Chemical Dependence of Core-Level Linewidths and Ligand-Field Splittings: High-Resolution Core-Level Photoelectron Spectra of I 4*d* Levels

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High-resolution I 4*d* photoelectron spectra (total instrumental resolution <0.06 eV) of several iodine molecules, ICl, IBr, I_2, and CH_2I_2, are reported. The inherent I 4*d* Lorentzian linewidths increase in the above order, due to the decrease in electronegativity of the moieties bound to I. The ligand-field splitting as measured by the C_2^0 crystal-field term decreases in the above order, and correlates extremely well with the electric-field gradient measured by ^{129}I quadrupole splittings.

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Recent advances in synchrotron radiation sources and beam lines have made it possible to study core-level photoabsorption and photoelectron spectra with the unprecedented experimental resolution of <0.1 eV. This resolution has made it possible to resolve and characterize vibrational structure on the C and N *K* shell by photoabsorption spectra [1] and the Si $L_{\mathrm{II,III}}$ levels using photoelectron spectra [2,3].

Vibrational structure is not the only core-level effect that can be observed with this improved resolution. Two other effects are of fundamental importance in core-level spectroscopy: the chemical dependence of core-level lifetime linewidths [4] and the ligand-field splitting on *p*, *d*, and *f* levels [5–10]. Until recently, little information has been available on these two effects. Coville and Thomas studied the chemical dependence of the C, N, and O *K*-shell linewidths using complete neglect of differential overlap–intermediate neglect of differential overlap calculations [4]. It was shown that the 1*s* linewidths of C decreased ($CH_4 > CH_3F > CH_2F_2 > CHF_3 > CF_4$) in the order of increasing electronegativity of the ligands. There is presently no convincing experimental evidence to support these results. In the ligand-field-splitting area, there have been a number of studies of the splitting on the *d* levels of Zn, Cd, Hg, In, and Sn containing gaseous compounds and metallic Sn having binding energies <25 eV [5–8], but only studies on the Xe 4*d* levels of XeF_x ($x=2,4,6$) above 25-eV [9,10] binding energy have been previously reported. An understanding of these two effects, along with vibrational splitting, is crucial for the future development of core-level spectroscopy of free molecules, adsorbates on surfaces, and solids. Without this understanding, and high-resolution spectra, it is often not possible to confidently distinguish between line broadening or splitting from the above three core-level effects. For example, two recent studies of the I 4*d* photoelectron spectra (at "medium" resolution) of I_2 [11] and HI [12] did not consider or ruled out both the chemical dependence of linewidths and ligand-field splittings as the line-broadening mechanism in these spectra.

The gas-phase iodine 4*d* spectra were recorded at the Canadian Synchrotron Radiation Facility located on the 1-GeV storage ring Aladdin [13–16], using a high-resolution photoelectron spectrometer [2,3,10,16]. The practical minimum photon and electron resolutions were 0.046 eV at 90-eV photon energy (0.07 Å at 25-μm slits) and 0.040 eV at 30-eV kinetic energy [16], respectively.

Samples of ICl, IBr, I_2, and CH_2I_2 were obtained from Aldrich Chemical Company in high purity. All the samples had high vapor pressures and were introduced directly into the gas cell of the spectrometer. At least five high-resolution spectra were obtained for each compound to enable standard deviations to be obtained. The I 4*d* spectra were calibrated with the Xe $4d_{3/2}$ and $4d_{5/2}$ lines of Xe gas at 69.525(10)- and 67.541(9)-eV binding energies [17], respectively. The experimental spectra were deconvoluted with a Lorentzian-Gaussian line shape using a nonlinear least-squares-fitting procedure [18]. None of the peak parameters (positions, widths, height, or line shape) were constrained during the fitting procedure. The peak shape from these fits were all 100% Lorentzian, reflecting the fact that the inherent Lorentzian linewidth is much larger than the total experimental Gaussian linewidth of <60 meV.

High-resolution photoelectron spectra of the I 4*d* core levels of ICl, IBr, I_2, and CH_2I_2 using 90-eV photons are shown in Fig. 1. At first glance, ICl and IBr look very similar by showing at least four peaks. The small peaks labeled "*A*" are due to the presence of I_2 when ICl and IBr decompose. In the case of I_2 and CH_2I_2, two peaks are evident which are due to the spin-orbit splitting of the d^9 ion state. If one takes a more careful look at the $d_{3/2}$ peak in both I_2 and CH_2I_2, it is evident that I_2 shows a very distinct shoulder on the high-binding-energy side and CH_2I_2 shows an asymmetry on the high-binding-energy side of the $d_{3/2}$ peak.

Apart from the small impurity I_2 peak (*A*) in the ICl and IBr spectra, all spectra were fitted with five peaks (Table I), yielding excellent fits in all cases (Fig. 1). These peaks are due to a combination of spin-orbit and ligand-field effects which remove the degeneracy of the d^9 final state. The Hamiltonian for the d^9 hole state in

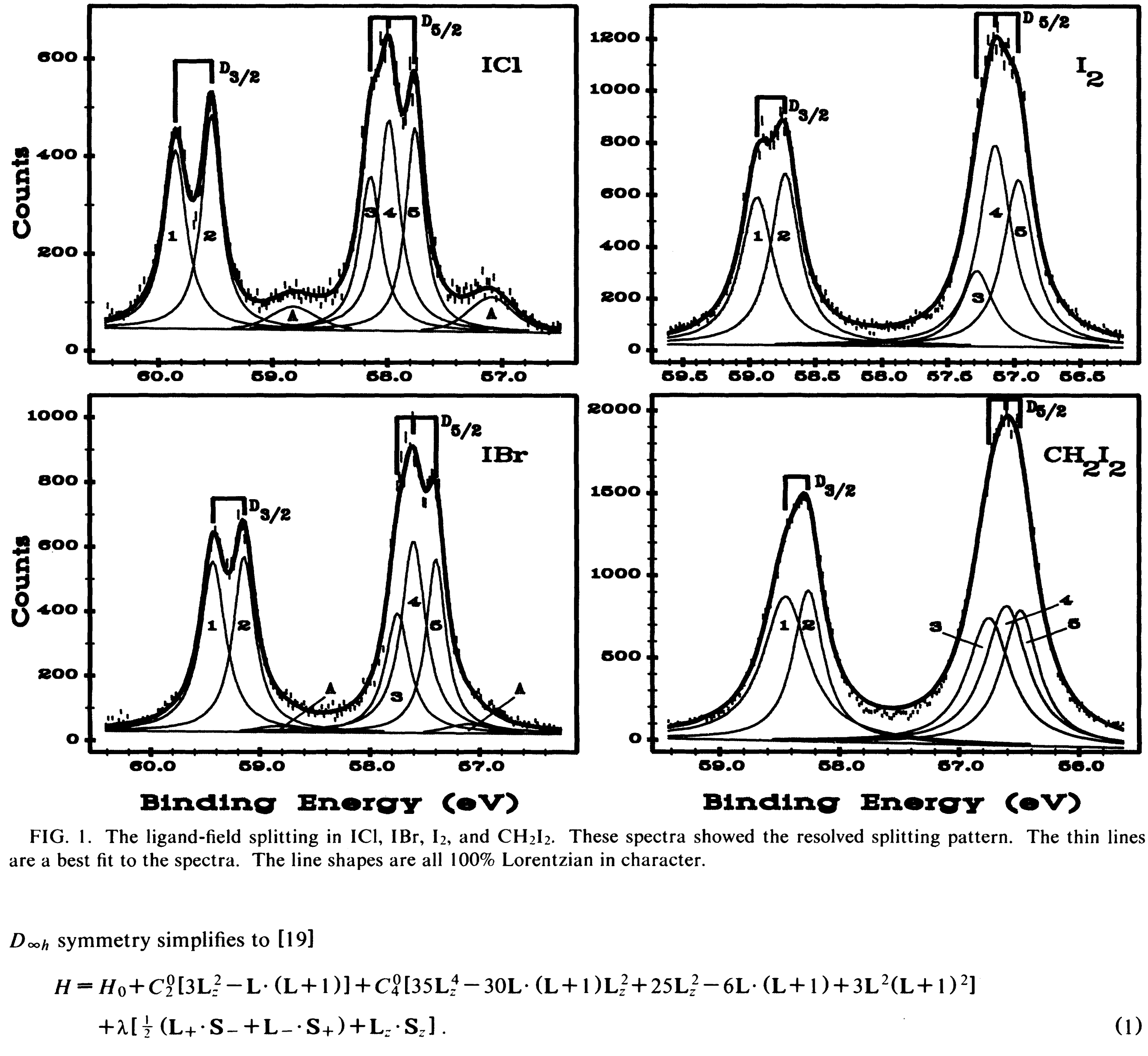

FIG. 1. The ligand-field splitting in ICl, IBr, I_2, and CH_2I_2. These spectra showed the resolved splitting pattern. The thin lines are a best fit to the spectra. The line shapes are all 100% Lorentzian in character.

$D_{\infty h}$ symmetry simplifies to [19]

$$H = H_0 + C_2^0[3L_z^2 - L\cdot(L+1)] + C_4^0[35L_z^4 - 30L\cdot(L+1)L_z^2 + 25L_z^2 - 6L\cdot(L+1) + 3L^2(L+1)^2] + \lambda[\tfrac{1}{2}(L_+\cdot S_- + L_-\cdot S_+) + L_z\cdot S_z]\,. \tag{1}$$

Diagonalizing the Hamiltonian in d-electron subspace and treating d^9 as d^1 with the usual sign changes, the eigenvalues and eigenfunctions can be calculated [5,19]. The C_2^0 values are reported in Table II, the λ values are all $\sim$0.695 eV ($\frac{5}{2}\lambda = 1.736$ eV), and the C_4^0 values are negligibly small. The eigenfunctions will be reported later.

Several points and/or trends are immediately apparent from Tables I and II. The standard deviations on peak positions and linewidths are extremely small. We observe no obvious charging shifts in our spectrometer, and this is extremely important for obtaining accurate positions, linewidths, and line shapes especially for these high-resolution spectra. Second, the binding energies increase in the order $CH_2I_2 < I_2 < IBr < ICl$, as expected from the increasing electronegativity $C < I < Br < Cl$. Third, the linewidths for corresponding peaks decrease in the above order, $CH_2I_2 > I_2 > IBr > ICl$, while peak 1 is always a bit broader than peak 2. Fourth, the $D_{3/2}$ splitting and C_2^0 values increase in the order $CH_2I_2 < I_2 < IBr < ICl$.

The last two trends are of particular importance to the study. Two different broadening mechanisms are present in the I 4d spectra. Vibrational broadening is small and only evident in peak 1 of Table I. This broadening is due to peak 1's high d_{z^2} character which is directed toward the ligand. The same effect was observed in the Xe 4d spectra of the XeF_x ($x = 2,4,6$) series [10]. Orbitals directed away from the ligand should show no vibrational contribution to linewidths. The other broadening mecha-

TABLE I. Photoelectron experimental data for ICl, IBr, I_2, and CH_2I_2.

Compound		Peak position (eV)	Peak width (eV)
ICl	1	59.850(10)	0.237(2)
	2	59.534(10)	0.198(5)
	3	58.147(22)	0.226(10)
	4	57.985(17)	0.235(10)
	5	57.756(11)	0.197(5)
IBr	1	59.430(6)	0.273(1)
	2	59.144(6)	0.250(1)
	3	57.747(22)	0.223(10)
	4	57.600(26)	0.244(10)
	5	57.394(19)	0.228(10)
I_2	1	58.940(6)	0.289(10)
	2	58.727(5)	0.261(3)
	3	57.278(33)	0.290
	4	57.141(28)	0.290
	5	56.968(20)	0.278
CH_2I_2	1	58.472(18)	0.457(3)
	2	58.258(11)	0.305(3)
	3	56.750	0.430
	4	56.606	0.430
	5	56.490	0.373

nism of much greater importance to this study is the chemical effect on the linewidths. As stated above, it was found that for all collected spectra the line shapes for all peaks of ICl, IBr, and CH_2I_2 were totally Lorentzian. This indicated that the instrumental effect (Gaussian character) is small and the line shape is controlled by the lifetime of the $4d$ core hole. This Lorentzian line shape allows for the first time the determination of inherent core hole lifetimes of any I-containing molecule using the photoelectron technique. McGuire [20] showed that for the $N_{4,5}$ shells, the Auger process is the major relaxation channel to fill the core hole. The Auger rate depends on the square of the Coulomb matrix element

$$\langle \psi_{4d}\chi | (1/r_{12}) | \psi_{v}\psi_{v'} \rangle , \qquad (2)$$

where χ and $\psi_v\psi_{v'}$ are the continuum electron and the wave function for the valence electrons that participate in the Auger process [4], respectively.

TABLE II. Ligand-field and nuclear-field-gradient (NFG) parameters for ICl, IBr, I_2, and CH_2I_2.

Compound	$\Delta D_{3/2}$ (meV)	C_2^0 (meV)	NFG [a] (10^{16} esu cm^{-3})
ICl	+316(5)	+37.3(2)	+7.85
IBr	+286(5)	+33.5(2)	+7.26
I_2	+213(8)	+27.4(2)	+5.41
CH_2I_2	+189(10)	+23.0(10)	+4.82
XeF_2 [b]	+330(5)	+39.1(2)	+8.38
XeF_4 [b]	−360(5)	−46.8(10)	−8.82

[a] Derived from e^2qQ values [22].

[b] Reference [17].

To examine this chemical effect, we will focus on the crystal-field-split $d_{3/2}$ peak labeled 2 in Table I which has high d_{xy} and $d_{x^2-y^2}$ character. The presence of the ligands (Cl, Br, I, CH_2I) along the z axis causes a change in the electron density in the I $5p$ valence shell due to the ligands' relative electronegativity. Ligands with stronger electron withdrawing ability than I (Cl, Br) will decrease the valence shell density, whereas those with weaker withdrawing abilities (C) will donate electron density to the valence shell. This change in electron density in the valence shell will decrease or increase the rate of Auger decay to fill the core hole [4], respectively. A decrease in Auger rate yields a longer lifetime and a smaller linewidth. Thus, it would be expected that the linewidth decreases ($CH_2I_2 > I_2 >$ IBr > ICl) with increasing electronegativity of the ligands (C<I<Br<Cl), as is observed in Table II.

The second trend, in C_2^0 values, is equally interesting and important. Figure 2 shows an excellent linear correlation between C_2^0 (and the $\Delta D_{3/2}$) and the electric-field gradient at the nucleus, eq_n, as measured by the quadrupole splittings in ^{129}I and ^{129}Xe Mössbauer spectroscopy. This correlation is not entirely unexpected because the crystal-field and quadrupole Hamiltonians transform identically [19]. However, C_2^0 is measured of course from the $4d^9$ ion state and not in the $4d^{10}$ ground state, and it is very important to observe that relaxation effects do not affect the trends. Thus, C_2^0 values can now be used to measure ground-state properties.

The spectra shown in Fig. 1 are by far the highest-resolution gas-phase photoelectron core I $4d$ level spectra yet reported. Such a decrease in resolution will always show that previous interpretations, based on lower-

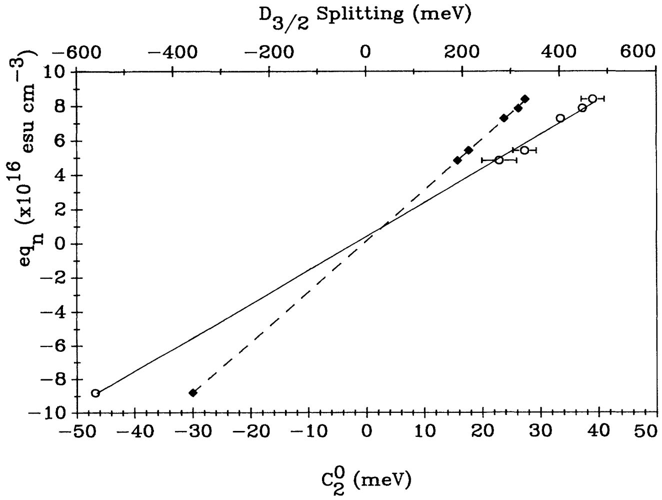

FIG. 2. Plots of C_2^0 and $\Delta D_{3/2}$ vs eq_n. ○ represents C_2^0 and ◆ represents $\Delta D_{3/2}$. The points are fitted with a line of best fit.

resolution spectra, are incomplete or incorrect. For example, a recent "medium"-resolution I $4d$ spectrum of I_2 [11] yielded a FWHM of the I $4d_{3/2}$ and I $4d_{5/2}$ lines of $\sim$0.8 eV. It was stated that no molecular effects (due to the crystal-field term) are present on the I $4d$ lines. More surprisingly, a photoabsorption study [21] of the I $4d \rightarrow$ Rydberg transitions was published at much higher resolution ($\sim$0.2 eV). They again noted no indication of ligand-field splitting.

Very-high-resolution I $4d$ photoelectron spectra of ICl, IBr, I_2, and CH_2I_2 have been reported. The crystal-field asymmetry parameter C_2^0 has been accurately determined and correlated to the nuclear field gradient at the nucleus, eq_n. We also show the first direct experimental evidence for the relationship between electronegativity of the ligand and the lifetime of the core hole.

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