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# The in-equivalence of the HCl molecules in $(\text{HCl})_2$ : An SCF *ab initio* calculation

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The geometry and the spectroscopic properties of  $(\text{HCl})_2$  have been calculated at the SCF level. A nearly orthogonal dimer with an almost linear H bridge has been found. The optimized Cl-Cl distance is  $R_e = 7.48$  a.u., while Cl-H bond lengths are found to be  $r_1 = 2.4133$  and  $r_2 = 2.4075$  a.u. for the proton donor and acceptor monomeric units, respectively. The binding energy corrected for basis set superposition error is computed to be  $B = 3.61$  kcal/mol. The spectroscopic properties (force constants, dipole and quadrupole moment derivatives) of monomeric units as a part of  $(\text{HCl})_2$  are discussed.

## I. INTRODUCTION

The existence of HCl dimers has long been recognized and their presence in the gas phase has been detected by infrared spectroscopy.<sup>1</sup> However, most of the structural studies have been undertaken by trapping the hydrogen chloride dimer in rare gas matrices. Conclusions derived from near<sup>2-4</sup> and far<sup>5</sup> infrared spectroscopic studies are uncertain and lead to colinear<sup>3</sup> or cyclic<sup>5</sup> conformations, in contrast with the zig-zag chain structure found in crystalline HCl.<sup>6-8</sup> Definitive structural experiments are still not available, except with regard to the inequivalence of the two monomeric units in the dimer, which automatically rules out the cyclic structure. More recent experiments (IR<sup>9</sup> and NMR<sup>10</sup> in matrices) are consistent with theoretical predictions that the two bonds of the monomeric units are almost orthogonal.

This prediction has been arrived at from two very different approaches. In one case, the interaction energy of the two monomers forming the dimer was calculated using a multipolar expansion of the intermolecular potential.<sup>11</sup> The equilibrium conformation corresponded to  $\theta_2 - \theta_1 \approx 4\pi/9$  and was independent of  $\phi$  (see Fig. 1 for the coordinates). The other approach is a quantum mechanical one, where the HCl dimer is considered as a typical example of a hydrogen bonded complex. The calculations performed to date are mostly limited to small and unpolarized basis set functions<sup>12-16</sup> or semi-empirical methods,<sup>17</sup> except for the work of Votava and Ahlrichs,<sup>18</sup> who have performed an extended SCF-CI calculation of the pair potential in the rigid body approximation. This calculation was essentially restricted to check the effect of correlation on the intermolecular potential without further investigation of the physical properties of the dimer. These calculations confirm the result of the intermolecular forces model. At this stage, the problem of the equilibrium geometry of the HCl dimer seems to be reasonably well resolved. It is however only a good starting point to a detailed description of its static and dynamic properties which are being revealed by increasingly detailed experiments. Of particular interest is a reliable intermolecular potential

in the calculations, for example, of the physical properties of crystalline HCl, where the atom-atom potential used to date is a poor approximation of the hydrogen bonding.<sup>19</sup> An important dynamical problem is the relative motion of the hydrogen atoms with respect to one other, which can be observed by NMR, and raises the question of the nature of the internal barrier to rotation within the loosely bound molecule. Furthermore, since the properties of the dimer are currently being measured in solid rare gas matrices, an understanding of its interaction with the environment, relies on an accurate internal potential.

With this in mind, we present an SCF calculation of the HCl dimer, which focuses on the changes in behavior of each of the monomeric units within the molecule and is divided into (a) the calculation of the first derivatives, with respect to internal stretching coordinate of the total dipole and quadrupole moments, in the respective local frames attached to each monomer, and (b) the calculation of the vibrational frequencies. These results contain the basic ingredients needed in a multipolar expansion of the intermolecular potential. This calculation also provided the justification for the intensity analysis of the infrared spectrum of  $(\text{HCl})_2$  recently presented by Maillard,<sup>20-22</sup> which relies on the introduction of a charge transfer parameter. Diagonal force fields are also presented. The general method and the nature of the basis set functions used in the SCF calculation are discussed in Sec. II. In Sec. III, electrical properties are given and a discussion concerning the  $\tau$  factor (charge transfer parameter introduced in Refs. 19-21) is presented. In Sec. IV, the perturbation of the spectral properties of the two monomeric units of the dimer are discussed and, finally, in Sec. V, the basis set superposition errors are given.

## II. CALCULATION OF THE HCl MONOMER

### A. Method and basis set

The SCF calculation has been performed using Gaussian lobe orbitals<sup>23-25</sup> as basis functions. These basis functions, together with the method used in the contrac-

TABLE I. Molecular properties of  $\text{HCl}$ .

		SCF			
		This work	Reference 26	Reference 31	Experiments
$E_T$	(a.u.)	-459.974 8	-460.098 1	-460.111 9	
$-\langle V \rangle / \langle T \rangle$		2.000 11	2.000 11	2.000 03	2.0
$M_Z (\mu_e)$	D	1.118	1.178	1.215	1.093 <sup>e</sup>
$M_Z^2 (\theta_{zz})$	$\text{D} \text{ \AA}^{-1}$	3.285	3.557	3.74	3.53 <sup>e</sup>
$M_Z^3 (\Omega_{zzz})$	$\text{D} \text{ \AA}^{-1}$	2.694	2.583		
$M_Z^4 (\Phi_{zzzz})$	$\text{D} \text{ \AA}^{-1}$	4.905	4.887		
$M_Z^5$	$\text{D} \text{ \AA}^{-1}$	6.708	6.904		
$M_Z^6$	$\text{D} \text{ \AA}^{-1}$	8.513	9.102		
$M_Z^7$	$\text{D} \text{ \AA}^{-1}$	10.283	11.485		
$M_Z^8$	$\text{D} \text{ \AA}^{-1}$	11.929	14.052		
$M_Z^9$	$\text{D} \text{ \AA}^{-1}$	13.222	16.740		
$M_Z^{10}$	$\text{D} \text{ \AA}^{-1}$	13.722	19.409		
$\omega_e$	( $\text{cm}^{-1}$ )	3127.7		3181 <sup>b</sup>	2989.7 <sup>c</sup>
$\langle 1/r_1 \rangle$	(a.u.)	64.812 4		64.821 8	
$\langle 1/r_2 \rangle$	(a.u.)	8.033 7		8.000 7	
$\langle z_1/r_1^3 \rangle$	(a.u.)	0.148 1		0.168 4	
$\langle z_2/r_2^3 \rangle$	(a.u.)	-2.927 7		-2.939 3	
$\langle (3z_1^2 - r_1^2)/r_1^5 \rangle$	(a.u.)	-3.673 1		-3.419 2	
$\langle (3z_2^2 - r_2^2)/r_2^5 \rangle$	(a.u.)	2.134 9		2.152 7	
$\frac{\partial \mu}{\partial r}$	$\text{D} \text{ \AA}^{-1}$	0.990	1.021 <sup>a</sup>		0.925 <sup>d</sup>
$\frac{\partial \theta_{zz}}{\partial r}$	D	3.704	3.369 <sup>a</sup>		

<sup>a</sup>CI values.<sup>b</sup>Cade P. and Huo W., J. Chem. Phys. 47, 649 (1967).<sup>c</sup>G. Herzberg, *Molecular Spectra and Molecular Structure* (Van Nostrand, New York, 1965).<sup>d</sup>E. W. Kaiser, J. Chem. Phys. 53, 1686 (1970).<sup>e</sup>F. H. De Leeuw and A. Dymanus, J. Mol. Spectrosc. 48, 427 (1973).

tion of the basis set, were chosen because they allow flexibility in the representation of the valence shells and accurately reproduce the electric properties of the monomeric species. It has been shown<sup>26</sup> that it is the electrostatic part of the intermolecular potential which effectively governs the relative orientation of the two molecules that form the dimer. The unpolarized chlorine basis set is the  $(10s, 6p)$  contracted into  $[6s, 4p]$  basis set of Roos.<sup>27</sup> The contractions were performed according to Dunning's rules.<sup>28</sup> The contraction leads to an energy loss of the order of  $9 \cdot 10^{-3}$  a.u. or less. For the hydrogen atom, the  $[2s]$  contraction<sup>29</sup> of Huzinaga's  $(4s)$  basis set<sup>30</sup> has been retained. The polarization functions, added to the chlorine and hydrogen atoms, are identical to those previously used by Maillard and Silvi in the calculation of electrical properties of hydrogen chloride.<sup>26</sup>

## B. Free monomer properties

The calculated molecular properties of monomeric  $\text{HCl}$  using the SCF wave functions described above at

the experimentally determined intermolecular distance ( $R_e = 2.4$  a.u.<sup>31</sup>) are reported in Table I. They are compared with experimental data whenever possible, and with other calculated values reported by McLean and Yoshimine<sup>32</sup> and, more recently, by Maillard and Silvi<sup>26</sup> using Hartree-Fock wave functions. For the sake of completeness, the multipole moments up to order ten have been recomputed using the wave function of Ref. 26. We have used the following convention: the origin of the coordinate system is taken at the molecular center of mass lying on the internuclear axis along the  $z$  direction, the position of chlorine atom being positive. Subscripts 1 and 2 designate the chlorine and hydrogen nuclei, respectively, which are chosen as the origin of coordinate system for the computation of potential, field, and field gradients at the nuclei.

It should be noted that the calculated total energy lies 0.1317 a.u. above the Hartree-Fock limit, mainly due to the use of a rather small chlorine basis set. The latter is also reflected in the dissociation energy of

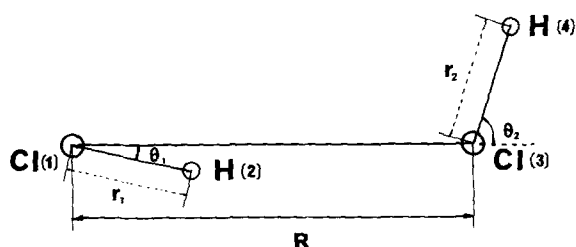


FIG. 1. Geometrical parameters characterizing the (HCl)<sub>2</sub> system  $\phi$  is the dihedral angle between the Cl(3)Cl(1)H(2) and Cl(1)Cl(3)H(4) planes.

3.41 eV, compared to 3.53 eV as calculated by McLean *et al.*<sup>32</sup> This deficiency in the description of the core orbitals may also be responsible for the small discrepancies between our calculated expectation values of the field and field gradient at the chlorine nucleus and those reported by McLean *et al.*<sup>32</sup> In spite of this, the overall agreement between the computed multipole moments, at least up to seventh order, shows that the electronic charge distribution is probably well described in the intermediate range, the region of interest for the dimerization process.

Optimization of the internuclear coordinates leads to a calculated equilibrium bond length slightly longer than the experimental one by  $6 \times 10^{-3}$  a.u. The calculated stretching force constant of  $5.603 \text{ aJ } \text{\AA}^{-1}$  leads to an harmonic frequency  $\omega_e = 3127.7 \text{ cm}^{-1}$ , which compares favorably with experimental values, namely,  $5.127 \text{ aJ } \text{\AA}^{-2}$  and  $2989.5 \text{ cm}^{-1}$ ,<sup>31</sup> respectively, or with the Hartree-Fock results of Cade and Huo<sup>33</sup> of  $5.838 \text{ aJ } \text{\AA}^{-2}$  and  $3181 \text{ cm}^{-1}$ , respectively. The dipole and quadrupole moment derivatives with respect to the stretching coordinate are found to be in fair agreement with experimental data<sup>34</sup> and with the more elaborate calculations that include configuration interactions.<sup>26</sup>

### III. STRUCTURE AND FORCE FIELD OF THE HCl DIMER

Since the main objective of this work is to examine the nonequivalent roles of the monomeric units in the

hydrogen bonded complex, the calculations have been restricted to the investigation of quasiorthogonal structures. The coordinate system for the molecule is depicted in Fig. 1. Optimized coordinates for the positions of the atoms are listed in Table II, where they are also compared with previous *ab initio* and intermolecular force type calculations. The complex is found to be planar, the angles  $\theta_1$  and  $\theta_2$  being equal, respectively, to  $-2.6^\circ$  and  $83^\circ$ . The later ( $\theta_2$ ) is in good agreement with previous calculations<sup>11-18</sup>; however,  $\theta_1$  is considerably smaller than values from earlier SCF 4.31G computations ( $-12.8^\circ$ ,<sup>16</sup>  $-7^\circ$ <sup>14</sup>). Also, our calculated Cl-Cl distance (7.48 a.u.) is slightly smaller than the value obtained from 4.31G calculations, but larger than the one predicted by the intermolecular potential model (6.63 a.u.). These differences suggest the following: (a) The larger value of  $\theta_1$  from the 4.31G calculations may be due to the fact that this method overestimates the HCl dipole moment (it is 90% too large) and consequently exaggerates the contribution of the dipole-dipole interaction to the total energy. (b) The larger Cl-Cl distance, calculated from the intermolecular potential, is a result of inadequately taking into account the short range interaction terms. It is well known, by comparison with experimental results,<sup>35</sup> that the intermolecular distances of hydrogen halide dimers<sup>36</sup> and codimers are always underestimated by this method, by at least 10%. Finally, it is of interest to note that the two HCl bond lengths of the dimer are slightly longer than the unperturbed monomers.

The force constants have been calculated by numerical differentiation of the potential energy hypersurface corresponding to the dimeric super system. Accordingly, for the monomeric units, the force constants and vibrational frequencies are given in Table III. The frequencies are larger than experimental values,<sup>20</sup> as expected from SCF calculations, but contrary to the results of Hobza and co-workers.<sup>14</sup> Furthermore, our calculated difference  $\omega_2 - \omega_1$  is  $25.3 \text{ cm}^{-1}$ , whereas the 4.31G calculation yields  $13 \text{ cm}^{-1}$  (Table III) (in solid Ar, the measured difference<sup>17</sup> is  $35.6 \text{ cm}^{-1}$ ).

The calculated diagonal force constants corresponding

TABLE II. Structure and external force constants of (HCl)<sub>2</sub>.

		This work	4.31G Reference 14	4.31G Reference 16	Potential Reference 34
$R_{\text{ClCl}}$	a.u.	7.48	7.532	7.552	6.63
$r_1$	a.u.	2.4133	2.4566	2.4566	...
$r_2$	a.u.	2.4075	2.4566	2.4548	...
$\theta_1$	deg	-2.6	-7.0	-12.8	-11.5
$\theta_2$	deg	83.0	78.0	74.7	86.6
$\phi$	deg	0.0	0.0	0.0	0.0
$F_{\text{RR}}$	$\text{aJ } \text{\AA}^{-1}$	0.0816	0.059		
$F_{\theta_1\theta_1}$	$\text{aJ rad}^{-1}$	0.109	0.071		0.031
$F_{\theta_2\theta_2}$	$\text{aJ rad}^{-2}$	0.375	0.038		0.029
$F_{\phi\phi}$		0.000 98	0.001		0.022

TABLE III. Spectroscopic properties of monomeric units in (HCl)<sub>2</sub>.

		Molecule 1	Molecule 2	Monomer
$r$	a. u.	2.4113	2.4075	2.4062
$F_{rr}$	aJ Å <sup>-1</sup>	5.494	5.585	5.6034
$\omega_e$	cm <sup>-1</sup>	3097.2	3122.5	3127.7
$\frac{\partial \mu}{\partial r}$	D Å <sup>-1</sup>	1.640	0.775	0.990
$\frac{\partial \theta_{xx}}{\partial r}$ <sup>a</sup>	D	6.813	5.069	3.704

<sup>a</sup>See the text.

to the relative motion of monomeric units are given in Table II, where they are compared with the force field determined by Hobza and co-workers.<sup>14</sup> Their force constants are lower than ours by an order of magnitude of 1.0 aJ Å<sup>-1</sup> unit, and this might be due to a simulation of correlation effects by a semiempirical procedure. The significance of these results is however quite uncertain for at least two reasons. First, the experimental data in the far IR region is sparse: only two bands at 231 and 241 cm<sup>-1</sup> have been tentatively attributed to dimers by Obriot,<sup>37</sup> whereas the normal coordinate analysis based on the quasiorthogonal model leads to four infrared active modes. Second, the validity of this normal coordinate analysis may be questionable. It is based on the model which leads to a rather rigid structure since the SCF calculation allows for only small amplitude internal motions in the dimer. This rigidity is characteristic of the SCF calculation and requires at least the inclusion of polarization functions<sup>38</sup> or configuration interactions to provide the necessary flexibility. Such a result would be more consistent with the results of the intermolecular force model,<sup>11,36</sup> where, at the outset, the two monomers are considered to be loosely bonded, allowing large coupling between vibrational, rotational, and librational modes.

#### IV. PERTURBATION OF THE SPECTROSCOPIC PROPERTIES OF THE TWO MOLECULES FORMING THE DIMER

As already stated in Sec. I, infrared experiments<sup>17</sup> clearly show that the two molecules in the dimer are inequivalent. The (HCl)<sub>2</sub> dimer trapped in rare gas matrices give rise to two stretching frequencies in the infrared region, located at 2856 cm<sup>-1</sup> ( $D_1$ ) and 2818 cm<sup>-1</sup> ( $D_2$ ) in solid argon. These features show some interesting characteristics, namely:

(a) The frequencies  $D_1$  and  $D_2$  remain unchanged in the isotopically mixed dimer HCl-DCI.

(b) The  $D_2/D_1$  intensity ratio is close to 10.

(c) The  $D_1$  frequency is very sensitive to the solid rare gas environment (the absorption bands in Ar, Kr, and Xe occur at 2856, 2845, and 2826.6 cm<sup>-1</sup>, respectively, whereas the  $D_2$  frequency, nearly constant at 2818 cm<sup>-1</sup>, is not).

From these observations, Schriver and co-workers<sup>17</sup> concluded that  $D_1$  and  $D_2$  are almost completely decoupled, leading to a small interaction force constant  $F_{r_1 r_2}$  and frequency shifts which are directly related to differences in the principal force constants  $F_{r_1 r_1}$  and  $F_{r_2 r_2}$ . They also calculated a value for the ratio of the dipole moment derivatives

$$\tau_\mu = \left( \frac{\partial \mu_1}{\partial r_1} / \frac{\partial \mu_2}{\partial r_2} \right)$$

close to 3, which is qualitatively verified by a MINDO/3 type calculation.<sup>17</sup> Subsequently, it was shown by Maillard *et al.*<sup>21</sup> that the results derived from an intermolecular forces type calculation could be noticeably improved by the introduction of two so called charge transfer parameters,  $\tau_\mu$  given above and

$$\tau_\theta = \left( \frac{\partial \theta_1}{\partial r_1} / \frac{\partial \theta_2}{\partial r_2} \right),$$

where  $\theta_1$  and  $\theta_2$  are the quadrupole moments associated with each monomer. These charge transfer parameters were evaluated by simply fitting the spectroscopic data. The present calculation, however, permits one to derive  $\tau_\mu$  and  $\tau_\theta$  directly from *ab initio* calculations.

Table III summarizes the calculated values of the quantities discussed above associated with each of the monomer units of the complex. Consistent with experiment, we find the force constant  $F_{r_1 r_1}$  is smaller than  $F_{r_2 r_2}$  and the corresponding red shifts of the frequencies 30.5 and 5.2 cm<sup>-1</sup>, respectively, in surprisingly good agreement with the observations.<sup>17</sup> This difference is reflected in the increase of the bond length, which is four times larger than that obtained for  $r_2$ .

The procedure used to calculate the derivatives of dipole and quadrupole moments, with respect to  $r_1$  and  $r_2$ , merits careful consideration because of their importance in the evaluation of the  $\tau$  factors introduced by Maillard *et al.*<sup>21</sup> In the intermolecular force type calculation based on a perturbative method, quantities such as  $\mu_1$ ,  $\mu_2$ ,  $\theta_1$ , and  $\theta_2$ , associated with the individual monomer units of the dimer, are natural. However, in our super system approach, only the overall charge distribution is calculable and its partition into contributions from various parts of the dimer molecule is arbitrary. Such a partition has not been attempted here but instead it has been assumed that  $(\partial \mu_i / \partial r_i) \approx (\partial \mu / \partial r_i)$ ,  $i = 1, 2$ . As for the quadrupole moment  $\theta$  where the choice of the origin is important, two functions  $\theta_1$  and  $\theta_2$  have been calculated in the Cartesian frames associated with the molecules 1 and 2, respectively, with  $\tau_\theta$  defined as

$$\left( \frac{\partial \theta_1}{\partial r_1} / \frac{\partial \theta_2}{\partial r_2} \right).$$

In these local reference frames, the origin is taken at the center-of-mass of the HCl molecule, the  $z$  axis is the molecular axis directed from Cl to H, and the  $x$  axis lies in the molecular plane. The calculated values of  $\tau_\mu$  and  $\tau_\theta$ , 2.11 and 1.34, respectively, are in very good agreement with the values chosen by Maillard *et al.*,<sup>21</sup> which best fit the experimental results and which both are taken within the same reference frame.

## V. BASIS SET SUPERPOSITION ERROR

The counterpoise method is now commonly used to take into account the basis set superposition error.<sup>39</sup> Most often, it is applied in the determination of dimerization energy. In the present case, the uncorrected value of dimerization energy is  $-8.01 \text{ kcal/mol}^{-1}$ . The corrected value is obtained by subtracting from the dimer energy the sum of the energies of the two monomer units, each one calculated with its own basis set augmented by the basis set of the other monomer. The spatial arrangement is that of the dimer but the charges are null on one of the monomer units. Applying the above correction, the dimerization energy becomes  $-3.61 \text{ kcal/mol}^{-1}$ . The basis set superposition error is obviously significant and a similar result has been found by Hobza *et al.*,<sup>14</sup> though our basis set is noticeably more flexible ( $d$  orbitals on Cl, and  $p$  and  $d$  functions of H). This may cast a doubt on the currently admitted correlation between the completeness of the basis set and the magnitude of the BSSE correction. The value given here appears to be only an upper bound to the true BSSE. Its effect on the multipole moments has also been evaluated; here again, the monomer internuclear distance is fixed at the value found in the dimer. The corrections are rather small up to the fifth order, but beyond this, serious discrepancies arise. This is not astonishing when one realizes that a moment of order  $l$  contains contributions from a density matrix element multiplied by  $(R_e)^l$  (the added basis set is located at a distance  $R_e$  from the isolated monomer). Consequently, an error of  $10^{-6}$  in such an element produces an error of 1 a.u. in the  $l$ th moment.

## VI. CONCLUSION

Extended basis set functions, including polarization functions, have been used to obtain the properties of an  $\text{HCl}$  monomer in isolated form or as part of a  $(\text{HCl})_2$  dimeric complex. The calculated constants for the molecule provides some interesting insight to the validity of intermolecular force type calculations. This is well illustrated in the calculation of the charge transfer coefficients first introduced by Maillard *et al.*<sup>21</sup> in accounting for the behavior of the dimer.

As for the properties of the dimer, an almost linear H bridge has been found between the two monomeric units, rather than the bent-bridge previously reported.<sup>14-16</sup> The calculation introduces an artificial rigidity in the dimer which cannot be resolved in the absence of correlation effects. This is especially important if one is to interpret the results of recent NMR experiments.<sup>10,40</sup>

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