Observation of Isotope Effects in Auger-Electron Spectra: The Predissociative $2\pi^{-2}\,{}^3\Sigma^-$ State in HCl and DCl

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(Received 31 March 1988)

The $L_2 \rightarrow 2\pi^{-2}\,{}^3\Sigma^-$ Auger-electron lines from HCl and DCl are recorded in very high resolution. The vibrational structure is resolved which reveals an isotope effect. The $2\pi^{-2}\,{}^3\Sigma^-$ state is shown to be predissociative with a potential barrier of 0.8(2) eV. The lifetime of the Cl $2p_{1/2}$ core-hole state in HCl and DCl was determined to 0.12(2) eV.

Auger-electron spectroscopy is a well-known method for the study of free molecules and solids. Most work on free molecules, however, has been dealing with Auger processes that only involve core electrons. As has been pointed out by Aksela et al.,[1] the list of experiments on KVV and LVV Auger spectra of molecules is far from exhaustive. Only in the cases of N_2 (Siegbahn et al.[2]) and CO (Correia et al.[3]) has it been possible to resolve the vibrational structure of an Auger line, and considerable theoretical effort has been spent to provide a theoretical description including correlation and interference effects.[3]

Isotope effects have been studied in uv-excited photoelectron spectroscopy since the early 1960's.[4] Recently it has been shown that it is possible to detect differences between isotope-substituted molecules also in x-ray-excited photoelectron spectra.[5] No isotope effects have, to our knowledge, been reported in Auger spectra.

The LVV Auger spectrum of HCl has earlier been studied by Aksela et al. This study was, however, focused on the overall assignment of the LVV Auger spectrum with use of ab initio configuration-interaction calculations. No attempt was made by these authors to resolve a vibrational fine structure of the lines.

In the electron-energy-loss spectrum reported by Shaw et al.[6] the $2p_{3/2}$-$4s\sigma$ transition shows up as a single line, corresponding to excitations mainly to the $v=0$ vibrational level in the excited state. One might assign a very small structure, discernible on the high-energy side of this line, to a $v=1$ vibrational level in the final state. This structure is, however, not discussed by the authors of Ref. 6.

We have examined the Cl $2p_{1/2,3/2}$ photoelectron lines in HCl excited with monochromatized x-rays.[7] These lines show very little vibrational broadening. This finding and the results of Shaw et al. are in line with the fact that the equilibrium bond distance of the ArH^+ ion (which is isoelectronic with a core-hole ionized HCl molecule) is approximately the same as for HCl in the ground state.[8] In conclusion, the $v=0$ vibrational component dominates in the core-hole ionized initial state of the Auger process. We therefore expect that any vibra-

tional fine structure appearing in the HCl and DCl LVV Auger spectra corresponds essentially to one single Franck-Condon progression, and moreover, that interference effects between the vibrational states, due to a finite lifetime, might be of minor importance.

We have performed a new study of the electron-beam–excited LVV Auger spectrum of HCl and DCl using very high resolution. We find that it is possible to resolve the first $L_2 \rightarrow 2\pi^{-2}\,{}^3\Sigma^-$ Auger line and several other lines into their vibrational components in the cases of both HCl and DCl and thus for the first time to detect isotope effects in Auger-electron spectra. In this paper we only discuss the $L_2 \rightarrow 2\pi^{-2}\,{}^3\Sigma$ vibrational band. The full spectrum will be presented in a forthcoming paper.[7] By determining the line positions and intensities we have obtained the potential curve of the doubly ionized $2\pi^{-2}\,{}^3\Sigma^-$ final state and we have also been able to estimate the lifetime of the Cl $2p$ core hole states in HCl.

HCl and DCl were produced by the introduction of H_2SO_4 and D_2SO_4, respectively, onto heated KCl in an evacuated flask. The spectra were run on a hemispherical electron spectrometer[9] at Uppsala at a pass energy of 40 eV. A 3-keV electron beam was used for excitation. The pressure in the analyzer was held constant at $\approx 1 \times 10^{-5}$ Torr. From runs at the same pressure on Ar gas the effect of inelastic scattering in the spectra was found to be negligible. Calibration of the spectrum was made by our mixing the sample gas with argon and simultaneously recording the LVV Auger spectrum and the $L_3M_1M_1({}^1S_0)$ and $L_3M_{2,3}M_{2,3}({}^1D_2)$ lines at 177.91 and 203.47 eV in Ar.[10]

Figure 1 shows the $L_2 \rightarrow 2\pi^{-2}\,{}^3\Sigma^-$ Auger band in HCl and DCl. In this figure we have, for clarity reasons, aligned the 0-0 transitions. As can be seen, three vibrational states are clearly resolved in each of the spectra. Two additional states can be found by a careful analysis of the line profiles. To the right of the strongest 0-0 transitions we discern a very small structure that may correspond to the $1 \rightarrow 0$ transitions.

Curve fitting was applied to the peaks in the two spectra. The spectrometer resolution was estimated by our running a very narrow satellite in argon at 176.60 eV
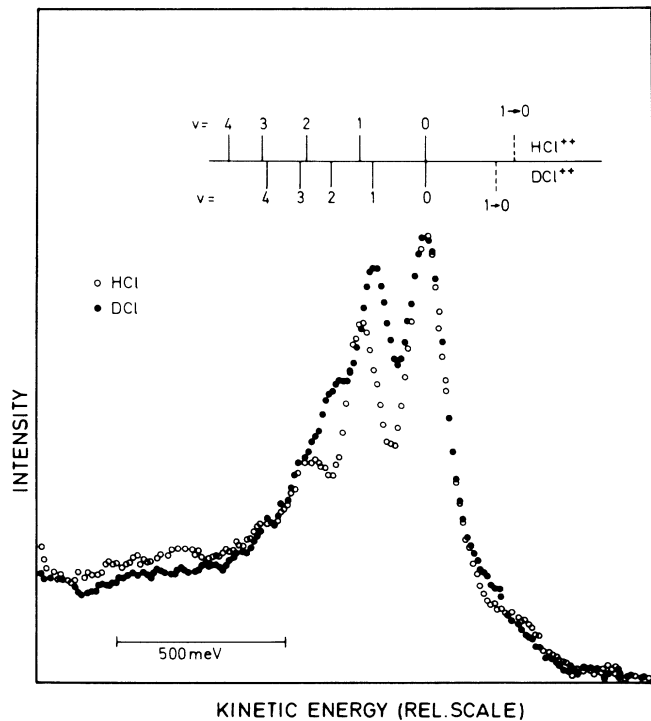
FIG. 1. The $L_2 \rightarrow 2\pi^{-2}\,^3\Sigma^-$ Auger-electron line in HCl and DCl. Notice the isotope shift between the respective vibrational sublevels. The 0-0 transitions were, for clarity reasons, put at the same energy.

TABLE I. Energies and intensities for vibrational states in the $L_2 \rightarrow 2\pi^{-2}\,^3\Sigma^-$ Auger line in HCl and DCl.

Molecule	Vibrational quantum No. v for the final state	Energy relative to the $v=0$ state[a] (meV)	Intensity relative to the $v=0$ state
HCl	0	0	1
	1	191(10)	0.64
	2	353(10)	0.28
	3	483(10)	0.13
	4	570(20)	0.09
	0[b]	−270(2)	~0.05
DCl	0	0	1
	1	158(10)	0.75
	2	278(10)	0.35
	3	370(10)	0.2
	4	470(20)	~0.1
	0[b]	−200(30)	~0.05

[a]In a calibration against the $L_3M_1M_1(^1S_0)$ and $L_3M_{2,3}M_{2,3}(^1D_2)$ lines in the Ar Auger spectrum (Ref. 10), at 177.91 and 203.47 eV, respectively, the Auger-electron energy of the 0-0 transitions was found to be 173.37(2) eV. The energy difference between the HCl and DCl 0-0 peaks was too small to be unambiguously determined.

[b]This line corresponds to the weak $1 \rightarrow 0$ transitions that can be seen to the right of the strong 0-0 transitions in Fig. 1.

(line 30 in Ref. 10). The FWHM of this line was 0.060 eV and thus we conclude that the spectrometer resolution is better than this figure. Lorentzian and Gaussian line profiles were tested and it turned out that Lorentzian lines with a FWHM of 0.130 eV gave the best description of the spectra. The resulting intensities and energies are displayed in Table I.

The isotope effects are clearly seen in Fig. 1. The vibrational states in the DCl spectrum are more closely spaced than in the HCl spectrum and the Franck-Condon distributions are also different.

From the energies of the peaks, given in Table I, it can immediately be seen that the potential curve for the final $2\pi^{-2}\,^3\Sigma^-$ state is markedly anharmonic. For a harmonic potential curve the ratio between the fundamental vibrational frequencies in HCl and DCl should be equal to the inverse of the square root of the ratio between the respective reduced masses. The latter ratio is in this case equal to 1.395, whereas the ratio between the energies for the $v=1$ states in Table I is $191/158 = 1.2$.

If we use, as a first approximation, a Morse potential this discrepancy gives an estimation of the dissociation energy of the $2\pi^{-2}\,^3\Sigma^-$ state. A fit by a second degree polynomial in $v + \frac{1}{2}$ of all the peaks in Table I, i.e., by the energy levels of a Morse potential, gives a vibrational energy constant $\hbar\omega_e = 0.23(3)$ eV and a dissociation energy of 0.8(2) eV from the HCl spectrum while the DCl

spectrum gives $\hbar\omega_e = 0.16(3)$ eV and $D = 0.8(3)$ eV. Alternatively, one can combine the $v=1$ energies for HCl and DCl to calculate these constants which gives a dissociation energy of 0.7(3) eV.

The fact that as many as five lines can be discerned in the HCl spectrum indicates an equilibrium distance for the doubly ionized $^3\Sigma$ state that is considerably different from the equilibrium distance of the initial state. In order to get an estimation of the change in equilibrium distance we used the harmonic approximation to calculate the vibrational intensities. As pointed out above, the x-ray photoemission spectrum, the electron-energy-loss spectrum, and the weak $1 \rightarrow 0$ transitions in Fig. 1 show that the core-hole state has approximately the same equilibrium distance as the molecule in the ground state. The fundamental vibrational energy for this state may be estimated from the energy of the $1 \rightarrow 0$ transition in the HCl spectrum in Fig. 1. In the harmonic approximation it is then possible to vary the equilibrium distance for the $^3\Sigma$ state to reproduce the experimental intensities with the use of the value 0.23 eV for the first vibrational constant. In this way we obtained a value of 1.41(3) Å for the equilibrium distance.

The Morse-potential curves are of course only a first approximation of the molecular potentials. It is, however, not meaningful to use more elaborate methods in this case since only five vibrational states can be observed. In addition, as a result of the lifetime effects, these states are not fully resolved.

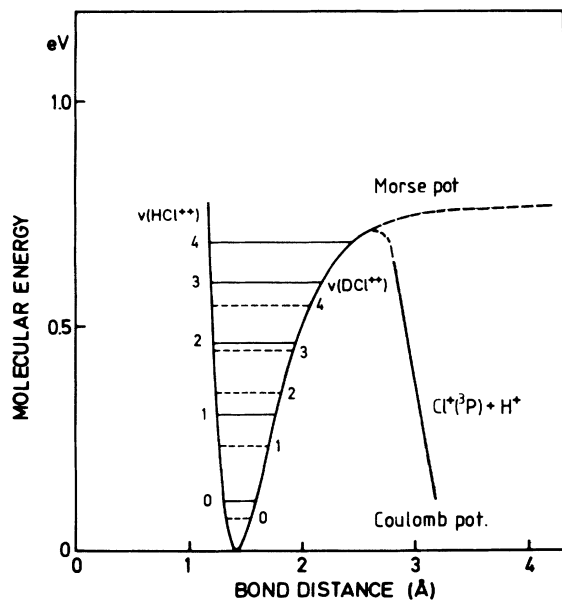The Cl $2p_{1/2}$ line in HCl has a binding energy of

FIG. 2. The potential energy curve for the $2\pi^{-2}\,{}^3\Sigma^-$ state in HCl and DCl together with the experimental vibrational energies. The curve was obtained by our fitting a Morse potential to the experimental vibrational energies and calculating the repulsive Coulomb potential for the $Cl^+ + H^+$ system. The total curve can obviously be regarded as the result of a repulsive interaction between the $(Cl^+ + H^+)$ ${}^3\Sigma^-$ and $(Cl^{++} + H)$ ${}^3\Sigma^-$ potentials.

209.03 eV.[6] Thus from Table I we conclude that the $v = 0$ level in the outermost ${}^3\Sigma$ state has an energy of $209.03 - 173.35$ eV $= 35.68$ eV. This state can dissociate either into $Cl^{++} + H$ or to $Cl^+ + H^+$. Both processes are symmetry allowed. The $(HCl)^{++}$ system therefore has one dissociation energy of about $36.80 - 35.68 + 4.31$ eV $= 5.43$ eV leading to $Cl^{++} + H$ and another at $26.61 - 35.68 + 4.31$ eV $= -4.76$ leading to $Cl^+ + H^+$, where the last term in the sums corresponds to the dissociation energy of HCl. (The atomic energies were taken from Moore.[11]) Hence, we conclude that we observe a *predissociative state*. The "dissociation energy" estimated from the Morse potential is therefore to be regarded as an approximate measure of the height of the dissociation barrier. The potential curves are illustrated in Fig. 2. These findings corroborate the results of a recent complete active space self-consistent-field–configuration-interaction calculation by Olsson and Larsson[12] and multireference single- and double-excitation configuration-interaction calculations of Fournier et al.[13]

The lines in the spectra of Fig. 1 could be fitted with Lorentzians with a FWHM of 0.130 eV. If we deconvolute a 0.060-eV Gaussian spectrometer contribution from

this line we obtain an inherent linewidth of 0.12(2) eV. This value is larger than the value obtained by Shaw et al.[6] for the inherent width of the Cl $2p_{1/2}$ core-hole state in HCl. It is also larger than the semiempirical value of the inherent width of the Cl $2p_{1/2}$ line in the Cl atom (0.083 eV) obtained by Krause and Oliver.[14] The comparison to the latter value could indicate a possible chemical effect on the inherent width. To a first approximation one would expect that the linewidth in the HCl molecule should increase to the value of approximately 0.12 eV found for the Ar $2p_{1/2}$ level.[14]

In conclusion we have observed vibrational levels in the HCl and DCl Auger-electron spectra. The analysis shows that the $2\pi^{-2}\,{}^3\Sigma^-$ state of HCl^{++} and DCl^{++} is predissociative and the potential barrier is approximately 0.8 eV. The inherent width of the Cl $2p_{1/2}$ core hole state is found to be 0.12(2) eV.

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