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Neon *K* Emission Spectrum

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The neon *K* emission spectrum, excited by direct electron bombardment of the neon gas, has been obtained with photon counting on a single-crystal potassium-acid-phthalate (KAP) planar spectrometer. The measured relative integrated intensity of the $\alpha'\alpha_3\alpha_4$ and $\alpha_5\alpha_6$ satellite groups was found to be larger than theoretical prediction, but in accord with the trend of previous comparisons for *K* satellites of neonlike ions in solids. A comparison of the present results for electron excitation and the preliminary results by O. Keski-Rahkonen and T. Åberg for photon excitation indicates that the relative integrated intensity of the neon *K* satellites is independent of excitation mode at the excess excitation energies employed. A weak increase of intensity on the low-energy side of $K\alpha_{1,2}$ in the (803–809)-eV region was recorded and can be attributed to a radiative Auger transition.

I. INTRODUCTION

A recent theory of x-ray satellites based on the sudden approximation has been successfully applied to calculate the integrated intensities of x-ray satellites relative to their parent line.[1-6] In particular, Åberg has found good agreement between theory and experiment for the $K\beta$ satellites[2] of Ar and KCl, and the $K\alpha$ satellites[3-6] of a number of neonlike ions. An estimate[5,6] of the relative integrated intensity of the neon $K\alpha$ satellites was obtained indirectly from the experimental total multiple-excitation probability,[7] from which the KL^2 ionization probability[8] was subtracted. This estimate for neon is in good agreement[5,6] with theory. However, it would be desirable to make a direct comparison from the neon *K* spectrum.

There have been four previous reports of the *K* spectrum of neon. The first, by Backovsky,[9] was obtained with a plane grating and a low-voltage discharge tube as a source. In the second report, by Kunzl and Svobodova-Joanelli,[10] a bent mica-crystal spectrometer and a similar source were used. Later, Backovsky and Drahokoupil[11] improved on the resolution by using a gypsum-crystal spectrometer with a similar source. In the fourth study, Moore and Chalklin[12] used a carefully focused bent mica-crystal spectrometer and an rf electrodeless discharge tube as a source to excite the neon atoms. All four investigations recorded the spectrum photographically, which requires that great care must be exercised to obtain accurate intensity measurements. In addition, a reliable estimate of the relative intensities is difficult to obtain[12] due to changes in the emission from the discharge tube. Keski-Rahkonen and Åberg[13] have recently measured the neon *K* spectrum in fluorescence, using a gypsum crystal in a single-crystal planar spectrometer with photon counting. Their primary radiation was from a chromium anode operated at 40 kV. In contrast, the presently reported results were obtained by electron excitation of a gas target.

II. EXPERIMENTAL METHOD

The neon *K* spectrum in this report was obtained by exciting neon gas, of research grade, by direct electron bombardment. This was done by crossing[14] a 10 kV, 100 mA electron beam from a Pierce-type electron gun with a continuous flow of gas from a conventional slit nozzle. The target gas was directed down the throat of a 6-in. oil diffusion pump. The nozzle slit, 0.5 in. long, 0.040 in. high, and 0.010 in. wide, was cut into the flat part of the beveled blind end of a 1-in.-diam stainless-steel tube 3 in. long and extending into the target chamber. The slit was oriented to be parallel to the path of the electron beam. A water-cooled copper tube with a blind end served to "catch" the incident electron beam after it traversed the ribbon of target gas about $\frac{1}{8}$ in. below the nozzle end. At a right angle to the plane of the electron beam and gas flow is a viewing port for aligning the electron beam. A vacuum single-crystal planar spectrometer is coupled through a window holder to the flange opposite the viewing port. Stretched polypropylene was used for window material in recording the neon *K* spectrum. The primary functions of this window in separating the spectrometer from the target chamber are to maintain the cleanliness of the spectrometer section and to facilitate safer handling of various molecular gases that were also studied with the equipment. Between the window and the source is a rectangular opening cut into sheet aluminum foil and positioned so that any radiation from the end of the nozzle cannot enter the spectrometer.

The spectrometer consists of 0.075° Soller slits to limit the lateral divergence, a potassium acid phthalate (KAP) analyzing crystal, and a flowing-gas proportional counter with a stretched poly-

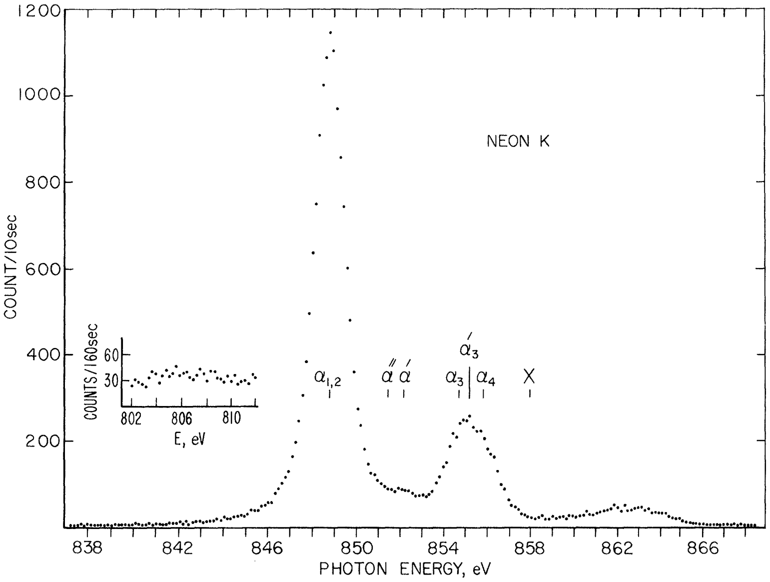

FIG. 1. Neon K spectrum obtained by direct electron excitation of neon gas. The energy positions of some K satellites, as determined by Moore and Chalklin (Ref. 12) are plotted relative to $K\alpha_{1,2}$ for comparison.

propylene entrance window. The counter gas used was methane at a pressure of about $\frac{1}{3}$ atm, whose number density was maintained by a pycnostat[15] to reduce any variations of gain. The proportional counter was followed by conventional electronic data logging to detect and record the radiation, while the spectrometer automatically step-scanned the spectral region of interest.

In Fig. 1 is shown the neon K spectrum obtained by averaging four different spectral scans without any instrumental corrections. The energy scale is set in terms of the nickel $L\alpha_{1,2}$ line (14.5612 Å)[16] excited by direct electron bombardment at 10 kV and 0.75 mA, with the nickel strip heated to a glowing red. The incident bombarding electrons and the emitted photons each made an angle of 45 ° to the normal of the nickel strip surface. The measured position of the main peak ($K\alpha_{1,2}$) in the neon spectrum is at 14.606 Å, relative to the nickel $L\alpha_{1,2}$ peak position, and considered in good agreement with the previous measurements[9-12] and the value of 14.610 Å accepted by Bearden.[16] A grating spacing of $2d = 26.6328$ Å, was used for the KAP analyzing crystal in this measurement.

III. RESULTS AND DISCUSSION

A. Low-Energy Region

The spectral region below the $K\alpha_{1,2}$ line to 788 eV was scanned with a counting time of 10 sec per point. No prominent spectral features were recorded in this region where the semi-Auger[17] and radiative-Auger[18,19] double-electron processes would be evident. There are other possible processes[18,19] that would result in changes of the emission intensity in this region, but these two processes are the most clearly identified to date. In the semi-Auger process, an $L_{2,3}$ electron fills the K hole and simultaneously another $L_{2,3}$ electron is excited with the emission of one photon. This emission would be expected as a broad peak in the 816-eV[20] region, tailing off to about 800 eV in analogy with the low-energy satellite in the argon and KCl $L_{2,3}$ emission.[17] Our experimental finding of no prominent feature in this region can be interpreted as evidence of no strong configuration mixing in the odd levels of the final ^2P state of neon II.

In the radiative-Auger effect, the second L-shell electron is emitted from the atom together with the photon. These transitions should be evident in the x-ray emission spectrum by a rise in intensity at each particular K-LL Auger energy of neon and tailing off to lower energy. The region of the inset in Fig. 1 was scanned repeatedly to accumulate a counting time of 160 sec per point. In this region, the K-$L_2L_3\,{}^1D_2$ at 804 eV[21] and the K-$L_2L_3\,{}^3P$ at about 807 eV would be expected to contribute to a radiative-Auger emission. The weak intensity above the background between about 803 and 809 eV, in the inset of Fig. 1, can possibly be attributed to these radiative-Auger transitions. A more complete study of this weak effect (by direct electron excitation with longer counting time per point) is not very practical with the present apparatus, due to the relatively large amount of gas specimen expended.

The spectral region up to energy 926 eV was scanned also, without observing any spectral features other than those shown in Fig. 1. In contrast to previous published experimental measurements, the neon K spectrum in Fig. 1 is relatively clean, without any evidence of a second-order Si $K\alpha_{1,2}$

TABLE I. Relative integrated intensities of high-energy satellites of neon *K* spectrum.

	$\frac{\alpha'\alpha_3\alpha_4}{\alpha_{1,2}}$	$\frac{\alpha_{5,6}}{\alpha_{1,2}}$
Experimental		
Electron excitation[a]	$30.2 \pm 2\%$	$8.3 \pm 1\%$
Photon excitation[b]	$32 \pm 3\%$	$8 \pm 1\%$
Theory[c]		
Photon excitation, sudden approximation	26%	3%

[a] This work.

[b] O. Keski-Rahkonen and T. Åberg, Ref. 13

[c] T. Åberg, Refs. 3, 5, and 6.

line or an "edge effect."

B. Relative Integrated Intensities of Satellites

The main peak $\alpha_{1,2}$ was separated from the first satellite group (referred to as the $\alpha'\alpha_3\alpha_4$ group) by assuming that $\alpha_{1,2}$ is symmetric. The high-energy side of the $\alpha'\alpha_3\alpha_4$ group was extended smoothly under the next satellite ($\alpha_5\alpha_6$ group) to zero intensity at 862 eV. The measured integrated intensity of $\alpha'\alpha_3\alpha_4$ and the $\alpha_5\alpha_6$ group centered at about 863 eV relative to $\alpha_{1,2}$, is presented in Table I together with preliminary secondary excitation results and theoretical calculations. The cumulative uncertainties in the primary excitation results were estimated from uncertainties due to (i) finite counting statistics of the overall spectrum, (ii) no intensity corrections for the energy dependence of absorption in the counter window and of the spectral response of the analyzing crystal KAP, (iii) no compensation for any background counts, and (iv) a possible inaccurate separation of the three groups of lines from the spectrum.

The agreement between the experimental results in Table I indicates an independence of mode of excitation of the $\alpha'\alpha_3\alpha_4$ ($KL \rightarrow L^2$) group and the $\alpha_5\alpha_6$ ($KL^2 \rightarrow L^3$) group relative intensities at the excitation energy greatly in excess of the threshold used in these experiments. This result is in excellent agreement with the independence of excitation mode of multiple excitation with *K*-Auger spectra of neon as measured by Krause *et al.*[22] The experimental results and the somewhat lower calculated value for the $\alpha'\alpha_3\alpha_4$ ratio are in accord with a recent comparison of measurements from solid targets of various neonlike ions in ionic compounds.[3-6]

A comparison of the relative intensity of the $\alpha_5\alpha_6$ group from solid targets indicated a larger value with photon excitation than with electron excitation,[4,5] as also suggested in the sudden approximation theory of x-ray satellites. These experimental $\alpha_5\alpha_6$ results from solids are at variance with the data in Table I. It is possible that, due to the high sensitivity of the $\alpha_5\alpha_6$ satellite group intensities to chemical effects, such as surface oxidation, the apparent experimental differences with mode of excitation in the solids comparison may be due to target contamination. Control of contamination for solid targets is far more difficult than with a monatomic gas target. The theoretically expected dependence of $\alpha_5\alpha_6$ intensity on mode of excitation is due to the calculated production probability of the *KK* double-vacancy states. In addition to the KL^2 triple-vacancy initial states produced by shake-off, almost all *KK* double-vacancy initial states will decay by Auger transitions to KL^2 states. The expected difference in intensity of the $\alpha_5\alpha_6$ group results from the calculated[4,5] greater production probability of *KK* states by photon excitation than by electron excitation, after taking into account correlation of the *K* electrons. Åberg[23] has estimated the difference of the relative intensity of $\alpha_5\alpha_6$ ratio to be about 0.5% greater for photon excitation. Since 0.5% is less than the uncertainties of the measurements, one cannot verify the calculated differences of the relative intensity due to excitation mode.

On comparison of the relative differences of experiment with theory of the data in Table I, the relative differences are larger for the $\alpha_5\alpha_6$ ratio. It is possible that this larger difference is due to the neglect of correlation[4,5] between the two $2p$ electrons ejected in the calculation of the production probability of the KL^2 state or the contributions of other processes occurring in the same spectral region but not included in the theory.

C. First Satellite Group Structure

The satellite structure up to about 857 eV was analyzed by Moore and Chalklin[12] into five individual lines α'', α', α_3, α_3', and α_4, whose positions measured from $\alpha_{1,2}$ are plotted in Fig. 1. They also estimated the satellite line intensities of this group relative to α_4. On examining Fig. 1, it is not unreasonable to ascribe the weak intensities in the 852-eV region to the presence of the two lines α'' and α'. Since this spectrum is not as well resolved as Moore and Chalklin's,[12] no attempt was made to decompose this satellite structure. Experimental confirmation of their analysis will have to await a higher-resolution study of the neon *K* spectrum. Assuming *LS* coupling in the neon atom, Horak[24] has identified the five satellite lines as one-electron transitions from the double-hole $KL \rightarrow L^2$ multiplet. More recently, Hartmann and Hendel[25] have extended the energy calculations for $8 \leq Z \leq 12$, and have agreed with Horak's assignment for the first satellite multiplet. The satellite intensities also have been shown by Sawada[26] to be reasonably explained by multiplet theory and some internal conversion.

In *LS* coupling the five lines can be divided into two groups with their initial states being KL_1 (α'' and α_3') and $KL_{2,3}$ (α', α_3, and α_4). The line intensity ratio in the two groups are 1 : 3 for KL_1 and 1 : 5 : 9 for $KL_{2,3}$, with the ratio of group $KL_{2,3}$ to KL_1 estimated by Åberg[2] to be about 7. Horak[24] has observed that for $Z > 10$, only the $KL_{2,3}$ group of three lines is obtained. The magnesium *K* spectrum by Bonnelle and Senemaud[27] is a recent example. Although the α_3' line for $Z > 10$ could be obscured possibly by overlapping with the more intense α_3 and/or α_4, the absence[28] of α'' is not as easily rationalized.

In accord with the suggestion by Horak[24] that the absence of the KL_1 group for $Z > 10$ may involve excitation and deexcitation processes, we would like to make the following observations. Calculations[29] of the probability of electron shakeoff as a result of β^- decay shows a trend of a more rapid decrease of shakeoff in the L_1 than the $L_{2,3}$ subshells for $Z > 10$. This will result in proportionately fewer initial KL_1 states. Secondly, the addition of the *M* shell in $Z > 10$ opens up another possible channel for decay of initial KL_1 states by the nonradiative Coster-Kronig process $KL_1 \rightarrow KL_{23}M$, as suggested by Demekhin and Sachenko.[30] Satellites resulting from radiative transitions of the type $KL_{23}M \rightarrow L_{23}L_{23}M$ would be expected to be very weak and closer in energy to the $\alpha'\alpha_3\alpha_4$ group ($KL \rightarrow L^2$), than the $\alpha_5\alpha_6$ group ($KL^2 \rightarrow L^3$).

D. *Kx* Line

Moore and Chalklin[12] observed a line at 858 eV and identified it as $K\beta_1$ by its relative position with respect to the extrapolation of *K*-series satellites from elements $Z > 10$. There is no indication of a line at 858 eV (*Kx* in Fig. 1) at the counting-time level and resolution used to record this spectrum. The $K\beta_1$ line which is found in the Na^+ *K* spectra but not in the *K* spectra of fluorides, has recently been identified[31] as a cross transition between cation and anion. Therefore, if a line should be resolved at 858 eV with longer counting time, it should not be labeled $K\beta_1$, as given in Refs. 12 and 16. The origin of this elusive line is still uncertain.

In view of the considerable theoretical and experimental progress made in the past few years, it would be desirable to systematically reinvestigate at high resolution the *K*-series spectra for light elements.

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Energy of the H_2O Molecule Calculated by Many-Body Perturbation Theory*

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Many-body perturbation theory is used to calculate a value of (-76.48 ± 0.07) a.u. for the total energy of the H_2O molecule. This value is obtained with a basis set of bound and continuum orbitals of angular momentum s, p, d, f, and g, computed in a potential appropriate to neutral oxygen. Diagrams involving the net interaction with passive unexcited states, minus the single-particle potential, and the hydrogen nuclei are evaluated through third order, and estimates of higher-order diagrams are made. Both pair and three-body correlation-energy diagrams are included in this calculation.

I. INTRODUCTION

Our methods for applying the many-body perturbation theory of Brueckner[1] and Goldstone[2] to atoms have been discussed previously.[3] Recently,[4,5] these methods have also been applied to simple molecules, provided a single-center expansion could be used as a starting point. This paper describes a calculation of the total nonrelativistic energy of the H_2O molecule by many-body perturbation theory. This is the first triatomic molecule to be treated by many-body perturbation theory. A complete set of single-particle states appropriate for neutral oxygen[6] was used as a basis set for the evaluation of many-body diagrams.[3] Orbitals of angular momentum s, p, d, f, and g were included in this basis set. With this choice of basis set, the most important classes of diagrams are those containing the net interaction with passive unexcited states, minus the single-particle potential, and the hydrogen nuclei. These diagrams were evaluated in first, second, and third order; and estimates of higher-order contributions are made. Pair and three-body correlations were also included. The energy which we obtained is -76.48 a.u. Our methods of calculation and numerical results are given in Sec. II, and a discussion of the results is given in Sec. III.

II. METHODS AND RESULTS

A. Methods

Using the Born-Oppenheimer approximation and neglecting relativistic effects, the Hamiltonian which determines the electronic structure of H_2O can be written in a.u. as

$$\mathcal{H}=\frac{16}{R_{\mathrm{OH}}}+\frac{1}{R_{\mathrm{HH}}}-\sum_{i=1}^{10}\left(\frac{\nabla_i^2}{2}+\frac{8}{r_i}+|\vec{r}_i-\vec{R}_A|^{-1}+|\vec{r}_i-\vec{R}_B|^{-1}\right)+\sum_{i<j=1}^{10}|\vec{r}_i-\vec{r}_j|^{-1}\,, \tag{1}$$

where $\vec{r}_i$ is the position vector of the ith electron relative to the oxygen nucleus as the origin, and $\vec{R}_A$ and $\vec{R}_B$ are the position vectors of the hydrogen nuclei relative to this origin. The equilibrium oxygen-hydrogen bond length is denoted by R_{OH}. It has been measured experimentally to be 1.8111 a.u.[7] The distance R_{HH} is determined by R_{OH} and the equilibrium bond angle; and it has a value of 2.8631 a.u. for the experimentally measured bond angle of 104° 27′.[7]

In order to apply perturbation theory, we write the Hamiltonian as

$$\mathcal{H}=\mathcal{H}_0+\mathcal{H}'\,, \tag{2}$$

with

$$\mathcal{H}_0=\frac{16}{R_{\mathrm{OH}}}+\frac{1}{R_{\mathrm{HH}}}+\sum_{i=1}^{10}\left(-\frac{\nabla_i^2}{2}-\frac{8}{r_i}+V(r_i)\right)\,, \tag{3}$$

$$\mathcal{H}'=\sum_{i<j=1}^{10}|\vec{r}_i-\vec{r}_j|^{-1}$$