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Zn I spectra in the 1300–6500 cm^{-1} range

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ABSTRACT

We study spectra of a plasma created by the laser ablation of ZnS targets in a vacuum and report 47 (not observed previously) Zn I lines in the range of 1300–6400 cm^{-1}. From the recorded spectra we determine energies of 5*g*, 6*g*, 7*f*, 6*h*, 7*h* and 8*h* Zn I levels. We also calculate a large list of transition probabilities and oscillator strengths for Zn I in the observed spectral range.

1. Introduction

The atomic data on zinc listed in databases are comparatively old. Zn I levels available in the NIST Database [1] are taken from a compilation by Sugar and Musgrove [2] which also contains a brief review of the previous studies of Zn I spectrum. The energies of $4s\,ns$ ^1S $(n=5..9)$, $4s\,ns$ ^3S $(n=5..7)$, $4s\,np$ ^1P $(n=4..7)$, $4s\,np$ ^3P $(n=4..9)$, $4s\,nd$ $^{1,3}D$ $(n=4..6)$, $4s\,4f$ and $4s\,5f$ $^1F_3$ levels were obtained from arc spectrum measurements by Johansson and Contreras [3]. More recently, Gullberg and Litzén [4] presented improved Zn I energy values for singlet and triplet levels of $4s\,4p$, $4s\,ns$ $(n=5..7)$ and $4s\,nd$ $(n=4..6)$ configurations. A number of $4s\,nl$ triplet levels with high orbital momentum $l=3..6$ with $n=5..9$ listed in NIST and in Sugar and Musgrove [2] are taken from hollow-cathode measurements of forbidden lines performed by Muntenbruch [5] in UV range of 2394–2839 Å (41771–35223 cm^{-1}).

As we show in our previous works on high-*l* atomic states [6–11], to access these states by electric dipole-allowed transitions, the infrared (IR) spectra should be studied. The strongest allowed transition (5*g*–6*h*) involving the lowest *g*- and *h*-states has wavenumber in a range of 1300–1350 cm^{-1}. The higher *l* appears for $n>6$, and the allowed transitions between them have even smaller wavenumbers.

The IR region plays an increasingly important role in modern astronomy, *e.g.* in studies of cool stars, planets, dust clouds, etc. The powerful capacities of IR astronomy cannot be fully utilized without detailed spectroscopic information on atomic line features (in particular, wavelengths and oscillator strengths) in the IR region [8].

To the authors' knowledge, only few laboratory measurements of Zn I IR spectrum have been reported up to now. Fisher et al. [12] reported four lines in 11,054–14,039 Å (9047–7123 cm^{-1}) range and Johansson and Contreras [3] reported 25 lines in 4100–10,000 cm^{-1} range. The aim of the present study is to observe Zn I lines in IR domain including the 1300–3100 cm^{-1} range where no laboratory

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Zn I spectra have been recorded previously. We also report some lines in the 4100–6400 cm^{-1} range which are absent in Johansson and Contreras [3]. From the observed spectra we extract revised energy values for several high-*l* levels which should be used instead of those currently recommended by NIST (measured from the forbidden UV transitions [5]).

2. Methods

We measured Zn I emission spectrum with the help of high-resolution FTIR spectroscopy of the plasma formed by the laser ablation of zinc sulphide (ZnS) target. The sample surface was irradiated by a high-repetition-rate, pulsed, nanosecond ArF laser ($\lambda = 193$ nm, laser pulse width 12 *ns*, frequency 1.0 kHz, output energy 15 mJ) in a vacuum (10^{-2} Torr). The emission from the plasma was focused into the spectrometer by a zinc selenide ZnSe (127 mm) lens for the spectral range below 1700 cm^{-1} and by a CaF_2 (100 mm) lens for the range above 2100 cm^{-1}. The emission spectra were recorded at the Molecular Spectroscopy Facility (MSF), J. Heyrovský Institute of Physical Chemistry, Czech Republic, using a Bruker Optics IFS 120 HR high-resolution Fourier transform spectrometer (FTS). A calcium fluoride (CaF_2) beamsplitter and indium antimonide (InSb) detector were utilized for measurements above 2100 cm^{-1}, with a potassium bromide (KBr) beamsplitter and a mid-band mercury cadmium telluride (MCT) detector used for measurements in the 1300–1700 cm^{-1} range. The FTS was equipped with suitable optical interference filters (Northumbria Optical Coatings Ltd.) and the aperture diameter (2.5 mm) chosen so that the intensity of infrared emission falling on the detectors was maximized in the spectral region of interest without saturation or loss of spectral resolution. The following filters were utilized in the corresponding spectral ranges: BP 3067-2 (1300–1700 cm^{-1}), BP 3555 (2100–3200 cm^{-1}), TFBP 351 (4100–4400 cm^{-1}), BP 4187 (5000–6400 cm^{-1}). The boxcar apodisation was applied to all interferograms. Due to the non-linear response of MCT detectors to the detected radiation, which results in baseline perturbations, all interferograms measured using the MCT detector were re-transformed using the non-linearity correction in Bruker's OPUS software.

The spectral resolution of FT spectrometer is given by $\Delta\nu = 1/\delta_{\max}$, where $\delta_{\max}$ is the maximum displacement of the moveable mirror. The best resolution of our measurements was of 0.02 cm^{-1} that corresponds to approximately 1.5–3.5 data points per full width at half maximum (FWHM). But to detect several weak lines, five-scan measurement was used since it gives better SNR. However, to preserve the sample from extra heating, we had to use less $\delta_{\max}$ for these five-scan measurements, and their resolution was about 0.06 cm^{-1}.

The wavelength calibration of the FT ablation spectra was performed using several CO lines from the spectra produced by discharge emission source [13,14] performed in the same operation conditions as used for the ablation experiment. The calibration was performed by linearly fitting the measured wavenumbers to high-precision values taken from HITRAN database [15]. The resulting wavenumbers ν were recalculated from the non-calibrated values ν' using $\nu = (1+\alpha)\nu'$ where α is a linear fit parameter. The α values were obtained for each spectral range with typical values of $\alpha \simeq 1.2 \times 10^{-6} \pm 2.7 \times 10^{-7}$ (with a relative uncertainty $\Delta\alpha/\alpha$ of about 20%).

Since, as it was mentioned above, several *f*-, *g*- and *h*-level energies given in NIST should be used with caution, for the transitions involving these levels we used the relative intensities of the corresponding observed lines as an additional criterion for their identification. Indeed, due to comparatively small quantum defects of non-penetrating high-*l* electronic states, the nl–$n'l'$ transitions for a fixed pair of the principal quantum numbers n, n' differ only by some tens of inverse centimeters for different pairs of orbital moments l, l'. Therefore, the relative intensity of the corresponding lines is the only criterion to identify them if no reliable information about the corresponding level energies is available beforehand. Note that such a comparison of the relative intensities can be used for line identification only within the same (of four listed above) spectral range. This is due to the reason that in our emission measurements several interference filters have been applied. Because of their non-linear characteristic it is difficult to compare the intensities of obtained emission lines between the different spectral windows (determined by the interference filter) in absolute units. However, since the wavenumbers of the above mentioned nl–$n'l'$ transitions with high l, l' lie in a same spectral range the same n and n', it is sufficient to use the relative intensities within the same range. The transitions involving low $l, l' < 3$ are easily identified from the upper and lower level energies which are known to a good accuracy.

To evaluate the relative intensities, we assumed the model of optically thin plasma at local thermal equilibrium (see discussion in our previous work [7]). Then the populations of the electronic states are described by the Boltzmann distribution, and the relative intensities are determined by the dipole transition matrix elements (transition probabilities or oscillator strengths). These *A*- or *f*-values were calculated using single-channel quantum defect theory (QDT) [16], which is much simpler than explicit two-electron calculations [17]. The QDT method has proved its efficiency for the calculation of first- [18,19] and second- [20–23] order matrix elements in atoms and molecules. We compare some QDT-calculated oscillator strengths with experimental and theoretical data available in the literature. As in our previous works [6,8,9, 24,25], the overall agreement of our QDT calculations with the results available in other sources is quite satisfactory. Approximately 80% of QDT-calculated values differ from the values calculated by other authors not more than by 25%, that is sufficient for the purpose of identification of our lines.

Note that, having calculated all the *A*-values and energies of the upper levels, in principle, it is not very difficult to bring all observed intensities to the same scale using the Bolzmann plots (see an example of such plots in [7]). However, on the one hand, the sensitivity of the detectors and transmission of the focusing lenses can depend on wavelength, and, on the other hand, such a unification is not necessary for our identification purposes, as it was stated above.

The uncertainties presented in the tables are described in Sections 3.1 and 3.2. For all tables, the uncertainties are reported in parentheses immediately following the values. They should be treated as the rightmost significant digits, *e.g.*, 123.4(56) means 123.4 ± 5.6.