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Measurement and analysis of blue shift on the helium 492.2 nm line in a liquid corona discharge

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Abstract

The helium singlet 1s4d-1s2p line (492.2 nm) has been measured in a corona discharge done in liquid helium at 4.2 K. A significant shift towards the blue direction is visible on the spectrum. Using an empirical model for the He-He* potential energy difference, we have performed a fitting of the line shape. The best-fit result is in good agreement with the experimental spectrum. It is shown that the blue shift is determined by the maximum of the potential energy difference function. Based on the fitting results, we give an estimate of this quantity.

Keywords:

1. Introduction

Corona discharge experiments in liquid helium have been performed in the framework of electrical engineering studies [1]. The experimental setup consists of a point-plane electrode system, which is placed inside a helium cryostat. By applying high voltage across the electrodes, a streamer of either positively or negatively charged particles, ions and electrons is produced, which leads to the formation of localized plasma. As a rule, information on the medium can be inferred from passive spectroscopy. The emission lines due to excited helium atoms are subject to collisional (pressure-)broadening, which is determined by the density and the temperature of the perturbers. In this article, we report on the spectral analysis of the light emitted at 492.2

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nm, corresponding to the $1s4d-1s2p$ transition of singlet helium. The spectrum presents a line which is strongly shifted to the blue direction. This shift is a feature of a potential energy difference having positive values at moderate internuclear distances, e.g. [2]. A blue shift has been observed on other lines visible in the same experiment and line shape fittings have been performed successfully, through the use of *ab initio* potential calculations [1] or with an analytical model [3]. Data on the helium 492.2 nm line shape in liquid are rather scarce. **The investigation reported in [4] concerned the same line in the same experiment, but in gaseous helium. In liquid, a specific issue is that simultaneous collisions between an emitter and the perturbors occur.** An accurate modeling requires a large number of nuclei to be accounted for, and the quasi-degeneracy of the upper level requires a large atomic base to be retained, which renders calculations prohibitive. We propose here a line shape model based on an empirical expression for the potential. Our approach is inspired by early investigations done using Lennard-Jones potentials, devoted to explain red shift and satellites on pressure-broadened lines [5, 6, 7]. We have adapted this model to the fitting of the experimental spectrum. The model involves three independent parameters. The article is organized as follows: in section 2, we give an overview of spectra observed in the experiment; in section 3, we present the line broadening model, to be used in the calculation of the 492.2 nm line; finally, we perform line shape fittings in section 4 and we infer the maximum of the potential energy difference function. A discussion about the inferred parameter values is done.

2. Observation of the helium 492.2 nm line in liquid corona discharges

A series of corona discharges have been performed at a temperature of 4.2 K, for pressures ranging from 1 bar to 100 bars, with the aim of probing the dielectric properties of liquid helium. Details on the experiment can be found elsewhere, e.g. [1, 3]. Passive spectroscopy measurements carried out in the visible range have indicated the presence of intense lines (see Fig. 1). These lines are broadened due to the interactions between the excited helium atoms that contribute to the emission and the bulk of the fluid, majorly made of helium atoms in their ground state. The line at 492.2 nm, due to the $1s4d-1s2p$ transition between singlet states, has the particularity to be strongly shifted to the blue side. Figure 2 illustrates this point. The line observed at 4.2 K and 1 bar is located approximatively at 490.5 nm. The line shift

Figure 1: Spectra presenting atomic lines have been recorded in liquid helium corona discharges. Here, the two most intense lines correspond to the $1s4d-1s2p$ and $1s3p-1s2s$ transitions of singlet helium.

is due to the collisions with perturbers; the blue direction indicates that the potential difference $\Delta u = u_{1s4d-1s^2} - u_{1s2p-1s^2}$ has positive values at moderate internuclear distances. In the next section, we present the formalism involved in the modeling of spectral line shapes and we apply it to the calculation of the helium 492.2 nm line broadened by collisions.

3. Line broadening model

As a rule, the modeling of a spectral line shape involves the calculation of the Fourier transform of the emitter dipole autocorrelation function $C(t)$, according to

$$I(\omega) \propto \text{Re} \int_0^\infty dt e^{i\omega t} C(t), \quad (1)$$

Figure 2: Plot of the helium 492.2 nm line obtained at room temperature (squares) and at 4.2 K, in liquid phase (circles). In both cases, the discharge was carried out at a 1 bar pressure. In liquid helium, the spectrum is strongly shifted to the blue direction.

with

$$C(t) = \text{Tr}(\rho \mathbf{d}(0) \cdot \mathbf{d}(t)). \quad (2)$$

Here, the trace Tr is performed over the whole space including the emitter and the perturbers surrounding it, and ρ and $\mathbf{d}$ are the density operator and the emitter dipole operator, respectively, expressed in the Heisenberg picture. Details on the formalism can be found in reviews, e.g., [8, 9, 10]. In the following, we retain the 1s4d and 1s2p levels only and we describe them as if they were non-degenerate. This simplification allows one to use a formulation of Eq. (2) in classical terms, suitable for fast calculations and, hence, appropriate for a fitting. In this framework, the atom is described as an oscillator with the single frequency $\omega_0 = (E_u - E_l)/\hbar$, where $E_u \equiv E_{1s4d} = 23.736$ eV and $E_l \equiv E_{1s2p} = 21.218$ eV are the energies of the upper and lower levels contributing to the transition. Assuming the perturbations are additive, the autocorrelation function factorizes and the problem amounts to the description of binary interactions between the emitter and each of the perturbers; explicitly, one has [11]

$$C(t) = e^{-NV(t)}, \quad (3)$$

where N is the atomic density and $V(t)$ (“collision volume”) is given by

$$V(t) = \int d^3r \int d^3v f(\mathbf{r}, \mathbf{v}) \left\{ 1 - \exp \left[-i \int_0^t dt' \Delta u(|\mathbf{r} + \mathbf{v}t'|) \right] \right\}. \quad (4)$$

Here, $\mathbf{r}$ and $\mathbf{v}$ are the perturber’s position and velocity relative to the emitter and $f(\mathbf{r}, \mathbf{v})$ is the corresponding distribution function. Equations (3) and (4) have been designed initially for the description of line broadening by neutrals with the assumption that collisions can be incomplete; they serve as a starting point in the so-called “unified theory” [12]. A similar approach also exists for the modeling of line broadening by charged particles (Stark effect) [13, 14]; in this case, specific treatments, based on kinetic theory, are required in order to account for collective behavior, e.g. [15]. A further simplification consists in neglecting the perturber’s motion during the line’s time of interest $\tau_i \sim \Delta\omega^{-1}$ (static approximation). This simplification holds provided that the collision time $\tau_c = r_0/v_0$ (with $r_0 \sim N^{-1/3}$ being the mean interparticle distance and $v_0 \sim \sqrt{k_B T/m_{He}}$ being the thermal velocity) is much smaller than the time of interest. This criterion is usually satisfied in the line wings where $\Delta\omega$ is large, but it is also satisfied here at half-maximum, given the

low temperature conditions (numerical application: $\tau_c \simeq 2 \times 10^{-12}$ s and $\tau_i \simeq 9 \times 10^{-14}$ s). Within this approximation, the collision volume is given by the following one-dimensional integral

$$V(t) = 4\pi \int_0^\infty dr r^2 g(r) \{1 - \exp[-i\Delta u(r)t]\}, \quad (5)$$

and the model becomes equivalent to the early formulation of the line broadening problem at the static limit, referred to as being the “statistical theory” [16]. The quantity $g(r)$ denotes the pair correlation function. It tends to one at large r and it falls abruptly to zero for small values of r due to repulsion [17]. Deviations to the static approximation are usually significant at the line center. The neglect of the perturber’s motion can result in an underestimate of the line broadening. In this case, if accuracy is sought, the line shape description should involve the more general formula (4). Whatever the model used [either based on Eq. (4) or Eq. (5)], the spectral profile of a line is governed by the structure of the potential energy difference function $\Delta u(r)$. Figure 3 shows an example of calculation assuming the van der Waals power law $-C_6/r^6$, compared to the non-monotonic Lennard-Jones function $C_{12}/r^{12} - C_6/r^6$, taking both C_6 and C_{12} positive. The static approximation has been used, i.e., the integral (5) has been evaluated. The pair correlation function has been set equal to 1. As can be seen in the figure, the two spectra are shifted to the red side, both are asymmetric, but their shape is different. The van der Waals function is always negative, which results in an increase of the radiation wavelength for each emitter-perturber interaction. As a result, the overall line shape is both shifted and broadened to the red direction. In the Lennard-Jones case, the positive part of the potential difference leads to a decrease of the radiation wavelength for perturbers that are located close to the emitter. The resulting spectral profile has a blue wing of larger intensity than the red wing. Note that the magnitude of this asymmetry is related to the perturber density; see [5, 6, 7].

4. Fitting of the experimental line shape

While being shifted to the blue direction, the experimental profile of the helium 492.2 nm line has a red wing larger than the blue wing; this result is apparent on the plot in Fig. 2 and it was observed on all spectra recorded in the experiment. A model capable of reproducing this trend should involve positive values of Δu at moderate or large r , and negative values at smaller

Figure 3: Plot of the spectral profile obtained using the static approximation, assuming van der Waals (dashed line) and Lennard-Jones (solid line) potential models with positive C_6 and C_{12} coefficients. See text for details. Arbitrary units are used. Both spectra are shifted to the red side, but they have different shapes. The van der Waals line profile is broader on the red side, whereas the Lennard-Jones line profile is broader on the blue side. This difference stems from the structure of the potential function.

r . Based on the analysis done in the previous section, we have performed a line shape fitting using a Lennard-Jones function, with negative C_6 and C_{12} coefficients in order to reproduce correct shift and asymmetry. The repulsion between the emitter and the perturber at short distances has been retained through the following model for the pair correlation function:

$$g(r) = \begin{cases} 0 & \text{if } r < r_m \\ 1 & \text{if } r \geq r_m \end{cases} . \quad (6)$$

The radius r_m is left as an adjustable parameter. Before proceeding to the fitting, the line shape function has been rewritten in terms of the reduced frequency $\tilde{\omega} = \omega/4\varepsilon$, the reduced density $\tilde{N} = (\pi/3)N\sigma^3$, and the reduced cut-off $\tilde{r}_m = r_m/\sigma$, where $\varepsilon = C_6^2/4|C_{12}|$ and $\sigma = (C_{12}/C_6)^{1/6}$ are the usual Lennard-Jones parameters. The ε parameter value has been set in such a way so that the calculated spectrum has precisely the same shift as the experimental spectrum. The other parameters involved in the fitting are the reduced density and the reduced cut-off; they control the line width and the asymmetry, respectively. We have used this property to infer σ and r_m . Figure 4 shows the obtained result. The best-fit result is in good agreement with the experimental spectrum. The inferred values are $\varepsilon = 14$ K, $\sigma = 3.4$ Å, and $r_m = 3.1$ Å. These values fall in the same range as that for other He_2^* interaction potentials [1]. The ε parameter is interpretable as the maximum value of a hump present at moderate r values; it is located at the distance $2^{1/6} \times \sigma \simeq 3.8$ Å.

5. Conclusion

We have applied a line shape model to the fitting of an experimental spectrum of the helium 492.2 nm line observed in a liquid helium corona discharge. **This line presents a significant shift towards the blue direction, indicating that the** spectral profile is mainly sensitive to collisions with the atoms surrounding the emitters. Using an empirical model for the potential energy difference between an emitter and a perturber, we have performed a fitting of the line shape. **The best-fit result is in good agreement with the experimental spectrum.** The model involves a function presenting a hump at moderate internuclear distance; **the amplitude and location of this hump** were inferred from the best-fit result. An extension of this work, devoted to account for the quasi-degeneracy of the levels involved in the transition, is presently underway. Dedicated calculations will be performed on the basis of

Figure 4: A fitting of the experimental line profile has been performed based on the potential model reported in the text. The best-fit result, in close agreement with the experimental spectrum, yields a potential hump of amplitude 14 K and located at 3.8 Å.

quantum chemistry software such as the MOLPRO code [18]. An issue that remains to be addressed is the role of finite atom velocity on the spectrum; an extension of the line broadening model accounting for this effect, e.g., through the use of the unified theory [12] or with molecular dynamics simulations [19], will be applied to the analysis of spectra. The sensitivity of the line shape to the collisions with neutrals is less important in gaseous phase. In previous works, it was shown that the 492.2 nm line presents features of an important Stark broadening, with the presence of a forbidden satellite [4]. The relative importance of the Stark effect with respect to the neutral broadening still remains to be addressed. An investigation will be done using computer simulations. Cross-checks between available Stark broadening codes (e.g., [20, 21, 22]) will be performed.

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