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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 $\chi_{aa}(\text{X})$. Significantly different values of $\chi_{aa}(^{14}\text{N}_i)$ and $\chi_{aa}(^{14}\text{N}_o)$ establish chemical inequivalence of the two ^{14}N nuclei and an average zero-point oscillation angle of $19.8(5)^\circ$ for the N_2 subunit. A distance $r_{\text{N}\cdots\text{I}} = 3.441(1) \text{ \AA}$ only slightly shorter than the sum of the N and I van der Waals radii, a small intermolecular stretching force constant $k_\sigma = 2.94 \text{ N m}^{-1}$ 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. Trifluoroiodomethane 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_2H_4 , CO, H_2O , H_2S 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_{σ} can be calculated from the measured rotational and centrifugal distortion constants and reveal that the ICl halogen bond is stronger than that formed by ICF₃ for any given B [2]. There is a systematic relationship between the k_{σ} of the halogen bond across the series B = Kr, C₂H₄, CO, H₂O, H₂S, NH₃ for B⋯ICl and the same quantity across the series for B⋯ICF₃. In every case, the lengths of the halogen bonds in B⋯ICF₃ and B⋯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⋯ICl.

This Letter presents an analysis of the rotational spectrum of a complex formed between N₂ and ICF₃ within the cold environment of a gas sample undergoing supersonic expansion. The geometry of N₂⋯ICF₃ 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 N–I halogen bonds in N₂⋯ICF₃ and N₂⋯ICl are compared to assess whether the trends identified for other B⋯ICF₃ and B⋯ICl hold for B = N₂.

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 ¹⁴N₂⋯ICF₃ and ¹⁵N₂⋯ICF₃ 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 N₂⋯ICF₃ at frequencies below 11 GHz allowed hyperfine structure associated with the nitrogen nuclei to be unambiguously resolved.

The method employed to generate N₂⋯ICF₃ was the same for both spectrometers. A gas sample is prepared to contain ~0.5 % CF₃I and ~1.5 % N₂ 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 ¹⁴N₂ (>95%) was obtained from BOC Ltd. ¹⁵N₂⋯ICF₃ was generated using a synthetically-enriched sample of ¹⁵N₂ (>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 $\sim 1 \mu\text{s}$. The FID is measured over a period of $20 \mu\text{s}$ 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 $1 \mu\text{s}$ in duration but the FID is recorded over a longer period ($100 \mu\text{s}$) 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 $^{14}\text{N}_2 \cdots \text{ICF}_3$ were measured with $\text{S/N} > 5$ 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 $\text{FWHM} \cong 80 \text{ kHz}$. 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) $\cong 10 \text{ kHz}$. 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 $^{14}\text{N}_2$, CF_3I 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_3I 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 $^{14}\text{N}_2 \cdots ^{127}\text{I}^{12}\text{C}^{19}\text{F}$ 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 N_2 and CF_3I 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

$$H = H_{\text{R}} - \frac{1}{6}\mathbf{Q}(\text{I}) : \nabla\mathbf{E}(\text{I}) - \frac{1}{6}\mathbf{Q}(\text{N}_i) : \nabla\mathbf{E}(\text{N}_i) - \frac{1}{6}\mathbf{Q}(\text{N}_o) : \nabla\mathbf{E}(\text{N}_o) \quad (1)$$

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 N_i and 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 ICF_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, $\chi_{aa}(\text{I})$, (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 $^{14}\text{N}_2 \cdots \text{ICF}_3$ 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, $\chi_{aa}(\text{N}_o)$ and $\chi_{aa}(\text{N}_i)$. More than a hundred hyperfine components were so measured and fitted. This analysis was challenging because $\chi_{aa}(\text{N}_o)$ and $\chi_{aa}(\text{N}_i)$ 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 $\chi_{aa}(\text{N})$. Fitting of transition frequencies so measured leads to two significantly different values of $\chi_{aa}(\text{N})$, as shown in column 2 of Table 1 (see Figure 2 for atom labelling). Finally, $\chi_{aa}(\text{N}_o)$ and $\chi_{aa}(\text{N}_i)$, 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 $^{15}\text{N}_2 \cdots \text{ICF}_3$, 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 $\chi_{aa}(\text{I})$. The evaluated D_J , D_{JK} and $\chi_{aa}(\text{I})$ are consistent with values of the same quantities determined for $^{14}\text{N}_2 \cdots \text{ICF}_3$. The implications of the measured change in B_0 on substituting $^{14}\text{N}_2$ for $^{15}\text{N}_2$ 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 $^{14}\text{N}_2 \cdots \text{ICF}_3$ are in Supplementary Tables S1 (chirped-pulse spectrometer) and S2 (Balle-Flygare spectrometer) while the $^{15}\text{N}_2 \cdots \text{ICF}_3$ 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 $\text{N}_2 \cdots \text{ICF}_3$ consistent with this assignment would require that the centre of mass of N_2 is located on the C_3 axis of the CF_3I monomer. However, several possibilities fulfil this condition. First, the internuclear axis of N_2 could be collinear with the C_3 axis of CF_3I 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_3I but on the opposite side of the CF_3I 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_3I 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_3I .

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_3I while the linear axis of N_2 is perpendicular to the C_3 axis of CF_3I is ruled out. The evidence available from studies of other halogen-bonded complexes $\text{B}\cdots\text{ICF}_3$ [2] is that N_2 should coordinate to iodine rather than the opposite face of the CF_3I 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_3I 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 $\text{N}_2\cdots\text{ICF}_3$.

3.2 Nuclear Quadrupole Coupling Constants

The values of $\chi_{aa}(\text{I})$, $\chi_{aa}(\text{N}_\text{i})$ and $\chi_{aa}(\text{N}_\text{o})$ in $\text{N}_2\cdots\text{ICF}_3$ 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. $\chi_{aa}(\text{X})$ 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_3I . Such a reduction was observed in $\chi_{aa}(I)$ on the formation of $Kr\cdots ICF_3$ [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 $B\cdots ICF_3$, ($B = NH_3$ [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_3I . The contributions of the two effects to the observed shifts in $\chi_{aa}(I)$, $\chi_{aa}(N_i)$ and $\chi_{aa}(N_o)$ on formation of $N_2\cdots ICF_3$ cannot be separated. However, it is possible to make reasonable assumptions and thereby assess whether the observations are consistent with those of $B\cdots ICF_3$ complexes studied previously. The effects of charge rearrangement and zero-point motions were considered in detail during a recent study [2] of $Kr\cdots ICF_3$ and $OC\cdots ICF_3$.

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_3I , are connected by a rigid bond, denoted R_{CM} . The zero-point oscillation amplitudes of the two subunits are defined instantaneously by the angles φ and θ (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

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

where $\chi_0(I)$ is $-2144.9949(28)$ MHz [6]. It is then possible to define operationally an average value $\varphi_{av.} = \cos^{-1}\langle \cos^2\varphi \rangle^{1/2}$. Application of the corresponding expression in θ 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 $^{14}N_2\cdots ICF_3$ 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 $\varphi_{av.} = 5.0(5)^\circ$ correctly describes the amplitude of zero-point bending motions of CF_3I in $Kr\cdots ICF_3$. The change in $\chi_{aa}(I)$ from $\chi_0(I)$ on formation of $N_2\cdots ICF_3$ lies midway between those observed to accompany the formation of $Kr\cdots ICF_3$ and $OC\cdots ICF_3$. It will be shown that the force constant, k_σ , of the intermolecular bond in $N_2\cdots ICF_3$ is intermediate between those determined for $Kr\cdots ICF_3$ and $OC\cdots ICF_3$. Applying the same arguments as presented previously, and given that $\varphi_{av.}$ was assumed to be $4.0(5)^\circ$ for $OC\cdots ICF_3$, it will be assumed that the range defined by

$\varphi_{av.} = 4.5(5)^\circ$ contains the correct value for $N_2 \cdots ICF_3$. Under this assumption and using Eq. (2), it is possible to estimate the value of $\chi_{aa}(I)$ that would be observed in the absence of any contribution from charge re-distribution on formation of this complex. The result is $-2116.8(50)$ MHz, where the uncertainty reflects the assumed range of $\varphi_{av.}$ According to the Townes-Dailey model [18], when applied to complexes such as $B \cdots ICF_3$ [2], the equilibrium value of the iodine coupling constant, $\chi_{zz}^e(I)$, can be related to the value appropriate to the free CF_3I molecule, $\chi_0(I)$, as follows:

$$\chi_{zz}^e(I) = \chi_0(I) + \delta \cdot \chi_A(I) \quad (3),$$

in which δ is the net increase in the magnitude of the electronic charge in the $5p_z$ orbital of the iodine atom brought about (by intermolecular transfer from N_2 to I and by intramolecular transfer from I within ICF_3) on complex formation. The nuclear quadrupole coupling constant of the free, ground-state iodine atom is denoted by $\chi_A(I)$ and has the value 2292.8 MHz [18]. It is possible to combine Eq. (2) and (3) to give

$$\chi_{aa}(I) = \frac{1}{2} \{ \chi_0(I) + \delta \cdot \chi_A(I) \} \langle 3 \cos^2 \varphi - 1 \rangle \quad (4)$$

and thus calculate δ from the measured value of $\chi_{aa}(I)$ under the assumption that $\varphi_{av.} = 4.5(5)^\circ$ to obtain the result that $\delta = 0.005(2)$. The angle describing the zero-point bending vibration of N_2 within the complex, defined as θ_{av} , will be somewhat greater than φ_{av} , owing to the comparatively light mass of N_2 . It has been shown through *ab initio* calculations [19] that the approach of N_2 towards a molecule such as CF_3I to form a complex that contains a linear $N_o-N_i \cdots I$ arrangement of atoms at equilibrium has the effect of increasing and decreasing the respective magnitudes of $\chi_{aa}^e(N_o)$ and $\chi_{aa}^e(N_i)$ by almost equal amounts. Hence, the difference between the mean value, $\frac{1}{2} [\chi_{aa}(N_i) + \chi_{aa}(N_o)]$, and the value of $\chi_0(N) = -5.538$ MHz in the free N_2 molecule [17] results only from zero-point averaging of vibrational motion. Equation 2 can now be re-written [14]

$$\frac{1}{2} [\chi_{aa}(N_i) + \chi_{aa}(N_o)] = \frac{1}{2} \chi_0(N) \langle 3 \cos^2 \theta - 1 \rangle \quad (5),$$

which allows $\theta_{av} = 19.8(5)^\circ$ to be calculated for $N_2 \cdots ICF_3$. This is somewhat larger than the value of $\theta_{av} \approx 8.3^\circ$ obtained for the zero-point vibrational motion of CO within $OC \cdots ICF_3$ from substitution coordinates [2] but is similar to $\theta_{av} = 17.8(5)^\circ$ determined from measured values of $\chi_{aa}^e(N_o)$ and $\chi_{aa}^e(N_i)$ for $N_2 \cdots ClF$ [14]. It will be shown that the intermolecular bond length determined from the experimental results is somewhat insensitive to the value determined for θ_{av} .

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 ¹³C did not allow the observation of spectra of complexes containing ¹³CF₃I and a synthetically-enriched source of ¹³CF₃I was not available. Spectra were measured therefore only for the isotopologues ¹⁴N₂...¹²⁷I¹²C¹⁹F₃ and ¹⁵N₂...¹²⁷I¹²C¹⁹F₃, 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 φ_{av} and θ_{av} allow calculation of the distance R_{CM} between the mass centres of N₂ and ICF₃ through eq.(6);

$$I_b \cong \langle I_{bb} \rangle = \mu r_{cm}^2 + \frac{1}{2} I_{bb}^{N_2} \langle 1 + \cos^2 \theta \rangle + \frac{1}{2} I_{bb}^{CF_3I} \langle 1 + \cos^2 \varphi \rangle + \frac{1}{2} I_{aa}^{CF_3I} \langle \sin^2 \varphi \rangle \quad (6)$$

in which $\mu = m^{N_2} m^{CF_3I} / (m^{N_2} + m^{CF_3I})$ is the reduced mass of the complex and $I_{bb}^{N_2}$, $I_{aa}^{CF_3I}$ and $I_{bb}^{CF_3I}$ 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 N_i atoms within the complex from

$$r(N \cdots I) = r_{cm} - r - r' \quad (7)$$

The results obtained when $\varphi_{av} = 4.5(5)^\circ$ and $\theta_{av} = 19.8(5)^\circ$ are $r(N \cdots I) = 3.441(1)$ Å and $3.442(1)$ Å for ¹⁴N₂...ICF₃ and ¹⁵N₂...ICF₃, respectively, where the quoted uncertainties reflect the range of values assumed for φ_{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 φ_{av} and θ_{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 $\varphi_{av} = 4.5^\circ$, 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 θ_{av} , changing φ_{av} from 4° to 5° leads to a change in R_{CM} of $\cong 1.25 \times 10^{-3}$ 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_3I and N_2 . The simplest approach is to represent the complex as a pseudo-diatomic molecule, with CF_3I 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_3I and N_2 sub-units. 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 $\text{N}_2 \cdots \text{ICF}_3$ is;

$$k_\sigma = (16\pi^2 \mu B_0^3 / D_J) \{1 - (B_0 / B^{\text{N}_2}) - (B_0 / B^{\text{ICF}_3})\} \quad (8)$$

In which μ is as defined in eq.(6) and B_{N_2} and $B_{\text{CF}_3\text{I}}$ are the rotational constants of free N_2 [20] and CF_3I [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_σ and ω / 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 $\text{N}_2 \cdots \text{ICF}_3$ where N_2 coordinates to iodine to yield a linear $\text{N}_o\text{--N}_i \cdots \text{I}$ arrangement of atoms. The determined length of the intermolecular bond in $\text{N}_2 \cdots \text{ICF}_3$ is compared with those in other halogen-bonded complexes containing CF_3I in Table 2. The halogen bond in $\text{N}_2 \cdots \text{ICF}_3$ is of similar length to those in $\text{OC} \cdots \text{ICF}_3$ and $\text{C}_2\text{H}_4 \cdots \text{ICF}_3$ while shorter than those in $\text{H}_2\text{S} \cdots \text{ICF}_3$, $\text{H}_2\text{O} \cdots \text{ICF}_3$ and $\text{H}_3\text{N} \cdots \text{ICF}_3$. 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 $\text{H}_3\text{N} \cdots \text{ICF}_3$. The contraction of $0.09 \text{ \AA}$ observed in $\text{N}_2 \cdots \text{ICF}_3$ is the smallest seen in any complex of CF_3I 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_3I . The result that $\delta = 0.005(2)$ in $\text{N}_2 \cdots \text{ICF}_3$ is slightly smaller than $\delta = 0.007(2)$ determined for $\text{OC} \cdots \text{ICF}_3$, suggesting slightly smaller charge re-distribution on formation of $\text{N}_2 \cdots \text{ICF}_3$ relative to $\text{OC} \cdots \text{ICF}_3$. 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···ICF₃. It has been shown previously [4,29] that the force constant of the halogen bond in B···ICF₃ can be predicted from

$$k_{\sigma} = cN_{\text{B}}E_{\text{XY}} \quad (9),$$

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···ICF₃ complexes for which B = Kr, CO, H₂S, H₂O and NH₃ [2] suggested a value of 3.9 for E_{ICF_3} which when used with $N_{\text{N}_2} = 2.1$ previously assigned [27] to N₂ in eq.(9), predicts $k_{\sigma} = 1.95$ N m⁻¹ for N₂···ICF₃. Given the broad assumptions involved, the level of agreement with the experimental result is acceptable.

In summary, the observed length of the bond separating N₂ from CF₃I, the force constant of this bond and the extent of charge re-distribution on the formation of N₂···ICF₃ are all consistent with the existence of a weak halogen bond between iodine and a nitrogen atom within the complex.

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Appendix A.

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

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Tables

Table 1. Spectroscopic constants of $\text{N}_2\cdots\text{ICF}_3$.

Spectroscopic constant	$^{14}\text{N}_2\cdots\text{ICF}_3$ [CP-FTMW]	$^{14}\text{N}_2\cdots\text{ICF}_3$ [BF-FTMW]	$^{15}\text{N}_2\cdots\text{ICF}_3$ [CP-FTMW]
B_0 / MHz	547.368428(89) ^a	547.367982(72)	526.580437(68)
D_J / kHz	0.22627(22)	0.22770(49)	0.21536(20)
D_{JK} / kHz	6.5426(79)	6.4915(97)	6.2152(52)
$\chi_{aa}(\text{I})$ / MHz	-2135.71(13)	-2136.508(56)	-2135.55(11)
$\chi_{aa}(\text{N}_i)$ / MHz	[-4.489]	-4.489(37)	-
$\chi_{aa}(\text{N}_o)$ / MHz	[-4.683]	-4.683(40)	-
N^b	1623	110	186
$\sigma_{\text{r.m.s.}}$ / kHz	27	2.7	6.4
k_σ / (N m^{-1}) ^c	4.65	-	4.62
k_σ / (N m^{-1}) ^d	2.94	-	2.99
ω / cm^{-1} ^d	45	-	44

^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 $\sigma_{\text{r.m.s.}}$ is the standard deviation of the fit.

^c The stretching force constant, k_σ , determined under the simple pseudo-diatomic approximation.²⁵

^d The stretching force constant, k_σ , is determined by Millen's method²⁷ 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...ICF₃ and B...ICl

B...IY	$r(Z\cdots I)/\text{\AA}$	$\{\sigma(Z)+\sigma(I)\}/\text{\AA}$	$\Delta r/\text{\AA}^a$	$k_\sigma/(\text{N m}^{-1})$	Angular geometry
N ₂ ...ICF ₃ ^b	3.441(1)	3.53	0.09	2.94	C _{3v}
N ₂ ...ICl ^c	3.180(2)	3.53	0.35	5.35(2)	Linear, C _{∞v}
OC...ICF ₃ ^d	3.428(1)	3.68	0.25	3.95(1)	C _{3v}
OC...ICl ^e	3.011(1)	3.68	0.57	7.96(3)	Linear, C _{∞v}
C ₂ H ₄ ...ICF ₃ ^f	3.434(2)	3.85	0.42	4.95(1)	C _{2v}
C ₂ H ₄ ...ICl ^g	3.032	3.85	0.82	14.0(1)	C _{2v}
H ₂ S...ICF ₃ ^h	3.559(1)	3.78	0.22	6.7(1)	C _s , pyramidal at S at equilibrium, and in zero-point state, $\psi = 93.7(2)^\circ$
H ₂ S...ICl ⁱ	3.154(3)	3.78	0.64	16.55(5)	C _s , pyramidal at S at equilibrium and in zero-point state, $\psi = 91.9(2)^\circ$
H ₂ O...ICF ₃ ^h	3.052(2)	3.50	0.44	8.1(1)	C _s , pyramidal at O at equilibrium. Inverting in zero-point state, $\psi = 36(2)^\circ$
H ₂ O...ICl ^j	2.828(1)	3.50	0.67	15.9(2)	C _s , pyramidal at O at equilibrium. Inverting in zero-point state, $\psi = 46(2)^\circ$
H ₃ N...ICF ₃ ^k	3.039(1)	3.53	0.49	11.6(2)	C _{3v}
H ₃ N...ICl ^l	2.711(2)	3.53	0.82	30.4(3)	C _{3v}

$\Delta r = \{\sigma(Z)+\sigma(I)\} - r(Z\cdots I)$, where $\sigma(Z)$ and $\sigma(I)$ are van der waals radii of the acceptor atom Z of B and of I, respectively. ^bThis work. ^cRef.[16]. ^dRef.[2]. ^eRef.[23]. ^fRef.[13]. ^gRef[22]. ^hRef.[21]. ⁱRef.[24]. ^jRef.[25]. ^kRef.[12]. ^lRef.[26]

Figures

Figure 1

The top panel is the experimental spectrum that results with a gas mixture of 0.5% CF_3I and 1.5% N_2 in 2 bar argon after averaging 660k FIDs (22 hr). The intense transitions in this panel belong to CF_3I . The bottom panel, highlighting the $J = 13 \rightarrow 12$ transition of $\text{N}_2 \cdots \text{ICF}_3$, 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.

Figure 2

Model used to interpret the spectroscopic constants of $\text{N}_2 \cdots \text{ICF}_3$ in terms of the molecular geometry.

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 θ and ϕ 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 $r(\text{N}\cdots\text{I})$ in $\text{N}_2\cdots\text{ICF}_3$ with the angles θ and φ , as calculated from the spectroscopic constants using the model discussed in the text and shown in Figure 2.