Vibrational structure in core-level photoelectron spectra: Periodic trends

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High-resolution (~ 0.1 eV) core-level photoelectron spectra of gas-phase SiH_4, PH_3, GeH_4, and AsH_3 have been recorded using monochromatized synchrotron radiation. These spectra, multiconfiguration self-consistent-field calculations of the vibrational profile, and the core-equivalent model all show that core-level vibrational structure decreases dramatically, both down a group of congeneric molecules and across a periodic row of isoelectronic molecules. The theoretical calculations also show that the Franck-Condon factors do not change for relatively shallow core levels (e.g., Si $2p,2s$ or Ge $3d,3p$) but increase significantly for deep core levels (e.g., Si $1s$).

Resolved vibrational splitting on a core-level photoelectron spectrum was first observed by Gelius *et al.* in the C $1s$ photoelectron spectrum of CH_4 [1,2]. Very recently, high-resolution (~ 0.1 eV) Si $2p$ photoelectron spectra of gas-phase silicon molecules (e.g. SiH_4, SiD_4, SiF_4) have enabled us to resolve and characterize vibrational splitting and broadening [3–6]. The core-equivalent model has been widely used to interpret not only the above resolved splitting [7], but also a large number of spectra where unresolved vibrational splitting dominates the observed linewidth and line shape (e.g., the C, N, and O $1s$ linewidth for adsorbates on Ni(100) [8–10].

However, the importance of vibrational splitting and broadening on core-level photoelectron spectra of gases, solids, and adsorbates is still generally not appreciated, as illustrated by two very recent examples. On one hand, vibrational contributions have often not been considered. For example, we have shown [11] that Si-H vibrational splitting has to be considered when interpreting the broad complex Si $2p$ spectrum of H adsorbed on silicon surfaces [6]. Very recently, experimental Ge $3d$ spectra of H adsorbed on Ge show unexpectedly that the Ge linewidths are narrower than those for Si $2p$, despite the fact that the Ge $3d$ linewidth is supposed to be broader than Si $2p$ [12]. On the other hand, vibrational contributions are sometimes used to rationalize any unexpected broadening on a medium-resolution ($\Delta E \sim 0.4$ eV) I $4d$ spectrum of HI, which is not due to vibrational structure as previously assigned [13]. Clearly, it is critical to understand trends in vibrational effects on core levels, especially with the high resolution now achievable with monochromatized synchrotron radiation.

In this paper we present high-resolution (~ 0.1 eV) core-level photoelectron spectra of several molecules, and Franck-Condon vibrational profiles from multiconfiguration self-consistent-field (MCSCF) calculations, to show the relative importance of vibrational structure: first, for isoelectronic species (e.g., SiH_4,PH_3) across a row in the Periodic Table; second, for analogous congeneric molecules (e.g., CH_4, SiH_4, GeH_4) down a row of the Periodic Table; and third, for different core levels (e.g., Si $2p,1s$) in the same molecule.

The core-level spectra (Si $2p$ of SiH_4, P $2p$ of PH_3, Ge $3d$ of GeH_4, and As $3d$ of AsH_3) were recorded at the Canadian Synchrotron Radiation Facility (CSRF) located at the 1-GeV Alladin storage ring using a high-resolution photoelectron spectrometer [3–6,14,15] recently equipped with a Quantar 3395A position-sensitive detector. This enabled us to record excellent spectra in a few minutes. The electron resolution ($\Delta E /E = 1/720$) gave an effective electron resolution of 0.04–0.05 eV at the 30–40 eV kinetic energy used for the spectra. The grazing-incidence grasshopper monochromator [16] used a 1800-groove/mm grating, which gave a practical minimum photon resolution of 0.07 Å at 25-μm slits [0.04 eV at 80 eV for Ge $3d$ and As $3d$, 0.11 eV at 130 eV (Si $2p$), and 0.14 eV at 170 eV (P $2p$)]. Samples of SiH_4, PH_3, GeH_4, and AsH_3, obtained commercially with high purity, were introduced directly into the gas cell of the spectrometer. The experimental core-level spectra were deconvoluted with a Lorentzian-Gaussian line shape using a nonlinear least-squares procedure constrained to use only one peak shape split by the metal spin-orbit and vibrational splitting [4,5].

MCSCF calculations were performed within the complete active space self-consistent-field approximation, using the SIRIUS program [17]. By varying the M—H bond length ($M =$ Si,Ge), potential surfaces were obtained for the ground and core-hole states of SiH_4 and GeH_4 and
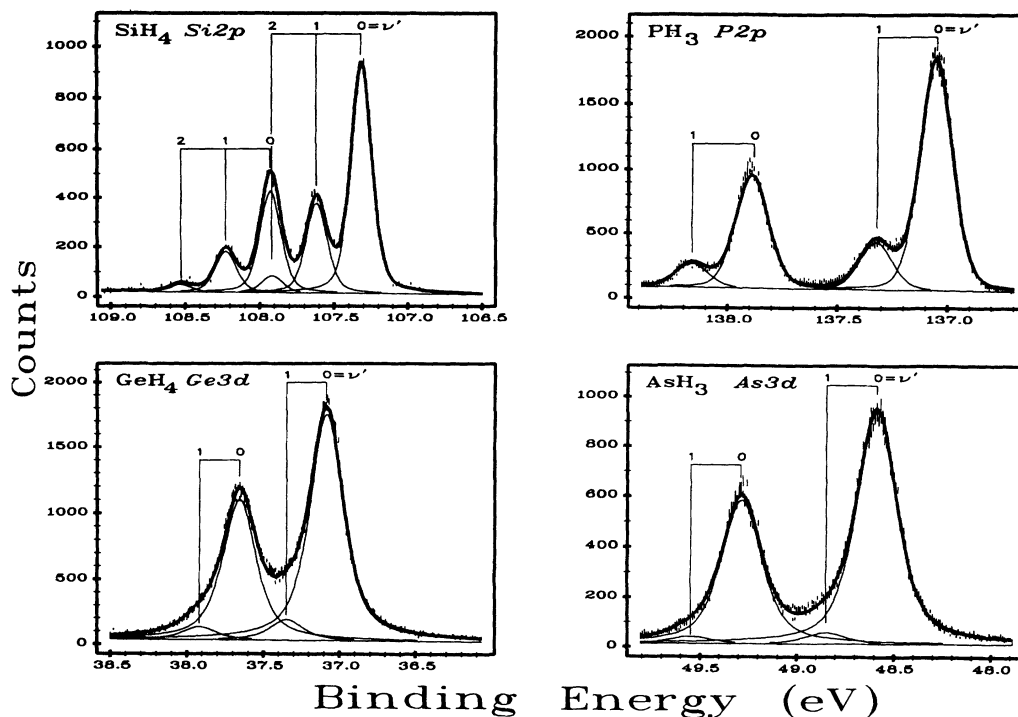
FIG. 1. Experimental photoelectron spectra of the following core level: Si $2p$ of SiH_4, P $2p$ of PH_3, Ge $3d$ of GeH_4, and As $3d$ of AsH_3.

then fitted to polynomials. Vibrational wave functions and frequencies for symmetrical stretching were calculated by treating the cubic term and terms above it as perturbations. Integration of Hermitian polynomials were calculated numerically. The Franck-Condon factors can easily be calculated once the vibrational wave functions are available. Details of the calculations will be fully reported in another paper [18].

The experimental spectra of SiH_4, PH_3, GeH_4, and AsH_3 are shown in Fig. 1, while the simulated theoretical spectra for SiH_4 and GeH_4 are shown in Fig. 2. The experimental and theoretical binding energies, vibrational frequencies, and Franck-Condon factors are summarized in Table I. There are several significant observations.

First, both theory and experiment show immediately that the vibrational structure decreases dramatically from the second and third rows of the Periodic Table (CH_4, SiH_4) to the fourth row (GeH_4). This trend clearly explains the trend in linewidths of H on Si and Ge [12]. Second, although not quite as dramatic, the vibrational structure decreases significantly from SiH_4 to PH_3 and from GeH_4 to AsH_3. Other recent studies show that the vibrational intensity of the transitions other than $v=0 \rightarrow v'=0$ on the $2p$ spectra drops even further from PH_3 to H_2S [19]. Third, the agreement between theory and experiment (Figs. 1 and 2 and Table I), although not quantitative, is still rather good, and certainly reproduces the dramatic trends from SiH_4 to GeH_4. Fourth, the theoretical
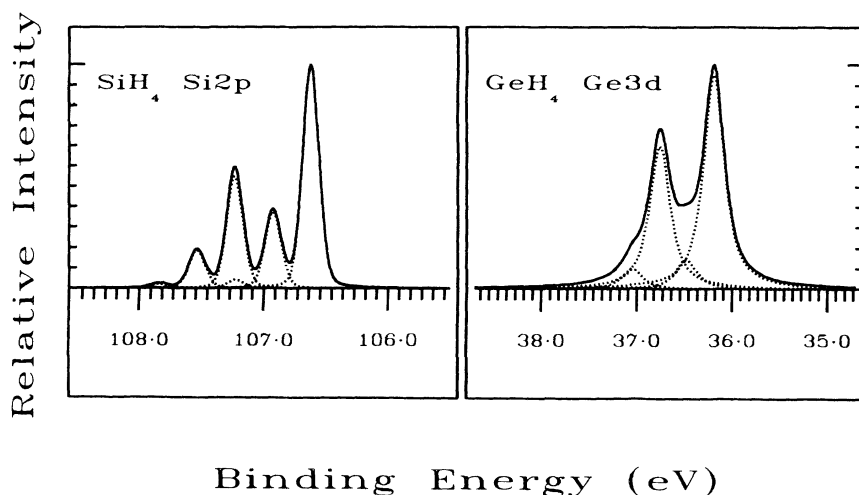
FIG. 2. MCSCF theoretical spectra of the following core level: Si $2p$ of SiH_4 and Ge $3d$ of GeH_4.

TABLE I. Experimental and calculated adiabatic ionization potentials (IP), vibrational frequencies, and Franck-Condon factors.

Molecule	Core level	IP (eV) Expt.	IP (eV) Theory	v (eV) Expt.	v (eV) Theory	v'	Franck-Condon factors Expt.	Franck-Condon factors Theory
SiH$_4$	Si $2p$	107.32	106.62	0.295	0.304	$v'=0$	66.3	72.3
						$v'=1$	29.1	24.5
						$v'=2$	5.1	2.6
SiH$_4$	Si $1s$		1851.4		0.333	$v'=0$		44.7
						$v'=1$		37.3
						$v'=2$		13.6
						$v'=3$		2.7
GeH$_4$	Ge $3d$	37.09	36.19	0.261	0.294	$v'=0$	91.5	87.2
						$v'=1$	8.5	12.0
GeH$_4$	Ge $3p$		129.07		0.295	$v'=0$		87.3
						$v'=1$		11.9
PH$_3$	P $2p$	137.05		0.298		$v'=0$	82.9	
						$v'=1$	17.1	
AsH$_3$	As $3d$	48.59		0.263		$v'=0$	95.3	
						$v'=1$	4.7	
CH$_4^1$	C $1s$	290.71	290.26	0.391	0.436	$v'=0$	63.0	66.8
						$v'=1$	29.0	23.0
						$v'=2$	6.0	7.2

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Franck-Condon factors do not differ substantially between the very shallow Ge $3d$ core level and the Ge $3p$ level (or between Si $2p$ and Si $2s$). The result shows conclusively that the very small vibrational structure on the Ge $3d$ level is not due either to its low binding energy or symmetry. However, the large change in the Franck-Condon profile between the Si $2p$ and Si $1s$ levels (Table I) shows that very deep core levels will show more significant vibrational structure. The Si $1s$ vibrational structure will probably never be resolved because of the large inherent linewidth (≥ 0.5 eV) [20] and even larger photon widths at the present time. Fifth, the experimental line shape for the GeH$_4$ and AsH$_3$ spectra are about 70% Lorentzian because the inherent linewidth dominates the spectra. These linewidths (0.25 eV for Ge $3d$ and 0.23 eV for As $3d$) should be no more than 0.03 eV broader than the inherent linewidth, although we do not fully understand why the line shapes are not 100% Lorentzian as observed for the molecular I $4d$ lines at similar experimental resolutions [11,14]. It is possible that other vibrational modes contribute to these spectra. In any case, these linewidths are much larger than earlier theoretical values [20] and larger than other measured $3d$ widths of Zn, Ga, and Kr of ≤ 0.05, 0.12 [21], and 0.10 eV [22], respectively. In the Si $2p$ and P $2p$ spectra, the instrumental width of > 0.1 eV dominates the observed spectra, leading to a more Gaussian line shape (80% Gaussian for PH$_3$). Inherent Si $2p$ and P $2p$ widths are < 50 meV [3,23].

TABLE II. Bond lengths (in angstroms). Most data are from Structure Data of Free Polyatomic Molecules, edited by K. H. Hellwege and A. M. Hellwege (Springer, Berlin, 1987), unless noted otherwise.

CH$_4$	NH$_3$	NH$_4^+$	HF	NeH$^+$
1.094	1.030	1.034	0.917[a]	0.991[b]
SiH$_4$	PH$_3$	PH$_4^+$	HCl	ArH$^+$
1.481	1.420	1.42	1.275[a]	1.280[b]
GeH$_4$	AsH$_3$		HBr	KrH$^+$
1.525	1.520		1.414[a]	1.421[b]
SnH$_4$	SbH$_3$		HI	XeH$^+$
1.7108	1.7039		1.609[a]	1.603[c]

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The above trends in vibrational structure can also be readily rationalized by examining bond lengths for core-equivalent molecules or molecules close to being core equivalent (Table II). Note the large change in bond length (~ 0.06 Å) between CH_4 and NH_4^+ (or NH_3), and SiH_4 and PH_4^+ (or PH_3). In contrast, there is less than a 0.01 Å change in bond length between GeH_4 and AsH_3, and between SnH_4 and SbH_3. The bond lengths for the hydrogen halides and their core equivalents (expect for HF) are all very similar, suggesting little or no vibrational structures as observed already for HI [11].

Although these trends have only been elucidated here for hydride molecules, they should be generally valid for many other ligands. For example, we already know that Si molecules such as SiF_4 give more vibrational structures than for Ge or Sn analogs [24], or Xe or I molecules [11,14,15]. These trends then should hold widely for many adsorbates, solids, and gases, although it must be realized that so far we have only considered high-symmetry molecules where the symmetric stretch dominates the vibrational structures.

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