Emission profiles of K-He exciplexes in cold helium gas

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Abstract. Emission spectra of exciplexes composed of a light alkali atom in the first excited state and $^4$He atoms have been observed in cryogenic gas in the spectral range from the atomic D lines to 6300 cm$^{-1}$. A unified semi-classical theory of line broadening has been used to determine the total profile from the center to the far wings of emission profiles of potassium perturbed by helium at low temperatures and high He density. The agreement of the theoretical peak positions of K$^*$He$_n$ exciplexes compared to the experimental determinations is fairly good. Such comparisons provide a critical test of the calculated molecular potentials and the relevance of the theoretical approach which has been used.

1. Theory
A unified theory of spectral line broadening 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. 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 $n_p \Phi(s) = e^{-n_p g(s)}$, (1)

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

$$g_\alpha(s) = \sum_{e,e'} |d_{ee'}|^2 \int_0^{+\infty} 2\pi \rho d\rho \int_{-\infty}^{+\infty} dx \tilde{d}_{ee'}[R(0)]$$

$$[e^{i} \int_0^{dt} V_{ee'}[R(t)] d\tilde{d}_{ee'}[R(s)] - \tilde{d}_{ee'}[R(0)]].$$

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

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

(2)
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.

In [1] we define \( \tilde{d}_{ee'}(R(t)) \) as a modulated dipole

\[
D(R) \equiv \tilde{d}_{ee'}[R(t)] = d_{ee'}[R(t)] e^{-\frac{V_e[R(t)]}{2kT}},
\]  

(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. Note that over regions where \( V_e(R) < 0 \), the factor \( e^{-\frac{V_e[R(t)]}{2kT}} \) 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.

![Figure 1](image1.png)

**Figure 1.** Potential curve for the \( X^2 \Sigma \) state of the He\(_2\) molecule [2], \((R_e=2.96 \text{ Å})\).

![Figure 2](image2.png)

**Figure 2.** Potential curves for the \( 4p \Pi \) states of the K-He molecule [3], \( A^2 \Pi_{1/2} \) (full line) and \( A^2 \Pi_{3/2} \) (dashed line) \((R_e=2.8 \text{ Å})\).

Laboratory spectra of K with H\(_2\) and He [4, 5] agree exceptionally well with the semi-classical profiles based on molecular potentials of [3] and [6]. The comparison with theoretical profiles establishes the accuracy of the interaction potentials, which are difficult to compute \textit{a priori}.

2. Emission profiles

While \( B \) states radiates in the blue wing, \( A \) states radiate in the red wing. Full quantum mechanical calculations in the binary approximation done by Zhu et al. 2006 [7] predict a K-He blue line satellite about 7080 nm in agreement with laboratory spectra whereas a broad plateau is obtained at around 830 nm on the red wing of emission profiles.

We present in figure 2 the excited-state potentials \( A^2 \Pi \) as a function of internuclear distance. They have minimum values, \( V_{\text{min}}=212/193 \text{ cm}^{-1} \), situated at the equilibrium distance, \( R_e=2.8 \text{ Å} \) respectively for \( A^2 \Pi_{3/2} \) and \( A^2 \Pi_{1/2} \) states. The well depth has six bound vibrational levels for zero angular momentum \( J=0 \). Table 1 of Zhu et al. et al. 2006 [7] gives the binding energies of the vibrational levels of KHe. The \textit{ab initio} energy curve for the ground state of He\(_2\) is shown in figure 1. The equilibrium distances for all these potentials are around 3 Å. The bound-free coefficients is a weighted sum of the emission rates of the individual rovibrational levels of the \( A^2 \Pi \) state. In the high pressure limit the bound and continuum states are thermally populated and the emission coefficient is the sum of the bound-free and free-free coefficients. Figure 12 of [7] shows the variation with temperature between 158 and 3000 K of emission.
coefficients. At lower temperature it results an enhancement of the maximum at 830 nm, it arises, for bound upper states, through the Boltzmann factor in the relative population:

$$g(v, j) = (2J + 1)e^{-\frac{V_{v,j}}{kT}}$$  \hspace{1cm} (5)

![Figure 3](image1.png)

**Figure 3.** High pressure semi-classical profiles of the D$_2$ line at temperatures T=158 (full line), 100 (dashed line), and 50 K (dotted line). The helium density is $n_{\text{He}} = 9 \times 10^{19}$ cm$^{-3}$.

![Figure 4](image2.png)

**Figure 4.** Emission profile at T=50 K and $n_{\text{He}}=9 \times 10^{19}$ cm$^{-3}$.
Figure 5. Emission spectra of KHe$_n$ in the case of D$_2$ excitation at various temperatures in gaseous helium ($n_{\text{He}} = 9 \times 10^{19}$ cm$^{-3}$). Vertical lines labelled as a-e indicate the peak positions of five Gaussian curves for $n=1$-5 (extracted from Enomoto et al. 2004 [8]).

3. Semi-classical profiles
We present figure 3 the variation of the semi-classical emission profiles for $T$ decreasing from $T=158$ K to 50 K. The intensity of the red wing increases as expected from Eqs. (4-5) corresponding to emission from the bottom of the $A^2\Pi$-state well. At this small internuclear separation $R_e$ the transition moment given by the modulated dipole moment gets very large at low temperature.

Broad peak was already observed in the NaHe wing spectrum of Havey et al. 1980 [9]. Such peaks are present in the red wing of the alkali-rare gas molecules when $D_e \gg kT$. For a temperature of 50 K, the thermal energy $kT$ becomes 70 cm$^{-1}$. At high density, $n_{\text{He}} = 9 \times 10^{19}$ cm$^{-3}$, multiple-perturber effects appear (figures 3-4), not only we obtain the excimer K*He but also the exciplexes K*He$_2$ and K*He$_3$ (K* represents the potassium atom in the first excited $p$ state).
Comparison with experimental spectra

Figure 5 shows emission spectra of Enomoto et al. 2004 [8] for KHe at various temperatures, the helium density is $n_{\text{He}} = 9 \times 10^{19} \text{ cm}^{-3}$. The emission spectra are a superposition of spectral components of KHe$_n$ and each peak of the observed spectra corresponds to the spectrum for different $n$. In order to determine experimentally the peak positions and the widths of spectral components of K$^*$He$_n$, they fitted superposition of five Gaussian curves.

The positions of the peaks of the emission bands (figure 4) and the experimental determinations of the observed peaks are summarized in table 1. The agreement of our theoretical peak position of KHe$_n$ exciplex compared to the experimental ones gives confidence in the determination of the potential of the $A^2\Pi$ state at short distance responsible of the red wing. The full width at half maximum (FWHM) is also very close, 700 cm$^{-1}$ for the KHe satellite compare to 726 cm$^{-1}$ determine from the Gaussian fits of the observed spectra.

Table 1. Comparison of theoretical peak positions at T=50 K with experimental determinations.

| $n$ | $\nu_{\text{theor}}$ (cm$^{-1}$) | $\nu_{\text{exp}}$ (cm$^{-1}$) |
|-----|---------------------------------|-------------------------------|
| 1   | 11884                           | 11914                         |
| 2   | 10824                           | 10826                         |
| 3   | 9823                            | 9608                          |

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