Characterisation of the Intermediate $C_2H_4\cdots Cl_2$ in a Gaseous Mixture of Ethene and Chlorine by Rotational Spectroscopy: A Weak π-Type Complex

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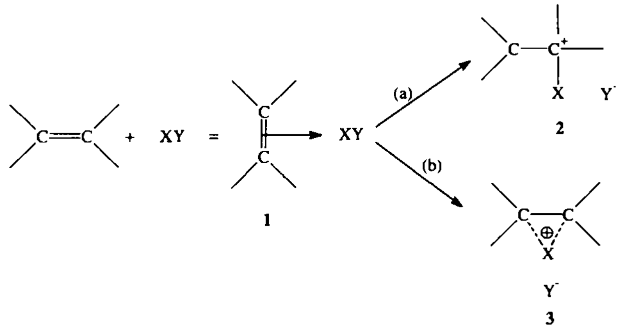
Abstract: A complex of ethene and Cl_2 has been characterised in the gas phase. Rotational spectra of the isotopomers $C_2H_4\cdots{}^{35}Cl_2$, $C_2H_4\cdots{}^{35}Cl^{37}Cl$ and $C_2H_4\cdots{}^{37}Cl^{35}Cl$ were recorded by using a fast-mixing nozzle in an FT microwave spectrometer. Rotational constants, centrifugal distortion constants and Cl nuclear quadrupole coupling constants $\chi_{gg}(Cl)$ are reported in each case. The complex is of the π-donor–acceptor type and has a C_{2v} geometry in which Cl_2 lies along the C_2 axis perpendicular to the plane of the C_2H_4 nuclei. The binding is weak, and only small changes in the $\chi_{gg}(Cl)$ attend complex formation. A simple model attributes these changes to a transfer of around $0.02\,e$ from the inner to the outer Cl nucleus, thus confirming that the complex is of the Mulliken outer type. Similarities in the properties of $C_2H_4\cdots Cl_2$ and $C_2H_4\cdots HCl$ indicate that the angular geometry is in both cases determined mainly by the electrostatic part of the interaction. The distance from the π-bond midpoint to Cl decreases from $C_2H_4\cdots HCl$ to $C_2H_4\cdots Cl_2$; this suggests that Cl_2 is "snub-nosed".

Keywords
chlorine complexes · ethene complexes · intermediates · rotational spectroscopy

1. Introduction

The nature of the initial interaction between an ethene molecule and a chlorine molecule holds a special position in chemistry for several reasons. First, ethene is the prototype unsaturated aliphatic hydrocarbon, while chlorine is the most commonly available halogen. Secondly, the interaction of alkenes and halogens leads to complexes belonging to a group that featured centrally in Mulliken's classification of charge-transfer complexes.[1,2] In the nomenclature proposed by Mulliken, the complex of ethene and chlorine is described as being of the bπ·aσ type, that is to say, involving donation of electrons from the π bonding orbital of ethene into the σ antibonding orbital of Cl_2. A question of immediate interest is whether the complex belongs to the inner (strong, significant charge transfer) or outer (weak, minor charge transfer) class defined in refs. [1] and [2].

The third reason for interest in the interaction of ethene and Cl_2 arises because it leads to chemical reaction. The addition of halogens or interhalogens XY to C=C double bonds constitutes an important class of reactions that has been the subject of intense and extended investigations.[3–6] There appears to be general agreement that in the dark and in polar solvents these reactions proceed via a mechanism of the type shown in Scheme 1 (a) or (b). However, the exact nature of the carbonium ion in solution (i.e., open structure **2** or the cyclic ion **3**) was for some years a matter of some controversy.[7] Recent experimental[8] and theoretical[9] investigations of the bromination of alkenes in polar solvents provide evidence for the bromonium ion **3**, which would be described as an inner bπ·aσ complex. While it is accepted that a complex of type **1** is formed when the alkene and halogen first interact and before the charge separation that characterises the second step, the precise character of this pre-equilibrium complex remains to be established experimentally.



Scheme 1. Generally accepted mechanisms for the addition of halogens or interhalogens XY to C=C double bonds in the dark and in polar solvents.

The existence of complexes of type **1** has been inferred from kinetic studies[3–5] and was first established spectroscopically by Dubois and Garnier[10] who used a spectrophotometric kinetic technique of short mixing time and rapid response to record the UV spectra of these species in solution. Later, a complex of ethene and Cl_2 was isolated in a low-temperature argon matrix and its infrared spectrum obtained.[11] However, in neither of these experimental investigations was a detailed

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characterisation (as defined below) of the intermediate **1** possible. To do this requires the answers to the following questions: What is the geometry of the complex (molecular point group, intermolecular distance)? What is the strength of the interaction? What is the extent of electric charge rearrangement on formation of the complex? Is the charge redistribution minor, implying that **1** in Scheme 1 consists of a pair of weakly interacting, largely unperturbed molecules (an outer complex), or is it major, indicating that **1** already possesses some of the character of **3** (an inner complex). The purpose of the present paper is to provide such a detailed experimental characterisation of the ethene $\cdots$ Cl_2 complex through its rotational spectrum.

On the theoretical side, several ab initio calculations[12] have had the ethene/Cl_2 system as their subject. For example, Kochanski et al.[12] predicted that ionic forms of type **2** and **3** have too high an energy for a chemically possible intermediate state in a gas-phase reaction. They found that the most stable form of complex was of type **1**, which for ethene $\cdots$ Cl_2 was of C_{2v} symmetry, with the Cl_2 molecule lying along the C_2 axis of ethene perpendicular to the molecular plane. They also concluded that the binding in **1** was very weak with only a small amount of charge transfer from ethene to chlorine. The present paper provides an experimental test of these predictions.

The rotational spectra of the three isotopomers $C_2H_4\cdots{}^{35}Cl_2$, $C_2H_4\cdots{}^{35}Cl^{37}Cl$ and $C_2H_4\cdots{}^{37}Cl^{35}Cl$ were recorded by using a pulsed-nozzle, Fourier-transform microwave spectrometer that was fitted with a fast-mixing nozzle.[13] The relevant feature of the latter device is that it keeps the two reactive materials separate until the point at which they expand simultaneously into the evacuated chamber of the spectrometer. The time between the first C_2H_4/Cl_2 encounter and the collisionless phase of the supersonic expansion is then only about 10 μs, long enough for formation of complex **1**, but too short to allow further progress along the reaction coordinate of Scheme 1. A detailed analysis of the spectra led to precise rotational constants, centrifugal distortion constants and Cl nuclear quadrupole coupling constants for each isotopomer. The straightforward interpretation of these spectroscopic constants led to an unambiguous and detailed characterisation of $C_2H_4\cdots Cl_2$ of the type alluded to above. A preliminary account of this work was published earlier.[14]

2. Results

2.1. Identification of $C_2H_4\cdots Cl_2$ and Determination of its Spectroscopic Constants: A rotational spectrum that could be attributed to the complex $C_2H_4\cdots Cl_2$ was observed when Cl_2 gas was flowing continuously through the inner of the two concentric tubes that constitute the fast-mixing nozzle and a gas mixture composed of 2% ethene in argon was pulsed down the outer tube. When the flow of Cl_2 gas was stopped or when the ethene was removed from the argon, the spectrum was not detected. The observed spectral pattern was characteristic of that of a nearly prolate, asymmetric-top molecule in which only the *a* component of the electric dipole moment is nonzero. The transitions were quite weak, as expected of a complex in which both components possess no permanent dipole moment and for which the highest order electric moment is of the quadrupole-induced dipole type.

Each of the observed *a*-type transitions exhibited a complicated nuclear quadrupole hyperfine structure consistent with the presence of two Cl nuclei lying on or close to the *a* axis of the complex. This hyperfine structure pattern allowed an unambiguous assignment of the rotational transitions. The observed frequencies of hyperfine components in the $4_{14}\leftarrow 3_{13}$, $4_{04}\leftarrow 3_{03}$, $4_{13}\leftarrow 3_{12}$, $5_{15}\leftarrow 4_{14}$, $5_{05}\leftarrow 4_{04}$ and $5_{14}\leftarrow 4_{13}$ transitions of the three isotopomers $C_2H_4\cdots{}^{35}Cl_2$, $C_2H_4\cdots{}^{35}Cl^{37}Cl$ and $C_2H_4\cdots{}^{37}Cl^{35}Cl$ are recorded in Table 1. The assignment of the spectrum of $C_2H_4\cdots{}^{37}Cl^{35}Cl$ was complicated by the near-coincidence in frequency of its transitions with those of the most abundant isotopomer $C_2H_4\cdots{}^{35}Cl_2$, especially in the $J = 5\leftarrow 4$ transitions. The reason for this is that the inner Cl atom (Cl_i) lies very close to the centre of mass of the complex. As a result, fewer components of the $C_2H_4\cdots{}^{37}Cl^{35}Cl$ transitions could be measured. No transitions having $K_{-1} > 1$ were observed for any of the isotopomers, presumably because of the relatively high energy of K_{-1} rotational states (the $K_{-1} = 2$ levels lie at 3.2 cm^{-1} above the $K_{-1} = 0$ levels), coupled with the low temperature of the supersonically expanded gas.

The observed frequencies of each isotopomer were fitted in an iterative, nonlinear least-squares analysis to give rotational constants (A_0, B_0, C_0), centrifugal distortion constants (Δ_J, Δ_{JK} and δ_J), and the Cl nuclear quadrupole coupling constants $\chi_{aa}(Cl_x)$ and $\{\chi_{bb}(Cl_x) - \chi_{cc}(Cl_x)\}$, where x = i or o and refers to the inner or outer Cl nucleus. The determined spectroscopic constants are given in Table 2 together with the standard deviation of the fit σ, while the residuals $\Delta\nu = \nu_{obs} - \nu_{calc}$ obtained in the final cycle of the least-squares fit are included in Table 1. As expected for a nearly prolate top ($\kappa = -0.899$) exhibiting only *a*-type transitions, A_0 is less well determined than the other rotational constants but is nevertheless unchanged (within two standard errors) among the three isotopomers. We note that σ is similar to the estimated error of frequency measurement (2 kHz); this indicates that the Hamiltonian employed in the spectral analysis was adequate. The form of the Hamiltonian is shown in Equation (1), where H_R is the effective semi-rigid rotor

$$H = H_R + H_Q \qquad (1)$$

operator appropriate to the Watson A reduction[15] truncated after fourth power terms in the angular momentum (Eq. (2)). In

$$\begin{aligned} H_R = {} & A_0J_a^2 + B_0J_b^2 + C_0J_c^2 - \Delta_J J^4 \\ & - \Delta_{JK}J^2J_a^2 - \Delta_K J_a^4 - 2\delta_J J^2(J_b^2 - J_c^2) \\ & - \delta_K[J_a^2(J_b^2 - J_c^2) + (J_b^2 - J_c^2)J_a^2] \end{aligned} \qquad (2)$$

fact, Δ_K and δ_K could not be determined from the transitions available and were therefore set to zero in the least-squares fit. The term H_Q is the operator describing the interaction of the electric quadrupole moment $\mathbf{Q}(Cl_x)$ of each Cl nucleus with the electric field gradient (e.f.g.) $\nabla\mathbf{E}(Cl_x)$ at the nucleus and is given by Equation (3). The matrix of H was constructed in the coupled basis $\boldsymbol{I}_i + \boldsymbol{I}_o = \boldsymbol{I}$, $\boldsymbol{I} + \boldsymbol{J} = \boldsymbol{F}$ and diagonalised in blocks of F.

$$H_Q = -\,{}^1\!/_6\,\mathbf{Q}(Cl_i):\nabla\mathbf{E}(Cl_i) - {}^1\!/_6\,\mathbf{Q}(Cl_o):\nabla\mathbf{E}(Cl_o) \qquad (3)$$

The matrix elements of Equation (3) in this basis have been given by Keenan et al.[16] Only the diagonal elements of the nuclear quadrupole coupling tensor $\chi_{gg}(Cl_x) = -(eQ/h)\partial^2V/\partial g^2$ ($g = a, b, c$) were determinable.

2.2. Molecular Symmetry of $C_2H_4\cdots Cl_2$: It is clear from the discussion in Section 2.1 that both C_2H_4 and Cl_2 are required to obtain the observed spectrum and that the responsible species contains two Cl nuclei. In addition, the determined spectroscopic constants (Table 2) for the three observed isotopomers allow an unambiguous conclusion about the symmetry and angular geometry of the complex.

Table 1 Observed and calculated transition frequencies of three isotopomers of $C_2H_4\cdots Cl_2$.

Transition		$C_2H_4\cdots{}^{35}Cl_2$		$C_2H_4\cdots{}^{35}Cl^{37}Cl$		$C_2H_4\cdots{}^{37}Cl^{35}Cl$	
$J'_{K_{-1}K_1} \leftarrow J''_{K_{-1}K_1}$	$I'F' \leftarrow I''F''$	ν_{obs} [MHz]	$\Delta\nu$ [kHz][a]	ν_{obs} [MHz]	$\Delta\nu$ [kHz][a]	ν_{obs} [MHz]	$\Delta\nu$ [kHz][a]
$4_{04} \leftarrow 3_{03}$	3 7 ← 3 6	9634.9629	0.4	9426.8508	0.2	9634.5609	1.7
	0 4 ← 0 3	9633.6594	1.0	9425.6865	2.1		
	1 5 ← 1 4	9631.8502	3.9			9632.1244	0.4
	2 5 ← 2 4	9633.2508	−4.5			9632.6712	−12.8[b]
	2 6 ← 2 5	9633.2984	−0.5	9425.5109	0.9	9633.1452	−5.3
	1 4 ← 1 3	9632.7057	−1.0	9424.4860	0.8	9632.3429	0.7
	3 6 ← 3 5	9636.6147	0.0	9428.1826	0.7	9635.9612	2.3
	3 4 ← 3 3	9627.7900	0.5	9420.4550	−0.2		
	3 3 ← 3 2	9625.5885	0.6	9419.2052	−0.5		
	2 3 ← 2 2	9633.2508	−3.1	9424.4403	−0.3		
	3 5 ← 3 4	9633.3556	0.9	9425.4375	−2.8		
	2 4 ← 2 3	9632.9186	1.8	9425.3208	−1.0		
$4_{14} \leftarrow 3_{13}$	3 7 ← 3 6	9556.0520	0.6	9351.1887	−0.7	9555.4890	2.8
	0 4 ← 0 3	9555.2813	−1.6	9350.6379	1.3	9554.8756	−4.9
	1 5 ← 1 4	9551.9749	−0.8				
	2 5 ← 2 4	9552.7717	5.9			9552.2270	−0.1
	2 6 ← 2 5	9552.7973	−0.5	9348.4656	1.4	9552.6831	5.9
	1 4 ← 1 3	9555.1578	−1.4	9350.2307	−2.0	9554.6069	−0.6
	3 6 ← 3 5	9553.7611	−1.4	9348.9497	0.9	9553.3561	−2.3
	3 4 ← 3 3	9546.6975	−1.1				
	2 3 ← 2 2			9347.3549	0.4		
	3 5 ← 3 4	9549.5315	0.4	9345.3621	−1.3	9549.6818	−0.8
$4_{13} \leftarrow 3_{12}$	3 7 ← 3 6	9716.9773	1.4	9505.2492	−0.7	9716.3902	−1.4
	0 4 ← 0 3	9716.2077	−2.1	9504.6970	1.6		
	1 5 ← 1 4	9712.9036	0.2				
	2 5 ← 2 4	9713.7067	5.2				
	2 6 ← 2 5	9713.7226	−3.1	9502.5227	−0.6	9713.5885	0.9
	1 4 ← 1 3	9716.0939	−0.8	9504.3047	−2.0		
	1 3 ← 1 2	9711.7190	−0.1				
	3 6 ← 3 5	9714.6851	1.2	9503.0110	0.2	9714.2595	0.5
	3 4 ← 3 3	9707.6469	1.4				
	2 3 ← 2 2			9501.4433	0.3		
	3 5 ← 3 4	9710.4583	−1.8	9499.4276	1.2	9710.5911	0.1
	2 4 ← 2 3	9711.1953	−1.3				
$5_{15} \leftarrow 4_{14}$	3 8 ← 3 7	11942.7213	0.9	11686.8747	−0.3	11942.2352	−0.7
	1 5 ← 1 4	11941.8491	−2.5				
	2 7 ← 2 6	11940.6833	−0.1				
	0 5 ← 0 4	11941.9186	1.7				
	3 7 ← 3 6	11941.9895	−0.1	11686.0546	−2.1	11941.5066	0.6
	3 6 ← 3 5			11683.9242	2.5		
$5_{14} \leftarrow 4_{13}$	3 8 ← 3 7	12143.8656	1.7	11879.4433	2.3	12143.3578	−0.1
	2 6 ← 2 5	12141.7933	1.0				
	1 5 ← 1 4	12142.9989	−4.3				
	2 7 ← 2 6	12141.8287	−0.5				
	0 5 ← 0 4	12143.0624	1.3				
	1 6 ← 1 5	12141.2990	−0.3				
	3 7 ← 3 6	12143.1325	1.2	11878.6226	−2.0		
	3 6 ← 3 5			11876.4886	−0.3		
$5_{05} \leftarrow 4_{04}$	3 8 ← 3 7	12042.1723	1.5	11782.1715	0.6	12041.7699	0.8
	2 6 ← 2 5	12040.9730	−0.3				
	1 5 ← 1 4	12040.7569	−2.1				
	2 7 ← 2 6	12041.0232	2.1	11781.2775	−1.0		
	0 5 ← 0 4	12041.1921	0.5				
	1 6 ← 1 5	12040.2841	−0.1				
	1 4 ← 1 3	12040.3526	0.3				
	3 7 ← 3 6	12043.3135	−0.6			12042.7185	−0.6
	3 3 ← 3 2	12035.7888	−1.8				
	3 4 ← 3 3	12037.6281	−1.4				
	3 5 ← 3 4	12038.3192	1.6				
	2 4 ← 2 3	12040.9730	2.5				
	3 6 ← 3 5	12041.4556	−0.1	11781.5434	1.6		
	2 5 ← 2 4	12040.8481	−2.1	11781.1769	−1.3		

[a] $\Delta\nu = \nu_{obs} - \nu_{calc}$. [b] Excluded from the fit.

We note first that the rotational constant A_0 is identical, within two standard deviations, for all three isotopomers, but is a few percent larger than the rotational constant C_0 of the free ethene molecule given in Table 3.[17] These observations can be readily understood in terms of an *equilibrium* geometry of $C_2H_4\cdots Cl_2$ having C_{2v} symmetry and in which the Cl_2 internuclear axis coincides with the C_2 axis of free ethene perpendicular to the molecular plane (i.e., with the principal inertial axis *c* of ethene, see Fig. 1).

In the zero-point state of the complex, the two subunits will undergo angular oscillations with respect to their mass centres. If the amplitude of the motion of C_2H_4 subunit is larger than that of Cl_2, these zero-point oscillations will lead to an A_0 for the complex that exceeds C_0 of ethene. The invariance of A_0 to

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Table 2. Ground-state spectroscopic constants of the three isotopomers of $C_2H_4\cdots Cl_2$.

Constant	$C_2H_4\cdots{}^{35}Cl_2$	$C_2H_4\cdots{}^{35}Cl^{37}Cl$	$C_2H_4\cdots{}^{37}Cl^{35}Cl$
A_0 [MHz]	25520(90)	25230(70)	25410(120)
B_0 [MHz]	1224.3817(4)	1197.5235(2)	1224.3508(4)
C_0 [MHz]	1184.1446(4)	1159.0036(2)	1184.1201(4)
Δ_J [MHz]	1.242(5)	1.156(4)	1.230(7)
Δ_{JK} [kHz]	54.5(2)	53.0(2)	54.5(3)
δ_J [kHz]	0.038(4)	0.031(3)	0.029(5)
$\chi_{aa}(Cl_i)$ [MHz]	−111.99(2)	−112.09(1)	−88.28(2) −112.01(4)[a]
$\chi_{aa}(Cl_o)$ [MHz]	−107.24(2)	−84.507(8) −107.22(1)[a]	−107.23(3)
$\{\chi_{bb}(Cl_i)-\chi_{cc}(Cl_i)\}$ [MHz]	−0.55(6)	−0.50(4)	−0.35(6)
$\{\chi_{bb}(Cl_o)-\chi_{cc}(Cl_o)\}$ [MHz]	−0.07(5)	0.01(4)	0.00(8)
σ [kHz][b]	2.1	1.6	3.2

[a] $\chi_{aa}(^{37}Cl)$ multiplied by the ratio of the nuclear electric quadrupole moments $^{35}Q/^{37}Q$ from A. C. Legon, J. C. Thorn, *Chem. Phys. Lett.* **1993**, *215*, 554–560. [b] Standard deviation of fit.

Table 3. Some properties of the ethene and chlorine molecules.

Property	C_2H_4[a]	$^{35}Cl_2$[b]	$^{35}Cl^{37}Cl$[b]
A_0 [MHz]	145837.75(14)	–	–
B_0 [MHz]	30010.79(5)	7287.95(60)	7090.99(60)
C_0 [MHz]	24824.17(5)	7287.95(60)	7090.99(60)
r_0 [Å]	–	1.9915(1)[c]	1.9917(1)[c]

[a] Ref. [17]. [b] Ref. [19]. [c] Calculated from $B_0 = h/8\pi^2\mu r_0^2$.

isotopic substitution within the Cl_2 subunit is also consistent with the equilibrium structure in Figure 1, since both Cl atoms lie on the *a* axis. These conclusions are reinforced when the so-called planar moments P_α ($\alpha = a$, *b* or *c*) of the complex are compared with the corresponding quantities of free ethene, as shown in Table 4. The P_α are defined in terms of the principal moments of inertia by Equation (4), where α, β and γ are to be

$$P_\alpha = {}^1/_2(I_\beta + I_\gamma - I_\alpha) = \textstyle\sum_i m_i\alpha_i^2 \qquad (4)$$

permuted over *a*, *b* and *c*. If the complex has a structure of C_{2v} symmetry of the type shown in Figure 1 and the ethene geometry were unperturbed on complex formation, the equilibrium values of P_b and P_c of the complex would be identical to the corresponding quantities P_a^E and P_b^E (E refers to free ethene), respectively. A comparison of the zero-point values of these quantities, which are listed in Table 4, reveals that this is nearly so. The following argument suggests that the difference $P_b^E - P_c$ in the ground-state values arises mainly from zero-point averaging effects rather than from significant changes in the ethene geometry.

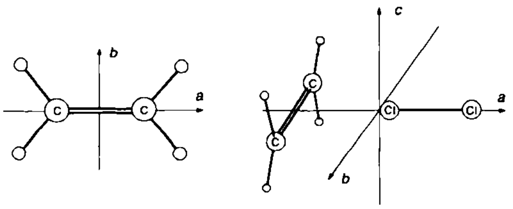

Fig. 1. Directions of the principal inertial axes in ethene (left) and ethene$\cdots Cl_2$ (right).

Table 4. Planar moments of $C_2H_4\cdots{}^{35}Cl_2$, $C_2H_4\cdots{}^{35}Cl^{37}Cl$, $C_2H_4\cdots{}^{37}Cl^{35}Cl$ and C_2H_4

Planar moment[a]	$C_2H_4\cdots{}^{35}Cl_2$	$C_2H_4\cdots{}^{35}Cl^{37}Cl$	$C_2H_4\cdots{}^{37}Cl^{35}Cl$	C_2H_4
P_α [uÅ^2]	409.87(3)	419.02(3)	409.84(4)	0.0531(2)
P_β [uÅ^2]	16.91(3)	17.03(3)	16.96(4)	16.8665(2)
P_γ [uÅ^2]	2.89(3)	3.00(3)	2.93(4)	3.4919(2)
Δ_0 [uÅ^2][b]	1.20(6)	0.98(6)	1.12(8)	-

[a] For the complexes $C_2H_4\cdots Cl_2$ the following identification is to be made: $\alpha = a$, $\beta = b$ and $\gamma = c$, while for C_2H_4 the appropriate identification is $\alpha = c$, $\beta = a$ and $\gamma = b$. [b] Δ_0 is the pseudoinertia defect of $C_2H_4\cdots Cl_2$ defined by Equation (7).

We assume that the equilibrium geometry of the complex is as shown in Figure 1 and that only the intermolecular modes of $C_2H_4\cdots Cl_2$ contribute to its zero-point motion. If the ground-state moments of inertia of free ethene are taken as equilibrium values, Equation (5) then follows, where b_H is the distance of

$$P_b^E = {}^1/_2(I_a + I_c - I_b) = 4m_Hb_H^2 \qquad (5)$$

each H atom from the *ac* plane. If the complex has a pseudoinertia defect of Δ_0 in its ground state, that is, the inertia defect after removal of the contribution of out-of-plane atoms, then Equation (6) follows, where the term $4m_Hc_H^2$ is the contribution

$$P_c = {}^1/_2(I_a^0 + I_b^0 - I_c^0) = -{}^1/_2\Delta_0 + 4m_Hc_H^2 \qquad (6)$$

of the out-of-plane (*ab*) hydrogen atoms. Recalling that the *c* axis of the complex corresponds to the *b* axis of ethene, we can replace $4m_Hc_H^2$ in Equation (6) by P_b^E, and Equation (6) turns into Equation (7).

$$P_b^E - P_c = {}^1/_2\Delta_0 \qquad (7)$$

The values of the pseudoinertia defect for the three isotopomers of $C_2H_4\cdots Cl_2$ are included in Table 4 and lie in the range $\Delta_0 = 1.1 \pm 0.1$ uÅ^2. The value for the analogous but planar complex of ethyne and Cl_2[18] is $\Delta_0 = 1.15(5)$ uÅ^2. The agreement between these two quantities provides evidence that the difference $P_b^E - P_c$ arises from zero-point effects rather than structural changes in ethene when the complex is formed.

All of the above arguments are also consistent with a potential energy surface having two equivalent minima of C_s symmetry separated by a low energy barrier at the C_{2v} form. Such a surface seems unlikely on grounds of chemical intuition, however, and the conclusion of a C_{2v} equilibrium geometry is to be preferred.

2.3. Molecular Geometry of $C_2H_4\cdots Cl_2$: Once the molecular symmetry of $C_2H_4\cdots Cl_2$ is known, it is possible to determine values for the intermolecular distance $r(*\cdots Cl_i)$, where * represents the midpoint of the C=C double bond, and the length $r(Cl_i - Cl_o)$ of the Cl_2 bond from the rotational constants of the three isotopomers given in Table 2.

We shall assume initially that the geometries of C_2H_4 and Cl_2 are unchanged when the complex is formed and later produce evidence in favour of this assumption from various sources, namely the weakness of the intermolecular interaction (as measured by the force constant k_σ—see Section 2.4) and the very small changes in the Cl nuclear quadrupole coupling constants when Cl_2 is subsumed into the complex.

Given that $C_2H_4\cdots Cl_2$ has the C_{2v} geometry of the type shown in Figure 1, it is readily shown that at equilibrium the principal moments of inertia I_α ($\alpha = a, b$ or c) of the complex are related to those of the free Cl_2 and ethene molecules, $I_b^{Cl_2}$ and I_α^E ($\alpha = a, b, c$), respectively, by the Equations (8), (9) and (10),

$$I_a = I_c^E \tag{8}$$

$$I_b = \mu r_{cm}^2 + I_b^{Cl_2} + I_a^E \tag{9}$$

$$I_c = \mu r_{cm}^2 + I_b^{Cl_2} + I_b^E \tag{10}$$

where r_{cm} is the distance between the centres of mass of the ethene and Cl_2 subunits, and $\mu = m_E m_{Cl_2}/(m_E + m_{Cl_2})$. Strictly, to use these equations with the observed ground-state moments of inertia, allowance should be made for the zero-point oscillations of the two subunits about their respective centres of mass. Although we have no information about the motion of the ethene subunit, the Cl nuclear quadrupole coupling constants do provide, in the manner described in Section 2.5, a source of the oscillation angle $\theta_{av} = \cos^{-1} <\cos^2\theta>^{1/2}$ of the Cl_2 subunit, where the instantaneous angle θ is as defined in Figure 2 together with r_{cm}. We shall first use the zero-point moments of inertia in Equations (9) and (10) as though they were equilibrium values and then modify Equations (9) and (10) to allow for θ. The necessary rotational constants (and hence moments of inertia through $B = h/8\pi^2 I_b$, etc.) are in Table 2 (for the complex) and Table 3 (for the ethene[17] and Cl_2 molecules.[19])

The values of r_{cm} resulting from use of Equations (9) and (10) are given in Table 5. We note from Table 5 that r_{cm} becomes either shorter or longer by 0.028 Å when ^{37}Cl substitution is made at either Cl_i or Cl_o, respectively, in $C_2H_4\cdots{}^{35}Cl_2$. Such changes are consistent with the proposed C_{2v} geometry of the complex. To obtain $r(*\cdots Cl_i)$ from r_{cm}, we use the expression $r(*\cdots Cl_i) = r_{cm} - r$, where r is the distance of Cl_i from the Cl_2 subunit mass centre. The errors in r_{cm} and $r(*\cdots Cl_i)$ are those generated from the errors in the rotational constants employed and do not take account of systematic errors in the model. The main part of the error arises from the uncertainty[19] in $B_0^{Cl_2}$. We note from Table 5 that for a given isotopomer $r(*\cdots Cl_i)$ is systematically larger by 0.004 Å when determined from I_b by means of Equation (9) than when Equation (10) is used. This value gives some indication of the error arising from neglect of zero-point effects. On the other hand, when $r(*\cdots Cl_i)$ is determined from a given equation it is approximately 4.5×10^{-4} Å shorter for the isotopomer $C_2H_4\cdots{}^{37}Cl^{35}Cl$ and around 1.5×10^{-4} Å shorter for $C_2H_4\cdots{}^{35}Cl^{37}Cl$ than for the parent isotopomer $C_2H_4\cdots{}^{35}Cl_2$. Such shrinkages on isotopic substitution with a nuclide of larger mass are commonly encountered.[20]

Table 5. The properties of r_{cm}, $r(*\cdots Cl_i)$, δr and k_σ for three isotopomers of $C_2H_4\cdots Cl_2$.[a]

Property	$C_2H_4\cdots{}^{35}Cl_2$	$C_2H_4\cdots{}^{35}Cl^{37}Cl$	$C_2H_4\cdots{}^{37}Cl^{35}Cl$
r_{cm} [Å][b]	4.12170(4) 4.12564(4)	4.14933(4) 4.15322(4)	4.09371(4) 4.09764(4)
$r(*\cdots Cl_i)$ [Å][b]	3.12595(4) 3.12989(4)	3.12583(4) 3.12972(4)	3.12551(4) 3.12944(4)
$10^4\,\delta r$ [Å][b]	0.0 0.0	1.2 1.7	4.4 4.5
k_σ [Nm^{-1}][c]	5.84(2)	5.92(2)	5.91(2)

[a] Errors are those propagated from the spectroscopic constants used to calculate the property. Systematic errors arising from the model employed are significantly larger (see text), but only the spectroscopic errors are included to allow identification of, for example, the small shortening δr. [b] The first row of distances results from the use of I_b in Equation (9) while the second row is from I_c in Equation (10). See text for definition of appropriate distance. [c] Calculated with Δ_J in Equation (15).

Equations (9) and (10) can be modified to allow for the zero-point angular oscillations θ and ϕ of the Cl_2 subunit defined in Figure 2. Since no information about the corresponding motion of the C_2H_4 subunit is available, this will again be ignored. If the motion of the Cl_2 subunit is two dimensionally isotropic in the plane perpendicular to the line r_{cm} (see Fig. 2), it is readily shown[21] that Equations (9) and (10) become Equations (11) and (12), respectively. The angular brackets denote the average

$$I_b = \mu\langle r_{cm}^2\rangle + {}^1/_2 I_b^{Cl_2}\langle 1 + \cos^2\theta\rangle + I_a^E \tag{11}$$

$$I_c = \mu\langle r_{cm}^2\rangle + {}^1/_2 I_b^{Cl_2}\langle 1 + \cos^2\theta\rangle + I_b^E \tag{12}$$

over the zero-point motion, and $\langle r_{cm}^2\rangle$ is the corresponding average of r_{cm}.

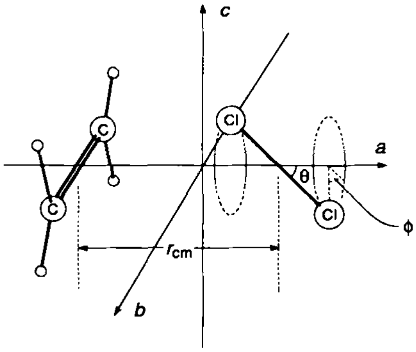

Fig. 2. Definition of the distance r_{cm} and the oscillation angle θ in ethene$\cdots Cl_2$.

It will be shown in Section 2.5 that a proper consideration of the Cl nuclear quadrupole coupling constants leads to an upper limit of $\theta_{av} = \cos^{-1}\langle\cos^2\theta\rangle^{1/2} = 9.5°$ and a best estimate of $\theta_{av} = 6.5(8)°$. When these values are used in Equations (11) and (12) for the isotopomer $C_2H_4\cdots{}^{35}Cl_2$, for example, the results for r_{cm} are 4.124(1) and 4.128(1) Å (for $\theta_{av} = 6.5(8)°$) and 4.127 and 4.131 Å (for $\theta = 9.5°$). Thus, the distances quoted in Table 5 are not very sensitive to the neglect of the Cl_2 motion, which tends to increase the values by between 0.002 and 0.005 Å. The effect of allowing for the oscillation of the ethene subunit would presumably be similar increases and so the values in Table 5 are lower limits, but are unlikely to be in error by more than about 0.01 Å.

In principle, a value of the r_s bond length of the Cl_2 subunit in the complex is available from the rotational constants in Table 2, because isotopic substitution by ^{37}Cl has been carried out separately at Cl_i and Cl_o in $C_2H_4\cdots{}^{35}Cl_2$. The a coordinate of each Cl nucleus is given by use of zero-point moments of inertia in Kraitchman's equation[22, 23] (Eq. (13)) appropriate

$$a_{Cl}^2 = (\Delta I_b + \Delta I_c)/2\mu_s \tag{13}$$

for substitution on the symmetry axis of a C_{2v} molecule, where $\mu_s = \Delta m M/(\Delta m + M)$ is the reduced mass for the substitution and ΔI_α are the changes in moments of inertia accompanying isotopic substitution. The results for the a coordinates, referred to $C_2H_4\cdots{}^{35}Cl_2$ as the parent molecule, are $a_{Cl_i} = 0.070$ Å and

$a_{\mathrm{Cl_o}} = 2.175$ Å. If the Cl_2 subunit is undergoing an angular oscillation of θ_{av}, the distance $r(\mathrm{Cl{-}Cl})$ in the complex is given by Equation (14), and for $\theta_{av} = 6.5(8)°$ leads to $r(\mathrm{Cl{-}Cl}) = 2.119(3)$ Å. A lengthening of the Cl_2 bond by approximately

$$r(\mathrm{Cl{-}Cl}) = (a_{\mathrm{Cl_o}} - a_{\mathrm{Cl_i}})/\cos\theta_{av} \qquad (14)$$

0.127 Å is thus implied when the complex is formed, but this is almost certainly an overestimate and should be treated cautiously. It is well known[24] that small substitution coordinates of <0.1 Å determined through Kraitchman's equations are usually seriously underestimated. The reason for this is that when a nuclide of larger mass is substituted near to the centre of mass of a molecule the change in zero-point motion causes the average lengths of the bonds in which the atom is involved to shrink.[20] The result is that ΔI_b for the substitution is decreased from its equilibrium value and hence $a_{\mathrm{Cl_i}}$ is too small. The shrinkage effect can swamp the small changes in equilibrium moments of inertia when the atom is very close to the centre of mass and can lead to imaginary coordinates.[25] Table 5 shows that $^{37}Cl_i$ substitution gives to relatively large shrinkages of $r(*\cdots \mathrm{Cl_i})$, and hence the underestimation of $a_{\mathrm{Cl_i}}$ is likely to be serious here. An underestimate of as much as 0.1 Å is possible, and it is therefore likely that the Cl_2 is barely lengthened in the complex. A very small lengthening would be entirely consistent with the weakness of the complex (Section 2.4) and the small perturbation of the electric charge distribution of Cl_2 (Section 2.5).

2.4. Strength of the Intermolecular Bond in $C_2H_4\cdots Cl_2$: One measure of the strength of the intermolecular bond of $C_2H_4\cdots Cl_2$ is the quadratic stretching force constant k_σ, which is the force required to produce a unit infinitesimal displacement of $r(*\cdots \mathrm{Cl_i})$ from its equilibrium value by moving Cl_2 along the a axis. It can be shown[26] that, for a complex in which the Cl_2 molecule is perpendicular to a planar subunit such as ethene, the centrifugal distortion constant Δ_J is related to k_σ in the quadratic approximation and under the assumption of rigid subunits by Equation (15), where the rotational constants B and C refer

$$k_\sigma = (8\pi^2\mu/\Delta_J)[B^3(1-b) + C^3(1-c)] \qquad (15)$$

refer to the complex, while $b = (B/B_{\mathrm{Cl_2}}) + (B/B_{\mathrm{E}})$, and c has a corresponding definition. $B_{\mathrm{Cl_2}}$, B_{E}, etc., are the rotational constants of the monomers (Table 3) and μ has been defined in connection with Equations (9) and (10). The values of k_σ determined from Equation (15) for the three isotopomers investigated are included in Table 5. It should be noted that these differ systematically from that reported in ref. [14] because of an error in calculating the preliminary result. We note that k_σ is almost isotopically invariant; this gives some confidence in the applicability of the model in this case. In fact, k_σ for $C_2H_4\cdots Cl_2$ is quite small and indicates that the complex is weakly bound and of the outer bπ·aσ type discussed by Mulliken.[1] Interestingly, k_σ is identical to that of the analogous complex $C_2H_4\cdots HCl$ ($k_\sigma = 5.9\ \mathrm{N\,m^{-1}}$),[27] slightly smaller than $k_\sigma = 6.6\ \mathrm{N\,m^{-1}}$ for $HCN\cdots Cl_2$[28] and much reduced from $k_\sigma = 12.7\ \mathrm{N\,m^{-1}}$ for $H_3N\cdots Cl_2$.[29]

2.5. Interpretation of the Cl nuclear Quadrupole Coupling Constants: The Cl nuclear quadrupole coupling constants of the three observed isotopomers of $C_2H_4\cdots Cl_2$ (see Table 2) are revealing in several ways about the nature of the complex, especially about the changes in the electric charge distribution of the Cl_2 molecule that accompany formation of complex.

First, we note that $\chi_{aa}(^{35}\mathrm{Cl_i})$ and $\chi_{aa}(^{35}\mathrm{Cl_o})$ are each very similar in magnitude to, and of the same sign as, the Cl nuclear quadrupole coupling constant $\chi_0(^{35}\mathrm{Cl}) = -111.790(4)$ MHz of the free $^{35}Cl_2$ molecule.[30] This observation is consistent with the angular geometry shown in Figure 1, in which the Cl_2 subunit lies along the a axis in the equilibrium conformation. It also shows that the electric charge distribution of Cl_2 in the complex is at most perturbed to only a small extent, because $\chi_{aa}(\mathrm{Cl}_x)$ (x = i or o) is proportional to the electric field gradient $-\partial^2 V/\partial a^2$ at nucleus x. Also consistent with this observation is the isotopic invariance of the e.f.g. (see Table 2) even though there is an apparent shrinkage of $r(*\cdots \mathrm{Cl_i})$ on ^{37}Cl substitution (see Table 5).

Secondly, the differences $\{\chi_{bb}(\mathrm{Cl}_x) - \chi_{cc}(\mathrm{Cl}_x)\}$ are very small for both x = i and o. This anisotropy is, of course, identically zero in the free Cl_2 molecule, but when C_2H_4 is brought to its equilibrium position in the complex the axial symmetry of the e.f.g. tensor will necessarily be destroyed. Moreover, the nucleus nearer to C_2H_4 will undoubtedly exhibit the largest anisotropy, and this allows unambiguous assignment of the labels i and o, as does the change in rotational constants for ^{37}Cl substitution at each of the two positions. It is clear that the anisotropy of the e.f.g. at the inner nucleus is very small, while it is undetectable within experimental error at the outer nucleus. These observations too are consistent with only a very small perturbation of the electric charge distribution of Cl_2 by the presence of C_2H_4.

The third piece of information available from the Cl nuclear quadrupole coupling constants is the mean fractional change f in the e.f.g. along a at the inner and outer Cl nuclei induced by complex formation. This provides an estimate of the net transfer of electronic charge from $\mathrm{Cl_i}$ to $\mathrm{Cl_o}$ that results. Recent ab initio SCF calculations[31] have demonstrated that, relative to free Cl_2, $\chi_{aa}(\mathrm{Cl_i})$ increases in magnitude while $\chi_{aa}(\mathrm{Cl_o})$ decreases. In particular, the value of $\chi_{aa}(\mathrm{Cl_o})$ is in good agreement with experiment. The ab initio values, of course, refer to the equilibrium conformation while the observed values of the $\chi_{aa}(\mathrm{Cl}_x)$ are zero-point expectation values. It is found[31] for $C_2H_4\cdots {}^{35}Cl_2$ that the mean value of the equilibrium coupling constants $^1/_2\{\chi^e_{aa}(\mathrm{Cl_i}) + \chi^e_{aa}(\mathrm{Cl_o})\}$ is within 0.5% of the free $^{35}Cl_2$ value. A similar conclusion was established[32] for $^{14}N_2$ in $N_2\cdots HCN$. This result allows the reduction in magnitude of the observed zero-point quantity $^1/_2\{\chi_{aa}(\mathrm{Cl_i}) + \chi_{aa}(\mathrm{Cl_o})\}$ from $\chi_0(\mathrm{Cl})$ of free $^{35}Cl_2$ to be attributed to zero-point averaging in the complex and, for the most part, to the contribution of the angular oscillation θ of the Cl_2 subunit. In that case, we have[32] Equation (16), which leads to $\theta = 6.5\,(8)°$, where the error is that

$$^1/_2\{\chi_{aa}(\mathrm{Cl_i}) + \chi_{aa}(\mathrm{Cl_o})\} = {}^1/_2\,\chi_0(\mathrm{Cl})\langle 3\cos^2\theta - 1\rangle \qquad (16)$$

arising from an assumption that $^1/_2\{\chi^e_{aa}(\mathrm{Cl_i}) + \chi^e_{aa}(\mathrm{Cl_o})\}$ is different from $\chi_0(\mathrm{Cl})$ by at most ±0.5%. Clearly, an upper limit to θ is obtained if all the reduction in magnitude of $\chi_{aa}(\mathrm{Cl_o})$ relative to $\chi_0(\mathrm{Cl})$ is attributed to zero-point effects. The result is $\theta_{av} = 9.5°$. This completes the justification of the choices for θ_{av} in Section 2.3.

Under the assumption that $^1/_2[\chi^e_{aa}(\mathrm{Cl_i}) + \chi^e_{aa}(\mathrm{Cl_o})]$ is unaffected by the presence of the C_2H_4 electric charge distribution, the quantity f (Eq. (17)) defines the mean fractional change in

$$\begin{aligned} f &= [\chi^e_{aa}(\mathrm{Cl_i}) - \chi^e_{aa}(\mathrm{Cl_o})]/[\chi^e_{aa}(\mathrm{Cl_i}) + \chi^e_{aa}(\mathrm{Cl_o})] \\ &= [\chi_{aa}(\mathrm{Cl_i}) - \chi_{aa}(\mathrm{Cl_o})]/[\chi_{aa}(\mathrm{Cl_i}) + \chi_{aa}(\mathrm{Cl_o})] \end{aligned} \qquad (17)$$

the e.f.g. at the inner and outer chlorine nuclei that attends complex formation, since $\chi^e_{aa}(\mathrm{Cl}_x)$ is proportional to the e.f.g. at nucleus x. The second equality holds only if the effects of zero-point averaging on the terms in the numerator cancel with those in the denominator. The value of f that results for $C_2H_4\cdots{}^{35}Cl_2$ is then 0.022. According to the Townes–Dailey model for interpreting nuclear quadrupole coupling constants,[33] the valence bond structures Cl–Cl and Cl^+Cl^- of the chlorine molecule would have values of $\Delta\chi(Cl) = \chi_{aa}(Cl_i) - \chi_{aa}(Cl_o)$ of 0 and -219 MHz, respectively. Hence, transfer of a single electron from Cl_i to Cl_o in $C_2H_4\cdots{}^{35}Cl_2$ would, on the basis of this simple model, lead to $f = 1$. We conclude therefore that the observed value $f = 0.022$ corresponds to a polarization of the electric charge distribution of Cl_2 by C_2H_4 that is equivalent to a transfer of only around 0.02e from Cl_i to Cl_o. In view of this very small estimate of the *intramolecular* charge transfer, it seems unlikely that there is significant *intermolecular* charge transfer when $C_2H_4\cdots Cl_2$ is formed.

3. Discussion

The observed ground-state rotational spectra of the three isotopomers $C_2H_4\cdots{}^{35}Cl_2$, $C_2H_4\cdots{}^{37}Cl^{35}Cl$ and $C_2H_4\cdots{}^{35}Cl^{37}Cl$ of a complex formed by ethene with molecular chlorine have been analysed to yield a range of spectroscopic constants. A detailed interpretation of the rotational constants has established unambiguously that the observed complex has a effective geometry in the ground state of C_{2v} symmetry and almost certainly an equilibrium geometry of this symmetry in which the Cl_2 subunit lies along the ethene C_2 axis that is perpendicular to the plane containing all the nuclei (i.e., along the symmetry axis of the π bonding orbital). The intermolecular stretching force constant k_σ determined from the centrifugal distortion constant Δ_J indicates that the interaction of C_2H_4 and Cl_2 is weak, a conclusion confirmed by an analysis of the changes in the magnitudes of the Cl_2 nuclear quadrupole coupling constants that accompany formation of the complex. Indeed, in the approximation of the Townes–Dailey model for interpreting quadrupole coupling constants,[33] the electric charge redistribution in Cl_2 induced by C_2H_4 can be understood in terms of a transfer of only 0.02e from the inner to the outer chlorine nucleus. These results establish that the observed complex $C_2H_4\cdots Cl_2$ is of the outer b$\pi\cdot$aσ type.[1, 2] There is no evidence of any ionic character of the type required of intermediates **2** and **3** (Scheme 1) discussed in the Introduction. This conclusion is consistent with the results of ab initio calculations.[12]

It is of interest to compare the properties of $C_2H_4\cdots Cl_2$ determined here with those of the analogous hydrogen-bonded complex $C_2H_4\cdots HCl$ (Table 6).[27, 34] Both complexes have an identical angular geometry and identical values of k_σ. The main difference lies in the distance $r(*\cdots Cl)$ from the ethene centre of mass to the nearest Cl atom, which is shorter by 0.60 Å in the Cl_2 complex. It has been pointed out that such distances in hydrogen-bonded complexes are determined by the contact of van der Waals spheres[35] if a radius of zero is assigned to the H atom. If, as suggested by Pauling,[36] spheres of radius 2 Å are placed on the C atoms of C_2H_4 to represent CH_2 and a sphere of radius 1.80 Å is centred on Cl, the distance $r(*\cdots Cl)$ in $C_2H_4\cdots HCl$ is predicted to be 3.74 Å, which is close to the observed value for $C_2H_4\cdots HCl$ (3.724 Å) (shown graphically in Fig. 3). When this approach is applied to $C_2H_4\cdots Cl_2$ an interpenetration of van der Waals spheres of the CH_2 groups and Cl_i is required (see Fig. 3). This interpenetration would be energetically very expensive and therefore unlikely. An alternative explanation has been offered by Buckingham,[37] who suggests the Cl atom in Cl_2 is shorter along the internuclear axis than it is perpendicular to the axis, that is, Cl_2 is "snub-nosed".

Table 6 Comparison of observed properties of $C_2H_4\cdots Cl_2$ and $C_2H_4\cdots HCl$.

Property	$C_2H_4\cdots Cl_2$	$C_2H_4\cdots HCl$
Angular geometry	C_{2v} symmetry; Cl_2 lies along C_2 axis of C_2H_4	C_{2v} symmetry; HCl lies along C_2 axis of C_2H_4
$r(*\cdots Cl_i)$ [Å]	3.128	3.724
k_σ [Nm^{-1}]	5.9	5.9
f[a]	0.02	-

[a] f is the mean fractional difference in electric field gradient of Cl_i and Cl_o induced by C_2H_4 and is given in terms of the Cl nuclear quadrupole coupling constants $\chi_{aa}(Cl_x)$ by Equation (17). In the approximation of the Townes–Dailey model for interpreting nuclear quadrupole coupling constants, f is a measure of the fractional electronic charge transferred from Cl_i to Cl_o.

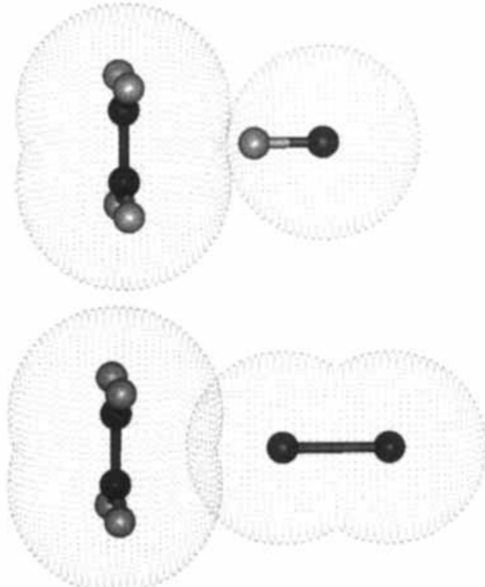

Fig. 3. The "snub-nosed" character of the Cl_2 molecule in the $C_2H_4\cdots Cl_2$ complex compared with the HCl molecule in $C_2H_4\cdots HCl$: The stick diagrams are to scale. Van der Waals spheres of 2.0 Å radius are used for the CH_2 groups, and spheres of radius 1.80 Å for each Cl atom (see text for discussion). The interpenetration of the CH_2 group spheres with that of the inner Cl atom in $C_2H_4\cdots Cl_2$ is physically unreasonable and provides evidence that the Cl atom must be shorter along the axis of the molecule than transverse to it (i.e., Cl_2 is "snub–nosed"). Note that the CH_2 and Cl van der Waals spheres just touch in $C_2H_4\cdots HCl$.

In fact, the parallelism in the observed properties of $C_2H_4\cdots Cl_2$ and $C_2H_4\cdots HCl$ is also apparent for each pair $B\cdots Cl_2$ and $B\cdots HCl$ in the series B = CO,[38, 39] HF,[40, 41] PH_3,[42, 39] HCCH,[18, 43] HCN[28, 39] and NH_3.[29, 39] In other words, for a given B both complexes have identical angular geometries, $\Delta r = r(B\cdots HCl) - r(B\cdots Cl_2) \approx 0.4 - 0.6$ Å for each pair and $k_\sigma(B\cdots Cl_2) \leq k_\sigma(B\cdots HCl)$. It has been known for some time that the angular geometries of, for example, $B\cdots HCl$ can be predicted either by empirical rules that are electrostatic in origin[44, 45] or by a quantitative electrostatic model in which the electric charge distributions of B and HCl are described in terms of a distributed multipole analysis.[35] In view of the parallelism in the experimental properties of $B\cdots Cl_2$ and $B\cdots HCl$, it seems likely that these electrostatic models can also be applied to the series $B\cdots Cl_2$. Certainly, the quantity f, which provides a measure of the perturbation of the electric charge distribution of Cl_2 when within B_{Cl_2}, is small even for the most strongly bound members of the series. This can be

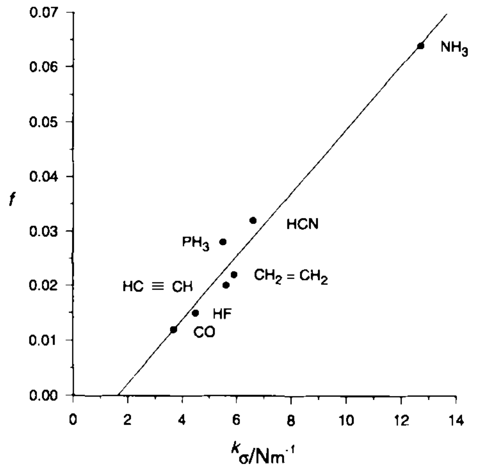

Fig. 4. A plot of f, the mean fractional difference in electric field gradient at Cl_i and Cl_o, against the intermolecular stretching force constant k_σ for the series of complexes $B \cdots Cl_2$, where B is CO, HF, PH_3, C_2H_4, C_2H_2, HCN and NH_3.

seen from Figure 4 which shows f plotted against k_σ for the series $B \cdots Cl_2$ defined above. We note a virtually monotonic increase in f as the intermolecular binding strength (measured by k_σ) increases. Even for the most strongly bound member, f is only approximately 0.06, corresponding to a transfer of $0.06e$ from Cl_i to Cl_o.

The set of empirical rules for predicting the angular geometries of hydrogen-bonded complexes such as $B \cdots HCl$ requires that the axis of the HCl molecule lies along the supposed axis of a nonbonding electron pair on the acceptor atom of B or along the symmetry axis of a π bonding orbital.[44, 45] In the crudest approximation, the electrophilic end $^{\delta+}H$ of the HCl seeks the axis of greatest electron density in B. A consideration of the electric charge distribution of the Cl_2 molecule at this level of approximation indicates why these rules are also likely to apply to $B \cdots Cl_2$ and why the properties of each pair in the series $B \cdots Cl_2$ and $B \cdots HCl$ are similar. Taking the distributed multipole analysis (DMA) of Cl_2 and ignoring the dipoles, quadrupoles, etc.,[35] the charge distribution of Cl_2 consists of a positive charge $\delta+ = 0.259e$ on each atom and a negative charge $\delta- = -0.518e$ at the bond centre. At the same level of approximation, HCl has charges $\delta+ = 0.213e$ on H, $\delta+ = 0.324e$ on Cl and $\delta- = -0.537e$ at the bond midpoint.[35] To the charge distribution of B, the Cl_2 and HCl molecules appear similar.

Experimental Procedure

The ground-state rotation spectrum of the complex $C_2H_4 \cdots Cl_2$ was observed by using a pulsed-nozzle, Fourier-transform microwave spectrometer[46] of the type originally described by Balle and Flygare.[47] To avoid the chemical reaction of ethene and chlorine that occurs when the two gases are mixed and allowed to remain in contact, a fast-mixing nozzle was incorporated into the spectrometer. The device used in the present experiments was similar to that described earlier[13] except in the materials used to construct the concentric tubes which keep the components separate until they expand into the evacuated Fabry–Pérot cavity of the spectrometer. The inner tube was a glass capillary of ca. 0.3 mm diameter through which pure chlorine gas (Aldrich) flowed continuously into the evacuated cavity to give a nominal pressure of 2×10^{-4} mbar. Concentric and coterminal with this capillary was a larger bore tube of Teflon down which a mixture composed of 2% ethene (Argo International) in argon was pulsed from a solenoid valve (General Valve Corp.) at a rate of 4 Hz. The stagnation pressure of the ethene/argon mixture was 3 atm. The gases issuing from the coterminal tubes mixed in a concentric flow which allowed the rapid formation of complexes in three-body collisions at the cylindrical interface. All collisions effectively cease at about 10 nozzle diameters downstream[48] of the mixing point and as long as the chemical reaction cannot increase its extent significantly in the time it takes the molecules in supersonic expansion to travel this distance (ca. 10 µs), the complexes formed initially are frozen. After a short delay (ca. 2 ms) to allow the complexes to reach the axis of the Fabry–Pérot cavity, a 2 µs pulse formed from monochromatic microwave radiation was propagated into the region between the mirrors. The subsequent spontaneous coherent emission from complexes in the gas pulse that had been rotationally polarized by the microwave radiation was collected and detected in the usual way. The observed spectra were relatively weak because $C_2H_4 \cdots Cl_2$ has only a small electric dipole moment that results from polarization of the charge distribution of one molecule by the electric quadrupole moment of the other and because each rotational transition is split into many components by the nuclear quadrupole coupling of the two Cl nuclear spins ($I = {}^3/_2$) to the framework angular momentum. Individual, well resolved Cl nuclear quadrupole hyperfine components had a full width at half-height of ca. 16 kHz (Fig. 5). As a consequence, frequencies could be measured with an estimated accuracy of 2 kHz.

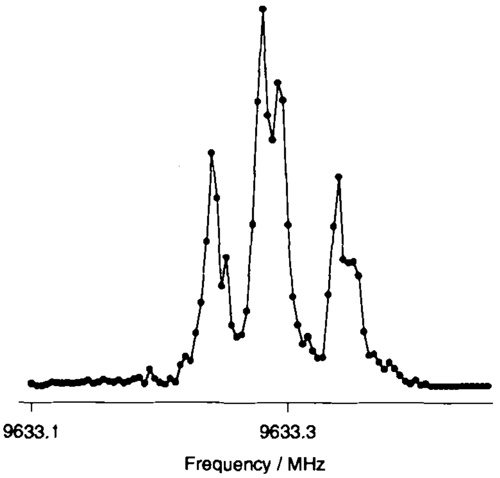

Fig. 5. Three Cl nuclear quadrupole hyperfine components in the $4_{04} \leftarrow 3_{03}$ transition of $C_2H_4 \cdots {}^{35}Cl_2$. The assignments ($I', F' \leftarrow I'', F''$) in order of increasing frequency are (2,5 ← 2,4), (2,6 ← 2,5), and (3,5 ← 3,4). The (2,5 ← 2,4) component is degenerate with (2,3 ← 2,2). Adjacent dots are separated by 3.90625 kHz and have been joined by straight lines. A small Doppler doubling is just discernable for each component. The spectrum was recorded with 860 gas-pulse cycles under the conditions described in the Experimental Procedure.

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