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The complex OC... ClF identified as a pre-chemical intermediate by rotational spectroscopy of carbon monoxide–chlorine monofluoride mixtures

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Abstract

The ground-state rotational spectra of four isotopomers of the complex OC... ClF have been observed by using a fast-mixing nozzle in a pulsed-nozzle, Fourier-transform microwave spectrometer. The spectrum of the reaction product carbonyl chloride fluoride was detected but its intensity indicated that the extent of the reaction was small. The observed spectroscopic constants B_0, D_J, χ_{aa}(Cl) and M_{bb}(Cl) were interpreted to show that the pre-chemical complex has the nuclei collinear in the order OC... ClF, with r(C... Cl) = 2.770(3) Å and the intermolecular stretching force constant k_σ = 7.03(3) N m^{-1}. There is only a minor electric charge redistribution within ClF on complex formation.

1. Introduction

Carbon monoxide and chlorine monofluoride undergo a chemical reaction in the gas phase at normal temperatures and pressures. Evidently, the reaction is vigorous and can be complex, as indicated by the following description [1] of the preparation of carbonyl chloride fluoride according to the stoicheiometry

ClF + CO = COClF.

"Streams of ClF and CO are mixed at −18°C in an iron reaction vessel. The CO must always be present in excess. The slower the rate of reaction the greater the yield of COClF." It is of interest to isolate and characterise the pre-chemical complex, i.e. the complex formed when the two molecules meet but before they can make progress along the reaction coordinate. The detailed characterisation of OC... ClF is the subject of this Letter.

Recently, we have demonstrated that a fast-mixing nozzle incorporated in a pulsed-nozzle, Fourier-transform microwave spectrometer is an effective means of forming and investigating pre-chemical complexes involving substances that would react when mixed under normal conditions [2]. For example, several complexes B... Cl_2, where B is a Lewis base, have been detected in this way [3]. Because reaction of B with Cl_2 could be precluded, it was possible to choose the bases B on the grounds of their intrinsic interest as σ- or π-electron donors rather than their inertness with respect to Cl_2, which is not a particularly desirable attribute in the context. It was then possible to examine how various properties vary along the series B... Cl_2, where B is CO, HF, C_2H_2, C_2H_4, PH_3, H_2S, HCN and NH_3, and

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thereby draw conclusions about the nature of the interaction, especially its geometrical implications and the extent of the electric charge redistribution within B. A question of interest here is the effect of replacing the nonpolar Cl_2 molecule by the interhalogen ClF. We now report the ground-state rotational spectra of four isotopomers of the pre-chemical intermediate OC...ClF and, from a detailed interpretation of the spectroscopic constants, present some of its properties.

2. Experimental

The ground-state rotational spectrum of OC...ClF was obtained by using a pulsed-nozzle, Fourier-transform microwave spectrometer [4,5]. To avoid the reaction of CO and ClF a fast-mixing nozzle [2] was used. Carbon monoxide (Aldrich) was flowed continuously down the central 0.3 mm diameter glass capillary of this device from a reservoir at ≈ 0.75 atm pressure and room temperature into the vacuum chamber of the spectrometer. The flow rate was adjusted to give a nominal pressure of $\approx 1 \times 10^{-4}$ mbar in the chamber. A mixture of $\approx 1\%$ of chlorine monofluoride in argon was pulsed, via a solenoid valve (General Valve Corp. Series 9), down the outer tube of the fast-mixing nozzle at a rate of 2 Hz from a stagnation tank having a pressure of ≈ 3 atm. Complexes OC...ClF formed at the interface of the coaxial flows of gas were polarized with microwave pulses and their rotational spectra recorded in the usual manner. Individual Cl-nuclear quadrupole hyperfine components in the observed spectra had a full width at half-maximum of ≈ 10–15 kHz (see Fig. 1) and allowed frequency measurements to be made with an estimated accuracy of 2 kHz.

The spectrum of the reaction product was also observable but weakly. On monitoring the 1_{01}–0_{00} transition of ^{35}Cl-carbonyl chloride fluoride, a known product of the CO/ClF reaction [1], we observed signals at the published frequencies of its three Cl-nuclear quadrupole hyperfine components [6] which allowed unambiguous identification of the compound. The $F = 5/2 \leftarrow 3/2$ component had a signal-to-noise ratio of approximately 5 : 1 in the time domain after averaging the signal from 80 gas pulses. The ratio of this signal to that from the $9/2 \leftarrow 7/2$ component of the $J = 3 \leftarrow 2$ transition of $^{16}O^{12}C...^{35}ClF$ under identical conditions was 1 : 70, indicating that the reaction product was present to the extent of approximately one percent or less.

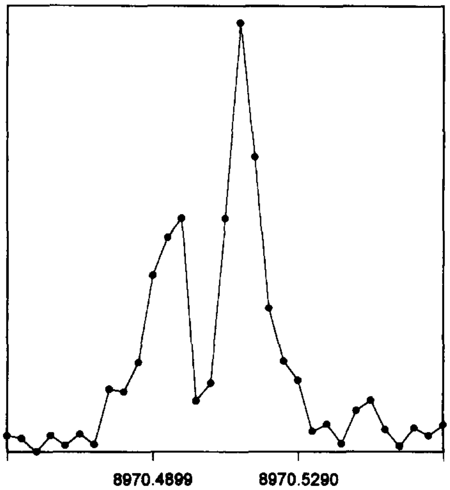

Fig. 1. Frequency domain recording of the $7/2 \leftarrow$ and $5/2$ and $9/2 \leftarrow$ and $7/2$ Cl-nuclear quadrupole hyperfine components of the $J = 3 \leftarrow 2$ transition in $^{16}O^{13}C...^{35}ClF$ observed in natural abundance. The signals from 85 gas pulses were averaged to obtain this spectrum. Adjacent dots are separated by 3.90625 kHz.

Chlorine monofluoride was prepared by the reaction of equimolar amounts of ClF_3 and Cl_2 in the presence of CsF in a prefluorinated nickel reactor fitted with an Autoclave Engineers 316 stainless steel valve (30 VM Series). After cooling to −196°C traces of non-condensible substances were pumped away. Following fractional condensation using traps at −142°C (methylcyclopentane slush) and −196°C to isolate the product, ClF was collected and stored above CsF in the original reaction vessel. ^{13}C-carbon monoxide (99 at%) was supplied by Aldrich.

3. Results

3.1. Spectral analysis

The observed ground-state rotational spectrum of OC...ClF is typical of that of a linear molecule carrying a single Cl nucleus ($I = 3/2$). The frequencies of Cl-nuclear quadrupole hyperfine components

Table 1
Observed and calculated transition frequencies of three isotopomers of ^{16}OC...ClF

$J' \leftarrow J''$	$F' \leftarrow F''$	$O^{12}C...^{35}ClF$		$O^{12}C...^{37}ClF$		$O^{13}C...^{35}ClF$	
		ν_{obs} (MHz)	$\Delta\nu$ (kHz) [a]	ν_{obs} (MHz)	$\Delta\nu$ (kHz) [a]	ν_{obs} (MHz)	$\Delta\nu$ (kHz) [a]
$3 \leftarrow 2$	$7/2 \leftarrow 7/2$	9036.3399	−0.1	9013.1276	−0.1	8934.5129	0.8
	$5/2 \leftarrow 7/2$	9053.2412	−0.4	9026.4311	0.1	8951.4167	−0.8
	$5/2 \leftarrow 3/2$	9063.3393	−0.8	9034.4225	−0.7	8961.5163	0.4
	$3/2 \leftarrow 1/2$	9063.4283	−1.0	9034.4773	−1.2	8961.6058	−0.3
	$7/2 \leftarrow 5/2$	9072.3168	−3.5	9041.4877	−2.9	8970.4952	−3.3
	$9/2 \leftarrow 7/2$	9072.3372	4.5	9041.5023	3.6	8970.5136	2.5
	$5/2 \leftarrow 5/2$	9089.2225	0.6	9054.7940	0.1	8987.4043	0.3
	$3/2 \leftarrow 3/2$	9099.2834	0.2	9062.7607	−0.1	8997.4632	−1.1
	$3/2 \leftarrow 5/2$	9125.1648	−0.2	9083.1309	−0.6	9023.3537	1.4
$4 \leftarrow 3$	$9/2 \leftarrow 9/2$	12059.0042	0.0	12025.7740	0.0	11923.2394	0.1
	$7/2 \leftarrow 5/2$	12090.7872	−1.9	12050.8295	−3.8	11955.0278	−1.5
	$5/2 \leftarrow 3/2$	12090.8152	2.9	12050.8527	5.3	11955.0548	2.0
	$9/2 \leftarrow 7/2$	12095.0008	3.8	12054.1476	2.6	11959.2425	4.1
	$11/2 \leftarrow 9/2$	12095.0008	−3.5	12054.1476	−2.3	11959.2425	−3.3
	$7/2 \leftarrow 7/2$	12107.6905	−0.2	12064.1368	0.2	11971.9340	−0.8
	$5/2 \leftarrow 5/2$	12126.7554	0.0	12079.1854	0.4	11991.0005	−0.6
$5 \leftarrow 4$	$11/2 \leftarrow 11/2$	15081.7619	1.0	–	–	–	–
	$9/2 \leftarrow 7/2$	15115.2762	3.4	15064.8698	1.8	–	–
	$7/2 \leftarrow 5/2$	15115.2762	−5.0	15064.8698	−3.1	–	–
	$11/2 \leftarrow 9/2$	15117.7635	2.6	15066.8283	2.0	–	–
	$13/2 \leftarrow 11/2$	15117.7635	−2.5	15066.8283	−1.5	–	–
	$9/2 \leftarrow 9/2$	15127.9664	−0.1	–	–	–	–
	$7/2 \leftarrow 7/2$	15151.2477	0.2	–	–	–	–

[a] $\Delta\nu = \nu_{obs} - \nu_{calc}$.

in the $J = 3 \leftarrow 2$, $4 \leftarrow 3$ and $5 \leftarrow 4$ transitions of the isotopomers $^{16}O^{12}C...^{35}ClF$, $^{16}O^{12}C...^{37}ClF$ and $^{16}O^{13}C...^{35}ClF$ are recorded in Table 1. All three species were observed in natural abundance (see Fig. 1), although some transitions of the ^{13}C isotopomer were measured using a sample of ^{13}CO (99 at%). In fact, it was also possible to observe the $\Delta F = +1$ components of the $J = 3 \leftarrow 2$ and $4 \leftarrow 3$ transitions of $^{18}O^{12}C...^{35}ClF$ in natural abundance, the measured frequencies of which are given in Table 2. Because of the extreme weakness of the $^{18}O^{12}C...^{35}ClF$ transitions, it was necessary to record them at a higher sensitivity and therefore at lower resolution. Hence, their observed frequencies have a reduced accuracy of ≈ 5 kHz.

Observed Cl-nuclear quadrupole hyperfine frequencies were fitted in an iterative nonlinear least squares analysis. The matrix of the Hamiltonian operator appropriate to a linear molecule,

$$H = B_0 J^2 - D_J J^4 - \tfrac{1}{6}\mathbf{Q}(\mathrm{Cl}) : \nabla\mathbf{E}(\mathrm{Cl}) - \boldsymbol{I} \cdot \mathbf{M}(\mathrm{Cl}) \cdot \boldsymbol{J}, \qquad (1)$$

was constructed in the coupled basis $\boldsymbol{F} = \boldsymbol{I} + \boldsymbol{J}$ and diagonalized in blocks of F. In Eq. (1) the symbols have their conventional meanings. The third and fourth terms account for the energy of interaction of the Cl-nuclear electric quadrupole moment with the electric field gradient at Cl along the molecular axis and of the Cl-nuclear magnetic moment with the magnetic field generated by the rotational motion,

Table 2
Observed and calculated transition frequencies of the isotopomer $^{18}O^{12}C...^{35}ClF$

$J' \leftarrow J''$	$F' \leftarrow F''$	$^{18}O^{12}C...^{35}ClF$	
		ν_{obs} (MHz)	$\Delta\nu$ (kHz) [a]
$3 \leftarrow 2$	$5/2 \leftarrow 3/2$	8581.6726	−0.4
	$3/2 \leftarrow 1/2$	8581.7678	0.5
	$7/2 \leftarrow 5/2$	8590.6507	−3.7
	$9/2 \leftarrow 7/2$	8590.6710	3.6
$4 \leftarrow 3$	$7/2 \leftarrow 5/2$	11448.5927	−0.3
	$9/2 \leftarrow 7/2$	11452.7979	−3.6
	$11/2 \leftarrow 9/2$	11452.8130	3.9

[a] $\Delta\nu = \nu_{obs} - \nu_{calc}$.

respectively. The matrix elements of these terms in the coupled basis are well known [7]. For a linear molecule, only the diagonal elements $\chi_{aa}(\mathrm{Cl}) = -(eQ/h)\partial^2 V/\partial a^2$ and M_{bb} of the Cl-nuclear quadrupole and spin–rotation coupling tensors, respectively, can be determined. Values of these quantities together with those of the rotational constant B_0 and the centrifugal distortion constant D_J resulting from the converged least squares fit are given in Table 3 for each of the four isotopomers of OC...ClF investigated. Because of the limited data set for $^{18}\mathrm{O}^{12}\mathrm{C}\ldots{}^{35}\mathrm{ClF}$, M_{bb} was fixed at its value in $^{16}\mathrm{O}^{12}\mathrm{C}\ldots{}^{35}\mathrm{ClF}$. This approach is justified when it is noted that M_{bb} is unchanged within experimental error by substitution of $^{13}\mathrm{C}$ in the isotopomer $^{16}\mathrm{O}^{12}\mathrm{C}\ldots{}^{35}\mathrm{ClF}$ (see Table 3). The residuals $\Delta\nu = \nu_{\mathrm{obs}} - \nu_{\mathrm{calc}}$ from the final cycles of the least squares fits are included in Tables 1 and 2. The standard deviation σ of each fit is given in Table 3 and is in each case of the same order as the estimated error of frequency measurement, namely ≈ 5 kHz for $^{18}\mathrm{O}^{12}\mathrm{C}\ldots{}^{35}\mathrm{ClF}$ but 2 kHz for the other isotopomers.

3.2. Molecular geometry

The observed ground-state rotational spectra of the four isotopomers of OC...ClF investigated are characteristic of a linear molecule but it is difficult to rule out small deviations from linearity on the basis of ground-state spectroscopic constants alone. However, the observed invariance of the $\chi_{aa}(\mathrm{Cl})$ (including $\chi_{aa}(^{37}\mathrm{Cl})$ when scaled by the ratio $Q(^{35}\mathrm{Cl})/Q(^{37}\mathrm{Cl})$ of the Cl-nuclear electric quadrupole moments [8]) to $^{18}\mathrm{O}$, $^{13}\mathrm{C}$ or $^{37}\mathrm{Cl}$ substitution means that the equilibrium conformation does not deviate substantially from collinearity. For example, if, in the equilibrium structure, the CO and ClF subunits each made of an angle 10° with the axis through their mass centres, the a axis rotations on $^{13}\mathrm{C}$ and $^{18}\mathrm{O}$ substitution would be 0.030° and 0.121°, respectively. If substitution in the CO subunit does not affect the zero-point oscillation of the ClF subunit, and hence the zero-point averaging of the $\chi_{aa}(\mathrm{Cl})$ value, this nonlinear model predicts that $\chi_{aa}(^{35}\mathrm{Cl})$ should change from $-143.998(3)$ MHz in $^{16}\mathrm{O}^{12}\mathrm{C}\ldots{}^{35}\mathrm{ClF}$ to $-144.035(3)$ MHz in $^{16}\mathrm{O}^{13}\mathrm{C}\ldots{}^{35}\mathrm{ClF}$ and $-143.882(3)$ MHz in $^{18}\mathrm{O}^{12}\mathrm{C}\ldots{}^{35}\mathrm{ClF}$. The observed values are $-144.023(3)$ MHz and $-143.96(2)$ MHz, respectively. It therefore seems unlikely that the equilibrium geometry differs significantly from linearity and this will be assumed in what follows.

Isotopic substitution at the O, C, and Cl nuclei allows the a coordinates of these atoms to be determined by the r_s method [9]. By using the change ΔI_b in I_b that accompanies isotopic substitution at the atom i in $^{16}\mathrm{O}^{12}\mathrm{C}\ldots{}^{35}\mathrm{ClF}$, the r_s coordinate of the substituted atoms can be obtained from Kraitchman's equation [10],

$$a_i^2 = \Delta I_b/\mu_s, \tag{2}$$

where $\mu_s = M\Delta m/(M + \Delta m)$ is the reduced mass for the substitution. The values of a_i referred to the principal axis system of $^{16}\mathrm{O}^{12}\mathrm{C}\ldots{}^{35}\mathrm{ClF}$ as the parent molecule are then $a_{\mathrm{O}} = 3.9056$ Å, $a_{\mathrm{C}} = 1.9568$ Å and $a_{\mathrm{Cl}} = -0.7602$ Å. When determined in weakly bound complexes, r_s coordinates obtained from zero-point moments of inertia can suffer considerable errors because of the contribution of the large amplitude intermolecular vibrations to the zero-point

Table 3
Ground-state spectroscopic constants of 4 isotopomers of OC...ClF

	$^{16}\mathrm{O}^{12}\mathrm{C}\ldots{}^{35}\mathrm{ClF}$	$^{16}\mathrm{O}^{12}\mathrm{C}\ldots{}^{37}\mathrm{ClF}$	$^{16}\mathrm{O}^{13}\mathrm{C}\ldots{}^{35}\mathrm{ClF}$	$^{18}\mathrm{O}^{12}\mathrm{C}\ldots{}^{35}\mathrm{ClF}$
B_0 (MHz)	1511.8045(2)	1506.7269(2)	1494.8334(3)	1431.5228(4)
D_J (kHz)	2.085(5)	2.080(5)	2.05(1)	1.86(1)
$\chi_{aa}(\mathrm{Cl})$ (MHz)	−143.999(3)	−113.495(3) −144.013(7) [a]	−144.023(3)	−143.96(2)
$M_{bb}(\mathrm{Cl})$ (kHz)	−2.0(2)	−1.6(2)	−2.1(2)	−2.0 [b]
σ (kHz) [c]	2.5	2.5	2.2	3.7

[a] The observed $\chi_{aa}(^{37}\mathrm{Cl})$ multiplied by the ratio $Q(^{35}\mathrm{Cl})/Q(^{37}\mathrm{Cl}) = 1.26889(3)$, given in Ref. [8].

[b] Set at this value, see text for discussion.

[c] The σ are the standard deviations of the fits reported in Tables 1 and 2.

Table 4
Properties of the monomers CO and ClF

Molecule	B_0 (MHz)	χ_0(Cl) (MHz)	M_0(Cl) (kHz)	r_0 [a] (Å)
$^{12}C^{16}O$ [b]	57635.9687(26)			1.13089
$^{13}C^{16}O$ [b]	55101.0205(122)			1.13083
$^{12}C^{18}O$ [b]	54891.4239(122)			1.13082
$^{35}Cl^{19}F$	15418.251 [c]	−145.8718 [d]	−21.616 [d]	1.63176
$^{37}Cl^{19}F$	15125.652 [c]	−114.9613 [d]	−17.649 [d]	1.63173

[a] Calculated from $B_0 = (h/8\pi^2\mu r_0^2)$. [b] Ref. [13]. [c] Ref. [14]. [d] Ref. [21].

motion. Small coordinates in particular can be severely affected and hence a_{Cl} here should be treated cautiously. Nevertheless, the a_i for i = O, C and Cl establish unambiguously the order of the atoms in the complex. By using the first moment condition $\sum_i m_i a_i = 0$, these coordinates allow the value $a_F = -2.443$ Å to be estimated and thence the order OC...ClF. The value of a_F is sensitive to small errors in a_{Cl} and hence cannot be used to obtain a reliable value for the ClF bond length within the complex.

The values of a_O and a_C are reasonably large and presumably less in error than a_{Cl}. They lead to $a_O - a_C = 1.1388$ Å which, in view of the angular oscillations α and β executed by the CO and ClF subunits, respectively, in the zero-point state (as defined in Fig. 2), is related to the CO bond length in the complex by $a_O - a_C \approx r(\mathrm{CO})\langle\cos\alpha\rangle$. Evidently, r(CO) is increased slightly from its value $r_0(\mathrm{CO}) = 1.13089$ Å in the free molecule, but the qualification concerning r_s coordinates in weakly bound complexes should be borne in mind. The coordinate a_{Cl} is too small to use to obtain the intermolecular distance r(C...Cl).

A more satisfactory route to r(C...Cl) uses the model of the complex shown in Fig. 2. The CO and ClF bond lengths are assumed unchanged on complex formation and the rigid subunits execute the angular oscillations α and β with respect to their mass centres, the distance between which is fixed at $r_{c.m.}$. It can then be shown [11] that the moment of inertia I_b^C of the complex is related to I_b^{CO} and I_b^{ClF} of the monomers by

$$I_b^C \approx \mu r_{c.m.}^2 + \tfrac{1}{2} I_b^{CO}\langle 1 + \cos^2\alpha\rangle + \tfrac{1}{2} I_b^{ClF}\langle 1 + \cos^2\beta\rangle, \qquad (3)$$

where the angular brackets refer to the zero-point average. In the averaged structure, the line $r_{c.m.}$ coincides with the a axis of the complex [12]. Given $\alpha_{av} = \cos^{-1}\langle\cos^2\alpha\rangle^{1/2}$ and $\beta_{av} = \cos^{-1}\langle\cos^2\beta_{av}\rangle^{1/2}$, Eq. (3) can be used with the moments of inertia of the monomers available from their rotational constants [13,14] (Table 4) to obtain $r_{c.m.}$ and thence the distance r(C...Cl) via

$$r(\mathrm{C...Cl}) = r_{c.m.} - r - r', \qquad (4)$$

where r and r' are the distances from the CO and ClF centres of mass to the C and Cl atoms, respectively, and are available from the bond lengths given in Table 4. When the values $\alpha_{av} = 15(3)°$ and $\beta_{av} = 10(3)°$ are used the resulting $r_{c.m.}$ and r(C...Cl) for each isotopomer are as recorded in Table 5. It remains to justify the choices of α_{av} and β_{av}, which are not directly determined in this work.

The complex HCN...HBr is similar to OC...ClF in binding strength, as measured by the respective values $k_\sigma = 7.3$ N m^{-1} [1] and $k_\sigma = 7.0$ N m^{-1} (see Section 3.3) of the intermolecular stretching force

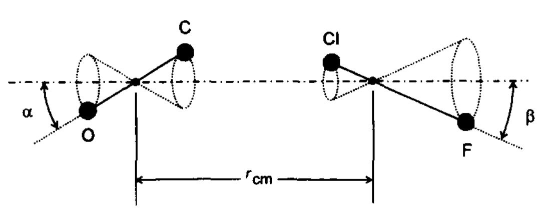

Fig. 2. Definition of the oscillation angles α and β and the distance $r_{c.m.}$ used in the discussion of the zero-point geometry of OC...ClF.

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[1] For a convenient source of k_σ values for hydrogen-bonded complexes, see Ref. [15].

Table 5
Values of $r_{c.m.}$, $r(C...Cl)$ and k_σ for four isotopomers of OC...ClF

Isotopomer	$r_{c.m.}$ [a] (Å)	$r(C...Cl)$ [b] (Å)	k_σ [c] ($N\ m^{-1}$)
$^{16}O^{12}C...^{35}ClF$	3.391(3)	2.770(3)	7.02(1)
$^{16}O^{12}C...^{37}ClF$	3.970(3)	2.770(3)	7.05(2)
$^{16}O^{13}C...^{35}ClF$	3.968(3)	2.771(3)	7.05(3)
$^{18}O^{12}C...^{35}ClF$	4.022(3)	2.769(3)	7.03(5)

[a] Calculated by using Eq. (3). The error is that generated by assuming $\alpha_{av} = 15(3)°$ and $\beta_{av} = 10(3)°$.
[b] Calculated from $r_{c.m.}$ by using Eq. (4).
[c] Calculated from D_J in Eq. (5). The error is that arising from the error in D_J.

constant. The angle $\alpha_{av} = 14.9°$ has been obtained from the ^{14}N-nuclear quadrupole coupling constant of $HC^{14}N...HBr$ after correcting for the change in the electric field gradient at N resulting from HBr [16]. Since HCN and CO are of similar moment of inertia, we assume $\alpha_{av} = 15(3)°$ for OC...ClF. The value for β_{av} can be obtained by considering $CO...Cl_2$ and OC...BrCl, which have k_σ values of 3.6 and 6.3 $N\ m^{-1}$ [17], respectively. The Cl-nuclear quadrupole coupling constants of $OC...Cl_2$ [18] interpreted according to an analysis set out elsewhere [19] lead to $\beta_{av} = 7.2°$ while that of OC...BrCl places an upper limit of 10.2° on β_{av} in OC...BrCl [17]. This suggests a value $\beta_{av} = 10(3)°$ is reasonable for OC...ClF, for, although more strongly bound than $OC...Cl_2$, the reduced mass for the oscillation of the ClF subunit is smaller than that of Cl_2.

We note from Table 5 that the $r(C...Cl)$ are invariant among the isotopomers while, of course, $r_{c.m.}$ is not. The errors quoted are those resulting from the assumed errors in α_{av} and β_{av}. Clearly, the geometry is not a sensitive function of these angles. If the CO and ClF bonds are each assumed to increase in length by 0.01 Å and the calculation repeated, we find a decrease of 0.016 Å in $r(C...Cl)$.

3.3. Nature of the interaction in OC...ClF

There are two ways of divining the nature of the interaction between the CO and ClF subunits in OC...ClF from the results presented here. The first concerns the strength of the interaction, as measured by the intermolecular stretching force constant k_σ. In the quadratic approximation and assuming unperturbed and rigid subunits, k_σ is related to D_J via the expression [20]

$$k_\sigma = \left(16\pi^2\mu B_0^3/D_J\right)\left(1 - B_0/B^{CO} - B_0/B^{ClF}\right), \tag{5}$$

where the rotational constants B_0, B^{CO} and B^{ClF} refer to the complex, CO and ClF, respectively, and the zero-point values of the last two, recorded in Table 4, can be used with sufficient approximation in place of equilibrium quantities. The values of k_σ obtained by using the D_J and B_0 values from Table 3 in Eq. (5) are included in Table 5. We note that k_σ of OC...ClF is similar to that (6.3 $N\ m^{-1}$) of OC...BrCl [17] but about twice that (3.6 $N\ m^{-1}$) of $OC...Cl_2$ [17,18]. Evidently the OC...ClF complex is not strongly bound and the nature of the binding is presumably similar to that in OC...BrCl for which a detailed interpretation of the Br and Cl nuclear quadrupole coupling constants allowed the conclusion that the extent of additional electron transfer from Br to Cl on formation of OC...BrCl was equivalent to only about 0.03 *e*.

The magnitude of the Cl-nuclear quadrupole coupling constant of $^{16}O^{12}C...^{35}ClF$ supports the view that the ClF subunit is not strongly perturbed electronically on complex formation. When the complex is formed, the free molecule value of the coupling constant $\chi_0(Cl)$ will be increased in magnitude to $\chi_0'(Cl)$ as a result of the additional electric field gradient at Cl due to the electric charge distribution of the CO subunit. If the effect of the angular oscillation α of the CO subunit (see Fig. 2) on $\chi_0'(Cl)$ is negligible, then the zero-point value $\chi_{aa}(Cl)$ of the Cl-nuclear quadrupole coupling constant in the complex is given by

$$\chi_{aa}(Cl) = \tfrac{1}{2}\chi_0'(Cl)\langle 3\cos^2\beta - 1\rangle. \tag{6}$$

If we assume $\beta_{av} = \cos^{-1}\langle\cos^2\beta\rangle^{1/2} = 10°$, for example, we estimate $\chi_0'(Cl) = -151$ MHz for $^{16}O^{12}C...^{35}ClF$, which should be compared with $\chi_0(Cl) = -145.8718$ MHz for free ClF [21]. Evidently, the electric field gradient at Cl is not greatly perturbed by complex formation.

According to the analysis of $\chi_0(Cl)$ for diatomic molecules such as ClF set out by Gordy and Cook [22], the value of this constant can be related to that,

$\chi_{\mathrm{atom}}(\mathrm{Cl})$, of a free Cl atom and the ionic character, i_c, of the ClF bond. For a singly bonded diatomic molecule AB, these authors assume a molecular orbital description $\psi_\sigma = a\psi_A + b\psi_B$ of the σ bond and define i_c by the equation $i_c = |a^2 - b^2|$, which reduces to $i_c = 1 - 2a^2$ when A carries the positive pole and the normalisation condition $a^2 + b^2 = 1$ is applied. Thus, the valence-bond structure $\mathrm{Cl}^+ \ldots \mathrm{F}^-$ requires that $i_c = 1$. It can then be shown that [22]

$$\chi_0(\mathrm{Cl}) = (1 + i_c)(1 - a_s^2)(1 + i_c\epsilon)\chi_{\mathrm{atom}}(\mathrm{Cl}), \qquad (7)$$

where a_s^2 is the amount of s character in the hybrid involved in the σ-bonding orbital and $1 + i_c\epsilon$ corrects the coupling per p electron to account for reduced nuclear screening when, as in the valence bond structure $\mathrm{Cl}^+ \ldots \mathrm{F}^-$, the coupling atom carries a formal positive charge. If we assume that formation of the complex OC...ClF results in an increased ionic character i'_c but leaves a_s and ϵ unchanged, the analogue of Eq. (7) can be written in terms of $\chi'_0(\mathrm{Cl})$ and i'_c. It can then be shown that the two equations lead in good approximation to

$$[\chi'_0(\mathrm{Cl}) - \chi_0(\mathrm{Cl})]/\chi_0(\mathrm{Cl}) \approx \Delta i_c/[1 + i_c], \qquad (8)$$

where $\Delta i_c = i'_c - i_c$. By using the values $i_c = 0.5$ and $\epsilon = 0.15$ suggested for ClF in Ref. [22], Eq. (8) leads to $\Delta i_c = 0.023$ for $\chi'_0(\mathrm{Cl}) = -151$ MHz. This provides justification a posteriori for the assumption $1 + i'_c\epsilon = 1 + i_c\epsilon$ implicit in obtaining Eq. (8) from Eq. (7), since these quantities then differ by only 0.3%. It is clear from the above analysis that the electric charge distribution of ClF is affected to only a minor extent by formation of OC...ClF. A similar analysis for the complex OC...BrCl leads to Δi_c of similar magnitude [17].

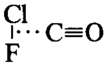
It is of interest to note that the projection formula for the spin–rotation coupling constant $M_{bb}(\mathrm{Cl})$ that is analogous to Eq. (6) is [23]

$$M_{bb}(\mathrm{Cl}) = (B_0/2B^{\mathrm{ClF}})\langle 1 + \cos^2\beta \rangle M_0(\mathrm{Cl}), \qquad (9)$$

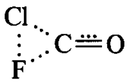
where $M_0(\mathrm{Cl})$ is the spin–rotation coupling constant of ClF [20] and is included in Table 4. When Eq. (9) is used to calculate $M_{bb}(^{35}\mathrm{Cl})$ for $^{16}\mathrm{O}^{12}\mathrm{C}\ldots{}^{35}\mathrm{ClF}$ and $^{16}\mathrm{O}^{12}\mathrm{C}\ldots{}^{37}\mathrm{ClF}$, the results are -2.09 and -1.76 kHz, respectively, for $\beta_{\mathrm{av}} = 10°$. The observed values of $-1.9(2)$ and $-1.5(2)$ kHz are in satisfactory agreement with the predicted values.

4. Discussion

The use of the fast-mixing nozzle has allowed the complex OC...ClF to be characterised in a mixture of CO and ClF. The fact that the reaction product (carbonyl chloride fluoride) could also be detected in small amount is of some chemical interest. Presumably, the isomer



of the complex is close to a plausible transition state



for the reaction. Although we have not detected the T-shaped isomer, it is worthy of note that the energy barrier to rotation of the ClF molecule in the linear isomer to give the T-shaped form must be small. Hence, it is possible that OC...ClF is actually on the reaction coordinate but our observations do not prove this.

The analysis of the ground-state rotational spectrum of the complex OC...ClF shows this to be a linear molecule, with the nuclei in the order indicated. The Cl-nuclear quadrupole coupling constant and the force constant k_σ both indicate that the interaction between the subunits is weak. For the series OC...XY, where XY = Cl_2, ClF and BrCl the force constants have the following approximate relationship: $k_\sigma(\mathrm{ClF}) \approx k_\sigma(\mathrm{BrCl})$ [17] $\approx 2\ k_\sigma(\mathrm{Cl}_2)$ [17,18]. Such a relationship has also been found for the series $\mathrm{H_2S}\ldots\mathrm{ClF}$ [24]. The contraction in the distance $r(\mathrm{C}\ldots\mathrm{Cl})$ between $\mathrm{OC}\ldots\mathrm{Cl}_2$ [18] and OC...ClF is 0.32 Å.

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