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Full hyperfine structure analysis of singly ionized molybdenum

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ABSTRACT

For a first time a parametric study of hyperfine structure of Mo II configuration levels is presented. The newly measured A and B hyperfine structure (hfs) constants values of Mo II $4d^5$, $4d^45s$ and $4d^35s^2$ configuration levels, for both 95 and 97 isotopes, using Fast-ion-beam laser-induced fluorescence spectroscopy [1] are gathered with other few data available in literature. A fitting procedure of an isolated set of these three lowest even-parity configuration levels has been performed by taking into account second-order of perturbation theory including the effects of closed shell-open shell excitations. Moreover the same study was done for Mo II odd-parity levels; for both parities two sets of fine structure parameters as well as the leading eigenvector percentages of levels and Landé-factor g_J, relevant for this paper are given. We present also predicted singlet, triplet and quintet positions of missing experimental levels up to 85000 cm^{-1}. The single-electron hfs parameter values were extracted in their entirety for ^{97}Mo II and for ^{95}Mo II: for instance for ^{95}Mo II, $a^{01}_{4d} = -133.37$ MHz and $a^{01}_{5p} = -160.25$ MHz for $4d^45p$; $a^{01}_{4d} = -140.84$ MHz, $a^{01}_{5p} = -170.18$ MHz and $a^{10}_{5s} = -2898$ MHz for $4d^35s5p$; $a^{10}_{5s} = -2529$ (2) MHz and $a^{01}_{4d} = -135.17$ (0.44) MHz for the $4d^45s$. These parameter values were analysed and compared with diverse ab-initio calculations. We closed this work with giving predicted values of magnetic dipole and electric quadrupole hfs constants of all known levels, whose splitting are not yet measured.

Contents

1. Introduction

The level structure analysis of singly ionized molybdenum was initiated by Meggers and Kiess in 1926, establishing 27 levels [2]. Later on, Schauls and Sawyer [3] extended this first study. It is in 1958 that a big overhang of this study occurred, done by Kiess alone this time, giving furthermore 179 experimental Landé-factor values of levels [4]. More recently, after a break of 45 years, a last but not the least fine structure (fs) study was published [5]: the spectrum of Mo II has been recorded with Fourier transform spectrometers in the wavelength interval: 1500–7000 Å and 110 new levels are reported. Moreover an accurate theoretical analysis of 5 even-parity configuration level set and 2 odd-parity

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configuration one were performed.

As regards Mo II hyperfine splitting only two lines were investigated up to now: the 293.4 nm ionic transition, $4d^45s^6D_{1/2}$ -$4d^45p^6F_{3/2}$ was explored for the stable Mo isotopes. A second 291.0 nm transition was studied to ascertain the sign of the magnetic hyperfine constant A since two solutions exist in the case of 293.4 nm transition. Furthermore some fast-ion-beam laser-induced-fluorescence measurements of Mo II splitting levels were just achieved [1], using the same experimental set-up as in [6]. In the present analysis we want to compare existing experimental hfs data with computed ones and to predict those which were not yet measured. In this aim we have to determine beforehand level eigenvectors to express the hyperfine structure constants A and B in intermediate coupling (Table 1).

2. Fine structure analysis

2.1. Even-parity configurations

The analysis methods for fine and hyperfine structures were described in our previous papers, for instance [7,8] when studying atoms like Zr and Hf or ions like Ti II, V II, Ta II… the procedure of fine structure analysis includes electrostatic and spin-dependent interactions Furthermore the spin-orbit integrals ζ_{4d} also effect the interactions with distant configurations. In the first step we try to obtain the best possible fit between calculated eigenvalues and observed energy levels considering the radial integrals Eav (configuration centre of gravity), ζ_{4d} (spin-orbit parameter), F_k and G_k (Slater integrals) and R_k (radial integral standing for interconfiguration electrostatic interaction) as adjustable parameters. In the second step we add in fitting procedure the two-body parameters α and β representing the one- and two-electron excitation respectively and three-body parameters T(d2s), T2(22) and T3(42) which stand for interaction effects with distant configurations influencing the term structure. We consider this fit procedure finished when we get the best standard deviation after taking, at the end, into account second-order of perturbation theory including the effects of closed shell-open shell excitations [9] (see the 5 last parameter values given in Table 2).

Rosner and Holt [1] have measured hfs splitting of only $4d^45s$ and $4d^5$ levels. The three lowest even-parity configuration centres of gravity of the Mo II are respectively: 26991 cm^{-1}, 34504 cm^{-1} and 55618 ccm^{-1} [4]. The fourth lowest even-parity configuration, $4d^46s$, has its centre of gravity located at: 100450 cm^{-1}. This means that the majority of the three lowest configuration levels mix only between themselves since they are isolated from levels of the other highest configurations. So for these two reasons we have decided to limit our configuration set study to the three lowest configurations: $4d^5$, $4d^45s$ and $4d^35s^2$.

The fs least square fitting procedure has been carried over 99 energy levels attributed to the three lowest even-parity configurations. With 82 parameters, 19 of which were treated as free, a goof fit has been achieved, with standard deviation of 27.12 cm^{-1}.

In Table 1, we give the energy levels, calculated eigenvalues, resulting LS-percentage of the largest and the second largest components of the wave functions and the corresponding LS-term designations. In this Table, the experimental Landé g_j-factor values are compared with the ab-initio ones, computed by means of Cowan code [10] and also with those deduced from the eigenvector compositions. Moreover we insert predicted level energies of missing experimental values up sometimes to 80000 cm^{-1}. We confirm the validity of the excellent huge work of Nilsson and Pickering [5] even if our fitting procedure gives closer eigenvalues to experimental energy levels on the whole.

Tables 2 and 3 contain the values of fs radial parameters resulted from the fitting procedure (fit). A description of these parameters can be found, for example, in Cowan [10] Some of the fs parameters, although predicted by theory but expected to be small, are not listed in these two tables.

2.2. Odd-parity configurations

Usually odd-parity level fine structure (fs) analysis is rather more difficult to perform than even-parity level one, due to presence of very complex mixing concerning odd-parity configurations: as regards Mo II the levels of $4d^35s5p$ overlap levels from both the $4d^45p$ and $4d^25s^25p$ configurations. It is clear, by analogy with elements located in the same column of the periodic table, that strong configuration interactions occur within $(4d+5s)^45p$. Furthermore, as it is commonly the case with the 4d-elements, Mo II has many low-lying levels below 60000 cm^{-1} which are members of the even-parity configurations as well as the odd-parity ones. To achieve a satisfactory interpretation of all observed hyperfine structure (hfs) constant values and finally to predict those, very numerous, which are missing we propose more refined treatment, including intermediate coupling and configuration mixing. The accuracy of the amplitude of the energy level eigenvectors is known to have a particular strong influence of the calculation of the effective single-electron hfs parameters extracted from experimental A and B constants.

The method used here was successfully tested in our previous works on Hf II [11], Zr I [12] and Ta II [13] for example and should find particular application for systems composed of many Rydberg configurations mutually interacting. The Hamiltonian used to describe the fs of an atom is given in numerous papers [14–16]. The configuration basis set-up used in this work consists simply of the main configurations: $4d^35s5p$ and $4d^45p$ whose experimental energy levels are available in literature [5,17]. Nevertheless it is a pity that experimental $4d^25s^25p$ configuration energy levels, expected to mix with other close odd configuration ones are not found yet in literature.

Although the total number of interaction integrals required for this basis is large, the situation was made tractable by imposing physically realistic ratios of radial integrals as constraints [7]. For this reason additional assumptions, which are taken mainly from Hartree-Fock calculations [10], had to be included in our fitting procedure. The coupling scheme used to describe the levels is usually LS coupling, also known as Russell-Saunders coupling. All the experimental known odd-parity levels [5] located up to 80×10^3 cm^{-1} were fitted. The whole main fs parameter sets of the configurations $4d^35s5p$ and 4^45p were adjusted. Thus the fs least square fitting procedure has been carried out over 176 energy levels listed in [5]. With 79 parameters, 21 of which were treated as free, a good fit has been achieved (standard deviation: 83 cm^{-1}). As in Table 1 for even-parity levels, the energy levels, calculated eigenvalues, resulting LS-percentages of first and second components of the wave functions, and the LS-term designations are given in Table 4. In this Table, the calculated g_J-factors, deduced from the eigenvector compositions, are compared with experimental ones when the latter are available. Tables 5 and 6 display fitted fs parameter values.

3. Hyperfine structure analysis and semi-empirical determination of the hfs radial parameters

3.1. Even-parity configurations

Concerning the hfs analysis we follow the many-body parameterization method [16] which permits to take advantage of similarities between configuration interaction effects observed independently in spin-orbit and hyperfine splitting. To our