The Quadrupole Moments of the Stable Nuclei of Sulphur and Chlorine*

M. Elbel and R. Quad
Fachbereich Physik der Universität Marburg, Renthof 5, D-3550 Marburg, W.-Germany

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By means of collinear laser spectroscopy the hyperfine structure of two transitions in the ionic spectra of sulphur and chlorine has been measured. The hyperfine constants of the involved levels have been determined. From them and by means of the spin-orbit coupling constants of the involved p-electrons the quadrupole moments of ^{33}S, ^{35}Cl and ^{37}Cl could be determined anew. The importance of the new values is seen in the fact that in the case of sulphur they result from measurements at the free ion or, in the case of chlorine, that they result from an electron other than 3 p.

Introduction

The quadrupole moment of sulphur 33 has never been measured at the free atom or ion. The tabulated value was derived from nuclear quadrupole resonance at rhombic sulphur [1] or microwave spectroscopy at several sulphur compounds [2]. Hence there is a lasting demand for confirmation of these values from atomic spectroscopy. However, until recently it seemed impossible to resolve the rather narrow hyperfine structure of the spectral lines of sulphur. Moreover, the atomic beam resonance fails because there is an apparent lack of detecting methods. Only the method of collinear laser spectroscopy at ion beams renders possible the resolution of the hyperfine structure in just one visible line of the sulphur ion. It belongs to the transition

$$\text{S II } 3p^2(^3P)\,3d\;^4F_{9/2} - 3p^2(^3P)\,4p\;^4D_{7/2}$$

and lies at 5608 Å. The lower one of the two states, $^4F_{9/2}$, is metastable due to its high angular momentum. Accordingly, in the ion beam extracted from a gas discharge into which SO_2 is fed, a sufficient amount of ions in that state may be found.

The situation in chlorine is a bit more favourable. The ground state of neutral chlorine is a $3p^5\,^2P_{3/2}$ [3, 4]. So far all the data on the nuclear moments of chlorine have been obtained by atomic beam resonance at this state. Although A-, B- and even C-values could be determined with unparalleled precision, the Sternheimer effect, which here amounts to 40%, renders unsure the Q-values of ^{35}Cl and ^{37}Cl which have been derived from them. Hence also a demand results for optical measurements at other states. Again there are some suitable lines in the ionic spectrum of chlorine at which collinear laser spectroscopy can be performed. Among these

$$\text{Cl II } \lambda 6664\text{:}\;\; 3p^3(^2D)\,3d\;^3G_5 - 3p^3(^2D)\,4p\;^3F_4$$

turned out to be the most favourable one. Again the lower state $^3G_5$ is metastable and may be formed in a gas discharge run in CCl_4-vapour.

Experimental

Our apparatus consists of a tuneable dye laser and an ion beam forming system. The latter is displayed in Fig. 1 and needs little explanation.

An ion source of the Penning type, consisting of a cylindrical anode and a tantalum cathode of large area heated by electron bombardment, is placed inside a magnetic field of axial direction. It is kept on high voltage (2.5 keV). The gas discharge inside the source was maintained in an atmosphere of some mTorr of SO_2 or CCl_4 depending on the species of ions desired. In the case of sulphur a few cubic centimeters of pure $^{33}SO_2$ were available, which sufficed for four recordings. An ion beam extracted

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Reprint requests to M. Elbel and R. Quad, Fachbereich Physik, Universität Marburg, Renthof 5, D-3550 Marburg.

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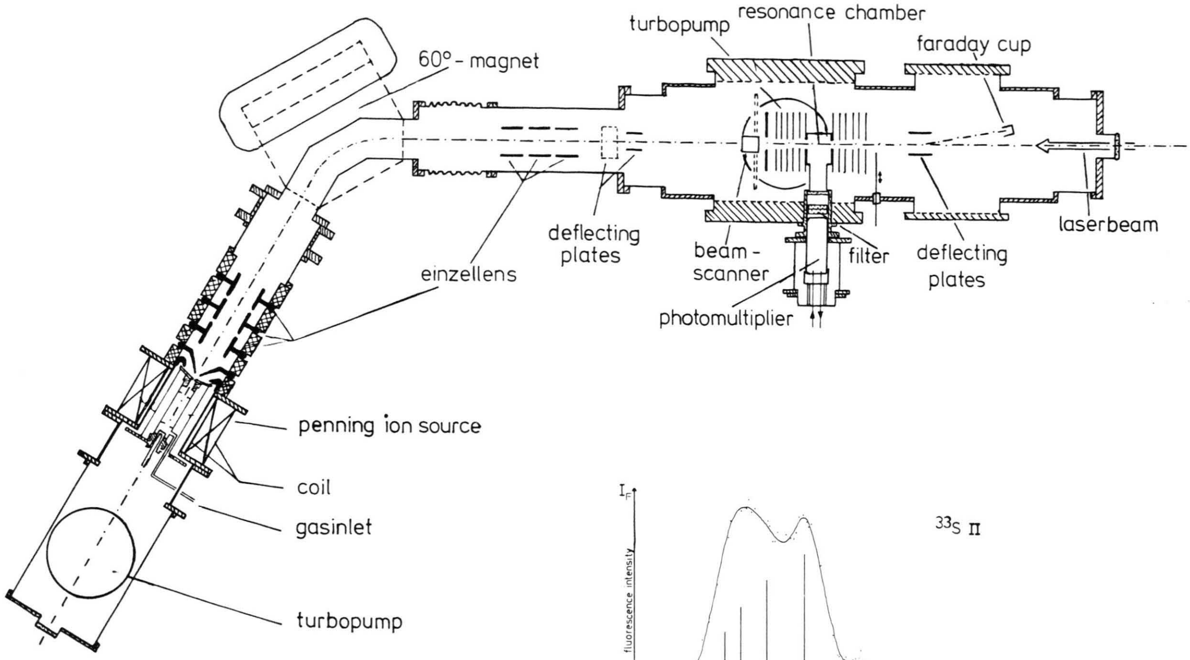

Fig. 1. The ion beam apparatus.

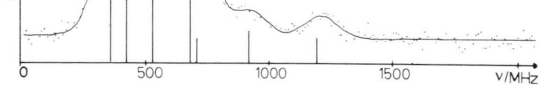

Fig. 2. Hyperfine structure of the ^{33}S-II-line at 5608 Å. Due to the nuclear spin $I = 3/2$ the structure consists mainly of a flag of four strong components with $\Delta F = \Delta J$ (bulk of the signal, left). At the right hand side two less intense components appear with $F \rightarrow F'$ being $7/2 \rightarrow 7/2$ and $5/2 \rightarrow 5/2$ (from right). The transition $3/2 \rightarrow 3/2$ almost coincides with the strongest component of the flag. The site of the weak components is influenced most strongly by quadrupole interaction.

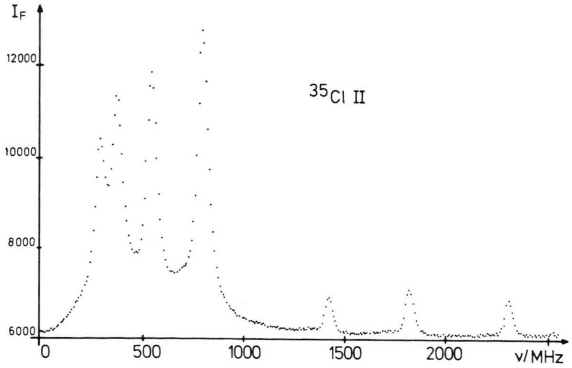

Fig. 3. Hyperfine structure of the ^{35}Cl-II-line at 6664 Å. Due to $I = 3/2$ for both nuclides of chlorine the pattern is very similar to the one of the sulphur line. Only the resolution which is mainly due to the pressure in the ion source, turns out to be much better. Also all the three $\Delta F = 0$ components are visible here. Only the ultraweak components with $\Delta F = +1$ could not be detected as in the case of sulphur.

from an orifice is accelerated and preselected by a 60° magnet. It is focussed to the resonance chamber which is kept at negative high voltage (− 4 ... − 5 keV). The latter voltage is scanned so that the chosen absorption line of the ions can be Doppler tuned to the frequency of the laser beam which is transmitted through the chamber from the other side. The reemitted photons of the excited ions are transmitted through a narrow banded filter and counted by a multiplier. The counts are stored into the memory of a computer (LSI 11/23) which likewise supplies the scanning voltage.

The hyperfine structures of sulphur and chlorine obtained in that manner are displayed in Figs. 2 and 3. The A- and B-values of the involved levels are determined by a least squares fit. The line widths are only 70 MHz in the case of chlorine but 160 MHz in the case of sulphur, where the pressure in the discharge was very low for lack of material.

Theoretical

The determined A- and B-values are listed in the Table 1. To evaluate the Q-values from them we

Table 1. Survey of the measured hyperfine constants A and B for the involved levels in the S II- and Cl II-spectra.

Nuclide	Configuration	State	A [MHz]	B [MHz]
^{33}S	$3p^2(^3P)\,3d$	$^4F_{9/2}$	80 ± 2	56 ± 7
	$3p^2(^3P)\,4p$	$^4D_{7/2}$	127 ± 3	50 ± 7
^{35}Cl	$3p^3(^2D)\,3d$	$^3G_5$	231.6 ± 0.2	-1.0 ± 0.5
	$3p^3(^2D)\,4p$	$^3F_4$	320.0 ± 0.2	-7.9 ± 0.4
^{37}Cl	$3p^3(^2D)\,3d$	$^3G_5$	192.6 ± 0.3	-1.0 ± 0.5
	$3p^3(^2D)\,4p$	$^3F_4$	266.1 ± 0.3	-7.7 ± 0.8

need the one-electron constants a and b of the 3p or 4p electron, respectively. Instead of the a-value the spin-orbit constant ζ may be used to derive $\langle 1/r^3 \rangle$ of the respective electron. For sulphur, by applying the energy sum rule, one shows easily that

$$B(3p^2(^3P)\,3d\,^4F_{9/2}) = -\,b(3p) + b(3d). \tag{1}$$

This explains the opposite sign of B in Table 1 with respect to Q of ^{33}S. ζ_{3p} can be derived by interpreting the fine structure of S II $3p^3\,^2P$ and ^2D to obtain

$$\zeta_{3p} = 515\ \mathrm{cm}^{-1}. \tag{2}$$

Neglecting in (1) the contribution of the 3d-electron, which can be estimated to a fraction of 1 MHz, one deduces from the well-known formulae (e.g. Kopfermann [5], eqs. (26,10) and (30,11))

$$Q(^{33}S) = (-\,8.4 \pm 0.8) \cdot 10^{-30}\ \mathrm{m}^2, \tag{3}$$

which confirms the value of Bird and Townes [2] surprisingly well. For Z_i, following a thumb rule for p-electrons, $Z-4$ was inserted.

For the evaluation of the Q-values of ^{35}Cl and ^{37}Cl the following relations are of crucial importance:

$$A(3p^3(^2D)\,4p\,^3F_4) = \tfrac{5}{8}A(3p^3\,^2D_{5/2}) + \tfrac{3}{8}a(4p_{3/2}); \tag{4}$$

furthermore

$$A(3p^3\,^2D_{5/2}) = \tfrac{4}{5}a(3p_{3/2}) + \tfrac{1}{5}a(3p_{1/2}) \tag{5}$$

and

$$B(3p^3(^2D)\,4p\,^3F_4) = b(4p_{3/2}). \tag{6}$$

Hence the quadrupole interaction is due to the valence electron 4p alone as the $3p^3$ shell is semicomplete. In (5) the ratio of $a(3p_{3/2})$ and $a(3p_{1/2})$ is well-known from the theory. Therefore in (4) there are only two free parameters: $a(3p_{3/2})$ and $a(4p_{3/2})$. Their ratio can be also concluded from spin orbit parameters since

$$\frac{a(3p_{3/2})}{a(4p_{3/2})} = \frac{\zeta_{3p}}{\zeta_{4p}}. \tag{7}$$

ζ_{3p} for Cl II can be evaluated from the fine structure in the $3p^3$ ns-series. ζ_{4p} can be taken from the fine structure of the $3p^3(^4S)\,4p\,^5P$ states. We find

$$\text{Cl II:}\quad \zeta_{3p} = (803 \pm 68)\ \mathrm{cm}^{-1},$$
$$\zeta_{4p} = (85 \pm 3)\ \mathrm{cm}^{-1}. \tag{8}$$

Inserting (7) and (8) into (4) and (5) we get

$$^{35}\mathrm{Cl}:\quad a(4p_{3/2}) = 31.2\ \mathrm{MHz}. \tag{9}$$

Equations (6) and (9) when inserted in Kopfermann's equation (30,13) yield

$$Q(^{35}\mathrm{Cl}) = (-\,7.6 \pm 0.5) \cdot 10^{-30}\ \mathrm{m}^2; \tag{10}$$

$$Q(^{37}\mathrm{Cl}) = (-\,6.8 \pm 1.0) \cdot 10^{-30}\ \mathrm{m}^2. \tag{11}$$

Korolkov and Makhanek [6] derive a value

$$Q(^{35}\mathrm{Cl}) = -\,8.5 \cdot 10^{-30}\ \mathrm{m}^2 \tag{12}$$

from measurements at the state Cl I $3p^5\,^2P_{3/2}$, which agrees quite well with our value.

Conclusions

By laser excitation of some levels in the ionic spectra of sulphur and chlorine their hyperfine constants could be determined. Several advantages enable us to derive quadrupole moments from them. First of all the states belong the highest *J*-value within their configuration. Then the spin-orbit constants of the electrons are known. Finally the investigated levels are almost undisturbed by spin-orbit coupling and they fit well into a Russell-Saunders scheme. Since *Z* is as low as 16 and 17, relativistic corrections are of little importance.

In the case of chlorine it had been possible to measure the quadrupole coupling constant of the 4p-electron. It completes the former measurements, which were only done at the 3p-electron, in a satisfactory way. In the case of sulphur the measurements are an order of magnitude less accurate due to the lack of material (pure ^{33}S). But here the quadrupole interaction is mainly due to the 3p-electron and is therefore an order of magnitude larger. Moreover the ^{33}S measurements are the first ones which have been done at the free ion or atom.

Acknowledgements

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