Absorption spectra of NaHe from white dwarfs to helium clusters

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Abstract. The absorption spectrum of Na produced in dense He shows line features, broadening and shift due to extrema in the $3s$-$3p$ potential differences of the transitions which contribute to the two fine-structure components. We present here a comprehensive study of Na-He collisional profiles at high density, and temperatures from 5000 K, the temperature prevailing in the atmosphere of ultra-cool white dwarfs, down to 1 K. At extremely low temperatures, experimental measurements and theoretical calculations of helium doped with alkali metals have been the subject of active study. The alkali-metal atoms are weakly bound to helium nanodroplets, and it appears that the dopants are trapped in a shallow dimple on the cluster’s surface, rather being solvated inside the cluster.

1. Theory

A unified theory of spectral line broadening (Allard et al. 1999 [1]) has been developed to calculate neutral atom spectra given the interaction and radiative transition moments for relevant states of the radiating atom with other atoms in its environment. This collisional theory goes beyond the Franck-Condon approximation but is quasi-classical for the ground state. 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 $n_p$

$$\Phi(s) = e^{-n_p \phi(s)}, \quad (1)$$

The dipole autocorrelation function $\Phi(s)$ is evaluated for a classical collision path with an average over all possible collisions. For a transition $\alpha = (i, f)$ from an initial state $i$ to a final state $f$, 

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we have
\[ g_\alpha(s) = \frac{1}{\sum_{e,e'}(\alpha)|d_{ee'}|^2} \sum_{e,e'}(\alpha) \left[ \int_0^{+\infty} 2\pi \rho d\rho \int_{-\infty}^{+\infty} dx \tilde{d}_{ee'}[R(0)] \right] \]
\[ \left[ e^{\frac{\pi}{2} \int_0^t dt V_{ee'}[R(t)]} \tilde{d}_{ee'}[R(s)] - \tilde{d}_{ee'}[R(0)] \right]. \] (2)

Our calculations are based on the \textit{ab initio} Na-He potentials of Nakayama and Yamashita 2001 [2] and radiative dipole moments of Pascale 1983 [3].

2. Quasi-molecular line satellites
The unified theory predicts that there will be line satellites centered periodically at frequencies corresponding to integer multiples of the extrema of the difference potential \( \Delta V(R) \):
\[ \Delta V(R) \equiv V_{ee'}[R(t)] = V_{e'}[R(t)] - V_e[R(t)], \] (3)
which represents the difference between the electronic energies of a quasi-molecular \( e-e' \) transition. In Allard et al. 1999 [1] we define \( \tilde{d}_{ee'}(R(t)) \) as a modulated dipole
\[ D(R) \equiv \tilde{d}_{ee'}[R(t)] = d_{ee'}[R(t)]e^{-\frac{V_{ee'}[R(t)]}{2kT}}, \] (4)
\( V_e \) is the lower state potential when we consider absorption profiles, or the upper state for the calculation of a profile in emission. Over regions where \( V_e(R) < 0 \) the factor \( e^{-\frac{V_{ee'}[R(t)]}{2kT}} \) accounts for bound states of the radiator-perturber pair, but in a classical approximation wherein the discrete bound states are replaced by a continuum; thus any band structure is smeared out. \( \Delta V \) and variation of the D(R) with temperatures of Na-He modulated dipole are displayed in figures 1 and 3.

2.1. High temperature

\[ \Delta V(R) \] and the temperature dependence of modulated dipole \( D(R) \) corresponding to the \( B - X \) transition.

The perturber density in the line-forming region of an ultra-cool white dwarf atmosphere can reach \( n_{\text{He}} = 10^{21} \text{ cm}^{-3} \), and it then requires a unified line profile calculation [4]. Because
of the large maximum in $\Delta V$ (figure 1), the line satellite at $T=5000$ K is very well-separated from the main line in the blue wing. It disappears for decreasing $T$ when the transition moment $\tilde{d}_{ee'}[R(t)]$ gets very small. Quantum mechanical calculations of absorption profiles of the Na 3s-3p transition perturbed by He [5, 6] are in agreement with our previous results [7]. The disappearance of the Na-He line satellite is seen at $T=158$ K in calculations by Zhu et al. 2006 [5]. Figure 2 shows quasi-molecular line satellites, positioned at about $\Delta V$ for NaHe, $2 \times \Delta V$ for NaHe$_2$, ... The dependence on the average number of perturbers is expected on the basis of the Poisson distribution, which indicates the probability of finding a select number of uncorrelated perturbers in the collision volume. Multiple perturber effects such as these are now well known, and were first identified in experimental alkali spectra by Exton and Snow 1978 [8] and by Kielkopf and Allard 1979 [9].

2.2. Low temperature

![Figure 3](image-url). $\Delta V(R)$ and the temperature dependence of modulated dipole $D(R)$ for the D1 line.

![Figure 4](image-url). Variation with He density (cm$^{-3}$) of the D1 component at $T=1$ K.

While the $^2\Pi_{3/2}$ state is purely attractive, the $^2\Pi_{1/2}$ state has a small barrier at 6.72 Å due to the spin-orbit coupling, the height of which relative to the $^2P_{1/2}$ state is 1.62 cm$^{-1}$ (figure 7 of Nakayama and Yamashita 2001 [2]). Because $\Delta V$ for the transition 3s $X \rightarrow 3p$ A $P_{1/2}$ is very small, there is no resolved quasi-molecular feature. It results an enhancement in the core of the line at $\Delta \omega = \Delta V = 3$cm$^{-1}$. At very low temperature and at the internuclear separation $R_e = 6.4$ Å close to the position where $\Delta V$ is an extremum (figure 3), the transition moment $\tilde{d}_{ee'}[R(t)]$ increases for decreasing temperature. This increasing of $D(R)$ can be explained by examining the potential energy curves given in figure 1 of Nakayama and Yamashita 2001 [2]. The ground state is repulsive at short range and very weakly attractive at intermediate range (6.6 Å) with a well depth of 1.22 cm$^{-1}$. Figure 4 shows clearly an asymmetrical shape of the D1 component due to the bound-free transition. Increasing the He density results in a shift of the D1 line towards the position of the extremum of $\Delta V$. The intensity variation in figure 4 is evidence of the presence of high order effects, and as $\Delta V$ is very small, we observe a blend of these structures.
3. Pressure dependence of the sum of the D1 and D2 components
Absorption cross-sections for $3s - 3p P_{1/2}$ and $3s - 3p P_{3/2}$ transitions are shown in figure 5. At low density the ratio for the components is 2, as expected for resonance doublets of light alkalies. Whereas the amplitude of the D2 line decreases exponentially, the blue wing of the D1 line gains in strength relative to the parent line. For $N_{He}=6 \times 10^{20}$ cm$^{-3}$ the peak amplitude of D1 becomes more important than the peak of D2 (figure 7) and for $N_{He}=9 \times 10^{20}$ cm$^{-3}$ (figure 6) there is a blend of the two fine-structure components. The same behaviour is observed in the experimental spectra (figure 8). The two vertical lines indicate the positions of the unperturbed D1 and D2 lines. In order to check whether we have reached the quasistatic limit we compare in figure 6 the unified profile and the one obtained using the quasistatic limit of the autocorrelation function. As we can expect at this high density the profiles are comparable with a perfect agreement in the wing.

4. Comparison with Path Integral Monte Carlo calculations
In recent years special attention has been focused on experimental measurements and theoretical calculations of helium nanodroplets doped with alkali metals [10, 11, 12, 13, 14]. Several theoretical works have described absorption spectra of Na atoms attached to helium nanodroplets (see Hernando et al. 2010 [13] and references therein). The first physical interpretation of the spectra was done by Nakayama and Yamashita 2001 [2]. Using a diatomics-in-molecules (DIM) type of calculation for describing the interaction potential between Na and helium atoms, they performed quantum path integral Monte Carlo (PIMC) simulations to obtain the helium density profile around Na in the ground state and also the absorption spectra of Ak-He$_n$ via the Franck-Condon (FC) approximation (Ak=Li, Na, K).

$$I_{eg}(\omega) \propto |M_{eg}|^2 \int dR \rho(R; \beta) \delta (V_e(R) - V_g(R) - \hbar \omega),$$

(5) where $V_g$ and $V_e$ are the potential energies in the electronic ground and excited states, respectively. $M_{eg}$ is the electronic transition dipole moment. The quantity $\rho(R; \beta)$ is the
quantum mechanical thermal density matrix on the electronic ground state surface. One can, therefore, obtain the absorption spectrum by calculating the potential energy difference at each nuclear coordinate generated by path integral Monte Carlo calculations. Figure 9 shows the average helium density profiles in the same range of internuclear distance as in figure 3 where ∆V is significant. We can see that both theoretical approaches have a dramatic change in the region where the bound-free transition takes place. They successfully reproduced the overall shapes of the spectra and explained their features through a discussion of potential difference and number of He atoms interacting with the Na atom in the region which is, from our point of view, the collision volume.

In our unified approach we use averages of independent Na-He pair collisions, emphasizing the collisional process rather the collective quantum description of the interaction of a Na atom with the He cluster (which may be important for very small He atom numbers). However the present approach goes beyond the FC approximation and provides a better description close to the line center. It can be seen that despite those differences, the two methods provide similar results. The complex behavior observed experimentally (figure 8) reflects the fact that the radiating alkali atom experiences multiple encounters with helium atoms and our collisional analysis gives a good physical understanding of the phenomena. Using the average helium density profile for NaHe₃₀ in the quasistatic limit instead of the modulated dipole moment, we obtained the profile shown in figure 10 compared to a quasistatic profile for (n_{He}=9 × 10^{20} \text{ cm}^{-3}). This interesting result demonstrates that the active region is as well described by the average profile as it is by the modulated dipole moment. It explains why our two approaches are in such close agreement. They both describe a radiating alkali atom surrounded by an equilibrium distribution of He atoms, with a spectrum given by multiple perturber phenomena in the high He density and very low temperature of liquid He.

5. Experimental spectra

Large liquid helium clusters produced in a supersonic jet are doped with alkali atoms (Li, Na, K) and characterized by means of laser induced fluorescence (Stienkemeier et al. 1996 [11]). The main feature of the spectra is that two absorption maxima are observed. One is near the D₂ line of the atomic transition and the other between the D₁ and D₂ lines. The spectrum broadens and the red maximum shifts slightly to the blue with increasing cluster size. The blue maximum is almost unshifted at all cluster sizes. The relative amplitude of the two absorption maxima changes slightly, that is, the red maximum becomes higher and dominant in larger clusters.

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Figure 7. Unified profiles for \((n_{\text{He}}=6\) and \(8.5\times10^{20}\text{cm}^{-3}\)) compared to PIMC calculations of [2]. \((\Delta\omega=\omega-\omega_0\), where \(\omega_0\) is relative to the center of gravity of the two fine-structure components).

Figure 8. Absorption spectrum of Na attached to large helium clusters \(\text{He}_N\) for different cluster sizes \((N = 12500, 10000, 5000, 2000, 900);\) from top to bottom). For sake of clarity individual curves are displaced vertically. (Extracted from Stienkemeier et al. 1996 [11]).

Figure 9. Average helium density profiles for the clusters at \(T=0.5\) K. Extracted partly from figure 2 of [2].

Figure 10. Quasistatic profiles obtained with average helium density profile and modulated dipole moment compared.

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