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Argon FTIR spectra between 800 and 2000 cm^{-1}: *h*- and *i*-levels and transition probabilities

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ABSTRACT

The new emission spectrum of atomic argon is measured using the time-resolved Fourier transform technique. Seventy-seven new Ar I lines in the 800–2000 cm^{-1} range with a resolution of 0.02 cm^{-1} are observed. The energies of 12 previously unknown 7*i* and 6*h* energy levels are extracted from the measured spectra. The probabilities of the transitions between the observed levels are calculated.

1. Introduction

Interest in the new spectroscopic data in the infrared region is currently growing. Numerous measurements and calculations are carried out to observe the new highly excited Rydberg states of different atoms. Among the various atoms, it is important to analyze the spectrum of atomic argon because of the wide use of argon in discharge experiments with different cathode materials. For example, Ar–La [1] and Ar–Th discharge lamps are applied for instrumental wavelength calibration in astronomy observation in visible [2] and infrared (IR) [3] ranges.

The energy levels of the neutral argon atom Ar I were determined a long time ago [4]. Most of the energy levels listed in the NIST Atomic Spectra Database [5] are taken from the grating spectrograph measurements [6] performed in the 313–1236 nm (8090–31,931 cm^{-1}) range with an accuracy of 0.001 nm (with the four lines at 104.8, 106.6, 87.9 and 87.6 nm measured with an accuracy of 5×10^{-5} nm).

More recently, two Ar I spectra in the infrared region were recorded in hollow cathode discharge using a high-resolution Fourier transform spectrometer (FTS) at the National Solar Observatory at Kitt-Peak (NSO). Engleman et al. [7] reported 447 Ar I lines in the 1798–9130 cm^{-1} range (resolution 0.013 cm^{-1}) obtained from the Th–Ar hollow cathode discharge at a current of 320 mA with an argon pressure of 2.2 Torr.

Using discharges with various cathodes (with a current of 150–600 mA and Ar pressure of 2–4 Torr), the Ar I spectrum was recorded by Whaling et al. [8,9] in the 1704–30,118 cm^{-1} range with a typical uncertainty of 0.003–0.0003 cm^{-1} (see also corrections by [10]).

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Table 1
Spectral ranges covered by the present measurement.

Spectral range	Filter specification	Serial no.	Detector	Beam splitter
700–1000	WBP 3067	–	MCT	KBr
1000–1250	WBP 3067	BP-3067-1-1-05	MCT	KBr
1250–1600	WBP 3067	BP-3067-2-1-05	MCT	KBr
1600–2000	WBP 3067	BP-3067-3-1-05	InSb	CaF_2

In the Kitt-Peak spectra mentioned above, the lines corresponding to the emission from the high orbital momentum ($l=3,4,5$) levels were identified using the results of Palmeri and Bièmont [11] who analyzed the NSO FTS spectra of Ar I in the 2073–1158 nm (4821–8634 cm^{-1}) range with an accuracy of 0.1–0.001 cm^{-1} to obtain the energies of the high-l levels (4f, ng with $n=4,5,6$ and 7h). The 6h levels have not been observed yet because the shortest wavelength of a dipole transition involving the 6h state corresponds to the 5g–6h transition at approximately 1340–1345 cm^{-1} [12]. For the 6h–7i transition, the corresponding wavenumber is estimated to be approximately 800–810 cm^{-1}, and therefore no i-levels (l=6) of Ar I have been observed yet.

The present work aims to report high-resolution Ar I spectra below 1700 cm^{-1} and to determine the energies of Ar I 6h and 7i levels.

2. Methods

To populate the higher energy Ar I levels, we applied pulsed discharge plasma produced in a 20 cm long glass discharge tube with water-cooled stainless steel electrodes. The tube was filled with a slow, constant flow of pure argon with a pressure of 1.0 Torr. Other discharge parameters were set as follows: pulse width=22 μs, voltage=0.9 kV and a peak-to-peak current=200 mA. The plasma radiation was collected by a ZnSe lens and focused into the spectrometer aperture. The spectra were measured with the resolution of 0.02 cm^{-1}.

The time-resolved Fourier transform spectrometric (TR-FTS) method used to record the IR spectra of Ar I is described in detail elsewhere [13–16]. This approach enables the measurement of IR spectra with a high spectral resolution (up to 0.0075 cm^{-1}) and a 1 μs time resolution over a wide spectral region. The time resolution scheme was necessary to increase the signal-to-noise ratio (SNR) of weak spectral lines by selecting the optimal time period after the discharge pulse [17]. To record the spectra, we used the Northumbria Optical Coatings Limited band pass interference filters, KBr and CaF_2 beam splitters, and Hg–Cd–Te or InSb detectors. These filters, detectors, and splitters are listed in Table 1 for all the spectral ranges covered in this work.

To increase the signal-to-noise ratio, we summed up several (from 5 to 20) time-shifted measurements of the spectra with a time step of 2 μs. In fact, this procedure means an averaging over the time periods (typically, from 3 to 15 μs after the beginning of the discharge pulse) where the intensity of the lines was maximal. The line features (wavenumber σ_{ki}, intensity I_{ki}, full width at half maximum, FWHM) listed in Table 2 were obtained by fitting the averaged spectral data using the Voigt profile function.

The measured wavenumbers were calibrated using 43 absorption lines of the water ν_2 (1596 cm^{-1}) band. Since the wavenumber dependence of the differences between our peak positions and the high-precision values taken from HITRAN [18] shows no significant trend (the multiplication factor obtained from the linear fit can be considered negligible) the wavenumber values were corrected by subtracting the factor (-0.0078 cm^{-1}) obtained as the mean of the differences between our peak positions and the high-precision values [18].

In the three spectral domains in Table 2, different filters, beam splitters and detectors were used so that the arbitrary units of intensity have a different scale in the different domains. The uncertainties are reported in the parentheses immediately following the values and should be interpreted using the rightmost significant digits in the main numbers, e.g., 123.4(56) represents 123.4 ± 5.6.

Following line classification, the energies of the previously unknown high-l-levels can be extracted (see Table 3) using the procedure described in earlier work [19]. The assignment of the lines listed in Table 2 was performed using the energy level list available in the NIST database [5]. Because the 6h and 7i states of Ar I have not been reported yet, the assignment of the lines corresponding to the transitions involving these levels was done as follows. First, we used approximate energy values for the high-l-levels calculated by the Rydberg formula with small quantum defects $\mu\sim0.001$. The error of the level energies determined in this way can be several cm^{-1}, so the observed lines should be classified according to their expected intensities, which can be assumed to be proportional to the line strengths (S-values). These values, as well as the f-values (oscillator strengths) or A-values (transition probabilities), are expressed in terms of squared dipole transition matrix elements, calculated here using the quantum defect theory (QDT) approximation with the J_1K coupling scheme.

QDT approach [20] is a good technique for such calculation for atoms [16,21] and molecules [22–24]. Like the modified Coulomb (Fues model potential) approximation [12,15,25–28], this technique can be used to evaluate effectively a large array of the dipole transition matrix elements in one-electron approximation. The QDT radial wavefunction of the optical electron in the nl_j state is given in terms of Whittaker functions by

$$R_{nlj}(r)=\frac{Z^{1/2}}{r\,n^*}\left[\frac{\Xi_l(E(nl_j))}{\Pi_l(n^*)}\right]^{1/2}W_{n^*,l+1/2}\left(\frac{2Zr}{n^*}\right)\times\left[\Gamma(l+1+n^*)\Gamma(n^*-l)\left(1+\frac{\partial\mu_{lj}(n^*)}{\partial n^*}\right)\right]^{-1/2}, \qquad (1)$$

where the effective principal quantum number n^* is connected to the energy level $E(nl_j)$ and quantum defect μ_{lj} via the Rydberg formula. The functions $\Xi_l(E(nl_j))$ and $\Pi_l(n^*)$ in (1) are connected with an interpolation of the quantum defect function $\mu_{lj}(n^*)$ [21]. The core polarization effects were taken into account accordingly [29].