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FEATURE ARTICLE

Pre-reactive intermediates in gas-phase chemical reactions: a contribution from rotational spectroscopy

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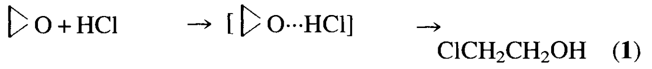
The detection and detailed characterisation of pre-reactive intermediates in gas mixtures through their microwave rotational spectra are described. Spectra were observed by using two special types of nozzle (a fast-mixing nozzle or a glow-discharge nozzle) in a pulsed-nozzle, Fourier-transform instrument. The pre-reactive intermediates are considered for one example of each of the following reaction types: a ring-opening reaction (1), the addition reaction of a halogen to a π bond (2), the abstraction reaction of H from a molecule by fluorine (3), a proton transfer reaction (4), a reaction in which a compound having a dative bond is formed (5), and a prototype unimolecular reaction (6).



O + HCl → [O···HCl] → $ClCH_2CH_2OH$ (1)

$CH_2{=}CH_2 + Cl_2 \rightarrow [CH_2{=}CH_2\cdots Cl_2] \rightarrow CH_2Cl{-}CH_2Cl$ (2)

$NH_3 + F_2 \rightarrow [H_3N\cdots F_2] \rightarrow NH_2F + NHF_2 + NF_3$ (3)

$Me_3N + HI \rightarrow [Me_3NH^+\cdots I^-] \rightarrow$ solid trimethyl ammonium iodide (4)

$NH_3 + BF_3 \rightarrow [H_3N\cdots BF_3] \rightarrow$ solid $H_3N{\cdot}BF_3$ (5)

Ar + HCl (v = 1) → [(10^00) Ar···HCl] → Ar + HCl (v = 0) (6)

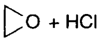
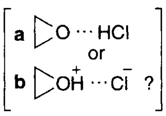
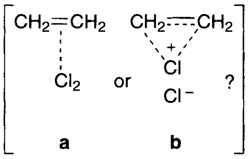
Introduction

This review describes some recent research aimed at identifying intermediates in binary gas mixtures, the components of which, if allowed to, react with each other. The term 'reaction' is here interpreted in a broad sense to include chemical reactions of the conventional type, the precipitation of an ionic solid when two gases are mixed, the formation/precipitation of a molecular solid composed of complexes involving a dative bond, or a prototype unimolecular reaction. The technique involved in detecting and characterising the intermediates is pulsed-nozzle, Fourier-transform microwave spectroscopy which allows ground-state rotational spectra of such species to be observed with both high resolution and high sensitivity. This method has been reviewed elsewhere recently[1] and will not be discussed in detail. The only experimental facet to be highlighted in the present article will be two special nozzles that allow the transient intermediates to be formed and then rapidly isolated. The rotational spectroscopy is then conventional. Most of the article will be concerned with the conclusions of chemical interest that result from characterising the various intermediate species.

Some prototype reactions in the gas phase and pre-reactive intermediates

Some reactions of fundamental interest in chemistry are shown in Table 1. In each case, two reactant molecules come together and form an encounter complex. We shall use the term 'pre-

Table 1 Six gas-phase reactions of interest in chemistry

Reaction	Reactants		Pre-reactive Intermediate		Product	Reaction type
1		→		→	$ClCH_2CH_2OH$	Ring-opening reaction
2	$CH_2{=}CH_2$	→		→	$CH_2Cl{-}CH_2Cl$	Addition of halogen to π bond
3	$NH_3 + F_2$	→	$[H_3N\cdots F_2]$	→	fluoramines	Violent substitution
4	$R_3N + HX$	→	a $R_3N\cdots HX$ or b $R_3NH^+\cdots X^-$?	→	solid ionic ammonium halides	Proton transfer before or after clustering?
5	$NH_3 + BF_3$	→	$[H_3N\cdots BF_3]$	→	solid $H_3N{\bullet}BF_3$	Formation of prototype dative bond
6	Ar + HCl(v = 1)	→	[(10^00)Ar ··· HCl]	→	Ar + HCl (v = 0)	Prototype unimolecular step

reactive intermediates' to describe such complexes because in each case the complex exists at a potential energy minimum but the system is reactive in one way or another, as described below for the particular examples. It is not possible to state with certainty that this potential energy minimum falls on the reaction coordinate in every example, although it does seem likely that the formation of the encounter complex is often a preliminary step.

Reaction 1 in Table 1 is the rapid opening of the three-membered ring that follows mixing oxirane and hydrogen chloride in the gas phase. When the components are so mixed, is the hydrogen-bonded species **1a** formed first, followed by proton transfer to give the protonated ring (a species invoked in proposed solution-phase mechanisms) or is there already incipient proton transfer, *i.e.* does the pre-reactive intermediate already have a substantial extent of ionic character of the type described by **1b**?

Reaction 2 involves the addition of molecular chlorine to ethene. There has been much discussion about the nature of the pre-equilibrium complex.[2] Is it a weak outer complex **2a**, of the type first classified by Mulliken, or is there a significant extent of charge transfer to give the strong inner complex **2b**?[3]

Reaction 3 is included in the discussion because of the legendary reactivity of fluorine with molecules containing hydrogen. When F_2 and NH_3 are mixed in the gas phase the result is a spectacular flame. Can an intermediate be detected in such a violently reactive mixture? What is the nature of this intermediate?

Proton transfer is a process of considerable interest in chemistry. There has been intense speculation about the nature of the ammonium and methylammonium halides in the gas phase.[4] When, say, ammonia and hydrogen chloride gases are mixed (reaction 4), does the formation of complexes $H_3N\cdots HX$ **4a** precede the precipitation of the ionic solid that constitutes the white smoke or is there already an appreciable extent of proton transfer in the complex, *e.g.* $H_3N^+H\cdots X^-$ **4b**? Can the extent of proton transfer in the gas phase be enhanced by progressive methylation of ammonia?

Reaction 5 also involves ammonia. The complex $H_3N{\cdot}BF_3$ was the first coordination compound to be discovered[5] and has been taken as the prototype of the dative bond. However, although the molecular solid has been well characterised, attempts to identify the gas-phase molecule $H_3N\cdots BF_3$ were fruitless, for when the gases NH_3 and BF_3 are mixed the solid is rapidly precipitated and reheating of the solid produces $H_2N{=}BF_2$ in the vapour,[6] not $H_3N\cdots BF_3$. Clearly, a detailed experimental description of various properties of $H_3N{\cdot}BF_3$ in the vapour phase (including the extent of electric charge redistribution) is of value in describing the dative bond.

Reactions 1–5 all involve complexes which presumably must undergo collisions if further reaction is to occur. Reaction 6, on the other hand, is an example of one proceeding by the unimolecular mechanism. Vibrationally excited (v = 1) HCl collides with argon atoms to produce the weakly bound complex (10^00) Ar···HCl, in which the excited vibration is that involving predominantly HCl stretching. But one quantum of the HCl stretching vibration has an energy *ca.* 25 times that required to dissociate the complex into Ar and HCl (v = 0). The second step in reaction 6 (called vibrational pre-dissociation) is the true unimolecular step in which the molecules having sufficient energy decompose. What is the lifetime of this excited complex before vibrational pre-dissociation? In classical language, how long does it take before sufficient vibrational energy leaks from the HCl stretching motion into the mode that leads to dissociation? Does the excited complex live long enough to be observed?

To answer the questions raised in the discussion of reactions 1–6 above, a means must be found for producing the pre-reactive intermediates alluded to and then inhibiting further progress along the reaction coordinate for long enough to detect and characterise these transient species.

How to produce, freeze and characterise pre-reactive intermediates

It is well known that rotational spectroscopy is a powerful method for measuring the precise properties of molecules in isolation in the gas phase. Indeed, much of our detailed knowledge of the structure of small molecules has been gained by this means and has been subsumed into textbooks, often without explicit acknowledgement of its source. In more recent times, it has become possible to investigate the rotational spectra of weakly bound complexes through the techniques of molecular beam electric resonance spectroscopy and pulsed-nozzle, Fourier-transform microwave spectroscopy, in which the pioneering work is associated with the names of Klemperer[7] and Flygare,[8] respectively. The central feature in each case is a supersonic beam or jet of gas formed when the pre-mixed components, heavily diluted in, *e.g.* argon, are expanded from a reservoir at a relatively high pressure through a nozzle (usually a small circular hole) into a vacuum. The gas emerging from the nozzle contains a high proportion of weakly bound complexes which rapidly achieve a state of collisionless expansion and which have very low rotational and vibrational temperatures. While in this collisionless state the complexes can interact with electromagnetic radiation of appropriate frequency (microwaves for rotational transitions) and their spectra recorded. The results to be discussed here have been obtained by using the pulsed-nozzle, Fourier-transform technique[1] in which, as the name implies, individual short pulses of gas are expanded through the nozzle *via* a solenoid valve. We shall not be concerned with the details of rotational spectroscopy, about which there are excellent texts.[9] It is sufficient to mention that several of the spectroscopic observables lead to important molecular properties. Those of relevance to the present discussions are summarized in Table 2, which will be referred to from time-to-time.

Given that rotational spectra of weakly bound complexes can be observed in the manner outlined, the only remaining problem is that the supersonically expanded gas is pre-mixed. Clearly, to observe pre-reactive intermediates in rapidly reacting systems, a method must be found of mixing the components on a sufficiently short timescale immediately prior to expansion. What is the time between mixing and the collisionless phase of the expansion? Is it fast enough for the purposes outlined above? To answer these questions it is necessary to be familiar with the properties of the supersonic expansion,[10] which are dominated by those of argon because it is usually the preponderant (98%) component of the gas mixture. The properties of the expansion are conveniently discussed in terms of the ratio X/d, where X is the distance travelled by the gas downstream from the nozzle exit and d is the nozzle diameter, as defined in Fig. 1. The ratio X/d is proportional to time because within only about one nozzle diameter the gas flow has reached its terminal speed ($\approx 5 \times 10^4$ cm s^{-1} for Ar under conditions appropriate to this discussion).

Gas dynamics calculations[10] show that the translational temperature of the expanded gas achieves a value of *ca.* 1 K within X/d = 10, *i.e.* within a time of about 10 μs if the nozzle has typical diameter $d \approx 0.5$ mm. Fig. 1 shows how the number of binary collisions Z_2 and the number of ternary collisions Z_3 *remaining* to each molecule vary with X/d.[10] Complexes are formed in three-body collisions which, as Fig. 1 shows, are effectively finished at $X/d \approx 2$, that is after a microsecond or two. But the nascent complexes can still undergo two-body collisions (which can lead to either dissociation or reaction) until $X/d \approx 10$, although after that (*i.e.* after *ca.* 10 μs) all such collisions cease. Hence, if the complexes survive until $X/d \approx 10$, no bimolecular reaction is possible thereafter. Moreover, the cooling of the internal energy modes, which accompanies the translational temperature drop, ensures that the complexes will usually have insufficient energy to allow a truly unimolecular decomposition to occur. In short, at *ca.* 10 μs after passing through the nozzle, no further reaction, clustering or precipitation is possible. Clearly, if the reactive gases can be kept separate and away from surfaces until the moment they expand through the nozzle, reactions requiring times > 10 μs can be precluded. This has been achieved by using the device described below.

The so-called fast-mixing nozzle[11,12] is illustrated in Fig. 2. It is usually bolted onto the bottom plate of a standard solenoid valve used in the pulsed-nozzle experiment and consists of a pair of concentric, approximately coterminal tubes of circular cross section. One of the reactive components (*e.g.* NH_3 in the NH_3–F_2 system) is flowed continuously through the central tube (typically of 0.3 mm internal diameter) into the vacuum chamber of the spectrometer. The other component (typically as a 1% mixture in argon) is pulsed from a stagnation pressure of 3 bar down the outer tube. Because the tubes are nearly coterminal, the reactive gases meet only in the roughly cylindrical interface between the concentric flows as they simultaneously undergo the expansion. According to the preceding discussion, complexes formed at the interface rapidly achieve collisionless expansion, are then effectively frozen and can be spectroscopically investigated. The efficacy of the fast-mixing technique is demonstrated by Fig. 3 which shows a rotational transition of $H_3N\cdots F_2$ observed when the component gases are pure NH_3 (central flow tube) and F_2–Ar (pulsed through the outer tube).[13]

The fast-mixing nozzle has been used to investigate the pre-reactive intermediates associated with reactions 1–5, as defined in Table 1. For the prototype unimolecular process (reaction 6), a different type of device, called a pulsed glow-discharge nozzle,[14] was used to produce the excited species (10^00) Rg···HCl, where Rg = Ar or Kr. It consists simply of a standard solenoid valve with a stainless steel ring held concentrically with its outlet orifice but insulated from it. The ring is maintained at a nominal dc potential of -1400 V while the case of the solenoid valve is at earth potential. When a pulse of gas mixture (*e.g.* 1% of HCl in Ar or Kr) is expanded from the solenoid valve in the usual way, it travels through the centre of this ring electrode. At some stage in the expansion through the ring into the vacuum chamber, the instantaneous pressure is appropriate to allow a dc glow-discharge to be sustained in the gas. A few percent of HCl molecules are thereby excited to the $v = 1$ state and these form complexes Ar···HCl or Kr···HCl in the (10^00) state during further expansion. Given that these vibrationally excited complexes do not have too short a lifetime before vibrational pre-dissociation, they can then be detected through their rotational spectrum in the usual way. Fig. 4 shows a region of the rotational spectrum of $^{84}Kr\cdots H^{35}Cl$ with the glow discharge off (*a*) and on (*b*).[15] The appearance of rotational transitions due to (10^00) $^{84}Kr\cdots H^{35}Cl$ is evident in (*b*).

Some conclusions of chemical interest

By using the technique of pulsed-nozzle, Fourier-transform microwave spectroscopy,[1] but modified to incorporate either a fast-mixing nozzle[12] or a glow-discharge nozzle,[14] it has been possible to observe and analyse the rotational spectra of the pre-reactive intermediates in reactions 1–6. From the spectroscopic constants so determined, conclusions of chemical interest concerning these species have been derived (see Table 2). Although the description of reactions 1–6 in Table 1 cited particular examples of complexes B···A, the conclusions of chemical interest have been generalised in the first four cases by applying the same techniques to a range of carefully chosen complexes in which either B or A or both have been systematically varied. These more general conclusions will be referred to in the discussion that follows and references given, as appropriate.

Reaction 1

The ground-state rotational spectra of several isotopomers of a complex of oxirane and hydrogen chloride could be detected when the components were mixed using the fast-mixing

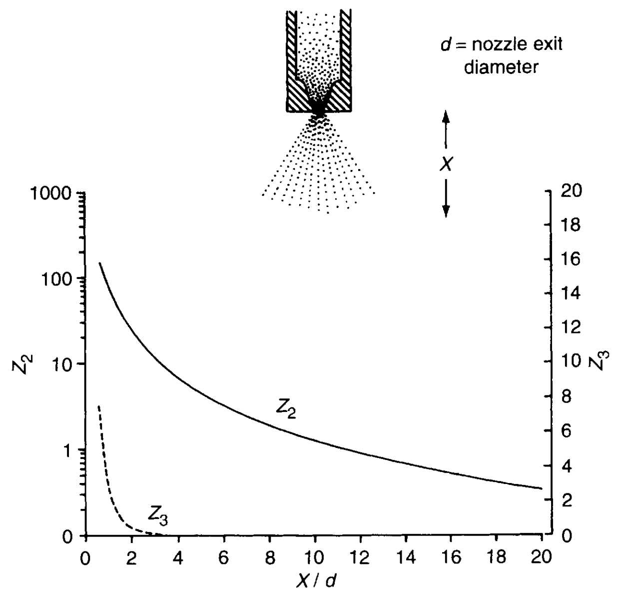


Fig. 1 The number of binary (Z_2) and ternary (Z_3) collisions remaining per molecule plotted against *X*/*d*, the number of nozzle diameters *d* travelled downstream *X* in an axisymmetric expansion of argon. For details, see ref. 10 (redrawn, with permission of Oxford University Press, from ref. 10).

Table 2 Spectroscopic constants from rotational spectroscopy and the molecular properties to which they lead

Spectroscopic constant	Molecular property	Comment
Nature of the spectrum	Symmetry	Special pattern is different for linear, symmetric-top and asymmetric-top molecules. Observation of a particular pattern often allows molecular symmetry to be established.
Rotational constants, A_0, B_0, C_0	Radial and angular geometry	$B_0 = h/8\pi^2 I_b$, where $I_b = \Sigma_i m_i\ (a_i^2 + c_i^2)$ is a principal moment of inertia. I_b depends on the relative positions (*i.e.* principal axis coordinates a_i, c_i) of atoms.
Centrifugal distortion constant, D_J or Δ_J	Intermolecular stretching force constant k_σ of a weakly bound complex	For weakly bound complexes B · · · A, the components B and A can in good approximation be assumed rigid. Then, if higher than quadratic force constants can be neglected, $D_J \propto k_\sigma^{-1}$.
Nuclear quadrupole coupling constants $\chi_{gg}(X) = eQ^x\ q_{gg}^x/h$	Electric field gradient q_{gg}^x at a nucleus X having a nonzero electric quadrupole moment Q^x	q_{gg}^x depends on the detailed electric charge distribution within the molecule. If a molecule X_2 is subsumed into a complex, q_{gg}^x changes and $\chi_{gg}(X)$ can be used as a probe of the change.

nozzle.[16] The rotational constants of the various isotopomers demonstrate that this complex has C_s symmetry and a geometry of the type shown in projection in the symmetry plane (*ac*) of the parent species in Fig. 5. Although it is straightforward to obtain the position of the Cl atom relative to that of the oxirane ring, it is notoriously difficult to place the H atom in a hydrogen-bonded complex in this way. However, the availability of the complete Cl-nuclear quadrupole coupling tensor, χ_{aa}(Cl), χ_{bb}(Cl) and χ_{ac}(Cl), allows an unambiguous conclusion in this case. It can be shown[16,17] that the off-diagonal element χ_{ac} leads in good approximation to the angle α_{az} between the HCl axis (z) and the a-inertial axis in the equilibrium form of the complex (see Fig. 5), that is after allowance has been made for the zero-point angular oscillation of the HCl subunit. Because the position of Cl is well determined from the rotational constants, α_{az} gives the position of H, as long as it can be assumed that the H atom remains attached to Cl at approximately the same distance as in free HCl. That this assumption is justified follows from a detailed interpretation of the component χ_{aa}(Cl) of the Cl-nuclear quadrupole coupling tensor.

Once α_{az} is known, it is a simple matter to obtain χ_{zz}(Cl), the value of the coupling constant along the equilibrium direction z of the HCl subunit, from the value χ_{aa}(Cl) along the inertial axis direction a. After allowance for the zero-point angular oscillation of the HCl subunit (discussed elsewhere),[16] it is found the χ_{zz}(Cl) is only a little changed from that, χ_0(Cl), of the free HCl

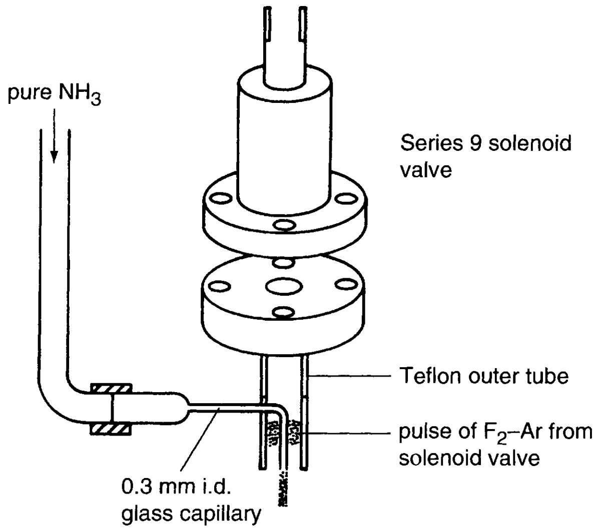


Fig. 2 The fast-mixing nozzle used to observe the rotational spectra of complexes B···XY (see text for discussion). A dilute mixture of one of the components (either B or XY) in argon is pulsed from a Series 9 (General Valve Corp.) solenoid valve down the outer of the two concentric tubes, as indicated. The other component is flowed, undiluted, down the inner glass capillary, the internal diameter of which at its end is *ca.* 0.3 mm. The example of the NH$_3$–F$_2$ system is illustrated.

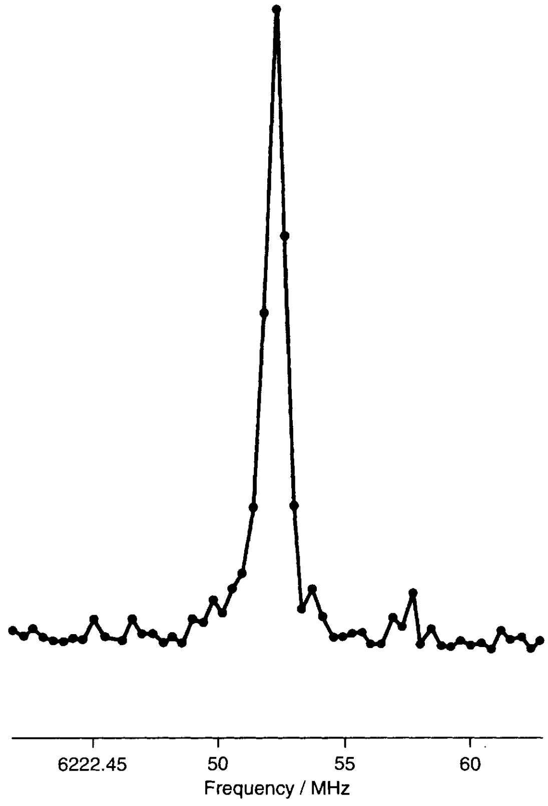


Fig. 3 The $F = 0 \leftarrow 1$ ^{14}N-nuclear quadrupole component of the $J = 1 \leftarrow 0$ transition of H$_3$^{14}N···F$_2$ at 6222.5235 MHz, as observed with the fast-mixing nozzle/FT microwave spectrometer combination

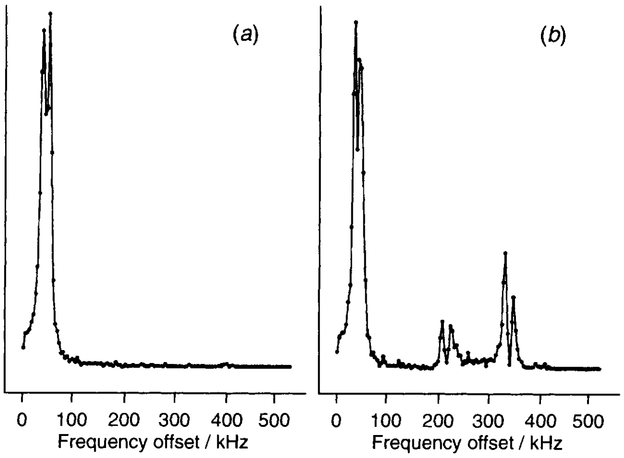


Fig. 4 (*a*) The $F = 9/2 \leftarrow 9/2$ Cl-nuclear quadrupole component of the $J = 5 \leftarrow 4$ transition of (00^00) ^{84}Kr···H^{35} Cl observed in the absence of a glow discharge. The transition is a doublet as a result of a Doppler effect. (*b*) The same region of the spectrum observed under the same conditions, except with the glow-discharge nozzle switched on. The new features arise from two $\Delta F = 1$ Cl-nuclear quadrupole components of the $J = 5 \leftarrow 4$ transition of (10^00) ^{84}Kr···H^{35} Cl. In both (*a*) and (*b*), frequencies are offset at a rate of 3.90625 kHz per point from 11922.0207 MHz. (Reproduced, with permission of the American Institute of Physics, from ref. 15).

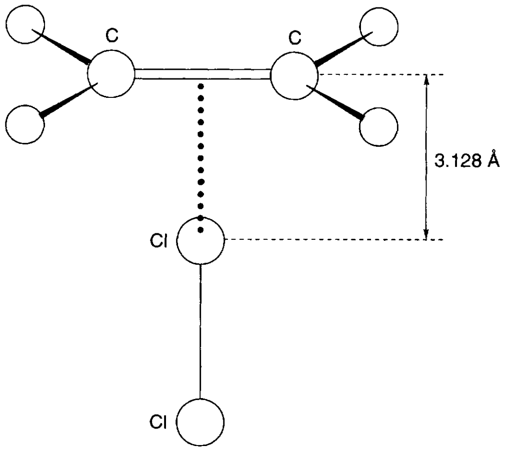


Fig. 5 The hydrogen-bonded complex (CH$_2$)$_2$O···H^{35}Cl formed by oxirane and hydrogen chloride shown in projection in the principal inertial plane *ac* which is also the symmetry plane of this C_s molecule. The angle α_{az} between the HCl axis z and the a axis and the angle θ defining the deviation of the O···H-Cl nuclei from collinearity are indicated. The axes are marked in Å. The hydrogen bond is significantly nonlinear.

molecule. What does this reveal about the nature of the HCl subunit when within the complex?

If there were a significant extent of transfer of the proton from HCl to $(CH_2)_2O$ in the detected complex of oxirane and hydrogen chloride, *i.e.* if the valence-bond description of the complex has a significant contribution from the structure $(CH_2)_2OH^+\cdots Cl^-$ (**1b** in Table 1), we would expect $\chi_{zz}(Cl)$ in the complex to be substantially decreased in magnitude relative to $\chi_0(Cl)$. This can be readily understood when it is recalled (Table 2) that $\chi_{zz}(Cl)$ is proportional to $q_{zz}{}^{Cl}$, the electric field gradient at Cl along the HCl axis z. In a free Cl^- ion, the spherically symmetric electronic charge distribution ensures that $q_{zz}^{Cl^-} = 0$. Of course, in $(CH_2)_2OH^+\cdots Cl^-$ there would be a nonzero value of $q_{zz}^{Cl^-}$ as a result of the presence nearby of the electric charge distribution of $(CH_2)_2O^+H$. However, this is expected to be a small effect, as it is in the diatomic ion-pair species $Na^+\cdots Cl^-$, for which $q_{zz}^{Cl^-}$ is less than 10% of q_{zz}^{Cl} in the covalent HCl molecule.[18] Hence, the fact that q_{zz}^{Cl} of the complex is close to that in free HCl and very much larger than that expected of the ion pair $(CH_2)_2OH^+\cdots Cl^-$ establishes that the HCl subunit is little perturbed when incorporated into the complex. Accordingly, the geometry is that shown in Fig. 5, with the HCl bond length effectively unchanged from free HCl. In those circumstances, knowledge of the angle α_{az} accurately places the H atom and we conclude (see Fig. 5) that the hydrogen bond is significantly nonlinear.[16,17] In fact, the $O\cdots H$–Cl nuclei deviate from collinearity by $\theta = 16.5°$.

The nonlinearities θ of several other $O\cdots H$–X and $S\cdots H$–X hydrogen bonds have been determined[16,17,19–25] in this way for a series of complexes $B\cdots HX$, where B = furan, SO_2, 2,5-dihydrofuran, oxirane, thiirane or formaldehyde and X = F, Cl, Br, CN or C≡CH. It has been possible to rationalise the behaviour of the angle θ when the Lewis base B and the acid HX are varied by introducing a refinement to a simple set of rules that had been proposed earlier.[26] The part of the original rules appropriate to the present discussion stated that the observed angular geometry of $B\cdots HX$ was that resulting if the HX axis were assumed to lie along the axis of a nonbonding electron pair carried by the acceptor atom of B. The pyramidal configuration at O in $(CH_2)_2O\cdots HCl$ and the C_s symmetry of the complex can then be readily understood[16] in terms of the usual (grossly exaggerated) pictorial representation of nonbonding pairs, as can the shallower pyramid in the complex of 2,5-dihydrofuran $\cdots HCl$[19] and the steeper pyramid in thiirane$\cdots$HCl.[22]

The refinement[17,19,23] to the rules requires that a linear hydrogen bond can be envisaged to be formed initially, as described above, but then, with the position of the H atom fixed, the Cl atom swings round in the plane of the C_s molecule until the sum of the force necessary to bend the hydrogen bond by the angle θ, the ring$\cdots$Cl repulsive force and the force of the secondary interaction of the CH_2 ring protons and the Cl atom is zero. Highly nonlinear primary hydrogen bonds experimentally observed in $H_2CO\cdots HCCH$,[24] $(CH_2)_2O\cdots HCCH$[25] and $(CH_2)_2S\cdots HCN$[23] have been rationalised in terms of a weak primary interaction that becomes significantly nonlinear in order to benefit from the stabilising secondary interaction.

Reaction 2

The aim of investigating this system is to determine the nature of the so-called pre-equilibrium complex formed by Cl_2 with alkenes. A detailed interpretation of the spectroscopic constants obtained from analysis of the rotational spectrum of ethene $\cdots Cl_2$, as observed with the fast-mixing nozzle/FT microwave spectrometer combination, characterises this prototype complex unambiguously.[27,28] The magnitudes of the rotational constants A_0, B_0 and C_0 of the species $C_2H_4\cdots{}^{35}Cl_2$, $C_2H_4\cdots{}^{37}Cl^{35}Cl$ and $C_2H_4\cdots{}^{35}Cl^{37}Cl$ demonstrate that the geometry is as shown in Fig. 6, *i.e.* with the Cl_2 internuclear axis lying along the C_2 axis of ethene that is perpendicular to the plane containing the C_2H_4 nuclei. This establishes that the complex is formally of the bπ·aσ type classified by Mulliken.[3] But the question remains: Is the complex of the weak, outer type (**2a** in Table 1) or the strong, inner type (**2b** in Table 1)? This question can be answered by considering the Cl-nuclear quadrupole coupling constants $\chi_{gg}(Cl_x)$ associated with the inner (x = i) and outer (x = o) Cl nuclei and the intermolecular stretching force constant k_σ, as determined from the centrifugal distortion constant Δ_J of the complex (see Table 2).

For a complex in which the Cl_2 internuclear axis (z) coincides with the inertial axis a and is also a C_n axis ($n \geqslant 2$) in the equilibrium geometry, it has been shown[28] that the electric field gradients $q_{zz}^{Cl_i}$ and $q_{zz}^{Cl_o}$ at the inner and outer Cl nuclei increase and decrease in magnitude, respectively, by equal and opposite amounts to a good degree of approximation. In view of the proportionality of $\chi_{gg}(Cl)$ and q_{gg}^{Cl} described in Table 2, the quantity defined by eqn. (1) then provides a measure of the

$$f = [\chi_{aa}^{e}(Cl_i) - \chi_{aa}^{e}(Cl_o)]/[\chi_{aa}^{e}(Cl_i) + \chi_{aa}^{e}(Cl_o)] \qquad (1)$$

mean fractional difference in the electric field gradient at the two nuclei, since in the above approximation $\frac{1}{2}[\chi_{aa}^{e}(Cl_i) + \chi_{aa}^{e}(Cl_o)] \approx \chi_o(Cl)$, the Cl-nuclear quadrupole coupling constant of free Cl_2. Moreover, the equilibrium values in eqn. (1) can be replaced by the observed zero-point values, since the effects of zero-point averaging would then cancel from the expression in good approximation. Hence, f is available from the experimental observables. The value obtained is only 0.022 for $C_2H_4\cdots Cl_2$, which means that the electric field gradients at Cl_i and Cl_o are affected to only a minor extent by complex formation.

The quantity f can be modelled by using the Townes–Dailey method[29] of interpreting nuclear quadrupole coupling constants in terms of valence p, d,...electrons. According to this model in its simplest form, the transfer of a fraction δ of a valence $3p_z$ electron from Cl_i and Cl_o on formation of the complex to give $C_2H_4\cdots Cl_i^{\delta+}Cl_o^{\delta-}$ would lead to coupling constants $(1 + \delta)\,\chi_0(Cl)$ at Cl_i and $(1 - \delta)\,\chi_0(Cl)$ at Cl_o, where $\chi_0(Cl)$ is the free Cl_2 value. Hence, the transfer of a single $3p_z$ electron ($\delta = 1$) to give the inner complex **2b**, $C_2H_4Cl^+\cdots Cl^-$, would lead to $\chi_{aa}(Cl_i) \approx 2\,\chi_0(Cl)$ and $\chi_{aa}(Cl_o) \approx 0$. In fact, the observed quantities $\chi_{aa}(Cl_i) \approx \chi_{aa}(Cl_o) \approx \chi_0(Cl)$ demonstrate that the Cl_2 molecule is essentially unperturbed by complex formation and therefore the complex is of the weak outer type **2a**, $C_2H_4\cdots Cl$–Cl. By substitution of the expressions $(1 \pm \delta)\chi_0(Cl)$ for $\chi_{aa}(Cl_i)$ and $\chi_{aa}(Cl_o)$ into eqn. (1), it is immediately clear that $f = \delta = 0.022$. Therefore, the electric perturbation of the Cl_2 subunit in the complex is very small and can be described in terms of a polarization of Cl_2 that is envisaged as a transfer of ≈ 0.02 e from Cl_i to Cl_o. This conclusion is reinforced by the small value $k_\sigma = 5.9$ N m^{-1} obtained for the restoring force per unit infinitesimal displacement along the C_2 axis of the complex.

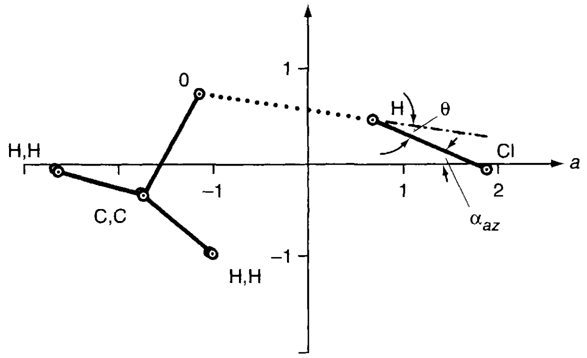


Fig. 6 The experimentally determined geometry of the ethene–chlorine complex. The CH_2 planes are perpendicular to the plane of the paper. The complex is formally of the bπ·aσ type defined by Mulliken (see ref. 3) but is of the weak, outer type with no significant extent of electric perturbation of the Cl_2 subunit (see text for discussion).

This magnitude of the force constant k_σ is typical of that of a weakly bound complex. An ion pair, such as $C_2H_4Cl^+\cdots Cl^-$, would have a much larger k_σ. For example, the force constant for $Na^+\cdots Cl^-$ is 108.6 N m^{-1}.[30]

Similar investigations to that referred to above for $C_2H_4\cdots Cl_2$ have been carried out for the whole series $B\cdots Cl_2$, where B = CO, HF, C_2H_2, C_2H_4, PH_3, H_2S, HCN or NH_3. It was found[31] that the strength of the interaction, as measured by k_σ, increases in the order CO < HF < HC≡CH ≈ PH_3 ≈ $H_2C{=}CH_2$ < H_2S < HCN < NH_3. In fact, $f = \delta$ plotted against k_σ leads to a reasonably straight line. Moreover, even in the case of the most strongly bound of these complexes, namely $H_3N\cdots Cl_2$, δ is only *ca.* 0.06, establishing that all members of the series are outer complexes of the Mulliken type.[3]

Two aspects of the geometry of the series $B\cdots Cl_2$ defined above are of interest. First, it is found[31] that the angular geometry of a given member of the $B\cdots Cl_2$ series is identical to that of the corresponding member of the $B\cdots HCl$ series, even though the angular geometries change considerably from one B to the next and the binding is *via* H in the $B\cdots HCl$ series but Cl in the $B\cdots Cl_2$. For the $B\cdots HCl$ series, the equilibrium angular geometries can be understood in terms of simple rules[26] (alluded to earlier) in which the molecular axis of HCl lies along the axis of a nonbonding or π-bonding electron pair of the acceptor B, as conventionally envisaged. Evidently, these rules also apply to the $B\cdots Cl_2$, except that the internuclear axis of Cl_2 now lies along the axis of the appropriate electron pair on B.[31] The reason for the parallelism of the angular geometries can be understood, and an explanation of why the rules apply to both series can be obtained, if the angular geometries are controlled predominantly by the electrostatic contribution to the interaction energy of the two subunits. In particular, a similarity in the electric charge distributions of HCl and Cl_2 means that, in so far as the electrostatic part of the interaction is concerned, these molecules appear very similar to the approaching Lewis base B.[32]

The second point of interest in the geometries of $B\cdots Cl_2$ and $B\cdots HCl$ lies in the distance $r(B\cdots Cl)$, which is found to be systematically shorter by 0.53(7) Å in the $B\cdots Cl_2$ series.[31] This contraction has been identified in the purely repulsive part of the interaction of a helium atom with HCl and Cl_2 through *ab initio* calculations and has been explained, in part at least, by an anisotropy of the chlorine atom in a chlorine molecule.[33]

A parallel series of investigations of the complexes $B\cdots BrCl$ has revealed a pattern similar to that in the $B\cdots Cl_2$ series as B is systematically varied.[34] There is now a congruence of the angular geometries with those of the $B\cdots HBr$ complexes and a systematic contraction of $r(B\cdots Br)$ from $B\cdots HBr$ to $B\cdots BrCl$. Although the extent of electron transfer from Br to Cl when $B\cdots BrCl$ is formed is larger [$\delta(B\cdots BrCl) \approx 2\delta\,(B\cdots Cl_2)$] it is still small, suggesting that the $B\cdots BrCl$ are also weak, outer complexes in which the interaction is dominated by the electrostatic term. This is reflected in the k_σ values, which are again small for the $B\cdots BrCl$ series, although in general $k_\sigma(B\cdots BrCl) \approx 2k_\sigma(B\cdots Cl_2)$.

It is also revealing to compare the properties of the complexes in a series $B\cdots XY$, where B is fixed and XY = F_2, Cl_2, ClF, Br_2 or BrCl. So far only the case B = NH_3 has been investigated for all the defined XY.[13,35–38] The order of the strength of the binding (as measured by the intermolecular stretching force constant k_σ) is XY = ClF > BrCl > Br_2 > Cl_2 > F_2, which is the order expected if electrostatics dominate the interaction in these complexes but not if charge transfer were predominant.

Reaction 3

Despite the spectacular nature of the flame produced when NH_3 and F_2 gases are mixed under normal conditions of temperature and pressure, it has been possible to observe the rotational spectrum of the complex $H_3N\cdots F_2$ by employing the fast-mixing nozzle.[13] Such an observation testifies to the power of this device as a tool for observing pre-reactive intermediates. The complex $H_3N\cdots F_2$ is found to have C_{3v} symmetry, with the weak interaction between the N atom of NH_3 and the inner F atom of F_2. The relative propensity of F_2 as an electron acceptor in the formation of $B\cdots XY$ donor–acceptor complexes has been discussed earlier in connection with reaction 2.

Reaction 4

The complexes $B\cdots Cl_2$ discussed earlier are of the weak, outer type in the gas phase. If inner complexes $[BCl]^+\ Cl^-$ are involved as intermediates in chlorination reactions in solution, it is likely that progress from $B\cdots Cl_2$ to $[BCl]^+\ Cl^-$ is solvent assisted. This raises the general question: Do inner complexes, implying significant transfer of charge, occur in the gas phase and can they be detected? If we include proton transfer in the general definition of charge transfer, the answer is yes.

To encourage proton transfer in the gas phase and favour an ion pair $BH^+\cdots X^-$ relative to the simple hydrogen-bonded species $B\cdots HX$, B should have a high proton affinity while the energy required to dissociate HX into ions H^+ and X^- should be as small as possible.

Ammonia has a high gas-phase proton affinity and this increases monotonically with progressive methylation. Among the hydrogen halides, the order of the appropriate dissociation energy is HF > HCl > HBr > HI. Hence, of the ammonium and methylammonium halides, $H_3N\cdots HF$ is the least likely and $Me_3N\cdots HI$ is the most likely to exhibit proton transfer in the gas phase.[39]

By using the fast-mixing nozzle it has been possible to observe the rotational spectrum of the complex that results from mixing Me_3N and HI.[40] The detected complex is definitely a symmetric top molecule and the nuclei $N\cdots H\cdots I$ lie in that order along the C_3 axis. But the central question is: where is the proton? This question can be answered by considering the iodine nuclear quadrupole coupling constant $\chi(I)$ and the intermolecular stretching force constant k_σ, which is available from the centrifugal distortion constant D_J.

Table 3 compares $\chi(I)$ for free HI, $HCN\cdots HI$, $H_3N\cdots HI$, $Me_3N\cdots HI$, $Na^+\cdots I^-$ and I^-. The complex $HCN\cdots HI$ provides an example in which the Lewis base is a poor proton acceptor, so that proton transfer to HCN from HI is not expected.[41] In the free ion I^- the iodine nuclear quadrupole coupling constant would be zero because the electronic distribution is spherically symmetric and therefore the electric field gradient at the nucleus would be zero. It is generally accepted that the diatomic molecule NaI is an ion pair $Na^+\cdots I^-$ in the gas phase, as indicated by the small magnitude of $\chi(I)$[42] which differs from zero only because of the presence nearby of the Na^+ ion. Table 3 illustrates that the values of $\chi(I)$ for $H_3N\cdots HI$ and $Me_3N\cdots HI$ are quite different.

Clearly, the $\chi(I)$ value of $H_3N\cdots HI$ is close to that of $HCN\cdots HI$, and both are a little reduced in magnitude from that of free HI. The reductions are readily understood in terms of a relatively large zero-point angular oscillation of the HI subunit in these complexes.[39] On the other hand, $Me_3N\cdots HI$ has a value of $\chi(I)$ close to that of $Na^+\cdots I^-$, indicating that a more accurate

Table 3 Iodine nuclear quadrupole coupling constants $\chi(I)$ and intermolecular stretching force constants k_σ of some $B\cdots HI$ complexes

Molecule	$\chi(I)$/MHz	k_σ/N m^{-1}
HI	−1823.4[a]	—
$HC^{14}N\cdots HI$	−1475.7(1)[b]	4.56(1)[b]
$H_3{}^{14}N\cdots HI$	−1324.891(18)[c]	7.18(9)[c]
$Me_3{}^{14}N\cdots HI$	−341.204(14)[d]	66.5(2)[d]
$Na^+\cdots I^-$	−262.14[e]	77.0[f]

[a] F. C. DeLucia, P. Helminger and W. Gordy, *Phys. Rev. A*, 1971, **3**, 1849. [b] Ref. 41. [c] Ref. 43. [d] Ref. 40. [e] Ref. 42. [f] Calculated from $\omega_e = (2\pi c)^{-1}(k/\mu)^{\frac{1}{2}}$ using ω_e given by J. R. Rusk and W. Gordy, *Phys. Rev. A*, 1962, **127**, 817.

description of the complex is $Me_3NH^+\cdots I^-$. This conclusion is reinforced by consideration of the magnitude of k_σ for trimethylammonium iodide, which is much larger than those of the simple hydrogen-bonded species $HCN\cdots HI$ and $H_3N\cdots HI$ but is indeed similar to that of the ion pair $Na^+\cdots I^-$ (see Table 3).[39]

The conclusions about trimethylammonium iodide and ammonium iodide in the vapour phase have implications for proton transfer. In observing the rotational spectrum of the former, the starting materials were Me_3N and HI held separately until they met at the point of expansion into a vacuum at the coterminal exits of the concentric tubes that constitute the fast-mixing nozzle.[40] Yet within *ca.* 10 μs of the encounter the proton, which was attached to I, was observed to be associated with Me_3NH^+. Conversely, the experiments with $H_3N\cdots HI$ began with the ionic solid ammonium iodide which, on heating, led to the hydrogen-bonded species in the vapour.[43]

In fact, the rotational spectra of several $Me_{3-n}H_nN\cdots HX$ complexes in the methylammonium halide series have been observed. This work has been reviewed elsewhere.[39] The general conclusion is that as NH_3 is progressively methylated the proton, which is attached to Cl in the first member $H_3N\cdots HCl$ of the X = Cl series, gradually shifts towards the N of the base but is only partially transferred by the time $Me_3N\cdots HCl$ is reached. In the series $Me_3N\cdots HX$, where X = F, Cl, Br or I, the proton affinity of the base remains constant while the dissociation energy for $HX = H^+ + X^-$ becomes smaller. It is found that $Me_3N\cdots HF$ is a simple hydrogen-bonded complex, the proton is partially transferred in $Me_3N\cdots H^{\delta+}\cdots Cl^{\delta-}$ but $Me_3NH^+\cdots Br^-$ and $Me_3NH^+\cdots I^-$ are both ion pairs. These results are consistent with energetic considerations, as discussed elsewhere.[39] By contrast, all $Me_{3-n}H_nP\cdots HX$ (n = 3 and 0) so far investigated show no significant extent of proton transfer from X to P. Ultimately, the difference in behaviour in the N and P series can be attributed to the larger ionic radius of P^+ compared with N^+, which leads to a smaller Coulombic energy of interaction in $P^+H\cdots X^-$ than $N^+H\cdots X^-$ and this reflects unfavourably on the energy of the proton-transfer process $P\cdots H{-}X = PH^+\cdots X^-$.[39]

Reaction 5

$H_3N{\cdot}BF_3$ can be considered the prototype donor–acceptor complex. It was discovered by Gay-Lussac in 1809[5] and is the simplest member of the class of compounds $R_3B{\cdot}NH_3$ used by G. N. Lewis to introduce the idea of the dative bond when discussing exceptions to the octet rule.[44] Surprisingly, the compound $H_3N{\cdot}BF_3$ was not identified in the gas phase until recently. Evidently, it is not regenerated when the solid precipitated on mixing the component gases is heated.[6] In view of the place of $H_3N{\cdot}BF_3$ as the first coordination compound, its rôle as a prototype for the dative bond and the fact that it is composed entirely of first row atoms, this species provides an important link between theory and experiment. A detailed investigation of its experimental properties in isolation in the gas phase therefore seemed desirable.

The fast-mixing nozzle/FT microwave spectrometer combination offered an ideal means of detecting the rotational spectrum of $H_3N{\cdot}BF_3$ in mixtures of the components NH_3 and BF_3 before precipitation of the solid. Indeed, by this means the rotational spectra of the four isotopomers $H_3{}^{14}N{\cdot}{}^{10}BF_3$, $H_3{}^{14}N{\cdot}{}^{11}BF_3$, $H_3{}^{15}N{\cdot}{}^{10}BF_3$ and $H_3{}^{15}N{\cdot}{}^{11}BF_3$ were detected, albeit with unexpectedly low intensity.[45] After a difficult analysis, the ^{14}N, ^{10}B and ^{11}B nuclear quadrupole coupling constants were determined. The magnitudes of these quantities were small, thereby suggesting that the ^{14}N and B nuclei sit in tetrahedral environments since in that case the electric field gradients (and therefore the nuclear quadrupole coupling constants, see Table 2) would be reduced in magnitude relative to the free components. An *ab initio* calculation[46] has confirmed this conclusion and has demonstrated that when the electric field gradients q_{zz}^{N} and q_{zz}^{B} along the molecular symmetry axis z at N and B, respectively, are plotted against the separation $r(N\cdots B)$ both show a rapid increase in slope at a certain value of $r(N\cdots B)$, implying a sudden transfer of an electron pair from N to B at a well defined distance. This is presumably a characteristic of the dative bond.

Reaction 6

The interest in complexes (10^00) $Rg\cdots HX$, where Rg is a rare gas atom and X is a halogen atom, lies in the fact that the state (10^00) corresponds to one quantum of excitation in the HX stretching motion. In addition, the excitation energy is greatly in excess (by a factor of *ca.* 25 for $Ar\cdots HCl$) of the energy required to dissociate the van der Waals bond. If (10^00) $Rg\cdots HX$ molecules can be formed and brought to a state of collisionless expansion before collisional deactivation, they provide a model for the simplest possible unimolecular decomposition step in the familiar unimolecular mechanism, namely

$$A^* \rightarrow \text{products} \qquad (2)$$

or to use (10^00) $Ar\cdots HCl$ as a specific example

$$(10^00)\ Ar\cdots HCl \rightarrow Ar + HCl\ (v = 0) \qquad (3)$$

The rotational spectra of (10^00) $Ar\cdots HCl$ and (10^00) $Kr\cdots HCl$ have both been observed[14,15] by using the glow-discharge nozzle (described earlier) in a Fourier-transform microwave spectrometer. Interpretation of the observed spectroscopic constants showed that the properties of these excited state complexes (such as the intermolecular stretching force constant k_σ, the angular oscillation of the HCl subunit and the $Rg\cdots Cl$ distance) were only slightly changed by the vibrational excitation, although there was some indication of a minor strengthening of the interaction on vibrational excitation. The widths of individual rotational transitions were not detectably increased by the vibrational excitation (see Fig. 4, for example), so no measurement of the lifetime of (10^00) $Rg\cdots HCl$ before the vibrational pre-dissociation process (3) was available from line broadening. However, another manifestation of a significant rate of vibrational pre-dissociation for (10^00) $Rg\cdots HCl$ would be the loss of population of this species during the time of its collisionless flight between the point of vibrational excitation (the glow-discharge nozzle) and its detection in the appropriate region of the spectrometer. Loss of population by fluorescence from the (10^00) state is negligible. By means of a series of experiments in which this time of flight was varied over a range of 400 μs, it was found that the relative population N_1/N_0 of the excited and ground states of both $Ar\cdots HCl$ and $Kr\cdots HCl$ remained constant.[47] The conclusion was that the characteristic decay time for vibrational pre-dissociation τ_{vp} exceeds 1 ms for both (10^00) $Ar\cdots HCl$ and (10^00) $Kr\cdots HCl$. It is of interest to note that in 1 ms the HCl molecule executes in excess of 10^{11} vibrations. The van der Waals mode and the HCl stretching mode in these $Rg\cdots HCl$ are indeed extremely weakly coupled.

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