

Direct experimental determination of the K 2*p* and Cl 2*p* core-level binding energy shifts between molecular and solid KCl: Line broadening effects

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Using a technique used previously for metals, the K 2*p* and Cl 2*p* photoelectron spectra of KCl have been measured from the molecular vapor and nonconductor solid *simultaneously*—a direct measurement for a nonconductor. The Cl 2*p* core level in bulk-solid KCl has a 0.79-eV *larger* binding energy than its molecular KCl counterpart, but the K 2*p* core level in bulk-solid KCl has a 3.75-eV *smaller* binding energy than in molecular KCl. After correction for the instrumental resolution, the Cl 2*p* experimental linewidths (FWHM) for both molecular (0.40 eV) and solid spectra (0.56 eV) are much smaller than the corresponding K 2*p* molecular and solid linewidths (0.88 and 0.93 eV, respectively). It is concluded that final-state vibrational splitting is the dominant factor in determining both molecular and solid-state linewidths, with phonon broadening being a smaller effect for the solid.

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I. INTRODUCTION

Alkali-halide molecules and solids have been studied extensively in the history of photoelectron spectroscopy. Numerous photoelectron papers of vapor phase alkali halides have been published, beginning with the groups of Berkowitz *et al.*¹ and Potts and Lee² in the 1970s. These papers concentrated mainly on valence photoionization. Also, there were many core-level x-ray photoemission spectroscopy (XPS) papers on alkali halides in the 1970s.^{3–10} More recently, there have been various electron spectroscopy papers (core-level, valence-level, and Auger papers) on synchrotron radiation-excited vapor phase alkali halides (see Refs. 11–13 and other references in those papers). Very recently, in an XPS paper on Na 2*p* and Cl 2*p* core levels of NaCl clusters,¹¹ it was stated that even the simple model systems, such as alkali-halide molecules lack some essential XPS data. For example, they pointed out that there were no published values for Cl 2*p* core-level binding energies (BEs) in vapor phase alkali halides and more importantly, that there were no reliable direct determinations of the core-level shifts from the gas phase monomer to the solid due to the different references for core-level BEs in the gas phase, solid, and common sample charging on these nonconductor solids. For example, for supported NaCl crystals, quite different Na 2*p* BEs were observed from 36.4 eV in Ref. 3 to 37.5 eV over 20 years later.¹⁴ Such BE shifts between molecules and solids are very important for calculations that include all charge-charge and polarization interactions in both the bulk solid and the nanoscale solids^{3,11,15} and for serving as reference values for cluster studies. To obtain close to the equivalent of the molecule/solid shift from just a gas phase study, valence- and core-level spectra of unsupported NaCl clusters containing up to about 100 atoms were recorded simultaneously with the molecular NaCl spectrum.¹¹ It was noticed that the binding energy shift of the large cluster with respect to the vapor phase monomer is 3 eV toward lower binding energies in the case of Na 2*p* ionization but is 1 eV toward *higher* binding energies for Cl 2*p* ionization. However, there still were difficulties in quantifying the shift with this method. For example, the Na 2*p* spectrum of the clusters

shifted in energy by up to 0.4 eV (from 36.2 to 36.6 eV) with different clustering conditions.¹¹ In addition, there is still the problem of substantially different shifts for corner-, edge-, and face-centered atoms in the cluster.¹¹

A recent paper¹⁶ describes a simple direct method for obtaining the binding energy shift between gaseous metal atoms/clusters and a solid metal. In general, this shift is difficult to determine experimentally, even for metals, because of the difference in reference levels for solids and gases: Solid binding energies are referenced relative to the Fermi level, whereas, gas-binding energies are referenced relative to the vacuum level. This method¹⁶ employs a very small synchrotron beam as the photoelectron source, an effusive vapor beam from an inductively heated oven, and a cool needlelike surface inserted into the vapor beam. Spectra of both condensed solid and vapor can be obtained *simultaneously*, and it was shown conclusively that the referencing problem for solids and gases is overcome. The surface of the solid sample is covered by the work-function potential, and the vapor atoms are so close to the solid that both vapor and solid see the same potential, and no work-function correction is required. The above technique is used in this paper for a nonconductor. We show that excellent spectra with narrow linewidths of *both* gas phase monomer KCl and solid KCl can be obtained simultaneously. The gas/solid shifts in the K 2*p* and Cl 2*p* spectra are in semiquantitative agreement with the above gas phase monomer/cluster results, indicating strongly that even for nonconductor solids, our technique avoids the usual referencing problems.

In addition to the above BE referencing problem for alkali halides, the alkali and halide XPS linewidths in alkali halides have been of considerable interest since the Citrin *et al.* 1974 paper,¹⁷ which proposed that temperature-dependent phonon broadening was the dominant cause of line broadening in valence- and core-level XPS spectra of solid alkali halides. For K 2*p* core levels in K halides,¹⁷ shallow cation core levels [e.g., K 3*p*, Rb 4*p*, along with the one anion I 4*d* spectrum for RbI (Ref. 14)], and valence levels¹⁸ of many alkali halides, phonon broadening (as calculated in a detailed theoretical paper¹⁵),

was considered to be the only significant line-broadening mechanism (see Ref. 19). However, in 1980,¹⁵ it was surprising that there were no reports of any experimental linewidths for core-level anion spectra (e.g., the Cl $2p$ spectrum of KCl or NaCl), yet Mahan predicted that Δ_0 , the phonon widths at 0 K, were virtually identical for most of the anion- and cation-level linewidths (Table IV, Ref. 15). For example, the predicted Δ_0 values for the K $2p$ and Cl $2p$ spectra were 0.455 and 0.465 eV, respectively. Even in the next 30 years, the only anion core-level XPS spectrum apparently published has been the I $4d$ level in RbI (Ref. 14). Even the very recent detailed thin-film XPS paper on KCl did not report the Cl $2p$ spectra.²⁰ However, the I $4d$ spectrum¹⁴ already showed that the I $4d$ linewidth (total linewidth of 0.8 eV) was considerably narrower than cation linewidths in other alkali halides (normally > 1.0 -eV total linewidth). This surface sensitive I $4d$ synchrotron spectrum of RbI has an unresolved intense surface contribution, which would make the bulk and surface I $4d$ linewidths closer to 0.6 eV.

Recently, a detailed paper on Si $2p$ and O $1s$ linewidths in silicates²¹ showed that temperature-independent final-state vibrational broadening (FSVB), the only significant line-broadening contribution on Si $2p$ levels in gas phase Si molecules,^{22,23} also was the dominant line-broadening contribution in nonconductor solid silicates. For example, for a Si $2p_{3/2}$ linewidth of 1.1 eV, the FSVB contribution was estimated at > 0.8 eV at room temperature, with phonon broadening being a smaller but significant contribution. The gas phase and solid KCl and Cl $2p$ spectra reported in this paper give a marvelous opportunity to reexamine the importance of phonon broadening and FSVB on core-level linewidths in ionic nonconductor solids.

II. EXPERIMENTS

The synchrotron radiation-excited experiments for KCl were carried out at the I411 beamline in MAX-laboratory, Lund, Sweden.²⁴ A modified Scienta SES-100 electron energy analyzer²⁵ was used to record the emitted electrons at the magic 54.7° angle with respect to the polarization vector of the horizontally polarized synchrotron radiation. An inductively heated oven was used to heat the solid sample in a stainless-steel crucible where the vapor pressure was estimated to be about 10^{-3} mbar at a temperature around 400°C . Vapor flows out from the crucible through a narrow pipe and condenses on a Cu tip, which is used to measure spectra from the solid phase.¹⁶ Calibration was performed using Ar $2p_{1/2}$ and Ar $3/2$ photolines (BEs of 250.79 and 248.63 eV, respectively²⁶). Photon energies of 350 and 250 eV were used to measure all the K $2p$ and Cl $2p$ XPS spectra, respectively. The experimental broadenings defined by the monochromator exit slit (0.05 mm), electron energy analyzers entrance slit (0.8 mm, curved), and pass energy of the electron analyzer (50 eV) are 0.41 and 0.29 eV for K $2p$ and Cl $2p$ spectra in vapor and combined solid-vapor measurements. These experimental broadenings were obtained from the Ar $2p$ calibrant spectrum, fitted by keeping the Lorentzian lifetime linewidth fixed at 118 meV (Ref. 27) with the Gaussian linewidth defining the experimental broadening. For the pure solid measurements,²⁰ the experimental broadening was 0.32 eV. In the data handling,

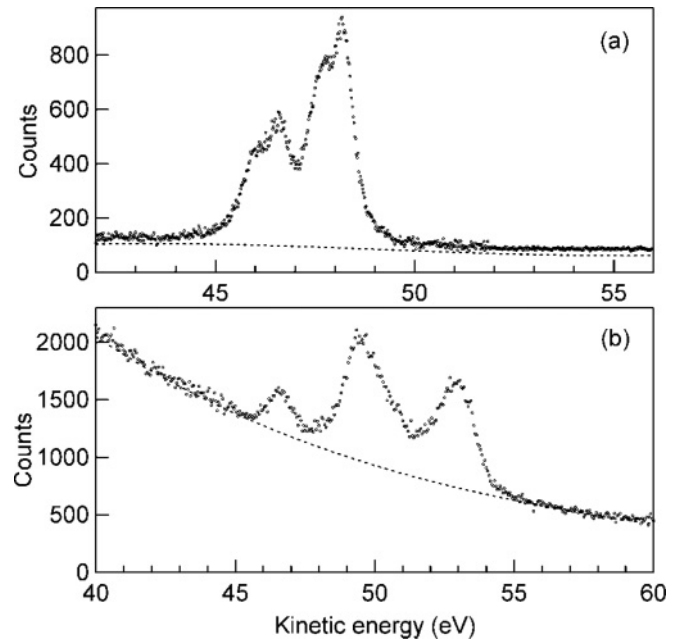


FIG. 1. Synchrotron radiation-excited (a) Cl $2p$ and (b) K $2p$ PES measured simultaneously from vapor and solid KCl. In all figures, the dashed lines are the approximated background contribution, which has been subtracted from the spectra shown in Figs. 4 and 5.

a curve fitting data package SPANCF was utilized,²⁸ which utilized convoluted Gaussian and Lorentzian functions. The inherent Lorentzian linewidths for the Cl $2p$ and K $2p$ lines are 100 and 150 meV, respectively.^{29,30} In principle, the charging of the insulator sample should not affect the binding energy shift when solid and vapor both are measured simultaneously because, even though there is an additional potential present in the interaction region due to the charging, the electrons emitted from the vaporous sample also feel this potential, and the reference level for solid and vapor remains the same. However, sample charging may cause linewidth broadening. Effects of the needle position were tested by measuring the vapor lines without the needle present and then slowly introducing the needle to the interaction region with a manipulator. The spectra were recorded as a function of the needle position. It was observed that the vapor lines shift gradually in energy when the needle is introduced slowly to the interaction region, but normally, no line broadening was observed. Line broadening was sometimes observed, but the data collection was made rapidly; and for the simultaneous measurement, only those spectra where the vapor linewidths were the same as in the vapor measurement alone were accepted for further data handling.

Figure 1 presents the raw data points for the Cl $2p$ and K $2p$ spectra of molecular and solid KCl. The flat background in the Cl $2p$ photoelectron spectrum (PES) [Fig. 1(a)] was modeled with a third-order polynomial and was subtracted from data points. For the K $2p$ spectrum [Fig. 1(b)], the shape of the background was modeled by an exponential function. In the curve-fitting process of the combined solid-vapor K $2p$ PES, a Shirley-type background also was utilized to compensate for inadequate background subtraction. The Shirley background cumulatively shifts intensity from the solid-state photoelectron

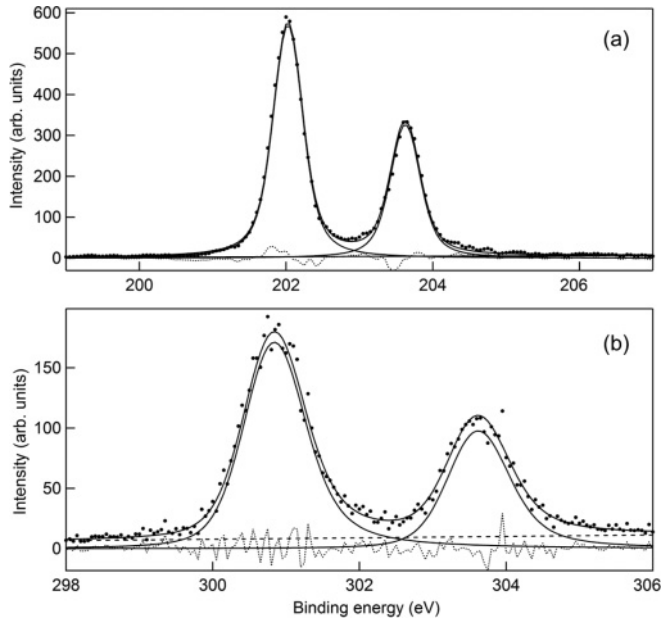


FIG. 2. Synchrotron radiation-excited (a) Cl $2p$ ($h\nu = 250$ eV) and (b) K $2p$ ($h\nu = 350$ eV) photoelectron spectra measured from vaporous KCl. The dots are measured data points, and the solid line is the fitted spectrum. The dotted line represents the difference between the measured data points and the fitted spectrum. The dashed line in (b) shows a linear background.

peaks toward lower kinetic energies. The Shirley background is shown as a dotted line in Fig. 5. It is important to emphasize that an inadequate background correction for this K $2p$ spectrum does not contribute to any significant error in the K $2p$ surface/vapor shift.

III. RESULTS AND DISCUSSION

A. The Cl $2p$ and K $2p$ spectra

To fit the combined gas phase and solid-state Cl $2p$ and K $2p$ spectra in Fig. 1, it is necessary to obtain the spectra of both gas phase and solid-state KCl separately. Figure 2 shows the calibrated Cl $2p$ and K $2p$ gas phase spectra of

just molecular KCl, and Table I gives the calibrated peak Cl $2p$ and K $2p$ peak positions along with the total full widths at half maxima (FWHM) obtained from the combined Voigt-Lorentzian/Gaussian fit. The K $2p$ spectrum is in good agreement with that reported previously by Patanen *et al.*³¹: The K $2p_{3/2}$ BE of 300.82 eV (Table I) agrees with the previous value of 301.0 eV,³¹ and the FWHM of 0.99 eV (Table I) agrees with a roughly measured value from the spectrum of 1.0 eV in Ref. 31. The Cl $2p$ spectrum previously has not been reported. Immediately, it is rather surprising that the Cl $2p$ FWHM of 0.53 eV is about one half the K $2p$ width of 0.99 eV in Table I, and the corrected Cl $2p$ FWHM of 0.40 eV is less than one half of the corrected K $2p$ width of 0.88 eV. The thin-film solid-state K $2p$ spectra of KCl, taken from the papers of Kisand and co-workers^{20,32} are shown in Fig. 3, and the corresponding unpublished Cl $2p$ spectra were very kindly given to us for analysis. They obtained the Cl $2p$ and K $2p$ spectra from a large range of film thicknesses (deposition times of 60–810 s), but we have chosen the Cl $2p$ and K $2p$ spectra from the 810-s deposition time. This spectrum gave the best results for our solid KCl spectra in the combined gas/solid spectrum (see below). These spectra were calibrated with a Cu $3p_{3/2}$ line at 75.13 eV. The BEs in Fig. 3 are several eV lower than for the gas phase as expected because of the Fermi-level reference for the solid spectra as compared to the vacuum-level reference for the gas phase. However, initially, it is a bit surprising that the Cl $2p$ and K $2p$ gas/solid BE shifts are quite different: about 3.5 eV for the Cl $2p$ spectra but about 6.5 eV for the K $2p$ spectra (Table I). This large difference indicates that the gas/solid shifts must be very different for the Cl $2p$ and K $2p$ lines as quantified below. The K $2p$ BEs (Table I) are in reasonable agreement with other values in the literature.^{3,10,20} These spectra were taken with 401-eV photon energies²⁰ so that the kinetic energy (KE) for the Cl $2p$ and K $2p$ spectra are close to 200 and 100 eV, respectively—close to the minimum of the escape depth curve.^{33,34} Thus, as is common with many other core-level spectra,³⁵ the core-level spectra contain two peaks of comparable intensity due to the surface layer and bulk layers. For the anion Cl⁻, the surface peak is at lower BEs than the bulk,³⁵ whereas, for the cation K⁺, the surface peak is at higher BEs than the bulk.³⁵ Because 100-eV KE is

TABLE I. K $2p$ and Cl $2p$ BEs, changes in BEs (Δ BE) and linewidths (FWHM) for gas phase and solid KCl.

Sample	K $2p_{3/2}$ spectra ^a			Cl $2p_{3/2}$ spectra ^a		
	K $2p_{3/2}$ BE	Δ BE	FWHM ^b	Cl $2p_{3/2}$ BE	Δ BE	FWHM ^b
Gas phase monomer ^c	300.82		0.99 (0.88)	201.97		0.53 (0.40)
Thin solid film—surface ^d	294.65		0.98 (0.93)	198.05		0.67 (0.56)
Bulk ^d	294.20	-0.45	0.98 (0.93)	198.46	+0.39	0.67 (0.56)
Gas/solid—gas ^c	300.82		0.99 (0.88)	201.97		0.53 (0.40)
Gas/solid—surface ^c	297.52	-3.30	1.18 (1.07)	202.37	+0.40	0.65 (0.56)
Gas/solid—bulk ^c	297.07	-3.75	1.18 (1.07)	202.76	+0.79	0.65 (0.56)

^aThe Cl $2p$ and K $2p$ spin-orbit splittings are 1.62 and 2.78 eV, respectively.

^bThe total fitted FWHM are given on the left with the FWHM corrected for the instrumental widths (photon plus electron) given in brackets.

^cThese BEs are referenced to the Ar $2p_{3/2}$ position of 250.79 eV. The errors for the gas phase peak positions and widths are <0.05 eV. The errors on the absolute solid positions and widths of the combined gas/solid spectra are 0.1 eV, but the errors on Δ BE should be less than 0.05 eV.

^dThese BEs are referenced to the Cu $3p_{1/2}$ line at 75.13 eV.²⁰ The errors on BE and FWHM are 0.05 eV.

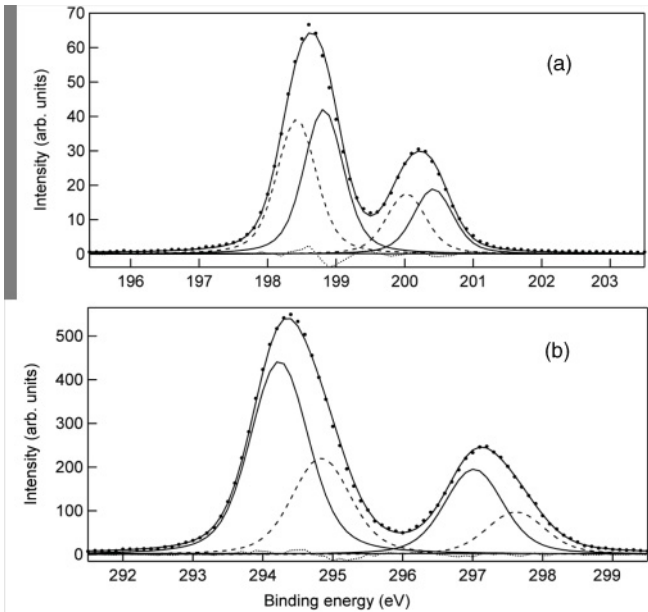


FIG. 3. Synchrotron radiation-excited (a) Cl $2p$ ($h\nu = 401.3$ eV) and (b) K $2p$ ($h\nu = 401.3$ eV) photoelectron spectra measured from solid KCl deposited on a Cu substrate with a deposition time of 810 s. The dots are measured data points, and the solid line is the fitted spectrum. Peaks drawn with solid and dashed lines are bulk and surface components, respectively. The dotted line represents the difference between the measured data points and the fitted spectrum. Reproduced from Ref. 32.

more surface sensitive than 200-eV KE, the surface peak is relatively more intense for the K $2p$ spectrum compared to the Cl $2p$ spectrum. The surface chemical shift for K $2p$ is -0.45 eV, whereas, the shift for Cl $2p$ is 0.39 eV. In other compounds,³⁵ the surface chemical shift for the anion also is slightly smaller in magnitude than for the cation. The surface chemical shift in the K $3p$ level in KCl has been reported,¹⁴ and our value of 0.45 eV is in good agreement with that given previously by Wertheim *et al.*¹⁴ (0.465 eV). However, their complex K $3p$ fits to one broad peak (unresolved spin-orbit splitting and surface shifts) were not shown, and the only anion spectrum shown for all the alkali halides was the I $4d$ spectrum of RbI (Ref. 14), which they suggested would have a surface chemical shift of less than 0.25 eV.

The solid K $2p$ total linewidths reported in Table I (0.98 eV) are again much larger than the Cl $2p$ total linewidths of 0.67 eV. It is interesting, perhaps, that inclusion of an intense surface peak with a surface chemical shift of close to 0.4 eV in the only anion spectrum in the literature—the I $4d$ spectrum of RbI—would yield a total I $4d$ width of 0.6 eV. That is one more indication that the anion linewidths are much smaller than the cation linewidths for alkali halides. More surprising, the measured total K $2p$ solid-state linewidth is no larger than the K $2p$ gas phase total linewidth. However, the gas phase K $2p$ spectra used an experimental resolution of 0.4 eV compared to the solid-state linewidth of 0.3 eV so that the gas phase linewidth after correction for the experimental resolution of 0.88 eV (brackets in Table I) indeed is slightly smaller than the solid-state linewidth of 0.93 eV. Our experimental total K $2p$ linewidths of 0.99 eV are smaller than the total

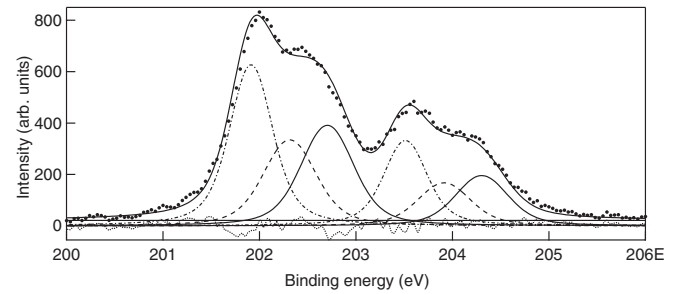


FIG. 4. Synchrotron radiation-excited ($h\nu = 250$ eV) Cl $2p$ photoelectron spectrum measured simultaneously from vapor phase and solid KCl. The dots are measured data points, and the solid line is the fitted spectrum. Peaks drawn with solid, dashed, and dashed-dotted lines are bulk, surface, and vapor components, respectively. The dotted line represents the difference between the measured data points and the fitted spectrum.

linewidths given by Citrin *et al.* of 1.1 eV at 300 K,¹⁷ but after correction for photon and electron contributions, our width of 0.93 eV is larger than their corrected width of 0.83 eV, which includes instrumental and lifetime linewidth corrections. Further correction for the K $2p$ lifetime width of 150 meV decreases our K $2p$ linewidth to 0.91 eV.

The combined gas/solid spectra (Figs. 4 and 5) can now be fit readily using the spectra in Figs. 2 and 3. For the Cl $2p$ spectrum (Fig. 4), the calibrated gas phase positions and widths are used directly from Fig. 2(a) along with the shifted solid-state spectrum (relative surface/bulk positions, widths, and relative intensities constrained) from Fig. 3(a). Only the relative gas/solid intensities and relative solid-state positions are varied in the initial fit with the linewidths unconstrained for the final fit in Fig. 4. The fit to the data is excellent, and all the Cl $2p$ linewidths are virtually identical to the separate gas and solid spectra [Figs. 2(a) and 3(a)]. This shows conclusively that there is no noticeable charging or differential charging in this spectrum, and the gas/solid shift can be obtained accurately. Somewhat surprisingly, the solid spectrum is shifted to higher BEs relative to the vapor spectrum: The shift in the bulk-solid peak is 0.79 eV higher than the gas phase peak (Table I).

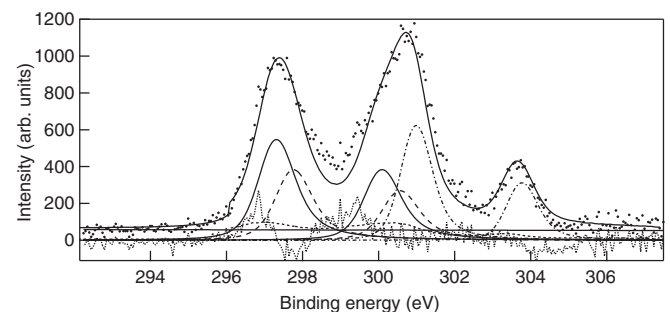


FIG. 5. Synchrotron radiation-excited ($h\nu = 350$ eV) K $2p$ photoelectron spectrum measured simultaneously from vapor phase and solid KCl. The dots are measured data points, and the solid line is the fitted spectrum. Peaks drawn with solid, dashed, and dashed-dotted lines are bulk, surface, and vapor components, respectively. The dotted line represents the difference between the measured data points and the fitted spectrum, and the dashed line is the contribution from the fitted Shirley background.

Using the same fitting procedure as above for the Cl $2p$ spectrum, the fit in Fig. 5 to the combined K $2p$ spectrum is acceptable but not as good as the Cl $2p$ fit. The solid linewidths (Table I) are a bit broader than given for the solid spectrum on its own, indicating some small differential charging for the solid. This K $2p$ spectrum was taken after the Cl $2p$ spectrum, so it is possible that this thicker sample is beginning to charge. In contrast to the Cl $2p$ spectrum, it is immediately apparent that the K $2p$ solid spectrum is shifted to much lower BEs relative to the vapor spectrum: The shift in the bulk-solid peak is 3.75 eV lower than in the gas phase peak. The very different gas/solid shifts for the Cl $2p$ and K $2p$ spectra observed here are in good semiquantitative agreement with the findings for the nanoscale solid in Zhang *et al.*¹¹ where a large negative shift (3 eV) in the Na $2p$ BE from monomer to nanoscale cluster is in contrast to the small positive shift (1 eV) in the Cl $2p$ BE. This agreement is one more confirmation that our method enables direct determination of both the gas and the solid spectra for nonconductor KCl without corrections. The reason behind very different gas/solid and gas/cluster BE shifts in the halogen and alkali atoms is related to the ionic nature of bonding characterizing the molecule and solid, and detailed calculations of these shifts have been presented for the NaCl monomer/cluster paper.¹¹ In short, the charge-charge interaction in the ionic solid consisting of alkali-metal cations and halogen anions (such as Na^+Cl^- or K^+Cl^-) depends on whether the cation or anion core level is ionized. In the case of anion ionization, the final-state halogen atom effectively is seen as a neutral atom by surrounding ions. Thus, the Cl $2p$ binding energy shift between the alkali-halide molecule and the ionic solid is determined by the different charge-charge interactions in the ground state. In contrast, after ionization of the cation site, the alkali-metal atom has an effective charge of $+2e$, and the charge-charge interaction is very important in the final ionized state, creating a negative K $2p$ BE shift in the solid compared to the alkali-halide molecule. Our results should now lead to more detailed calculations of the gas/solid shifts in KCl.

B. K $2p$ and Cl $2p$ linewidths for monomer and solid

The gas phase and solid-state Cl $2p$ and K $2p$ linewidths reported in this paper are very important for determining the major causes of both gas phase and solid-state broadening. As noted above for the gas phase monomer spectrum (Fig. 2), the first observation is that the Cl $2p$ total FWHM (0.53 eV) is much narrower than the K $2p$ FWHM (0.99 eV) with the corrected widths of 0.40 and 0.88 eV being even more different. The natural linewidths of 100 meV for Cl $2p$ (Ref. 29) and 150 meV for K $2p$ (Ref. 30) are small and do not contribute significantly to these linewidths. As for the Si gas phase molecules,^{21–23} the only significant broadening mechanism for the KCl monomer gas phase spectra is the unresolved final-state vibrational splitting (FSVS). We consider the potential-energy curves (PECs) for ground-state KCl and the Cl $2p$ and K $2p$ ionized states (Fig. 6). The equilibrium K-Cl bond distance in the $2p$ ionized molecule (2.38 Å) is significantly smaller than in the neutral molecule (2.75 Å).³¹ Optimal level configuration interaction calculations carried out with the GAMESS code³⁶ give a K-Cl bond length of 3.38 Å

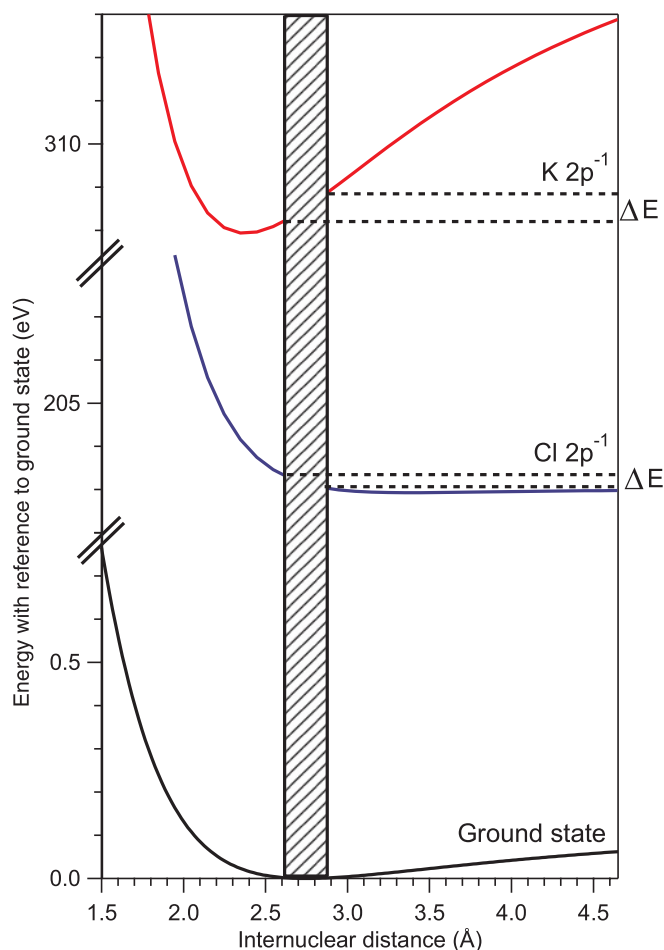


FIG. 6. (Color online) Calculated potential-energy curves for ground state Cl $2p^{-1}$ and K $2p^{-1}$ ionized states. The vertical lines show the Franck-Condon region of the transitions. The horizontal lines represent the energy regions for the Franck-Condon transitions.

for the Cl $2p$ ionized state. The shallow PEC is expected for ionized Cl $2p$ because the core equivalent of ionized Cl^- is Ar, and the KAr species is bonded very weakly.³⁷ The K and Cl atoms in the lowest vibrational state Δ_0 of the ground state are excited by a photon to produce a core ionized state in a number of vibrational states $\nu_1, \nu_2, \nu_3, \dots, \nu_n$ with n and vibrational intensities depending on the shape of the potential curve and the displacement Δr (the internuclear distance) of the ionized PECs from the ground-state PEC. For the K $2p$ ionization, Δr is very large (0.37 Å) compared to the Δr (0.05 Å) for Si $2p$ ionization²¹ in Si molecules. A very large vibrational envelope ($n > 10$) will be expected for the K $2p$ spectrum as shown in Fig. 6 by the large slope in the two extremes of the Franck-Condon region giving a ΔE of 1.3 eV between the two extremes of the Franck-Condon region. Unlike for Si molecules, this vibrational structure will never be resolved even at experimental resolutions < 0.1 eV because the calculated ion state vibrational splitting of 97 meV is much smaller than the inherent lifetime K $2p$ linewidth of 150 meV. Extensive FSVS, however, has been resolved recently in the absorption spectrum of the analog KF monomer on the K $3p$ -K $4s$ transition.³⁸ In this spectrum, the very narrow K $3p$ linewidths and extremely high photon resolution enable

complete resolution of the vibrational peaks. In contrast to the K $2p$ PEC, the Cl $2p$ PEC is almost flat in the Franck-Condon region, and the energy difference between the extremes of the Franck-Condon region is only about 0.5 eV. Compared to the K $2p$ linewidth, a much narrower Cl $2p$ peak is expected. Previous high-resolution Cl $2p$ gas phase XPS on HCl, for example,^{39,40} shows very little vibrational structure. Our analysis shows clearly that FSVS has to be the major contribution to both Cl $2p$ and K $2p$ monomer spectra, but a detailed theoretical analysis, such as obtained earlier on small molecules,^{23,40} now is required for quantitative comparison of experiment and theory.

Second, it is even more important to consider the very small increase in Cl $2p$ and K $2p$ linewidths from the gas phase monomers to the solid. The temperature of our solid sample is not known exactly, but it might be slightly higher than room temperature because of the heat radiation from the vaporizing oven. These small differences in widths between gas and solid immediately suggest that FSVS is the dominant line-broadening mechanism for the solid spectra as we showed for the Si $2p$ XPS spectra for Si gas phase and solid silicate compounds.²¹ Is a similar FSVS contribution expected for the KCl solid as for the gas phase monomer? Considering the K $2p$ linewidth, the K-Cl bond lengths and Fig. 6 show that the change in monomer K-Cl bond length between the ground state and the K $2p$ ion state (Δr) is 0.37 Å. For the solid, the expected change in bond length between the ground and ion states is given by the difference in ionic radius between the K⁺ ion and Ca²⁺, the core equivalent of K⁺ (Ref. 21 and references therein). The ionic radii of K⁺ and Ca²⁺ are 1.52 and 1.14 Å,⁴¹ and Δr is 0.38 Å—incredibly similar to the above difference in monomer bond lengths of 0.37 Å. Since the bond-length change is the major linewidth controlling factor for an ion PEC with a strong ionic or covalent bond, we, thus, expect a very similar FSVB for both solid and monomer. Detailed theoretical calculations on gas phase and solid Si molecules²¹ also showed almost identical changes in Si-O bond lengths between the gas and the solid phases. For the Cl $2p$ ionization in solid KCl, it is more difficult to predict the vibrational structure in the solid KCl, but the expected very shallow PEC for Cl $2p$ ionized KCl (core equivalent KAR) should yield an FSVS similar to that observed in the monomer Cl $2p$ spectrum. It is also important to note that the gas/solid linewidth change is larger for Cl $2p$ than for K $2p$ linewidths. This is expected for the expected constant phonon broadening contribution¹⁵ for both Cl $2p$ and K $2p$ spectra. Because of the quadratic dependence of the linewidths,²¹ a phonon contribution of 0.3 eV on the Cl $2p$ solid-state linewidths would increase the Cl $2p$ linewidth by about 0.1 eV; whereas, the same 0.3-eV contribution to the K $2p$ linewidth would increase that linewidth by only about 0.05 eV.²¹ We strongly suggest then that FSVB is the controlling factor on these solid-state linewidths and that

0.88 and 0.40 eV are very close to the overall Δ_0 values (the FWHM at 0 K) for the K $2p$ and Cl $2p$ linewidths, respectively, rather than those given earlier by Mahan (0.46 eV for both). Obviously, many more temperature-dependent cation and anion spectra along with more theoretical analyses now are required to fully define the phonon-broadening contributions.

IV. CONCLUSIONS

In this paper, we reported core-level solid-vapor binding energy shift values for KCl. The aim of this paper was to test whether the simultaneous measurement technique presented in Ref. 15 for metals also is applicable for nonconductors. Compared to the vapor-phase molecular KCl K $2p$ binding energies, it was observed that the $2p$ level binding energy is shifted to opposite directions depending on whether the anion or cation side was ionized; Cl $2p$ core level in bulk-solid KCl has a 0.79-eV larger binding energy than its molecular KCl counterpart, whereas, the K $2p$ core level in bulk-solid KCl has a 3.75-eV smaller binding energy than in molecular KCl. Simultaneous measurement also offered a possibility to directly observe line shape and width differences between molecular and solid KCl photoelectron spectra. The experimental linewidths (FWHM) exhibit a relatively small increase going from molecular lines to solid. However, a significant difference between linewidths of K and Cl $2p$ levels was observed: the Cl $2p$ experimental linewidths for both molecular (0.40 eV) and solid spectra (0.56 eV) being much smaller than the corresponding K $2p$ linewidths (0.88 and 0.93 eV for molecule and solid, respectively). It was shown that the final-state vibrational splitting contributes dominantly to the molecular and solid-state linewidths with phonon broadening being a smaller effect for the solid.

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