Electronic Supplementary Information for

An Insight Into The Halogen-Bond Nature Of Noble Gas-Chlorine Systems By Molecular Beam Scattering Experiments, Ab-Initio Calculations And Charge Displacement Analysis

Francesca Nunzi,^{*a,b**}Diego Cesario,^{*a,c*} Leonardo Belpassi,^{*b*} Francesco Tarantelli,^{*a,b*}Luiz F.

Roncaratti,^d Stefano Falcinelli,^e David Cappelletti, *^a Fernando Pirani^a

^a Dipartimento di Chimica, Biologia e Biotecnologie, via Elce di Sotto 8, I-06123 Perugia, Italy

^b Istituto di Scienze e Tecnologie Molecolari del CNR (ISTM-CNR), via Elce di Sotto 8, I-06123

Perugia, Italy

^c Department of Chemistry and Pharmaceutical Sciences and Amsterdam Center for Multiscale

Modeling, Vrije Universiteit Amsterdam, De Boelelaan 1083, 1081 HV Amsterdam, The

Netherlands

^d University of Brasilia, Institute of Fisics, POB 04455, BR-70919970 Brasilia, DF, Brazil

^e Dipartimento di Ingegneria Civile ed Ambientale, Università degli Studi di Perugia, via G. Duranti

93, 06215 Perugia, Italy

Corresponding Author *E-mail: francesca.nunzi@unipg.it; david.cappelletti@unipg.it

S1. Improved Lennard Jones functions:

The improved Lennard Jones (ILJ) model is formulated as:

$$V_{vdW}(R,\Theta) = \sum_{i=a,b} \varepsilon(\theta_i) \cdot \left[\frac{6}{n(r_i,\theta_i) - 6} \cdot \left(\frac{r_m(\theta_i)}{r_i} \right)^{n(r_i,\theta_i)} - \frac{n(r_i,\theta_i)}{n(r_i,\theta_i) - 6} \cdot \left(\frac{r_m(\theta_i)}{r_i} \right)^6 \right]$$
(1)

The values of $\varepsilon(\theta_i)$ and $r_m(\theta_i)$ are generated by the following relations:

$$\varepsilon(\theta_{i}) = \varepsilon_{\parallel} \cdot \cos^{2}(\theta_{i}) + \varepsilon_{\perp} \cdot \sin^{2}(\theta_{i})$$
(2)
$$r_{m}(\theta_{i}) = r_{m\parallel} \cdot \cos^{2}(\theta_{i}) + r_{m\perp} \cdot \sin^{2}(\theta_{i})$$
(3)

where the symbols \parallel and \perp refer, respectively, to the parallel ($\theta_i=0$) and perpendicular ($\theta_i=\pi/2$) limit configurations within each Ng-Cl_i pair (i=a,b). Moreover, for each interacting pair the long range attraction coefficient C_{6i} , provided by the asymptotic behavior of V_{vdW} formulation, is equal to $[\varepsilon(\theta_i) \cdot r_m^6(\theta_i)]$, while, the global attraction coefficient is simply given as sum of the two angular averaged C_{6i} components.

The parameter $n(r_{i}, \theta_{i})$, which modulates simultaneously the "fall off" of the repulsion and the radial dependence of the intermediate and long range attraction, depends on β , an additional parameter related to the hardness of both partners.¹ It is expressed as:

$$n(r_{i},\theta_{i}) = \beta + 4 \cdot \left(\frac{r_{i}}{r_{m}(\theta_{i})}\right)^{2}$$
(4)

The values of the ε and r_m parameters are reported in Table 1 and are expected to depend, as found for many other vdW systems, on the polarizability components, correlated with the electron density distribution on each interaction center (see text). The β parameters defining the fall off of the repulsion and the radial modulation attraction is fixed at 7.5 and 7.0 in the ground and excited states, respectively, for the Ng-Cl₂ systems.

SII. EXPERIMENTAL DATA ANALYSIS

As anticipated in the previous sections, in the thermal collision energy range the average component of Q(v) and the oscillatory pattern provide complementary information on the intermolecular interaction, namely on the strength of the long range attraction and on the features of the well depth, respectively. Moreover, under the used conditions, all collision events occur in the thermal energy range, involve molecular partners rotating sufficiently fast respect to the average collision time and their dynamics can be treated semi-classically. The adopted treatment applies properly to collisions of elastic type, dominant at intermediate and large impact parameter (the classical equivalent of the orbital angular momentum), such as those mainly probed by the present experiments, with no loss of any relevant information on the intermolecular interaction. Motivations of the adopted treatment mostly arise from the experimental observation in all cases of well resolved glory patterns, that suggests the occurrence of a collision dynamics mainly driven by a substantially isotropic central field. However, the interaction anisotropy must be explicitly taken into account when its role becomes more effective, generating a partial or total "glory" amplitude quenching, and this occurs when the collision velocity overcomes the value for which the collision time becomes significantly shorter than the average molecular rotation time. Under such conditions, the projectile interacts with the target molecule "suddenly" and the interacting complex, formed during the evolution of each collision event, tends to maintain "memory" of a limited number of specific configurations, to which it is associated a particular interaction. As previously made for similar cases,²⁻⁴ the collision dynamics, essential for the analysis of the experimental findings, has been confined in two different limiting regimes, emerging at low and high collision velocity, respectively. A spherical model has been employed to describe collisions at low velocities when the Cl₂ molecule has sufficient time to behave as isotropic partners. The scattering, mainly elastic, probes several relative configurations simultaneously and is driven by a central potential similar to the isotropic component (spherical average) of the full PES. An anisotropic molecular model, where the cross section is represented as a combination of independent contributions coming from all possible limiting configurations of each

S3

Ng-Cl₂ collision complex. That is, a sort of "Infinite Order Sudden" approximation is applied (see for instance Refs. 5-8). Accordingly, the two regimes selectively emerge as a function of the ratio between the mean molecular rotation time, (depending on the rotational temperature of Cl₂ into the scattering chamber), and the collision time, τ_{coll} , varying with the selected velocity v of Ng beam. During the analysis the Cl₂ molecules have been considered as targets rotating sufficiently fast only for collisions occurring at low v ($v \le 0.80$ km/s). In the low velocity range, the collisions have been then considered mainly driven by an "effective" radial potential V(R), related to the isotropic component of the PES. At each R it has been evaluated by averaging the interaction over all the angular coordinates. At higher velocity, *i.e.* when $\tau_{coll} < \tau_m$, the *anisotropic molecular* regime sets in. In this case, at each *v*, the individual cross sections are calculated for several different configurations and properly averaged over all the angular (O) coordinates. To this aim, a grid of 256 configurations have been used to evaluate the average value of each Q(v). The final theoretical Q(v) values, to be compared with the experimental data, have been then calculated within the *spherical model* at low v and according to the anisotropic molecular model at high v. At intermediate v, the switch between the dynamics of the spherical model and that of the anisotropic molecular model has been obtained as a weighted sum. depending on v, of the cross section contributions evaluate within the two different dynamical regimes,^{5, 8} according to the procedure detailed in Refs ^{2, 9}.

SIII. Polar flattening:

We can argue that the shift in the position of the repulsive wall is related to the shift of the Cl₂ density profile at lower distance with respect to that of the Cl atom. A measure of the shift may be provided by the Δz value, defined as the distance between two points of density profiles (for Cl₂ and Cl) taking the same density value (isodensity). As shown in Figure S4 (bottom panel), $\Delta z(\rho)$ assumes a narrow range of values, considering suitable values along the density profile. The polar flattening values Δz increase with the decreasing of the isodensity values, probably due to the role of the inner electrons that are strongly influenced by the nucleus. Nevertheless, the polar flattening values result almost constant for isodensity greater than 70 me bohr⁻³. Even if the choice of the isodensity value, at which the polar flattening is estimated, is to some extent arbitrary, the value of 1 me bohr⁻³, referring to a molecular surface which encompasses approximately 96% of the electronic charge of a molecule, is conventionally used to map the Coulomb potential for the analysis of the σ -hole.¹⁰ Accordingly, the polar flattening is estimated equal to 0.18 Å, a value consistent with the shift of the repulsion wall by about 4%.

SIV. Charge Displacement Function

Recently, an analogous approach has been successfully applied to the investigation of strength and nature of the interaction in Ng/H₂O complexes with CCl₄ / CF₄, from which we gained important features of the weak intermolecular halogen bond, formed in Ng/H₂O -apolar molecule systems.², ⁹Remarkably, the CD function represents a versatile tool for assessing the electron density adjustment, promoted by CT between two interacting fragments, unhampered by any specific decomposition scheme. In particular, the CD function is defined as:

$$\Delta q(z) = \int_{-\infty}^{+\infty} dx \int_{-\infty}^{+\infty} dy \int_{-\infty}^{z} \Delta \rho(x, y, z') dz'$$
(5)

S5

where $\Delta \rho$ is the difference between the electron density of the complex and that of the non-interacting fragments, placed in the same position of the complex geometry, and *z* is any suitable axis joining them. Δq measures the net electronic charge that, upon formation of the complex, has been displaced from right to left across the plane perpendicular to the axis and passing through *z*. A positive (negative) value corresponds to electrons flowing in the direction of decreasing (increasing) *z*. Accordingly, if the CD curve results appreciably different from zero and does not change in sign in the region between the fragments, we can unambiguously assert that a CT effect is operative. Conversely, if the curve crosses zero in this region, the CT may be uncertain (both in magnitude and direction). If CT really takes place, it is useful, for comparative purpose, to end up with a definite numerical estimation of it, by considering the CD function value at a specific point between the fragments along the *z* axis. As in previous cases, ¹¹⁻¹³our choice has been the point along *z* where the electron densities of the non-interacting fragments become equal (isodensity boundary).¹¹⁻¹³ Remarkably, the CD function returns a precise, in principle exact, and insightful picture of the electron cloud rearrangement arising from the formation of the intermolecular bond and from the polarization capabilities of the substrates.

Table S1. Geometrical parameter R (Å) and interaction energy E (meV) of He-, Ne- and Ar-Cl₂ adducts in three relative orientations (linear, L, T-shaped, T, and saddle, S) computed at the CCSD(T) level of theory with different basis sets. In parenthesis, the energy values with BSSE corrections. The values of energy extrapolated at the CBS limit are also reported.

				He-Cl ₂						
	Linear		T-Shaped		Saddle					
Basis	R	Е	R	E	R	Ε				
AVTZ	4.16	7.05 (4.59)	3.31	6.41 (3.98)	4.20	3.12 (2.06)				
AVQZ	4.11	6.17 (5.23)	3.38	5.83 (4.83)	4.27	2.89 (2.36)				
AV5Z	4.10	6.11 (5.48)	3.37	5.77 (5.22)	4.27	2.77 (2.52)				
CBS	4.15	6.10	3.34	5.79	4.18	2.70				
Ne-Cl ₂										
AVQZ	4.20	12.84 (9.50)	3.40	12.28 (9.43)	4.10	7.15 (5.17)				
AV5Z	4.20	11.68 (10.25)	3.40	11.68 (10.33)	4.10	6.58 (5.70)				
CBS	4.24	10.64	3.43	11.29	4.16	6.20				
Ar-Cl ₂										
AVQZ	4.40	28.58 (24.78)	3.7	27.3 (24.1)	4.40	16.44 (14.25)				
AV5Z	4.40	28.82 (26.36)	3.60	27.88 (25.39)	4.40	16.67 (15.23)				
CBS	4.47	28.96	3.68	29.21	4.40	17.10				

Table S2. Geometrical parameter R (Å) and interaction energy E (meV) of He-, Ne- and Ar- Cl_2 adducts in three relative orientations (linear, T-shaped, and saddle) computed at the HF level of theory with different basis sets. In parenthesis, the energy values with BSSE corrections. The values of energy extrapolated at the CBS limit are also reported.

He-Cl ₂							
	Linear		T-Shaped		Saddle		
Basis	R _m	Em	R _m	Em	R _m	E _m	
AVTZ	4.16		3.31		4.20		
AVQZ	4.11	-4.48 (-4.71)	3.38	-5.24 (-5.47)	4.27	-2.47 (2.70)	
AV5Z	4.10	-5.67 (-5.75)	3.37	-4.78 (-4.85)	4.27	-2.02 (-2.06)	
CBS	4.15	-4.13	3.34	-4.61	4.18	-2.46	
				Ne-Cl ₂			
AVQZ	4.20	-8.28 (-9.40)	3.40	-9.15 (-9.99)	4.10	-6.51 (-7.10)	
AV5Z	4.20	-9.13 (9.33)	3.40	-9.85 (-10.06)	4.10	-7.03 (-7.19)	
CBS	4.24	-8.41	3.43	-9.39	4.16	-5.93	
Ar-Cl ₂							
AVQZ	4.40	-24.73 (-25.35)	3.7	-20.15 (-20.67)	4.40	-13.30 (-13.81)	
AV5Z	4.40	-24.90 (-25.07)	3.60	-28.88 (-29.04)	4.40	-13.58 (-13.75)	
CBS	4.47	-19.12	3.68	-21.87	4.40	-13.67	

Table S3. CT value (me) at the isodensity boundary (IB, Å) of He-, Ne- and Ar-Cl₂ adducts in the X^{I} Σ_{g}^{+} ground state in three relative orientations (linear, T-shaped, saddle) computed at the CCSD(T)/AVQZ level of theory.

		Linear		T-shaped		Saddle	
		IB	СТ	Z	СТ	Z	СТ
	He	2.81	0.39	1.98	0.41	2.80	0.24
$X^{1}\Sigma_{g}^{+}$	Ne	1.98	0.80	1.98	0.76	2.80	0.48
	Ar	2.80	1.75	1.82	0.28	2.50	0.35

Table S4. CT value (me) at the isodensity boundary (IB, Å) of Ar-Cl₂ adduct in the $B^{3}\Pi_{0u}^{+}$ excited state in three relative orientations (linear, T-shaped, saddle) computed at the HF/AVTZ level of theory. For the T-shaped and saddle configurations the CT values related to the 3A' and 3A'' (parenthesis) states are shown.

		Linear		T-shaped		Saddle	
		IB	СТ	Z	СТ	Z	СТ
$X^{1}\Sigma_{g}^{+}$	Ar	3.07	0.61	1.82	0.97 (1.42)	2.39	2.04 (1.69)



Figure S1. Potential energy curves (Energy vs He-Cl_2 distance) of the He-Cl_2 complex in the linear (top), T-shaped (middle) and saddle (bottom) configurations computed at the CCSD(T) level of theory with different basis set compared to the parametrized potential energy curve (see text for details).



Figure S2. Potential energy curves (Energy vs Ne- Cl_{2CM} distance) of the Ne- Cl_2 complex in the the L (top), T (middle) and S (bottom) configurations computed at the CCSD(T) level of theory with different basis set compared to the parametrized potential energy curve (see text for details).



Figure S3. Potential energy curves (Energy vs $\text{Ar-Cl}_{2\text{CM}}$ distance) of the Ar-Cl_2 complex in the L (top), T (middle) and S (bottom) configurations computed at the CCSD(T) level of theory with different basis set compared to the parametrized potential energy curve (see text for details).



Figure S4. Top: electron density profile, ρ (me·Bohr⁻³), for Cl₂ (CCl₄) molecule along the Cl-Cl (C-Cl) bond – solid lines- and perpendicular to it at the Cl nucleus (dashed lines) compared to that of the (spherical) Cl atom, placed at the same position of Cl in Cl₂ (CCl₄) molecule – zero on the current z axis. Bottom: Δz (Å) behaviour for the Cl/Cl₂ system reported as a function of the density value ρ (me Bohr⁻³).



Figure S5. CD curves of the Ne-Cl₂ complex (X state) in the linear (a), T-shaped (b) and saddle (c) configurations computed at the CCSD/AVQZ level of theory. The 3D isodensity plots of the electron density change accompanying bond formation are also shown ($\Delta \rho = \pm 8 \times 10^{-5}$ me/bohr³, negative /positive values in red /blue). The dots on the dashed line represent the nuclei *z* coordinates. The vertical solid line identify a conventional boundary between the Ng and Cl₂ fragments (see text for details).



Figure S6. CD curves of the Ar-Cl₂ complex (X state) in the linear (a), T-shaped (b) and saddle (c) configurations computed at the CCSD/AVQZ level of theory. The 3D isodensity plots of the electron density change accompanying bond formation are also shown ($\Delta \rho = \pm 8 \times 10^{-5}$ me/bohr³, negative /positive values in red /blue). The dots on the dashed line represent the nuclei *z* coordinates. The vertical solid line identify a conventional boundary between the Ng and Cl₂ fragments (see text for details).



Figure S7. CD curves for the Ng-Cl₂ complexes (X state, top: He; middle: Ne; bottom: Ar) in the linear configuration computed at various distance R at the CCSD/AVQZ level of theory. The dots on the dashed line represent the nuclei z coordinates in the minimum energy structure, taken as a reference.



Figure S8: Ln CT as a function of the inter-fragments distance R (i.e. the distance from Ng to the Cl₂ CM) for the L configuration of the Ng-Cl₂ complexes (Ng = He, Ne, Ar). The best fitting of the data (dashed lines) using Eq. ln (*CT*) = ln (A_{CT})- γ ·*R* (with A_{CT} and γ as free parameters) is also shown.



Figure S9. CD curves of the Ar-Cl₂ complex (B state) in the linear (a), T-shaped (b) and saddle (c) configurations computed at the HF/AVTZ level of theory (solid/dashed lines: 3A'/3A'' state, see text) The 3D isodensity plots of the electron density change accompanying bond formation are also shown ($\Delta \rho = \pm 8 \times 10^{-5}$ me/bohr³, negative /positive values in red /blue; top/bottom inset: 3A'/3A'' state, see text). The dots on the dashed line represent the nuclei *z* coordinates. The vertical solid line identify a conventional boundary between the Ng and Cl₂ fragments (see text for details).



Figure S10. Molecular electrostatic surface potential (ESP) map of the Cl₂ molecule in the $(X^{I} \Sigma_{g}^{+})$ ground and $(B^{3} \Pi_{u})$ excited states, in kcal/mol¹ at the 1 me/Bohr³ isodensity surface.

References

- 1. M. Capitelli, D. Cappelletti, G. Colonna, C. Gorse, A. Laricchiuta, G. Liuti, S. Longo and F. Pirani, *Chem. Phys.*, 2007, **338**, 62-68.
- 2. A. Bartocci, L. Belpassi, D. Cappelletti, S. Falcinelli, F. Grandinetti, F. Tarantelli and F. Pirani, *J. Chem. Phys.*, 2015, **142**, 184304
- 3. D. Cappelletti, V. Aquilanti, A. Bartocci, F. Nunzi, F. Tarantelli, L. Belpassi and F. Pirani, *J. Phys. Chem. A*, 2016, **120**, 5197-5207.
- 4. D. Cappelletti, S. Falcinelli and F. Pirani, J. Chem. Phys., 2016, 145, 134305.
- 5. D. Cappelletti, M. Bartolomei, F. Pirani and V. Aquilanti, J. Phys. Chem. A, 2002, 106, 10764-10772.
- 6. V. Aquilanti, L. Beneventi, G. Grossi and F. Vecchiocattivi, J. Chem. Phys., 1988, 89, 751-761.
- 7. V. Aquilanti, D. Ascenzi, D. Cappelletti, M. de Castro and F. Pirani, *J. Chem. Phys.*, 1998, **109**, 3898-3910.
- 8. D. Cappelletti, M. Bartolomei, M. Sabido, F. Pirani, G. Blanquet, J. Walrand, J. P. Bouanich and F. Thibault, *J. Phys. Chem. A*, 2005, **109**, 8471-8480.
- 9. D. Cappelletti, A. Bartocci, F. Grandinetti, S. Falcinelli, L. Belpassi, F. Tarantelli and F. Pirani, *Chem. Eur. J.*, 2015, **21**, 6234-6240.
- 10. R. F. W. Bader, M. T. Carroll, J. R. Cheeseman and C. Chang, *J. Am. Chem. Soc.*, 1987, **109**, 7968-7979.
- 11. L. Belpassi, I. Infante, F. Tarantelli and L. Visscher, J. Am. Chem. Soc., 2008, **130**, 1048-1060.
- 12. G. Bistoni, L. Belpassi and F. Tarantelli, *Angew. Chemie Int. Ed.*, 2013, **52**, 11599-11602.
- 13. N. Salvi, L. Belpassi and F. Tarantelli, *Chem. Eur. J.*, 2010, **16**, 7231-7240.