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

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Abstract

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.

1. 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 dynamics accompanying the ionization process.

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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 intermolecular 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, e.g., 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.

2. 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).

3. Results and discussion

C 1s photoelectron spectra of methane clusters were 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 deconvo-