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Victor Solomonik
Ivanovo State University of Chemistry …

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University of Texas at Austin

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John F Stanton
University of Texas at El Paso

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The ground singlet and low-lying triplet electronic states of CuF_3

Victor G. Solomonik[1], James E. Boggs*, John F. Stanton

Department of Chemistry and Biochemistry, Institute for Theoretical Chemistry, The University of Texas at Austin, Austin, TX 78712, USA

Abstract

A computational study of the structure and properties of the ground and low-lying excited electronic states of the CuF_3 molecule is reported in this paper. Highly sophisticated methods were used, including the coupled-cluster singles and doubles level augmented by a perturbative correction for connected triple excitations, and the equation of motion coupled cluster method in the singles and doubles approximation. In agreement with a previous quantum chemical calculation, the present results predict a T-shaped C_{2v} equilibrium geometry for the singlet $^1A_1$ state, as expected. The triplet electronic states of CuF_3 were investigated for the first time. The lowest triplet, $^3A'_2$, is only 1700 cm^{-1} above the ground $^1A_1$ state and corresponds to a trigonal planar D_{3h} equilibrium structure. The ^3E triplet state was found to lie above the $^3A'_2$ state by 11 000 cm^{-1}. © 2000 Elsevier Science B.V. All rights reserved.

Keywords: Low-lying excited state; Equation of motion; Coupled-cluster method

1. Introduction

The CuF_3 molecule is one of the simplest tri-coordinated copper systems. It may serve as a model of other inorganic Cu^{III} systems in which a copper atom is bonded to strongly electronegative atoms [1]. A knowledge of the properties of CuF_3 may also be helpful for revealing the regularities in the structure and chemical bonding patterns of transition metal compounds. Unfortunately, the molecular structure of CuF_3 has not yet been well characterized. There are no published experimental structural studies of this molecule, and the only previous theoretical

investigation of CuF_3 was performed by Dorigo et al. [2], employing a medium-sized basis set at the Hartree–Fock and MBPT(2) levels of theory. Geometry optimization performed for the closed-shell electronic state gave a T-shaped (C_{2v}) equilibrium structure as expected since it was postulated [3] (see also references cited in Dorigo et al. [2]) that CuX_3 systems prefer a T-shaped structure due to a first-order Jahn–Teller distortion of the trigonal planar D_{3h} structure. However, the triplet states were not investigated. A study of the open-shell electronic states for CuF_3 should be useful to help elucidate the nature of chemical bonding in CuX_3 systems, and is a principal topic of this paper.

2. Computational methods

All calculations were carried out using a local version of the ACES II program package [4]. Standard basis sets of near triple-zeta quality augmented with d

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* Corresponding author. Tel.: + 1-512-471-7525; fax: + 1-512-471-8696.

E-mail addresses: sol@icti.ivanovo.su (V.G. Solomonik), james.boggs@mail.utexas.edu (J.E. Boggs).

[1] Permanent address: Department of Physics, Ivanovo State University of Chemical Sciences and Technology, Engels St. 7, Ivanovo 153460, Russia.

Table 1

Equilibrium geometries (R_1 is an equilibrium axial Cu–$F_{(1)}$ bond distance; R_2 is an equilibrium bond distance of the other two symmetrically equivalent bonds, Cu–$F_{(2)}$ and Cu–$F_{(3)}$; α is an equilibrium bond angle $\alpha_e(F_{(1)}–Cu–F_{(2)}) = \alpha_e(F_{(1)}–Cu–F_{(3)}))$ and the energies of the singlet and triplet electronic states of the CuF_3 molecule

Electronic state	Method[a]	R_1 (Å)	R_2 (Å)	α (deg)	Energy (au)	h (cm^{-1})
$^1A_1$	RHF	1.6642	1.6632	100.8	−1937.269006	0
(C_{2v})	MBPT(2)	1.6947	1.7021	93.4	−1938.849782	0
	SDQ–MBPT(4)	1.7305	1.7148	95.4	−1938.837063	0
	CCSD(T)	(1.7305)[b]	(1.7148)[b]	(95.4)[b]	−1938.849600	0
$^3A_2'$	UHF	1.6811	1.6811	120	−1937.299659	−6727
(D_{3h})	MBPT(2)	1.6890	1.6890	120	−1938.823863	5688
	SDQ–MBPT(4)	1.7025	1.7025	120	−1938.812416	5409
	CCSD(T)	1.7171	1.7171	120	−1938.841807	1710
$^3B_2$	UHF	2.5566	1.7428	90.9	−1937.378175	−23960
(C_{2v})	MBPT(2)	2.4775	1.7309	91.0	−1938.833951	3474
	SDQ–MBPT(4)	2.4615	1.7297	91.0	−1938.811640	5580
	CCSD(T)	(2.4615)[b]	(1.7297)[b]	(91.0)[b]	−1938.817397	7068

[a] RHF and UHF—spin-restricted and unrestricted Hartree–Fock methods; MBPT(2)—second-order many-body perturbation theory; SDQ–MBPT(4)—fourth-order MBPT in which triple excitation effects are ignored; CCSD(T)—coupled cluster singles and doubles (CCSD) method [11] augmented by a perturbative correction for connected triple excitations [12,13].

[b] Fixed value.

and f-type polarization functions were adopted for both fluorine and copper atoms [5].[2] We believe that this basis set, coupled with the effectiveness of the CCSD(T) procedure in treating electron correlation, can give a reliable prediction of the geometric and electronic properties of CuF_3. Geometries at potential energy stationary points were optimized using analytical gradients, except those of the D_{3h} structures.[3] Harmonic vibrational frequencies and infrared (IR) intensities were calculated using analytical second derivatives of the potential energy and first derivatives of the dipole moment [10].

[2] The fluorine basis was the TZ2P basis as implemented in ACES II [4]. It comprises the 5s3p contracted sets [5] augmented with a (3/2) double-zeta set of d-type polarization functions (exponents: 3.57, 1.0575, 0.70; contraction coefficients: 0.357851, 0.759561). An exponent of the 5th s-type primitive basis function is equal to 66.70 (66.73 in the original Dunning's paper). The copper basis set was the TZVP basis implemented in the GAMESS program package [6]. This is the modified s and p Wachters' (14s9p) basis [7], augmented with the (6/3) triple-zeta d set published by Goddard et al. [8]. The f-type function with exponent 3.0 [9] was also added. A final copper basis set was (14s11p6dlf) $\rightarrow$ (10s8p3dlf). Only the pure spherical harmonic components of d- and f-type Gaussian functions were retained in the calculations.

[3] The D_{3h} geometry equilibrium internuclear distances $R_e(M–F)$ at the MBPT(2) and CCSD(T) levels were computed numerically using a polynomial fit of energies calculated for a grid of six $R(M–F)$ values (the grid step was 0.02 Å).

3. Results and discussion

The molecular geometries of CuF_3 computed at the CCSD(T) level of theory are listed in Table 1. Results at several intermediate theoretical levels are also shown to illustrate the importance of the high-level correlation treatment that we have adopted. In contrast to the previous theoretical study [2], we found open-shell UHF wave functions that have a lower energy than the singlet RHF wave function for both D_{3h} and C_{2v} geometries. Nevertheless, as expected, electron correlation favors the relative stability of the closed-shell $^1A_1$ state, which appears to be the true ground state of the molecule. The calculations result in an equilibrium geometry of C_{2v} symmetry for this state with an axial Cu–$F_{(1)}$ bond longer than the other two symmetrically equivalent bonds, Cu–$F_{(2)}$ and Cu–$F_{(3)}$, by 0.015 Å. The equilibrium bond angles $\alpha_e(F_{(1)}–Cu–F_{(2)}) = \alpha_e(F_{(1)}–Cu–F_{(3)})$ are quite close to 90°, thereby resulting in a nearly T-shaped structure.[4] The distortion from D_{3h} symmetry results from a first-order Jahn–

[4] The computed values of the total energy and equilibrium geometry parameters of the CuF_3 molecule in $^1A_1$ state listed in Table 1 may be compared to that calculated at the MBPT(2) level in Ref. [2]: $E = −1937.66913$ a.u., $R_1 = 1.726$ Å, $R_2 = 1.703$ Å, $\alpha = 92.6°$.

Teller effect; the nominal electron configuration of the high symmetry structure is $(e'')(a'_1)^2(e')^2$, as expected based on qualitative arguments [3] (see also references cited in Dorigo et al. [2])

The SDQ–MBPT(4) harmonic vibrational frequencies in cm^{-1} and IR intensities in km/mol (given in parentheses) of the $^1A_1$ state are: 636(2), 562(7), 225(10)—a_1 symmetry; 213(28)—b_1 symmetry; 786(161), 189(12)—b_2 symmetry. The antisymmetric $Cu-F_{(2)}$, $Cu-F_{(3)}$ stretching mode located at 786 cm^{-1} has the highest IR intensity. This absorption may serve as a guide for identifying the CuF_3 molecular species in IR matrix-isolation experiments. One more potentially observable property of the CuF_3 ($^1A_1$) molecule is the dipole moment, which is 0.59 D at the SDQ–MBPT(4) level of theory.

When D_{3h} symmetry is enforced, our calculations indicate that the lowest triplet state of CuF_3 having this symmetry is $^3A'_2$ (high spin) $(e'')^4(a'_1)^2(e')^2$. Adiabatically, this triplet lies 1700 cm^{-1} above the $^1A'_1$ ground state. The potential energy surface governing planar asymmetric (e') vibrational motion in the $^3A_2$ state is greatly complicated due to the presence of a small negative eigenvalue in the UHF orbital stability matrix.[5] Harmonic vibrational frequencies calculated at the UHF level are: $\omega_1(a'_1) = 737$, $\omega_2(a''_2) = 319$, $\omega_3(e') = 2188$ and $\omega_4(e') = 279$ cm^{-1}; the anomalous value of 2188 cm^{-1} is caused by the instability (for a discussion of these effects, see Ref. [14]). The broken symmetry solution corresponds to a $^3B_2$ electronic state that adopts a strongly asymmetric geometry at the UHF level. Qualitatively, this behavior persists at the MBPT(2) level of theory, but SDQ–MBPT(4) and single-point CCSD(T) calculations indicate that the symmetric D_{3h} ($^3A_2$) structure is lower in energy. The problem here is simply due to the fact that the reference function used in the calculation for the $^3B_2$ states does not correlate with that used for the $^3A'_2$ state, but rather to one of the three symmetry-equivalent solutions to the UHF equations that do not transform as pure irreducible representations of the D_{3h} point group. While the CCSD(T) calculations strongly suggest that the computed $^3B_2$ state of C_{2v} symmetry is

an artifact of the orbital instability, another procedure was followed to verify this supposition. Specifically, the $^3A'_2$ state was studied with the Brueckner coupled-cluster doubles (B-CCD) method [15]. B-CCD is known to be particularly suitable for problems of this kind as it employs orbitals that are optimized at the correlated level of theory, and therefore avoids problems associated with reference function instabilities and near-instabilities [15].[6] Following this procedure, the minimum energy was found at $R_e = 1.698$ Å. Harmonic vibrational frequencies of e' symmetry calculated by numerical differentiation [16] of the B-CCD energy were found to be 775 and 155 cm^{-1}. It should be noted that the former is considerably more reasonable than the value obtained at the UHF level, and supports the idea that the D_{3h} structure of $^3A'_2$ symmetry is a minimum on the potential energy surface of CuF_3.

Low-lying excited triplet states at the D_{3h} conformation were characterized with the equation-of-motion coupled cluster method in the singles and doubles approximation [17]. All the excited triplet states lie above the $^3A'_2$ reference-state by more than 6000 cm^{-1}. The vertical excitation energies computed at the $^3A'_2$ state CCSD(T) geometry are equal to 6340 cm^{-1} for the $^3A''_2$, $(e'')^3(a'_1)^2(e')^3$ state, 7010 cm^{-1} for the $^3A''_1$, $(e'')^3(a'_1)^2(e')^3$ state, and 10 980 cm^{-1} for the $^3E'$, $(e'')^4(a'_1)^1(e')^3$ state.

The orbitally-degenerate $^3E'$ electronic state should be distorted to lower energy C_{2v} structures due to the Jahn–Teller effect. However, the Jahn–Teller distortion energy is expected to be much less than the splitting between the lowest $^3A'_2$ and excited $^3E'$ triplet electronic states.

In conclusion, we should note that the theoretical parameters of both the singlet and triplet state of CuF_3 are strongly influenced by electron correlation. Lower theoretical levels such as the MBPT(2) method are obviously unable to provide an adequate treatment in this difficult case. The present results clearly show the importance of a sufficiently complete

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[5] One negative eigenvalue of the orbital rotation hessian was found within each one of the four irreducible representations of the computational symmetry point group, C_{2v}.

[6] The frequencies were determined numerically using single-sided numerical differentiation. As a result of the small magnitude of the force constants, a certain amount of numerical imprecision is unavoidable. Uncertainty in the quoted values is about ± 20 cm^{-1}. Nevertheless, there is no question that a stable D_{3h} structure is predicted at the B-CCD level and the force constants for the e' vibrational motion are physically reasonable.

accounting for electron correlation effects in theoretical studies of copper compounds.

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