J. Phys. Chem. A **2004,** *108,* 9267−9273

CaF_2 As a Quasilinear Molecule: the Vibrational−Rotational Energy Levels Predicted by Ab Initio Quantum Chemistry Approach

Jacek Koput* and Agnieszka Roszczak

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

Received: July 26, 2004; In Final Form: August 19, 2004

The equilibrium structure and potential-energy surface of calcium difluoride, CaF_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 CaF_2 molecule was found to be quasilinear, with an equilibrium FCaF angle of 154.3° and barrier to linearity of 54 cm^{-1}. The vibrational−rotational energy levels of the $^{40}CaF_2$ and $^{44}CaF_2$ isotopomers were predicted using the variational method. In particular, the FCaF bending fundamental (the ν_2 mode) was determined to be very low at only 9 cm^{-1}. The calculated spectroscopic constants could be used to guide future high-resolution spectroscopic experiments on calcium difluoride.

1. Introduction

Calcium difluoride, CaF_2, has attracted considerable interest because of its unusual equilibrium structure. Because the CaF_2 molecule is ionically bonded and the charge distribution closely resembles the structure $F^-Ca^{2+}F^-$, its equilibrium structure could be expected to be linear on the basis of a simple electrostatic model. Such a linear structure was found in the early electron-diffraction study.[1] However, in the electric-deflection experiments by Wharton et al.[2] and Büchler et al.,[3] the CaF_2 molecule was shown to have a permanent electric dipole moment and, therefore, a bent equilibrium configuration. The infrared spectra of two CaF_2 isotopomers, $^{40}CaF_2$ and $^{44}CaF_2$, were investigated by Snelson[4] using the matrix-isolation technique. The CaF_2 molecule was concluded in this study to be nonlinear at equilibrium. The strong absorption bands at 581, 561, and 555 cm^{-1} in matrixes of neon, argon, and krypton, respectively, were assigned to the antisymmetric CaF stretching mode ν_3 of the main $^{40}CaF_2$ isotopomer. The weak absorption bands at 504, 489, and 487 cm^{-1}, respectively, were assigned to the symmetric CaF stretching mode ν_1. The fundamental frequencies of the ν_3 and ν_1 modes for the $^{40}CaF_2$ species in the gas phase were estimated[4] to be 595 and 520 cm^{-1}, respectively, with an error limit of about ± 10 cm^{-1}. Absorption bands due to FCaF bending mode ν_2 were not observed,[4] and the ν_2 fundamental was estimated to be considerably lower than the ν_1 fundamental. The infrared spectrum of gaseous calcium difluoride at about 2100 K was observed by Baikov.[5] A broad band at 115 cm^{-1} was assigned to various hot-band ν_2 transitions, and the ν_2 fundamental was estimated to be 120 cm^{-1}. The infrared spectra of the two CaF_2 isotopomers in a krypton matrix were measured by Calder et al.[6] The bands at 485, 163, and 554 cm^{-1} were assigned to the ν_1, ν_2, and ν_3 modes, respectively, of the main isotopomer. From the observed fundamental frequencies of the two isotopic species, the equilibrium FCaF angle was determined[6] to be 140 ± 5°. These results were confirmed in the subsequent spectroscopic studies by Ramondo et al.[7,8] From the $^{40}Ca-^{44}Ca$ isotopic frequency shift of the ν_3 fundamental, the equilibrium FCaF angle was found to be 142 and 131° for the CaF_2 molecules isolated in argon and krypton matrixes, respectively. Using the same matrix-isolation technique, the structure of the CaF_2 molecule trapped in various matrixes was investigated by Beattie et al.[9] The equilibrium FCaF angle was determined to range from 139 to 156° depending on the matrix's nature.

There are a number of theoretical studies on calcium difluoride.[10−24] The results of calculations at the Hartree−Fock (HF) level of theory were not definitive concerning the equilibrium structure of the CaF_2 molecule. It was shown that the predicted structure changes from bent to linear, with the equilibrium FCaF angle ranging from 126 to 180°, depending on the size and quality of a one-particle basis set. (See Table 1 of ref 15.) The results reported by Salzner and Schleyer,[15] Wright et al.,[17] and Hassett and Marsden[21] indicate that, with an spdf basis set of approximately triple-ζ quality, the HF total energy difference between the linear and bent configurations is very small. The FCaF bending potential-energy function was predicted to be extremely flat near the equilibrium configuration. Seijo et al.[18] and Kaupp et al.[19,20] came to similar conclusions using the effective core potentials instead of all-electron basis sets. The inclusion of the electron correlation effects within the second-order Møller−Plesset (MP2) approach[13−15,17,21,23] was found to favor the bent configuration. With the largest spdf basis sets applied to date,[13,17,21,23] the equilibrium FCaF angle was predicted by the MP2 method to range from 151.8 to 153.8°. The barrier to linearity was determined to be 120 (ref 13), 125 (ref 17), and 61 cm^{-1} (ref 21). In the single-reference configuration interaction calculations,[19] CISD+Q/spdf, the equilibrium FCaF angle and barrier to linearity were found to be 157.5° and 66 cm^{-1}, respectively. Using the density functional theory (DFT) approach, the CaF_2 molecule was predicted to be bent at equilibrium, with the FCaF angle being 148.6 and 142.4° (refs 22 and 23, respectively). However, the barrier to linearity was determined[22] to be about 320 cm^{-1}, much higher than that found using the ab initio methods. The vibrational harmonic frequencies ω_1, ω_2, and ω_3 of the $^{40}CaF_2$ species were determined at the HF level of theory to be in the range of 484−541, 9−94, and 609−704 cm^{-1}, respectively, (See Table 7 of ref 15.) By accounting for the electron correlation effects using the MP2 or CI approach,[13−15,21] the harmonic frequencies were found to be 479−554, 30−90, and 549−656 cm^{-1}, respectively.

---

* Corresponding author. E-mail: koput@amu.edu.pl.

10.1021/jp046682k CCC: $27.50

TABLE 1: Molecular Parameters of CaF_2 Determined Using the CCSD(T) Method and Various cc-pV*n*Z Basis Sets

	CVQZ/VQZ[a]	CV5Z/V5Z	CVQZ/aug-VQZ	CV5Z/aug-V5Z
equilibrium configuration				
r(CaF) (Å)	2.0053	2.0043	2.0079	2.0046
∠(FCaF) (deg)	154.86	154.14	156.28	154.55
energy + 876 (hartree)	−0.816764	−0.852141	−0.827596	−0.856252
linear configuration				
r(CaF) (Å)	2.0130	2.0124	2.0147	2.0125
barrier (cm^{-1})	58	57	37	50

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

A comparison of the structural parameters and harmonic frequencies of the CaF_2 molecule determined at various levels of theory can also be found in Tables 1 and 2 of the recent paper by Levy and Hargittai.[23] The unusual equilibrium structure of calcium difluoride, as well as some other alkaline-earth dihalides, can be rationalized using “sd hybridization” and/or “polarized-ion” models. Both models have been discussed in detail in recent reviews by Hargittai[25] and Kaupp.[26] The sd hybridization model invokes a small (but significant) covalent character of CaF bonding arising from the 4s and 3d orbitals of the calcium atom rather than from the valence 4s and 4p orbitals. The charge transfer from the 4s to 3d orbital results in a small deviation from pure ionic CaF bonding and, therefore (due to the shape of the sd hybrid orbitals), in a slightly nonlinear equilibrium structure. In the polarized-ion model, a dipole moment on the polarizable Ca^{2+} cation is induced by the electric field of both F^- anions and the polarization energy tends to favor a bent equilibrium structure. Both models were combined into the “softness criterion”.[14,24]

In this study, we present an accurate characterization of the 3D potential-energy surface and vibrational−rotational energy levels of calcium difluoride. 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 by taking into account the “outer-core” correlation effects of the calcium atom. This approach has been successfully applied previously to predict the potential-energy surfaces and vibrational−rotational energy levels of alkaline-earth (Be, Mg, and Ca) monohydroxides.[27−29] In particular, the calculated spectroscopic constants of the CaOH radical were found[28] to be in remarkably good agreement with experimental data. To our knowledge, neither the experimental nor the theoretical anharmonic force field of calcium difluoride has been reported in the literature.

2. Method of Calculation

The molecular parameters of calcium difluoride were calculated using the coupled-cluster method including single and double excitations and a perturbational correction due to connected triple excitations, CCSD(T).[30−33] 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.[28,34] 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.[28] 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 (14s8p4d3f2g1h)/[6s5p4d3f2g1h] set for fluorine. 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- and 1s-like core orbitals of the calcium and fluorine atoms, respectively, were excluded from the active space. The calculations were performed using the MOLPRO-2002 package of ab initio programs.[35]

The vibrational−rotational energy levels were calculated variationally using the 6D Hamiltonian of a triatomic molecule developed by Carter and Handy.[36−38] 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. Symmetry-adapted stretching coordinates (symmetric and antisymmetric) were used. Vibrational basis set functions were formed as products of the contracted 2D stretching functions and 1D bending functions. For each value of the rotational quantum number J, 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 energy levels. The number of contracted 2D stretching functions was 48, and the number of contracted bending functions was 32, leading to a total of 1536 vibrational basis functions.

3. Results and Discussion

The equilibrium structural parameters and the total energy computed for the ground electronic state of calcium difuoride are listed in Table 1. As found at the MP2/spdf[13,17,21,23] and CISD+Q/spdf [19] levels of theory, the CaF_2 molecule is predicted by the CCSD(T) method to be bent at equilibrium. The calculated equilibrium CaF bond length, the FCaF angle, and the height of the barrier to linearity are close to the best estimates of 2.0032 Å, 153.8°, and 61 cm^{-1}, respectively, reported by Hassett and Marsden.[21] Because the CaF bond is strongly polarized, we investigated the effects of diffuse functions for fluorine. The additional calculations were performed with the augmented correlation-consistent basis sets, aug-cc-pV*n*Z.[39] The calculated molecular parameters are also listed in Table 1. Although changes in the molecular parameters are quite sizable for the quadruple-ζ basis set, inclusion of the diffuse functions does not significantly affect the parameters determined with the quintuple-ζ basis set. These changes are much smaller, amounting to only 0.0003 Å, 0.4°, and 7 cm^{-1} for the CaF bond length, the FCaF angle, and the barrier to linearity, respectively. The changes in the calculated total energy and structural parameters with the one-particle basis set indicate that the convergence is nearly complete with the quintuple-ζ basis set. We take the average of the CV5Z/V5Z and CV5Z/aug-V5Z results to be the best estimates for the equilibrium CaF bond length (2.0044 Å), the FCaF angle (154.34°), and the barrier to linearity (54 cm^{-1}). By analogy to the CaOH radical,[28] for which the experimental value of the equilibrium CaO bond length (r_e) is known, an uncertainty in the predicted equilibrium CaF bond length can be estimated to be ±0.002 Å. It is a bit difficult to assign uncertainties reliably to the predicted equilibrium FCaF angle and barrier height, but we believe that the calculated values are accurate to about ±1° and ±10 cm^{-1}, respectively. The predicted equilibrium FCaF angle falls in the range of the experimentally determined[6−9] values (131−156°). Note, however, that all of the experimental data quoted refer to the CaF_2 molecules isolated in various rare-gas matrixes at very low temperatures. Because the matrix effects were shown to be significant,[9] the predicted equilibrium FCaF angle cannot be compared directly with these experimental values. Moreover, as noted previously by Snelson,[4] the FCaF angle derived from the experimental isotopic frequency shifts can be seriously in error for two reasons. First, the apex angle of a triatomic molecule is calculated from an equation that can be rigorously applied only for harmonic motion. Second, the isotopic frequency shift is not a very sensitive function of the apex angle. For the ν_3 mode of the CaF_2 molecule,[4] varying the fundamental frequencies of the isotopic species by ±1 cm^{-1} results in an error of ±30° in the calculated FCaF angle. Considering the error limits of the measured frequencies and the role of (unknown experimentally) anharmonicity, an uncertainty of about ±10° in the derived FCaF angle seems likely.

To determine the shape of the potential-energy surface of calcium difluoride, we calculated the total energy at the CCSD(T)/cc-pCV5Z/cc-pV5Z level of theory at 162 points in the vicinity of the equilibrium configuration. The computed energies ranged to approximately 10000 cm^{-1} above the minimum. The potential-energy surface was then approximated by a 3D expansion along the internal valence coordinates. The internal coordinates for the CaF stretching modes were chosen as Simons−Parr−Finlan coordinates,[40] $q = (r - r_e)/r$, where r and r_e are instantaneous and equilibrium bond lengths, respectively. For the FCaF bending mode, a curvilinear displacement coordinate was used;[41] it was defined as the supplement of the valence FCaF angle measured from a linear reference configuration. The coordinates for the CaF stretching modes are referred to as q_1 and q_2, whereas that for the FCaF bending mode are referred to as θ. Thus, the potential-energy surface of calcium difluoride can be written as the polynomial expansion

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

where V_{lin} is the total energy at the linear configuration of the CaF_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 rms deviation of the fit was 4.2 μhartree (0.9 cm^{-1}). Because the reference configuration was assumed to be linear and the equilibrium configuration of the CaF_2 molecule was, in fact, calculated to be bent, the quadratic force constant for the FCaF bending mode (the coefficient c_{002}) is negative.

TABLE 2: Anharmonic Force Field[a] of CaF_2

i	j	k	c_{ijk}
0	0	2	−0.002596
2	0	0	1.096928
0	0	4	0.007894
1	1	0	0.300805
1	0	2	0.053826
3	0	0	−1.113681
0	0	6	−0.002606
1	2	0	−0.212019
1	0	4	−0.027027
2	0	2	−0.096135
1	1	2	−0.181620
4	0	0	−0.099556
0	0	8	0.000880
1	3	0	0.110026
1	0	6	0.008591
3	0	2	0.039045
2	2	0	0.186059
2	0	4	0.036146
1	1	4	0.093589
1	2	2	0.222725
5	0	0	1.038457
0	0	10	−0.000175
1	0	8	−0.001271
2	0	6	−0.007452
3	0	4	−0.013515
1	1	6	−0.014757
1	2	4	−0.070400
0	0	12	0.000019

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

TABLE 3: Predicted Fundamental Vibrational Wavenumbers (in cm^{-1}) for $^{40}CaF_2$ and $^{44}CaF_2$

	$^{40}CaF_2$	$^{44}CaF_2$
ν_1 (sym CaF stretch)	496.8	496.0
ν_2 (FCaF bend)	9.1	8.6
ν_3 (asym CaF stretch)	591.2	578.4
ZPE[a]	574	566

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

The anharmonic force field was used to calculate variationally the vibrational−rotational energy levels of the two isotopic species, $^{40}CaF_2$ and $^{44}CaF_2$. The predicted values of the fundamental vibrational wavenumbers are given Table 3. The calculated ν_1 and ν_3 values can be compared with the experimental gas-phase wavenumbers, which were estimated by Snelson[4] to be 520 and 595 cm^{-1}, respectively, for the main isotopomer. The predicted ν_3 fundamental coincides with the experimental value to within its error bar (±10 cm^{-1}),[4] whereas the predicted ν_1 fundamental underestimates the experimental value by 23 cm^{-1}. The $^{40}Ca-^{44}Ca$ isotopic frequency shift of the ν_3 fundamental is calculated to be 12.8 cm^{-1}, as compared with the experimental shifts of 11.2−12.3 cm^{-1} observed in various matrixes.[4,6−9] As could be expected for a heavy-ended nearly linear triatomic molecule, the $^{40}Ca-^{44}Ca$ isotopic frequency shifts of the other fundamentals are predicted to be much smaller. They amount to merely −0.5 and −0.8 cm^{-1} for the ν_2 and ν_1 fundamentals, respectively. The ν_2 fundamental is determined to be an order of magnitude lower than any of the experimental values of 120 (gas phase[5]), 163 (Kr matrix[6]), or 157 cm^{-1} (Ar matrix[7,8]). This is in line with previous theoretical studies predicting the ν_2 fundamental to lie in the range of 30−90 cm^{-1} at the correlated level of theory.[13−15,21] As for the equilibrium FCaF angle, the predicted ν_2 fundamental frequency cannot be compared directly with the values obtained in the matrix-isolation experiments. The matrix effects are expected to change significantly the shape of the FCaF bending potential-energy function and, in particular, the height of the barrier to linearity. On the other hand, the experimental wavenumber of 120 cm^{-1} that was derived by Baikov[5] from the infrared spectrum (the broad band at about 115 cm^{-1}) was measured at a temperature of about 2100 K. Because the ν_2 fundamental frequency is predicted to be anomalously low, highly excited FCaF bending energy levels are expected to be significantly populated at this temperature. As shown below, the ν_2 mode is also highly anharmonic, and the spacing of the FCaF bending energy levels increases significantly upon excitation. The ν_2

TABLE 4: 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 $^{40}CaF_2$ and $^{44}CaF_2$

	$^{40}CaF_2$		$^{44}CaF_2$	
$(v_1, v_2^{l_2}, v_3)$	energy	ΔB_v	energy	ΔB_v
$(0, 0^\circ, 0)$	0	0	0	0
$(0, 1^1, 0)$	9.1	23.0	8.6	21.6
$(0, 2^2, 0)$	26.5	45.9	25.2	43.5
$(0, 2^0, 0)$	47.1	−4.1	45.9	−6.4
$(0, 3^3, 0)$	49.6	67.6	47.4	64.5
$(0, 3^1, 0)$	70.6	32.2	68.4	29.1
$(0, 4^4, 0)$	77.3	88.2	74.0	84.4
$(0, 4^2, 0)$	98.2	60.5	94.9	56.9
$(0, 4^0, 0)$	107.6	40.0	104.4	36.1
$(0, 5^5, 0)$	108.7	107.9	104.3	103.4
$(0, 5^3, 0)$	129.4	84.4	125.0	80.1
$(0, 5^1, 0)$	142.3	64.2	137.9	59.4
$(0, 6^6, 0)$	143.4	126.8	137.7	121.7
$(0, 6^4, 0)$	163.7	106.2	158.1	101.3
$(0, 6^2, 0)$	178.3	87.2	172.7	82.3
$(0, 6^0, 0)$	183.7	78.1	178.1	73.2
$(1, 0^0, 0)$	496.8	−30.1	496.0	−28.5
$(0, 0^0, 1)$	591.2	−14.6	578.4	−14.5

fundamental transition can thus be expected to lie at the low-wavenumber end of the absorption feature[5] centered at 115 cm^{-1}.

Table 4 lists some predicted low-lying vibrational−rotational energy levels of both isotopomers in question. Because the barrier to linearity of the CaF_2 molecule was found to be quite low, calcium difluoride can be considered as a nonrigid linear molecule undergoing highly anharmonic FCaF bending motion. Therefore, the quantum numbers v_2 and l_2 for the doubly degenerate bending mode of a linear molecule were used in this study to label the FCaF bending energy levels. In this linear-molecule perspective, the ν_2 fundamental corresponds to the $(v_1, v_2^{l_2}, v_3) = (0, 1^1, 0)$ energy level. In an alternative bent-molecule picture,[42,43] the energy levels can be labeled by the FCaF bending (n) and rotational (J, k) quantum numbers. The quantum number n is the number of nodes in a FCaF bending wave function over the range $(0, \pi)$. k is the quantum number for the component of the rotational angular momentum along the molecule-fixed a axis ($|k| = K_a$). The quantum numbers n and k can be related to the vibrational quantum numbers v_2 and l_2 used here by relations $v_2 = 2n + |k|$ and $l_2 = k$. Note that for a nearly linear triatomic molecule undergoing highly anharmonic bending motion, both notations can be legitimately applied. Moreover, because of strong vibration−rotation interactions, the quantum numbers v_2 and l_2 (or alternatively n and k) can only be used as near quantum numbers.

The location of the FCaF bending energy levels relative to the bending potential-energy function is shown in Figure 1. The function depicted is a slice through the potential-energy surface $V(q_1, q_2, \theta)$ for the CaF bond length fixed at its reference value

$$V(q_1 = 0, q_2 = 0, \theta) = -570\theta^2 + 1733\theta^4 - 572\,\theta^6 + 193\theta^8 - 38\theta^{10} + 4\theta^{12} \quad (2)$$

where the potential energy and θ coordinate are given in wavenumbers and radians, respectively. The function $V(q_1 = 0, q_2 = 0, \theta)$ has a minimum at the FCaF angle of 156° with a barrier to linearity of 50 cm^{-1}, and it differs only insignificantly from the minimum-energy path along the FCaF bending coordinate θ. By solving the 1D Schrödinger equation with the potential-energy function of eq 2, the ground FCaF bending state was calculated to lie 25 cm^{-1} below the top of the barrier to linearity. The classical turning points for this state are located at the FCaF angle of 167 and 148°.

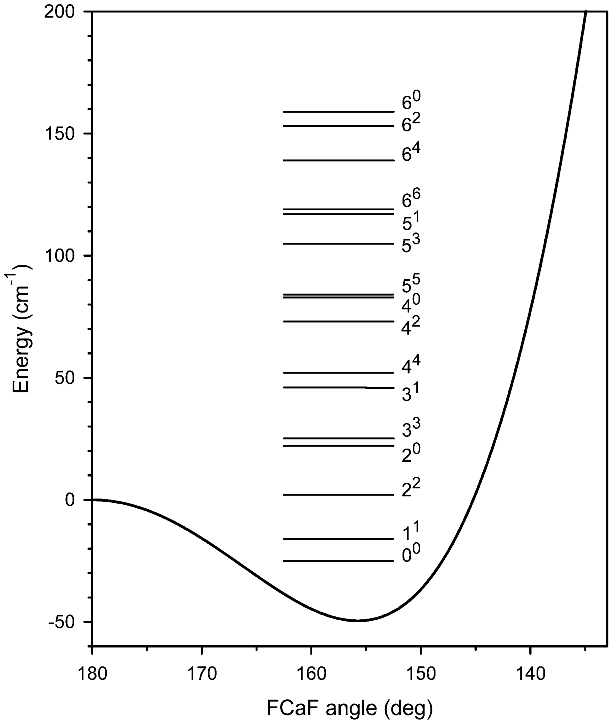

Figure 1. The FCaF bending potential-energy function and location of the $v_2^{l_2}$ energy levels for the main CaF_2 isotopomer.

The spacing of the FCaF bending energy levels changes significantly upon excitation, thus reflecting the high anharmonicity of the ν_2 mode. For example, the $(v_2 + 1)^1 \leftarrow v_2^0$ transition wavenumbers are predicted to be 23.5, 34.7, 49.8, 62.6, and 76.1 cm^{-1} for v_2= 2, 4, 10, 20, and 40, respectively. The rotationless energies of these v_2^0 states are calculated to be 47.1, 107.6, 366.2, 931.2, and 2325.0 cm^{-1}, respectively. Transitions between the FCaF bending energy levels thus span a broad region extending from the submillimeter wave into the far-infrared region. In the context of the experimental study by Baikov[5] (discussed above), we note that even the $v_2^{l_2} = 40^0$ state is significantly populated at a temperature of 2100 K. By using a Boltzmann distribution, its population factor is calculated to be about 0.2 of that for the ground vibrational state. At such high temperatures, the significant fraction of the CaF_2 molecules populates highly excited ν_2 energy levels, leading to the maximum of infrared absorption due to the FCaF bending motion observed in the far-infrared region.

For each vibrational energy level, the effective rotational constant B_v was then determined by fitting an odd-order power series in $(J + 1)$ to the calculated rotational transition energies. The effective rotational constant B_0 for the ground vibrational state of the $^{40}CaF_2$ and $^{44}CaF_2$ isotopic species is determined in this way to be 3394.4 and 3394.0 MHz, respectively. Varying the equilibrium structural parameters of calcium difluoride within their estimated error bars (± 0.002 Å for the CaF bond length and ± 1° for the FCaF angle) results in a change of the B_0 value of about ± 10 MHz. The predicted changes in the effective rotational constant due to excitation of the vibrational modes (ΔB_v) are also listed in Table 4. As can be seen, the effective rotational constant B_v changes substantially and quite irregularly with excitation of the FCaF bending mode. In particular, the rotational constant for the excited $v_2^{l_2} = 2^0$ state is predicted to be smaller than that of the ground vibrational state. The determined pattern of the effective rotational constants in the excited ν_2 states is highly anomalous in the usual semirigid

TABLE 5: Harmonic Wavenumbers ω_i and Anharmonic Constants x_{ij}(in cm^{-1}) of $^{40}CaF_2$

ω_1	502.8	x_{11}	−1.8
ω_2	16.9	x_{22}	1.7
ω_3	596.7	x_{33}	−1.5
		x_{12}	0.1
		x_{13}	−4.7
		x_{23}	−0.2

TABLE 6: Total Energy[a] of CaF_2 (in cm^{-1}) as a Function of the FCaF Angle that was Determined Using the cc-pCV5Z/cc-pV5Z Basis Set at Various Levels of Theory

∠(FCaF)	180	170	160	150	140	130
HF	0	−4.3	−0.1	59.5	242.2	626.0
MP2	0	−16.7	−47.3	−41.5	69.3	362.4
CCSD	0	−12.5	−31.5	−8.1	125.4	445.0
CCSD(T)	0	−16.0	−44.7	−35.8	78.3	373.8
ΔE_{corr}[b]	0	−11.7	−44.6	−95.3	−163.9	−252.2

[a] Relative to the total energy for the linear configuration that was calculated for the CaF bond length of 2.0124 Å. The total energy for the linear configuration is calculated to be −875.899455 (HF), −876.818693 (MP2), −876.820453 (CCSD), and −876.851882 hartree (CCSD(T)). [b] Correlation energy at the CCSD(T) level, relative to the correlation energy for the linear configuration of −0.952427 hartree.

molecule perspective because it resembles neither that characteristic of a linear molecule nor that of a well-bent molecule. A similar pattern of the effective rotational constants in the excited bending states has been recently observed experimentally[44] and predicted theoretically[45,46] for two halofulminates, ClCNO and BrCNO. However, changes in the effective rotational constant B_v due to the excitation of the CaF stretching modes, ν_1 and ν_3, are consistent with what is usually expected for small-amplitude stretching modes. For the $^{40}CaF_2$ isotopomer, the *l*-type doubling constant q_v is calculated to be 43.5, 23.4, and 20.0 MHz for the $v_2^{l_2} = 1^1$, 3^1, and 5^1 states, respectively. For the $^{44}CaF_2$ isotopomer, the corresponding constants q_v are determined to be 45.4, 24.0, and 20.2 MHz.

The vibrational energy levels of calcium difluoride can be further characterized by the harmonic frequencies ω_i and anharmonicity constants x_{ij}. The values predicted for the main $^{40}CaF_2$ isotopomer are given in Table 5. These were determined from the nine low-energy vibrational levels with $l_2 = 0$, including the fundamental, overtone, and combination levels (v_1 and $v_3 = 1$ and 2, and $v_2 = 2$, 4). The vibrational constant g_{22} for the $v_2 = 2$ state is predicted to be −5.2 cm^{-1}. For the $v_2 = 4$ and 6 states, the constant g_{22} is calculated to be smaller by a factor of ~2, being −2.6 and −1.5 cm^{-1}, respectively. Moreover, the l_2 dependence of the FCaF bending energy indicates a significant quartic contribution. The quartic anharmonic constant g_{2222} is determined to be 0.04 and 0.01 cm^{-1} for the $v_2 = 4$ and 6 states, respectively. The harmonic frequencies predicted in this study are consistent with those found previously at the correlated level of theory,[13−15,21] being 479−554, 30−90, and 549−656 cm^{-1} for the ν_1, ν_2, and ν_3 modes, respectively. Note that, in the previous studies, the harmonic frequency of the FCaF bending mode was determined for calcium difluoride treated as a bent molecule; therefore, it corresponds to the $v_2^{l_2} = 2^0$ energy level in the linear-molecule picture adopted in this study.

The shape of the FCaF bending potential-energy function, irregular spacing of the energy levels, and unusual dependence of the effective rotational constants upon excitation of the FCaF bending mode clearly indicate that the CaF_2 molecule is quasilinear. Interpretation of the structure and vibrational−rotational spectra of calcium difluoride thus requires an explicit model of the quasilinear dynamics. To quantify the quasilinearity of the CaF_2 molecule, the parameter γ_0 can be calculated [47] as $\gamma_0 = 1 - 4[E(0, 1^1, 0)/E(0, 2^0, 0)]$. Here, $E(v_1, v_2^{l_2}, v_3)$ denotes the vibrational−rotational term value determined for $J = l_2$. The parameter γ_0 ranges from −1, for an ideal linear molecule, to +1, for an ideal bent molecule. From the calculated energy levels of the main $^{40}CaF_2$ isotopomer, the parameter γ_0 is determined to be 0.23.

To estimate intensities of rotational transitions, we calculated the electric dipole moment of calcium difluoride at the CCSD(T)/cc-pCV5Z/cc-pV5Z level of theory using the finite field approach. For the equilibrium configuration, the dipole moment was determined to be 3.217 D. Upon inclusion of the diffuse basis-set functions for fluorine (aug-cc-pV5Z), this value changes insignificantly to 3.220 D. The electric dipole moment of the CaF_2 molecule was previously[14] determined at the MP2/spd level of theory to be 3.340 D. Note that, in the linear-molecule picture of calcium difluoride, there will be no pure rotational transitions because the electric dipole moment for the equilibrium configuration is calculated to lie along the molecule-fixed *b* axis. The *b*-type spectrum of calcium difluoride will thus consist of "perpendicular" vibrational−rotational transitions with the selection rules $\Delta v_2 = \pm 1$, $\Delta l_2 = \pm 1$, and $\Delta J = 0, \pm 1$; however, in the alternative bent-molecule picture, these transitions can be viewed as pure *b*-type rotational transitions with the selection rules $\Delta n = 0$ and $\Delta k = \pm 1$. Because the calculated dipole moment depends strongly on the FCaF angle and the ν_2 mode is predicted to be highly anharmonic, large vibrational averaging effects in intensities of the rotational transitions are expected to be observed experimentally. Using the HF wave function, the charge distribution was computed by the Mulliken population analysis to be −0.71e and +1.42e at the F and Ca atoms, respectively. The calcium s, p, and d basis-set functions were found to be populated with 6.03, 12.09, and 0.31 electrons, respectively. This occupation changes merely by some 0.01e upon going from the linear to well-bent configuration of the CaF_2 molecule. As already noted by Kaupp et al.,[19] the absolute d valence population for calcium in the CaF_2 molecule is much higher than the absolute s and p populations.

To investigate the effect of electron correlation on the shape of the FCaF bending potential-energy function, we performed the calculations at various levels of theory, namely Hartree−Fock (HF), second-order Møller−Plesset (MP2), and coupled-cluster (CCSD and CCSD(T)). The quintuple-ζ basis set was used, and the CaF bond length was fixed at the reference value. The potential-energy functions thus determined are given in Table 6 and are also shown in Figure 2. At the HF level, the CaF_2 molecule is predicted to be barely bent at equilibrium. The potential-energy function is determined to be extraordinary flat in the vicinity of a minimum (at the FCaF angle of 166°). The HF total energy changes by less than ± 6 cm^{-1} (± 30 μhartree) for the FCaF angle varying from 180° to 158°. The inclusion of the correlation effects within the perturbational MP2 framework favors the bent configuration, with a minimum at the FCaF angle of 155° and a barrier to linearity of 53 cm^{-1}. Changes in the shape of the potential-energy function upon accounting for the correlation effects by both coupled-cluster methods are similar. The potential-energy function predicted at the CCSD(T) level of theory is nearly identical (within about 10 cm^{-1} in the region under consideration) with that predicted at the MP2 level. As shown by results of Table 6, the electron-correlation effects play an important role in determining the shape of the FCaF bending potential-energy function. In fact, this shape is due to a balance between changes in the HF total

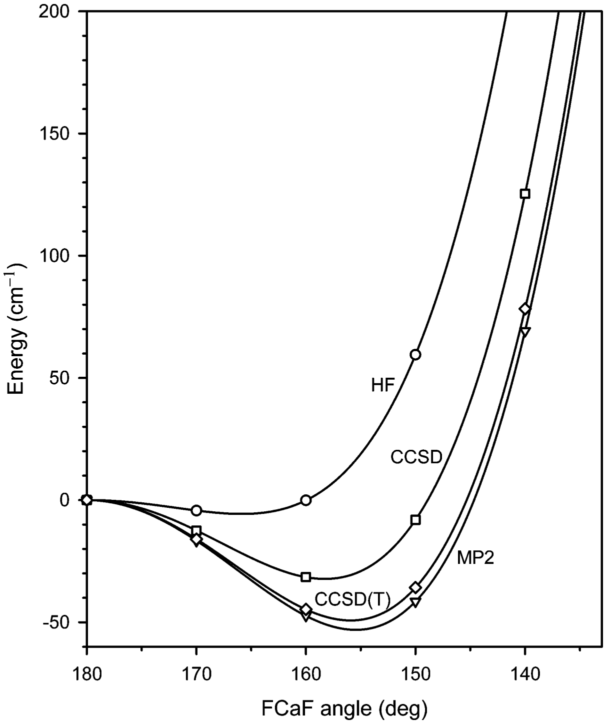

Figure 2. The (relative) total energy of calcium difluoride as a function of the FCaF angle that was determined using the cc-pCV5Z/cc-pV5Z basis set at the HF, MP2, CCSD, and CCSD(T) levels of theory. The functions are drawn to a common scale.

and correlation energies with the FCaF angle. The correlation energy falls with the decreasing FCaF angle, whereas the HF total energy raises. At large FCaF angles, a change in the correlation energy predominates slightly over that in the HF total energy, thus resulting in the highly anharmonic FCaF bending potential-energy function with a minimum at the bent configuration.

Because the relativistic effects might be important for determining the shape of the FCaF bending potential-energy function,[18] expectation values of the mass−velocity and one-electron Darwin contact term integrals[48] were calculated by the single-reference configuration interaction method including single and double excitations, CISD, in conjunction with the cc-pCV5Z/cc-pV5Z basis set. For the linear configuration, the scalar relativistic correction to the total energy was determined to be −3.023156 hartree. The correction appeared to be essentially independent of the FCaF angle because it was found to change evenly by merely 12 μhartree (2.6 cm^{-1}) upon varying the FCaF angle from 180° to 130°. Upon the inclusion of the scalar relativistic corrections, the barrier to linearity of calcium difluoride thus decreases insignificantly by about 1 cm^{-1}.

In conclusion, the high-quality ab initio approach has been applied to characterize the 3D potential-energy surface and vibrational−rotational energy levels of calcium difluoride. The CaF_2 molecule was confirmed to be indeed quasilinear. The FCaF bending potential-energy function was determined to be highly anharmonic, with a barrier to linearity of 54 cm^{-1}. The electron-correlation effects were shown to play an important role in determining the shape of this function. The pattern of FCaF bending−rotational energy levels was predicted to be anomalous in the usual semirigid molecule perspective. In particular, the ν_2 fundamental was determined to be only 9 cm^{-1}. The vibrational and rotational constants of various energy levels of the $^{40}CaF_2$ and $^{44}CaF_2$ isotopic species are reported. Because of the large amplitude and high anharmonicity of the FCaF bending mode, the variational treatment in conjuction with the rigorous vibration−rotation Hamiltonian is necessary for calculating the energy levels of calcium difluoride from the potential-energy surface. Because of the combination of low volatility of calcium difluoride and expected high irregularity of its vibrational−rotational spectrum, the CaF_2 molecule may appear as a challenge for experimental spectroscopic studies in the gas phase; therefore, we hope that the results reported in this study will be a useful guide for characterizing this interesting species by high-resolution spectroscopic techniques.

Acknowledgment. We thank Dr. Brenda P. Winnewisser and Dr. Manfred Winnewisser for critically reading and commenting on the manuscript. J. K. thanks also Dr. Stuart Carter for providing a copy of the RVIB3 program.

References and Notes

(1) Akishin, P. A.; Spiridonov, V. P. *Kristallografiya* **1957**, *2*, 475.

(2) Wharton, L.; Berg, R. A.; Klemperer, W. *J. Chem. Phys.* **1963**, *39*, 2023.

(3) Büchler, A.; Stauffer, J. L.; Klemperer, W. *J. Chem. Phys.* **1964**, *40*, 3471.

(4) Snelson, A. *J. Phys. Chem.* **1966**, *70*, 3208.

(5) Baikov, V. I. *Opt. Spektrosk.* **1968**, *25*, 356.

(6) Calder, V.; Mann, D. E.; Seshadri, K. S.; Allavena, M.; White, D. *J. Chem. Phys.* **1969**, *51*, 2093.

(7) Ramondo, F.; Rossi, V.; Bencivenni, L. *Mol. Phys.* **1988**, *64*, 513.

(8) Ramondo, F.; Bencivenni, L.; Nunziante Cesaro, S.; Hilpert, K. *J. Mol. Struct.* **1989**, *192*, 83.

(9) Beattie, I. R.; Jones, P. J.; Young, N. A. *Inorg. Chem.* **1991**, *30*, 2250.

(10) Gole, J. L.; Siu, A. K. Q.; Hayes, E. F. *J. Chem. Phys.* **1973**, *58*, 857.

(11) Yarkony, D. R.; Hunt, W. J.; Schaefer, H. F., III. *Mol. Phys.* **1973**, *26*, 941

(12) Klimenko, N. M.; Musaev, D. G.; Charkin, O. P. *Zh. Neorg. Khim.* **1984**, *29*, 639.

(13) Dyke, J. M.; Wright, T. G. *Chem. Phys. Lett.* **1990**, *169*, 138.

(14) von Szentpály, L.; Schwerdtfeger, P. *Chem. Phys. Lett.* **1990**, *170*, 555.

(15) Salzner, U.; Schleyer, P. v. R. *Chem. Phys. Lett.* **1990**, *172*, 461.

(16) DeKock, R. L.; Peterson, M. A.; Timmer, L. K.; Baerends, E. J.; Vernooijs, P. *Polyhedron* **1990**, *9*, 1919.

(17) Wright, T. G.; Lee, E. P. F.; Dyke, J. M. *Mol. Phys.* **1991**, *73*, 941.

(18) Seijo, L.; Barandiaran, Z.; Huzinaga, S. *J. Chem. Phys.* **1991**, *94*, 3762.

(19) Kaupp, M.; Schleyer, P. v. R.; Stoll, H.; Preuss, H. *J. Am. Chem. Soc.* **1991**, *113*, 6012.

(20) Kaupp, M.; Schleyer, P. v. R. *J. Am. Chem. Soc.* **1992**, *114*, 491.

(21) Hassett, D. M.; Marsden, C. J. *J. Mol. Struct.* **1995**, *346*, 249.

(22) Wang, S. G.; Schwarz, W. H. E. *J. Chem. Phys.* **1998**, *109*, 7252.

(23) Levy, J. B.; Hargittai, M. *J. Phys. Chem. A* **2000**, *104*, 1950.

(24) von Szentpály, L. *J. Phys. Chem. A* **2002**, *106*, 11945.

(25) Hargittai, M. *Chem. Rev.* **2000**, *100*, 2233.

(26) Kaupp, M. *Angew. Chem., Int. Ed.* **2001**, *40*, 3534.

(27) Koput, J.; Carter, S.; Peterson, K. A.; Theodorakopoulos, G. *J. Chem. Phys.* **2002**, *117*, 1529.

(28) Koput, J.; Peterson, K. A. *J. Phys. Chem. A* **2002**, *106*, 9595.

(29) Koput, J.; Peterson, K. A. *J. Phys. Chem. A* **2003**, *107*, 3981

(30) Čižek, J. *J. Chem. Phys.* **1966**, *45*, 4256.

(31) Purvis, G. D., III.; Bartlett, R. J. *J. Chem. Phys.* **1982**, *76*, 1910.

(32) Raghavachari, K.; Trucks, G. W.; Pople, J. A.; Head-Gordon, M. *Chem. Phys. Lett.* **1989**, *157*, 479.

(33) Scuseria, G. E.; Lee, T. J. *J. Chem. Phys.* **1990**, *93*, 5851.

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

(35) MOLPRO-2002 is a package of ab initio programs designed by H.-J. Werner and P. J. Knowles, with contributions from R. D. Amos, A. Bernhardsson, A. Berning, P. Celani, D. L. Cooper, M. J. O. Deegan, A. J. Dobbyn, F. Eckert, C. Hampel, G. Hetzer, T. Korona, R. Lindh, A. W. Lloyd, S. J. McNicholas, F. R. Manby, W. Meyer, M. E. Mura, A. Nicklass, P. Palmieri, K. A. Peterson, R. Pitzer, G. Rauhut, M. Schütz, U. Schumann, H. Stoll, A. J. Stone, R. Tarroni, and T. Thorsteinsson.

(36) Carter, S.; Handy, N. C. *Mol. Phys.* **1986**, *57*, 175,

(37) Carter, S.; Handy, N. C. *Comput. Phys. Rep.* **1986**, *5*, 117.

(38) Handy, N. C. *Mol. Phys.* **1987**, *61*, 207.

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

(40) Simons, G.; Parr, R. G.; Finlan, J. M. *J. Chem. Phys.* **1973**, *59*, 3229.

(41) Hoy, A. R.; Mills, I. M.; Strey, G. *Mol. Phys.* **1972**, *24*, 1265.

(42) Hougen, J. T.; Bunker, P. R.; Johns, J. W. C. *J. Mol. Spectrosc.* **1970**, *34*, 136.

(43) Bunker, P. R.; Stone, J. M. R. *J. Mol. Spectrosc.* **1972**, *41*, 310.

(44) Lichau, H.; Gillies, C. W.; Gillies, J. Z.; Ross, S. C.; Winnewisser, B. P.; Winnewisser, M. *J. Phys. Chem. A* **2001**, *105*, 10065.

(45) Koput, J. *J. Phys. Chem. A* **1999**, *103*, 2170.

(46) Koput, J. *J. Phys. Chem. A* **1999**, *103*, 6017.

(47) Yamada, K.; Winnewisser, M. *Z. Naturforsch., A: Phys. Sci.* **1976**, *31*, 139.

(48) Cowan, R. D.; Griffin, D. C. *J. Opt. Soc. Am.* **1976**, *66*, 1010.