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A Floating Gaussian Orbital Calculation on Argon Hydrochloride (Ar·HCl)

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The electronic structure, properties and binding of the argon hydrochloride (Ar·HCl) complex are discussed in connexion with simple *ab initio* Floating Gaussian Orbital calculations on the system.

Key words: Argon hydrochloride (Ar·HCl) – Van der Waals molecules

1. Introduction

The experimental study of van der Waals molecules has grown considerably over the past few years [1], but, except for relatively small systems, little *ab initio* theoretical work has appeared in the literature. The conventional SCF method is able to calculate dipole-dipole and even dipole-induced dipole (induction) interactions between atomic and molecular systems, but the long-range dispersion interaction is not directly calculable by the SCF approach. In order to produce the multipole interactions included in the dispersion energy [2], two basic methods have been used. Firstly, there is the SCF-CI approach, which can now obtain the He_2 well depth [3], but it is uncertain as to whether the immediate future will see very extensive use of this method for large systems. This is because of the computational effort involved. The second approach involves the use of perturbation theory to obtain values of the C_6, C_8 and C_{10} coefficients in the multipole expansion [2]

$$\varepsilon_{\mathrm{disp}} \sim \frac{C_6}{r^6} + \frac{C_8}{r^8} + \frac{C_{10}}{r^{10}} \tag{1}$$

The dispersion energy $\varepsilon_{\mathrm{disp}}$ is added to the SCF interaction energy (if any). The evaluation of these coefficients from a large basis SCF calculation is not too straightforward, requires iteration and can give unpredictably poor results [2]. Conversely, as Amos and Yoffe have shown [4], these coefficients may be computed

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very simply and with apparently good accuracy from Frost-model wavefunctions [5]. In this article it will be shown how the electronic structure, properties and binding of the argon hydrochloride (Ar·HCl) complex may be described from Floating Gaussian Orbital (FGO) calculations.

Ar·HCl is one of the most experimentally studied of van der Waals molecules [1]. Its geometry and several of its spectroscopic constants have been determined by Klemperer and co-workers [6], but there is disagreement over the Ar···HCl bond energy. Whereas the early infrared work of Rank *et al.* [7] and the more recent results of Miziolek and Pimental [8] and of Boom *et al.* [9] suggest a value of between 4.6 and 5.0 $\mathrm{kJ\ mol^{-1}}$, the molecular beam scattering experiments of Farrar and Lee [10] gave $1.59 \pm 0.08\ \mathrm{kJ\ mol^{-1}}$. This latter well depth has been used in theoretical treatments of the Ar·HCl potential [11, 12].

2. Calculations

The *ab initio* Floating Spherical Gaussian Orbital (FSGO) approach of A. A. Frost [5] has been used extensively in calculations on the electronic structure of molecules. It gives good results for systems which include induction interactions, because of the polarisation built into the floating orbitals [13]. The FSGO model has been adapted slightly for the calculations on Ar·HCl to include floating *s*-type and *p*-type (lobe) functions (hence the generic abbreviation FGO). In the method, the variational energy of a Slater determinant of doubly-occupied FGO's is minimised by varying the position and exponent of each orbital function. The use of floating *s*-type and *p*-type functions is described elsewhere [13, 14]. The FGO configuration is illustrated in Fig. 1.

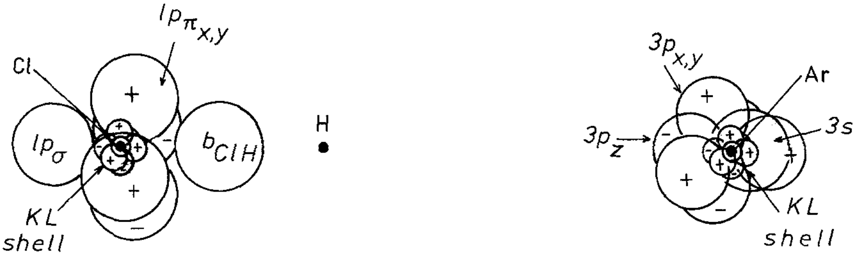

Fig. 1. FGO orbital configuration for the Ar·HCl complex

The Ar·HCl FGO wavefunction was carefully optimised, to determine how certain specific constraints would affect the size and position of the SCF minimum. First, however, the wavefunctions of the Ar and HCl systems were optimised separately. In Calculation I (Table 1) the Ar···HCl distance was varied, but other parameters were fixed. This produced the negligible binding energy of 5 $\mathrm{J\ mol^{-1}}$. Attempted optimisation of the valence orbitals at this geometry (Calculation II) led to no improvement in the binding energy. Polarisation of the argon atom's 3*s* (III) and 3*p* (IV) orbitals was then undertaken, by allowing the orbitals to float along the H···Ar internuclear axis. The 3*s* orbital was very slightly displaced away from the molecule, but little improvement in total energy resulted. The

$3p_{x,y}$ orbitals, however, produced a relatively large lowering in energy when they were moved towards the HCl molecule. The final calculation (V) included all parameters. This gave an SCF binding energy of 0.140 kJ mol^{-1} at an Ar $\cdots$ H distance of 2.827 Å and a very slight increase in the H–Cl bond length of *ca.* 0.00006 Å.

Table 1. Parameter variation and binding energy

Calculation[a]	r(Ar–H), Å	$\Delta\varepsilon_{\mathrm{HF}}$[b]
I [r(Ar–H)]	3.199[c]	0.005
II [Valence orbitals]	···	0.005
III [II+polarised Ar $3s$]	···	0.005
IV [II+polarised Ar $3p$]	···	0.089
V [I–IV+r(H–Cl)]	2.827[d]	0.140[e]

[a] Parameters varied in square brackets.
[b] Hartree–Fock binding energy, kJ mol^{-1}.
[c] r(H–Cl) = 1.198714 Å (calculated).
[d] r(H–Cl) = 1.198778 Å (calculated).
[e] $E_{\mathrm{total}} = -853.67015513$ a.u.

A further calculation on the Ar ···Cl–H isomer (that is, with the argon atom on the other side of the HCl molecule) produced "negligible" binding at the SCF level, with r(Ar ···Cl) apparently optimised near 4 Å. Including the dispersion interaction, evaluated by Amos and Yoffe's expressions [4] for the C_n coefficients between pairs of orbitals in atom and molecule[1], the binding energy of Ar ···Cl–H is calculated to be *ca.* 1.5 kJ mol^{-1}. This should be compared with the binding energy of Ar ···H–Cl (at the FGO optimised geometry) of 0.140 plus 2.545 kJ mol^{-1} ($\varepsilon_{\mathrm{disp}}$), totalling 2.685 kJ mol^{-1}.

During these calculations, several phenomena were noted which may be of interest to others carrying out more conventional large basis calculations. As mentioned above, the imposition of certain constraints on the system led to little or no binding at the SCF level. The most important involved the non-polarisation of the argon $3p_{x,y}$ orbitals. The implication here is that Ar-centred d-orbitals should not be excluded from large basis set calculations, when evaluating induction energies. In the final wavefunction it was noticed that the Cl–H 2π orbitals were also significantly displaced, so that Cl-centred d-functions (as well as H $2p$ orbitals) are likely to be helpful in producing the induction interaction at the SCF level. Naturally the implementation of this will depend upon the precise method, but it would necessarily lead to a considerable increase in computer time.

The geometry of the system was found to depend significantly upon the H–Cl bond length. It should be observed of course, that the FGO H–Cl distance is rather shorter than experiment (about 6%), although it is not clear how this may adversely

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[1] The dispersion energy with respect to the n'th power of R in the multipole expansion is given by $\varepsilon^{n}_{\mathrm{disp}} = \sum_{i=1}^{\mathrm{Ar}} \sum_{j=1}^{\mathrm{HCl}} C^{ij}_{n}/r^{n}_{ij}$, for which C^{ij}_{n} and r_{ij} are the coefficient and distance between orbitals i and j.

affect the calculation of the Ar · HCl complex. It is encouraging, however, that such a simple model can still include some of the effects involved in the binding of asymmetric van der Waals molecules. The optimum exponents in the complex were similar to those obtained in the separated atom and molecule calculations.

Since the binding energy of the Ar · HCl complex is found to be mostly due to the dispersion interaction, it is important that the geometry of the system should be well characterised. This is because of the inverse power dependence in expression (1) for $\varepsilon_{\text{disp}}$. The induction energy calculated here may well be too low, but past experience has shown that the FGO model produces values for this kind of interaction in good agreement (better than 10%) with more extensive calculations [13].

Table 2. Geometry of the Ar · HCl complex (Å)

	Calculated (r_e)	Experiment (r_0)
r(Cl ···Ar)	4.025961	4.006
r(Cl–H)	1.198778	1.284[b]
r(H ···Ar)	2.827184	2.722

[a] Ref. [6]. [b] Assumed value.

The experimental and calculated geometry of the complex is given in Table 2. The Ar–HCl bond energy for the FGO geometry is 2.685 kJ mol^{-1}, to be compared with the experimental estimates of *ca.* 1.6 kJ mol^{-1} [10] or 4.6–5.0 kJ mol^{-1} [7–9]. The FGO results clearly do not agree with the lower scattering value, especially since the calculated r_e (Ar ···Cl) distance is longer than the experimental r_0 result (r_e values are always shorter than r_0). If a rough estimate of the experimental r_e (Ar ···H) were ca. 2.7 Å, then $\varepsilon_{\text{disp}}$ is found to be 3.5 kJ mol^{-1} when recalculating the energy at this geometry. Unfortunately, there is little evidence at the present to indicate how accurate the C_n coefficients are; such as there is [4], implies that calculated values of $\varepsilon_{\text{disp}}$ are reasonably close to experiment. For example, using the most recent empirical results for Ar–Ar [15], Table 3, gives a value for $\varepsilon_{\text{disp}}$ at $r = 3.8$ Å within 0.5% of that obtained by the use of the FGO coefficients[2]. The present calculations therefore concur with the larger experimental values of the Ar ···HCl bond energy.

Table 3. C_n coefficients of the dispersion interaction

	Ar/Ar[a]	Ar/HCl	HCl/HCl
C_6, 10^5 °K Å^6	5.289 (4.694)	7.098	9.621
C_8, 10^6 °K Å^8	1.711 (2.191)	2.567	3.816
C_{10}, 10^7 °K Å^{10}	0.679 (1.34)	4.069	6.636

[a] Experiment [15] in parentheses.

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[2] The following relationship between the coefficients holds to within about 1%: $C_n(\text{A–B}) = [C_n(\text{A–A}) \cdot C_n(\text{B–B})]^{1/2}$.

Table 4. Dipole[a] and quadrupole[b] moments

	Ar	Ar·HCl	HCl
μ_D Ground states	0	1.05274	0.99094[c]
μ_D Complex states	0.05707[d]	—	0.99567[e]
θ_B Ground states	0	···	+2.21443[f]
θ_B Complex states	−0.00034[g]	—	+2.22074

[a] In Debyes (1 D ≈ 3.335641 × 10^{-30} C m).

[b] Calculated, in Buckinghams (1 B ≈ 3.335641 × 10^{-40} C m^2), with respect to the centre of mass using Cl = 35, H = 1: $\theta_B = \Sigma Z_k R_k^2 - \langle z^2 - \frac{1}{2}(x^2 + y^2) \rangle$.

[c] Experiment 1.12 D [16].

[d] Induced dipole moment.

[e] Augmented dipole moment = 0.00473 D.

[f] Experiment 3.84 B [17].

[g] Induced quadrupole moment along z (internuclear) axis (Fig. 2).

3. Electronic Properties

Various electronic properties were calculated for the Ar·HCl complex and separated Ar and HCl systems a) at optimum isolated results (ground states) and b) at optimum complex results (complex states). Table 4 lists dipole and quadrupole moments which show how the induction interaction between atom and molecule perturbs the ground state moments (Fig. 2). The overall dipole moment of the complex, 1.05274 D, may be said to consist of the sum

$$\mu_{\text{total}} = \mu_{\text{HCl}} + \mu^{\text{ind}} + \mu^{\text{overlap}}.$$

This neglects the augmentation of the HCl dipole in the complex, which amounts to ca. 0.5%. When μ^{aug} is included, the overlap dipole is less than 10^{-6} D. The HCl quadrupole moment increases slightly in the complex state. This indicates that the charge distribution becomes slightly more oblate in shape. At the same time, the charge distribution in the argon atom is drawn out along the internuclear axis (that is, it has become prolate along the z axis). The changes in shape, given by the quadrupole moments, for the atom and molecule are mutually "perpendicular" or "compensating" in character (Fig. 2).

The direction and extent of charge transfer in the complex is of considerable interest. This may be inferred from changes in the one-electron potential, evaluated

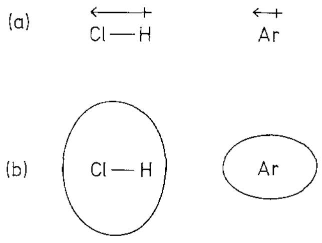

Fig. 2. (a) Dipole-induced dipole and (b) quadrupole-induced quadrupole interactions in the Ar·HCl complex

Table 5. Total one-electron potentials[a]

	Separated systems	Complex
$\langle 1/r_{\mathrm{Ar}} \rangle$	-61.24558	-61.22851
$\Delta\langle 1/r_{\mathrm{Ar}} \rangle$		$+0.01707$
$\langle 1/r_{\mathrm{H}} \rangle$	-0.85866	-0.85902
$\Delta\langle 1/r_{\mathrm{H}} \rangle$		-0.00036
$\langle 1/r_{\mathrm{Cl}} \rangle$	-56.45350	-56.45393
$\Delta\langle 1/r_{\mathrm{Cl}} \rangle$		-0.00043

[a] In a.u.$^{-1}$ ($\approx 3.027705 \times 10^{-9}$ C m^{-1}).

at the nuclei (Table 5). The potential is the sum of a nuclear and an electronic part, respectively:

$$\langle 1/r \rangle = \sum{}' Z/r - \sum \langle \psi | 1/r | \psi \rangle$$

In the complex, $\langle 1/r_{\mathrm{Ar}} \rangle$ increases because a) the distribution of electron density in the HCl molecule is displaced towards the chlorine and b) electrons are transferred from Ar into the region between atom and molecule. If the electron populations in HCl were divided according to the charge on each nucleus (that is, $\mu_{\mathrm{HCl}} = 0$), then the contribution from a) would be zero. The transfer of electrons in b) is suppressed in Calculation I (Table 1). $\langle 1/r_{\mathrm{Ar}} \rangle$ in this case is -61.23222 a.u.$^{-1}$,[3] showing that only about 20% of the increase in $\langle 1/r_{\mathrm{Ar}} \rangle$ calculated in the complex may be ascribed to charge transfer. However, there is no simple quantitative relationship between charge transferred and $\Delta\langle 1/r \rangle$. Nevertheless, the relatively small decreases in $\langle 1/r_{\mathrm{H}} \rangle$ and in $\langle 1/r_{\mathrm{Cl}} \rangle$ in the complex imply that there has been a movement of electron density from Ar towards H, mostly in the region between atom and molecule. This may be attributed to the induced dipole on the argon atom.

A population analysis [18] of the FGO wavefunction is given in Table 6. For

Table 6. Population analysis

	Separated systems	Complex
N_σ (Ar)	10	10
N_π (Ar)	8	7.995892
ΔN_π (Ar)		-0.004108
N_σ (H)	1.064942	1.064382
ΔN_σ (H)		-0.000560
N_π (H)	0.056516	0.060420[a]
ΔN_π (H)		$+0.003904$
ΔN (H)		$+0.003344$
N_σ (Cl)	8.935058	8.935618
ΔN_σ (Cl)		$+0.000560$
N_π (Cl)	7.943484	7.943688
ΔN_π (Cl)		$+0.000204$
ΔN (Cl)		$+0.000764$

[a] Consists of 0.004108e from Ar and 0.056312e from HCl 2π MO.

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[3] a.u.$^{-1}$ = a.u. of potential (Table 5).

Frost-model wavefunctions, according to the relative position of an orbital along a bond, such an analysis is useful for determining how a pair of electrons is shared between two centres. However, because there is no relation between the electron population and the electron density, it is doubtful whether changes in electron population can demonstrate that charge transfer has occurred. Table 6 shows that the argon atom loses 0.1% of its valence π-electrons (with respect to the z axis) to produce a minute Ar–H "double π-bond". This is associated with a population of about 0.004e at the hydrogen nucleus. Further movement of electrons has occurred, from H to Cl (reflected in the augmented complex state dipole moment). None of these changes is reflected in an appropriate increase or decrease of electron density at the nuclei.

Table 7. Stabilisation of Argon 3*s* and 3*p* orbitals in the Ar·HCl complex[a]

	η_i^{observed}	$\eta_i^{\text{complex b}}$
3*s*	27.629	28.443
3*p*	15.759 ($^2P_{3/2}$)	16.790 (σ) 16.637 (π)
	15.937 ($^2P_{1/2}$)	16.980 (σ) 16.825 (π)

[a] In eV. [b] Definition in text.

The SCF orbitals were calculated for the complex and for the isolated atom and molecule. Little change occurs in the HCl orbitals and orbital energies in the complex, the largest being a 0.2% increase in orbital energy for the 2π MO. In fact, all the HCl SCF orbitals are displaced slightly towards higher energies. The Ar atomic orbitals, however, undergo considerable perturbation and stabilisation in the complex. The 3*s* orbital energy decreases by virtually 3%, whilst the 3*p* orbitals split into σ and π components, being stabilised by 6.5 and 5.6%, respectively, in the complex. The FGO orbital energies are poorly calculated with respect to experiment, nevertheless, the relative displacement in energy of the valence orbitals may be less subject to the errors associated with the Gaussian functions. Therefore, Table 7 gives the apparent stabilisation of the argon atomic orbital energy η_i with respect to experiment:

$$\eta_i^{\text{complex predicted}} = \eta_i^{\text{observed}} \frac{\eta_i^{\text{complex calc.}}}{\eta_i^{\text{atom calc.}}}$$

The changes are, in principle, observable in a photoelectron experiment, although a) the Ar^+ $^2P_{3/2}$ and $^2P_{1/2}$ states and components would be shifted into the vibrational structure of the HCl^+ $^2\Sigma^+$ state [19] and b) the concentrational of Ar·HCl is apparently even lower than $(HCl)_2$ [9], which in turn, to all appearances, is not discernible even in high-resolution photoelectron spectra.

4. Electronic Structure

The observed structure of the Ar·HCl complex (and of other van der Waals molecules [20, 21]) raises two interesting questions:

a) why is the arrangement Ar·H–Cl and not Ar·Cl–H?

b) what is the nature of the bonding in the complex?

For the Ar·ClF van der Waals molecule, Harris *et al.* [20] predict that there is charge transfer from Ar to ClF, and that, following arguments similar to Walsh's rules, the charge resides on the terminal F. This approach is often used as a rationalisation for the universal preference of triatomics to have the most electropositive atom at the centre. In polar van der Waals molecules involving the Noble gases, however, it is not necessary to invoke the bonding properties of particular orbitals in this way. A simpler explanation for the observed preference may be as follows: the two possible (linear) structures for the Ar·HCl complex are $\mathrm{H^+Cl^-} \cdots {}^+\mathrm{Ar}^-$ (*I*) and $\mathrm{Cl^-H^+} \cdots {}^-\mathrm{Ar}^+$ (*II*), for which the dipole-induced dipole interactions have similar energies. The observed structure evidently depends upon how readily the polarised Ar atom can *accept* electrons from the HCl molecule, because *I* will inevitably lead to some charge transfer at van der Waals distances. However, argon (in common with the other Noble gases) does not form stable negative ions and so *II* is preferred over *I*. Charge transfer is not required to stabilise *II*.

Klemperer has observed [21] that the polar molecule–Noble gas atom complexes invariably obey Lewis acid–Lewis base configurations. The Noble gas supplies the electron pair and therefore acts as a Lewis base. The implication is that these complexes have bonds which are at least partly chemical and so some charge transfer will have taken place from atom to molecule. The distinction to be made between a chemical and a physical bond may be related partly to the question of charge transfer and partly to the fraction of the binding energy which may be attributed to chemical (that is, overlap) forces. The calculations described above indicate that only a comparatively small fraction of the binding energy of the Ar·HCl complex may be attributed to inductive forces, perhaps no more than 5%. It was also shown that the overlap dipole between atom and molecule was a negligible quantity, much less than one ten thousandth the size of the dipole induced on the argon atom. It follows that even the energy which may be ascribed to induction may not have a chemical (overlap) origin and is simply that due to the interaction of the two dipoles. Nevertheless, this conclusion is naturally subject to the qualification that it was obtained using simple Gaussian functions.

The present calculations imply that the size and extent of the repulsive interactions between atom and molecule need not be entirely responsible for the position of the observed energy minimum. The repulsion between the electrons in the region between the systems and the anisotropy of the dispersion interactions brought about by the axially symmetric molecule may be contributing factors towards determining the lower energy conformation. However, the predicted augmentation of the HCl dipole moment, which is itself brought about by the moment induced in the Ar atom, may well be a consequence of an alternative physical mechanism capable of fixing an optimum geometry. Closer approach of the polarised atom to the molecule would lead to greater augmentation of the HCl dipole moment. This self-reinforcing effect, whilst strengthening the attractive induction energy, automatically increases somewhat the total molecular energy by stretching the H–Cl bond. A point of equilibrium is therefore reached, which may be quite independent of the sum of the van der Waals radii of atom and molecule.

In dipolar systems, such a mechanism may well limit the size of even the dispersion interaction.

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