Jahn−Teller Effect in VF_3

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A computational study of the two lowest-lying electronic states, $^3A'_2$ and $^3E''$, of the VF_3 molecule is reported. 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 contrast to previous theoretical and experimental data, the present results predict the $^3E''$ state to be the ground electronic state of VF_3 in its trigonal planar D_{3h} conformation. The $A^3A'_2$ state is 1300 cm^{-1} above the X^3E'' state. The Jahn−Teller (JT) effect in the X^3E'' state was studied. The three equivalent minima on the Jahn−Teller surface corresponding to the $^3B_1$ minimum are 270 cm^{-1} below the D_{3h} energy and separated by only 24 cm^{-1} barriers corresponding to $^3A_2$ saddle points. The JT distortions of the D_{3h} structure are appreciable; at the $^3B_1$ minimum (C_{2v} symmetry), the molecule has one long V−F bond with R_{1e} (V−$F_{(1)}$) = 1.768 Å, two short bonds with R_{2e} (V−$F_{(2)}$) = R_{3e} (V−$F_{(3)}$) = 1.748 Å, and the bond angle $\alpha_e(F_{(2)}-V-F_{(3)})$ = 129°. The available experimental data on the VF_3 molecular structure and spectra (gas-phase electron diffraction and matrix IR and Raman spectroscopy) are discussed in light of the present results.

I. Introduction

The molecular structure and vibrational spectrum of VF_3 have been studied both theoretically[1,2] and experimentally by high-temperature gas-phase electron diffraction[3] and by IR and Raman matrix-isolation spectroscopy.[4] Quantum chemical spin-restricted open-shell Hartree−Fock (ROHF) calculations predict a planar trigonal D_{3h} equilibrium structure[1,2] and a ground electronic state of $^3A'_2$ symmetry.[1] Both electron diffraction[3] and vibrational spectroscopy[4] data were interpreted on the basis of the symmetrical D_{3h} equilibrium structure of VF_3. Thus, a consensus apparently exists on the structure of this molecule. However, the problem of the molecular structure of VF_3 may be much more complicated than has been anticipated, since the molecule may possess very low-lying excited electronic states. ROHF calculations[1] predict that the molecule has a low-lying electronic state of $^3E''$ symmetry, which is above the $^3A'_2$ state by 4060 cm^{-1}. However, an electron correlation effect could change this value appreciably. Furthermore, a Jahn−Teller distortion[5,6] of the $^3E'$ state D_{3h} structure could lower its energy sufficiently to make it the ground state. These possibilities needed to be investigated. The present paper reports the results of the first high-precision quantum chemical investigation of the electronic and molecular structure of the VF_3 molecule.

II. Computational Details

The molecular properties of VF_3 were studied by the coupled-cluster singles and doubles (CCSD) method[7] augmented by a perturbative correction for connected triple excitations[8,9] (CCSD(T)) and by the equation-of-motion coupled-cluster method in the singles and doubles approximation[10] (EOM-CCSD). The calculations have been carried out using a local version of the ACES II program package.[11] Standard basis sets were adopted for both fluorine and metal atoms. The fluorine basis was a triple-ζ plus double polarization (TZ2P) one, as implemented in the ACES II program.[12] The s and p functions for the metal atoms, taken from Wachters' (14s9p5d) basis,[13] were contracted to [10s8p] with the following modifications: the most diffuse s function was removed, one s function spanning the 3s−4s region was added, and two p functions were added to describe the 4p region. The (6/3) triple-ζ d set was that published by Goddard et al.[14,15] The f-type polarization functions were also added.[16] The final contracted metal basis set (14s11p6d1f) → [10s8p3d1f] was of near triple-ζ quality. Only the pure spherical harmonic components of d-type and f-type Gaussian functions have been retained in the calculations. Thus, the basis set adopted for the VF_3 molecule comprises 128 functions. The minimum energy D_{3h} internuclear distance R_e(M−F) and the wavenumber ω_1, of the totally symmetric vibration were computed numerically using a polynomial fit of the energies calculated for a grid of five R(M−F) values.

III. Results and Discussion

Our procedure was to start with a D_{3h} structure and the $^3A'_2$, $(e'')^2$ electronic state, which was expected to be the ground state of VF_3 according to the results of the previous investigations. The spin-unrestricted Hartree−Fock (UHF) wave function was used as a reference function in the electron correlation computations. The UHF equilibrium geometry in the $^3A'_2$ state has D_{3h} symmetry with R_e(V−F) =1.7773 Å (E_{min} = −1241.518 305 au). The UHF harmonic vibrational frequencies (in cm^{-1}) and IR intensities (in km/mol, given in parentheses) of this state, calculated using analytical second derivatives of the energy and first derivatives of the dipole moment, are $\omega_1(a'_1)$ = 692, $\omega_2(a''_2)$ = 157 (128), $\omega_3(e')$ = 784 (583), $\omega_4(e')$ = 187 (48). These results are very close to those of the ROHF calculations reported before.[2] The CCSD(T) R_e(V−F) = 1.7770

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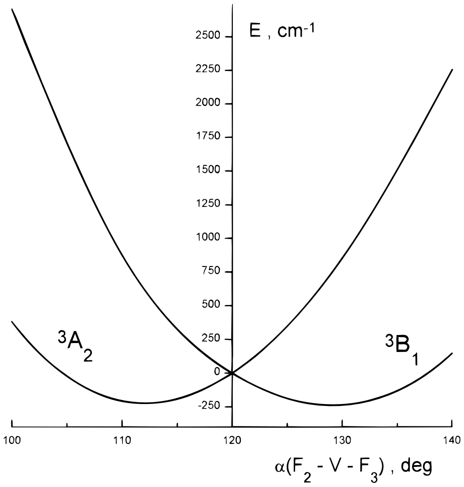

Figure 1. VF_3 Jahn−Teller C_{2v} energy as a function of bond angle $\alpha(F_{(2)}-V-F_{(3)})$.

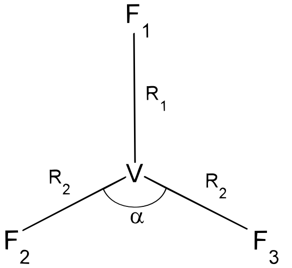

Figure 2. Internal coordinate notation for VF_3 of C_{2v} symmetry.

TABLE 1: C_{2v} Symmetry Equilibrium Geometries and Jahn−Teller Stabilization Energies ΔE_{JT} of VF_3 Calculated by EOM-CCSD Theory

	$^3A_2$	$^3B_1$
$R_{1e}(V-F_{(1)})$, Å	1.7440	1.7678
$R_{2e}(V-F_{(2)}) = R_{3e}(V-F_{(3)})$, Å	1.7605	1.7485
$\alpha_e(F_{(2)}V- V-F_{(3)})$, deg	112.2	128.7
ΔE_{JT}, cm^{-1}	245	269

Å ($E_{min} = -1242.790359$ au) and $\omega_1(a'_1) = 676$ cm^{-1} values demonstrate the lack of a strong correlation effect on these molecular properties of VF_3 in the $^3A'_2$ state. The closed-shell singlet $^1A'_1$ state was found to lie above the $^3A'_2$ state by 4004 cm^{-1} (single-point CCSD(T) calculation for a D_{3h} structure optimized at the RHF level: $R_e(V-F) = 1.7475$ Å).

The EOM-CCSD treatment of the lowest-lying electronic states was started with a D_{3h} CCSD(T) theoretical structure. The only low-lying electronic state possessing an energy close to that of the reference $^3A'_2$ state is the $^3E''$, $(a'_1)^1(e'')^1$ state. In contrast to the previous study,[1] its energy appeared to be *lower* than that of the $^3A'_2$ state; the magnitude of the difference found in our calculations is 820 cm^{-1}. In order to check the reliability of this prediction we have computed the relative energies of the two electronic states using the QRHF-CCSD(T) approach, which employs open-shell quasi-restricted Hartree−Fock (QRHF) reference functions.[17] The results obtained with QRHF-CCSD closely approximate those from CCSD calculations using UHF or ROHF reference functions.[18] The QRHF reference functions applied here were those formed from a closed-shell determinant of the VF_3^{2+} dication by adding two electrons. The QRHF-CCSD(T) relative energy of the $^3E''$ state is -1197 cm^{-1}, strongly supporting the result of the EOM-CCSD calculation. Therefore, we believe that *the $^3E''$ state is the ground electronic state of the VF_3 molecule.* The equilibrium V−F internuclear distance for the $^3E''$ (D_{3h}, constrained) state computed by the EOM-CCSD method is $R_e(V-F) = 1.7574$ Å, shorter by ca. 0.02 Å than that in the $^3A'_2$ state.[19] The $^3E''$ state energy lowering following D_{3h} geometry optimization is 147 cm^{-1}. This value combined with the previously computed vertical excitation energy gives the following estimate of the adiabatic $A^3A'_2 \leftarrow X^3E''$ excitation energy of VF_3: 967 cm^{-1} at the EOM-CCSD level or 1344 cm^{-1} at the QRHF-CCSD(T) level of theory (the latter value is presumably more reliable).

The Jahn−Teller effect in the $^3E''$ state was studied using an EOM-CCSD approach. There are two JT active vibrations (of e' symmetry): a stretch and a bend. The bend was investigated first, keeping the three $R(V-F)$ distances constant and equal to 1.7574 Å. Figure 1 displays the EOM-CCSD energies of the $^3A_2$ and $^3B_1$ electronic states arising on distortion of the planar trigonal structure from 3-fold D_{3h} symmetry to C_{2v}, computed for several values of the bond angle $\alpha(F_{(2)}-V-F_{(3)})$ (as shown in Figure 2). The interpolation procedure gave the $^3A_2$ state minimum at $\alpha = 112.1°$, lower than the $^3E''$ state energy by 224 cm^{-1}, and the $^3B_1$ state minimum at $\alpha = 129.1°$, lower than the $^3E''$ state energy by 238 cm^{-1}. Next, a complete C_{2v} geometry optimization was performed for the two states within an EOM-CCSD approach using analytical gradients.[20] The results are given in Table 1. The JT distortions of the D_{3h} structure appeared to be quite pronounced, although the pseudorotation linking equivalent C_{2v}, states is likely to be facile. At the $^3B_1$ minimum, the molecule has a bond angle $\alpha_e(F_{(2)}-V-F_{(3)}) = 129°$, one long V−F bond, and two symmetry-equivalent short bonds with a bond length difference of 0.019 Å. At the $^3A_2$ minimum, the molecule has a bond angle $\alpha_e(F_{(2)}-V-F_{(3)}) = 112°$, one short V−F bond, and two long bonds with a bond length difference of 0.017 Å. The $^3A_2$ "minimum" corresponds to the pseudorotation transition state on the potential-energy surface; the associated barrier height $[E(^3A_2)-E(^3B_1)]$ is only 24 cm^{-1}.

The low value of the JT stabilization energy and the shallow minima on the JT surface with respect to both bending and stretching JT-active vibrational coordinates shows a highly fluxional behavior of the VF_3 molecule in its ground electronic state. This feature of VF_3 coupled with the existence of a very low-lying excited electronic state extremely complicates the problem of a rigorous determination of the VF_3 molecular structure both theoretically and experimentally. The results of the computations provide evidence in favor of the multimode character of the JT effect in this molecule. This will require much more extensive theoretical treatment than that in the ordinary single-mode $E \otimes e$ case.[21]

The VF_3 molecule is also a real challenge for both gas-phase electron diffraction and spectroscopy. At high temperatures, its effective structure will presumably resemble that of a regular XY_3 molecule possessing an equilibrium geometry of D_{3h} symmetry. This was apparently the case in the electron diffraction study of VF_3 performed by Zasorin et al.[3] for the VF_3 gas temperature of 1220 K. The authors[3] concluded that the VF_3 molecule has a planar trigonal equilibrium structure of D_{3h} symmetry with an effective bond length $R_g(V-F) = 1.751$ (3) Å. This value is in agreement with the computed averaged equilibrium bond lengths in the $^3B_1$ and $^3A_2$ states, $R_e^{av}(V-F) = 1.755$ Å, and is also close to the $R_e(V-F) = 1.777$ Å theoretical value for the low-lying excited $^3A'_2$ electronic state. However, this agreement may be accidental. On the basis of the assumption of existence in the gas-phase of VF_3 of only the $^3A'_2$ state molecular species, the V−F bond distance $\Delta R = R_g - R_e$ correction estimate is equal to 0.037 Å at 1220 K.[2] A correction of similar magnitude may presumably be applied to estimate the value for the ground JT perturbed electronic state. Then the R_g(V−F) value should be equal to ca. 1.79 Å. An even larger R value might be expected because of the coexistence in the VF_3 gas phase of both the ground $^3E''$ and the excited $^3A'_2$ electronic states, since the latter possesses a longer V−F bond distance and would be strongly populated at high temperatures. If the above arguments are reasonable, there is a disagreement between the present results and the results of the electron-diffraction study of VF_3. The reason for the discrepancy is not clear. The same kind of discrepancies were noted,[2,22,23] however, for the other two transition-metal trifluoride molecules studied in the electron-diffraction work,[3] ScF_3 and CrF_3. For ScF_3, R_g(Sc−F) = 1.847(2) Å at 1750 K as derived in ref 3 but R_g(Sc−F) = 1.926(2) Å at 1600 K as measured in the other electron-diffraction study.[24] The latter value is in agreement with the R_g(Sc−F) = 1.920 Å (1600 K) derived from an ab initio data.[22] For CrF_3, R_g(Cr−F) = 1.732(2) Å at 1220 K as derived in ref 3 but R_g(Cr−F) = 1.785 Å at 1220 K as derived from ab initio data.[23] So the discrepancies are systematic and perhaps have the same source.

The IR and Raman spectra of VF_3 isolated in solid Ne and Ar were studied by Predtechenskii et al.[4] Only one band located at 649 cm^{-1} was recorded in the Raman argon matrix spectrum (neon matrix was not used in the Raman studies). Its counterpart in the IR spectrum was not observed. Therefore, the authors[4] have assigned this band to the $\nu_1(a'_1)$ totally symmetric stretching mode of VF_3 and concluded that the molecule possesses an equilibrium structure of D_{3h} symmetry. The absorptions, assigned by Predtechenskii et al. to the $\nu_3(e')$ stretching mode of VF_3 were observed in the IR spectra in both neon and argon matrices. A doublet band with maxima at 733.2 and 731.8 cm^{-1} was observed in argon matrix, and a triplet band with maxima at 742.7, 739, and 737.2 cm^{-1} was observed in a neon matrix. The multiplet structure of the bands was explained[4] as a matrix effect. The results of our study suggest another explanation of the complex structure of the bands observed in the IR spectrum of VF_3. The observed splitting of the bands in a matrix IR spectra may be due in part to the Jahn−Teller effect. The strong Jahn−Teller distortions might lead to appreciable splitting of the $\nu_3(e')$ band. For example, in the MnF_3 molecule, which exhibits strong Jahn−Teller distortions (up to 0.02 Å for bond lengths and 25° for bond angles) and a large JT stabilization energy (∼2500 cm^{-1}),[25−27] this splitting is equal to 46 cm^{-1}.[28,29] The splitting of only 1.4 cm^{-1} in Ar may be evidence in favor of a much weaker JT effect in VF_3 compared to that in MnF_3. The absence of the IR counterpart of the band at 649 cm^{-1} observed in the Raman spectrum is apparently due to the very low IR intensity of this mode and supports the conclusion for a very weak JT effect in VF_3. A subtle JT effect on the stretching region of the VF_3 vibrational spectrum observed in the work of Predtechenskii et al.[4] is in obvious agreement with the present results.

Computation of the wavenumbers and intensities in the infrared and Raman spectra of VF_3 would require much more extensive work and is beyond the scope of the present paper. Nevertheless, the present results give opportunity for some speculations regarding the stretching region of the VF_3 vibrational spectrum. As long as the JT effect on this region of the spectrum is weak, the frequency of the totally symmetric stretching vibration computed for the constrained (JT-unperturbed) D_{3h} structure of VF_3 in the $^3E''$ electronic state should not differ appreciably from the corresponding frequency computed more rigorously accounting for the JT effect. The $\omega_1(a'_1)$ harmonic frequency, computed at the EOM-CCSD level of theory, is equal to 680 cm^{-1}. The corresponding value computed for the first excited $^3A'_2$ electronic state at a comparable level of theory (CCSD) is 684 cm^{-1}. Therefore, the $\omega_1(a'_1)$ frequency is predicted to be slightly lower in the ground $^3E''$ state than that in the excited $^3A'_2$ state. The most reliable theoretical estimate of the $\omega(a'_1)$ frequency of VF_3 in the $^3A'_2$ state is that computed at the CCSD(T) level: $\omega(a'_1)$ = 676 cm^{-1}. Therefore, the corresponding frequency of VF_3 in the $^3E''$ state may be expected to lie around 670 cm^{-1}. This prediction is in a reasonable agreement with the wavenumber 649 cm^{-1} of the band observed[4] in the Raman spectrum of the Ar matrix-isolated VF_3, since the matrix shift of the band is expected to be around 10−20 cm^{-1}.

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