

Paper IV

First observation of vibrations in core-level photoelectron spectra of free neutral molecular clusters

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Core-level photoelectron spectra of free neutral methane clusters have been recorded. These spectra exhibit well-resolved surface and bulk features as well as vibrational fine structure. The vibrational structure in the cluster signal is well reproduced by a theoretical model that assumes independent contributions from inter- and intramolecular modes. The intramolecular contribution to the vibrational lineshape is taken to be equal to that of the monomer in the gas phase, while the intermolecular part is simplified to line broadening. An estimate of the cluster size has been made on the basis of the observed surface-to-bulk intensity ratio.

I. INTRODUCTION

Clusters are unique in that they enable studies of how physical and chemical properties evolve with size. In the small-cluster regime, quantum effects may give each cluster size unique properties. In the next size range, it is primarily the change in surface curvature and the surface-to-bulk ratio which govern the evolution with size. [1] The importance of surface chemical phenomena makes it interesting to study properties of monomers in a surface compared to those of monomers in the bulk, and clusters are useful in this respect due to the abundance of surface atoms and the possibility of changing the surface curvature by changing the size of the clusters.

A promising technique for cluster studies is core-level photoelectron spectroscopy (XPS), for which the primary observables are the energy position and width of cluster-specific peaks in the photoelectron spectrum. In order to separate the cluster signal into peaks pertaining to molecules in the surface and bulk (interior), respectively, it is useful to decompose the observed spectrum in terms of theoretical model spectra that represent each of these fractions. For one, such a decomposition gives access to the surface-to-bulk ratio, which in turn can be used to estimate the size of a cluster. [2] More than that, from the derived shifts in ionization energies and widths, it is possible to learn about the structure of heterogenous clusters [3, 4] and to obtain insight into the bonding mechanism in a cluster.

Recently, there has been considerable progress in the construction of theoretical lineshape models for core-level photoelectron spectra of van-der-Waals-bonded atomic clusters. The spectra may be understood in terms of convolution of three contributions, representing the distribution of cluster sizes, the distribution of ionization energies for monomers within a cluster of a given size, and a Voigt function representing the lineshape of a monomer in a cluster surrounding. [5] While spectra of inert gas clusters display well resolved surface and bulk features, the situation may be more complicated for molecular clusters because of the possibility of pronounced nuclear dynam-

ics accompanying the ionization process.

For many years, core-level ionization was believed not to give rise to vibrational excitations, since core orbitals are non-bonding. However, in a classical model, the removal of a core electron sets up Coulomb forces that act on the charged atoms, possibly shifting them to new equilibrium positions (*vide infra*). Moreover, ionization may lead to large electronic relaxation, including contraction of valence orbitals at the ionized atom, transfer of electron density to the ionized atom to delocalize the positive charge, and also polarization of atoms and bonds. The resulting change in molecular geometry leads to vibrational excitations and is well described in terms of the Franck-Condon principle. [6] In core-level spectra of free molecules, vibrational structure was first observed in 1973 [7, 8], for the case for methane. Through the years, reported C1s spectra of methane have reflected the rapid improvement in experimental resolution. In 1985 the vibrational structure in the C1s spectrum of methane was fully resolved [9] and in 1999 even evidence for anharmonic vibrational coupling was reported. [10] Today vibrational fine structure is commonplace in gasphase XPS [11], and has even been reported for molecules adsorbed on surfaces. [12]

In a molecular cluster, the nuclear dynamics following core ionization can conceivably become very complicated, due to the high number of vibrational degrees of freedom and also because of the presence of both intra- and inter-molecular modes. Force constants of intramolecular modes are typically considerably larger than those associated with intermolecular modes. This fact has been used to decompose the vibrational lineshape of a cluster photoelectron spectrum into two parts, describing intra- and intermolecular vibrations, respectively. The intramolecular component has been assumed to be identical to that of the free monomer, while the intermolecular part has been described in the Gaussian limit of the linear-coupling approximation. [13, 14]

The approach just outlined has been applied successfully to describe core-level photoelectron spectra of i.e. methanol [15] and water. [16] However, due to the large

inherent width of these spectra, which in turn is caused by the distribution of ionization energies within the cluster, the vibrational structure is not apparent except for possibly a minor contribution to the overall width of the photoelectron peaks. Hence, to our knowledge, there does not exist experimental evidence for ionization-induced vibrations in molecular clusters, let alone validation of the approximation of decoupled intra- and intermolecular vibrations. In this contribution we report on the first observation of vibrational fine structure in core-level photoelectron spectra of free neutral clusters.

II. EXPERIMENTAL DETAILS

Methane clusters were produced in a supersonic beam expansion setup described in [17], using a nozzle with a opening diameter of 150 μm and a half opening angle of 10° . To increase the degree of condensation a mixture of 8% CH_4 in helium was expanded through the nozzle. The temperature of the nozzle was kept between 110 and 120 K during all experiments. Spectra were recorded for two different backing pressures, 2.5 and 1.2 bar.

C 1s photoelectron spectra of methane clusters were recorded at beamline I411 at MAX-Lab in Lund, Sweden, [18] using a photon energy of 350 eV. The hemispherical analyzer was set to 54.7° with respect to the polarization plane of the photon beam in order to eliminate angular distribution effects.

The experimental spectra were fit by least-squares technique to theoretical lineshape models that include the effect of vibrational excitation, post-collision interaction (PCI), the finite lifetime of the core hole, and the finite experimental resolution. The vibrational Franck-Condon envelope for gasphase methane was adopted from Ref. [10]. This was subsequently convoluted by the lineshape given by eq 12 in Ref. [19] to account for the natural linewidth (100 meV for C1s) and interaction between the photoelectron and the Auger electron emitted in the deexcitation of the core-hole state (PCI). Finally, the finite experimental resolution was represented by a Gaussian distribution which for these experiments has a full width at half maximum (fwhm) of 115 meV. The cluster peaks are treated similarly, except that we allow for a free Gaussian width in order to include a distribution of ionization energies as well as additional broadening due to intermolecular vibrations.

The spectra are fit with eight variable parameters. These are the positions (2) and heights (2) of the adiabatic peaks corresponding to molecules in the surface and bulk fractions of the clusters, respectively, relative to those of gasphase methane; Gaussian linewidths (2) for the two cluster contributions; and a linear background (2).

III. RESULTS AND DISCUSSION

C 1s photoelectron spectra of methane clusters are recorded under two different stagnation conditions, realized by using different backing pressures. The spectra are shown in Fig. 1, where the upper spectrum (A) is recorded using higher backing pressure than when recording the lower spectrum (B). In both spectra, the well-defined peak near 290.7 eV is the adiabatic peak of uncondensed methane, and the two peaks at higher ionization energy (to the left in the figure) correspond to states that are vibrationally excited in the symmetric C–H stretching mode. The spectra have been calibrated using the adiabatic ionization energy of gas phase methane. [20] The structure at lower ionization energy than the peak at 290.7 eV, represents ionization of molecules in clusters, to be discussed next.

In both spectra shown in Fig. 1, the part due to clusters is dominated by a strong peak just above 290 eV, modulated by a pronounced shoulder toward lower ionization energy and a shoulder (spectrum A) or an asymmetry (spectrum B) toward higher ionization energy. By deconvoluting the observed spectrum in terms of separate lineshape models for the surface and bulk molecules, we find that the peak near 290 eV is due to molecules at the cluster surface that are not vibrationally excited. Surface molecules that are excited into the $v=1$ level in the symmetric C–H stretching mode, give rise to the shoulder observed between the monomer and surface adiabatic peaks in spectrum A. The shoulder found at low ionization energy in the cluster part of the spectrum, is found to be the adiabatic peak of bulk molecules. The present assignment is consistent with lower ionization energy for molecules in the bulk than at the surface of a cluster, caused by differences in electrostatic screening of the final state. This is a well known phenomenon for atomic clusters. [21] The surface is less screened than the bulk since the coordination of a surface atom is lower than for a bulk atom.

Determining the size of neutral clusters is a non-trivial task. However, based on experience from rare-gas clusters, it is reasonable to assume that higher backing pressure leads to larger clusters and hence that spectrum A corresponds to larger clusters than does spectrum B.

Studying spectrum A in more detail, it can be seen that using the monomer lineshape with an increased Gaussian width to represent the surface and bulk peaks affords an excellent fit the experimental spectrum, including the vibrational satellite. From this we conclude that the vibrational spectrum can be well described by performing a full Franck-Condon analysis of the monomer and treating all intermolecular vibrations within the Gaussian limit of the linear-coupling approximation. [13, 14]

The total Gaussian widths obtained from fitting spectrum A are 0.32 eV for the surface and 0.23 eV for the bulk fraction. For comparison we note that methanol clusters, held together by hydrogen bonds, shows linewidths that are more than twice as large [15],

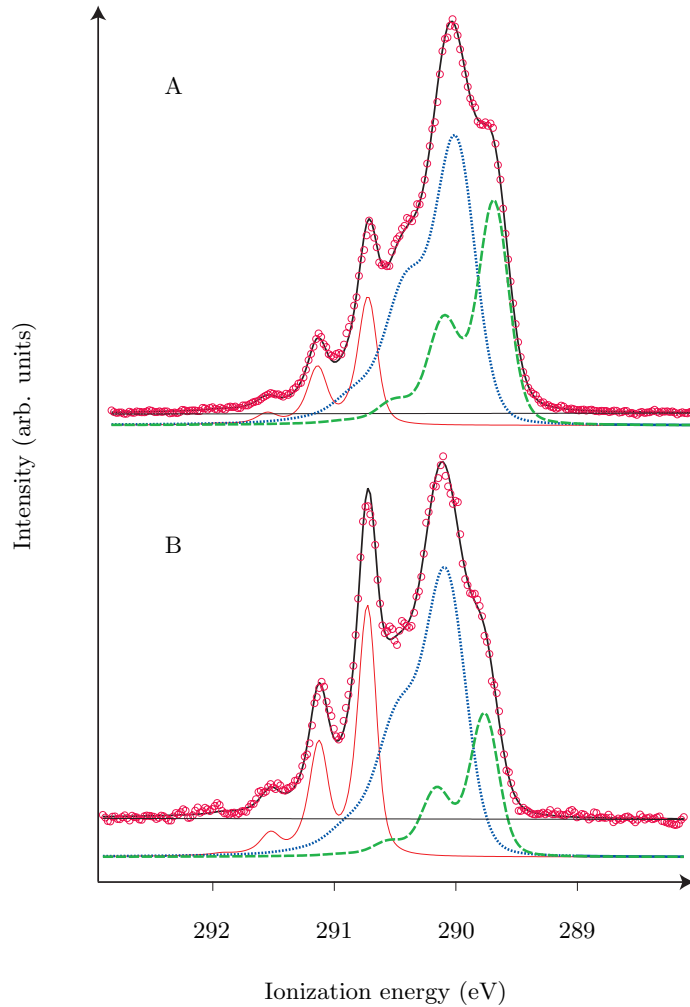


FIG. 1: (Color online) Experimental C 1s photoelectron spectra of cluster beams of methane, corresponding to two different values of backing pressure. The spectra was recorded at a photon energy of 350 eV. The upper spectrum corresponds to higher pressure and presumably larger clusters than does the lower spectrum. In both cases, experimental data points are shown as circles and lines are used to represent fitting models. The thin solid line at higher ionization energy represents uncondensed methane molecules; the dotted line represents methane molecules in the surface layer of a cluster; the dashed line represents methane molecules in the bulk (interior) of a cluster; and a thicker solid line shows the full model spectrum.

TABLE I: Summary of fitting parameters obtained for the two cluster sizes in Fig. 1. Spectrum A refers to the upper spectrum and Spectrum B refers to the lower spectrum.

	Spectrum A		Spectrum B	
	Surface	Bulk	Surface	Bulk
Intensity as % of total cluster intensity	62	38	73	27
Vertical chemical shift relative to gas phase (eV)	-0.70	-1.00	-0.65	-0.97
Gaussian linewidth (fwhm) (eV)	0.32	0.23	0.34	0.22

whereas rare gas clusters typically show widths somewhat smaller than reported here for methane. Subtracting (in squares) the width associated with the monomer line, we find a combined contribution from the distribution of ionization energies and intermolecular vibrations, of 0.30 eV and 0.20 eV for the two cluster fractions. We note that

these values are consistent with our assignment of surface and bulk peaks, as both contributions to line broadening are expected to be more pronounced for the surface than for the bulk. The distribution of chemical shifts is broader for the surface since there are sites at the surface with different coordination, whereas all bulk atoms have

the same coordination. The vibrational broadening has previously been calculated for argon clusters, and found to be around 60 meV for the surface and around 30 meV for the bulk. [5] The vertical chemical shifts of the surface and bulk peaks compared to the monomer peak are -0.7 and -1.0 eV respectively. These values are in the same size range as shifts obtained for rare gas clusters.

Turning to spectrum B, the Gaussian widths of the surface and bulk peaks are 0.34 eV and 0.22 eV, respectively. These values are similar to and bracket those discussed for the upper spectrum in Fig. 1. This finding is consistent with the notion that spectrum B corresponds to smaller clusters than those that give rise to spectrum A. Smaller clusters have a larger contribution from low-coordinated sites, which gives a broader surface peak, and fewer bulk layers, which gives a narrower bulk peak. We note, however, that the differences in width between the two spectra lies in the same size regime as the statistical uncertainties. Nonetheless, both the surface-to-bulk ratio and the energy shifts relative to the gasphase monomer, support our assessment of the relative cluster size, cf Tab. I. The surface fractions are 62 and 73 % as obtained from spectrum A and B, respectively. Additionally, the bulk shift is larger for spectrum A than for spectrum B, if only by 0.03 eV.

The clearly resolved surface and bulk peaks as well as the observable vibrations in the cluster peaks of Fig. 1 make methane a rare case among molecular clusters. We attribute this to the combination of the small Gaussian broadening in the cluster peaks and the strong intramolecular vibrational excitations. The narrow cluster peaks can be explained by the bonding pattern. Methane is a highly symmetric molecule, the highest electrostatic multipole component is a small octupole. Hence the bonding in methane clusters can largely be ascribed to dispersion forces. Dispersion forces are known to give rise to smaller variations in ionization energies within clusters than low-order electrostatic interactions, due to the absence of initial-state effects. The strong vibrational fine structure in the monomeric line is known to be caused by substantial contraction in the C-H bond upon core-ionization.

The problem of establishing the size of free neutral clusters is a severe limitation in interpreting the spectra of weakly bound clusters. Mass spectrometry is not very reliable, since massive fragmentation can be expected upon ionization. Due to the molecular nature of the monomer, and also due to the use of a gas mixture, cluster size estimates based on stagnation conditions [22], which are commonplace for size estimation of atomic clusters, can not be used. It would be possible to estimate the size distribution from the XPS spectra, in the same way as in Ref. [5] for argon clusters. Here, we develop a crude estimate of the cluster size.

The surface fraction of a cluster decreases with increasing cluster size. This can be used to estimate the cluster size by comparing the intensity of the surface peak to that of the bulk peak [2]. The cross section for ionization

is assumed equal for all atoms in a cluster. Hence the relative number of electrons emitted from the surface of a cluster is determined by the cluster size. However, not all electrons emitted from the interior of a cluster reach the surface, some scatter inelastically. This has to be accounted for in order to convert the surface fraction of a spectrum into a cluster size. In Ref. [2], this is done by assuming a simple exponential attenuation of the signal as an electron travels through the cluster. Furthermore the cluster is assumed to consist of spherical shells, with a spacing between layers given by that of the fcc(111) surface. For methane this number is 3.67 Å. [23] To estimate the cluster size one needs knowledge about the escape depth of the electron. Lacking such detailed information for methane we note that for rare gases the electron attenuation length at 60 eV kinetic energy is between 10 and 20 Å. [2, 24] By calculating relative intensities for methane clusters in the same way as in Ref. [2] and by assuming an attenuation length of 10 Å, we find that the clusters expressed in spectrum B have between four and five complete shells, assuming icosahedral clusters, i.e. consist of between 147 and 309 atoms, whereas the clusters that gave rise to spectrum A consist of close to 1000 atoms. An attenuation length of 20 Å would reduce these numbers to 55-147 and close to 309 atoms respectively.

IV. CONCLUSIONS

C 1s photoelectron spectra have been recorded for a beam of methane clusters. The spectra exhibit well resolved surface and bulk features as well as vibrational fine structure. To the best of our knowledge this is the first observation of vibrational fine structure in XPS of free neutral molecular clusters. We find that the modulation of the spectrum caused by vibrational excitation, may be accurately described in a model in which a Franck-Condon profile of the monomer has been broadened by a Gaussian distribution that represents intermolecular vibrations and a distribution of ionization energies. A crude size estimate has been prepared from the observed surface-to-bulk intensity ratio.

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