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Ionization of Kr.CF₄ and Xe.CF₄ van der Waals clusters: from face to vertex geometry

R. Püttner^{*1}, V. A. Alekseev^{†2}, G. A. Garcia[‡], R. Kevorkyants[†], L. Nahon[‡]

^{*} Institut für Experimentalphysik, Freie Universität Berlin, Arnimallee 14, D-14195, Germany

[†] Institute of Physics, St.Petersburg State University, Uljanovskaja St.1, Peterhof, 198504 Russia

[‡] Synchrotron Soleil, Orme des Merisiers, St. Aubin BP 48, 91192 Gif sur Yvette cedex, France

Synopsis We report on photoionization studies of Xe.CF₄ and Kr.CF₄ van-der-Waals (vdW) clusters produced in a supersonic expansion and detected using synchrotron radiation and photoelectron-photoion coincidence techniques. Complementary *ab initio* calculations of the potential energy surfaces for the ground state and the first ionized state are performed and show generally good agreement with the experimental results. In particular, the calculation reveals a change in the equilibrium configuration from face to vertex geometry upon ionization. This observation is fully in line with the lineshapes of the Xe.CF₄ and Kr.CF₄ clusters in the photoelectron spectra.

Recent studies of Xe-CF₄ and Kr-CF₄ quasi-molecules (collision pairs) in static gas cell experiments revealed an interesting coupling effect induced by an interaction of transient dipole of IR active CF₄ ($\nu_3 = 0 \leftrightarrow \nu_3 = 1$) vibrational transition with transient dipoles of IR transitions between excited states of the Rg atom. This coupling manifests itself via intense satellite bands at energies of the Rg atom states increased by the energy of one ν_3 quantum of CF₄ ([1] and references therein).

In this paper, we report on photoionization studies of the rare gas (Rg) vdW clusters Xe.CF₄ and Kr.CF₄. The experiments were performed on the DESIRS VUV beamline located at the French national synchrotron facility, SOLEIL. The ions and electrons were detected in coincidence using the DELICIOUS III double imaging photoelectron-photoion coincidence (i²PEPICO) spectrometer [2]. In this way, both conventional photoelectron spectra at fixed photon energies and threshold photoelectron spectra were recorded. For the interpretation of the experimental results complementary *ab initio* calculations for the ground and the first ionized state of the Rg.CF₄ vdW clusters are performed. These calculations show that the vertex geometry is energetically most favorable for the ionized states, which differs from the well-known face geometry for the ground state of Rg.CH₄ and Rg.CF₄ clusters.

For both clusters, the lineshapes of the photoelectron spectra show an asymmetric structure with a main peak approximately 0.05 eV below the Rg⁺+CF₄ dissociation asymptote as well as a shoulder with an onset approximately 0.2 eV below the asymptote. Based on the calculations the

main peaks can be explained with vertical transitions in the face geometry while the shoulders are due to adiabatic transitions to vibrational states which are mainly located around the vertex geometry.

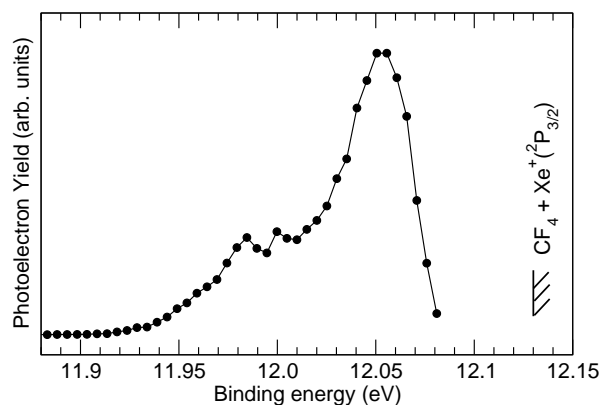


Figure 1. Threshold photoelectron spectrum for Xe.CF₄. The dissociation limit Xe⁺+CF₄ is also indicated.

For Xe.CF₄ also the energy range above the first ionization threshold of Xe⁺ was probed. However, in this region no photoelectron - Xe.CF₄⁺ ion coincidence signal was found. This suggests a fast decay of the Xe.CF₄⁺ clusters above the first dissociation limit, in agreement with previous PEPICO measurements for Kr₂ and Xe₂ dimers [3].

References

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¹E-mail: puettnr@physik.fu-berlin.de

²E-mail: v.alekseev@spbu.ru

