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ScienceDirect
Journal of Electron Spectroscopy and Related Phenomena 162 (2008) 30–35
JOURNAL OF ELECTRON SPECTROSCOPY and Related Phenomena
www.elsevier.com/locate/elspec

Valence photoelectron spectrum of KBr: Effects of electron correlation

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Received 8 June 2007; received in revised form 10 August 2007; accepted 17 August 2007
Available online 23 August 2007

Abstract

The valence photoelectron spectrum has been measured for molecular KBr. Experimental energies of the main and satellite structures have been compared with the results of *ab initio* calculations based on molecular orbital theory including configuration and multiconfiguration interaction approaches. Comparison between the experimental KBr spectrum and previously reported Kr valence photoelectron spectrum has also been performed in order to find out if electron correlation is of the same importance in the valence ionized state of KBr as in the corresponding state of Kr.

PACS: 32.80.Hd

Keywords: KBr; Valence photoionization; Molecular calculations

1. Introduction

The physical and chemical properties of alkali halide molecules have been the subject of numerous investigations (see e.g. [1,2] and references therein) because of the ionic character of their molecular bond that allows the application of simple theoretical models. Most lately we studied both the electronic decay of the valence VUV resonances and also the Auger decay following the core ionization in either the alkali or the halide side of the molecule (see [1–4] and references therein). In the study of the Br normal Auger spectra (MNN) in the alkali bromide series [3], the experimental results were compared with the results of single configuration calculations for Br^-decay spectrum [5,6]. It was noticed that the molecular Auger decay resembles in great extend the decay in Br^-ions when the final state of the Auger transition involves the electrons from the outermost molecular orbitals (MOs) (4p in Br^-). However, great differences between the spectrum of Br^-ion and the alkali bromide spectra were seen in the Auger groups involving the inner valence (Br 4s) MO. Single configuration calculations for Br^- failed completely in describing the features of these Auger groups. It is known that electron correlation plays a dramatic role in the same Auger group of Kr, shifting the energies and redistributing the intensity between the main and satellite lines [7]. Valence photoelectron spectrum of Kr is also accompanied by a rich satellite structure, due to the many-electron effects related to the valence ionization (see ref. [8] and references therein). The study of the inner valence photoelectron spectra of the alkali bromides was thus assumed to provide information not only on the structure of the molecular orbitals but also on the Br MNN Auger final states.

The outer valence spectrum of KBr has been recorded earlier [9,10] with the HeI and HeII discharge lamp excitation, covering the spectral range of Br^- 4p and K^+ 3p orbitals. However, the existing data does not show any indications of the Br^- 4s or the K^+ 3s orbitals. As far as we know, no synchrotron radiation excited high resolution experiments for gas-phase KBr have been reported so far.

In the present study we have measured the synchrotron radiation excited molecular KBr valence photoelectron spectrum including the 4p and 4s orbitals of Br^- and also the 3p and 3s orbitals of K^+. We also investigated whether the valence photoelectron spectrum of Br^- reflects similar satellite structure as seen in the spectra of the isoelectronic Kr atom [8].

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doi:10.1016/j.elspec.2007.08.006

2. Computational details

Calculations were performed using the quantum chemistry software package GAMESS [11,12]. Configuration interaction (CI) [13] and multiconfigurational self-consistent field (MCSCF) [14–16] wavefunctions, in a full optimized reaction space (FORS), also known as complete active space (CASSCF), were adopted. Calculations including the spin-orbit (SO) interaction were not performed. While the use of the MCSCF calculations was favorable for the higher quality level of their results, the CI calculations turned out to be very useful because of their less demanding nature, allowing us to reach deeper photoionization levels within our memory and computational time limits. Through the Mulliken [17–21] and the Lowdin [22] population analysis we could estimate the atomic orbitals (AO) contribution for each MO. This allowed us to determine if and how the ionic character of the molecule changes across the studied range of MO, indicating possible limits of the ionic model. For K we used the Pople's 6-311** valence triple zeta with polarization basis set [23]. For Br the augmented Dunning type correlation consistent aug-cc-pVDZ [24] was used. The ionization energies (IE) have been calculated in the minimum of the potential energy curve (PEC) for the neutral KBr molecule, corresponding to a calculated internuclear distance of 2.915 Å, in nice agreement with previous evaluations [25].

3. Experiments

Measurements were performed at the beamline I411 [26] in MAX-laboratory in Lund, Sweden. The beamline uses synchrotron radiation of an undulator located at the 1.5 GeV MAX-II storage ring. A modified Scienta SES-100 electron spectrometer was used to record the spectra of the emitted electrons at the "magic" 54.7° angle from the polarization vector, corresponding to angle-independent measurements. For a detailed description of the electron energy analyzer see ref. [27]. The molecular beam of KBr was produced from solid KBr in stainless steel crucible using a computer controlled inductively heated oven, designed and built at the University of Oulu [28]. The temperature of the crucible in the measurements was around 500 ° C corresponding the vapor pressure of 10^{-2} mbar [29,30] inside the crucible. Temperature was controlled with thermocouple sensors connected to the oven. The photon energy of 61.5 eV was used in the measurements of the KBr valence photoelectron spectrum (PES). Also other photon energies (60, 66, 70 eV) were used to identify possible Auger transitions and second order contributions at the kinetic energy region of the measurements. The binding energy calibration of the KBr photoelectron spectrum was obtained by introducing Xe gas to the interaction region and recording the Xe 5p photolines at 12.130 and 13.436 eV binding energy [31] simultaneously with the spectrum of KBr. The KBr photoelectron spectrum was measured with 20 eV pass energy of the electron spectrometer corresponding to approximately 70 meV analyzer contribution to the linewidths. The photon bandwidth was estimated to be 40 meV with the 100 μm exit slit of the monochromator.

4. Results and discussion

The valence photoelectron spectrum of KBr is presented in Fig. 1. The main KBr related structures are seen at the binding energies around 9, 19, 25 and 41 eV. In addition to the structures related to the inner and outer valence orbitals of KBr, the spectrum also includes some contributions related to the evaporation of background gases from the oven construction. The main residuals have been identified [32] to originate from CO_2 but small contributions of H_2O and CO have also been noticed.

Experimental and theoretical results are summarized in Tables 1–3 . In order to provide a systematic assignment for the whole range of experimental findings, we have used molec-

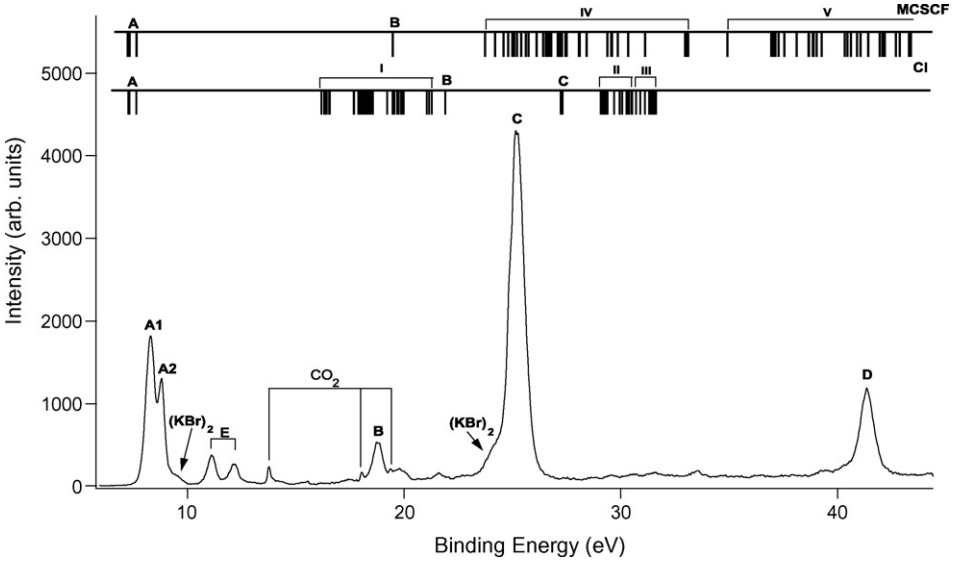

Fig. 1. Valence photoelectron spectrum of KBr molecule measured at 61.5 eV. In the top of the figure we schematically reported the results from the theoretical calculations.