

K-SHELL EXCITED LI-LIKE IONS: ELECTRON SPECTROSCOPY OF THE DOUBLET TERM SYSTEM

M. MACK and A. NIEHAUS

Fysisch Laboratorium, Rijksuniversiteit Utrecht, Princetonplein 5, 3584 CC Utrecht, The Netherlands

Electron energies of autoionising doubly excited $1s2ln'l'$ ($n' = 2, 3$) L-states of Li-like ions are reported for C IV, N V, and O VI. The autoionising states are produced in electron capture reactions from two-electron targets (He, H₂) by slow ($E_{\text{ion}} \leq 5$ keV/amu) charge selected ion beams. In this way, differentiation of doublet and quartet terms is possible and the charge state of the emitting ion is unambiguously defined. Comparison is made with available data from other experiments and with relativistic atomic structure calculations. A multiconfiguration variational approach as well as a Z -expansion calculation are found to give better agreement with experimental data than a multiconfigurational Dirac-Fock method.

1. Introduction

During the last few years considerable efforts, both theoretically and experimentally, were made to establish energy values and transition rates for the Li-like doubly excited ($1s2ln'l'$) states. Most of the experimental work has been confined to the quartet states, which are accessible to optical spectroscopy due to their high fluorescence yield. Little is known about the doublet system, where the dominant decay mode is autoionisation. Electron spectroscopy on fast ion beams has been performed with sufficient accuracy (± 0.5 eV) only for autoionisation of B III and C IV ([1–3]); the autoionising decay of FVII has been determined with insufficient resolution only [4], and the measurement suffers from an error in energy calibration (compare refs. [5,6]). For some selected states which decay as well by K X-ray emission K X-ray wavelengths are available either measured in laser produced plasmas [7,8] or on fast beams [9,10]. In this article we report electron energies of autoionising doublet states $1s2/2l'$ and $1s2s3l'$ of C IV, N V and O VI.

2. Experimental method

The autoionising states are produced in electron capture reactions from the interaction of a slow ($E_{\text{ion}} \leq 5$ keV/amu) charge selected beam of multiply charged ions with thin gas targets (typically $\sigma nl < 5 \times 10^{-4}$, with σ the cross section, n the target density, l the interaction length). The emitted electrons are detected by an electrostatic cylindrical mirror analyzer (CEMA) which accepts electrons under an angle of $50^\circ \pm 2^\circ$ with respect to the beam axis. The spectrometer resolution is typically $\Delta E_{\text{rwhm}}/E \leq 5 \times 10^{-3}$. The actual reso-

lution is limited by Doppler broadening. However, due to the high spectral resolution a substructure is observed in the Doppler-broadened peaks: there appear two maxima with a sharp dip in between (fig. 1). The two maxima are due to the finite divergence of the ion beam (maximum divergence angle ± 10 mrad); they correspond to the cases that the velocity component of the ion in the direction of the emitted electron is at its maximum or minimum, i.e. electron and emitting ion moving in the same or in opposite azimuthal directions, respectively. The dip in between corresponds to a Doppler-angle of 50° precisely, and it is this well-defined

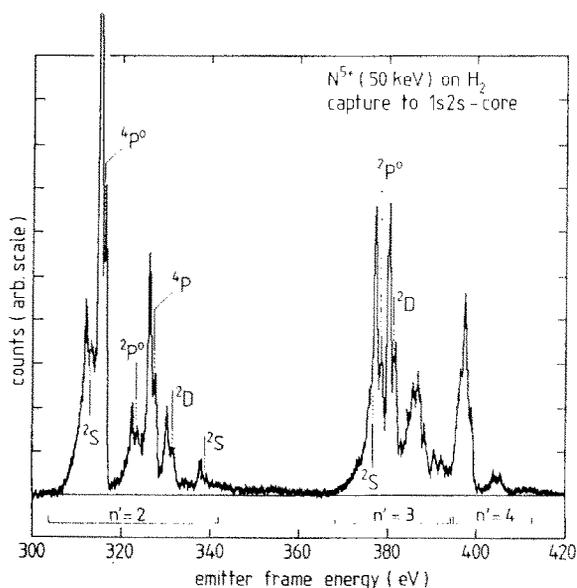


Fig. 1. Autoionising K LX-decay of N^{4+} ($1s2ln'l'$) produced in collisions of N^{5+} ($1s2s$)³S with H₂; collision energy 50 keV.

energy position which is used for evaluation. Where peaks started partly to overlap, the precise peak position was determined by a fit of the peak shape (taken from well isolated peaks) to our spectra. Note that since we work with slow ion beams the Doppler-shift amounts only to a fraction of the emitter rest frame energy and is therefore less a source of uncertainty than with fast beams [1,3].

Energy calibration was done as follows: for a CEMA the ratio of voltage difference between the cylinders (U) and the electron energy (T)

$$k = T/U, \quad (1)$$

is in principle fixed by the geometrical dimensions used [11]. Slight deviations from this value may occur because of field imperfections. For our geometry we derive (using the values given by Draper and Lee [11])

$$k_{\text{geo}} = 1.5196 \pm 3 \times 10^{-4}. \quad (2)$$

To assess the unknown influence of field penetrations at the large open entrance and exit slits to the inner cylinder, we calibrated our relative energy scale to the differences of the (center of gravity) energies of the peak $1s2s2p\ ^4P^0$ in C IV, N V and O VI. As is shown in table 1, the three most recent theoretical calculations agree on these differences within ± 50 meV. The calibration constant had to be slightly raised in order to match these differences:

$$k_{\text{calib}} = 1.002k_{\text{geo}} = 1.5230 \pm 1.5 \times 10^{-3}. \quad (3)$$

The relative scale obtained in this way was then fixed to the $^4P^0$ -value for C IV which has been recommended as a calibration point [3]. Actually, our unfixed energy scale met this value within 50 meV.

Let us briefly comment on some special features of our method: we use two-electron targets (He, H₂); Li-like ions can then be produced either via double capture by H-like ions (C⁵⁺, N⁶⁺, O⁷⁺), or via single capture by core-excited He-like ions (configuration $1s2s\ ^3S$). We have demonstrated that the spin of the captured electrons is not changed in the collision [12], which means that double capture from the singlet targets He or H₂ can only yield doublet states. Quartet terms are popu-

Table 1

Differences in term energies (eV) for the $1s2s2p\ ^4P^0$ state of different ions; the third column is the difference of the first two columns and given for completeness only. The fine structure splittings of [18] have been used where necessary to obtain center of gravity energies.

	C IV–N V	C IV–O VI	N V–O VI
ref. [13]	86.367	186.371	100.017
ref. [17]	86.332	186.330	99.998
ref. [16]	86.350	186.420	100.070
this work	86.29 ± 0.1	186.44 ± 0.1	100.15 ± 0.1

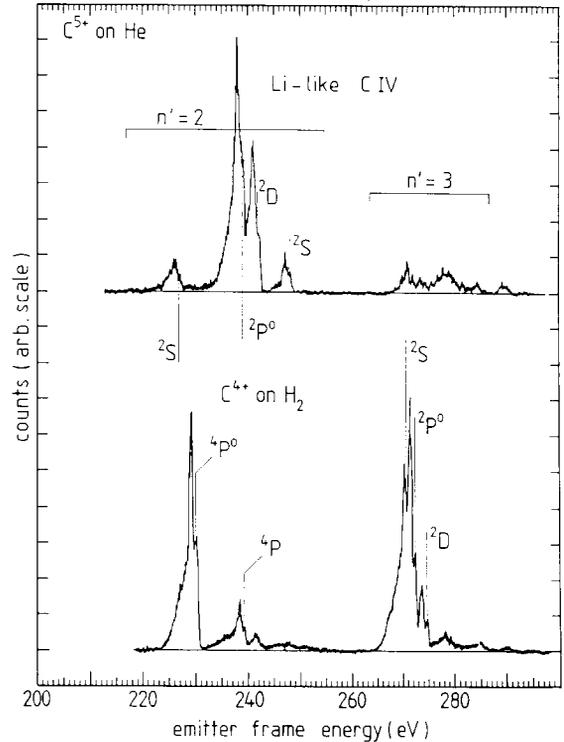


Fig. 2. Spin-conserving capture allows separation of otherwise blended lines: KLX-decay of C³⁺ ($1s2ln''$), produced by double capture from He (projectile C⁵⁺, 62.5 keV) or by single capture from H (projectile C⁴⁺, 40 keV).

lated in single capture reactions, but we have shown [12] that the quartet states $1s2s3l''$ do not autoionise at all, which means we have to deal only with the $1s2p^2\ ^4P$ and $1s2s2p\ ^4P^0$ quartet states. Generally, double capture by the core excited He-like ions is very weak and the decay of the resulting Be-like ions does not interfere with the decay of the Li-like ions. The only exception is the system C⁴⁺ – He, where double capture is dominant. The peaks due to Be-like ions can be easily identified because they appear in the spectra produced by H-like ions only when a multi-electron target like neon or argon is used.

With this approach: two-electron targets, two primary charge states, and at least two different targets the charge state of the emitting ion can be unambiguously identified. Moreover, spin selective capture allows separation of peaks which would otherwise be blended, such as $1s2s^2\ ^2S$ and $1s2s2p\ ^4P^0$ or $[1s(2s2p)^1P]^2P^0$ and $1s2p^2\ ^4P$, as is shown in fig. 2 for the C IV ion.

3. Results

The electron energies (which correspond to term energies above the $1s^2$ He-like ground state, because the

Table 2

Measured electron energies (eV); the value for C IV $1s2s2p\ 4P^0$ is used as common calibration point and it fixed to the theoretical value given by Chung [3]

	C IV	N V	O VI
$1s2s2p\ 4P^0$	[229.639]	315.93	416.08
$1s2s^2\ 2S$	227.00 ± 0.1	312.88 ± 0.7	412.67 ± 0.08
$1s(2s2p)^3P\ 2P^0$	235.15 ± 0.3	323.23 ± 0.08	424.81 ± 0.08
$1s(2s2p)^1P\ 2P^0$	238.90 ± 0.07	327.00 ± 0.15	429.38 ± 0.15
$1s2p^2\ 2D$	241.93 ± 0.1	331.18 ± 0.13	434.31 ± 0.08
$2S$	248.10 ± 0.1	338.72 ± 0.1	442.92 ± 0.08
$1s2s^3S3s\ 2S$	270.00 ± 0.15	376.80 ± 0.15	500.40 ± 0.15
$1s2s^3S3p\ 2P$	271.95 ± 0.1	378.18 ± 0.15	501.90 ± 0.1
$1s2s^3S3d\ 2D$	274.33 ± 0.1	381.23 ± 0.1	505.57 ± 0.1

autoionisation proceeds to the $1s^2\epsilon l_\epsilon$ continuum) are obtained from the spectra in the following way: the energy difference between the peak considered and the $1s2s2p\ 4P^0$ -peak is added to the energy of $4P^0$ (see table 1), which is an averaged value from more than ten measurements. We have corrected our energies for pos-

sible postcollision-interaction shifts, which will occur due to the very short lifetimes of some doublet states; for this correction we used the lifetimes as calculated by Chen (ref. [13]); for the quartet states his lifetimes are in good agreement with experimentally determined lifetimes [14]. The resulting correction is largest for the $1s2p^2\ 2D$ state and does not exceed 100 meV; for states $1s2s3l'$ it is negligible compared to our error bars.

Error bars refer to the difference in energy between the peak considered and the state $4P^0$. They are calculated by

$$e^2 = 2(d/2)^2 + s^2 + c^2, \tag{4}$$

where

e – the uncertainty of the energy difference between the term energy and the energy of $1s2s2p\ 4P^0$,

d – the scanning step of the cylinder voltage multiplied by k_{calib} ,

s – one standard deviation of the average of usually more than five different measurements,

c – the error inherent to the calibration of the relative energy scale (eq. (3)).

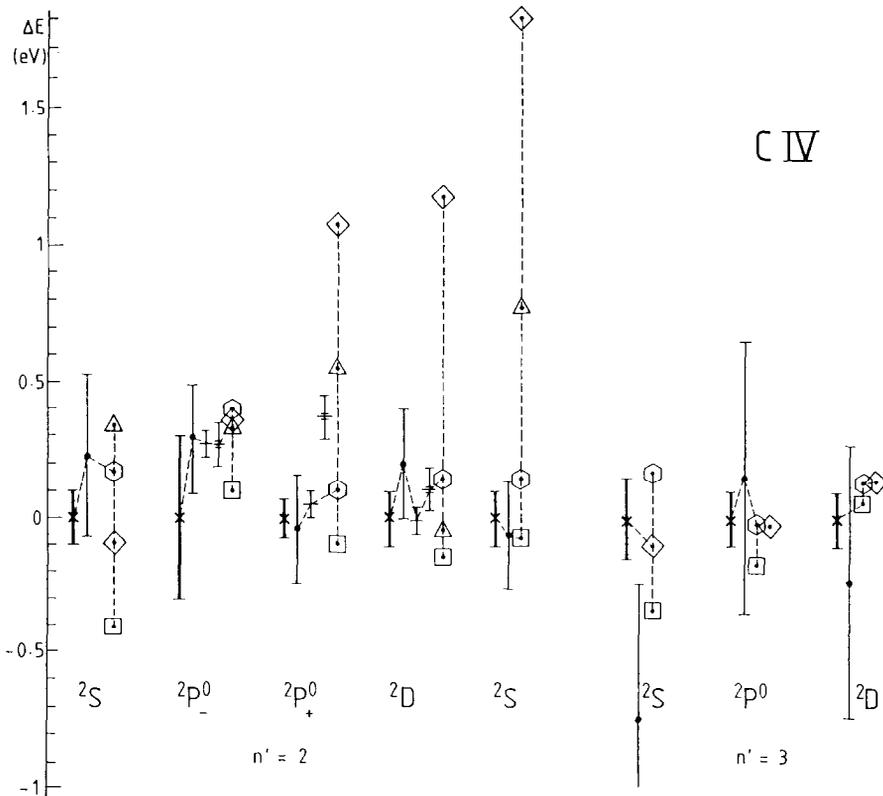


Fig. 3. Term energies from other work compared to our measurements. The vertical scale gives the published energy minus our values. Shown are experimental values from electron spectroscopy, * this work, † ref. [3]; from optical spectroscopy, ‡ ref. [8], † ref. [7], · ref. [10] and theoretical values, Δ ref. [15], □ ref. [16], ⊙ ref. [3], ◇ ref. [13]; $2P^0_-$ denotes $[1s(2s2p)^3P]^2P^0$, $2P^0_+$ means $[1s(2s2p)^1P]^2P^0$. Dashed lines only to guide the eye.

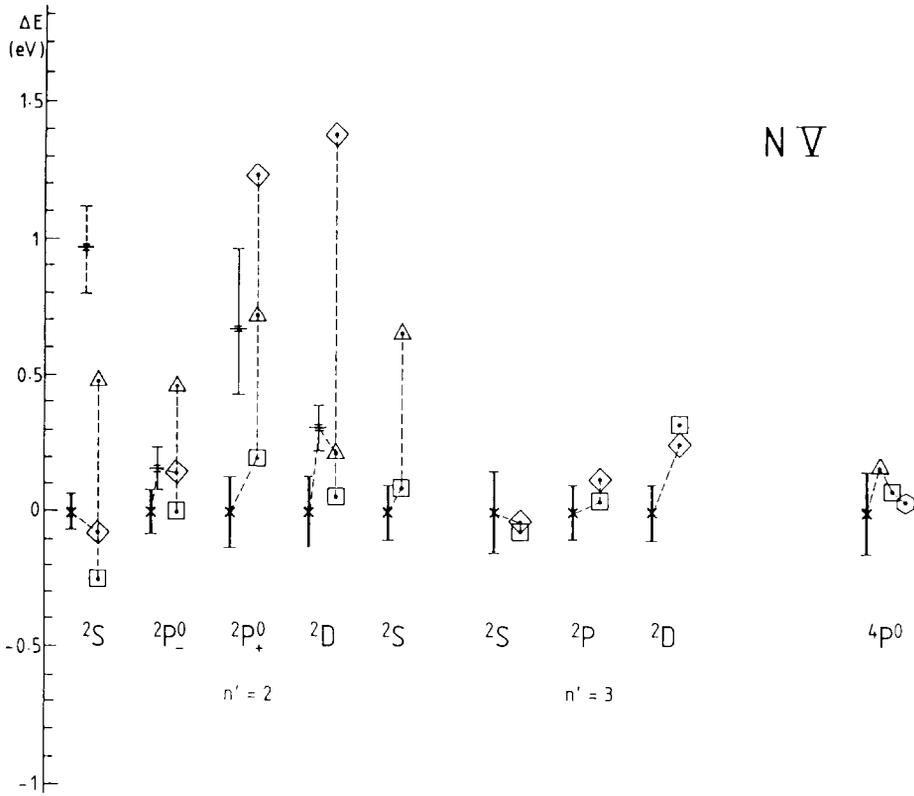


Fig. 4. Same as fig. 3.

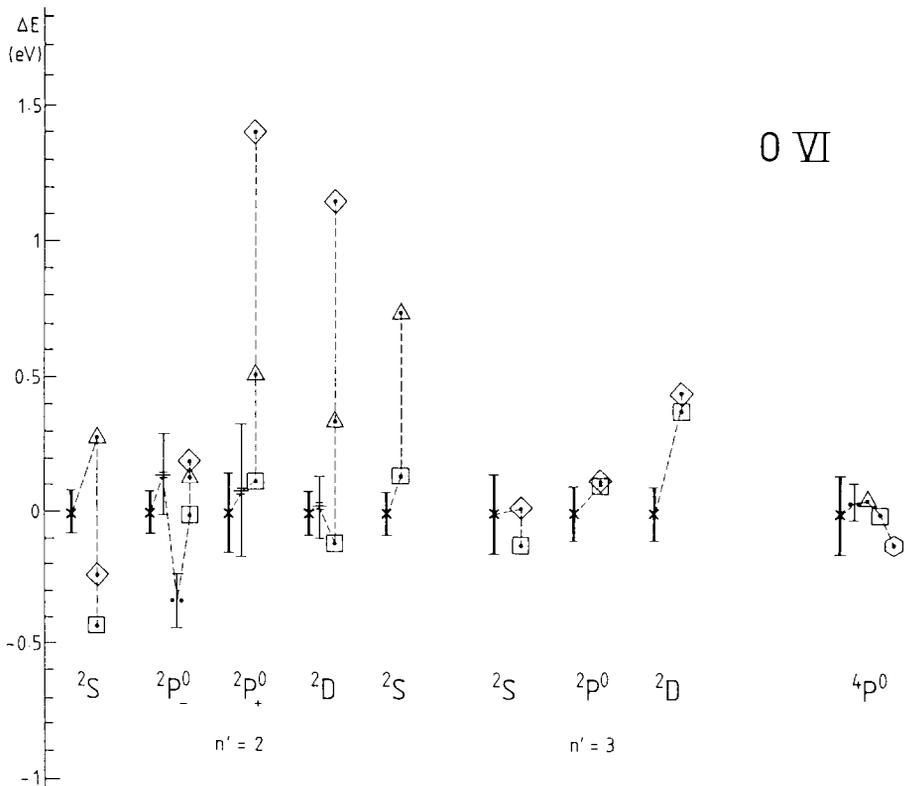


Fig. 5. Same as fig. 3.

Our results are presented in table 2 and compared with other experimental and theoretical work in figs. 3–5.

4. Discussion

For C IV, excellent agreement is obtained with the energies measured by Bruch et al. (ref. [3]); our $^2P^0(1)$ value is certainly less precise due to the very low intensity it has for carbon. From the values of ref. [3], refs. [7,8], together with our energies we have formed a weighted average (table 3), which should be regarded as the best set of experimental values available for C IV. For all systems, good agreement is obtained between the (absolute) energies derived from K X-ray wavelengths and our energy values, which means that the energy scale we use agrees with an absolute energy scale within the common error bars. The 2S -value in N V derived from optical spectroscopy [8] is given for completeness only: in ref. [8] it is stated that it should be less accurate.

Theoretical calculations with which we compare are a semiempirical Hartree–Fock calculation with relativistic corrections by Gabriel [15], a calculation using a Z -dependent perturbation theory with relativistic effects included by Vainshtein and Safronova [16], a relativistic multiconfiguration variational method developed by Chung [2,3,17] and a very recent multiconfigurational Dirac–Fock calculation by Chen [13], fully relativistic and including QED corrections. The absolute values of the latter are in disagreement with all available experimental data. In figs. 4 and 5 the calculation by Chen is shown recalibrated to the $^4P^0$ -values given by Chung

[17]: then the states with a 3S -core agree quite well with the experimental energies, but for all other states the differences remain large (up to 2 eV). We suggest that an error may have occurred either in the calculation of the final states (the calculation gives transition wavelengths) or that correlation effects have not been accounted for properly. It has been noted previously [17], that multi-configurational Dirac–Fock (MCDF) calculations cannot easily compute correlation effects to high accuracy. Chung [17] states, that a nonrelativistic variational method would be most suited for calculating correlation effects; indeed, his calculation for C IV is in very close agreement with the experimental spectrum (see table 3).

The Z -expansion method [16] yielded values nearly as close to experiment, except for the $1s2s^2\ ^2S$ state, which is off by about 0.5 eV in all systems. This was quite surprising, because in ref. [16] it was stated that the values given by Gabriel [15] should be superior, which is obviously not the case. Actually, the values of Gabriel compare quite badly with experiment.

So far, we have no explanation for the difference between theory and experiment seen for the $1s2s3d\ ^2D$ -state in N V and O VI. Blending by a quartet state ($1s2s3d\ ^4D$) can be excluded.

5. Conclusions

We have determined term energies above $1s^2$ for the doubly excited doublet states $1s2l2l'$ and $1s2s3l'$ of the Li-like ions C IV, N V, O VI. Typical accuracy is ± 100 meV. For most of the determined states in N V and O VI no experimental data are available for comparison; where we can compare with other work good agreement is found.

The recent relativistic MCDF calculation of Chen [13] is found to disagree severely with all experimental data; recalibrating his energies to the $^4P^0$ -values given by Chung [17] gets only the states with a 3S -core close to experiment. For C IV the multiconfiguration variational method used by Chung [17] yields term energies very close to the experimental values; for all systems considered, the Z -expansion method calculation by Vainshtein and Safronova is in good agreement with experiment as well, except for $1s2s^2\ ^2S$. Our results indicate that for the low Z -values treated here and as long as one considers only center of gravity energies, correlation effects will dominate any effects due to relativistic corrections.

This work is part of the research program of the Stichting voor Fundamenteel Onderzoek der Materie (FOM) and was made possible by financial support from Nederlandse Organisatie voor Zuiver-Wetenschappelijk Onderzoek (ZWO).

Table 3

Weighted average of doublet term energies (eV) for the KLL-, KLM-decay in C IV compared to theoretical values. Averaged are the experimental values of refs. [3,7,8] and this work

Weighted average experimental spectra C IV			Theory	
			ref. [3]	ref. [16]
$1s2s2p$	$^4P^0$	Calibrated to ref. [3]	229.64	229.66
$1s2s^2$	2S	227.06 ± 0.09	227.17	226.59
$1s(2s2p)^3P$	$^2P^0$	235.40 ± 0.04	235.55	235.25
$1s(2s2p)^1P$	$^2P^0$	238.92 ± 0.04	239.01	238.81
$1s2p^2$	2D	241.98 ± 0.04	242.08	241.79
$1s2p^2$	2S	248.25 ± 0.10	248.25	248.03
$1s2s^3S3s$	2S	270.70 ± 0.15	270.91	270.40
$1s2s^3S3p$	2P	271.98 ± 0.10	271.93	271.78
$1s2s^3S3d$	2D	274.29 ± 0.10	274.47	274.39

References

- [1] M. Rødbro, R. Bruch and P. Bisgaard, *J. Phys.* B12 (1979) 2413.
- [2] K.T. Chung and R. Bruch, *Phys. Rev.* A28 (1983) 1418.
- [3] R. Bruch, K.T. Chung, W.L. Luken and J.C. Culberson, *Phys. Rev.* A31 (1985) 310.
- [4] J. Newcomb, T.R. Dillingham, J. Hall, S.L. Varghese, P.L. Pepmiller and P. Richard, *Phys. Rev.* A29 (1984) 82. The K-X-electron energies given in this reference must be raised by 8.3 eV in order to match the K X-ray wavelengths given in [5,6].
- [5] M. Terasawa, T.J. Gray, S. Hagmann, J. Hall, J. Newcomb, P. Pepmiller and P. Richard, *Phys. Rev.* A27 (1983) 2868.
- [6] I. Martinson, B. Denne, J.O. Ekberg, L. Engström, S. Huldt, C. Jupén, U. Litzén, S. Mannervik and A. Triqueiros, *Phys. Scripta* 27 (1983) 201.
- [7] N.J. Peacock, M.G. Hobby and M. Galanti, *J. Phys.* B6 (1973) L298.
- [8] P. Nicolosi and G. Tondello, *J. Opt. Soc. Am.* 67 (1977) 1033.
- [9] R. Bruch, K.T. Chung, E. Träbert, P.H. Heckmann, B. Raith and H.R. Müller, *J. Phys.* B17 (1984) 333.
- [10] D.L. Matthews, W.J. Braithwaite, H.H. Wolter and C.F. Moore, *Phys. Rev.* A8 (1973) 1397.
- [11] J.E. Draper and C.Y. Lee, *Rev. Sci. Instr.* 48 (1977) 1397.
- [12] M. Mack and A. Niehaus, these Proceedings (Conf. on the Physics of Multiply Charged Ions, Groningen, The Netherlands, 1986) *Nucl. Instr. and Meth.* B23 (1987) 109/116/291.
- [13] M.H. Chen, *At. Data Nucl. Data Tables* 34 (1986) 301.
- [14] J.H. Blanke, P.H. Heckmann and E. Träbert, *Phys. Scripta* 32 (1985) 509.
- [15] A.H. Gabriel, *Mon. Not. R. Astron. Soc.* 160 (1972) 99.
- [16] L.A. Vainshtein and U.I. Safronova, *At. Data Nucl. Data tables* 21 (1978) 49/*At. Data Nucl. Data Tables* 25 (1980) 311.
- [17] K.T. Chung, *Phys. Rev.* A29 (1984) 682.
- [18] J. Hata and I.P. Grant, *J. Phys.* B16 (1983) 2412.