaCl_2$ isotopomers were predicted by the variational method. The calculated spectroscopic constants could be used to guide future high-resolution spectroscopic experiments on calcium dichloride.

1. Introduction

The differences between equilibrium structures of alkaline-earth dihalides and dihydrides are of experimental and theoretical interest.[1,2] Although the bonding in these molecules is almost entirely ionic, some of them were found in the electric deflection experiments[3,4] to have a bent equilibrium configuration. In particular, among the calcium-containing molecules, calcium difluoride (CaF_2) and dihydride (CaH_2) were found both experimentally and theoretically to be slightly bent at equilibrium, see refs 5 and 6, and references therein. In contrast, the $CaCl_2$ molecule was found to be linear at equilibrium.[3,4,7−19]

The infrared spectrum of gaseous calcium dichloride at about 1650 K was observed by Baikov.[7] A broad featureless band at 395 cm^{-1} was assigned to vibration−rotation transitions of the antisymmetric CaCl stretching mode ν_3. The infrared spectra of various $CaCl_2$ isotopomers were investigated by Hastie et al.[8] and White et al.[9] using the matrix-isolation technique. The strong absorption band due to the ν_3 fundamental transition was observed at about 414, 397, and 402 cm^{-1} in neon, argon, and krypton matrices, respectively. From the calcium and chlorine isotopic frequency shifts of the ν_3 fundamental, the equilibrium configuration of the $CaCl_2$ molecule was concluded to be linear. These results were confirmed in the subsequent spectroscopic study by Ramondo et al.[11] Concerning the ClCaCl bending mode ν_2, Hastie et al.[8] suggested the fundamental transition to be about 122 cm^{-1}. On the other hand, White et al.[9] and Ramondo et al.[11] assigned the weak band observed at 72 and 65 cm^{-1} in argon and krypton matrices, respectively, to the ν_2 fundamental transition. The symmetric CaCl stretching mode ν_1 was found to be infrared inactive. In the electron-diffraction study by Vajda et al.,[10] the $CaCl_2$ molecule was found to be linear at equilibrium, with the thermal-average CaCl bond length (r_g) of 2.483 Å. The equilibrium CaCl bond length (r_e) was then estimated by Levy and Hargittai[17] to be 2.455 Å.

There are a number of theoretical studies on calcium dichloride.[12−19] In the ab initio calculations, ranging from the Hartree−Fock (HF) to coupled-cluster (CCSD(T)) level of theory, the equilibrium configuration of the $CaCl_2$ molecule was predicted to be linear. The equilibrium CaCl bond length was calculated to be 2.46−2.56 Å depending on the method and one-particle basis set employed. The density functional theory (DFT) methods are not conclusive concerning the equilibrium structure of $CaCl_2$.[16,19] Using the B−VWN and B3-LYP exchange-correlation functionals, the $CaCl_2$ molecule was predicted to be linear. Using the S−VWN and PW91 functionals, the $CaCl_2$ molecule was predicted to be bent, with the equilibrium ClCaCl angle of 160−150°. The vibrational harmonic frequencies ω_1, ω_2, and ω_3 of calcium dichloride were calculated to be in the ranges 270−456, 17−64, and 417−637 cm^{-1}, respectively.[12−19] In the most extensive calculation to date by Haworth et al.,[18] the equilibrium CaCl bond length of $CaCl_2$ was predicted to be 2.469 Å at the CCSD(T)/(aug-)cc-pWCVQ+dZ level, and the vibrational frequencies ω_1, ω_2, and ω_3 were predicted to be 270, 31, and 417 cm^{-1}, respectively, at the CCSD(T)/(aug-)cc-pWCVT+2dZ level. To our knowledge, neither the experimental nor theoretical anharmonic force field of calcium dichloride was reported so far in the literature.

In this study, we present an accurate characterization of the three-dimensional potential energy surface and vibration−rotation energy levels of calcium dichloride. 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 the core-correlation and scalar relativistic effects.

2. Method of Calculation

The molecular parameters of calcium dichloride were calculated with the coupled-cluster method including single and double excitations and a perturbational correction due to connected triple excitations, CCSD(T).[20−23] 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.[24] Because a proper treatment of a calcium-containing molecule requires explicit consideration of the Ca valence 4s and “outer-core’’ 3sp electrons, the valence basis sets for calcium were augmented with sets of tight functions.[25] The resulting core-valence basis sets, cc-pCV*n*Z, were designed to describe both valence and “outer-core’’ spaces of the calcium atom. For chlorine, the extended correlation-consistent aug-cc-pV(*n*+d)Z basis sets were used.[26] The extended basis set includes an additional tight d function, and it is further augmented with diffuse functions to allow the basis set to adjust to a negative charge on the chlorine atoms. The largest one-particle basis set applied in this study consists of a (26s18p12d6f4g2h)/

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TABLE 1: Molecular Parameters of $CaCl_2$, Determined with the CCSD(T) Method and Various cc-pV*n*Z Basis Sets

	$n = Q^a$	$n = 5$
r(CaCl) (Å)	2.4698	2.4652
energy + 1596 (hartree)	−0.825204	−0.848178

[a] The cc-pCV*n*Z/aug-cc-pV(*n*+d)Z basis sets for the Ca/Cl atoms, respectively.

[12s10p9d6f4g2h] set for calcium and a (21s13p6d4f3g2h)/[8s7p6d4f3g2h] set for chlorine. 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 and chlorine atoms were excluded from the active space unless otherwise noted. This active space is referred to as V. The calculations were performed with the MOLPRO-2006 package of ab initio programs.[27]

The vibration−rotation energy levels were calculated variationally with the six-dimensional Hamiltonian of a triatomic molecule developed by Carter and Handy.[28−30] 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 vibration−rotation energy levels were calculated by using atomic masses. Vibrational basis set functions were formed as products of the contracted two-dimensional stretching functions and one-dimensional bending functions. For each value of the rotational quantum number J, the secular matrix was constructed by 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 vibration−rotation energy levels. For the calculated potential energy surface of calcium dichloride (see below), the number of contracted two-dimensional stretching functions was 48 and the number of contracted bending functions was 32, leading to a total of 1536 vibrational basis functions for each symmetry block. This size of the basis set ensured the convergence in the energy to better than 10^{-6} cm^{-1} for the vibration−rotation energy levels of interest.

3. Results and Discussion

As shown in the previous ab initio studies,[12−19] the $CaCl_2$ molecule in its ground electronic state is predicted to be linear at equilibrium. The calculated equilibrium CaCl bond length and total energy of $X^1\Sigma_g^+$ $CaCl_2$ are given in Table 1. To determine the shape of the potential energy surface of calcium dichloride, the total energy was calculated by using the quintuple-ζ ($n = 5$) basis set at 165 symmetry unique points in the vicinity of the equilibrium configuration. The CaCl bond lengths were sampled in the range 2.1−3.2 Å, and the ClCaCl valence angle was in the range 180−80°. The computed energies ranged thus to approximately 9000 cm^{-1} above the minimum. The potential energy surface was then approximated by a three-dimensional expansion along the internal valence coordinates. The internal coordinates for the CaCl stretching modes were chosen as Simons-Parr-Finlan coordinates,[31] $q = (r - r_e)/r$, where r and r_e are instantaneous and equilibrium bond lengths, respectively. For the ClCaCl bending mode, a curvilinear displacement coordinate was used.[32] It was defined as the supplement of the ClCaCl valence angle measured from a linear equilibrium configuration. The coordinates for the CaCl stretching modes are referred to as q_1 and q_2, whereas that for the ClCaCl bending mode as θ. The potential energy surface of calcium dichloride can be written as the polynomial expansion

$$V(q_1,q_2,\theta) = V_e + \sum_{ijk} c_{ijk} q_1^i q_2^j \theta^k \tag{1}$$

where V_e is the total energy at the equilibrium configuration of the $CaCl_2$ 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 22 coefficients appeared to be statistically significant. The optimized values of the expansion coefficients are given in Table 2 in the column headed "V". Only the coefficients that are not equivalent by symmetry are quoted. The root-mean-square deviation of the fit was 1.8 μhartree (0.4 cm^{-1}).

The potential energy surface just determined was corrected for the correlation effects of the 2sp electrons of the calcium ("inner-core'') and chlorine atoms, and then for the scalar relativistic effects. These calculations were performed by using the quadruple-ζ (n = Q) basis set, namely the uncontracted cc-pCVQZ basis set for calcium[25] and the aug-cc-pCV(Q+d)Z basis set for chlorine.[33] Only the 1s-like core orbitals of the calcium and chlorine atoms were excluded from the active space in the correlation treatment. This active space is referred to as A. For the core-correlation corrections, the total energy of the $CaCl_2$ molecule was computed with the CCSD(T) method at the same 165 points, using either V or A active space. At each point, a difference between these total energies was calculated and subsequently added to the total energy computed with the quintuple-ζ basis set and the V active space. The core-correlation corrections to the molecular energy amount to about −0.964 hartree and vary by less than ±0.001 hartree for all of the data points. The values of the expansion coefficients c_{ijk} optimized for the corrected potential surface are given in Table 2 in the column headed "$V + C$". The scalar relativistic correction to the molecular energy was determined as the sum of the expectation values of the mass-velocity and one-electron Darwin contact term integrals.[34] The calculations were performed with the single-reference configuration interaction method including single and double excitations, CISD, with the A active space. Although the relativistic corrections appeared to be quite large of about −5.660 hartree, they vary as little as the core-correlation corrections along the potential energy surface. The values of the expansion coefficients c_{ijk} optimized for the corrected potential surface are given in Table 2 in the column headed "$V + C + R$". Inclusion of the core-correlation corrections shortens the equilibrium CaCl bond length by 0.0028 Å, whereas inclusion of the relativistic corrections shortens it further by 0.0017 Å. The best estimate of the equilibrium CaCl bond length of calcium dichloride is thus 2.460 Å, as compared with the experimental electron-diffraction estimate of 2.455(8) Å by Levy and Hargittai.[17] Considering convergence of the calculated values with the one-particle basis set size (see Table 1) and errors inherent to the CCSD(T) method, the predicted equilibrium CaCl bond length is believed to be accurate to ±0.003 Å. The predicted equilibrium CaCl bond length coincides with the experimental value to within its errors bars.

The three anharmonic force fields of Table 2 were used to calculate variationally the vibration−rotation energy levels of the main isotopic species $^{40}Ca^{35}Cl_2$, with the rotational quantum number J ranging from 0 to 6. The predicted fundamental vibrational wavenumbers are given in Table 3. Inclusion of the core-correlation and relativistic effects has a very small effect on the calculated values, as differences between the vibrational wavenumbers determined with the V and $V + C + R$ force fields do not exceed 1 cm^{-1}. The predicted fundamental wavenumbers of $CaCl_2$ are believed to be accurate to better than ±5 cm^{-1}. The best anharmonic force field $V + C + R$ was used to

TABLE 2: Anharmonic Force Fields[a] of $CaCl_2$

i	j	k	V	$V + C$	$V + C + R$
0	0	2	0.003180	0.003211	0.003213
2	0	0	1.059644	1.060885	1.060001
0	0	4	0.003400	0.003359	0.003327
1	1	0	0.193818	0.193818	0.192911
1	0	2	0.026978	0.026923	0.026874
3	0	0	−1.131667	−1.133336	−1.131796
0	0	6	−0.000379	−0.000349	−0.000319
1	2	0	−0.038734	−0.038533	−0.037985
1	0	4	−0.008061	−0.007971	−0.007862
2	0	2	−0.051387	−0.051320	−0.051133
1	1	2	−0.076130	−0.075654	−0.075346
4	0	0	−0.019962	−0.020852	−0.012558
0	0	8	−0.000031	−0.000040	−0.000049
1	3	0	0.028708	0.030885	0.030261
1	0	6	0.000913	0.000886	0.000846
3	0	2	0.013612	0.013720	0.013400
2	2	0	−0.005888	−0.005934	−0.003526
2	0	4	0.005258	0.005195	0.005126
1	1	4	0.024827	0.024499	0.024151
1	2	2	0.073791	0.073169	0.072912
5	0	0	0.617434	0.622788	0.608815
0	0	10	0.000040	0.000041	0.000042

[a] Expansion coefficients c_{ijk} of eq 1, in hartrees. The coordinates q_1 and q_2 are dimensionless; θ is in radians. The equilibrium CaCl bond length is determined to be 2.4652, 2.4624, and 2.4607 Å for the V, $V + C$, and $V + C + R$ force fields, respectively.

TABLE 3: Fundamental Vibrational Wavenumbers[a] (in cm^{-1}) of the Main $^{40}Ca^{35}Cl_2$ Isotopomer

	V	$V + C$	$V + C + R$
ν_1 (sym CaCl stretch)	284.0	284.5	284.5
ν_2 (ClCaCl bend)	36.9	37.1	37.1
ν_3 (asym CaCl stretch)	426.0	426.7	426.9

[a] Calculated with the corresponding anharmonic force fields of Table 2.

TABLE 4: Ab Initio Predicted and Experimental Fundamental Vibrational Wavenumbers (in cm^{-1}) of Various $CaCl_2$ Isotopomers

	$^{40}Ca^{35}Cl_2$	$^{44}Ca^{35}Cl_2$	$^{40}Ca^{37}Cl_2$	$^{40}Ca^{35}Cl^{37}Cl$	$^{44}Ca^{35}Cl^{37}Cl$
			Ab Initio		
ν_1	284.5	284.3	276.8	280.6	280.4
ν_2	37.1	36.0	36.8	37.0	35.8
ν_3	426.9	414.5	422.7	424.9	412.4
ZPE[a]	393	386	387	390	383
			Experimental[b]		
ν_2	63.6/71.5	62.0/...	.../...	.../...	.../...
ν_3	402.3/397.2	390.7/385.5	.../393.5	400.9/395.3	389.2/383.5

[a] The zero-point energy. [b] From the infrared spectra of $CaCl_2$ in Kr/Ar matrices, ref (9) and (11), respectively.

calculate the vibration−rotation energy levels of various $CaCl_2$ isotopomers, and the predicted fundamental vibrational wavenumbers are given in Table 4. Assignments of the predicted $J = 0$ and 1 vibration−rotation energy levels of the main isotopic species $^{40}Ca^{35}Cl_2$ up to about 1500 cm^{-1} above the ground state are given in Table S1 of the Supporting Information. As can be seen, this region includes all of the vibrational energy levels up to $\upsilon_1 = 5$, $\upsilon_2 = 28$, and $\upsilon_3 = 3$ (altogether 208 vibrational states). The ν_3 fundamental is determined to be about 13, 30, and 25 cm^{-1} higher than the experimental values derived from infrared spectra of calcium dichloride in neon, argon, and krypton matrices, respectively.[8,9,11] Such differences are consistent with the matrix effects observed for several molecules.[35] Note that the experimental gas-phase estimate[7] of the ν_3 fundamental of 395 cm^{-1} is lower than the values determined by the matrix-isolation technique. This is somewhat unexpected, because just opposite large matrix shifts have been usually observed for the stretching modes of polar molecules.[35] Because the infrared spectrum of gaseous $CaCl_2$ was measured at about 1650 K,[7] the observed broad band consists likely of several hot-band transitions. The fundamental frequencies of calcium dichloride, especially the ν_2 one, are predicted to be low, and therefore, highly excited vibrational energy levels are expected to be significantly populated at this temperature. Because, as shown below (see Table 6), the anharmonic constants related to the ν_3 mode are all predicted to be negative, the ν_3 hot-band transitions are expected to extend to lower frequencies, with the ν_3 fundamental transition lying at the high-wavenumber end of the observed[7] absorption feature. The ν_2 fundamental of calcium dichloride is predicted to be nearly twice lower than the experimental values of 65 cm^{-1} (Kr matrix)[9] and 72 cm^{-1} (Ar matrix).[11] This is in line with previous ab initio studies[18,19] predicting the ν_2 fundamental to lie in the range 31−41 cm^{-1} at the correlated level of theory. The difference between the theoretical and experimental values is presumably due to the matrix effects, which can be expected to change significantly the shape of the soft ClCaCl bending potential energy function. These are the isotopic frequency shifts observed in the matrix-isolation experiments,[9,11] which can be compared most directly with the ab initio predicted values. The isotopic frequency shifts of the ν_3 fundamental are calculated to be −2.0 ($^{40}Ca^{35}Cl^{37}Cl$), −4.2 ($^{40}Ca^{37}Cl_2$), −12.4 ($^{44}Ca^{35}Cl_2$), and −14.5 cm^{-1} ($^{44}Ca^{35}Cl^{37}Cl$), as compared with the experimental values[9,11] of −1.4/−1.9, −3.6/−3.7, −11.6/−11.7, and −13.1/−13.7 cm^{-1}, respectively, in Kr/Ar matrices. The ^{44}Ca−^{40} Ca frequency shifts of the ν_2 fundamental is predicted to be −1.1 cm^{-1}, as compared with the experimental value[9] of −1.6 cm^{-1} in a Kr matrix. The experimental isotopic frequency shifts are reproduced to better than 1 cm^{-1}.

TABLE 5: $J = l_2$ Vibration−Rotation Term Values (in cm^{-1}) and Changes in the Effective Rotational Constant B_υ (in MHz) for the Low-Lying Energy Levels of the Main $^{40}Ca^{35}Cl_2$ Isotopomer

$(\upsilon_1, \upsilon_2^{l_2}, \upsilon_3)$	energy	ΔB_υ
$(0, 0^0, 0)$	0.	0.[a]
$(0, 1^1, 0)$	37.1	6.1
$(0, 2^0, 0)$	75.0	11.8
$(0, 2^2, 0)$	75.0	12.0
$(0, 3^1, 0)$	113.6	17.4
$(0, 3^3, 0)$	113.6	17.7
$(0, 4^0, 0)$	152.7	22.7
$(0, 4^2, 0)$	152.8	22.9
$(0, 4^4, 0)$	152.9	23.3
$(1, 0^0, 0)$	284.5	−2.3
$(0, 0^0, 1)$	426.9	−4.3

[a] The ground-state rotational constant B_0 is predicted to be 1197.2 MHz.

Table 5 lists some predicted low-lying vibration−rotation energy levels and changes in the effective rotational constant B_υ of the main isotopic species $^{40}Ca^{35}Cl_2$. For each vibrational energy level, the effective rotational constant B_υ was determined by fitting an odd-order power series in J to the calculated rotational transition energies. The effective rotational constant B_0 for the ground vibrational state of $^{40}Ca^{35}Cl_2$ is determined in this way to be 1197 MHz. Varying the equilibrium CaCl bond length within its estimated error bar (±0.003 Å) results in a change of the B_0 value of ±3 MHz. The quartic centrifugal distortion constant D_0 is determined to be 0.11 kHz. The l-type doubling constant q_υ is calculated to be 2.64 and 2.57 MHz for the $\upsilon_2^{l_2} = 1^1$ and 3^1 states, respectively. As can be seen, both spacing of the ClCaCl bending energy levels and effective

TABLE 6: Harmonic Wavenumbers ω_i and Anharmonic Constants x_{ij} (in cm^{-1}) of the Main $^{40}Ca^{35}Cl_2$ Isotopomer

ω_1	284.5	x_{11}	−0.4
ω_2	35.5	x_{22}	0.3
ω_3	430.3	x_{33}	−1.0
		x_{12}	1.6
		x_{13}	−1.9
		x_{23}	−0.5

rotational constant B_v change almost linearly with the vibrational quantum number v_2, thus indicating low anharmonicity of the ν_2 mode. Changes in the effective rotational constant B_v due to excitation of the CaCl stretching modes, ν_1 and ν_3, are also consistent with what is usually expected for slightly anharmonic stretching modes.

The vibrational energy levels of calcium dichloride can be further characterized by the harmonic frequencies ω_i and anharmonic constants x_{ij}. The values predicted for the main isotopic species $^{40}Ca^{35}Cl_2$ are given in Table 6. 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). Note that the anharmonic coupling between the normal modes of $CaCl_2$ is weak. In particular, as follows from the results given in Table S1, the ClCaCl bending frequency in the excited CaCl stretching states $v_1 = 5$ and $v_3 = 3$ is predicted to be 45.1 and 35.6 cm^{-1}, respectively, as compared with the ν_2 fundamental of 37.1 cm^{-1}. The vibrational constant g_{22} for the $v_2 = 2$ state is predicted to be −0.0046 cm^{-1}. The harmonic frequencies predicted in this study are consistent with those found previously at the correlated level of theory,[18,19] being 270−275, 31−41, and 417−425 cm^{-1} for the ν_1, ν_2, and ν_3 modes, respectively. The quasilinearity parameter[36] γ_0 of $CaCl_2$ is calculated to be −0.98, close to the limit of −1 for an ideal linear molecule.

In conclusion, the high-quality ab initio approach has been applied to characterize the three-dimensional potential energy surface and vibration−rotation energy levels of calcium dichloride. The $CaCl_2$ molecule was confirmed to be linear at equilibrium. The pattern of vibration−rotation energy levels was predicted to be characteristic of a typical semirigid linear molecule. This is in a striking contrast to other calcium-containing molecules CaF_2 and CaH_2, although perfectly consistent with popular models of structural chemistry.

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Supporting Information Available: Assignments of the predicted $J = 0$ and 1 vibration−rotation energy levels of the main isotopic species $^{40}Ca^{35}Cl_2$ are given in Table S1. This material is available free of charge via the Internet at http://pubs.acs.org.

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