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SAC-CI general-*R* study of the ionization spectrum of HCl*

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Abstract. The valence ionization spectrum of HCl is studied by symmetry-adapted-cluster configuration-interaction general-*R* and SD-*R* methods. The general-*R* method describes well the peak positions and intensities of seven satellite lines observed below the double ionization threshold. The twinning shake-up states due to the $(4\sigma)^{-1}$ state and the Rydberg states of HCl^+ are correctly reproduced.

Key words: Symmetry-adapted-cluster configuration-interaction – HCl – Ionization spectrum – Electron correlation – Shake-up state

1 Introduction

Many satellite peaks are found in the inner-valence region of the ionization spectrum. These peaks are of considerable interest since they reflect electron correlations in molecules. Recently, these peaks have been intensively studied by high-resolution X-ray photoelectron spectroscopy (XPS), synchrotron radiation photoelectron spectroscopy (SRPS), and electron momentum spectroscopy. The satellite lines of HCl [1–5] were studied in detail by Adam [3, 4] and Svensson et al. [5] and the valence ionization spectrum was recorded up to 52 eV using XPS and SRPS [5]. Eleven satellite lines were observed and seven of them were found to lie below the continuum of the doubly ionized state. Some of the potential curves were also studied by the isotope effect and the photon-energy dependence of the intensity.

The satellite peaks of HCl [6] have also been studied theoretically by the Green function method, algebraic diagrammatic construction (ADC) (3) and approximated ADC (4) [7–9]. Seven satellite lines were analyzed with respect to vertical ionization [6]. Some of the potential curves for HCl^+ were studied by the multireference configuration interaction method and five lines were assigned by taking account of the Franck–Condon factors from the neutral ground state [10]. However, it still seems to be important to perform reliable calculations with extended basis sets including sufficient amount of electron correlation, especially for the assignment of the high-lying shake-up states. In particular, there are congested satellite peaks which are considered to be due to the Rydberg states converging to the doubly ionized states [5, 6, 10].

The symmetry-adapted-cluster configuration-interaction (SAC-CI) method [11–16] has been successfully applied to several molecular spectroscopic problems including ionization spectroscopy [17–24]. There are two standard choices of the linked operators (*R*) in the SAC-CI methods, namely, single double (SD)-*R* and general-*R* methods [25–28]. Details of the general-*R* method can be found in Ref. [25] The SAC-CI general-*R* method is designed to describe multiple-electron processes with high accuracy and has been shown to be useful for studying many different kinds of states in ionization spectra [25, 29]. In a recent series of applications [29–31], we studied the details of the shake-up states using the SAC-CI general-*R* method.

In this paper, we study the ionization spectrum of HCl up to the double ionization threshold by the SAC-CI general-*R* and SD-*R* methods.

2 Computational details

In the preceding study of HCl by ADC [6], several basis sets were systematically examined and diffuse functions were found to be important, while the *f* functions on Cl and the *d* functions on H did not have much effect on the results. Therefore, we chose “basis set I” in Ref. [6] for our basis set; $(12s9p)/[8s6p]$ GTOs of McLean and Chandler [32] augmented with two diffuse *s* and *p* functions of $\zeta_s = 0.06, 0.015$ and $\zeta_p = 0.04, 0.01$, plus four *d* functions of $\zeta_d = 0.7$, 0.25, 0.08, and 0.02 for the Cl atom, and $(5s)/[3s]$ GTOs [33] plus two *p* functions of $\zeta_p = 1.0$ and 0.3 for the H atom. The resultant basis set is $(14s11p4d/5s2p)/[10s8p4d/3s2p]$. The internuclear distance is 1.2746 Å of the experimental ground state [34] and vertical ionizations are studied.

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Both SAC-CI general-*R* and SD-*R* calculations are performed. Since most of the shake-up states of HCl are described by two-electron processes, higher excitation operators in the general-*R* method were limited up to triples. In the SD-*R* method, unlinked terms written as $R_iS^{ab}_{jk}$ and $R^a_{ij}S^{bc}_{kl}$, were included; namely the "3,4-excited" calculation [18] is performed. In the SAC-CI calculation, 1*s*, 2*s*, and 2*p* orbitals of Cl were frozen as cores and then the active space consists of 4 occupied MOs and 58 unoccupied MOs. Perturbation selection was performed for the linked operators higher than doubles to reduce the computational effort. For the ground state, the threshold for the linked doubles is $\lambda_g = 1 \times 10^{-5}$ a.u. and the unlinked terms are written as the products of the important linked terms whose SDCI coefficients are larger than 0.005. For the ionized states, the threshold for the linked operators is $\lambda_e = 1 \times 10^{-5}$ a.u. The thresholds of the CI coefficients for calculating the unlinked operators are 0.1 and 0.001 for the *R* and *S* operators which are the SAC and SAC-CI operators, respectively.

The HONDO8 program [35] is used for the HF SCF calculations and the SAC-CI96 program [36] is used for the SAC-CI calculations.

3 Results and discussion

The ionization spectrum up to the double ionization threshold, i.e. about 35 eV, was studied by the SAC-CI general-*R* and SD-*R* methods. The satellite states belong mainly to $^2\Sigma$, so that 40 and 15 ionized states were calculated for $^2\Sigma$ and $^2\Pi$ symmetries, respectively. The number of reference configurations used for the perturbation selection, and the dimensions of the linked operators in the general-*R* calculations together with those before perturbation selection are summarized in Table 1. Since most of the shake-up states are described predominantly by two-electron processes, the reference configurations are 73 and 56 singles and doubles configurations selected for the $^2\Sigma$ and $^2\Pi$ states, respectively. The dimensions of the SAC-CI general-*R* calculations are about 7,600 and 5,800 for the $^2\Sigma$ and $^2\Pi$ states, respectively.

The ionization spectra of HCl calculated by the SAC-CI general-*R* and SD-*R* methods are compared with the X-ray photoelectron spectrum [5] in the energy region 10–40 eV in Fig. 1. The spectrum includes $(2\pi)^{-1}$ and $(5\sigma)^{-1}$ states and the seven higher bands which are due to the shake-up states borrowing their intesities mainly from the $(4\sigma)^{-1}$ single-hole state. The intensity of the peak is calculated by the monopole approximation including initial- and final-state correlation effects [37], though the monopole intensity does not necessarily give the quantitative cross-section of the photoelectron spectroscopy. Each peak in the theoretical spectrum is convoluted with the different line width as obtained from experiment [5]. The present convolution is symmetric in higher- and lower-energy directions, though the line shape should be asymmetric when the Franck–Condon factor is taken into account [10]. The main configurations of each peak, together with the peak position and intensity are shown in Table 2. They are shown for the states up to 35 eV and 38 eV for general-*R* and SD-*R*, respectively, with calculated intensities greater than 0.005 except for some low-lying $^2\Pi$ states. The experimental ionization potentials (IPs) and intensities are

Table 1. Numbers of the reference configurations and the dimensions of the linked operators in the symmetry-adapted-cluster configuration-interaction (SAC-CI) general-*R* calculations for the ionized states of HCl

State	Singles	Doubles	Triples	Total
Numbers of reference configurations				
$^2\Sigma$	2	71	–	73
$^2\Pi$	1	55	–	56
Dimensions of SAC-CI general-*R* calculations[a]				
$^2\Sigma$	2/2	237/272	7,360/17,536	7,599/17,810
$^2\Pi$	1/1	185/224	5,682/17,220	5,868/17,445

[a] Dimensions after perturbation selection/before perturbation selection

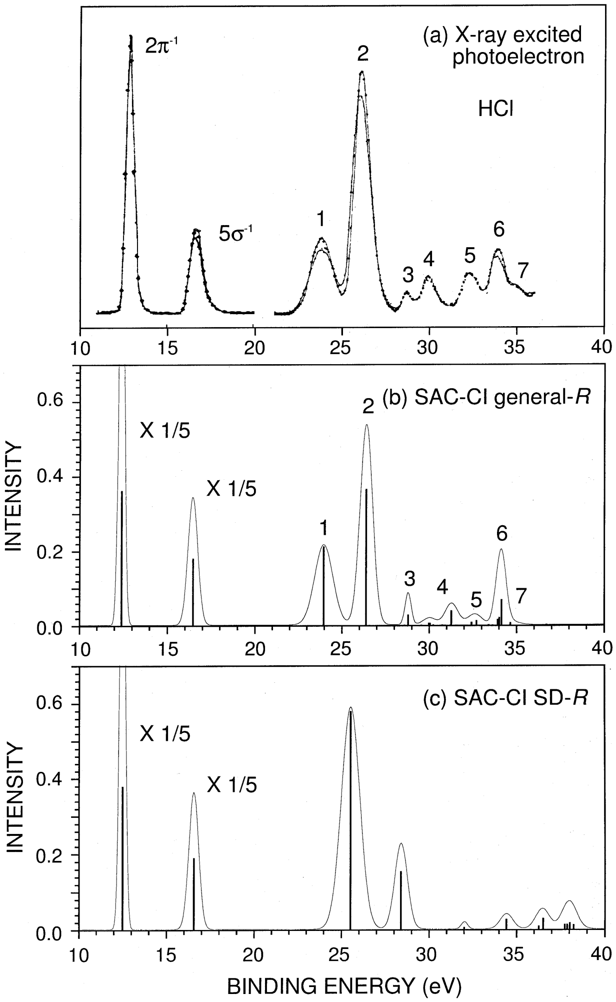

Fig. 1. Ionization spectra of HCl by **a** X-ray photoelectron spectroscopy, **b** the symmetry-adapted-cluster configuration-interaction (SAC-CI) general-*R* method, and **c** the SAC-CI single double (SD)-*R* method. Each peak in the theoretical spectra is convoluted with the different line widths as obtained from experiment [5]. Intensity of $(2\pi^{-1})$ is normalized to 2

from XPS and SRPS [5]: the intensities are shown relative to that of line 2.

The two main peaks at 12.8 and 16.6 eV in the experimental spectrum [5] are reproduced well by both the SAC-CI general-*R* and SD-*R* methods. The general-*R* method calculates the $(2\pi)^{-1}$ and $(5\sigma)^{-1}$ states to be at 12.41 and 16.46 eV, while they are calculated to be at 12.50 and 16.56 eV by the SD-*R* method. Inclusion of higher excitations in the SAC-CI operators *R* does not affect much the main-peak positions and their intensities; this has also been shown by other examples [25, 29–31].

For the seven bands above 20 eV, remarkable differences are seen between the general-*R* and SD-*R* results. The general-*R* method nicely reproduces the positions and the intensities of the shake-up states. It is important to include higher-than-doubles excitation operators in the linked operators to describe well the shake-up states, which are essentially the two-electron processes relative to the ground state. This was also found in a series of recent applications [29–31]. Among the seven bands observed in the energy region 22–36 eV, the first twinning peaks centered at about 25 eV originate from the $(4\sigma)^{-1}$ state [5, 6, 10]. They are calculated to be at 23.96 and 26.38 eV in comparison with the experimental IPs of 23.5 and 25.8 eV. These states have the character of $(2\pi^{-2}n\sigma)$ as shown in Table 2. The relative intensity of line 1 to line 2 is evaluated as 0.58 by the general-*R* method; this is slightly larger than the experimental value of 0.417. By the SD-*R* method, the twinning states are calculated to be at 25.51 and 28.39 eV and their relative intensities are reversed. The difference between the general-*R* and SD-*R* methods for describing these states is shown in Table 3. In the general-*R* method, the weight of the configuration $(2\pi^{-2}n\sigma)$ is larger in the $2^2\Sigma$ state than in the $3^2\Sigma$ state, while the SD-*R* method gives the opposite picture; therefore, the relative intensity of these peaks is calculated differently by the two methods. The weight of triples is not so large for these states. Small asymmetry of the peak was observed for band 2 and this was attributed to the $3^2\Pi$ state [10]. This $^2\Pi$ state is calculated by the present general-*R* method to be at 27.88 eV with a small monopole intensity of 0.001 as shown in Table 2.

Table 3. Main configurations ($C > 0.2$) of the $2^2\Sigma$ and $3^2\Sigma$ states calculated by the SAC-CI general-*R* and SD-*R* methods

State	SAC-CI general-*R*	SAC-CI SD-*R*
$2^2\Sigma$	$0.46(4\sigma^{-1})+0.42(2\pi^{-2}11\sigma)$ $+0.42(2\pi^{-2}11\sigma)$	$0.76(4\sigma^{-1})+0.26(2\pi^{-2}11\sigma)$ $+0.26(2\pi^{-2}11\sigma)$
$3^2\Sigma$	$0.60(4\sigma^{-1})-0.24(2\pi^{-2}11\sigma)$ $-0.24(2\pi^{-2}11\sigma)$	$0.39(4\sigma^{-1})-0.45(2\pi^{-2}11\sigma)$ $-0.45(2\pi^{-2}11\sigma)$ $+0.24(2\pi^{-2}9\sigma)+0.24(2\pi^{-2}9\sigma)$

Table 2. Excitation level, ionization potential (IP) (in eV), monopole intensity, and main configurations of the ionized states of HCl calculated by the SAC-CI general-*R* and single double (SD)-*R* methods

State	Exptl.[a]			SAC-CI general-*R*				SAC-CI SD-*R*	
	Line No.	IP	Intensity[b]	Excitation level	IP	Intensity	Main configurations ($C > 0.3$)	IP	Intensity
$^2\Sigma$		16.6		1	16.46	0.899	$0.94(5\sigma^{-1})$	16.56	0.947
	1	23.65	0.417	2	23.96	0.211	$0.46(4\sigma^{-1})+0.42(2\pi^{-2}11\sigma)$ $+0.42(2\pi^{-2}11\sigma)$	25.51	0.578
	2	25.85	1.0	2	26.38	0.365	$0.60(4\sigma^{-1})$	28.39	0.153
	3	28.5	0.043	2	28.78	0.028	$0.33(2\pi^{-2}9\sigma)+0.33(2\pi^{-2}9\sigma)$ $+0.32(2\pi^{-2}12\sigma)+0.32(2\pi^{-2}12\sigma)$	32.01	0.006
	4	29.8	0.164	2	30.04	0.006	$0.43(5\sigma^{-2}11\sigma)-0.36(2\pi^{-2}2\delta)$ $-0.36(2\pi^{-2}2\delta)$	34.41	0.027
				2	31.27	0.039	$0.43(5\sigma^{-2}11\sigma)$	36.26	0.009
	5	32	0.194	2	32.43	0.009	$0.46(5\sigma^{-1}2\pi^{-1}5\pi)$	36.52	0.030
					32.71	0.012	$0.41(5\sigma^{-1}2\pi^{-1}6\pi)+0.41(5\sigma^{-1}2\pi^{-1}6\pi)$ $-0.30(2\pi^{-2}1\delta)$	37.74	0.013
	6	33.2	0.164	2	33.92	0.016	$0.58(2\pi^{-1}5\sigma^{-1}5\pi)-0.58(2\pi^{-1}5\sigma^{-1}5\pi)$ $+0.36(2\pi^{-1}5\sigma^{-1}3\pi)-0.36(2\pi^{-1}5\sigma^{-1}3\pi)$ $+0.33(5\sigma^{-1}2\pi^{-1}5\pi)-0.36(5\sigma^{-1}2\pi^{-1}5\pi)$	37.88	0.018
				2	34.01	0.021	$0.42(2\pi^{-2}8\sigma)+0.42(2\pi^{-2}8\sigma)$		
				2	34.14	0.069	$0.34(2\pi^{-2}8\sigma)+0.34(2\pi^{-2}8\sigma)$ $+0.32(2\pi^{-1}5\sigma^{-1}6\pi)+0.32(2\pi^{-1}5\sigma^{-1}6\pi)$		
	7	34.65	0.143	2	34.65	0.007	$0.53(2\pi^{-2}7\sigma)+0.53(2\pi^{-2}7\sigma)$		
$^2\Pi$		12.8		1	12.41	0.907	$0.95(2\pi^{-1})$	12.50	0.950
				2	27.88	0.001	$0.50(2\pi^{-2}6\pi)-0.47(5\sigma^{-1}2\pi^{-1}11\sigma)$ $+0.38(2\pi^{-2}6\pi)+0.30(5\sigma^{-1}2\pi^{-1}9\sigma)$	34.34	0.007
				2	28.58	0.001	$0.56(2\pi^{-2}5\pi)$		
				2	29.55	0.001	$0.48(2\pi^{-2}6\pi)-0.34(5\sigma^{-1}2\pi^{-1}9\sigma)$		
				2	29.98	0.006	$0.56(2\pi^{-2}5\pi)+0.35(2\pi^{-2}5\pi)$ $+0.34(2\pi^{-2}3\pi)-0.34(2\pi^{-2}5\pi)$ $+0.33(2\pi^{-2}5\pi)$		
				2	30.24	0.002	$0.58(2\pi^{-2}6\pi)-0.30(2\pi^{-2}5\pi)$		

[a] Ref. [5]

[b] Intensity relative to the second line

The next five bands with smaller intensities were observed above the twinning peaks and were considered to be due to the Rydberg states converging to the doubly ionized state [5, 6, 10]. For these peaks, many shake-up states are calculated both by the general-*R* and SD-*R* methods with relatively small intensities as in the experimental spectrum. Their intensities are due to $^2\Sigma$ states, mostly from $(4\sigma)^{-1}$ and $(5\sigma)^{-1}$ states, through final-state correlations: main configurations have the nature of $2h1p$. Band 3, observed at 28.5 eV, is clearly assigned to the $^2\Sigma$ state calculated to be at 28.78 eV, and is characterized as a $(2\pi^{-2}n\sigma)$ state, though the assignment of this state is the subject of controversy [5, 6]. The $^2\Pi$ state is also calculated to be at 28.55 eV.

For the other peaks, our assignments are given in the general-*R* spectrum shown in Fig. 1. Two or three shake-up states are assigned to each band. Here, our assignment is based on the calculated IPs, since the intensity is a rather delicate quantity. We calculate two $^2\Sigma$ shake-up states, both $(5\sigma^{-2}n\sigma)$, at 30.04 and 31.27 eV and they are the candidates for line 4 observed at 29.8 eV. The convolution of these states gives two bands, however. In this region, $^2\Pi$ states with small intensities are also calculated to be at 29.98 and 30.24 eV as seen from Table 2. For line 5, found at 32 eV, we assign two $^2\Sigma$ states calculated to be at 32.43 and 32.71 eV, both of which are characterized as $(5\sigma^{-1}2\pi^{-1}n\pi)$. Three shake-up states calculated to be at 33.92, 34.01, and 34.14 eV are attributed to line 6 measured at 33.2 eV. These states are described by a linear combination of $(5\sigma^{-1}2\pi^{-1}n\pi)$ and $(2\pi^{-2}n\sigma)$. Finally, the $^2\Sigma$ shake-up state calculated to be at 34.65 eV whose dominant configuration is $(2\pi^{-2}n\sigma)$ is assigned to line 7 observed at 34.65 eV. Considerable mixing of δ orbitals is found for these shake-up states, indicating the importance of the *d*-type Rydberg functions as pointed out in Ref. [6]. The SD-*R* method also gives these shake-up states, however, their IPs are evaluated to be 2–3 eV higher than the general-*R* method as shown in Table 2.

4 Conclusion

The valence ionization spectrum of HCl is studied by the SAC-CI general-*R* and SD-*R* methods. The main peaks, $(1\pi)^{-1}$ and $(5\sigma)^{-1}$ states, are described well by both the general-*R* and SD-*R* methods, but the general-*R* method is necessary for describing the shake-up states in a higher-energy region. In particular, seven satellite peaks in the range 20–35 eV are well-reproduced by the general-*R* method. The twinning peaks centered at 25 eV are very nicely reproduced and are due to $(4\sigma)^{-1}$ interacting with $(2\pi^{-2}n\sigma)$. The next five bands with small intensities are attributed to the Rydberg states of HCl^+ converging to the doubly ionized state. These states are described by linear combinations of the configurations $(5\sigma^{-2}n\sigma)$, $(5\sigma^{-1}2\pi^{-1}n\pi)$, $(2\pi^{-2}n\sigma)$, and $(2\pi^{-2}n\delta)$.

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