

Systematics of autoionization widths of doubly excited states of atoms

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We analyze the autoionization widths of doubly excited states of two-electron atoms using the $(K, T)^A$ classification scheme introduced previously. It is shown that the widths of all the states along each truncated rotor series are comparable except for the last two states. This novel systematic is interpreted qualitatively in terms of the molecular or the correlated motion of the two electrons, except for the last two states which are explained in terms of the independent-electron model.

The first photoabsorption spectra of doubly excited states of helium below the $N=2$ threshold of He^+ ions were taken in 1963 (Ref. 1). Two series, one broad and another very narrow, were observed. This striking difference in the autoionization widths between the two series was interpreted as a first indication of the failure of the independent-electron model. According to Cooper, Fano, and Prats,² the two series, instead of being designated as $2snp$ and $2pns$ series, are to be replaced by the two linear combinations $2snp + 2pns$ and $2snp - 2pns$, which are called the $+$ and $-$ series.

Since these early investigations, our understanding of doubly excited states has been greatly enhanced over the years by the many theoretical models and computational methods developed. It is well established now that a certain class of doubly excited states display molecular rovibrational normal modes with the same supermultiplet structure of energy levels of a triatomic molecule.³⁻⁵ These studies treat doubly excited states as stable and deal only with their wave functions and energy levels. In this communication, we address instead the systematics of their autoionization widths. This can be achieved only for states classified by the new schemes.

One such a classification scheme for all doubly excited states of two-electron atoms was given previously by one of us.⁴⁻⁵ In this scheme, each doubly excited state, in addition to the usual L , S , and π , is designated by a symbol ${}_n(K, T)_N^A$, which replaces the $nLNl'$ notations of the independent electron model. In this notation, n and N denote the principal quantum numbers of the outer and the inner electrons, respectively. The quantum numbers K , T , and A replace l and l' ; they are used to characterize the correlation of the two electrons. The procedure for assigning K , T , and A quantum numbers have been described elsewhere.⁴⁻⁶ In this scheme, only states with $A = \pm 1$ display rovibrational normal modes.^{4,5} The quantum number K has to do with angular correlation, with large positive K corresponding to two electrons tending to stay on the opposite sides of the nucleus and negative K for the two electrons to stay on the same side of the nucleus. The quantum number T is the projection of L along the interelectronic axis. These approximate quantum numbers (or labels) can be related to other approximate quantum numbers used for triatomic molecules⁷ or to those in the linear diatomic model⁸ of doubly

excited states.

There are a number of spectral regularities when doubly excited states are thus classified. For states designated with $A = +1$ or $A = -1$, the spectra display: (1) the rotor structure, meaning that states with the same K , T , and A have rotorlike energies $BL(L+1)$ vs L ; (2) the T -doubling, similar to the Λ -doubling in molecules since states with identical K , T , A , and L and opposite π and S form tight degenerate doublets. However, there are limitations to these molecular models.⁷ First, states which are similar to singly excited states do not exhibit molecular behavior^{4,5} in their spectra. These states have been designated with $A=0$. Second, the rotor series is truncated.

The discussion of autoionization widths has been quite sparse. Experimentally very few have been measured.⁹ Theoretical calculations have been scarce,¹⁰⁻¹² especially for doubly excited states below the higher N thresholds. The existing data are still not adequate for us to explore their systematics. Some of the widths have been calculated by us. Our methods of calculations are quite simple. The "bound" state parts are calculated by the configuration-interaction method and the continuum states are represented by pure Coulomb wave functions. The width of each state is then obtained by evaluating the dielectronic interaction matrix elements between the bound and the continuum states. To ensure the reliability of our method we apply our calculations to positive ions for $Z \geq 6$ only. Comparison of our results with others¹⁴ for a number of states indicates that our calculations for widths are reliable to better than 20%. These results are adequate for the purpose of analyzing the systematics of the widths. For the analysis of the widths the states are labeled according to the K , T , and A quantum numbers for each n and N . In the following we address the observed systematics.

(1) *The variation of autoionization widths along the rotor series.* In Fig. 1(a) we display the widths along the rotor series for the intrashell states of H^- for $(K, T) = (N-1, 0)$ with $N=3-6$. The rotor series terminates at $L_{\max} = 2(N-1)$ at each N for this group. Note that for $N=3$, the widths for the first three members of the rotor series are comparable. The ${}^3F^0$ state, next to the last of the series, is very narrow, while the last member, ${}^1G^e$, is broad again. This pattern ap-

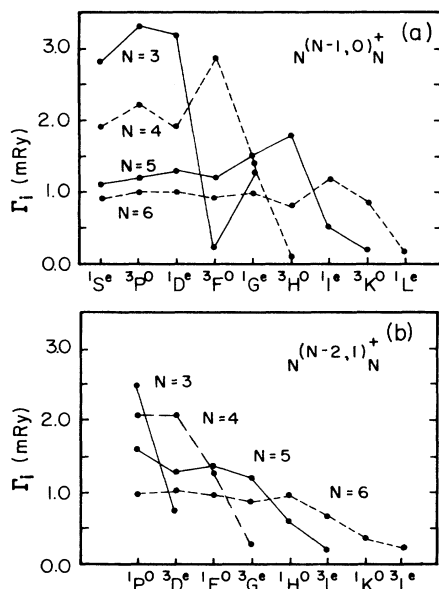


FIG. 1. Autoionization widths of H^- vs the angular momentum along the rotor series. (a) For the $N(N-1,0)_N^+$ rotor series; (b) for the $N(N-2,1)_N^+$ rotor series. Data from Refs. 10.

pears for higher N as well. In this figure the data for the last member of each of the rotor series for $N \geq 4$ are not available, but we expect them to be large (see other examples below).

In Fig. 1(b) we show a similar plot for the widths of the intrashell states for $(K, T) = (N-2, 1)$, $N=3-6$. The rotor series in this case starts with $L=1$ and terminates at $L_{\max} = 2(N-1) - 1$. We note that the widths of the first few members of the rotor series are about equal. The next to the last member of the rotor series is very narrow; the last one is not available, but we expect it to be large. This striking regularity of widths along the rotor series has been observed for other values of (K, T) (see Figs. 2 and 3 below).

(2) *The widths along an isoelectronic sequence.* In Table I we show the autoionization widths for $Z=1, 2, 6, 7$, and

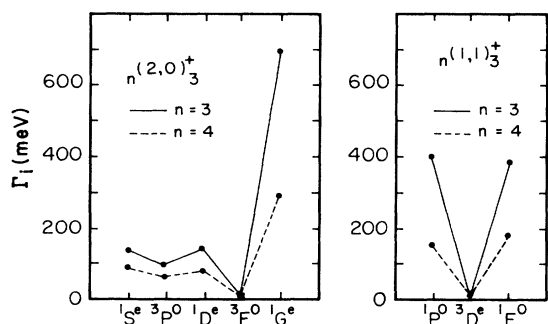


FIG. 2. Autoionization widths for the $n(2,0)_3^+$ and $n(1,1)_3^+$ rotor series for intrashell states ($n=3$) and intershell states ($n=4$) of C^{4+} obtained from the present calculation.

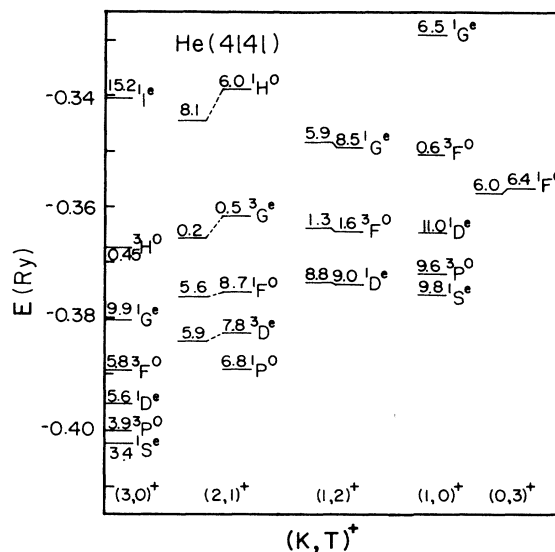


FIG. 3. Energy levels (horizontal lines) and autoionization width (entries above each line, in units of 10^{-3} Ry) of doubly excited states of He below the He^+ ($N=4$) thresholds arranged using the $(K, T)^A$ classification scheme. Only intrashell states are shown. Data from Ref. 10(d). For the pair of T -doubling states only the designation of $\pi = (-1)^L$ state is given. Data for the $(2,1)^+ 3P^e$ are not available. From the table one expects that the energy of this state is about -0.391 Ry, and the width is about 6.0×10^{-3} Ry.

8 along the rotor series for $n=N=3$, $(K, T) = (2, 0)$ and $(1, 1)$. We note that the pattern of the widths along the rotor series for each Z is identical to those shown for H^- in Fig. 1 and the width for each state becomes nearly independent of Z for higher Z . We also note that the width for the last member of rotor series for higher Z is very large.

(3) *The widths along the rotor series of intershell states.* According to the classification scheme of Ref. 4, intershell states of a Rydberg series are designated by $n(K, T)_N^A$ for $n > N$. The variation of widths along the ro-

TABLE I. Autoionization widths (in 10^{-3} Ry) along the isoelectronic sequence for the $3(2,0)_3^+$ and $3(1,1)_3^+$ rotor series. Results from Refs. 10(c), 11(b), 12, and 13.

| | H^- | He | C^{4+} | N^{5+} | O^{6+} |
|--------------|-------|------|----------|----------|----------|
| $3(2,0)_3^+$ | | | | | |
| $1S^e$ | 2.8 | 6.0 | 9.5 | 10.0 | 10.0 |
| $3P^o$ | 3.3 | 5.9 | 7.5 | 7.8 | 7.7 |
| $1D^e$ | 3.2 | 10.5 | 12.9 | 12.9 | 13.2 |
| $3F^o$ | 0.2 | 0.05 | 0.06 | 0.08 | 0.09 |
| $1G^e$ | 1.6 | 13.4 | 47.0 | 50.0 | 54.0 |
| $3(1,1)_3^+$ | | | | | |
| $1P^o$ | 2.5 | 14.0 | 28.6 | 29.5 | 30.8 |
| $3D^e$ | 0.7 | 1.4 | 1.9 | 1.6 | 2.0 |
| $1F^o$ | ? | 6.5 | 24.0 | 25.0 | 28.0 |

TABLE II. Comparison of autoionization widths between $A=+1$ and $A=-1$ states for fixed K , T , $N=3$, $n=4$ along the rotor series, for $Z=6$. Results are from the present calculation. The widths are in meV.

| $(K, T)=(2,0)$ | | | | $(K, T)=(1,1)$ | | | | | | | |
|----------------|-----|--------|---------|----------------|-----|--------|---------|---------|----|-----|---------|
| $A=+1$ | | $A=-1$ | | $A=+1$ | | $A=-1$ | | | | | |
| $^1S^e$ | 90 | 1.4 | $^3S^e$ | $^1P^o$ | 155 | 4.5 | $^3P^o$ | $^3P^e$ | 85 | 0.2 | $^1P^e$ |
| $^3P^o$ | 59 | 1.5 | $^1P^o$ | $^3D^e$ | 11 | 3.4 | $^1D^e$ | $^1D^o$ | 2 | 0.7 | $^3D^o$ |
| $^1D^e$ | 78 | 2.1 | $^3D^e$ | $^1F^o$ | 42 | 6.1 | $^3F^o$ | $^3F^e$ | 15 | 2.2 | $^1F^e$ |
| $^3F^o$ | 2 | 3.8 | $^1F^o$ | | | | | | | | |
| $^1G^e$ | 293 | 0.9 | $^3G^e$ | | | | | | | | |

tor series observed above for intrashell states also applies to intershell states which have the same K , T , A , and N . This is shown in Fig. 2 where we show the widths calculated by us for C^{4+} for the $(K, T)=(2,0)$, and $(1,1)$ rotor series, for the case of $N=3$, and for both the intrashell states ($n=3$) and intershell states ($n=4$).

(4) *The widths of "vibrationally" excited rotor series.*

The rotor series which have smaller K corresponding to vibrationally bending molecular excited states. In Fig. 3 we show the widths of the $4l4l'$ intrashell states of He arranged according to the $(K, T)^A$ classification scheme. Short horizontal lines indicate each level's position while the entry above each line gives its width. For $T \neq 0$, doublings are shown. We note that along each rotor series, the width of the second to the last member of the rotor series is always much smaller, while the last member of the series is always broad. Such pattern for each rotor series is again identical to those shown in Figs. 1 and 2.

(5) *The widths of + and - series.* The introduction of the so-called + and - series by Cooper, Fano, and Prats² in the 1960s implied that states belonging to the + series have large widths and states belonging to the - series have small widths. This result is quite general.¹⁵ In Table II we compare the widths along the rotor series for intershell states which have identical K and T but different A ($A=+1$ and -1). The data are for $n=4$, $N=3$ of C^{4+} , $(K, T)=(2,0)$ and $(1,1)$, with the latter being separated into states where $\pi=(-1)^L$ and $\pi=(-1)^{L+1}$, respectively. We again note the strong contrast of the widths between the + and - states which have identical K and T .

(6) *The autoionization widths of doubly excited states of Be-like ions.* For doubly excited states which have a non-Coulombic ionic core, the energy levels deviate from

the rotor structure¹⁶ (the relative ordering remains the same), but their autoionization widths,¹⁷ when ordered according to the $(K, T)^A$ classification scheme, show similar patterns as those with two-electron only. In Table III we compare the widths of doubly excited states of C^{4+} and of O^{4+} for the cases where $n=N=3$, $(K, T)=(2,0)$ and $(1,1)$. We again note that the widths along the rotor series vary in the same way as those shown in Fig. 1, and that the width of each state is not influenced by the presence and the structure of the ionic core.

The examples above show two major features in the systematics of widths of doubly excited states along the rotor series. The first is that the widths of the first few members of a rotor series are comparable. This can be explained qualitatively. For example, consider the ${}_3(2,0)_3^+$ rotor series. Autoionization tends to favor invariance in A and invariance in the vibrational quantum number ($\nu=N-K-1$), i.e., $\Delta A=0$ and $\Delta \nu=0$ (Ref. 7). (In hyperspherical terminology $\Delta \nu=0$ preserve the nodal structure in angle θ_{12} , see Ref. 4.) This means that each state in this rotor series tends to autoionize to the $(1,0)_2^+$ continuum states. However, the truncation of the rotor series restricts the maximum L for the $(1,0)_2^+$ channels to $L=2$. Thus, the first three states ($^1S^e$, $^3P^o$, and $^1D^e$) of the ${}_3(2,0)_3^+$ rotor series are allowed to autoionize to the $(1,0)_2^+$ channel and condition $\Delta A=0$ and $\Delta \nu=0$ can be satisfied. Thus the widths of all these states tend to be comparable. On the other hand, the two uppermost states ($^3F^o$ and $^1G^e$) of the ${}_3(2,0)_3^+$ rotor series cannot autoionize to the $A=+1$ channels and $\Delta A=0$ cannot be satisfied. Thus the last two members of the rotor series behave differently. We note that the last two members of each rotor series cannot decay to the $A=+1$ continuum

TABLE III. Comparison of widths (in meV's) of doubly excited states of C^{4+} (from the present calculation) and of O^{4+} (from Ref. 17).

| | $(K, T)=(2,0)^+$ | | | $(K, T)=(1,1)^+$ | | | | |
|---------|------------------|----------|---------|------------------|----------|----------|----------|-----|
| | C^{4+} | O^{4+} | | C^{4+} | O^{4+} | C^{4+} | O^{4+} | |
| $^1S^e$ | 142 | 79 | $^1P^o$ | 399 | 393 | $^3P^e$ | 148 | 199 |
| $^3P^o$ | 99 | 105 | $^3D^e$ | 19 | 32 | $^1D^o$ | 4 | 17 |
| $^1D^e$ | 138 | 240 | $^1F^o$ | 385 | 353 | $^3F^e$ | 101 | 102 |
| $^3F^o$ | 5 | 3 | | | | | | |
| $^1G^e$ | 676 | 724 | | | | | | |

states is *universally true*.

The striking difference in the width for the last two members of the series, on the other hand, can be explained using the independent electron model. We observed that the energies and widths of the last two members of each rotor series are usually adequately calculated using *single configuration* wave functions. For example, the widths of ${}^3F^o(3p3d)$ and ${}^1G^e(3d^2)$ states (both have $K=2$ and $T=0$) for C^{4+} calculated with a single configuration are 0.37 and 77.6, in units of 10^{-3} Ry, as compared to the accurate values of 0.06 and 47, in the same units, as shown in Table I. The large contrast was traced to the strong cancellation of Slater integrals for the former and strong enhancement for the latter. We have checked a few other cases along the rotor series

such as those for $(K, T)=(2,1)$, $n=N=4$ of He to confirm this statement.

In summary we have shown that the widths of doubly excited states display striking regularities along the rotor series if the states are grouped using the (K, T) ⁴ classification scheme of Lin.⁴ The origin of the regularity was explained qualitatively. Quantitative interpretations in terms of wave functions formulated in hyperspherical coordinates are currently underway.

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