PHYSICAL REVIEW A **75**, 032510 (2007)

Core-level electron spectroscopy on the sodium dimer Na 2*p* level

T. Rander,[1] J. Schulz,[1,2,3] M. Huttula,[3] A. Mäkinen,[3] M. Tchaplyguine,[2] S. Svensson,[1] G. Öhrwall,[1] O. Björneholm,[1]
S. Aksela,[3] and H. Aksela[3]
[1]*Department of Physics, Uppsala University, P.O. Box 530, SE-751 21 Uppsala, Sweden*
[2]*MAX-Lab, Lund University, Box 118, SE-221 00 Lund, Sweden*
[3]*Department of Physical Sciences, P.O. Box 3000, FIN-90014, University of Oulu, Finland*

(Received 20 December 2006; published 19 March 2007)

The lifetime broadening and molecular field splitting of the sodium dimer 2*p* core level is studied by x-ray photoelectron spectroscopy and by Auger electron spectroscopy. The lifetime of the Na 2*p* core hole has been determined to be 15±8 fs, much shorter than what has previously been reported for solid sodium. The molecular field splitting of this core level has been determined to be 42±10 meV. The Auger measurements have experimentally confirmed that the sodium dimer is a good example of when the Coulomb explosion mechanism determines the spectral shape.

DOI: 10.1103/PhysRevA.75.032510 PACS number(s): 33.15.Pw, 33.15.Ry, 33.60.Fy, 33.80.Eh

I. INTRODUCTION

With the introduction of modern x-ray and photoelectron spectrometers and modern x-ray sources the study of core hole lifetimes has attracted much interest. Recent studies have shown that there are considerable variations of the core hole lifetimes owing to molecular effects [1–4], and one can find state dependent core hole lifetimes in atoms. In certain cases such atomic core hole states may have comparatively long lifetimes and ways to produce atoms in such states selectively [5] have been proposed.

The core hole lifetimes are normally very short, typically only a few femtoseconds or less. The reason for this is that for almost all core hole states Auger decay processes are possible, and such processes are faster by several orders of magnitude than radiative decay. This was known at a very early stage and the pioneering reports of Mc Guire [6] gave the first detailed compilation, covering essentially the whole periodic system.

The decay of the Na 2*p* core hole is a particularly interesting case. The ground state configuration in the free atom is $1s^2 2s^2 2p^6 3s^1$. This configuration prohibits Auger decay of the Na 2*p* core holes due to the trivial reason that there is only one electron in the 3*s* subshell. The reported atomic lifetimes of different multiplets of the 2*p* core hole state are therefore determined by optical decay and lie in the nanosecond range [7]. In a dimer Na_2, the situation drastically changes. The 2*p* core-ionized valence molecular orbital configuration, $2p^{-1}1\sigma_g^2$ has two electrons in the valence level and consequently, Auger decay of a Na 2*p* core hole state becomes possible. The Na_2 molecule is therefore a prototype system to study this type of lifetime changes.

The system is also of interest because of the similarity with the so called interatomic Coulombic decay (ICD) effect for inner valence states [8]. In the latter case in dimers and clusters an additional decay mechanism can occur, leading to the formation of final state vacancies on the neighboring atoms. The removal of two $1\sigma_g$ electrons from a Na dimer leaves the system containing two Na^+ ions at an interatomic distance of the ground state of the dimer. Such a system is easy to describe, since the sum of the atomic radii of these ions are smaller (2.32 Å) [9] than the interatomic distance in the dimer molecule (3.08 Å) [10]. The two ions will repel each other, and move on an almost pure Coulombic repulsive potential. Therefore, the Na_2 molecule is an ideal example of the Coulomb explosion phenomenon.

In addition the dimer is of interest as a starting point for the studies of clusters. It has recently been possible to obtain Na 2*p* core photoelectron spectra of free clusters [11], and understanding the dimer is a necessary step to describe the evolution of the spectra from the atom, to the clusters and further on to the infinite solid. In this work, we aim to accurately describe the Na dimer 2*p* XPS feature, and to present a model for the Auger decay in the system.

II. EXPERIMENT

The x-ray photoelectron (XPS) measurements were performed at the undulator gas-phase beam-line I411 at MAX-lab, Lund, Sweden [12,13]. For our purposes, we used the interchangeable part of this beam-line. The end station that was utilized in the present case consisted of a Scienta SES-100 spectrometer, with a resistively heated oven mounted perpendicular to the electron lens [14]. The whole arrangement was rotated to an angle of 54.7° (the so-called magic angle) with respect to the synchrotron light polarization. This was done to eliminate angle dependent effects in the spectra. The experimental resolution was 60 meV for the Na_2 2*p* XPS. The Auger measurements were performed at Oulu university, Oulu, Finland. The same chamber and spectrometer set-up was used as in the XPS measurements, with the difference that an electron gun was used as excitation source. The experimental resolution in the measurement of the Auger spectrum was 20 meV.

The sample, in both the XPS and Auger measurements, was about 5 *g* Na, which was kept at a temperature of about 230 °C to provide a stable effusive beam. To characterize the contents of the sample beam, a time-of-flight [15] spectrum was recorded (Fig. 1) with the same evaporation oven. It shows that the beam is mainly atomic, but also has a substantial (9±1%) Na_2 content.

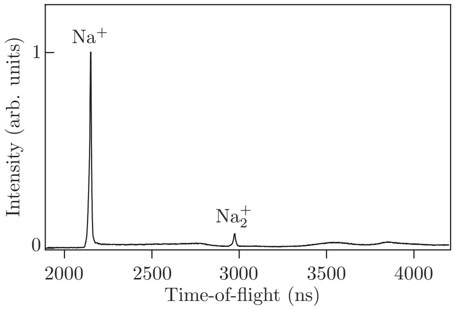

FIG. 1. Time-of-flight spectrum of the metal-vapor beam. The main contribution is atomic, but there is also a substantial amount of dimers. No large contribution from trimers is seen.

III. CALCULATIONS

A calculation using the $Z+1$ approximation was performed to obtain a first approximation of the XPS line shape. This means that we used NaMg$^+$ as our model system for the excited state. The calculation was done using the GAUSSIAN 03 [16] program package and the G2FC [17] program for further calculation of the Franck-Condon factors. We used DFT [Becke three-parameter Lee-Yans-Parr (B3LYP)] and a correlation-consistent polarized valence triple zeta (cc-PVTZ) basis set in all the calculations. The results of the calculations are summarized in Table I.

Values for the ground-state equilibrium distance and vibrational frequency ω_e are in good agreement with the experimental results of Ref. [10]. The calculated values for the excited state have not, as far as we know, been experimentally confirmed. When performing the Franck-Condon analysis, the sensitivity of the results to the core-ionized state vibrational frequency has been tested by manually varying the equilibrium distance of the ionic intermediate state. Since this variation did not give rise to any large deviations in the final spectrum we used the geometry obtained from the DFT calculation. The dimer lines were fitted with the SPANCF package for IGOR [18] with the help of the calculated vibrational profiles.

IV. RESULTS AND DISCUSSION

Figure 2 shows an overview spectrum of the Na $2p^{-1}$ spectral region. Between 37.8 and 38.6 eV we observe the atomic multiplet lines which are due to the coupling between the Na $2p$ core hole to the $3s$ valence electron. This first part of the spectrum is well known [19]. The dimer feature can be seen between 36 eV and 36.3 eV. The latter feature consists only of two spin-orbit split sodium dimer lines [20], since the Na$_2$ $1\sigma_g^2$ is a closed shell. Thus it is not simply a broadened version of the monomer spectrum. The formation of the closed shell also explains the difference in binding energy, together with the additional screening provided by the $1\sigma_g$ electrons. The atomic lines were used for energy calibration and to find the experimental resolution.

TABLE I. Experimental and calculated values of the equilibrium distance and vibrational frequency of the ground state and ionic state of the Na$_2$ dimer. The equilibrium distance R_e is given in Å and the vibrational constant ω_e in meV.

		Experimental	Calculated
Na$_2$	R_e	3.08	3.04
	ω_e	19.7	19.6
NaMg$^+$	R_e		3.19
	ω_e		18.8

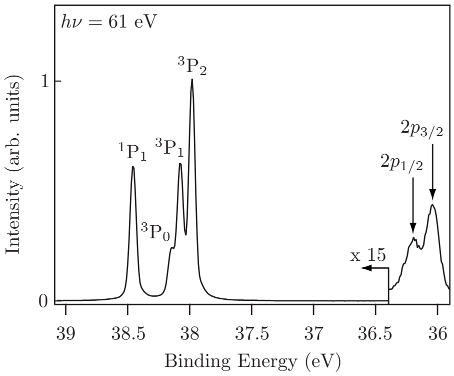

FIG. 2. Photoelectron spectrum of the Na $2p$ region. The features between 37.8 and 38.7 eV are atomic lines, the features between 36 and 36.3 eV are the dimer lines.

The Lorentzian contribution to the atomic lines should be in the range of μeV [7], since the $2p^5 3s$ state can only decay radiatively. In the case of the Na$_2$ molecule, the situation is different from that of the Na atom. Here, lifetime effects play a significant role, since Auger decay becomes possible. This means that a majority of decays from the core-ionized $2p^{-1}1\sigma_g^2$ state goes through this channel. The final state in the Auger process is antibonding, where each Na atom has the configuration $1s^2 2s^2 2p^6$, i.e., in a (Na$^+$)$_2$ system. A fit of the Na$_2$ $2p$ lines is displayed in Fig. 3. The two spectral components are fitted with the help of the calculated vibrational bar spectrum. The bar spectrum was convolved with a Gaussian broadening of 60 meV, obtained from the atomic spectrum, to take experimental broadening into account. It was not possible to get a good fit of the dimer $2p$ spectrum using two

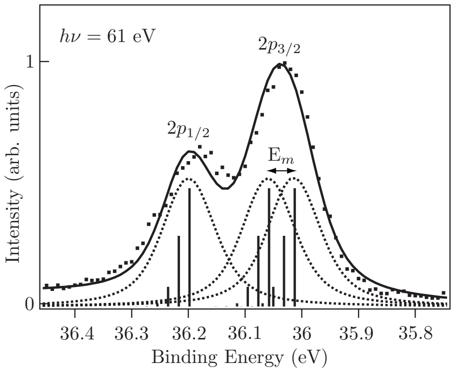

FIG. 3. The spin-orbit split sodium dimer photoelectron lines. The dots represent the experimental data, the dashed lines are the fit components, the whole line is the sum of the fit components and the vertical bars are the calculated vibrational progressions. The molecular field splitting is marked E_m.

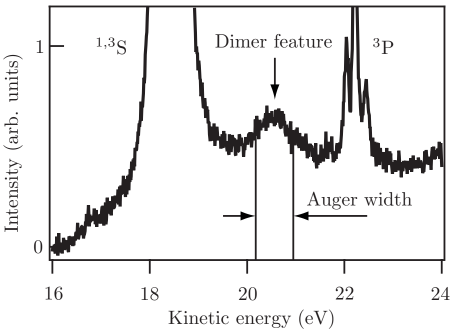

FIG. 4. Auger spectrum showing the dissociative dimer contribution. The features to the left and right of the dimer feature stem from atomic Auger decay.

peaks of the same form and with a statistical ratio 1:2. Instead, to fit the lower binding energy ($2p_{3/2}$) component, two identical progressions were used to take molecular field splitting into account, as was previously done for example in Ref. [21]. The magnitude of the molecular field splitting was determined to be 42±5 meV. The splitting between the $2p_{1/2}$ feature and the center-of-mass of the $2p_{3/2}$ features was determined to be 0.16 eV, which corresponds well to what has been determined in experiments in the solid state (160 meV) [22].

The shorter lifetime of the $2p$ core hole in the dimer manifests itself in the Lorenzian width of the photoelectron line, which was fitted to be 45±23 meV, corresponding to a lifetime of 15±8 fs. Our results for the dimer show a larger broadening than has previously been reported for solid Na [23], where a Lorenzian width of 13 meV, corresponding to a lifetime of 51±7 fs was measured. Thus, while the spin-orbit splitting seems to be the same in the solid and the dimer, the lifetime is not. This short experimental lifetime confirms that the Auger process dominates in the decay of Na$_2$ molecular core-hole states. The uncertainty in our values stems mainly from the fact that due to the small vibrational energy, many of the Na$_2$ molecules are not in their vibrational ground state, which means that hot bands contribute to the final spectrum.

The Auger spectrum presented in Fig. 4 shows three features, since this spectrum was acquired using an electron gun as excitation source. One can see the atomic Na$^+$ $2s2p^63s\ ^{1,3}S$ feature to the left, and the atomic Na$^+$ $2s2p^63p\ ^3P$ feature to the right, due to the $2s$ excitation. These features are used for the energy scale calibration [24]. The middle feature, at 20.5 eV, stems from the dimer Na$_2$. This Auger feature position has been reported earlier, by Breuckmann *et al.* [24], but without any discussion of the final state character. The structureless, broad (width 0.7±0.1 eV) shape of the Auger feature confirms the above discussed dissociative character of the final, doubly ionized state.

It is possible to estimate the width of the Auger feature, assuming that the final state is described by a pure, repulsive Coulomb potential curve. A comparison between the vibrational time of the dimer (35 fs) and the lifetime of the core hole (15±8 fs) shows that the wave packet will have time to propagate outside the ground-state Frank-Condon (FC) region before the Auger decay takes place. We take this into account by defining an effective FC region for the system. For simplicity, we define this effective FC region as being limited at the low-distance side by the ground state FC region boundary, and on the high-distance side by the intermediate state FC region. Figure 5 shows a schematic picture of this definition. Projecting this effective FC region onto the repulsive Coulomb potential directly yields the width of the Auger feature.

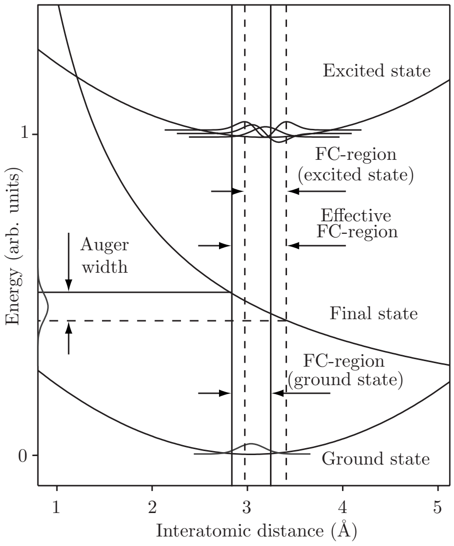

FIG. 5. Schematic picture of the Auger linewidth estimation. The effective Franck-Condon region is projected onto the Coulomb potential, which allows for a direct read-out to the Auger width.

Performing such an estimation for the sodium dimer yields a value of the Auger width of 0.7±0.1 eV, which is what is also found when extracting a value of the width directly from the experimental spectrum itself. This approach ignores lifetime vibrational interference, but seems to be sufficiently accurate to describe the investigated system to within our experimental accuracy. Thus, the $2p$ core-ionized sodium dimer is a good prototype system, where the Coulomb explosion mechanism determines the Auger spectral width.

The XPS data presented in this work show a clear contribution to the core-hole lifetime from Auger decay. For a Na$_2$ molecule the lifetime is much shorter than what has been reported earlier in the works on solid Na. Since the Na $2p$ spectrum of solid Na is very similar to that of the Na$_2$ molecule when decomposed into the surface and bulk components [22], this might indicate that the core-hole lifetime in the earlier works in the solid state (51 fs), which has been determined by use of the many-body theory of Almbladh [25], might have been underestimated, even though the overlap between the $3s$ orbitals is larger in the molecule than in the solid due to the covalent nature of the bond. Also, the situation in the solid state is more complex than in the dimer, due to the influence on the lifetime determination by, for example, shake up from the Fermi level to the conduction band and phonon broadening. In the solid state, this is taken into account by using a Doniach-Sunjic line shape and Gaussian broadening. In the present case, there are no such effects which could explain that the dimer spectrum shows Lorenzian tails, meaning that the lifetime in the dimer can be established with reasonable reliability. Molecular field splitting explains that the intensity ratio between the $2p_{3/2}$ feature and the $2p_{1/2}$ feature at first sight appears to be less than 2:1. The ratio is, however, confirmed as the $2p_{3/2}$ feature consists of two, molecular field split components, each of which has the same width and intensity as the $2p_{1/2}$ component.

V. CONCLUSIONS

In conclusion, we have determined the Na $2p$ core-hole lifetime and the molecular field splitting in the sodium dimer by measuring the XPS of free sodium dimers. Auger measurements confirm that the system behaves in a way that is consistent with the final state ions moving on a repulsive Coulomb potential.

ACKNOWLEDGMENTS

We would like to thank The Swedish Research Council (VR), the Knut and Allice Wallenberg foundation, the Swedish Foundation for Strategic Research (SSF), the Nordic Academy for Advanced Studies (NorFA), the Göran Gustafsson foundation, and the Research Council for Natural Sciences and Engineering of the Academy of Finland. We also thank the MAX-lab staff for their support.

[1] K. C. Prince, M. Vondràček, J. Karvonen, M. Coreno, R. Camilloni, L. Avaldi, and M. de Simeone, J. Electron Spectrosc. Relat. Phenom. **101–103**, 141 (1999).
[2] E. Kukk, J. D. Bozek, J. Sheehy, P. Langhoff, and N. Berrah, J. Phys. B **33**, L51 (2000).
[3] T. X. Carroll, K. J. Børve, L. Sæthre, J. D. Bozek, E. Kukk, J. A. Hahne, and T. D. Thomas, J. Chem. Phys. **116**, 10221 (2002).
[4] A. Machado Bueno *et al.*, Phys. Rev. A **67**, 022714 (2003).
[5] R. F. Fink, A. Eschner, M. Magnuson, O. Björneholm, I. Hjelte, C. Miron, M. Bässler, S. Svensson, M. N. Piancastelli, and S. L. Sorensen, J. Phys. B **39**, 269 (2006).
[6] E. J. McGuire, Phys. Rev. A **14**, 1402 (1976).
[7] E. Träbert, Phys. Scr. **53**, 167 (1996).
[8] N. V. Dobrodey, A. I. Streltsov, and L. S. Cederbaum, Phys. Rev. A **65**, 023203 (2002).
[9] P. Atkins and J. de Paula, *Physical Chemistry*, 7th ed. (Oxford University Press, 2002).
[10] K. K. Verma, J. T. Bahns, A. R. Rejei-Rizi, W. C. Stwalley, and W. Zemke, J. Chem. Phys. **78**, 3599 (1983).
[11] M. Tchaplyguine *et al.* (unpublished).
[12] M. Bässler *et al.*, Nucl. Instrum. Methods Phys. Res. A **469**, 382 (2001).
[13] M. Bässler *et al.*, J. Electron Spectrosc. Relat. Phenom. **101**, 953 (1999).
[14] M. Huttula, S. Heinäsmäki, H. Aksela, E. Kukk, and S. Aksela, J. Electron Spectrosc. Relat. Phenom. (to be published).
[15] M. Huttula, M. Harkoma, E. Nõmmiste, and S. Aksela, Nucl. Instrum. Methods Phys. Res. A **467–468**, 1514 (2001).
[16] M. J. Frisch *et al.*, *GAUSSIAN 03, Revision C.02* (Gaussian, Inc., Wallingford, CT, 2004).
[17] K. J. Børve, *G2FC*, University of Bergen, 2000.
[18] E. Kukk (unpublished).
[19] S. Krummacher, V. Schmidt, J. M. Bizau, D. L. Ederer, P. Dhez, and F. Wuilleumier, J. Phys. B **15**, 4363 (1982).
[20] J. Schulz, M. Tchaplyguine, T. Rander, O. Björneholm, S. Svensson, R. Sankari, S. Heinäsmäki, H. Aksela, S. Aksela, and E. Kukk, Phys. Rev. A **72**, 010702(R) (2005).
[21] S. Svensson *et al.*, Phys. Rev. Lett. **72**, 3021 (1994).
[22] D. M. Riffe, G. K. Wertheim, and P. H. Citrin, Phys. Rev. Lett. **67**, 116 (1991).
[23] T. A. Callcott, E. T. Arakawa, and D. L. Ederer Phys. Rev. B **18**, 6622 (1978).
[24] E. Breuckmann, B. Breuckmann, W. Mehlhorn, and W. Schmitz, J. Phys. B **10**, 3135 (1977).
[25] C.-O. Almbladh, A. L. Morales, and G. Grossmann, Phys. Rev. B **39**, 3489 (1989).