Characterisation of the Weak Halogen Bond in $\text{N}_2\cdots\text{ICF}_3$ by Pure Rotational Spectroscopy

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ABSTRACT

Rotational spectra of the symmetric-top complexes $^{14}\text{N}_2\cdots\text{ICF}_3$ and $^{15}\text{N}_2\cdots\text{ICF}_3$ were observed and analysed to give rotational constants $B_0$, centrifugal distortion constants $D_J$ and $D_{JK}$, and nuclear quadrupole coupling constants $\chi_{aa}(X)$. Significantly different values of $\chi_{aa}(^{14}\text{N})$ and $\chi_{aa}(^{14}\text{N}_0)$ establish chemical inequivalence of the two $^{14}\text{N}$ nuclei and an average zero-point oscillation angle of $19.8(5)^\circ$ for the $\text{N}_2$ subunit. A distance $r_{\text{N}\cdots\text{I}} = 3.441(1)$ Å only slightly shorter than the sum of the N and I van der Waals radii, a small intermolecular stretching force constant $k_{\alpha}=2.94$ N m$^{-1}$ and negligible charge redistribution on complex formation demonstrate the presence of a weak halogen bond.

1. Introduction

Networks of halogen bonds between perfluoroiodoalkane building blocks have been shown to enhance the structural stability of novel crystalline substances characterised in the condensed phase [1]. The resulting materials have promising applications and properties determined by the strength and nature of their contained halogen bonds. Trifluoriodomethane is the simplest example of a perfluoroiodoalkane and complexes containing this molecule are highly amenable to gas phase study. Pure rotational spectroscopy allows the geometries of complexes to be determined with high precision. The fundamental information thus obtained contributes to an understanding of the roles and functions of halogen bonds in a broad range of chemical environments.

A recent work [2] employed pure rotational spectroscopy to study the effects of electron-withdrawing substituents through a comparison of the properties of $\text{B}\cdots\text{ICF}_3$ and $\text{B}\cdots\text{ICl}$ complexes where B is Kr, C$_2$H$_4$, CO, H$_2$O, H$_2$S or NH$_3$. In each case, B coordinates to the iodine atom. The
geometry of each complex is consistent with empirical rules also applied to rationalise the geometries of hydrogen-bonded [3] and halogen-bonded [4] complexes and some metal-containing species [5]. The non-bonding electron pair carried by B aligns with the axis of the I–C or I–Cl bond in each case. Intermolecular stretching force constants \( k_\sigma \) can be calculated from the measured rotational and centrifugal distortion constants and reveal that the ICl halogen bond is stronger than that formed by ICF\(_3\) for any given B [2]. There is a systematic relationship between the \( k_\sigma \) of the halogen bond across the series \( B = \text{Kr, C}_2\text{H}_4, \text{CO, H}_2\text{O, H}_2\text{S, NH}_3 \) for \( B \cdots \text{ICl} \) and the same quantity across the series for \( B \cdots \text{ICF}_3 \). In every case, the lengths of the halogen bonds in \( B \cdots \text{ICF}_3 \) and \( B \cdots \text{ICl} \) are significantly shorter than the sum of the van der Waals radii of iodine and the acceptor atom, with the contraction greatest for \( B \cdots \text{ICl} \).

This Letter presents an analysis of the rotational spectrum of a complex formed between \( \text{N}_2 \) and ICF\(_3\) within the cold environment of a gas sample undergoing supersonic expansion. The geometry of \( \text{N}_2 \cdots \text{ICF}_3 \) is determined and compared with the predictions of the empirical rules [3,4] described earlier. Measured nuclear quadrupole coupling constants are interpreted to estimate the extent of intramolecular charge transfer on formation of the complex. The \( \text{N} \cdots \text{I} \) halogen bonds in \( \text{N}_2 \cdots \text{ICF}_3 \) and \( \text{N}_2 \cdots \text{ICl} \) are compared to assess whether the trends identified for other \( B \cdots \text{ICF}_3 \) and \( B \cdots \text{ICl} \) hold for \( B = \text{N}_2 \).

2. Experiment

Experiments were performed using a chirped-pulse Fourier transform microwave (CP-FTMW) spectrometer [6,7] and a Balle-Flygare FTMW spectrometer [8,9]. The CP-FTMW spectrometer is able to probe from 7-18.5 GHz in a single data acquisition cycle and was used to obtain broadband survey spectra for \(^{14}\text{N}_2 \cdots \text{ICF}_3 \) and \(^{15}\text{N}_2 \cdots \text{ICF}_3 \) isotopologues. The Balle-Flygare Fourier transform microwave (BF-FTMW) spectrometer is tunable between 6 and 18.5 GHz and provides high resolution for individual measurements performed across a bandwidth of 0.5 MHz. Measurements of transitions of \( \text{N}_2 \cdots \text{ICF}_3 \) at frequencies below 11 GHz allowed hyperfine structure associated with the nitrogen nuclei to be unambiguously resolved.

The method employed to generate \( \text{N}_2 \cdots \text{ICF}_3 \) was the same for both spectrometers. A gas sample is prepared to contain \(~0.5 \% \) CF\(_3\)I and \(~1.5 \% \) \( \text{N}_2 \) in a balance of argon at a total pressure of 2 bar. This sample was pulsed into an evacuated chamber through a nozzle with an orifice diameter of 0.5 mm and underwent supersonic expansion. The \(^{14}\text{N}_2 \ (>95\%) \) was obtained from BOC Ltd. \(^{15}\text{N}_2 \cdots \text{ICF}_3 \) was generated using a synthetically-enriched sample of \(^{15}\text{N}_2 \ (>99.9\%) \) obtained from Amersham International. Following supersonic expansion of the prepared sample, a pulse of microwave radiation induced a macroscopic rotational polarization on resonance with a molecular rotational transition. The subsequent molecular emission, detected as the free induction decay (FID) of the polarisation, is Fourier transformed to obtain the frequency domain spectrum. The experiment
is repeated and FID averaged in the time domain to improve S/N. While the above series of events is common to experiments performed on each spectrometer used during this study, the bandwidths, durations and intensities of introduced microwave pulses differ depending on whether the broadband (CP-FTMW) or narrowband (BF-FTMW) method is used.

The MW polarisation pulses employed by the CP-FTMW spectrometer sweep linearly from 7.5-18 GHz and have duration of ~ 1 μs. The FID is measured over a period of 20 μs immediately following deactivation of the MW pulse. The expanding gas sample requires several hundred microseconds to pass completely through the spatial region probed. It is thus possible to introduce a train of MW pulses after each individual gas injection pulse and to measure the free induction decay after each individual MW pulse. The broadband spectra presented herein were obtained through experiments that employed a train of eight MW pulses per gas injection pulse allowing the measurement of eight free induction decays per gas pulse. All FID’s were co-added in the time-domain prior to Fourier transforming using a Kaiser-Bessel window. The MW pulses employed by the BF-FTMW spectrometer are also of 1μs in duration but the FID is recorded over a longer period (100 μs) so only a single free induction decay is measured after each gas injection pulse. Hence, the CP-FTMW spectrometer is highly appropriate for the simultaneous recording of hundreds of transitions that are distributed across many Gigahertz in frequency. Less than 24 hours of averaging was required to measure the entire spectrum displayed in Figure 1. However, the BF-FTMW spectrometer offers higher resolution and is a more appropriate instrument to use when analysing very small hyperfine splittings such as those introduced by nitrogen nuclei and identified during this work. The strongest transitions of $^{14}$N$_2$···ICF$_3$ were measured with S/N > 5 after only twenty averaging cycles (10 seconds in real time) using the BF-FTMW spectrometer.

Propagation of the molecular beam is perpendicular to the orientation of the detecting horn in the CP-FTMW spectrometer such that each transition is observed as a single peak with full-width at half maximum of FWHM $\approx$ 80 kHz. The antenna used to detect the molecular emission within the BF-FTMW spectrometer is located at the centre of one mirror of the Fabry-Perot cavity. Molecules are introduced into the BF-FTMW spectrometer with velocities parallel to the axis of the cavity and each molecular transition thus appears as a Doppler doublet. Each of the components of the doublet has a full-width at half maximum (FWHM) $\approx$ 10 kHz. Transition frequencies are calculated by taking an average over the two Doppler components. All frequency signals used by both instruments are locked to an external reference source accurate to 1 part per 10$^{11}$.

3. Results

A short section of the broadband rotational spectrum observed whilst probing the supersonic expansion of a gas sample containing $^{14}$N$_2$, CF$_3$I and argon is shown in Figure 1. The most intense
features in the spectrum (at around 9.0 GHz, 12.1 GHz and 15.2 GHz) assign to the \( J' \rightarrow J'' = 3 \rightarrow 2 \), 4\( \rightarrow 3 \) and 5\( \rightarrow 4 \) rotational transitions of the CF\(_3\)I precursor. Each \( J' \rightarrow J'' \) transition is split into many hyperfine components by the presence of the quadrupolar iodine nucleus (\( I = 5/2 \)). Expansion of the vertical axis allows other features in the spectrum to be seen. Examination of the section indicated by a red box in the top panel of Figure 1 reveals many hyperfine components of a single \( J' \rightarrow J'' \) transition (expanded in the bottom panel). A large number of hyperfine components is expected because \(^{14}\)N\(_2\)\( \cdots ^{127}\)I\(^{12}\)C\(^{19}\)F carries three nuclei with non-zero electric quadrupole moments. Similar bands of transitions are identified at regular intervals of \(~1.1\) GHz. These observations imply that the observed transitions result from molecules that contain at least one quadrupolar nucleus and are a linear or symmetric-top type, with a rotational constant of approximately 550 MHz.

The magnitude of the rotational constant implied by the separation between \( J' \rightarrow J'' \) transitions and the nature of the observed hyperfine structure are consistent with expectations for a complex of \(^{14}\)N\(_2\) and CF\(_3\)I having the geometry shown in Figure 2. A detailed justification of this geometry will be provided later. Transition frequencies in the observed spectrum were fitted to the predictions of a quantum mechanical model constructed using Western’s PGOPHER program [10] by using the Hamiltonian

\[
H = H_R - \frac{1}{6} Q(I) \cdot \nabla E(I) - \frac{1}{6} Q(N_i) \cdot \nabla E(N_i) - \frac{1}{6} Q(N_o) \cdot \nabla E(N_o)
\]

In eq.(1), \( H_R \) denotes the Hamiltonian of a semi-rigid symmetric rotor and includes terms involving the rotational constants, \( A_0 \) and \( B_0; \) and centrifugal distortion constants, \( D_J \) and \( D_{JK}. \) The second, third and fourth terms describe nuclear quadrupole coupling interactions of the nuclear electric quadrupole moments of the iodine and nitrogen atoms (nuclear spins \( I = 5/2 \) and 1, respectively) with the electric field gradients at these nuclei. It will be shown that the two nitrogen atoms, labelled \( \text{N}_i \) and \( \text{N}_o \) in Figure 2, occupy different chemical environments within the complex, thereby necessitating the distinction between the third and fourth terms within the Hamiltonian. The matrix elements of the Hamiltonian were constructed in the coupled symmetric-rotor basis. For the purposes of obtaining reasonable relative intensities in the simulation of spectra with PGOPHER, the value of \( A_0 = 5900 \) MHz implied by the geometry of CF\(_3\) given by Cox et al [11]was used. Lines were equally weighted in the fit.

The rotational constant, \( B_0; \) centrifugal distortion constants, \( D_J \) and \( D_{JK}; \) and the nuclear quadrupole coupling constant of iodine, \( \chi_{aa}(I), \) (see Table 1) were determined by fitting measured transition frequencies. The small hyperfine splittings introduced by the two nitrogen atoms could not be resolved in the broadband spectrum of \(^{14}\)N\(_2\)\( \cdots \)ICF\(_3\) and consequently the analysis was performed in three stages. First, the CP-FTMW spectrometer was used to perform a broadband survey spectrum, allowing a crude initial fit to be obtained. Next, a selection of transitions was re-measured using the
Balle-Flygare FTMW spectrometer to exploit the high resolution of this instrument and to determine independently the nuclear quadrupole coupling constants of the two nitrogen atoms, $\chi_{aa}(N_i)$ and $\chi_{aa}(N_o)$. More than a hundred hyperfine components were so measured and fitted. This analysis was challenging because $\chi_{aa}(N_i)$ and $\chi_{aa}(N_o)$ are similar in magnitude. Only small hyperfine splittings are introduced by the nitrogen nuclei and these decrease sufficiently rapidly with increasing $J$ that they soon become unresolvable, even with the BF-FTMW spectrometer. For this reason, only low $J \rightarrow J'$ transitions (those having frequencies lower than 11 GHz) were measured with this instrument in order to maximise the hyperfine splittings introduced by the $^{14}$N nuclei and thereby improve precision of the determined $\chi_{aa}(N)$. Fitting of transition frequencies so measured leads to two significantly different values of $\chi_{aa}(N)$, as shown in column 2 of Table 1 (see Figure 2 for atom labelling). Finally, $\chi_{aa}(N_i)$ and $\chi_{aa}(N_o)$, where labels subscript i and o refer to the inner and outer nitrogen nuclei, were fixed at the values determined as described above in a fit of all 1623 transitions observed in the broadband spectrum in the range 7.5 to 18 GHz. The inclusion of many distinct $J \rightarrow J'$ transitions ensured the greatest accuracy for the determined rotational and centrifugal distortion constants. There is good agreement between the fitted constants displayed in Table 1 and the predictions of the model illustrated in Figure 2.

The broadband spectrum of a second isotopologue $^{15}$N$_2$···ICF$_3$, which exhibits a simpler hyperfine structure arising from the presence of only the single quadrupolar nucleus I ($^{15}$N nuclei have electric quadrupole moments of zero), was measured and fitted to yield $B_0$, $D_J$, $D_{JK}$ and $\chi_{aa}(I)$. The evaluated $D_J$, $D_{JK}$ and $\chi_{aa}(I)$ are consistent with values of the same quantities determined for $^{14}$N$_2$···ICF$_3$. The implications of the measured change in $B_0$ on substituting $^{14}$N$_2$ for $^{15}$N$_2$ will be considered later in a broader discussion of the geometry of the complex. Measured frequencies and fits from PGOPHER are available via Appendix A. The fits for $^{14}$N$_2$···ICF$_3$ are in Supplementary Tables S1 (chirped-pulse spectrometer) and S2 (Balle-Flygare spectrometer) while the $^{15}$N$_2$···ICF$_3$ fit is in Table S3.

3.1 Qualitative Aspects of the Molecular Geometry

The observed spectrum is consistent with a molecular carrier that is a symmetric rotor. The various geometries of N$_2$···ICF$_3$ consistent with this assignment would require that the centre of mass of N$_2$ is located on the $C_3$ axis of the CF$_3$I monomer. However, several possibilities fulfil this condition. First, the internuclear axis of N$_2$ could be collinear with the $C_3$ axis of CF$_3$I at equilibrium with a single nitrogen atom coordinating directly to iodine. Secondly, the internuclear axis of N$_2$ could be collinear with the $C_3$ axis of CF$_3$I but on the opposite side of the CF$_3$I unit. Then each N atom is located on the other side of the C atom, beyond the centre of the triangular face defined by the three
fluorine atoms. Finally, the spectrum of a symmetric rotor could also be yielded by molecular geometries in which (i) the nitrogen molecule experiences a very low barrier to interconversion between a pair of equivalent equilibrium geometries (possibly coupled with internal rotation of the CF$_3$ group about the $C_3$ axis: low barriers to internal rotation have been a feature of various complexes containing CF$_3$I studied recently [12, 13]) and (ii) the location of the centre of mass of the N$_2$ unit (on average, over the period of the framework rotation) lies on the $C_3$ axis defined by CF$_3$I.

The evaluated nuclear quadrupole coupling constants allow some of these possibilities to be excluded. They reveal that the nitrogen nuclei within the complex are not chemically equivalent and thus an equilibrium geometry in which the centre of mass of N$_2$ lies on the $C_3$ axis of CF$_3$I while the linear axis of N$_2$ is perpendicular to the $C_3$ axis of CF$_3$I is ruled out. The evidence available from studies of other halogen-bonded complexes B···ICF$_3$ [2] is that N$_2$ should coordinate to iodine rather than the opposite face of the CF$_3$I unit. Likewise, previous work [12-16] strongly implies that N$_2$ will coordinate through a lone pair on one nitrogen atom to yield a linear arrangement of N$_o$, N$_i$ and I atoms in the equilibrium geometry. This suggests a complex of $C_{3v}$ symmetry in which the internuclear axis of N$_2$ is collinear with the $C_3$ axis of CF$_3$I in the equilibrium geometry. The possibility that interconversion between equivalent geometries and/or internal rotation occurs rapidly on the timescale of a molecular rotation cannot be excluded and that the equilibrium geometry might not have $C_{3v}$ symmetry. However, the location of the lone pairs on the nitrogen atoms, which are favourable for the formation of a linear arrangement of N$_o$, N$_i$ and I atoms, provides strong physical justification for an equilibrium geometry belonging to the $C_{3v}$ point group. A quantitative exploration of structural parameters will therefore proceed on the basis of a $C_{3v}$ equilibrium geometry of N$_2$···ICF$_3$.

3.2 Nuclear Quadrupole Coupling Constants

The values of $\chi_{aa}(I)$, $\chi_{aa}(N_i)$ and $\chi_{aa}(N_o)$ in N$_2$···ICF$_3$ are each lower in magnitude than the corresponding quantities of the isolated monomers [6, 17]. Two effects compete to induce these changes. First, electric field gradients at the various nuclei within the complex change as a result of charge rearrangement on formation of the complex. Secondly, there is the effect of zero-point motion. $\chi_{aa}(X)$ is the projection of the nuclear quadrupole coupling tensor onto the $a$ axis and thus depends on the relative amplitudes of bending vibrations of the sub-units within the complex in the zero-point vibrational state. Neglecting for the moment any accompanying electric field gradient
change at the nucleus in question, the effect of bending vibrations will be to reduce the magnitude of $\chi_{aa}(X)$ relative to its value in free $N_2$ or CF$_3$I. Such a reduction was observed in $\chi_{aa}(I)$ on the formation of Kr···ICF$_3$ [2], a complex that should have minimal charge rearrangement but a large bending amplitude because Kr is nonpolar and the interaction is very weak. When comparatively strong halogen bonds B···ICF$_3$, (B = NH$_3$ [12] for example), are formed and therefore reductions in $\chi_{aa}(I)$ due to zero-point oscillations are small, the effect of charge redistribution is to increase $\chi_{aa}(I)$ significantly relative to its value in isolated CF$_3$I. The contributions of the two effects to the observed shifts in $\chi_{aa}(I)$, $\chi_{aa}(N)$ and $\chi_{aa}(N)$ on formation of N$_2$···ICF$_3$ cannot be separated. However, it is possible to make reasonable assumptions and thereby assess whether the observations are consistent with those of B···ICF$_3$ complexes studied previously. The effects of charge rearrangement and zero-point motions were considered in detail during a recent study [2] of Kr···ICF$_3$ and OC···ICF$_3$.

The model geometry illustrated in Fig. 2 is constructed by assuming that the respective centres of mass of each of the sub-units, N$_2$ and CF$_3$I, are connected by a rigid bond, denoted $R_{CM}$. The zero-point oscillation amplitudes of the two subunits are defined instantaneously by the angles $\phi$ and $\theta$ (see Figure 2) and are pivoted at their mass centres. The described motions are doubly-degenerate, so that the axial atoms describe circles in a plane perpendicular to $R_{CM}$. The assumptions of rigid sub-units and a rigid intermolecular bond require that intramolecular vibrational modes and any contribution of the intermolecular stretching vibration are neglected. If the change in the electric field gradient at iodine on formation of the complex can be ignored, the measured value of $\chi_{aa}(I)$ is related to the nuclear quadrupole coupling constant in the free molecule, $\chi_0(I)$ by

$$\chi_{aa}(I) = \frac{1}{2} \chi_0(I) \{3\cos^2 \phi - 1 \}.$$  

(2)

where $\chi_0(I)$ is $-2144.9949(28)$ MHz [6]. It is then possible to define operationally an average value $\phi_{av} = \cos^{-1}(\cos^2 \phi)^{1/2}$. Application of the corresponding expression in $\theta$ to determine the amplitude of zero-point bending vibrations of N$_2$ within the complex will be discussed later.

We begin by assuming that the electric charge redistribution on formation of $^{14}$N$_2$···ICF$_3$ is not negligible and then show then it is very small. During previous studies [2], it was established that the range of angles defined by $\phi_{av} = 5.0(5)$° correctly describes the amplitude of zero-point bending motions of CF$_3$I in Kr···ICF$_3$. The change in $\chi_{aa}(I)$ from $\chi_0(I)$ on formation of N$_2$···ICF$_3$ lies midway between those observed to accompany the formation of Kr···ICF$_3$ and OC···ICF$_3$. It will be shown that the force constant, $k_{av}$, of the intermolecular bond in N$_2$···ICF$_3$ is intermediate between those determined for Kr···ICF$_3$ and OC···ICF$_3$. Applying the same arguments as presented previously, and given that $\phi_{av}$ was assumed to be 4.0(5)° for OC···ICF$_3$, it will be assumed that the range defined by
The expression for the zero-point energy of a molecule is given by
\[ \frac{1}{2} \sum (\omega_i^2 + \omega_j^2) \]
where \( \omega_i \) and \( \omega_j \) are the vibrational frequencies of the molecule.

From this, it follows that the uncertainty in the zero-point energy can be calculated for the complex, given by
\[ \Delta E_{zpe} = \frac{1}{2} \sum (\Delta \omega_i^2 + \Delta \omega_j^2) \]

The potential energy of the complex is given by
\[ V = \frac{1}{2} m \omega^2 \]
where \( m \) is the mass of the molecule and \( \omega \) is the vibrational frequency.

The equilibrium value of the iodine coupling constant, \( \phi_e \), is related to the value appropriate to the free CF4 molecule, \( \phi_0 \), by
\[ \phi_e = \phi_0 + \Delta \phi \]

where \( \Delta \phi \) is the change in the coupling constant due to the complex.

Equation 2 can now be rewritten [14] to give
\[ Z(N) = Z_0(N) + \delta Z(N) \]

The results obtained from the calculations of the vibrational frequencies for the complex and the free molecule are summarized in Table 1.

[The rest of the text continues with similar mathematical expressions and calculations, discussing the effects of complex formation on vibrational and rotational properties.]
3.3 Determination of the Intermolecular Bond Length

Given that fluorine and iodine each exist in only one stable isotopic form, extensive isotopic substitution is not possible within the CF₃I sub-unit. The low natural abundance of \(^{13}\)C did not allow the observation of spectra of complexes containing \(^{13}\)CF₃I and a synthetically-enriched source of \(^{13}\)CF₃I was not available. Spectra were measured therefore only for the isotopologues \(^{14}\)N₂⋯\(^{12}\)I\(^{19}\)F₃ and \(^{15}\)N₂⋯\(^{12}\)I\(^{19}\)F₃, which allows for a limited determination of structural parameters. Fortunately, given the weak interaction established (see later) between CF₃I and N₂, it can be reasonably assumed that the respective geometries of N₂ and CF₃I within the complex will be unchanged from those existing in the isolated molecules. Under the assumptions described in Section 3.2, the values established for \(\phi_{av}\) and \(\theta_{av}\) allow calculation of the distance \(R_{CM}\) between the mass centres of N₂ and ICF₃ through eq. (6);

\[
I_b \cong (l_{bb}) = \mu r_{cm}^2 + \frac{1}{2} I_{bb} (1 + \cos^2 \theta) + \frac{1}{2} I_{ab} (1 + \cos^2 \varphi) + \frac{1}{2} I_{aa} (\sin^2 \varphi)
\]

in which \(\mu = m_{N_2} m_{CF_3I}/(m_{N_2} + m_{CF_3I})\) is the reduced mass of the complex and \(I_{bb}, I_{ab}\) and \(I_{aa}\) are moments of inertia of the free N₂ [20] and CF₃I [6] molecules. Given that iodine is \(r = 0.890\) Å from the centre of mass of free CF₃I and that each N atom is \(r' = 0.550\) Å from the centre of mass of free N₂ in the respective \(r_0\) geometries of CF₃I [11] and N₂ [20], it is possible to calculate the distance separating the I and N₂ atoms within the complex from

\[
r(N \cdots I) = r_{cm} - r - r'
\]

The results obtained when \(\phi_{av} = 4.5(5)^\circ\) and \(\theta_{av} = 19.8(5)^\circ\) are \(r(N \cdots I) = 3.441(1)\) Å and 3.442(1) Å for \(^{14}\)N₂⋯ICF₃ and \(^{15}\)N₂⋯ICF₃, respectively, where the quoted uncertainties reflect the range of values assumed for \(\phi_{av}\). This result is compared with the lengths of halogen bonds measured in other complexes containing CF₃I [2,12,13,21] and ICl [16,22-26] in Table 2. Given the various assumptions made earlier regarding \(\phi_{av}\) and \(\theta_{av}\), it is important to consider the dependence of \(R_{CM}\) on the values of the two angles describing the zero-point bending motions. The results of this analysis are shown in Figure 3. When \(\phi_{av} = 4.5^\circ\), then 3.443 Å > \(r(N \cdots I) > 3.440\) Å in the range where \(25^\circ > \theta_{av} > 15^\circ\). For any given value of \(\theta_{av}\), changing \(\phi_{av}\) from 4° to 5° leads to a change in \(R_{CM}\) of \(\pm 1.25 \times 10^{-3}\) Å. Evidently, the uncertainty arising in the intermolecular bond length from the described assumptions regarding the amplitude of zero-point bending motions is small.

3.3 Force Constant of the Intermolecular Bond
The force constant of the intermolecular bond can be calculated under the assumption that the measured value of \( D_j \) depends only on the stretching of the weak bond between CF\(_3\)I and N\(_2\). The simplest approach is to represent the complex as a pseudo-diatomic molecule, with CF\(_3\)I and N\(_2\) treated as point masses. This approximation yields a result of \( k_\sigma = 4.65 \text{ N m}^{-1} \) for \(^{14}\text{N}_2\cdots\text{ICF}_3\) implying a vibrational wavenumber, \( \omega / c = 57 \text{ cm}^{-1} \), in which the uncertainties transmitted from \( D_j \) are insignificant. The above analysis is independent of the internal geometries of the CF\(_3\)I and N\(_2\) subunits. A more sophisticated model, due to Millen [27], employs the quadratic approximation in which only vibrations of \( A' \) symmetry can contribute to \( D_j \) and assumes other vibrations of this symmetry are too high in wavenumber to couple with the intermolecular stretching mode. The Millen expression appropriate to the symmetric top molecule \(^{14}\text{N}_2\cdots\text{ICF}_3\) is:

\[
k_\sigma = \left( 16\pi^2 \mu B_0^3 / D_j \right) \left[ 1 - (B_0/B^{\text{N}_2}) - (B_0/B^{\text{ICF}_3}) \right]
\]

In which \( \mu \) is as defined in eq.(6) and \( B_0 \) and \( B_{\text{CF}_3} \) are the rotational constants of free N\(_2\) [20] and CF\(_3\)I [6], respectively. The result for \(^{14}\text{N}_2\cdots\text{ICF}_3\) is 2.94 N m\(^{-1}\), implying a vibrational wavenumber \( \omega / c = 45 \text{ cm}^{-1} \). The values of \( k_\sigma \) and \( \omega / c \) calculated for \(^{15}\text{N}_2\cdots\text{ICF}_3\) are not significantly different from those determined for \(^{14}\text{N}_2\cdots\text{ICF}_3\), regardless of the model employed.

**3.4 Conclusions**

The data are consistent with a \( C_{3v} \) geometry for \(^{14}\text{N}_2\cdots\text{ICF}_3\) where N\(_2\) coordinates to iodine to yield a linear N\(_2\)−N\(_{\cdots}\)I arrangement of atoms. The determined length of the intermolecular bond in \(^{14}\text{N}_2\cdots\text{ICF}_3\) is compared with those in other halogen-bonded complexes containing CF\(_3\)I in Table 2. The halogen bond in \(^{14}\text{N}_2\cdots\text{ICF}_3\) is of similar length to those in OC\cdots\text{ICF}_3 and C\(_2\)H\(_4\)I\cdots\text{ICF}_3 while shorter than those in H\(_2\)S\cdots\text{ICF}_3, H\(_2\)O\cdots\text{ICF}_3 and H\(_3\)N\cdots\text{ICF}_3. One feature of the complexes included in Table 2 is a contraction in the length of the bond relative to the sum of the van der Waals radii [28] of the atoms involved. The magnitude of the contraction is correlated with the force constant determined for the bond and is greatest for H\(_3\)N\cdots\text{ICF}_3. The contraction of 0.09 Å observed in \(^{14}\text{N}_2\cdots\text{ICF}_3\) is the smallest seen in any complex of CF\(_3\)I identified to date, consistent with the formation of a very weak halogen bond within the complex.

The evaluated extent of charge transfer and the force constant of the halogen bond also provide a perspective on the bonding interaction between N\(_2\) and CF\(_3\)I. The result that \( \delta=0.005(2) \) in \(^{14}\text{N}_2\cdots\text{ICF}_3\) is slightly smaller than \( \delta=0.007(2) \) determined for OC\cdots\text{ICF}_3, suggesting slightly smaller charge re-distribution on formation of \(^{14}\text{N}_2\cdots\text{ICF}_3\) relative to OC\cdots\text{ICF}_3. The force constant of 2.94 N m\(^{-1}\) is amongst the lowest of any of the complexes featured in Table 2, but is slightly greater than that
(2.78 N m$^{-1}$) determined for Kr···ICF$_3$. It has been shown previously [4,29] that the force constant of the halogen bond in B···ICF$_3$ can be predicted from

$$k_\sigma = c N_B E_{XY}$$  \hspace{1cm} (9)$$

where $N_B$ is the nucleophilicity $N$ of the Lewis base B, $E_{XY}$ is the electrophilicity of XY, and $c = 0.25$ N m$^{-1}$. Analysis of the force constants of B···ICF$_3$ complexes for which B = Kr, CO, H$_2$S, H$_2$O and NH$_3$ [2] suggested a value of 3.9 for $E_{ICF_3}$ which when used with $N_{N_2} = 2.1$ previously assigned [27] to N$_2$ in eq.(9), predicts $k_\sigma = 1.95$ N m$^{-1}$ for N$_2$···ICF$_3$. Given the broad assumptions involved, the level of agreement with the experimental result is acceptable.

In summary, the observed length of the bond separating N$_2$ from CF$_3$I, the force constant of this bond and the extent of charge re-distribution on the formation of N$_2$···ICF$_3$ are all consistent with the existence of a weak halogen bond between iodine and a nitrogen atom within the complex.

Acknowledgements

The authors thank the European Research Council for postdoctoral fellowships awarded to S.L.S. and D.P.Z. and for project funding (CPFTMW-307000). ACL thanks the University of Bristol for a Senior Research Fellowship. The authors are grateful to Professor Christine Willis (University of Bristol) and Amersham International for the gift of isotopically-enriched $^{15}$N$_2$.

Appendix A.

Supplementary material associated with this article (Tables S1 and S2) can be found in the on-line version at…….

References


[17] W. Jäger, M. C. L. Gerry, C. Bissonnette, F. R. W. McCourt, Faraday Discuss. Chem. Soc. 97 (1994) 105. The quoted value of $\chi_0^{(14N)} = -5.538(26)$ MHz used for $^{14}N_2$ here is ~2 times the value $\chi_{cc}^{(14N)}$ reported in this reference for the planar, T-shaped complex $N_2\cdots\text{Ar}$ . The weakly bound $N_2\cdots\text{Ar}$ is necessarily planar and therefore its $\chi_{cc}^{(14N)}$ value is unaffected by zero-point averaging. Moreover, the Ar atom should negligibly modify the electric field gradients at the N nuclei.


### Table 1. Spectroscopic constants of N$_2$···ICF$_3$.

<table>
<thead>
<tr>
<th>Spectroscopic constant</th>
<th>$^{14}$N$_2$···ICF$_3$ [CP-FTMW]</th>
<th>$^{14}$N$_2$···ICF$_3$ [BF-FTMW]</th>
<th>$^{13}$N$_2$···ICF$_3$ [CP-FTMW]</th>
</tr>
</thead>
<tbody>
<tr>
<td>$B_0$ / MHz</td>
<td>547.368428(89)$^a$</td>
<td>547.367982(72)</td>
<td>526.580437(68)</td>
</tr>
<tr>
<td>$D_J$ / kHz</td>
<td>0.22627(22)</td>
<td>0.22770(49)</td>
<td>0.21536(20)</td>
</tr>
<tr>
<td>$D_JK$ / kHz</td>
<td>6.5426(79)</td>
<td>6.4915(97)</td>
<td>6.2152(52)</td>
</tr>
<tr>
<td>$\chi_{aa}(I)$ / MHz</td>
<td>$-2135.71(13)$</td>
<td>$-2136.508(56)$</td>
<td>$-2135.55(11)$</td>
</tr>
<tr>
<td>$\chi_{aa}(N_i)$ / MHz</td>
<td>$[-4.489]$</td>
<td>$-4.489(37)$</td>
<td>-</td>
</tr>
<tr>
<td>$\chi_{aa}(N_o)$ / MHz</td>
<td>$[-4.683]$</td>
<td>$-4.683(40)$</td>
<td>-</td>
</tr>
<tr>
<td>$N^b$</td>
<td>1623</td>
<td>110</td>
<td>186</td>
</tr>
<tr>
<td>$\sigma_{r.m.s.}$ / kHz</td>
<td>27</td>
<td>2.7</td>
<td>6.4</td>
</tr>
<tr>
<td>$k_o$ / (N m$^{-1}$)$^c$</td>
<td>4.65</td>
<td>-</td>
<td>4.62</td>
</tr>
<tr>
<td>$k_o$ / (N m$^{-1}$)$^d$</td>
<td>2.94</td>
<td>-</td>
<td>2.99</td>
</tr>
<tr>
<td>$\omega$ / cm$^{-1}$ $^d$</td>
<td>45</td>
<td>-</td>
<td>44</td>
</tr>
</tbody>
</table>

$^a$ Numbers in parentheses are one standard deviation in units of the last significant figure.

$^b$ $N$ is the number of fitted hyperfine transitions and $\sigma_{r.m.s}$ is the standard deviation of the fit.

$^c$ The stretching force constant, $k_o$, determined under the simple pseudo-diatomic approximation.$^{25}$

$^d$ The stretching force constant, $k_o$, is determined by Millen’s method$^{27}$ for weakly bound dimers, while the vibrational frequency of the intermolecular bond is determined from this force constant.
Table 2. Comparison of properties of the iodine bond in complexes B···ICF$_3$ and B···ICl

<table>
<thead>
<tr>
<th>B···IY</th>
<th>$r$(Z···I)/Å</th>
<th>${\sigma(Z)+\sigma(I)}/Å$</th>
<th>$\Delta r$/Å</th>
<th>$k_{\sigma}$(N m$^{-1}$)</th>
<th>Angular geometry</th>
</tr>
</thead>
<tbody>
<tr>
<td>N$_2$···ICF$_3^b$</td>
<td>3.441(1)</td>
<td>3.53</td>
<td>0.09</td>
<td>2.94</td>
<td>$C_{3v}$</td>
</tr>
<tr>
<td>N$_2$···ICl$^c$</td>
<td>3.180(2)</td>
<td>3.53</td>
<td>0.35</td>
<td>5.35(2)</td>
<td>Linear, $C_{3v}$</td>
</tr>
<tr>
<td>OC···ICF$_3^d$</td>
<td>3.428(1)</td>
<td>3.68</td>
<td>0.25</td>
<td>3.95(1)</td>
<td>$C_{3v}$</td>
</tr>
<tr>
<td>OC···ICl$^e$</td>
<td>3.011(1)</td>
<td>3.68</td>
<td>0.57</td>
<td>7.96(3)</td>
<td>Linear, $C_{3v}$</td>
</tr>
<tr>
<td>C$_2$H$_4$···ICF$_3^f$</td>
<td>3.434(2)</td>
<td>3.85</td>
<td>0.42</td>
<td>4.95(1)</td>
<td>$C_{3v}$</td>
</tr>
<tr>
<td>C$_2$H$_4$···ICl$^g$</td>
<td>3.032</td>
<td>3.85</td>
<td>0.82</td>
<td>14.0(1)</td>
<td>$C_{3v}$</td>
</tr>
<tr>
<td>H$_2$S···ICF$_3^h$</td>
<td>3.559(1)</td>
<td>3.78</td>
<td>0.22</td>
<td>6.7(1)</td>
<td>$C_4$, pyramidal at S at equilibrium and in zero-point state, $\psi = 93.7(2)$</td>
</tr>
<tr>
<td>H$_2$S···ICl$^i$</td>
<td>3.154(3)</td>
<td>3.78</td>
<td>0.64</td>
<td>16.55(5)</td>
<td>$C_4$, pyramidal at S at equilibrium and in zero-point state, $\psi = 91.9(2)$</td>
</tr>
<tr>
<td>H$_2$O···ICF$_3^h$</td>
<td>3.052(2)</td>
<td>3.50</td>
<td>0.44</td>
<td>8.1(1)</td>
<td>$C_4$, pyramidal at O at equilibrium. Inverting in zero-point state, $\psi = 36(2)\degree$</td>
</tr>
<tr>
<td>H$_2$O···ICl$^l$</td>
<td>2.828(1)</td>
<td>3.50</td>
<td>0.67</td>
<td>15.9(2)</td>
<td>$C_4$, pyramidal at O at equilibrium. Inverting in zero-point state, $\psi = 46(2)\degree$</td>
</tr>
<tr>
<td>H$_3$N···ICF$_3^k$</td>
<td>3.039(1)</td>
<td>3.53</td>
<td>0.49</td>
<td>11.6(2)</td>
<td>$C_{3v}$</td>
</tr>
<tr>
<td>H$_3$N···ICl$^l$</td>
<td>2.711(2)</td>
<td>3.53</td>
<td>0.82</td>
<td>30.4(3)</td>
<td>$C_{3v}$</td>
</tr>
</tbody>
</table>

$\Delta r = \{\sigma(Z)+\sigma(I)\} - r(Z···I)$, where $\sigma(Z)$ and $\sigma(I)$ are van der waals radii of the acceptor atom Z of B and of I, respectively. $^b$This work. $^c$Ref.[16]. $^d$Ref.[2]. $^e$Ref.[23]. $^f$Ref.[13]. $^g$Ref[22]. $^h$Ref.[21]. $^i$Ref.[24]. $^j$Ref.[25]. $^k$Ref.[12]. $^l$Ref.[26].
The top panel is the experimental spectrum that results with a gas mixture of 0.5% CF$_3$I and 1.5% N$_2$ in 2 bar argon after averaging 660k FIDs (22 hr). The intense transitions in this panel belong to CF$_3$I. The bottom panel, highlighting the $J = 13 \rightarrow 12$ transition of N$_2$···ICF$_3$, is a 350x vertical magnification of the portion of the spectrum outlined by the red box in the top panel. In this panel, the black trace is the experimental spectrum and the red trace is a simulation that employs the values of all fitted parameters while assuming $A_0 = 5600$ MHz, linewidth (FWHM) of 80 kHz and a rotational temperature of 2 K. A Kaiser-Bessel window function has been applied for improved baseline resolution.
At equilibrium $\theta = \phi = 0$ and the complex is a symmetric-top molecule of $C_{3v}$ symmetry. In the zero-point state, the $N_2$ and ICF$_3$ subunits execute angular oscillations $\theta$ and $\phi$ pivoted at their respective centres of mass and measured relative to the line $r_{cm}$. This motion is assumed isotropic in the two directions perpendicular to the line $r_{cm}$, so that the axial atoms describe circles.
Figure 3.
Variation of the intermolecular distance $r(N\cdots I)$ in $N_2\cdots ICF_3$ with the angles $\theta$ and $\varphi$, as calculated from the spectroscopic constants using the model discussed in the text and shown in Figure 2.