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Photoabsorption of Atomic Sodium in the VUV

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The aboomption spectrom of atomic sodium in the photon energy region from 30 eV to 150 eV has been investigated. A great number of sharp absorption tines which ean be attributed to the excitation of a 2p-or a 2s-eteciron has been detected. Simultaneous excitalion of one $2 p$ - and one $3 s-$ evectron gives rise to conotiderably strong Broad and asymmetric absorption strmotixes above the nighest series limit ( $1 P$, for the excitations of a single 2p-electron. Some of the asGignments have been eonfirmed by Hortree-Fock calculations. The relative speotral dependence of the absorpition cross-section in this energy range has been determined for the first time. The spectrum of free Wa atoms has been compared with the $L_{I I}$, ITI spectrum of solid sodizm.

## I. INTRODUCTION

The sharp lines showing up in absorption spectra at the onset of inner shell transitions of free atoms give detailed information on the electron states. This information has in many cases also turned out to be of great use for the interpretation of the absorption spectra of solids formed by these atoms ${ }^{1}$. In this respect the atomic absorption spectra due to transitions of the tightly bound core electrons to continum states can also be very helpful. The investigation of the $2 p$-absorption of atomic sodium has been initiated by absorption measurements on the simple metals Na, Mg and $\mathrm{Al}^{2}$. The $\mathrm{L}_{\text {II, III }}$ absorption spectra of these metals show broad periodic structures up to 100 eV above threshold. These structures cannot be explained in terms of the one-electron band model. Lundquist et al. ${ }^{3,4}$ have tried to interprete these maxima with the help of the so-called "plasmaron theory" which demands simultaneous excitation of collective modes and the core electron. This theory correctly describes the position of these peaks for Al; it fails, however, to give the positions of these peaks for Na and Mg .

Absorption measurements in the VUV showed that the continuum absorption of many solids is very similar to that of the corresponding free atoms ${ }^{1}$. Most of the absorption spectra can be understood, at least qualitatively, in terms of a one-electron model for free atoms ${ }^{5}$. Taking into account, however, multiplet splitting, configuration interaction and electroncorrelation Dehmer et al. ${ }^{6}, 7$ and Amusia et al. ${ }^{8}$ achieved quantitative agreement between their calculations and the experimental results.

Calculations ${ }^{9}$ of the photoionization cross-section for the 2 p -absorption of atomic $\mathrm{Na}, \mathrm{Mg}$ and A 1 in terms of a one-electron model only give one broad maximum above the onset of the 2 p -absorption. Atomic data, on the other hand, indicate that transitions from the 2 s-states and simultaneous excitations of one 2 p-electron and one 3 s-electron or two $2 p$-electrons respectively might be responsible for at least part of the structures detected in the 2 p -absorption spectra of these simple metals. As there were no measurements of the $2 p$-continuum absorption of atomic $N a$ available we measured the $2 p$ absorption of sodium vapour in the energy region from 30 eV to 150 eV . One major object of these measurements was to find out how closely the 2 pabsorption of solid sodium resembled the 2 p -spectrum of atomic sodium and whether the periodic structures mentioned above were due to solid state effects.

## II. EXPERIMENTAL PROCEDURE

The 7.5 GeV electron synchrotron DESY served as a continuum background source 10,11 . The fine structure at the onset of the $2 p-t r a n s i t i o n s$ of sodium was measured with a 2 m grazing incidence Rowland spectrograph (McPherson Model 247). The spectra were recorded on photographic plates (Kodak SWR, Ilford Q2). Two different aluminum coated gratings were used, one with 600 lines/mm and one with 1, 200 lines/mm. The blaze angle was $2^{\prime} 4^{\prime}$ for both gratings. Measurements at an angle of incidence of $82^{\circ} 30^{\prime}$ and of $84^{\circ} 30^{\prime}$ were performed. The resolution achieved was better than 0.08 A with the 1,200 lines/mm grating and better than $0.15 \AA$ with the 600 1ines/mm grating over the entire energy region. The exposure times varied between some minutes and several hours depending on the electron current in the accelerator, the pressure conditions in the sodium vapour furnace and the thickness and materials of the windows used for confining the vapour.

In order to avoid the tedious and difficult task of calibrating the intensity response of the photographic plates the spectral dependence of the absorption cross-section was measured with a 1 m grazing incidence Rowland spectrometer. In this case an open magnetic type multiplier (Bendix M 306), mounted behind the exit slit was used as a detector. A gold coated grating with 2,400 lines/mm and a blaze angle of $4^{\circ} 16^{\prime}$ with an angle of incidence of $77014^{\prime}$ was used. Because of the high absorption of the sodium vapour we had to open the entrance slit and, as a result, the wavelength resolution was limited to 0.2 A over the measured energy range. Details of the experimental set-up and the experimental procedure are given in Refs. 11,12. The spectrometer was calibrated by the known He resonance lines ${ }^{13}$. The He resonance lines and some very sharp absorption
lines of atomic Na determined by Connerade et al. ${ }^{1 /+}$ were used for the wavelengtin calibration of the photographic plates.

The sodium vapour furnace using the heat pipe principle was mounted in front of the spectrographs. A buffer gas of helium prevented the sodium from reaching the aluminum, magnesium or zapon windows which confined the vapour region. The thickness of the windows ranged from $500 \AA$ to $1,000 \AA$. They were supported by a 75 copper mesh. These windows also served as filters suppressing higher orders reflected from the grating. We additionally used si prefilters in the energy region from 70 eV to 100 eV . The sodium vapour pressures varied from 0.1 Torr up to 0.5 Torr (temperature up to $410^{\circ} \mathrm{C}$ ). The temperature profile along the stainless steel furnace was measured by thermocouples. The absorption path 1 ength was 40 to 70 cm . As the spectrum of the synchrotron radiation is completely smooth and continuous, any structure found in the spectra car, with a high degree of reliability, be attributed to the sodium vapour. The well-known structures due to the absorption of the windows and the He buffer gas could easily be separated from the structures due to the sodium vapour.

## III. EXPERIMENTAL RESULTS

The absorption spectrum of sodium vapour in the measured energy region is shown by the solid line in Fig. 1. Since the temperature profile along the furnace and consequently the pressure and the length of the sodium vapour column could not be determined very exactly only the relative shape of the absorption spectrum was measured. The absorption spectrum shown in Fig. 1 has been adjusted to the absolute cross-section calculated by McGuire ${ }^{9}$ (dotted curve). The same holds for the absorption spectrum of solid $\mathrm{Na}^{2}$ given by the dashed curve. As for atomic sodium no absolute crosssections have been determined for solid sodium. Under the conditions of our measurements the percentage of Na molecules is expected to be about $3 \%{ }^{16}$. Though the absorption due to this molecular contribution is expected to be small compared to the absorption due to Na atoms we cannot exclude that some of the weak structures showing up in the spectra are due to $\mathrm{Na}_{2}$ molecules. Careful study of the temperature dependence of the spectra over a considerable temperature range might help to clarify this question but these experiments still remain to be done.

At the onset of transitions from the 2 p-shell of atomic sodium we find two strong sharp lines. The background due to transitions of the outer 3 selectron seems to be almost exhausted in this energy region ${ }^{9}$. Apart from some broader and weaker structures a considerable number of sharp lines show up in the spectrum towards higher energies. The appearance of these lines changes abruptly above 38.5 eV . Above this energy the spectrum is dominated by relatively broad and asymmetric structures. These structures could be detected up to 47 eV . Above 47 eV the absorption cross-section increases smoothly. Between 65 and 71 eV transitions from the 2 s -level give
rise to prominent, broad and asymmetric absorption lines. Towards still higher emergies the cross-section decreases smoothly. Up to 150 eV no further structures could be detected.

Part of this spectrum has already been reported by Connerade et al. ${ }^{14}$. Probably due to a lower vapour pressure, lower intensity of the BRV source used in these measurements and the difficulties caused by the line structure already present in the spectrum emitted by the source, Connerade et al. have only been able to detect the strongest lines in the energy range up to 50 eV . Only the first strong line at 66 eV due to the excitation of the 2s-elcctrons has shown up in their measurements. Simultaneous to our measurements Ederer et al. ${ }^{17}$ measured the absorption of atomic sodium using synchrotron radiation. According to preliminary results there seems to be good agreement between their results and ours in the energy region up to 50 eV. They have not examined the structures between 65 eV and 71 eV .

The relative spectral dependence of the absorption coefficient between 30 eV and 150 eV has been determined by our measurements using photoelectric detection for the first time.

IV. DISCUSSION

For the purpose of discusion the measured absorption spectrum (Fig. 1) will be divided into four parts. In part A the overall behaviour of the measured absorption spectrum will be discussed and compared to the aisorption spectrum of solid sodium" and to the results of McGuire's calculations for free sodium atoms. Part $B$ deals with the absorption lines in the energy range from 30 eV to 38.5 eV beeing due to transitions from the $2 p^{-s h e l l}$ of atomic Na. The double excitations givjng rise to the structures between 38.5 eV and 50 eV will be discussed in part C . Transitions from the 2 s -shell showing up between 65 eV and 72 eV will be treated in part $D$.

## A. Continuum Absorption

McGuire ' has calculated the photoionization cross-section for atomic sodium by a one-clectron model using the atomic potential tabulated by Herman and Skillman'. The dotted line in Fig. l gives the results of these calculations. The onsel of the transitions of the $N a 2 p-e l e c t r o n s$ into continuma states given by McGuire lies about 4 eV below the experimentally determined
 $\mathrm{P}_{1} 38.081 \mathrm{eV}, \mathrm{F}_{0}, 38.15 \mathrm{j} \mathrm{eV}, \quad \therefore \mathrm{P}_{1} 38.462 \mathrm{eV}$, these energies have beer obtained by adding the ionization energy of Na to the energy of the lowest excited states of $\mathrm{Na}^{+}$, all values taken from the tables by C.E. Moore : ) Both theory and experiment show a considerable increase in the absorption cross-section at threshold. Above this threshold the absorption crosssection increases giving rise to a broad maximum at about 60 eV. Towards stili higher energies the absorption decreases. This general feature is shown by both the theoretical and the experimental curve. 'The broad maximum can be explained in terms of a one-electron model for free atoms as beeing
due to the delayed onset of transitions ${ }^{5}$ from the 2 p-states to d-symmetric final states. A potential barrier at the edge of the atom depresses these transitions at threshold and shifts the oscillator strength towards higher energies. Transitions to bound final states are not included in McGuire's calculations. The sharp absorption lines and the prominent structures due to double excitations are, therefore, not to be found in the theoretical curve. The onset of the transitions from the $2 s-s t a t e s$ of Na to continuum states given by the calculations also lies at about 4 eV below the series limits $2 \mathrm{~s} 2 \mathrm{p}^{6} 3 \mathrm{~s}{ }^{3} \mathrm{~S}_{1},{ }^{\circ} \mathrm{S}_{0}$. Again the structures found experimentally between 65 eV and 71 eV are not reproduced by the calculations.

The absorption spectrum of solid sodium given by the dashed line in Fig. 1 also shows a broad maximum at about 60 eV . Three prominent maxima are superimposed at $48.5 \mathrm{eV}, 65.5 \mathrm{eV}$ and 90 eV . Similar maxima have been detected in the 2 p -absorption spectra of solid $\mathrm{Mg}, \mathrm{Al}^{2}$ and $\mathrm{Si}^{27}$. These maxima cannot be explained by one-electron band models. They might as has already been pointed out ${ }^{3}, \therefore$ be due to the simultaneous excitation of one $2 \mathrm{p}-\mathrm{electron}$ and one, two, or three plasmons. By coupling the plasmon to the $2 p$-core hole the energy of the plasmon is shifted to higher energies as compared to the energy of the normal bulk mode.

From atomic data and from the results of Hartree-Fock calculations one can estimate the highest series limit for the simultaneous excitation of one 2 p-electron and one 3 s-electron to be at about 53 eV , for the excitation of one 2 s -electron at 72 eV , and for the simultaneous excitation of two 2 p-electrons at about 110 eV . This means that these series limits approximately coincide with the high energy tail of the three maxima found in the absorption spectra of solid sodium. The same holds for the $2 p-$
absorption spectra of solid Mg and Al . Part of these three maxima might, therefore, be due to these excitations. However, no maxima show up in the spectrum of sodium vapour at the energy where we find the first and the third maximum in the solid. Only at the position of the second maximum around 65 eV do we find strong absorption structures in the spectrum of sodium vapour being due to $2 s$-transitions. These structures might be broadened when going from the free atoms to the solid and at least part oi this peak might, therefore, be due to 2 s-excitations. All this leads to the conclusion that these three maxima cannot be explained by atomic excitations alone. Solid state effects seem to be very importani. At present a convincing explanation for those maxima has not, as yet, been given.

## B. Region irom 30 eV to 38.5 eV

At the onsel of the 2 p-transitions two strong 1 ines show up at 30.768 eV and at 30.934 eV . These lines are due to the transitions $2 \mathrm{p}^{5} 3 \mathrm{~s}^{7} \mathrm{~S} .1$ $2 \mathrm{p} 3 \mathrm{~s} \mathrm{p}, 1 \%$ of atomic sodium. The energy positions of these 1 ines are very close to the position of the $\mathrm{L}_{\text {III }}(30.68,0.1 \mathrm{eV})$ and $\mathrm{L}_{\text {II }}$ (30.84:0.1 eV) edges in solid sodium. The value of the spin orbit splitting ( 0.16 eV ) agrees well with the result of Hartree-Fock ${ }^{2}$ calculations for free sodium atoms and with the energy separation of the ${ }^{1}$ III and the $L_{\text {If }}$ edge found for solid sodium. The structures detected between 31 eV and 35 eV cannot be explained by atomic excitations and are pussibly due to excitations of Na, molecules.

The 1 ines experimentally determined in the region up to 38.5 eV are tabulated together with a tentative interpretation in Tables I and 1 I .

The lines alove 35 eV are shown on an enlarged scale in Fig. 2. These lines are due to following type of transitions:

$$
\begin{array}{ll}
2 \mathrm{p} 3 \mathrm{~s}: / 5 & 2 \mathrm{p} 3 \mathrm{sin} \quad \mathrm{n}-4 \\
& 2 \mathrm{p} 3 \mathrm{snd} \mathrm{n}-3
\end{array}
$$

Taking into account the selection rules for dipole allowed transitions there are 17 series converging to the serics $1 \mathrm{imits} 2 \mathrm{p} 3 \mathrm{~s}, \mathrm{p}, \mathrm{P}$, It is impossible to pick out series by eye below the "p series limit because of the complicated experimental spectrum due to the great number ol overlapping series. Connerade et al. carculated the eftective quantum number for all the lines detected by them and thereby obtained a tentative assignment of the lines. Because of the great number of very closely spaced Iines and the effect of interaction between overlapping conligurations which has to be taken into account, we question the reliability of assignments based on this procedure. Furthermore, the strength and the appearance of the lines du not load to an unambiguous identification.

By diagonalizing the energy matrices we calculated the encrgy pusition and the relative oscillator strength of the lines belonging to the $2 p$ 3s4s and the 2 p 3 s 3 d contiguration of atomio sodium. These matrices have bern obtained with the help of the tables given by $S l a t e r$ and by Condon and Shortiey . Furthermore, the energy matrires obtained in this way have bean wherked using tine graphical tensor operator techriques givea by Brigess and the code deveioped by Hibjert : The periinent values for the Coulomb, exchange and spin-orbit energies have been calculated by the Hartree-Fock code developed by Froese Fischer: These two configurations should correspond to the 1 ines found in the spectru: up to 36.7 ev. The results of the calculations are included in Fig. 2. The center of
gravity of the calculated configurations has been adjusted to the experimental results. No adjustment has been applied to the splitting of the lines calculated ior one configuration. Between the calculated energy splitting and the experimental results we find reasonable agreement for the four lines with lowest energy. Furthermore, the relative oscillator strengths calculated for these lines are in reasonable agreement with those determined experimentally. Towards higher energies there are considerable differences between the calculated and the experimental spectrum. This might be due to the interaction between the $2 p^{\prime} \cdot 3 s 4 s$ configuration and the overlapping 2 p 3 s 3 d configuration. We have not taken configuration interaction into account ir our calculations.

Simiiar calculations have been made for the configurations $2 \mathrm{p} \cdot 3$ sns and 2 p'3snd with $n$ up to 15 . Because of the complexity of the spectra no unambiguous correlation between the results of these calculations and the experimertal results could be found. The interaction between the overlapping configurations seems to modify the spectrum considerably. In order, therefore, to give a reliable interpretation calculations taking into account the interactions between all overlapping configurations have to be perlormed. We have not tried to tackle this extensive task.

Above the ${ }^{*} P_{0}$ series limit series converging to the $P_{1}$ series limit can be seen clearly. The energy position of these lines and their interpre:ation are listed in Table II. The strong, broader lines are due to the following transitions:

$$
2 p^{6} 3 s^{2} S_{y / 2} \rightarrow 2 p^{5} 3 s\left({ }^{1} \mathrm{P}\right) \text { nd }{ }^{2} \mathrm{P}: / 2,3 / 2,{ }^{2} \mathrm{D}_{3} / \%
$$

These lines seem to be broadened by the interaction with the underlying continum. The different levels could, therefore, not be resolved. The
sharp weaker lines are due to the transitions

$$
2 \mathrm{p} \cdot 3 \mathrm{~s} \mathrm{~S}_{1 / 2} \cdot 2 \mathrm{p}^{5} 3 \mathrm{~s}\left({ }^{\mathrm{l}} \mathrm{P}\right) \mathrm{ns} \cdot \mathrm{p}_{1 / \%}, 3 / ?
$$

The interaction of these lines with the underlying continum seems to be smaller. This can be concluded from the narrow 1 ine width which, in some cases, even permitted us to separate both components.

## C. Region from 38.5 eV to 50 eV

Above the ${ }^{1} P_{1}$ series limit simultaneous excitations oi a 2 p-ciectron and a 3 s-electron give rise to broad asymmetric structures extending up to 47 eV . These structures are shown on an enlarged scale in Fig. 3. According to the selectrion rules the following dipole transitions can take place.

$$
\begin{aligned}
& 2 p^{i} 3 s \quad \cdot \quad 2 p^{5} n \sin s \quad n, n^{\prime} \geq 4 \\
& 2 p^{5} n s n^{\prime} d \quad n>4 n^{\prime} \geq 3 \\
& \text { 2p npa'p } n, n^{\prime}=3 \\
& 2 \mathrm{p}^{\prime} \mathrm{ndn}^{\prime} \mathrm{d} \quad \mathrm{n}, \mathrm{n}^{\prime}=3 \\
& \text { 2pmpn'f } n-3 n^{\prime}-4
\end{aligned}
$$

Because of the large number of overlapping series converging to excited slates of the $\mathrm{Na}^{+}$ion the interpretation of this part of the spectrum seems to be very difficult. Part of the lower lying series limits taken from C.E. Moore's Lables are included in Fig. 3. There setms to be considerable interaction between the overlapping serics and between the serias and the underlying continua which gives rise to a broadening of the structures. The interaction of the series with the underlying continua also gives rise to asymmetric and window-type lines. One series of window-type lines converging
towards the $2 \mathrm{p}^{5}\left({ }^{2} \mathrm{P}: /\right)^{3} \mathrm{p} \quad{ }^{3} \mathrm{~S}$, level of $\mathrm{Na}^{+19}$ can easily be picked out by eyc. There seems to be another series converging to the $2 \mathrm{p}^{\prime}\left(\mathrm{P}_{1 / 2}\right) 3 \mathrm{p} \mathrm{S}_{0}^{\mathrm{S}}$ level of $\mathrm{Na}^{+} \%$. The spectrum becomes even more complicated towards higher energies due to the increasing number of series. According to atomic datala the high energy limit of these double excitations should be at 52.612 eV which corresponds to the energy position of the $2 \mathrm{~s}^{2} 2 \mathrm{p}^{2}$ states of $\mathrm{Na}{ }^{++}$. The spectrum becomes smooth already at 47 eV .
D. Region from 65 eV to 7 ? eV

Transitions from the 2 s -level give rise to the strong asymmetric lines found in the energy region between 65 eV and 72 eV . These lines are shown on an enlarged scale in Fig. 4. According to Hartree-Fock calculations the onset of the simultaneous excitation of two 2 p-electrons or the simultaneous excitation of one $2 \mathrm{~s}-$ and one 3 s-electron should lie above 73 eV . We do not, therefore, have to take these double excitations in the energy range under consideration into account. Consequently, in the following we will concentrate on transitions of the type:

$$
2 s^{2} 2 p^{6} 3 s^{2} s=2 s^{6} 3 \operatorname{snp} n 3
$$

These transitions should give rise to series converging to the $2 s^{2} 2 \mathrm{p}^{3} \mathrm{~S}$, and $2 s 2 p^{4} 3 \mathrm{~S}$ level of $\mathrm{Na}^{+}$. Hartree-Fock calculations place the center of this configuration between 70 eV and 72 eV . The energy splitting between the ${ }^{3} S_{1}$ and the ${ }^{1} S_{\text {states }}$ is expected to be about 0.9 eV . The energy position of the 2 s 2 p 3 s configuration of $\mathrm{Na}^{+}$can also be estimated from atomic data. . The $2 \mathrm{~s} 2 \mathrm{p}^{\prime \prime}$ configuration of $\mathrm{Na}^{++}$lies 85.2 eV above the ground state of Na. The binding energy of the $3 s$-electron in the $2 s^{2} 2 p^{6} 3$ configuration of $\mathrm{Na}^{+}$ should be very close to the binding energy of the 3 s-electron in the state
$2 s^{\prime 2} 2 p^{6} 3 s$ of $\mathrm{Mg}^{+}$, thus replacing the $\mathrm{Na}^{+} 2 \mathrm{~s}$ hole by a proton inside the $\mathrm{Mg}^{+}$nucleus. By subtracting this binding energy of 15 eV from 85.2 eV we end up with an energy of 70.2 eV which is in agreement with the results of the Hartree-Fock calculations.

Hartree-Fock calculations for the 2 s 2 p 3 s 3 p and the $2 \mathrm{~s} 2 \mathrm{p} 3 \mathrm{~s} / 4 \mathrm{p}$ configurations of sodium, taking into account oscillator strengths, lead to the assignment of the strong line at 66.6 eV to the $2 \mathrm{~s} 2 \mathrm{p} 3 \mathrm{~s}\left({ }^{3} \mathrm{~S}\right) 3 \mathrm{p}{ }^{\gamma} \mathrm{p}$ states and to the assignment of the line at 69.6 eV to the $2 \mathrm{~s} 2 \mathrm{p}^{\mathrm{f}} 3 \mathrm{~s}$ ( $\left.{ }^{2} \mathrm{~S}\right) 4 \mathrm{p}$ ? P states. These lines are highly asymmetric indicating a considerable interaction with the underlying continua. We tried, therefore, to fit these lines by profiles respresented by the formula

$$
\begin{aligned}
& a(c)=o_{a} \frac{(q+\varepsilon)}{(1+c)}+\sigma_{b} \\
& \quad=\left(E-E_{r}\right) / \frac{1}{2}
\end{aligned}
$$

given by L. Fano and J.W. Cooper . Here $\because$ gives the departure of the incident photon energy $E$ from the resonance energy $E_{r}$. This departure is expressed in a scale whose unit is the half-width $\frac{1}{2}$ of the line. u(.) represents the absorption cross-section for photon energy $F$ whereas a and $b$ represent two portions of the cross-section corresponding, respectively, to transitions to states of the continum which do and do not interact with the discrete state. $q$ is a numerical index which characterizes the line profilc. These relations hold for the interaction of one discrete line with one continuum.

The calculated profiles, giving the best fit to the experimental data, are shown by the dashed curves in Fig. 4. The parameter $q$ we used was -2 for the line at 66.6 eV and -1.8 for the line at 69.6 eV . A value - -6 for the $q$ parameter has also been found for the auto-ionizing - $s \cdot 2 p^{\prime} \rightarrow 2 s 2 p^{\circ} 3 p$ line in $N e^{\prime \prime}$, which is next to Na in the periodic table. The shoulder at 66 eV might be due to the $2 \mathrm{~s} 2 \mathrm{p}^{5} 3 \mathrm{~s}$ ( ${ }^{3} \mathrm{~S}$ ) $3 \mathrm{p}{ }^{4} \mathrm{P}$ states. Ihe maximum at 68 eV has been assigned to the $2 s 2 p^{6} 3 \mathrm{~s}$ ( s ) 3 p p states. Tite suggested energy positions of the ${ }^{i} S$ and 'S series 1 imits are indicated by bars in Fig. 4. The splitting of the LS terms due to the spin orbit interaction is not expected to show up in the spectrum due to the small


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Table I
Observed 2 p -electron excitation up to the $2 \mathrm{p}^{3} 3 \mathrm{~s}{ }^{3} \mathrm{P}$, ionization limits ${ }^{9}$. Identified transitions are given in column 5. The assignments for the 1 ines above 35.8 eV are less reliable than those for the lines at lower energy because of the differences between the calculated energy positions and oscillator strengths and the experimental results (see chapter IV B and Fig. 2). "C" denotes the 1 ines previously published in Ref. 14.

Table II Series of lines converging to the $2 \mathrm{p}^{5} 3 \mathrm{~s} \mathrm{~V}^{\mathrm{P}}$, ionization limit: The effective quantum number $\mathrm{n}^{+}$is given in column 5. "C" denotes the lines previously published in Ref. 14.

## Figure Captions

Fig. 1 Spectral dependence of the absorption cross-section of atomic sodium (solid line) and solid sodium ${ }^{2}$ (dashed line) in the energy range $30-150 \mathrm{eV}$ given in arbitrary units. For comparison the absolute cross-sections calculated by McGuire ${ }^{9}$ are included (dotted line).

Fig. 2
Absorption of atomic sodium in the energy range $35-39 \mathrm{eV}$. Since in the photoelcctric measurements not all ine structure found in this energy range could be resolved, the relative oscillator strengths of the absorption lines has been obtained by taking into account both the photoelectric and the photographic measurements. Most of the absorption 1 ines are due to transitions of the type $2 p^{3} 3 s \rightarrow 2 p 3$ ns and $2 p^{6} 3 s \rightarrow 2 p^{5} 3$ snd. The energy positions of the series limits are taken from Ref. 19. The calculated energy splittings and relative oscillator strengths of the lines of the $2 p^{5} 2 s^{4} 4$ and $2 p^{5} 3 s 3 d$ configurations are included.

Fig. 3 Absorption spectrum of atomic sodium in the energy range $38.5-46.5 \mathrm{ev}$. The structure is due to the simultancous excitation of one 2 p - and one 3 s-electron. The energy position of the ten lowest series limits, all of them belonging to the $2 \mathrm{p}^{5} 3 \mathrm{p}$ configuration of the $\mathrm{Na}^{+}$ion, have been taken from Ref. 19.

Fig. 4 Absorption Lires due to 2 s-electron excitation. The series limits have been obtained from Hartree-Fock calculations. The best fit of the data by a Fano proiile" is given by the dashed curves.


| i | $\begin{aligned} & h v \\ & \text { fev) } \end{aligned}$ |  | Appeara | nce |  |  | Assignment |
| :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: |
| 332.64 | 37.273 | fairly | broad, | fairly | strong | C | $2 \mathrm{p} 3 \mathrm{~s}(2 \mathrm{p}) 5 \mathrm{~d}$ |
| 332.47 | 37.292 | fairly | broad, | fairly | strong | C | 2p.3s (\%) bd |
| 332.27 | 37.315 |  | sharp, | very | weak |  |  |
| 331.76 | 37.372 |  | sharp, |  | weak |  |  |
| 331.69 | 37.380 |  | sharp, |  | weak |  |  |
| 331.58 | 37.392 |  | sharp, | very | weak |  |  |
| 331.15 | 37.441 | fairly | broad, | fairly | strong | C | $2 \mathrm{p}^{\prime} 3 \mathrm{~s}$ (3p) 5 d |
| 330.98 | 37.460 |  | sharp, |  | weak | C |  |
| 330.65 | 37.497 | fairly | broad, | fairly | strong | C |  |
| 330.37 | 37.529 |  | sharp, | very | weak |  |  |
| 330.24 | 37.544 |  | sharp, |  | weak | C |  |
| 330.10 | 37.560 |  | simarp, | very | weak |  |  |
| 329.78 | 37.596 |  | sharp, |  | weak | C |  |
| 329.70 | 37.606 |  | sharp, | very | weak |  |  |
| 329.58 | 37.619 |  | sharp, | very | weak | C |  |
| 329.47 | 37.632 |  | sinarp, | very | weak |  |  |
| 329.37 | 37.643 |  | sharp, | very | weak |  |  |
| 329.24 | 37.658 |  | sharp, | very | weak | C |  |
| 329.07 | 37.678 |  | sharp, | very | weak |  |  |
| 328.97 | 37.689 |  | sharp, | very | weak |  |  |
| 328.94 | 37.692 |  | sharp, | very | weak |  |  |
| 328.88 | 37.699 | fairly | broad, |  | strong | C |  |
| 328.57 | 37.735 |  | sharp, | very | weak |  |  |
| 328.46 | 37.747 |  | sharp, | very | weak |  |  |
| 328.35 | 37.760 | rairly | broad, |  | strong | C |  |
| 328.22 | 37.775 |  | sharp, | very | weak |  |  |
| 328.13 | 37.785 |  | sharp, |  | weak | C |  |
| 328.00 | 37.800 | Lairly | broad, | fairly | strong | C |  |
| 327.93 | 37.808 |  | sharp, | very | weak |  |  |
| 327.82 | 37.821 |  | sharp, | very | weak |  |  |
| 327.70 | 37.835 |  | sharp, | very | weak |  |  |
| 327.64 | 37.842 |  | sharp, | fairly | strong | C |  |
| 327.53 | 37.85 .5 |  | sharp, | very | weak |  |  |
| 327.44 | 37.865 | fairly | broad, |  | strong | C |  |
| 327.28 | 37.884 |  | sharp, |  | weak |  |  |
| 327.16 | 37.897 |  | sharp, | iairly | strong | C |  |
| 327.06 | 37.909 |  | sharp, | very | weak |  |  |





Fig. 1


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