Physical interpretation of the blue shift of spectra obtained by corona discharge in liquid helium

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Abstract. We discuss the major importance of temperature and perturber density in the broadening and shift of the He 706 nm triplet 3s-2p transition within a unified line shape semi-classical theory which contains the impact as well the quasistatic limits. In a previous paper we presented the first calculations of He-He collisional profiles for this transition using ab-initio molecular potentials. The excellent agreement between our theoretical determination of the near wing of the line profiles and reported experimental spectra of a corona discharge in gaseous He at 300 K established the validity of our interpretation of the spectra and the accuracy of the interaction potentials. In liquid He, the experimental line profiles are formed under conditions where two or more perturbers are likely to act simultaneously. Such phenomena determine the character of a spectral line at high perturber density. In this work we show that it is possible to determine the physical conditions of temperature and pressure from the experimental spectra of an electric discharge in liquid He. We show that at 4 K the theoretical line shift is negative in disagreement with an incorrect analysis reported in a recent paper and also presented at this conference.

1. Unified profile calculations
A unified theory of spectral line broadening yields the complete profile from the line center to the far wing, and includes the effect of the dependence of the transition probability on interatomic distance for all states that contribute to the line. Complete details and the derivation of the theory are given by [1]. In our theoretical work, the spectral line is computed from the Fourier transform (FT) of a dipole autocorrelation function. A pairwise additive assumption allows us to calculate the total profile \( I(\Delta \omega) \), when all the perturbers interact as the FT of the \( N \)th power of the autocorrelation function \( \phi(s) \) of a unique atom-perturber pair. We obtain for a perturber density \( n_p \)

\[
\Phi(s) = e^{-n_p g(s)},
\]

where decay of the autocorrelation function with time leads to atomic line broadening.

For a transition \( \alpha = (i, f) \) from an initial state \( i \) to a final state \( f \), we have

\[
g_{\alpha}(s) = \frac{1}{\sum_{e,e'}|d_{ee'}|^2} \sum_{e,e'}^{(\alpha)} \int_0^{+\infty} 2\pi \rho d\rho \int_{-\infty}^{+\infty} dx \tilde{d}_{ee'}[R(\rho) - \tilde{d}_{ee'}[R(0)]].
\]
The $e$ and $e'$ label the energy surfaces on which the interacting atoms approach the initial and final atomic states of the transition as $R \to \infty$ ($R$ denotes the internuclear distance between the radiator and the perturber). $\Delta V(R)$, the difference potential, is given by

$$\Delta V(R) \equiv V_{e'}[R(t)] - V_e[R(t)],$$

and represents the difference between the electronic energies of the quasi-molecular transition. The interatomic interactions are the main physical quantities needed for a good understanding of collisional processes. The \textit{ab initio} computation of the adiabatic potential energy curves of He$_2$ have been carried out using the MOLPRO 2009 package \(^1\) (see figure 1). Complete details are given by Allard \textit{et al.} 2009 \([2]\). In a previous study, we have checked that this approach leads, for the lowest quintet, results comparable to a full CI, within less than a few thousandths of a wavenumber. Moreover errors due to BSSE are also far below the wavenumber thanks to the huge basis set involved.

\[\text{Figure 1. Potential energies for the triplet 3s (full line) and 2p (dashed line) states of the He}_2\text{ molecule. For comparison, a full CI potential calculation for the 3s }^3\Sigma_g\text{ state is overplotted (extracted from table 1 of [3]).}\]

Emission measurements of the self-broadened lines of He due to 3s $^1\Sigma - 2p$ $^1\Sigma$ transitions show that beyond a symmetrical Lorentzian center these lines exhibit a blue asymmetric behaviour \([2, 4]\). The observed asymmetries are a consequence of maxima in the 3s-2p potential difference curves at an intermediate internuclear distance (figure 2). This blue asymmetry is due to a blend of four quasi-molecular satellites in proximity to the atomic lines. Because of the blending, it can be accurately described \textit{only} with a \textit{unified} spectral line shape theory that is valid from the center to the far wing.

\section{Density effects}

The general behaviour of the profiles, particularly of the distribution of energy among multiple satellites, is simply related to the probability $W(m, h)$ of finding $m$ perturbers in a volume $\tau$ near the perturbed atom (collision volume) at any instant.

When the perturber density is $n$, $W(m, h)$ is given by the Poisson distribution

$$W(m, h) = \frac{n^m}{m!} \exp(-n)$$

\(^1\) http://www.molpro.net
with $h = n\tau$.

The effects of two or more perturbers becomes quite significant at high densities where the peak of the line profile corresponds to the most probable distribution of perturbers.

To interpret what would be seen for an electrical discharge in a liquid, where the He density may be in excess of $10^{21}$ cm$^{-3}$, it is interesting to follow the evolution of the profiles as the perturber density increases from the regime of binary collisions to one where many more perturbers act simultaneously. The line core disappears completely when the probability of finding more than one perturber interacting at a time is large. The profile of the line then shifts by the mechanism of the redistribution of its oscillator strength in higher order satellites, rather than a shift of the ”impact” line core.

![Figure 2](https://example.com/figure2.png)

**Figure 2.** $\Delta V$ and the corresponding electric dipole moment $D(R)$ in atomic units for 300 to 4 K. Left: $3s\,^3\Sigma_g \rightarrow 2p\,^3\Pi_u$ (full line) and $3s\,^3\Sigma_g \rightarrow 2p\,^3\Sigma_u$ (slashed dotted line). Right: $3s\,^3\Sigma_g \rightarrow 2p\,^3\Pi_u$ (full line) and $3s\,^3\Sigma_g \rightarrow 2p\,^3\Sigma_u$ (slashed dotted line).

### 3. Temperature effects

While the position of the line satellites critically depends on the interaction potential, their strength depends on the radiative dipole moments, $D(R)$, in the internuclear region where the line satellite is formed [1]. In Allard et al. 1999 [1] we define $\tilde{d}_{ee'}(R(t))$ as a modulated dipole

$$D(R) \equiv \tilde{d}_{ee'}[R(t)] = d_{ee'}[R(t)]e^{-\frac{V_0[R(t)]}{kT}},$$

The values of $D(R)$ for the maxima of the difference potential energy $\Delta V$ are pointed out using $\times$ in figure 2. The decreasing strength of the satellites with temperature is illustrated in figure 4. They disappear for about $T \leq 10$ K when the transition moments $d_{ee'}[R(t)]$ get too small in the region of the maximum of the difference potential of $\Delta V(R)$ for all contributing transitions.

The simplest way of characterizing a line shape is in terms of the parameters: $w$, the full width at half maximum (HWHM), $d$, the shift and the asymmetry. We have studied the variations of these parameters versus the density for $T=300$, 80 and 40 K in Allard et al. 2011 [5]. As an example here, we will consider experimental spectra recorded at 4 K, (figure 3 of Li et al. 2009 [6]), to show that it is possible to determine the physical conditions of temperature and
Figure 3. Same as figure 2 for T=4 K at long range distance. For comparison CI potential calculation (table 1 of [3]) for the 3s $^3\Sigma_g$ state is overplotted (red ×).

Figure 4. Evolution of the line profiles, with decreasing temperature for $n_{\text{He}} = 10^{20}$ cm$^{-3}$ (left), with increasing helium density (right) at T=4 K.

pressure in the emitting region of an electric discharge in liquid helium. We determined the line parameters from these published spectra, and show them on the parameter curves in figure 5. The deduced values of $T$ and $n_{\text{He}}$ have to be consistent for the width ($w$) and the shift ($d$) to uniquely define the temperature and density close to the electrode tip. For the experiment at 1.4 MPa, the deduced helium density is not the same for the width and the shift, which means that the temperature must be higher than 40 K. A grid of the parameter curves shown in figure 5, should be done at different temperatures from about 60 K to 30 K, with a step size of 5 K. It would allow us to obtain the physical conditions in the medium close to the electrode tip for all of the experimental spectra. In the following we will consider the two extreme physical conditions of pressure reported in figure 3 of Li et al. 2009 [6]. At 0.1 MPa the profile is almost unshifted and the parent line at 706 nm is still apparent. This contrasts with
2.3 MPa, where the maximum of the experimental spectrum has shifted to the position of the quasi-molecular satellites (figure 6). It is noteworthy that there is a close agreement between the experimental and theoretical profiles, and we conclude from this that the source temperature for these experiments varies from about 60 K to 30 K.

4. Study of the theoretical profiles at 4 K in the quasistatic limit
Our unified line shape theory contains the impact as well the quasistatic limits [1], however in order to get a closer comparison with results presented in Bonifaci et al. 2012 [3] we will use specifically the quasistatic limit of Eq. 2.

To explain the negative shift obtained at very low temperature shown in figures 4 and 5, we have plotted in figure 3 the potential difference in the “active” region where the modulated dipole moment \( \tilde{d}_{ee}(R(t)) \) at \( T=4 \) K is different from zero. This region is the same one identified...
Figure 7. Quasistatic profiles at $T=4$ K, $n_{\text{He}}=2.65 \times 10^{22}$ cm$^{-3}$. MRCI potentials [2] (full line) Truncated CI potentials [3] (dashed line).

Table 1. Comparison of line parameter determinations from quasistatic profiles at $T=4$ K, for $n_{\text{He}}=2.65 \times 10^{22}$ cm$^{-3}$.

|                | $w$ (cm$^{-1}$) | $d$ (cm$^{-1}$) |
|----------------|----------------|-----------------|
| this work MRCI | 39.5           | -140            |
| this work CI truncated | 42.6 | 86.5            |
| Bonifaci et al. 2012 [3] | 140 | 200             |

“liquid helium” density profiles in figure 6 of [3]. Because they noticed that the $2p$ potentials for the triplet potentials appear to be essentially flat when $R \geq 5$ Å, we overplot in figure 3 their tabulated potential for the $3s \ 3\Sigma_g$ state obtained with our basis set [2].

As can be seen in figure 3, $\Delta V$ is repulsive at intermediate range while very weakly attractive at long range with a well depth of 0.4 cm$^{-1}$. It should be noted that these values are close to the limit of ab initio calculations and that they can be expected to be sensitive to the methodology or basis sets employed in the calculations. Taking into account the fact that CI calculations of Bonifaci et al. [3] use the same reference functions as ours, this overall agreement is remarkable.

Unfortunately, table 1 of Bonifaci et al. [3] truncates $R$ at $R_{\text{cut}}=16$ Å, which consequently neglects the critical long range part of the potential. It is well known that the shift of a spectral line profile is very sensitive to the long range part of the interaction potential, and for line shape calculations such truncation leads to unphysical results. We see that there is a dramatic effect on the resultant profiles in figure 7. The calculations have been done for $n_{\text{He}}=2.65 \times 10^{22}$ cm$^{-3}$ close to the asymptotic value of helium density for $P=3.5$ MPa, according to figure 6 of Bonifaci et al. 2012 [3]. The line parameter determinations from these quasistatic profiles are summarized in table 1. An examination of figure 7 and table 1 reveals that the width of the profiles are very similar because the intermediate range of the potentials are the same. This sensitivity to the long range potential leads to opposite shifts of the profile in the two calculations. Truncation of
the long range part of the potentials produces an incorrect result. We evaluated the line parameters of Bonifaci et al. 2012 [3] from the results shown in their figures 7 and 8. The width of a spectral line profile, has to be small at low temperature, the large theoretical values obtained for the width at 4 K reported in [3, 9] are consequently unphysical.

It is noteworthy that Path Integral Monte Carlo (PIMC) calculations by [7] are in close agreement with our theoretical approach for the study of absorption spectra of helium doped with sodium. This interesting result is also presented at this conference (Allard et al. 2012 [8]).

5. Conclusions
The positive shift observed in spectra of a corona discharge in liquid He must be due to quasi-molecular lines in the blue wing which arise from potential extrema. These satellites are sensitive to temperature because, at higher temperature, the perturbers are more likely to climb the excited-state potential barrier that generates the difference-potential maximum. Large values of the width and shift are characteristic of quasi-molecular features.

From the results described above compared with published experiments we infer that the temperature in the corona discharge is above 10 K. The temperature and the density are not those in the He liquid.

As it is well known, the shift of a spectral line profile is very sensitive to the long range part of the interaction potential. Even when there is an uncertainty in the long-range van der Waals well, truncating the long range part of the potentials leads to inaccurate values of the shift. On the other hand, the width of a spectral line profile, mainly due to collisions at intermediate distance, has to be small at low temperature.

As a final caution, we note from our experience that the Fourier Transform connecting temporal physics to observed spectra is a powerful tool for line profile analyses. However as we see here, it may give completely erroneous results when used with ad hoc computational assumptions without considering the underlying physical phenomena. Furthermore, unless the time series is finely sampled and very long, and the windowing function is carefully chosen for the problem at hand, spurious oscillations will appear on the FT which are unreal and easily misinterpreted.

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