## Theoretical and experimental studies of the doubly charged ion $HCl^{2+}$

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Energies of excited states of  $HCl^{2+}$  have been determined experimentally by the technique of double charge transfer and are compared with present results of a multireference single- and double-excitation configuration-interaction calculation. The calculation shows the existence of four bound states. The good agreement obtained permits a direct assignment of the four lowest-energy excited states with singlet symmetry. Comparison of our work with previous information obtained from photoion-photoion coincidence, electron impact, charge stripping, and also from HCl xuv Auger analysis is given. We report the double-ionization energies of stable states  ${}^{3}\Sigma^{-}$ ,  ${}^{1}\Delta$ , and  $\Sigma^{+}$  HCl<sup>2+</sup> as  $35.9\pm0.2$ ,  $37.4\pm0.15$ , and  $38.6\pm0.3$  eV, respectively, while dissociative states  ${}^{1}\Pi$  and  ${}^{2}\Sigma^{+}$  are at  $40.9\pm0.3$  and  $45.6\pm0.3$  eV.

# I. INTRODUCTION

The study of molecular doubly ionized states has received growing attention in recent years. Potentialenergy surfaces, dissociative pathways, vertical doubleionization energies, and transition rates have been accurately calculated for small dications. In this case straightforward comparison between experiment and calculation may be made because of the relatively small number of low-lying doubly ionized states.

In order to obtain diverse experimental information on molecular doubly ionized states, several different techniques are required. In Auger<sup>1</sup> spectroscopy doubly charged ions are reached from core hole states of singly charged precursors. In the photoion-photoion coincidence technique<sup>2,3</sup> (PIPICO) dissociative doubly charged ions formed by photon impact are detected by mass spectrometry. In special cases laser dissociation<sup>4</sup> can be used to achieve high-resolution spectroscopy. Single-charge-stripping experiments<sup>5</sup> permit the measurement of energy defects for  $A^+ \rightarrow A^{2+}$  transitions. Inelastic translational energy-loss measurements have also been successfully applied to determine bound states of dications.<sup>6,7</sup> The double-charge-transfer technique used here and originally developed by one of us<sup>8</sup> gives complementary information to that of the above techniques.

Various theoretical methods such as the multiconfiguration self-consistent-field technique, configurationinteraction (CI) and Moller Plesset calculations,<sup>9,10</sup> and the Green's-function approach<sup>11,12</sup> have been employed. Recently, energies of the singlet states of the doubly charged chlorine dication have been determined experimentally and were compared with the results of a multireference single- and double-excitation configurationinteraction (MRSD-CI) calculation.<sup>13</sup> This dication served as a good test for the selection rules governing double charge transfer to homonuclear diatomics and for theoretical calculations.

In the present work we have extended the previous studies of homonuclear  $H_2$  (Ref. 14) and  $Cl_2$  (Ref. 13) to the heteronuclear molecule HCl. In this paper we present both double-charge-transfer experimental data and MRSD-CI results.

Only a few experimental results are available on  $HCl^{2+}$ .

(i) In 1961 Dorman and Morrison<sup>15</sup> induced transitions by electron impact using two single focusing mass spectrometers with different flight times from source to detector. They found  $HCl^{2+}$  to be stable with an ionization threshold of  $35.5\pm0.5$  eV. This result is in agreement with the value of  $36.0\pm0.8$  eV found earlier by Thorburn<sup>16</sup> who used a similar electron-impact ionization technique but with a less sophisticated apparatus.

(ii) In a charge-stripping experiment<sup>17</sup> an energy of  $23.5\pm0.5$  eV was measured for the energy difference between the single- and double-ionization energy of HCl. From this result the double-ionization energy of HCl $\rightarrow$ HCl<sup>2+</sup> was estimated to be  $36.2\pm0.5$  eV using the value of 12.748 eV for the ionization energy of the HCl ground state.

(iii) In PIPICO studies<sup>3</sup> a relatively small production rate for dissociative double photoionization of HCl has been noted when using 304-Å (40.8-eV) helium resonance radiation. The H<sup>+</sup> and Cl<sup>+</sup> fragments were found to be released with a dissociation energy of  $6.4\pm1.1$  eV. It was suggested than an  $HCl^{2+}$  unbound state exists at  $37.3\pm1.1$  eV, assuming that the two fragments are correlated to the first  $H^+ + Cl^{+}({}^{3}P)$  dissociation limit.

(iv) xuv Auger spectroscopy<sup>18</sup> has yielded information on both ground and excited double ionic states with singlet and triplet symmetry. The experimental  $L_{2,3}M_{2,3}M_{2,3}$  Auger spectrum<sup>18</sup> has received two theoretical interpretations<sup>18,19</sup> based on a comparison between HCl and the isoelectronic rare-gas argon. Both interpretations of the experimental data were in agreement; the HCl<sup>2+</sup> ground state  $X^{3}\Sigma^{-}$  lies between 1.3 and 1.8 eV below the  $^{1}\Delta$  state and between 3.5 and 4.0 eV below the <sup>3</sup>II state. Also, excited singlet states  ${}^{1}\Sigma^{+}$ and <sup>1</sup>II were determined to be 1.2 eV and between 3.1 and 3.8 eV (Refs. 18 and 19), respectively, above the singlet ground state <sup>1</sup> $\Delta$ . Part of the  $L_{2,3}M_{2,3}M_{2,3}$  Auger super product state  $\Delta$ . Further the  $L_{2,3}M_{2,3}M_{2,3}M_{2,3}$  reactions spectrum corresponding to the final states  $5\sigma^{-1}2\pi^{-1}\Pi$  and  $5\sigma^{-2}\Sigma^+$  overlaps the  $L_{2,3}M_{2,3}M_{2,3}$  Auger spec-trum corresponding to the final states  $2\pi^{-2}\Sigma^+$  and  $5\sigma^{-1}2\pi^{-1}$ <sup>3</sup> $\Pi$ . Tentative assignment requires the support of theoretical evaluation of the binding energy values of these states, and a hypothesis on the  $(L_2M_{2,3}M_{2,3})$ ,  $(L_3M_{2,3}M_{2,3})$  branching ratio. For this reason a large difference between the results presented by Refs. 18 and 19 exists for the <sup>1</sup>II state. Also a large discrepancy is present in the calculated position of the next higher excited singlet state  $2^{1}\Sigma^{+}$  and a reassignment has been suggested by Kvalheim.<sup>19</sup>

Nevertheless, all the above identifications show that singlet and triplet states of  $HCl^{2+}$  are well spaced compared to the resolving power of the present charge-transfer technique. Therefore, HCl is a good candidate for testing spin selection rules for double-charge-transfer collisions involving heteronuclear diatomic molecules. Also, the details of these states are not known, and it is of interest to determine how many states are bound and whether we might expect optical emission<sup>20</sup> from  $HCl^{2+}$ .

Consequently, in this work we have undertaken a MRSD-Cl calculation together with a double-charge-transfer experiment. Comparing these new experimental and theoretical results to the previous data, we have obtained a clearer understanding of the spectroscopy of  $HCl^{2+}$ .

## **II. EXPERIMENTAL PROCEDURE**

Here only a brief description of the experimental arrangement will be presented; a detailed discussion has been given previously.<sup>13</sup> The double-charge-transfer technique involves measurement of the translational energy of  $H^-$  ions arising from the acquisition of two electrons by incident protons impinging on a gaseous target. This can happen either in a one-step double-charge-transfer process:

$$\mathbf{H}^{+} + \mathbf{H}\mathbf{C}\mathbf{I} \rightarrow \mathbf{H}^{-} + \mathbf{H}\mathbf{C}\mathbf{I}^{2+} \tag{1}$$

or in two successive single-charge exchanges:

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$$\mathbf{H}^{+} + \mathbf{H}\mathbf{C}\mathbf{I} \rightarrow \mathbf{H} + \mathbf{H}\mathbf{C}\mathbf{I}^{+}(i) , \qquad (2a)$$

$$\mathbf{H} + \mathbf{H}\mathbf{C}\mathbf{I} \to \mathbf{H}^{-} + \mathbf{H}\mathbf{C}\mathbf{I}^{+}(j) , \qquad (2b)$$

in which the HCl<sup>+</sup> produced in each collision may not be in the same electronic state. For process (1) the value of the double-ionization energy  $I^{2+}$  is determined using the following relation (neglecting recoil of the target, see Refs. 13 and 14):

$$I^{2+} = (E_0 - E) - E(\mathbf{H}^-) , \qquad (3)$$

where  $E_0$  is the initial kinetic energy of the protons, E is the measured kinetic energy of the H<sup>-</sup> ions, and  $E(H^-)$ is the double-ionization energy of H<sup>-</sup> (-14.35 eV). Single-ionization potentials of HCl are given by process (2) with

$$I^{+} + I^{+'} = (E_0 - E) - E(\mathbf{H}^{-}), \qquad (4)$$

where  $I^+$  and  $I^{+'}$  are the ionization energies required to produce HCl<sup>+</sup> in states (i) and (j).

The two  $H^-$  production processes differ in pressure dependence: process (1) varies linearly with pressure while process (2) varies quadratically. These pressure characteristics aid in identifying the energy-analyzed  $H^-$  spectra.

The apparatus is based on a highly collimated double mass spectrometric technique which permits the detection of energy-selected  $H^-$  ions with a resolving power of 5000. A voltage-labeling technique is used to discriminate the  $H^-$  signal which does not originate from target-gas interactions in the collision cell.<sup>13,14</sup>

Absolute-energy calibration of the  $H^-$  spectra was achieved using argon as a reference gas since the excitation energies involved for single and double charge transfer are known precisely and are comparable with those expected for hydrogen chloride. Accurate energy differences between peaks were obtained by measuring the shift in the spectrum of energy-selected H<sup>-</sup> ions resulting from either a change of 10 eV in the primary H<sup>+</sup> collision energy or a change of 5 V on the voltagelabeled collision chamber. For the low-pressure data the H<sup>-</sup> signal was quite small and typically five hours were required to obtain a good signal-to-noise ratio. To ensure that there were no energy shifts a spectrum of a mixture of HCl + Ar was also recorded using separate needle valves for each gas.

# **III. CALCULATIONS**

The atomic-orbitals (AO) basis set employed for the calculations<sup>21</sup> has been partially optimized for the study of the excited states of the singly-ionized system HCl<sup>+</sup>. The chlorine functions are derived from the Veillard (12s, 9p) set in the Dunning (7s, 5p) contraction.<sup>22</sup> The four most diffuse s functions with exponents between 6.4 and 0.19 in the original basis have been expanded by one additional function and reoptimized; the new exponents are 8.464 97, 3.025 67, 0.92, 0.35, and 0.14. Similarly, the 5p space is modified so that the three AO's with exponents between 0.95 and 0.125 are replaced by four p functions with exponents 2.353 60, 0.458 27, 0.21, and 0.085. In addition, four Cartesian six-component Gaussian d functions with exponents 12.25, 3.50, 0.80, and 0.30 plus one Gaussian (ten-component) f function  $(\alpha = 0.60)$  have been added. Thus the chlorine basis can

be described as a contracted (8s, 6p, 4d, 1f) set. The functions for hydrogen are chosen from the work of Lie and Clementi<sup>23</sup> on the basis of a comparative study of various hydrogen functions for the description of HF, HCl, and OH.<sup>24</sup> They consist of eight primitive *s* functions contracted to five groups with two additional *p* functions with exponents 1.4 and 0.25. Together with this (5s, 2p) basis the total number of AO functions is 69.

The configuration-interaction (CI) calculations are of the standard multireference single- and double-excitation (MRSD-CI) type.<sup>25</sup> A set of reference configurations (ref) is chosen for each spatial and spin symmetry, i.e., the set which forms the dominant part of the CI expansion of the states under consideration. All single and double excitations with respect to this set are generated and form the MRSD-CI space, from which those configurations are selected which contribute to all states under consideration (various roots of a given symmetry) more than a chosen energy threshold (based on their interaction in a secular equation including the test species and the reference set). The Hamiltonian matrix for the selected subset is diagonalized directly while the contribution of the more weakly interacting configurations is taken into account in a perturbationlike manner. The total result is then the energy E(MRSD-CI) which corresponds to the total MRSD-CI space. The full CI energy E(full CI) in the given AO basis is also estimated in the standard manner<sup>25-27</sup> in analogy to the formula of Davidson<sup>28</sup> as

$$E(\text{full CI}) = E(\text{MRSD-CI}) + \left(1 - \sum_{\text{ref}} c_i^2\right) [E(\text{MRSD-CI}) - E(\text{ref})],$$

where the sum runs over all reference configurations and E(ref) is the corresponding energy.

In all actual calculations a core of two shells corresponding to the 1s shell and 2s shell of chlorine is held doubly occupied while all other electrons are correlated. The size of the reference sets varied between 11 and 18 configurations while the total MRSD-CI space reached more than a million symmetry-adapted functions (SAF's). Details are contained in Table I. It is seen that the reference configurations amount in each case to more than 91% of the total wave function. The molecular



FIG. 1. Calculated full CI potential-energy curves for  $HCl^{2+}$ . The right ordinate  $I^{2+}$  represents the double-ionization energy. (a) and (b) show the turning points of the ground state (v = 0) of HCl.

basis consists in each case of the  ${}^{4}\Sigma^{-}(\sigma^{2}\pi_{x}\pi_{y}\sigma)$  selfconsistent-field (SCF) molecular orbitals (MO's) of HCl<sup>+</sup> which have the advantage of being produced in a field of equal occupation of  $\pi_{x}$  and  $\pi_{y}$  and also occupation of the  $\sigma^{*}$ -type MO. The total energy of HCl<sup>+</sup> in its  $X^{2}\Pi$ state at R = 2.48 a.u., i.e., the approximate minimum, is E(MRSD-CI) = -460.05013 hartrees or estimated E(fullCI) = -460.07665 hartrees.

The ground state of  $\text{HCl}^{2+}$  is  ${}^{3}\Sigma^{-}$  with the electronic configuration  $\sigma^{2}\pi^{2}$ . Two close-lying states with the same occupation follow, i.e.,  ${}^{1}\Delta$  and  ${}^{1}\Sigma^{+}$ . All three are expected to possess approximately the same geometric behavior. The calculated potential-energy curves for these

TABLE I. Technical details for the MRSD-CI calculation. Given are the number of reference (main) configurations and the number of roots according to which configuration selection is carried out, the total number of symmetry-adapted configurationstate functions (SAF's) which have been generated, and the largest selected subspace which has been diagonalized explicitly. Furthermore, the weight of the reference configurations in the final MRD-CI wave function for a calculation at R = 2.484 a.u. is given in the last column. Since the calculations are carried out in the  $C_{2v}$  subgroup, the irreducible representation correlation is indicated.

State			SAF's				
	$C_{2v}$ notation	Number of mains	Number of roots	Number of total	Number of selected	$\sum_{\rm ref} c_i^2 \ (\%)$	
$X^{3}\Sigma^{-}, 2^{3}\Sigma^{-}$	${}^{3}A_{2}$	15	2	1 410 519	7225	94.7,93.8	
$^{1}\Delta, ^{1}\Sigma^{+}, 2^{1}\Sigma^{+}, 2^{1}\Delta$	${}^{1}A_{1}$	18	4	593 340	9585	93.6,93.8,93.0,92.2	
$^{1}\Delta, ^{1}\Sigma^{-}, 2^{1}\Delta, 2^{1}\Sigma^{-}$	${}^{1}A_{2}$	13	5	660 276	11 263	94.6,91.6,92.0,92.4	
<sup>3</sup> П,2 <sup>3</sup> П	${}^{3}B_{1}$	11	2	918 625	7275	93.9,93.0	
$^{1}\Pi, 2^{1}\Pi, 3^{1}\Pi$	${}^{1}B_{1}$	15	4	622 460	11 469	93.9,92.6	

		Electronic		$\Delta E(R)^{a}$			$\Delta E(R)^{b}$	$\Delta E(R)^{c}$
	State	configuration	2.41 a.u.	2.48 a.u.	2.69 a.u.	2.86 a.u.		2.4087 a.u.
HCl <sup>2+</sup>	<sup>3</sup> Σ <sup>-</sup>	$\sigma^2 \pi^2$	0.0	-0.140	-0.276	-0.264	0.0	0.0
	$^{1}\Delta$	$\sigma^2 \pi^2$	1.54	1.43	1.29	1.30	1.8	1.74;1.88
	$1\Sigma^+$	$\sigma^2 \pi^2$	2.84	2.72	2.56	2.55	3.0	2.99;2.85
	<sup>3</sup> П	$\sigma \pi^3$	3.86	3.57	3.01	2.71	3.9	4.0;3.80
	$^{1}\Pi$	$\sigma \pi^3$	5.26	4.92	4.30	3.99	5.5	6.71;5.46
	$2^{1}\Sigma^{+}$	$\sigma^0\pi^4$	10.24	9.81	8.76	8.12	10.6	
	2 <sup>3</sup> П	$\sigma^2 \pi \sigma$	11.91	11.25	10.79	10.33		
	$2^{3}\Sigma^{-}$	$\sigma \pi^2 \sigma$	13.05	12.67	11.28	10.38		
	2 <sup>1</sup> П	$\sigma^2 \pi \sigma$	13.64	13.00	11.64	10.88		
	${}^{1}\Sigma^{-}$	$\sigma \pi^2 \sigma$	14.75	14.11	12.46	11.52		
	$2^{1}\Delta$	$\sigma \pi^2 \sigma$	17.31	17.03	15.77	14.74		
	3 <sup>1</sup> П	$\sigma\sigma^2\pi^3$						
		$\sigma^0\pi^3\sigma$	17.57	17.16	15.96	14.74		
	$2^{1}\Sigma^{-}$	$\sigma^2 \pi \pi$		17.47	17.32			
			$E(\mathbf{R})^{\mathrm{a}}$	$E(\mathbf{R})^{\mathrm{d}}$		<i>E</i> ( <i>R</i> ) <sup>a</sup>	<i>E</i> ( <i>R</i> ) <sup>b</sup>	<i>E</i> ( <i>R</i> ) <sup>c</sup>
HCl <sup>2+</sup>	$3\Sigma^{-}$	$\sigma^2 \pi^2$	-459.2357				-458.9521	-458.9862;-458.7432
HCl <sup>+</sup>	$X^2\Pi$	$\sigma^2 \pi^3$		-460.0766		460.0638		
	$A^{2}\Sigma^{+}$	$\sigma \pi^2$		-459.9373		-460.9496		

TABLE II. Calculated energies for the various states of  $HCl^{2+}$  at pertinent internuclear separations R in atomic units (see text). Relative values  $\Delta E(R)$  with respect to ground state  ${}^{3}\Sigma^{-}$  are given in eV; total energies E(R) are in hartrees.

<sup>a</sup>This work.

<sup>b</sup>Results obtained from Ref. 19.

<sup>c</sup>Results obtained from Ref. 18 where two different AO basis sets are used.

<sup>d</sup>Results from Ref. 21.

three states as well as for the  $1^{1}\Pi \sigma \pi^{3}$  state are displayed in Fig. 1; the calculations are undertaken at 19 internuclear separations between R = 2.0 and 6.0 a.u. In accordance with qualitative MO theory the  $\sigma^2 \pi^2$  states possess a potential well while the state occupying the  $\sigma$ MO only is repulsive. Various other excited states have also been calculated at four internuclear separations (i.e., the ground-state geometry of  $X^{1}\Sigma^{+}$  of HCl at 2.41 a.u., the geometry of the two lowest states of HCl<sup>+</sup> (i.e.,  $X^{2}\Pi$ at 2.48 a.u. and  $A^{2}\Sigma^{+}$  at 2.86 a.u., as well as close to the minimum of HCl<sup>2+</sup> which is found at 2.75 a.u.), and the results are contained in Table II while the technical details for the calculations are summarized in Table I. It is obvious that all higher-lying states which occupy the  $\sigma^*$ -type MO are strongly repulsive. The same is obviously true for  $2^{1}\Sigma^{+}$  which does not occupy the HClbonding  $\sigma$  MO at all and for the <sup>3,1</sup> $\Pi$  states which occupy this MO only once.

Comparison with two earlier calculations by Kvalheim<sup>19</sup> and by Aksela *et al.*<sup>18</sup> show fair agreement with the present results. The first work<sup>19</sup> employs a (7s, 5p, 3d and 2s, 1p) Gaussian basis for Cl and H of similar quality as in the present work and uses between 2747 and 3811 configuration-state functions in the CI (excluding the eight highest MO's from consideration with a fixed core of 1s, 2s, and 2p). The second<sup>18</sup> calculation employs three different AO basis sets from double- $\zeta$  quality to one with a (10s, 8p, 2d and 6s, 2p) contraction and carries out a direct CI with the CRAY-1s Daresbury package. In the present case with the exception of the 1 <sup>1</sup>II state the results show relatively little dependence on

the AO basis quality as seen from the last column of Table II. The differences between the earlier and the present work are probably due primarily to the choice of the CI space. Also the present calculation allows for higher roots and possesses the multireference feature.

The energy difference between HCl<sup>+</sup>  $X^{2}\Pi$  and HCl<sup>2+</sup>  $X^{3}\Sigma^{-}$  at the HCl<sup>+</sup> equilibrium distance is 22.51 eV from MRSD-CI and 22.74 eV from the estimated full CI level. Using this latter value together with (i) the energy difference of 0.14 eV (Table II) between 2.48 a.u. (the equilibrium distance of  $HCl^+$ ) and 2.341 a.u. (the equilibrium distance of HCl), (ii) the known ionization potential of HCl of 12.75 eV, and (iii) the zero-point energy of 0.165 eV for the  $X^{2}\Pi$  state of HCl, we have deduced 35.46 eV for the energy [referenced to  $X^{1}\Sigma^{+}(v=0)$  of HCl] of the  ${}^{3}\Sigma^{-}$  ground state of HCl<sup>2+</sup> at R = 2.41 a.u. Experience with our calculations is that the ionization potential is generally underestimated by between 0.3 and 0.5 eV because of the larger amount of correlation energy inherent in the system possessing one more electron, which is not fully accounted for in the theoretical treatment. Explicit comparison of the Cl  $({}^{2}P)$  and CL  $+({}^{3}P)$ and  $Cl^{+}({}^{1}D)$  results<sup>21</sup> in the given AO basis show an error of 0.35 eV, and consequently, the  ${}^{3}\Sigma^{-}$  ground-state curve of  $HCl^{2+}$  at R = 2.41 a.u. is expected to lie at 35.81 eV (+0.15 eV if the larger error of 0.5 eV is assumed) above the  $X^{1}\Sigma^{+}$  energy of HCl. This procedure has been adopted in order to improve the accuracy of the absolute energy of the double-ionization vertical transition.

## **IV. EXPERIMENTAL RESULTS**

The translational energy-loss spectrum of H<sup>-</sup> arising from 3-5-keV protons colliding with pure HCl was obtained at several pressures. Figure 2 shows two kineticenergy distributions of H<sup>-</sup> obtained for 3-keV H<sup>+</sup> at two different HCl pressures in the collision chamber  $(\sim 1 \times 10^{-6}$  torr and  $\sim 4 \times 10^{-6}$  torr). Measurements show that the intensity of the lower energy peaks *a,b* varies quadratically with pressure and is attributed to the double-collision processes (2) while the intensity of the three higher-energy peaks *A,B,C* varies linearly and is attributed to the single-step process (1).

Figure 3 shows the high-energy part of the kineticenergy distribution of  $H^-$  obtained for 5-keV  $H^+$  with low-pressure HCl in the collision chamber. In this case the transmission is high enough to reveal the presence of an additional single-collision state (labeled D) on the higher-energy side of state C.

Following the procedure given in the experimental section we were able to obtain energy differences between peaks with an accuracy of 0.2 eV. The energy scale of Figs. 2 and 3 are directly given in absolute units determined by using argon as a calibration gas. Figure 4(a) shows the experimentally determined H<sup>-</sup> spectrum using Ar at low pressure ( $\sim 1 \times 10^{-6}$  Torr) and shows two well-known peaks e and E with full width at half maximum (FWHM) of 0.8 eV which gives the energy resolution of the apparatus. Peak e is due to the double-collision process leaving argon ionized in each collision in states  ${}^{2}P_{3/2}$  or  ${}^{2}P_{1/2}$ , while peak E is due to the single-collision process leaving doubly ionized argon



FIG. 2. Translational energy spectra of  $H^-$  ions from 3-keV  $H^+$  impinging on HCl at high pressure and HCl at low pressure. The scale is directly calibrated in terms of ionization energies  $I^+ + I^+$  and  $I^{2+}$ .



FIG. 3. Translational energy spectra of  $H^-$  ions from 5-keV  $H^+$  impinging on HCl at low pressure. The scale is directly calibrated in terms of ionization energies  $I^{2+}$ . Shown is the energy region corresponding to process 1.

in the state  ${}^{1}D_{2}$ . Corresponding ionization energies  $I^{+}+I^{+'}$  and  $I^{2+}$  are, respectively, 31.7 and 45.112 eV (see Ref. 29). Figure 4(c) shows the translational energy of H<sup>-</sup> arising from the acquisition of two electrons on HCl at high pression ( $\simeq 4 \times 10^{-6}$  Torr) and Fig. 4(b) shows the H<sup>-</sup> spectra from a mixture of Ar and HCl in-



FIG. 4. Translational energy spectra of  $H^-$  ions from 3-keV  $H^+$  impinging on (a) Ar, (b) a mixture of Ar and HCl, and (c) HCl.

troduced in the collision chamber through two separate needle valves at the same partial pressure as in Figs. 4(a) and 4(c).

These spectra enable us to give absolute ionization energies of  $HCl^{2+}$ . On Fig. 4(b), peaks a,b and A,B,C,E are easily recognized by comparing spectra 4(a) and 4(c). However, we notice a new intense peak d and a weak shoulder labeled f. Peaks a and b, seen on Figs. 2 and 4(c), can be interpreted in terms of the photoelectron spectrum of  $HCl^{.30}$  Two states,  $X^{2}\Pi$  and  $A^{2}\Sigma^{+}$ , are known to have adiabatic ionization energies of 12.75 and 16.28 eV with an average FWHM of 0.1 and 0.7 eV.

Transitions through process (2) produce different combinations of these two states and give three possible values of  $I^+ + I^{+'}$  located at 25.50, 29.03, and 32.56 eV. Our measured values of 25.6 and 29.1 eV show that peaks a and b are unambiguously due to the formation of 2 HCl<sup>+</sup> ( $X^2\Pi$ ) and HCl<sup>+</sup> ( $X^2\Pi$ )+HCl<sup>+</sup>( $A^2\Sigma^+$ ). The third expected peak c due to 2 HCl<sup>+</sup> ( $A^2\Sigma^+$ ) is not clearly seen in our experiments and its contribution is estimated to be a few percent.

There are a few reports on differential cross sections in energy and angle in the single-charge-exchange processes (2a) and (2b). These processes are most intense at 0° angular scattering, so the heights of the peaks we observe can be estimated to be directly proportional to the cross sections.<sup>31</sup> Within this approximation and from the relative heights of the peaks we can determine the relative cross sections of the processes leading to  $H^-$  production from process 2(a):

$$\mathbf{H}^{+} + \mathbf{H}\mathbf{C}\mathbf{I} \rightarrow \begin{cases} \mathbf{H} + \mathbf{H}\mathbf{C}\mathbf{I}^{+}(X^{2}\mathbf{\Pi}), & \Delta E = +0.9 \text{ eV} (\sigma_{1}) \\ \mathbf{H} + \mathbf{H}\mathbf{C}\mathbf{I}^{+}(A^{2}\Sigma^{+}), & \Delta E = -2.7 \text{ eV} (\sigma_{2}) \end{cases}$$

and those of the two processes forming  $H^-$  by process 2(b):

$$\mathbf{H} + \mathbf{H}\mathbf{C}\mathbf{I} \rightarrow \begin{cases} \mathbf{H}^{-} + \mathbf{H}\mathbf{C}\mathbf{I}^{+}(X^{2}\Pi) , & \Delta E \simeq -12 \text{ eV} \quad (\sigma_{-1}) \\ \mathbf{H}^{-} + \mathbf{H}\mathbf{C}\mathbf{I}^{+}(A^{2}\Sigma^{+}) , & \Delta E \simeq -15.5 \text{ eV} \\ (\sigma_{-2}) , \end{cases}$$

where  $\sigma_1$  and  $\sigma_2$  are the cross sections for charge exchange forming HCl<sup>+</sup> in the ground and first excited state, respectively, while  $\sigma_{-1}$  and  $\sigma_{-2}$  refer to formation of the ion pair  $HCl^+ + H^-$  with  $HCl^+$  in the same two states.  $\Delta E$  is the energy defect at infinite separation corresponding to each reaction. After deconvolution of the experimental data, we have deduced values lower than 1 for the cross-section ratios,  $\sigma_2/\sigma_1$  and  $\sigma_{-2}/\sigma_{-1}$  (either 0.3 or a few percent). From this result we conclude that the most probable channel for the formation of both H and H<sup>-</sup> leaves the target in the ground state  $X^{2}\Pi$  rather than the excited  $A^{2}\Sigma^{+}$  state. In contrast, in the case of  $Cl_2$  it was<sup>13</sup> shown that the collision channel is enhanced when the target is left in the  ${}^{2}\Pi_{u}$  excited state rather than in the  $X^2 \Pi_g$  ground state. As mentioned previously, in the mixture of HCl + Ar shown in Fig. 4(b) we observe one peak d and a shoulder f which does not appear with either pure Ar [Fig. 4(a)] or pure HCl [Fig. 4(c)]. From these energy-loss measurements we conclude that peak d involves collisions producing  $Ar^{+}(^{2}P)$ 

+HCl<sup>+</sup>( $X^2\Pi$ ) while the shoulder is due to collisions producing Ar<sup>+</sup>( $^2P$ )+HCl<sup>+</sup>( $A^2\Pi$ ). We note the large intensity of peak d which implies that one process (either H or H<sup>-</sup> formation) is substantially larger in Ar than in HCl. An explanation of the process involved would require another apparatus having two collision chambers.

As already mentioned, single-collision peaks A,B,C,D involve doubly charged states of HCl<sup>2+</sup> and have double-ionization energies of 37.4, 38.6, 40.9, and 45.6 eV. The margin of error,  $\pm 0.3$  eV, in these values is due to (i) thermal drift during our five-hour scans, (ii) the difficulty associated with assigning the position of the maximum, and (iii) the uncertainty about the position of the calibration peak e which can be due to double collisions involving Ar<sup>+</sup> in the states  ${}^{2}P_{1/2}$  and  ${}^{2}P_{3/2}$ . Depending on the relative contribution of  ${}^{2}P_{1/2}$  and  ${}^{2}P_{3/2}$ in each collision, peak e can be located at 31.51 eV  $({}^{2}P_{3/2}, {}^{2}P_{3/2})$ , 31.687 eV  $({}^{2}P_{1/2}, P_{3/2} \text{ and/or } {}^{2}P_{3/2}, {}^{2}P_{1/2})$ , or 31.864 eV  $({}^{2}P_{1/2}, {}^{2}P_{1/2})$ . In order to overcome this difficulty and to reduce drift during long scans, the following procedure was used. A partial scan of  $I^{2+}$  energy loss in the 32-47-eV range was recorded using 3010eV H<sup>+</sup> on Ar. This spectrum identified a reference energy for doubly ionized Ar in the  ${}^{1}D_{2}$  state at 45.112 eV [peak E in Fig. 4(a)]. Immediately following this, a 3010-eV HCl scan was recorded, followed by a 3000-eV Ar scan which shifts peak E by 10 eV to 35.112 eV. This value is very close to peak A of HCl. With this procedure peak A was found at 37.40±0.15 eV. In order to reduce data-collection time, a computercontrolled scanning procedure was used in which we were able to scan quickly over regions where no peaks existed and slowly over regions containing information. Using a deconvolution program, which takes into account broadening due to the initial energy distribution of H<sup>+</sup> formed in the ion source and the energy resolution of the apparatus, the FWHM of peaks A,B,C,D was estimated to be 0.6, 0.7, 1.8, and 2 eV, respectively.

#### V. DISCUSSION

In Fig. 5 are represented the experimentally measured absolute energetic positions of the doubly charged states of  $HCl^{2+}$ , obtained by the present double-charge-transfer experiment. Also presented and discussed are photoion-photoion coincidence (PIPICO)<sup>3</sup> and electron-impact<sup>15,16</sup> data as well as absolute values derived from charge-stripping measurements,<sup>17</sup> from the present calculation, and from Auger results.<sup>18,19</sup>

Our present calculation for the  $HCl^{2+}$  states are referenced to the  $HCl^+ X {}^2\Pi$  ionic state, a state which has a well-known experimental energy<sup>30</sup> of 12.75 eV. The energy position of the ground  $X {}^3\Sigma^-$  state for  $HCl^{2+}$  at the equilibrium internuclear distance of  $HCl \ (R = 2.41 \text{ a.u.})$ was already discussed in the calculation part of this article. It was calculated to be at 35.46 eV and expected to lie between 35.6 to 36 eV when the correlation energy of 0.35 to 0.5 eV is taken into account. We have chosen 35.9 eV as the energy of the  $X {}^3\Sigma^-$  state. Using the numerical results of column 1 of Table II together with the preceding values, we have positioned our theoretical values for the excited states of  $HCl^{2+}$  on Fig. 5.

We have determined also the absolute position for the  $X^{3}\Sigma^{-}$  state using Auger spectroscopy experimental results,<sup>18</sup> together with absorption spectra for HCl in the extreme-ultraviolet region<sup>32,33</sup> and electron-impact energy loss.<sup>34</sup> The measured values of the <sup>2</sup>P ionization po-tential for HCl are 207.1 $\pm$ 0.5 eV,<sup>32</sup> 207.4 $\pm$ 0.2 eV,<sup>33</sup> 207.40 eV (Ref. 34) for  ${}^{2}P_{3/2}$  and 208.7±0.5 eV,<sup>32</sup> 209.0±0.2 eV,<sup>33</sup> 209.03 eV (Ref. 34) for  ${}^{2}P_{1/2}$  and correspond to the excitation of an electron from the  $3\sigma$  or  $1\pi$ molecular orbitals. The 2p vacancy state is essentially atomic in character, which means the degeneracy due to its molecular character  $(3\sigma^2 \text{ and } 1\pi^4)$  is in the HCl case of the same order as the inherent width of the Auger lines. For this reason we may use the terminology  ${}^{2}P_{3/2,1/2}$  for these core-hole ionic states.<sup>33</sup> The highenergy peak in the  $L_{2,3}M_{2,3}M_{2,3}$  Auger spectra has a unique interpretation and it lies at  $173.30\pm0.2$  eV in the kinetic-energy scale; it is attributed unambiguously to  $L_2(2\pi^{-2})^3\Sigma^-$ . It is therefore possible to deduce the ionization potential for the doubly charged ground state  $2\pi^{-2} {}^{3}\Sigma^{-}$  as 209.0-173.3=35.7±0.4 eV. This value agrees closely with that of our theoretical result and consequently for clarity we have again chosen 35.9 eV for the energy position of  $X^{3}\Sigma^{-}$  state for presentation of the energy differences between HCl<sup>2+</sup> excited states ob-



FIG. 5. Comparison between calculated and experimental energies of  $HCl^{2+}$  electronic states.  $\triangle, \Box, \circ, *$  are the experimental results from Refs. 15, 16, 5 and 3.  $\blacksquare$ ,  $\blacktriangle$  are the result of CI calculation of Ref. 19 and reassigned Auger experimental results from Ref. 18.  $\bullet$ , present MRSD-CI calculation for energy normalization of the  ${}^{3}\Sigma^{-}$  state for these three results (see text). Also no error bars are presented for these three cases.  $\blacklozenge$ , present double-charge-transfer work.

tained through previous Auger<sup>18,19</sup> analysis. The results are shown in Fig. 5. Theoretical values from Ref. 18 already reassigned in Ref. 19 are not plotted.

In Fig. 5 differences between Auger analysis and our calculations are noticeable. For example, the energy gap between  ${}^{1}\Delta$  and  ${}^{3}\Sigma^{-}$  states is calculated to be 1.54 eV for this work and 1.8 eV in the calculation of Ref. 19 which also overestimates by more than 0.3 eV the energy splitting between the  ${}^{1}D$  and  ${}^{3}P$  states of Ar<sup>2+</sup>. Consequently, 1.54 eV is the most likely energy difference between the  ${}^{3}\Sigma^{-}$  and  ${}^{1}\Delta$  state. This value is consistent with the value of  $1.6\pm0.1$  eV obtained from the Auger energy spectrum given as Fig. 4 in Ref. 18.

In our experimental spectrum (Fig. 2) no significant signal around  $I^{2+} = 35.9$  eV is seen, demonstrating that the  ${}^{3}\Sigma^{-}$  state is not populated in our experiment. This is consistent with the statement that in the case of doubly charged transfer experiments the transition  $M \rightarrow M^{2+}$  must obey the selection rule  $\Delta S = 0$ . This means that the electronic states of  $M^{2+}$  with the same symmetry as in the initial neutral state M are favored. Therefore, the state labeled A at 37.4 $\pm$ 0.15 eV has a  $^{1}\Delta$ symmetry. By subtracting 1.54 eV we find the  ${}^{3}\Sigma^{-}$  state to be at 35.9±0.2 eV in agreement with the values of  $35.7\pm0.4$  eV and 35.9 eV presented earlier in this paper. In conclusion, as seen in Fig. 1, vertical double ionization of  ${}^{3}\Sigma^{-}$  state is 35.9 eV while the value at equilibrium separation R = 2.7 a.u. is 35.6 eV and the maximum of the configuration barrier is at 36.1 eV at R = 4.2 a.u.

The experimental values obtained by electron impact are  $35.5\pm0.5 \text{ eV}$  (Ref. 15) and  $36\pm0.8 \text{ eV}$  (Ref. 16) are compatible within error bars with our value for the  ${}^{3}\Sigma^{-}$ state. In fact, the first value needs to be corrected by + 0.2 eV because the electron energy was calibrated using the appearance potential of HCl<sup>+</sup> which was estimated to be  $12.56\pm0.1 \text{ eV}$  at that time but is now known to be + 0.2 eV higher.

Charge-stripping experiments measure the vertical energy difference between  $AB^+$  and  $AB^{2+}$  and consequently do not necessarily measure the vertical energy difference between AB and  $AB^{2+}$ . The result  $36.3\pm0.4$ eV from Ref. 17 for HCl<sup>2+</sup> is presented in Fig. 5 assuming HCl<sup>+</sup> is initially populated in the ground vibrational level. In this experiment the  $HCl^{2+}$  stable state is expected to be reached by a vertical transition from the HCl<sup>+</sup> ground stable state. The well of the potentialenergy curve<sup>28</sup> for HCl<sup>+</sup> is shifted up in internuclear distance when compared to the neutral state;<sup>29</sup> therefore, we expect to obtain an energy value for the  ${}^{3}\Sigma^{-}$  HCl<sup>2+</sup> state in the charge-stripping experiment<sup>17</sup> which is in the well of the  ${}^{3}\Sigma^{-}$  state. The obtained value of 36.3 eV indicates that excited vibrational levels of the  ${}^{3}\Sigma^{-}$  state are populated. We can also suggest a contribution from the  $1\Delta$  state in the experimental spectra.

The observation of PIPICO<sup>3</sup> is difficult to analyze due to the large error bar in the measurement of the energy release (6.4±1.1 eV) obtained by the detection of the ionic fragments H<sup>+</sup> and Cl<sup>+</sup> in coincidence. When adding this energy release value to the known energy value 31 eV for the first dissociative limit  $[H^+ + Cl^+({}^{3}P)]$ , the authors proposed a position of 37.3±1 eV which as can

be seen from Fig. 5 could energetically correspond to the excitation of X  ${}^{3}\Sigma^{-}$  or more likely to the  ${}^{1}\Delta$  HCl<sup>2+</sup> state. This is possible because in the photoionization process the selection rule is less strict than in the double-charge-transfer experiment ( $\Delta S = 0, \pm 1$ ). However, in Fig. 1 we observe that even though the potentialenergy curves for the  $X^{3}\Sigma^{-}$  and  $^{1}\Delta$  states lead to fragmentation in the Franck-Condon region from the neutral state, the expected kinetic energy released does not explain the experimental observation even with the large error bar ( $\pm 1$  eV). The  ${}^{1}\Sigma^{+}$  state can also be reached by vertical transitions from the neutral excited by the 40.8eV resonant radiation obtained from a HeII discharge lamp. This state at 38.6 eV (see Fig. 1) correlates to the  $Cl^{+}({}^{1}D) + H^{+}$  limit, and consequently corresponds to a kinetic-energy release during fragmentation of 6.3 eV in good agreement with the PIPICO results. The emitted light used in the PIPICO<sup>3</sup> experiment is not monochromatized and consequently higher-energetic radiations (for example, 48.4 and 51.0 eV) could also participate in the double-ionization process by producing the  ${}^{1}\Sigma^{+}$  HCl<sup>2+</sup> state even if the He II lamp has a fairly low efficiency for these emissions.

The peak B at  $38.9\pm0.3$  eV (see Fig. 3) of our doublecharge-transfer experiment is within 0.2 eV of the values obtained from the  ${}^{1}\Sigma^{+}$  state of Auger and our calculation, and so the assignment appears straightforward (see Fig. 5). From spin selection rules<sup>35</sup> there is no reason to observe in our experiment the next excited state  ${}^{3}\Pi$ . This state is the first excited state with a triple symmetry and it is expected to be at 39.8 eV (see Fig. 5) on the higher-energy side of line B (Fig. 2) where no peak is observed. Based on the same energy comparison as for peak B, peak C at 40.9 $\pm$ 0.3 eV is assigned to the  ${}^{1}\Pi$ state. The full width at half maximum is 0.6 eV for peaks A and B, but is much larger for peak C (1.8 eV). This finding is interpreted as being due to the stable character of the  $^{1}\Delta$  and  $^{1}\Sigma^{+}$  states. Our calculations predict also the repulsive character for the  ${}^{1}\Pi$  state which explains the broadening observed for peak C.

On the higher-energy side of the spectrum a broad peak labeled D is observed at an energy of  $45.5\pm0.5$  eV (Fig. 3). At this energy our calculations predict the presence of a  $2^{1}\Sigma^{+}$  state. If we consider our error bar, this value is also in agreement with the value proposed by the theoretical analysis of Kvalheim.<sup>19</sup> This lower kinetic-energy part of the Auger spectrum is very difficult to interpret because of the lack of experimental intensity. The spectrum is obtained from the deconvolution of many lines and consequently it cannot serve as good support for the calculation. In fact the first theoretical interpretation proposed by Assela *et al.*<sup>18</sup> suggested a  $2 {}^{1}\Sigma^{+}$  state to lie at 42.7 eV and consequently far out of our experimental error bar. Peak D is assigned as  $2 {}^{1}\Sigma^{+}$  in agreement with our calculation and with the reassignment of Kvalheim.

## VI. CONCLUSION

In Fig. 5 we have presented the excited double ionic states of  $HCl^{2+}$  obtained in our double-charge-transfer experiment and our MRSD-CI calculation. Our experimental resolution was good enough to resolve the four lowest excited states with singlet symmetry and we have proposed absolute values for the double-ionization energy of these states which agree well with our calculation (except for a possible small shift in energy of 0.2 eV due to the uncertainty of estimating the correlation energy in the calculation).

With this work we have shown that HCl is a favorable candidate to study the spin conservation selection rule for our double-ionization process.<sup>35</sup> The ground double ionic state  ${}^{3}\Sigma^{-}$  has been experimentally observed as a well-resolved line in the Auger spectrum. From our results we have obtained an improved value of  $35.9\pm0.2$  eV for this state. We have compared our data with results of other techniques such as PIPICO,<sup>3</sup> charge stripping,<sup>17</sup> and electron-impact experiments<sup>15,16</sup> and satisfactory assignment of states is given. Our double-charge-transfer experimental results have also permitted us to clarify the discrepancy observed between the two theoretical analysis of the Auger spectrum.

Finally, the energy differences between excited states in the present calculation differ from the present experimental data by less than a few percent, and demonstrate the high degree of reliability of calculations of the present type. Stimulated by the present work a PIPICO experiment by Ollsson and co-workers using synchrotron radiation is presently underway in Orsay.<sup>36</sup>

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