# Rotational spectroscopy of mixtures of ethyne and iodine monochloride: isolation and characterisation of the $\pi$ -type complex C<sub>2</sub>H<sub>2</sub>···ICl

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The ground-state rotational spectrum of a complex formed by ethyne and iodine monochloride was observed by using pulsed-nozzle, Fourier-transform microwave spectroscopy. A fast-mixing nozzle was utilised to avoid chemical reaction of the component gases prior to their supersonic expansion. Rotational constants  $A_0$ ,  $B_0$ and  $C_0$ , quartic centrifugal distortion constants  $\Delta_J$ ,  $\Delta_{JK}$  and  $\delta_J$ , and halogen nuclear quadrupole coupling constants  $\chi_{aa}(X)$  and  $\{\chi_{bb}(X) - \chi_{cc}(X)\}$ , where X = Cl or I, were determined for the three isotopomers  $C_2H_2 \cdots I^{35}Cl, C_2H_2 \cdots I^{37}Cl$  and  $C_2D_2 \cdots I^{35}Cl$ . Detailed interpretation of the rotational constants established that the equilibrium geometry of the complex has a planar, T-shape of  $C_{2x}$  symmetry in which ethyne acts as the bar of the T. This geometry, with the zero-point distance  $r(*\cdots I) = 3.115(1)$  Å between the centre of the  $\pi$ -bond of ethyne and the nearest halogen atom I, establishes that the interaction in this complex is between ethyne as a  $\pi$  electron donor and I of ICl as the electron acceptor. The halogen nuclear quadrupole coupling constants  $\chi_{aa}(X)$  were interpreted on the basis of a simple model to show that, on complex formation, fractions  $\delta_1 = 0.026$  and  $\delta_2 = 0.056$  of an electronic charge are transferred from the ethyne  $\pi$  bond to I and from I to Cl, respectively, leading to a net decrease of 0.030e at I. The complex is weakly bound, according to the intermolecular stretching force constant  $k_{\sigma} = 12.2(1) \text{ Nm}^{-1}$  determined for the isotopomers  $C_2H_2 \cdots I^{35}Cl$  and  $C_2H_2\cdots I^{37}Cl$  from  $\Delta_J$  values. The opportunity is taken to compare the properties of  $C_2H_2\cdots ICl$  established here with those similarly determined for the series  $C_2H_2\cdots XY$ , where  $XY = Cl_2$ , CIF, or BrCl.

## 1. Introduction

We report the ground-state rotational spectra of three isotopomers of a complex formed by ethyne with iodine monochloride. This investigation is part of a continuing programme in which we are using rotational spectroscopy to determine the properties of several extended series of complexes  $B \cdots X_2$ or  $B \cdots XY$ , where B is a Lewis base and  $X_2$  and XY are homonuclear and heteronuclear dihalogen molecules, respectively. The properties of primary interest are the angular geometry of the complex, the strength of the interaction between the components, and the extent of the electric charge redistribution that accompanies formation of the complex. By varying B and the dihalogen molecule systematically and observing how the properties of  $B \cdots X_2$  or  $B \cdots XY$  change, we aim to draw conclusions about the nature of the interaction. Another aim of these investigations is to examine whether any parallelism exists between the properties of these so-called 'halogen-bonded' complexes  $B \cdots X_2$  or  $B \cdots XY$  and the corresponding hydrogen-bonded series B...HX. So far, some general conclusions have been advanced for the series  $B \cdots Cl_2 / B \cdots HCl,^1$  $B \cdots BrCl/B \cdots HBr^2$ and  $B \cdots ClF/$  $B \cdots HCl.^{3,4}$  We have recently begun considering the series B···ICl.<sup>5,6</sup>

Complexes of the type  $B \cdots ICl$  and  $B \cdots I_2$ , in which an iodine atom acts as the electron acceptor, featured centrally in early investigations of charge transfer complexes by both experimental and theoretical methods. Notable among these was the experimental work of Benesi and Hildebrand<sup>7</sup> on benzene/I<sub>2</sub> in the liquid phase, the X-ray diffraction study of complexes in the solid state by Hassel and Rømming,<sup>8</sup> and the theoretical analysis by Mulliken and Person,<sup>9</sup> who also introduced a detailed classification of complexes based on the type

of molecular orbital from which and into which electrons are donated and accepted, respectively, in forming a complex such as  $B \cdots XY$ . An important class contains complexes formally described as of the  $b\pi.a\sigma$  type, *i.e.* complexes in which electrons are donated from a  $\pi$ -bonding orbital of B into a  $\sigma$ antibonding orbital of XY.

Although the first charge-transfer complex to be investigated,<sup>7</sup> namely benzene  $\cdot \cdot I_2$ , is of the b $\pi$ .a $\sigma$  type, the simplest possible member in which I is the electron donor is ethyne...ICl. However, complexes of ethyne with halogens have been difficult to observe hitherto because of the facile chemical reaction that accompanies mixing of the components under normal conditions. This difficulty can be overcome in the solid state by isolation of the complex in cryogenic matrices<sup>10</sup> and, more recently, in the gas phase by using a fast-mixing nozzle<sup>11</sup> to accomplish supersonic expansion of the components to be mixed while avoiding chemical reaction. The latter method has been used to produce ethyne...Cl<sub>2</sub>, ethyne...ClF and ethyne...BrCl in isolation in a jet within the Fabry-Pérot cavity of a pulsed-nozzle, Fourier-transform microwave spectrometer and thereby to observe their rotational spectra.<sup>12-14</sup> The same method is employed here to characterise the simplest  $B \cdots ICl$  complex of the b $\pi.a\sigma$  type, namely ethyne $\cdots$ ICl, which is the subject of this paper.

The earlier studies of the rotational spectra of  $Ar \cdots ICl^5$ and  $OC \cdots ICl^6$  allowed us to develop a method of interpreting the changes in the iodine and chlorine nuclear quadrupole coupling on formation of the complex  $B \cdots ICl$  in terms of electric charge redistribution from B to I and from I to Cl. We take advantage of this method here to determine the extent of both inter- and intra-molecular charge transfer in the prototype  $b\pi.a\sigma$  complex of the type B··ICl. We also establish the angular geometry of ethyne···ICl unambiguously from an interpretation of the rotational spectra of  $C_2H_2 \cdots I^{35}Cl$ ,  $C_2H_2 \cdots I^{37}Cl$  and  $C_2D_2 \cdots I^{35}Cl$  and obtain a measure of the intermolecular binding strength (the intermolecular stretching force constant  $k_{\sigma}$ ) from the effects of centrifugal distortion.

## 2. Experimental

The ground-state rotational spectrum of the ethyne···ICl complex was observed by means of a pulsed nozzle, Fouriertransform microwave spectrometer of the Balle-Flygare design.<sup>15,16</sup> A fast mixing nozzle<sup>11</sup> was employed as a means of avoiding the chemical reaction that would occur between ethyne and ICl if they were mixed in the normal way in a stagnation vessel. ICl vapour was flowed continuously from above a sample of solid iodine monochloride (Lancaster Synthesis), through the central glass capillary (0.3 mm internal diameter) of this nozzle, into the evacuated Fabry-Pérot cavity of the spectrometer. The flow rate was adjusted so that a steady state pressure of  $ca. 2 \times 10^{-4}$  mbar was registered in the chamber. The solid was contained in a glass tube having a Teflon tap and the entire line up to the capillary was constructed in glass, thereby ensuring that the ICl did not come into contact with metal, with which it might react. Simultaneously, a mixture composed of ethyne (B.O.C. Gases Ltd.) in argon, having a partial pressure ratio of 2:100, respectively, and held at a total pressure of 3 bar was pulsed down the outer (Teflon) tube of the mixing nozzle at a rate of 2 Hz by means of a Series 9 solenoid valve (General Valve Corp.). Because the two concentric tubes of the nozzle are coterminal, the ICl and ethyne came into contact only as they both expanded into the Fabry-Pérot cavity. Complexes formed at the interface of the concentric gas flows were polarised with pulses of microwave radiation in the usual way and the freeinduction decay at rotational transition frequencies was collected and processed as described elsewhere.<sup>16</sup> Individual hyperfine components of transitions had a full-width at halfheight of ca. 16 kHz, which led to an accuracy of frequency measurement estimated at 2 kHz.

A sample of dideuterioethyne, prepared by the action of  $D_2O$  (99.8 atom%, Aldrich) on calcium carbide (BDH), was used to observe the spectrum of  $C_2D_2\cdots I^{35}Cl$ .

## 3. Results

## 3.1 Spectroscopic analysis

The observed ground-state rotational spectrum of each isotopomer of ethyne...ICl investigated was of the type normally associated with a nearly prolate asymmetric rotor for which the only non-zero component of the electric dipole moment is  $\mu_a$ . Each observed *a*-type transition carried an extensive hyperfine structure that clearly arose from the coupling of the iodine and chlorine nuclear spin vectors  $I_{I}$  and  $I_{CI}$ , respectively, to the framework rotational angular momentum J via the nuclear quadrupole interaction. The observed frequencies of hyperfine components in the  $J = 4 \leftarrow 3$ ,  $5 \leftarrow 4$  and  $6 \leftarrow 5$ sets of transitions are given in Table S1<sup>+</sup> for the isotopomers  $C_2H_2\cdots I^{35}Cl,\ C_2H_2\cdots I^{37}Cl$  and  $C_2D_2\cdots I^{35}Cl.$  Fewer transitions were observed for the last of these species, mainly because the transitions involving  $K_{-1} = 1$  were reduced in intensity relative to the  $K_{-1} = 0$  transitions. For the isotopomers  $C_2H_2\cdots I^{35}Cl$  and  $C_2H_2\cdots I^{37}Cl$ , the  $K_{-1} = 1$  transitions. sitions were considerably stronger than in  $C_2D_2\cdots \hat{I}^{35}Cl$ . This suggests a nuclear spin statistical weight effect that differs between the  $C_2H_2$  and  $C_2D_2$  species. Discussion of this effect is postponed until Section 3.2.

Observed frequencies were fitted by a standard, nonlinear least squares procedure in which the matrix of the Hamiltonian H defined in eqn. (1) was constructed in the coupled basis  $I_1 + J = F_1$ ,  $F_1 + I_{Cl} = F$  and diagonalised. The Hamiltonian

$$H = H_{\mathbf{R}} - 1/6\boldsymbol{Q}_{\mathbf{I}} : \nabla \boldsymbol{E}_{\mathbf{I}} - 1/6\boldsymbol{Q}_{\mathbf{CI}} : \nabla \boldsymbol{E}_{\mathbf{CI}} + \boldsymbol{I}_{\mathbf{I}} \cdot \boldsymbol{M} \cdot \boldsymbol{J}$$
(1)

proved sufficient to fit the observed frequencies with a standard deviation comparable with the estimated error of measurement (namely, 2 kHz). The first term in eqn. (1) is the energy operator for the semi-rigid asymmetric rotor, for which the Watson A reduction<sup>17</sup> in the  $I^r$  representation was employed. Centrifugal distortion effects were satisfactorily accounted for by including only quartic terms in the angular momentum operators. The second and third terms in eqn. (1), of the form  $-1/6\boldsymbol{Q}_{x}$ :  $\nabla \boldsymbol{E}_{x}(X = I \text{ or } CI)$ , described the energy of interaction of the nuclear electric quadrupole moment  $\boldsymbol{Q}_{x}$  of halogen X with the electric field gradient  $\nabla E_x$  at nucleus X. It was not necessary to consider the effects of centrifugal distortion on the nuclear hyperfine structure, even though the magnitude of the splitting due to I was large. The final term in eqn. (1) takes account of the coupling of  $I_1$  to J via the magnetic spin-rotation interaction. The quantity M is the spinrotation coupling tensor. Inclusion of the corresponding operator for the Cl spin-rotation coupling was found unnecessary.

The fitting was conducted using the program SPFIT written by H.M. Pickett.<sup>18</sup> The spectroscopic constants obtained in the final cycle of the fit are given in Table 1 for the three isotopomers  $C_2H_2\cdots I^{35}Cl$ ,  $C_2H_2\cdots I^{37}Cl$  and  $C_2D_2 \cdots I^{35}Cl$ , together with the standard deviations of the fits. The residuals  $\Delta v = v_{obs} - v_{calc}$  are included in Table S1. Despite the fact that only  $K_{-1} = 0$  and 1 transitions were observed for these very nearly prolate asymmetric rotors, we note that the large rotational constant  $A_0$  is moderately well determined in each case. Of the quartic centrifugal distortion constants only  $\Delta_J$ ,  $\Delta_{JK}$  and  $\delta_J$  could be determined from the data available. The only components of the halogen nuclear quadrupole coupling tensors  $\chi_{\alpha\beta}(X) = -(eQ/h)\partial^2 V_X/\partial\alpha\partial\beta$  ( $\alpha,\beta$ to be permuted over a, b and c) released in the fit were  $\chi_{aa}(X)$ and  $\{\chi_{bb}(X) - \chi_{cc}(X)\}$ , where X = I or Cl. Evidently, offdiagonal elements are either zero or make a negligible contribution to the observed hyperfine splittings. The components  $M_{aa}(I)$  and  $M_{bb}(I)$  of the iodine spin-rotation coupling tensor were both determined for  $C_2H_2\cdots I^{35}Cl$ , for which many hyperfine components were available. In view of the nearly zero-values of  $\{\chi_{bb}(X) - \chi_{cc}(X)\}$  (see Table 1), we set  $M_{bb}(I) =$  $M_{cc}(I)$ . The smaller number of transitions measured for  $C_2H_2{\cdots}I^{37}Cl$  and  $C_2D_2{\cdots}I^{35}Cl$  coupled with the small contribution of the iodine spin-rotation effect to the observed hyperfine frequencies obliged us to fix  $M_{aa}(I)$  for these isotopomers at the value determined for  $C_2H_2 \cdots I^{35}Cl$ .

## 3.2 Symmetry and angular geometry of C<sub>2</sub>H<sub>2</sub>…ICl

The complex  $C_2H_2$ ...ICl is readily shown to have the planar T-shaped geometry of  $C_{2v}$  symmetry shown in Fig. 1 by means of interpretation of the various observed spectroscopic constants.

First, the fact that the zero-point rotational constant  $A_0$  of each isotopomer  $C_2H_2\cdots I^{35}Cl$ ,  $C_2H_2\cdots I^{37}Cl$  and  $C_2D_2\cdots I^{35}Cl$  (see Table 1) is almost identical within experimental error to the rotational constant  $B_0$  of the corresponding isotopomer of free ethyne<sup>19,20</sup> (as given in Table 2) demonstrates that ICl lies along the  $C_2$  axis of the ethyne molecule. If the geometry of the ethyne subunit were unperturbed on complex formation, the geometry displayed in Fig. 1 would require that the equilibrium rotational constant  $A_e$  of the complex were identical with  $B_e$  of the free ethyne subunit. Unfortunately, equilibrium rotational constants are not available, but the small excess of  $A_0$  of each  $C_2H_2$  isotopomer over

<sup>&</sup>lt;sup>†</sup> Available as supplementary material (SUP **57599**, 4pp.) deposited with the British Library. Details are available from the Editorial Office. For direct electronic access see http://www.rsc.org/suppdata/cp/1999/3721.

**Table 1** Ground state spectroscopic constants for  $C_2H_2\cdots I^{35}Cl, C_2H_2\cdots I^{37}Cl$  and  $C_2D_2\cdots I^{35}Cl$ 

Spectroscopic constant	$C_2H_2\cdots I^{35}Cl$	$C_2H_2\cdots I^{37}Cl$	$C_2D_2$ ···I <sup>35</sup> Cl
A <sub>0</sub> /MHz	35611(120)	35316(260)	25037(100)
$B_0/MHz$	1145.9416(2)	1118.6947(4)	1099.1048(4)
$\tilde{C_0}/MHz$	1108.7254(2)	1083.1981(5)	1052.3151(4)
$\Delta_{I}/kHz$	0.443(3)	0.403(6)	0.37(1)
$\Delta_{IK}/kHz$	26.6(2)	25.9(3)	26.2(4)
$\delta_I/kHz$	0.013(2)	0.011(4)	0.013 <sup>a</sup>
$\chi_{ag}(I)/MHz$	-2969.03(2)	-2969.3(4)	-2969.02(6)
$\{\chi_{bb}(I) - \chi_{cc}(I)\}/MHz$	-83.29(4)	-83.27(7)	-86.6(2)
$\chi_{as}(Cl)/MHz$	-78.99(6)	-62.26(1)	-78.92(1)
$\{\chi_{bb}(Cl) - \chi_{cc}(Cl)\}/MHz$	-0.41(1)	-0.32(3)	-0.30(7)
$M_{aa}/MHz$	-0.0045(30)	$-0.0045^{a}$	$-0.0045^{a}$
$M_{bb}/MHz$	0.0062(2)	0.0071(4)	0.0055(7)
$\Delta_0/\mathrm{u}\mathrm{\AA}^{2}$ b	0.61(5)	0.49(10)	0.26(8)
Ň	114	65	45
$\sigma/\mathrm{kHz}$	1.4	3.1	3.8

the  $B_0$  value of free ethyne almost certainly originates from a small angular oscillation  $\alpha$  of the ethyne subunit in the zeropoint state of the complex of the type illustrated in Fig. 2. If the equilibrium angle  $\alpha_e$  is 90°, it is shown in Section 3.5 that the average value  $\alpha_{av} = \sin^{-1} \langle \sin^2 \alpha \rangle^{1/2}$ , where angular brackets denote the zero-point average, will be smaller than 90° and will lead to  $A_0$  larger than  $A_e$  in the case of the  $C_2H_2$ isotopomers. The fact that, on the other hand,  $A_0$  for  $C_2D_2 \cdots I^{35}CI$  is smaller than  $B_0$  for  $C_2D_2$  is also consistent with this interpretation, as will be elaborated in Section 3.5. An explanation of the increased value of  $A_0$  of  $C_2H_2 \cdots I^{35}CI$ in terms of a contraction of the C=C bond of ethyne on formation of  $C_2H_2 \cdots ICI$  seems unconvincing not only because  $A_0$ of  $C_2D_2 \cdots I^{35}CI$  is smaller than  $B_0$  of  $C_2D_2$  but also because the  $\pi$ -system of ethyne is acting as the electron donor in the



Fig. 1 The equilibrium geometry of ethyne $\cdots$ ICl drawn to scale.

complex and the C-C bond would be expected to lengthen.

The planar arrangement of the nuclei implied by the  $C_{2v}$  geometry shown in Fig. 1 requires that the relation  $I_c^e = I_b^e + I_a^e$  exists among the equilibrium moments of inertia, but the latter are unavailable. However, a small positive inertia defect  $\Delta_0 = I_c^0 - I_b^0 - I_a^0$  is often taken as an indication of a planar geometry. Values of this quantity are given in Table 1. For the two isotopomers  $C_2H_2\cdots I^{35}Cl$  and  $C_2H_2\cdots I^{37}Cl$ ,  $\Delta_0$  is identical within experimental error and is very similar in value to those of the corresponding isotopomers of  $C_2H_2\cdots ClF$ , namely 0.639(2) and 0.634(1) uÅ<sup>2</sup>, respectively.<sup>13</sup> The value of  $\Delta_0$  is somewhat smaller for the  $C_2D_2\cdots I^{35}Cl$ .



Fig. 2 Definition of the principal inertial axes *a* and *b* of ethyne...ICl, the distance  $r_{\rm cm}$  and the angles  $\alpha$ ,  $\beta$  and  $\psi$  used in the determination of the geometry of the complex.

Table 2 Some properties of ethyne, iodine monochloride and the atoms I and Cl

Molecule or atom	B <sub>0</sub> /MHz	$r/{ m \AA}^a$	$\chi_0(I)/MHz$	$\chi_0(\text{Cl})/\text{MHz}$
$\begin{array}{c} C_{2}H_{2}^{\ b} \\ C_{2}D_{2}^{\ c} \\ I^{35}CI^{d} \\ I^{37}CI^{d} \end{array}$	35273.8(4) 25418.2(3) 3414.36695(7) 3269.92335(9)	 0.50196 0.52414		-85.887(3) -67.687(3)
Atomic I <sup>e</sup> Atomic <sup>35</sup> Cl <sup>e</sup> Atomic <sup>37</sup> Cl <sup>e</sup>			-2292.71 	-109.74 -86.51

<sup>*a*</sup> r is the distance of I from the centre of mass in free ICl. Values were calculated from the  $r_0$  bond distances given in ref. 5. <sup>*b*</sup> Ref. 19. <sup>*c*</sup> Ref. 20. <sup>*d*</sup> Ref. 5. <sup>*e*</sup> Ref. 22.

A planar equilibrium geometry of the type shown in Fig. 1 requires that a rotation  $C_2^a$  about the *a*-axis exchanges a pair of equivalent protons in  $C_2H_2\cdots ICl$  isotopomers. The usual arguments based on Fermi-Dirac statistics then predict that, in the vibrational ground state, a-type transitions which originate in  $K_{-1} = 1$  levels have a nuclear spin statistical weight of 3 while those involving  $K_{-1} = 0$  levels have a weight of unity. Conversely, for  $C_2D_2$ . ICl, the exchange of the pair of equivalent D nuclei (I = 1, bosons) leads to a nuclear spin statistical weight ratio of 1 : 2 for  $K_{-1} = 1$  transitions relative to  $K_{-1} = 0$  transitions. Certainly, the intensities of the  $(J+1)_{1,J+1} \leftarrow J_{1,J}$  and  $(J+1)_{1,J} \leftarrow J_{1,J-1}$  transitions were considerably smaller than that of the  $(J+1)_{0,J+1} \leftarrow J_{0,J}$  transsition of a given J for the  $C_2D_2\cdots I^{35}Cl$  isotopomer. For the  $C_2H_2\cdots ICl$  isotopomers, on the other hand, the  $K_{-1} = 1$ transitions were at least as the strong as the  $K_{-1} = 0$  component. Given the difficulty of measuring relative intensities of transitions when using pulsed-nozzle FT microwave spectroscopy and given the unknown extent of rotational cooling of the higher energy  $K_{-1} = 1$  levels in the supersonic expansion, the nuclear spin statistical weight ratios required by the postulated angular geometry could not be established quantitatively. The qualitative evidence is consistent with the planar,  $C_{2v}$  geometry, however.

The signs and magnitudes of the determined nuclear quadrupole coupling constants  $\chi_{aa}(X)$  and  $\chi_{bb}(X) - \chi_{cc}(X)$  for both X = I and Cl (see Table 1) are also consistent with the proposed angular geometry. Thus, the former constant is similar in both respects to  $\chi_0(X)$  of free ICl<sup>5</sup> (values of which for the I and Cl nuclei are included in Table 2) while the latter is close to zero. The fact that none of the off-diagonal elements  $\chi_{ab}(X)$ ,  $\chi_{ac}(X)$  or  $\chi_{bc}(X)$  was required to give a fit of transition frequencies that is close to the error of frequency measurement is also evidence in favour of the preferred angular geometry. A more detailed discussion of the nuclear quadrupole coupling constants is postponed until Section 3.3.

#### 3.3 Charge transfer on formation of C<sub>2</sub>H<sub>2</sub>…ICl

Information about the extent of the electric charge redistribution on formation of  $C_2H_2\cdots$ ICl is available from the halogen nuclear quadrupole coupling constants but it is convolved with the zero-point angular oscillation of the ICl subunit. Some approximations, and the use of a simple model for interpreting nuclear quadrupole coupling constants, are necessary to extract the intermolecular and intramolecular charge transfer. These are set out below.

According to the arguments of Section 3.2, ethyne...ICl has a planar T-shaped geometry of  $C_{2v}$  symmetry (see Fig. 1). The changes in the rotational constants accompanying isotopic substitution of  ${}^{37}$ Cl for  ${}^{35}$ Cl in  $C_2H_2\cdots I^{35}$ Cl establish that I lies closer to the ethyne subunit than does Cl (see Section 3.5). Each component of the X nuclear quadrupole coupling tensor in the equilibrium state of the complex is defined by  $\chi_{qq}^{e}(X) =$  $-(eQ_x/h)\partial^2 V_x/\partial g^2$ , where g = a, b or c and  $Q_x$  is the conventional electric quadrupole moment of nucleus X. The fact that ethyne is nonpolar and that the Cl nucleus is remote from the centre (\*) of the ethyne subunit  $[r(*\cdots Cl) \approx 5.4 \text{ Å}, \text{ see Section}]$ 3.5] suggests that the cylindrical symmetry of the electric charge distribution at Cl is not likely to be significantly perturbed on formation of the complex. We thus expect  $\{\chi_{bb}^{e}(Cl)\}$  $-\chi^{e}_{cc}(Cl)$  to be very close to zero in the complex. The zeropoint values of this difference (see Table 2) are certainly very small, an observation suggesting that the zero-point angular oscillation  $\beta$  of the ICl subunit (see Fig. 2 for definition), which is the main contribution to the zero-point averaging of the coupling constants, can be assumed to be twodimensionally isotropic in the bc plane.

In the approximation that the intermolecular stretching

mode makes a negligible contribution to the difference between  $\chi_{gg}^{e}(X)$  and the corresponding zero-point quantity  $\chi_{gg}(X)$ , that the effects of the ethyne subunit angular oscillation ( $\alpha$  defined in Fig. 2) are also negligible, and that the motion of the ICl subunit is two-dimensionally isotropic, the  $\chi_{aa}(X)$  are related to the  $\chi_{aa}^{e}(X)$  for both X = I and X = Cl by

$$\chi_{aa}(\mathbf{X}) = \frac{1}{2} \chi_{aa}^{\mathsf{e}}(\mathbf{X}) \langle 3 \cos^2 \beta - 1 \rangle \tag{2}$$

The next step is to express the  $\chi_{aa}^{e}(X)$  values in terms of those  $\chi_{0}(X)^{5}$  of free ICl (see Table 2) and the electric charge redistribution when ICl is incorporated into the complex. We assume that a fraction  $\delta_{1}$  of an electronic charge is transferred from the  $\pi$ -bond of ethyne to the iodine atom. In addition, the ethyne electric charge distribution will produce an electric field and its various gradients at the X nuclei and the response of the ICl electronic distribution to these leads to an increased electric field gradient (efg) at I and a diminished efg at Cl, relative to the free ICl molecule. We shall assume that the latter changes can be described in terms of a polarization of the ICl electronic distribution equivalent to a transfer of a fraction  $\delta_{2}$  of an electron from I to Cl. Thus, in this model, there are net increases of  $(\delta_{1} - \delta_{2})e$  at I and  $\delta_{2}e$  at Cl.

According to the Townes–Dailey model<sup>21</sup> for interpreting nuclear quadrupole coupling constants, as applied to ICl, the transfer of a fraction  $\delta$  of an electron from the 5p<sub>z</sub> orbital on iodine into the 3p<sub>z</sub> orbital on Cl (z is the internuclear axis) leads to changes of  $\delta \cdot \chi_A(I)$  and  $-\delta \cdot \chi_A(Cl)$  in the free molecule coupling constants  $\chi_0(I)$  and  $\chi_0(Cl)$ , respectively, where  $\chi_A(X)$ is the coupling constant of the free halogen atom X.<sup>22</sup> On the basis of this model, we can write

$$\chi_{aa}^{e}(\mathbf{I}) = \chi_{0}(\mathbf{I}) - (\delta_{1} - \delta_{2})\chi_{A}(\mathbf{I})$$
(3)

$$\chi^{\rm e}_{aa}({\rm Cl}) = \chi_0({\rm Cl}) - \delta_2 \cdot \chi_{\rm A}({\rm Cl}) \tag{4}$$

In formulating eqn. (3), it is assumed that the net change  $(\delta_1 - \delta_2)e$  of the electronic charge on I involves the  $5p_z$  orbital.

If  $\beta_{av} = \cos^{-1} \langle \cos^2 \beta \rangle^{1/2}$  were known, eqns. (3) and (4) used in combination with eqn. (2) would afford a route to both  $\delta_1$  and  $\delta_2$ . Unfortunately, we do not have a method of determining  $\beta_{av}$  independently. We can make a reasonable estimate of this quantity by referring to a recent analysis<sup>5</sup> of the coupling constants  $\chi_{aa}(X)$  of Ar···ICl, however. When intermolecular charge transfer is assumed negligible in this weakly bound complex, it is possible to obtain simultaneously the fraction  $\delta_2$  of an electronic charge transferred from I to Cl and the angle  $\beta_{av}$ , as discussed in ref. 5. The results are  $\delta_2 =$  $5.4 \times 10^{-3}$  and  $\beta_{av} = 5.45(1)^\circ$ . The nearly zero value of  $\delta_2$  provides justification a posteriori of the assumption that  $\delta_1$  is negligible in the Ar···ICl case.

Given that Ar···ICl is much more weakly bound than ethyne···ICl according to the criterion of the intermolecular stretching force constant  $k_{\sigma}$ , which has values of 3.20(1) and 12.2(1) Nm<sup>-1</sup> respectively for these two complexes, it is reasonable to assume that the angular oscillation of the ICl subunit is attenuated in ethyne···ICl relative to Ar···ICl. Because  $\beta_{av}$  is small even in Ar···ICl, we do not expect a large decrease in  $\beta_{av}$  in ethyne···ICl. Accordingly, if we assume  $\beta_{av} = 4.5(5)^{\circ}$ , we can be reasonably confident that the actual value will lie in the range.

The values of  $\delta_1 - \delta_2$  and  $\delta_2$  obtained by using the observed  $\chi_{aa}(X)$  (Table 1), the known  $\chi_0(X)$  values<sup>5</sup> and  $\chi_A(X)$  values<sup>22</sup> (Table 2) and  $\beta_{av} = 4.5(5)^{\circ}$  in eqns. (2), (3) and (4) are recorded in Table 3 for each of the three isotopomers  $C_2H_2\cdots I^{35}Cl$ ,  $C_2H_2\cdots I^{37}Cl$  and  $C_2D_2\cdots I^{35}Cl$ . The errors quoted are those resulting from the assumed range of  $\beta_{av}$ , to which the values of  $\delta_1 - \delta_2$  and  $\delta_2$  are not very sensitive. The implication of the results in Table 3 is that  $\delta_1 = 0.026$ , *i.e.* the intermolecular charge transfer corresponds to *ca*. 2 to 3% of an electron from the ethyne  $\pi$  bond to I. The polarisation of

Table 3 Some determined properties of ethyne...ICl

	Isotopomer			
Property	$C_2H_2\cdots I^{35}Cl$	$C_2H_2\cdots I^{37}Cl$	$C_2D_2$ ···I <sup>35</sup> Cl	
$ \begin{array}{c} \delta_1 - \delta_2^a \\ \delta_2 \\ k_{\sigma} / \mathrm{Nm}^{-1} b \\ \alpha_{\mathrm{av}} / \mathrm{degrees}^c \end{array} $	-0.0300(3)	-0.0302(3)	-0.0300(3)	
	0.0561(2)	0.0560(2)	0.0568(2)	
	12.12(8)	12.3(2)	13.4(3)	
	75(2)	$75(2)^d$	80(2)	
$egin{array}{l} eta_{ m av}/{ m degrees}^e \ r_{ m cm}/{ m \AA}^f \ r(*\cdots { m I})/{ m \AA}^g \end{array}$	4.5(5)	4.5(5)	4.5(5)	
	3.6169(14)	3.6398(14)	3.6151(14)	
	3.1150(14)	3.1157(14)	3.1131(14)	

<sup>*a*</sup>  $\delta_1$  is the fraction of an electronic charge transferred from ethyne to I and  $\delta_2$  is the fraction of an electronic charge transferred from I to Cl on complex formation. See text for discussion. <sup>*b*</sup> Calculated from  $\Delta_J$  using eqn. (5). The errors are those propagated from  $\Delta_J$  and do not reflect systematic errors in the model. <sup>*c*</sup> Calculated from eqn. (7). See text for discussion. <sup>*d*</sup> Assumed value. <sup>*e*</sup> See text for method of estimation of  $\beta_{av}$ . <sup>*f*</sup> Calculated from eqn. (8). <sup>*g*</sup> Calculated from eqn. (9).

the ICl subunit corresponds to the transfer of 0.056e from I to Cl, leading to a net decrease of 0.030e at I.

## 3.4 Strength of the intermolecular binding

The extent of both inter- and intramolecular charge redistribution, estimated from the nuclear quadrupole coupling constants in the preceding section, is small and suggests that the complex ethyne.  $\cdot$  ICl is weakly bound. One criterion of the binding strength is the intermolecular stretching force constant  $k_{\sigma}$ , which measures the restoring force for unit infinitesimal displacement along the weak bond direction. In the approximation of rigid, unperturbed subunits and ignoring potential constants beyond the quadratic, the centrifugal distortion constant  $\Delta_J$  of a planar complex of  $C_{2v}$  symmetry, such as ethyne.  $\cdot$  ICl, is related to  $k_{\sigma}$  by<sup>23</sup>

$$k_{\sigma} = (8\pi^{2}\mu/\Delta_{J}) \times [(1-b)B^{3} + (1-c)C^{3} - {}^{1/4}(B-C)^{2}(B+C)(2-b-c)]$$
(5)

In eqn. (5),  $\mu = m^{C_2H_2} m^{ICl}/(m^{C_2H_2} + m^{ICl})$ , the rotational constants *B*,  $B^{C_2H_2}$  and  $B^{ICl}$  refer to the complex, ethyne<sup>19,20</sup> and ICl,<sup>5</sup> respectively,  $b = (B/B^{C_2H_2}) + (B/B^{ICl})$ , and *c* has the corresponding definition in terms of the rotational constants *C*.

The values of  $k_{\sigma}$  obtained by using eqn. (5) for each of the three isotopomers of ethyne...ICl investigated are included in Table 3. Zero-point spectroscopic constants were used for the complex (see Table 1) and for the free component molecules (Table 2). We note that  $k_{\sigma}$  so determined is isotopically invariant between the two isotopomers  $C_2H_2\cdots I^{35}Cl$  and  $C_2H_2\cdots I^{37}Cl$  within the error propagated from  $\Delta_J$ . The slightly larger value for  $C_2D_2\cdots I^{35}Cl$  is probably a result of the difficulties of determining  $A_0$  and  $\Delta_J$  separately in this case. The reduced number of  $K_{-1} = 1$  transitions available for this isotopomer (for reasons discussed in Section 3.2) means that the errors in the two quantities  $A_0$  and  $\Delta_J$  are probably underestimated.

## 3.5 The intermolecular distances $r_{cm}$ and $r(*\cdots I)$

It was argued in Sections 3.2 to 3.4 that ethyne...ICl has a planar, T-shaped geometry of the type shown in Fig. 1, that the intermolecular binding is weak (according to the  $k_{\sigma}$  criterion) and that the electric charge redistribution on complex formation corresponds to only a few percent of an electron. In this section, we determine the distance  $r_{\rm cm}$  between the centres of mass of ethyne and ICl and the distance  $r(*\cdots I)$ , where \* identifies the centre of mass of the ethyne subunit.

It is not possible from results presented here to determine any small structural changes in the ethyne and ICl subunits that attend formation of the complex. In view of the weak binding, we shall assume that the subunit geometries survive unchanged. The *a*-coordinate of the <sup>35</sup>Cl atom can be determined from the changes  $\Delta I_b$  and  $\Delta I_c$  in the zero-point moments of inertia on substitution of <sup>35</sup>Cl by <sup>37</sup>Cl in the usual way by using Kraitchman's equation<sup>24</sup> for substitution of an atom on the symmetry axis of a  $C_{2v}$  planar molecule. The appropriate expression is

$$a_{\rm Cl}^2 = (\Delta I_{\rm b} + \Delta I_{\rm c})/2\mu_{\rm s}, \qquad (6)$$

where  $\mu_s = M \cdot \Delta m/(M + \Delta m)$ . The result is  $a_{CI} = 2.332$  Å. If I lies closer to the ethyne subunit, as in the geometry shown in Fig. 1, this value of  $a_{CI}$  implies the iodine coordinate  $a_I \approx 0$ , since  $r_0 = 2.3236$  Å in free ICL<sup>5</sup> The alternative arrangement in which Cl lies closer to ethyne than I would require  $a_I \approx 4.6$  Å, which is clearly unreasonable, given the predominant contribution of I to the mass of the complex.

The model used to determine  $r_{\rm cm}$  and  $r(*\cdots I)$  from the observed zero-point moments of inertia is shown in Fig. 2. It assumes that the ethyne and ICl subunits execute the zero-point angular oscillations  $\alpha$ ,  $\beta$  and  $\psi$ , as defined in Fig. 2, but with the distance  $r_{\rm cm}$  between the mass centres fixed. The motion described by the angle  $\psi$  is assumed to be two-dimensionally isotropic. By averaging over the angles  $\alpha$ ,  $\beta$  and  $\psi$ , the following relations between the principal moments of inertia of the complex and those,  $I_b^{\rm C_2H_2}$  and  $I_b^{\rm ICl}$ , of the components can be established:

$$I_a = I_b^{C_2 H_2} \langle \sin^2 \alpha \rangle + I_b^{ICl} \langle \sin^2 \beta \rangle \tag{7}$$

$$I_b + I_c = 2\mu r_{\rm cm}^2 + I_b^{\rm C_2H_2} \langle 1 + \cos^2 \alpha \rangle + I_b^{\rm ICl} \langle 1 + \cos^2 \beta \rangle$$
(8)

The values of  $I_a$ ,  $I_b$ ,  $I_c$ ,  $I_c^{CH_2}$  and  $I_b^{ICI}$  are available from rotational constants in Tables 1 and 2. As discussed in Section 3.3,  $\beta_{av} = \cos^{-1} \langle \cos^2 \beta \rangle^{1/2}$  can be assigned the value 4.5(5)°. The value of  $\alpha_{av}$  can be determined from eqn. (7). For the isotopomer  $C_2H_2\cdots I^{35}Cl$ , for which the rotational constant  $A_0$  is best determined, the application of eqn. (7) with  $\beta_{av} = 4.5(5)^\circ$  leads to  $\alpha_{av} \approx 75(2)^\circ$ . The corresponding angle, similarly determined, for the isotopomer  $C_2D_2\cdots I^{35}Cl$  is 80(2)°. When the same approach is applied to the isostructural complex ethyne...ClF, the angles  $\alpha_{av} = 78(4)^\circ$  and 80(4)° are obtained 13 for  $C_2H_2\cdots 3^5ClF$  and  $C_2D_2\cdots 3^5ClF$ , respectively. A smaller oscillation angle for the  $C_2D_2$  subunit is reasonable in view of the larger reduced mass for the motion.

Given the angles  $\alpha_{av}$  and  $\beta_{av}$ , eqn. (8) may be used to determine  $r_{cm}$ . The results for the three isotopomers  $C_2H_2\cdots I^{35}Cl$ ,  $C_2H_2\cdots I^{37}Cl$  and  $C_2D_2\cdots I^{35}Cl$  are given in Table 3, in which the values of  $\alpha_{av}$  and  $\beta_{av}$  are also included. In view of the larger error in  $A_0$  for  $C_2H_2\cdots I^{37}Cl$ , the value of  $\alpha_{av}$  for this isotopomer was assumed unchanged from  $C_2H_2\cdots I^{35}Cl$ . The best approximation possible to the equilibrium value of the distance  $r(*\cdots I)$  is given by

$$r(*\cdots \mathbf{I}) = r_{\rm cm} - r,\tag{9}$$

where r is the distance of the I atom from the centre of mass in the free ICl molecule (see Table 3). Values of  $r(*\cdots I)$  so determined are given in Table 3.

## 4. Discussion

Use of a fast-mixing nozzle in a Balle–Flygare, Fouriertransform microwave spectrometer has led not only to the isolation of complexes ethyne...ICl in a mixture of the two components which would undergo chemical reaction under normal conditions but also to their characterisation through analysis of the rotational spectrum so detected. Interpretation

**Table 4** Comparison of some properties of the series of complexes ethyne...XY, where XY = ClF,  $Cl_2$ , BrCl or ICl

XY	$k_{\sigma}/\mathrm{Nm}^{-1}$	$\delta_2{}^a$	$r(*\cdot\cdot\cdot X)/\text{\AA}$	$\{\sigma(\mathbf{C}) + \sigma(\mathbf{X})\}/\mathbf{\mathring{A}}^{b}$	⊿r/Å <sup>c</sup>
$\begin{array}{c} \operatorname{Cl}_2^{\ d} \\ \operatorname{ClF}^{e,f} \\ \operatorname{BrCl}^{g,h} \end{array}$	5.6 10.0 9.4	0.020 0.016 0.032	3.163 2.873 3.059	3.50 3.50 3.65	0.34 0.63 0.59
ICl <sup>i</sup>	12.2	0.056	3.115	3.85	0.74

<sup>*a*</sup>  $\delta_2$  is the fraction of an electronic charge transferred from XY when ethyne···XY is formed. The method used to estimate  $\delta_2$  for the CIF complex is given in ref. 3. <sup>*b*</sup>  $\sigma(C)$  and  $\sigma(X)$  are van der Waals radii from ref. 25. The value used for C in C<sub>2</sub>H<sub>2</sub> is half the thickness of the benzene ring (1.7 Å) given in ref. 25. <sup>*c*</sup>  $\Delta r = \{\sigma(C) + \sigma(X)\} - r(*\cdots X)$ , where \* is the centre of gravity of the ethyne molecule. <sup>*d*</sup> Ref. 12. <sup>*e*</sup> Ref. 13. <sup>*f*</sup> Ref. 3. <sup>*g*</sup> Ref. 14. <sup>*h*</sup> Ref. 2. <sup>*i*</sup> This work.

of the spectroscopic constants of three isotopomers of ethyne...ICl has established the angular geometry of the complex, the intermolecular distance  $r(*\cdots I)$ , the strength of the interaction (as measured by  $k_{\sigma}$ ), and some details of the electric charge redistribution on association of the component molecules.

The corresponding sets of properties, similarly determined,<sup>12-14</sup> are now available for the series of complexes ethyne···XY, where  $XY = Cl_2$ , ClF, BrCl or ICl, and are compared in Table 4. Each member of the series has the planar, T-shaped angular geometry of  $C_{2v}$  symmetry of the type shown in Fig. 1 and in each case the halogen atom of higher atomic number is closest to the  $\pi$ -bond of ethyne. The distances  $r(*\cdots X)$  are systematically shorter by  $\Delta r = {\sigma(C) + \sigma(X)} - r(*\cdots X)$  than the sum of the van der Waals radii of C and X,<sup>25</sup> as may be seen from Table 4 which gives values of  $\sigma(C) + \sigma(X)$  and  $\Delta r$ . The value  $\sigma(C) = 1.7$  Å, which is the half-thickness of the benzene ring, suggested by Pauling<sup>25</sup> was adopted. The contraction  $\Delta r$  for a given XY in the series of ethyne...XY complexes given in Table 4 is almost identical to the corresponding  $\Delta r$  in the series OC···XY, which was reviewed recently.<sup>6</sup> The origin of the contraction lies in the so-called 'snub-nosed' character of the dihalogen molecules XY, i.e. the smaller van der Waals radius along the internuclear axis direction than perpendicular to it and has been discussed elsewhere.1,2,6

It is clear from the  $k_{\sigma}$  values given in Table 4 that the order of binding strength in the series ethyne···XY is XY = ICl > BrCl ~ ClF > Cl<sub>2</sub>. The same order prevails in the corresponding OC···XY series and was readily rationalised in terms of the electric moments of the XY subunits.<sup>6</sup> In fact, the ratio  $k_{\sigma}$  (OC···XY)/ $k_{\sigma}$  (C<sub>2</sub>H<sub>2</sub>···XY) has the values 0.65, 0.70, 0.67 and 0.66 for XY = Cl<sub>2</sub>, ClF, BrCl and ICl. This indicates that the type of systematic behaviour previously noted among the hydrogen-bonded complexes B···HX (X = F, Cl, Br, CN)<sup>26</sup> also occurs in the corresponding 'halogen-bonded' series.

Finally, we note that polarisation of the XY subunit by the ethyne molecule, as determined from the halogen nuclear quadrupole coupling constants  $\chi_{aa}(X)$  and expressed in terms

of a transfer of a fraction  $\delta_2$  of an electronic charge from X to Y, depends mainly on the atom X. Thus, the  $\delta_2$  values lie in the order  $\text{Cl}_2 \sim \text{ClF} < \text{BrCl} < \text{ICl}$ , which is that expected from polarizabilities. The molar refraction constants [R], which are proportional to the atom polarizabilities  $\alpha$  via  $[R] = (4\pi\epsilon_0)^{-1}(4\pi N_A \alpha/3)$ , assigned to the atoms Cl, Br and I by Ingold are 5.9, 8.8 and 13.8 cm<sup>3</sup> mol<sup>-1</sup>, respectively.<sup>27</sup>

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