The Observation of Electronic Energy Bands in Small Argon Clusters

M. Förstel[1,2], M. Mucke[1], T. Arion[1], T. Lischke[1], S. Barth[1], V. Ulrich[1], H.-P. Rust[1], G. Öhrwall[3], O. Björneholm[3], A. M. Bradshaw[1,4], U. Hergenhahn[1]

[1]Max-Planck-Institut für Plasmaphysik, EURATOM Association, 85748 Garching, [2]Max-Planck-Institut für Kernphysik, 69117 Heidelberg, [3]Division of Molecular and Condensed Matter Physics, Department of Physics and Astronomy, Box 516, SE-75120 Uppsala, Sweden, [4]Fritz-Haber-Institut der Max-Planck-Gesellschaft, 14195 Berlin

'new' set-up

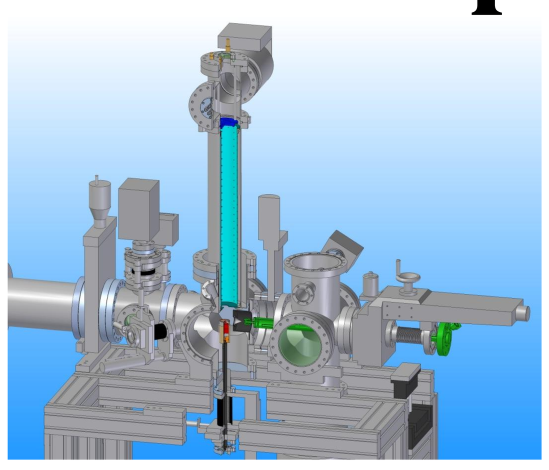

Fig. 2: *Sketch of the current experimental set-up, consisting of an expansion chamber for the molecular jet (rhs) and reaction chamber with the magnetic bottle spectrometer (central, pointing upward). Synchrotron radiation is directed perpendicular to the drawing plane.*

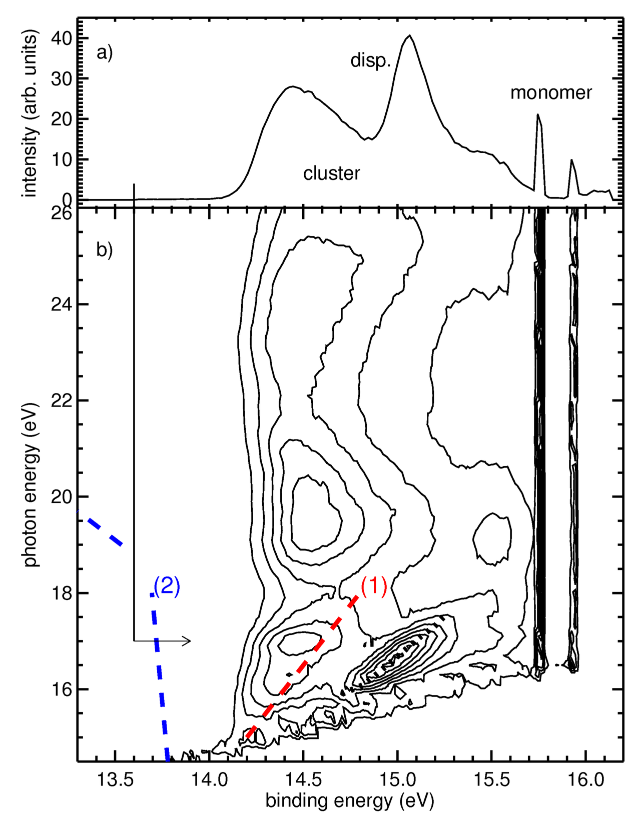

Fig. 1: *Contour plot (panel b) showing high resolution 3p photoelectron spectra of Ar clusters with mean size ⟨N⟩ = 1670 as a function of both photon energy and binding energy. The red dotted line indicates the feature for which strong electronic band dispersion is apparent. The lines designated '1' and '2' derive from the photoemission data for Ar(111) measured by Kassühlke et al. [3]. The feature '2' in fact extends further towards lower binding energies not plotted here. Panel a) shows a cut through the contour plot at an energy (marked with arrow), where the dispersing feature is maximally developed.*

introduction

One of the main motivations for the study of clusters is the search for the onset of bulk properties: How many atoms or molecules do we need to combine in order to make small piece of condensed matter?
Indeed, this question has been asked - and answered - many times, as different criteria where suggested to determine the transition to bulk-like behaviour. Here, we have observed electronic band dispersion in rare gas clusters for the first time. In Ar, the effect starts to appear at a mean cluster size of approx. 230 atoms.

experimental

Ar and Kr clusters were produced in a supersonic jet expansion through a conical nozzle. The stagnation pressure and the nozzle temperature were varied to control the mean of the cluster size distribution ⟨N⟩. The cluster beam was ionized with monochromatic light at the BESSY II synchrotron radiation source. Two different setups were used to detect the resulting photoelectrons.

The first one consisted of a hemispherical analyser with an energy resolution of about 20 meV [1]. For further experiments, a magnetic bottle type spectrometer (Fig. 2) was used. This instrument is capable of an energy resolution of about 20 = $E/\Delta E$, while recording electrons over almost 4π solide angle. The latter experiment was carried out in the BESSY single bunch mode.

the cluster size

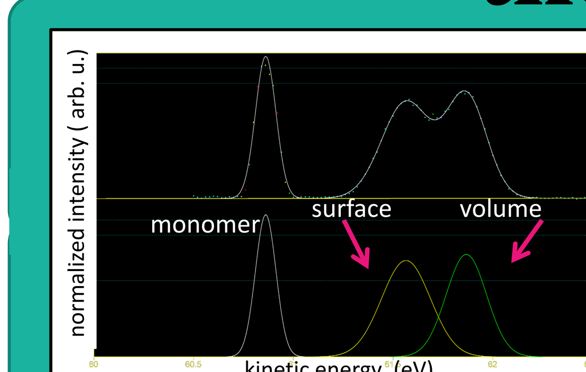

Fig. 2: Argon cluster 3s photoelectron spectrum showing contributions of argon atoms on the surface and within the cluster.

The mean cluster size ⟨N⟩ was determined using a scaling law due to Hagena *et al.* [2]. Additionally we have measured the contributions of bulk and surface atoms to the Ar 3s spectra (Fig. 2). From the ratio of bulk to surface contributions we get an alternative estimate for the mean size, N_{ph}. The mean sizes derived from the bulk to surface ratio are larger than those from the scaling law. There is less discrepancy at larger cluster sizes.

⟨N⟩ from scaling law	Measured area bulk to surface	N_{ph} estimated from bulk to surface ratio
40	0.63	160
90	0.7	200
150	0.9	300

Table 1: Comparison of the cluster size estimation methods.

results and discussion

The argon 3*p* valence region was measured for clusters of mean size ⟨N⟩ = 1670, from the threshold up to a photon energy of 28 eV. The resulting spectra are shown as a contour plot vs. binding energy and photon energy (Fig. 1). The spectra show the cluster valence band of approximately 1.5 eV width. In agreement with previous work [1,4] the cluster valence band is largely unstructured at most photon energies. However, in the photon energy range 15.5 - 17.5 eV a strong peak at ≈ 15 eV binding energy with a halfwidth of about 0.25 eV is visible. This feature shifts smoothly and continuously by 0.7 eV in binding energy from 14.6 to 15.3 eV over this photon energy range (red dashed line Fig. 1).
Also shown schematically are the corresponding photoemission data from Kassühlke *et al.* [3] for (111) single crystal bulk argon recorded in normal emission. They show two features in the binding energy range of 12.5 to 15.0 eV. One of these dominates the spectra between 16 and 18 eV photon energy. It also shifts to higher binding energy by about 0.6 eV (red dashed line marked '1'). The other, weaker feature in the data of Kassühlke *et al.* (blue dashed line '2') shifts slightly to lower binding energy with the slope increasing at about 18 eV photon energy. A dispersing feature similar to the present result was also seen in early work on polycrystalline Ar films by Schwentner et al [5].
We note the identical photon energy range, the very similar binding energy shift and the high intensity of the ≈ 15 eV feature in the bulk and cluster data. We conclude that the same effect is occurring in the cluster as in the bulk and may be attributed to energy band dispersion. In other words, there is direct evidence that at ⟨N⟩ = 1670 the clusters have bulk-like electronic properties.

more results and discussion

In a second experiment, using a magnetic bottle electron analyser, we again measured argon cluster photoelectron spectra as in Fig. 1 for a series of cluster sizes ranging from ⟨N⟩ = 24 to ⟨N⟩ = 200. The results are shown in Figures 4 and 5. For clusters with a mean size of ⟨N⟩ = 24 and 42 (panels a and b in Fig. 4), the band feature is developed only rudimentarily. For clusters with a mean size of ⟨N⟩ = 91 and above (panels c and d) we observe a nearly fully developed bandfeature as compared to ⟨N⟩ = 1670 (Fig. 1).

We thus conclude that the formation of energy bands in argon clusters already occurs in clusters with a mean size between ⟨N⟩ = 90 and ⟨N⟩ = 190. This corresponds to a cluster size N_{ph} of about 230. This perhaps surprising result can be understood within a simple tight-binding model.

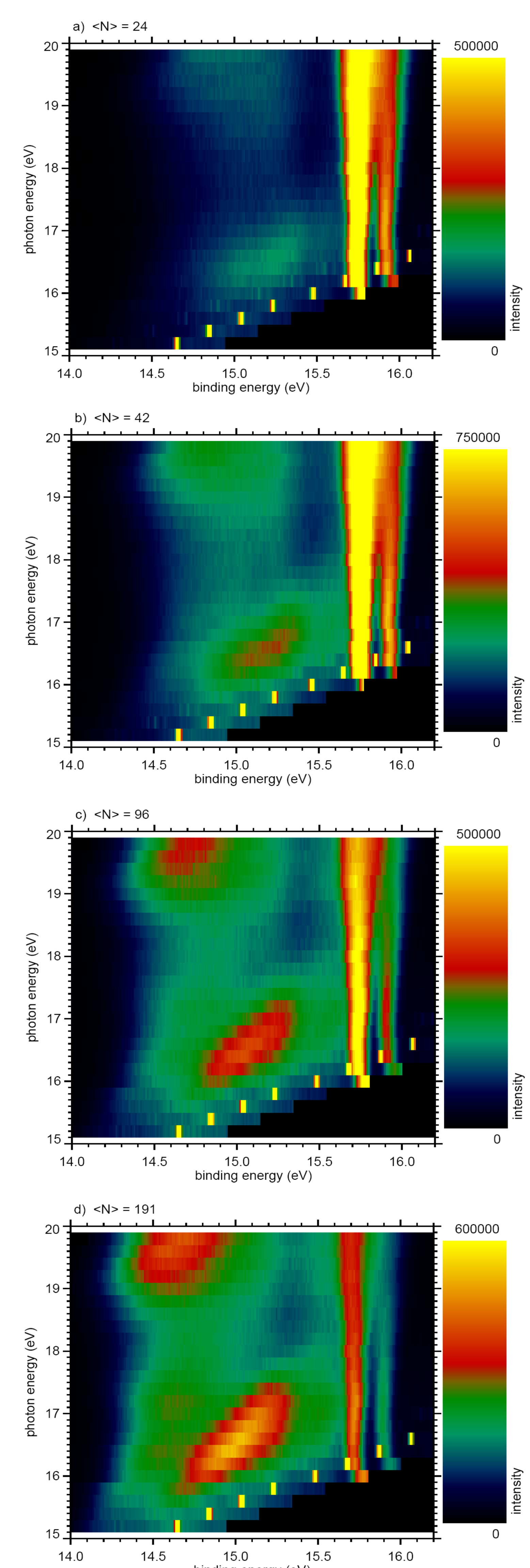

Fig. 4: *"Colour-coded" intensity plots of 3p photoelectron spectra of Ar clusters with various mean sizes of ⟨N⟩ = 24 (panel a), ⟨N⟩ = 42 (b), ⟨N⟩ = 96 (c) and ⟨N⟩ = 191 (d).*

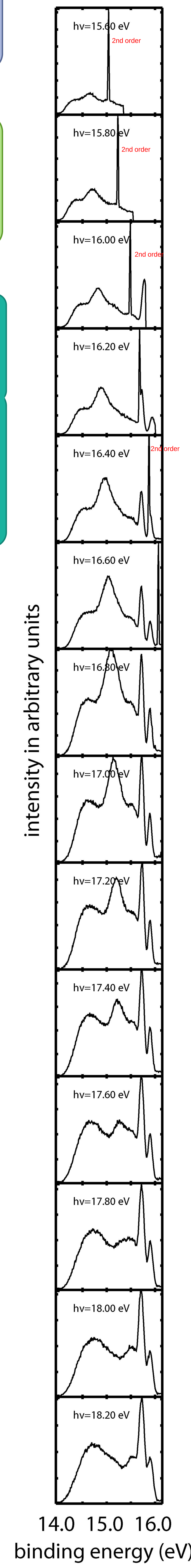

Fig. 5: 3p photoelectron spectra of argon clusters with ⟨N⟩ = 191, recorded with the magnetic bottle analyser at different excitation energies.

results for Kr

Most recently, we have extended our experiments to Kr. Very near to the photoemission threshold (in the photon energy range 13.8 – 14.7 eV) we also find a dispersing feature, but with a bandwidth in this case of only 0.2 eV. Similar to Ar, data from both single crystal [3] and polycrystalline krypton [5] show such a structure.

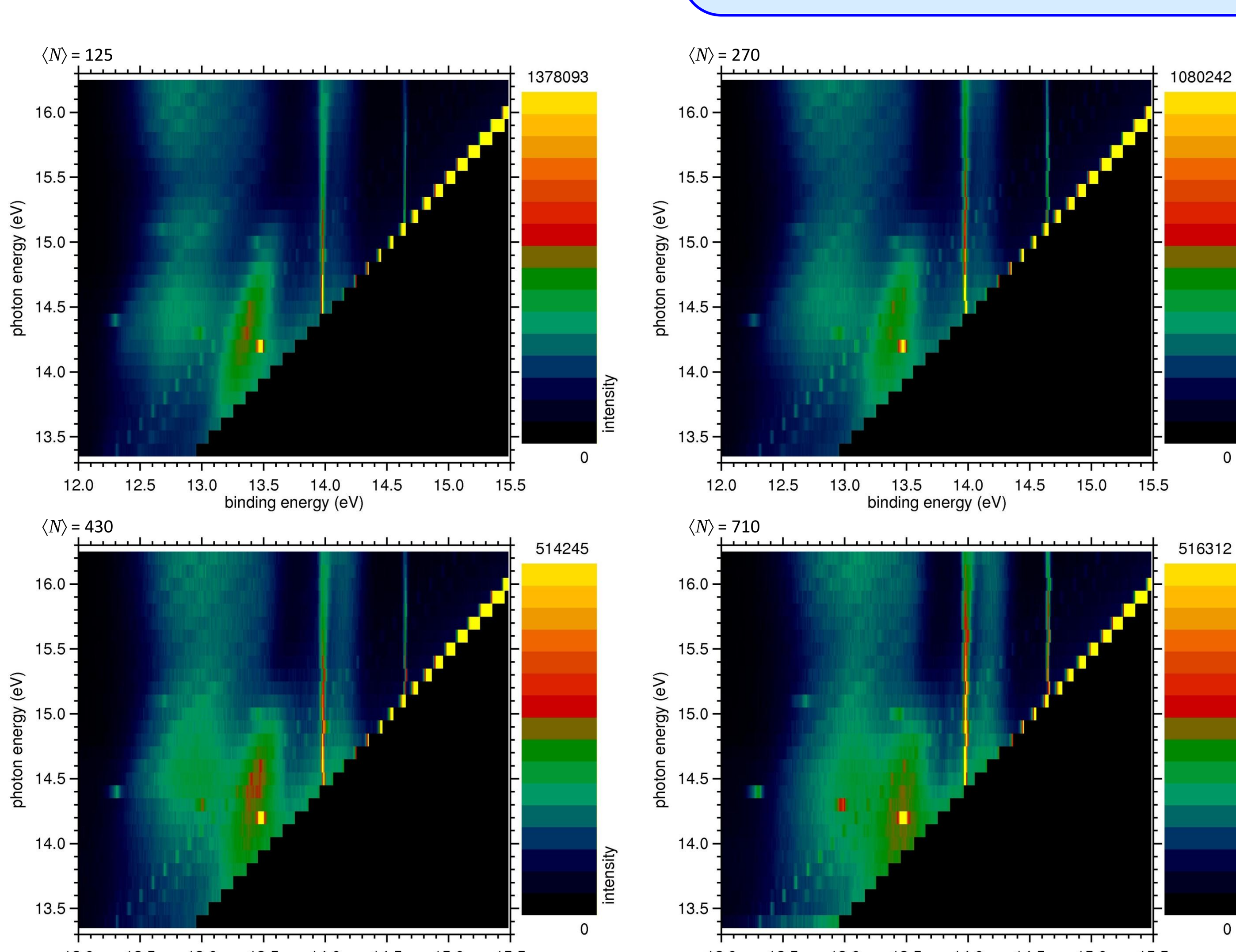

Fig. 6: 4p photoelectron spectra of krypton clusters with four different settings of ⟨N⟩, recorded with the magnetic bottle analyser.

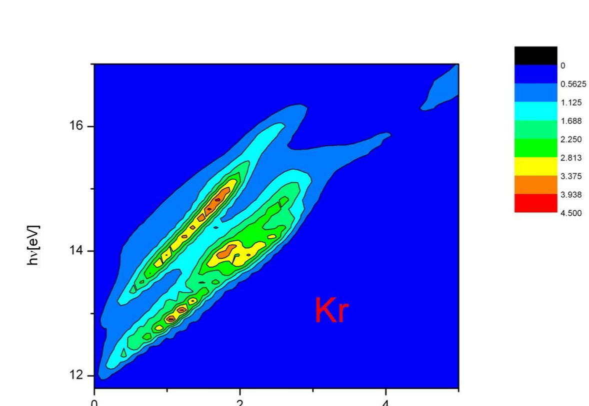

Fig. 7: Photoemission data of bulk single crystal Kr [3]. (Courtesy of P. Feulner.)

thanks

We thank P. Feulner, K. Horn, D. Menzel, A. Nilsson, M. Scheffler, A. Stampfl and G. P. Williams for useful discussions. We acknowledge financial support from the Deutsche Forschungsgemeinschaft, the Advanced Study Group of the Max-Planck-Society, the Fonds der chemischen Industrie, the Swedish Research Council (VR), and the Seventh Framework Programme of the European Community (FP7/2007-2013; grant agreement no. 226716).

references

This work: M. Förstel, U. Hergenhahn, A. M. Bradshaw *et al.*, Phys. Rev. B **79**, 155448 (2009);
M. Förstel, U. Hergenhahn, A. M. Bradshaw *et al.*, J. Electron Spectrosc. Relat. Phenom. **184**, 107 (2011).
[1]: U. Hergenhahn *et al.*, Phys. Rev. B **79**, 155448 (2009).
[2]: O. F. Hagena, Rev. Sci. Instrum. **63**, 2374 (1992).
[3]: B. Kassühlke , P. Feulner, and D. Menzel, private communication. See B. Kassühlke, PhD Thesis, Technical University of Munich, Herbert Utz Verlag, Munich (1998).
[4]: D. Rolles, H. Zhang, Z. D. Pesic, J. D. Bozek, and N. Berrah, Chem. Phys. Lett. **468**, 148 (2009).
[5]: N. Schwentner, F.-J. Himpsel, V. Saile, M. Skibowski, W. Steinmann, and E. E. Koch, Phys. Rev. Lett. **34**, 528 (1975).