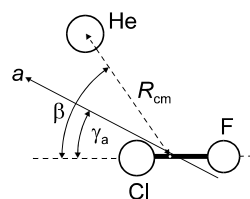


116	ClFHe	Chlorine fluoride – helium (1/1)	C_s
MW		(weakly bound complex)	(effective symmetry class)
			(large-amplitude motion)
			ClF · He

$r_0^a)$	Å		$\theta_0^a)$	deg	
	Σ_0	Σ_1		Σ_0	Σ_1
R_{cm}	3.9796(1)	3.7190(5)	$\gamma_a^b)$	13.665(15)	44.092(24)
	3.9746(26)	3.737(16)		12.93(40)	45.6(10)
He...Cl	3.4543(1)	4.0026(5)	$\beta^b)$	21.061(25)	116.216(21)
	3.4450(26)	4.011(16)		19.97(61)	114.9(9)

The He · ClF complex is highly nonrigid, undergoing large-amplitude oscillation in both angular and radial coordinates. The effect of zero-point oscillation is seen in the large difference, 22.9 cm⁻¹, between the calculated potential energy minima of –58.1 (lowest linear Σ_0) and –35.2 cm⁻¹ (excited T-shaped Σ_1) and the measured value (including zero-point energy) of 2.320 cm⁻¹. The potential surface is poorly represented as a sum of spherical atom-atom interactions. At both minima the He...Cl distance is shorter than the sum of van der Waals radii. The *ab initio* potential is too shallow since an appreciably better fit of the spectral transitions is obtained by uniformly increasing the magnitude of the interaction potential by 10%. Bound states calculated for a potential with the T-shaped minimum removed show significant differences from experiment, indicating that the T-shaped minimum does indeed exist. The large change in geometry between the Σ_0 and Σ_1 states is evidenced by the difference in rotational constants, dipole moments, and quadrupole coupling constants for each state. In addition, these values are consistent with a T-shaped Σ_1 state rather than an antilinear Σ_1 state.



^{a)} For $J = 1$ levels. The upper and lower values were obtained from the average values of Legendre polynomials $\langle P_2 \rangle$ and $\langle P_1 \rangle$, respectively.

^{b)} See figure for the definition.

Higgins, K., Tao, F.-M., Klemperer, W.: J. Chem. Phys. **109** (1998) 3048.