YU ISSN 0015-3206
FZKAAA 14 (4) 345 (1982)

LETTER TO THE EDITOR

SATELLITE BANDS IN THE FAR BLUE WING OF THE POTASSIUM FIRST RESONANCE DOUBLET

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Received 29 September 1982

UDC 539.186.3

Original scientific paper

We report the observation and theoretical interpretation of the quasi-static far blue wing of the self-broadened potassium first resonance doublet. Besides pronounced triplet satellite band at 721.4 nm, we observed a very weak satellite at 748.5 nm. The interpretation of both satellite bands is given by means of the calculated potential curves.

A very far blue wing of the light alkali first resonance doublet is mainly formed out of two difference potential curves $B\,^1\Pi_u - X^1\Sigma_g^+$ and $^3\Pi_g - {}^3\Sigma_u^+$. It has been recently shown that triplet difference potential is directly responsible for the occurence of the satellite band at 551.5 nm in the case of sodium[1] and at 603.7 nm in the case of lithium[2]. We were interested to observe similar satellite band in the case of potassium and other heavier alkali quasimolecules. The present analysis of the interaction of two potassium atoms could lead to a better understanding of the heavier alkali collisional molecules[3].

We have employed the heat-pipe oven of the modified version recently described by Scheingraber and Vidal[4]. Both horizontal and vertical heat-pipes have been filled with pure potassium and were operated in the heat-pipe regime. In that way the length of the vapour column was better defined than usual and we have been able to measure the absorption spectra of the dense alkali vapours in the almost-cell-conditions at high temperatures. The temperature in the cell was changed in the range from 713 K to 753 K while the concentration of potassium atoms varied from 1.26×10^{23} m^{-3} to 2.54×10^{23} m^{-3}. We used standard

absorption technique by means of a current stabilized halogen lamp, a high resolution monochromator (resolution better than 0.01 nm), a red sensitive photomultiplier, an amplifier and a strip-chart recorder.

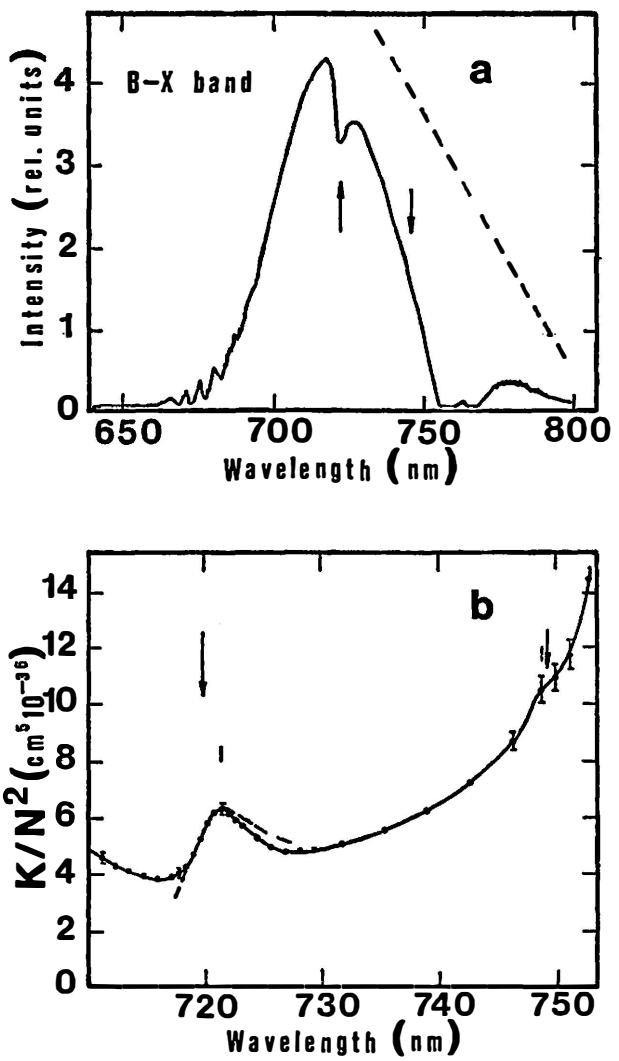

Figure 1. a) Absorption spectrum near the potassium first resonance doublet. The dashed line represent the continuum of a halogen lamp. The length of the vapour column was 5.4 cm and pressure of potassium was 10^3 Pa.

b) The reduced absorption coefficient for the blue wing of the potassium first resonance doublet. The dashed line represented calculated satellite shape which was obtained with scaled triplet potential curves of sodium. The intensity of the calculated curve is normalized to the experimental satellite peak value. Theoretical curve reproduces fairly well exponential fall-off beyond the maximum.

In Fig. 1a we present a portion of absorption spectrum near potassium first resonance doublet with the positions of the satellite bands indicated by arrows. In Fig. 1b, we present the plot of the absorption coefficient divided by the square of the particle density against the wavelength in the far blue wing of the merged potassium resonance lines. The points obtained are given with the erorr bars from the averaging procedure over four different potassium atom densities. The satellite band at 721.4 nm has a typical form corresponding to the maximum in the difference potential curve, but the satellite band closer to the line centre is rather weak and no attempt was done to analyse its peculiar form.

In order to explain the origin of the pronounced satellite band at 721.4 nm we recall that similar satellites were found for the cases of sodium and lithium, and explained in terms of the $^3\Pi_g - {}^3\Sigma_u^+$ difference potential curves[1,2]. We used the procedure suggested by Konowalow and Rosenkrantz[5] and scaled the results for sodium triplet potential curves so that the relevant difference potential fits the position of the triplet satellite in the case of potassium. The calculated satellite shape shown by the dashed lines in Fig. 1b fairly well reproduces the experimental satellite shape (we have employed the theory of Szudy and Baylis[6] using the quadratic approximation for the difference potential curve). In principle the physical model succesfully used in the case of lighter alkali dimers works well in the case of potassium triplet satellite. However, difficulties arise when we attempted to interpret the weaker satellite band closer to the line centre. Since the ab initio configuration interaction calculations[5] do not take into account the spin-orbit interaction we tried a different approach by treating the spin-orbit interaction explicitly and including the exchange interaction in an asymptotically correct way[7].

We have performed the interaction potential calculations in the longrange region in essentially the same way proposed by Umanskij and Nikitin[8], the main difference being in the careful evaluation of the dispersion energy. The results of these calculations are presented in the form of the relevant difference potential curves in Fig. 2a. At 0.5 nm the group of four difference potential curves corresponding to 2_g, 1_g and almost degenerate O_g^- and O_g^+ potentials forming $^3\Pi_g$ state have pronounced maximum which actually produced the observed satellite band at 721.4 nm. At about 0.9 nm a very interesting interaction of two O_g^+ potential curves occurs. The strong exchange interaction bends the upper O_g^+ potential curves downwards where it should cross several other potential curves (2_g, 1_g, O_g^- and O_g^+). However due to Wigner-Neumann theorem two O_g^+ curves cannot cross, but rather they are subjected to an avoided crossing. At still larger internuclear separations the difference potential curves resemble very much to those calculated by Movre and Pichler[9].

In Fig. 2b we show the molecular absorption oscillator strengths for the transitions from the ground states to two O_g^+ states involved in the avoided crossing. In the region of the avoided crossing, at about 0.9 nm of internuclear separation oscillator strengths of both O_g^+ (1/2) and O_g^+ (3/2) drastically change their values. The rate of change of the oscillator strengths and their magnitudes at relevant internuclear separations explain, at least qualitatively, why we observe only one satellite band instead of three. The maximum of the upper O_g^+ potential curve will not produce a satellite band since the corresponding oscillator strength is almost negligible in the small region of interest (around 1 nm of internuclear separation). The minimum of the same difference potential will appear as a satellite band, since the relevant oscillator strength, $f(O_g^+ [^3\Pi_g])$, suddenly increases in the region

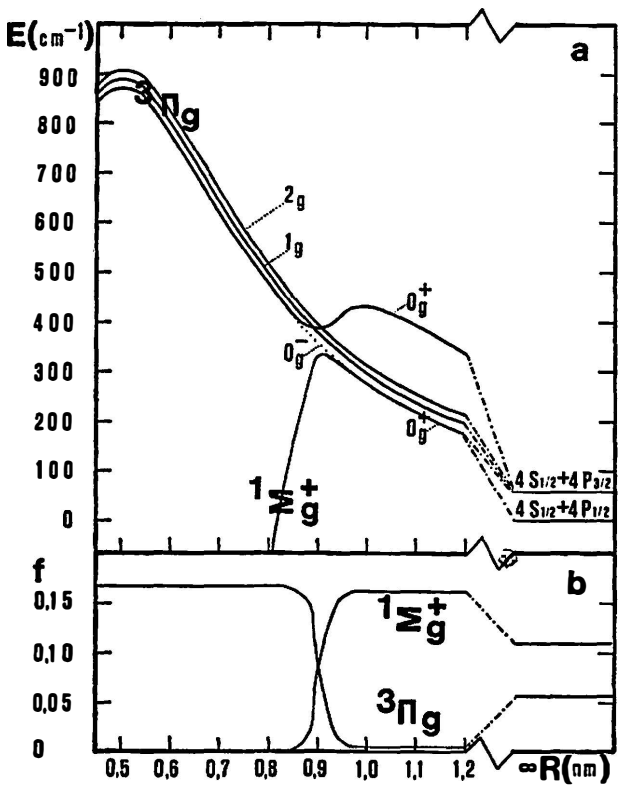

Figure 2. a) The relevant difference potential curves ($^3\Pi_g - {}^3\Sigma^+$ and $^1\Sigma_g^+ - {}^3\Sigma_u^+$) in the long-range region of interatomic distances.

b) The molecular absorption oscillator strengths for transitions from $^3\Sigma_u^+$ to O_g^+ ($^1\Sigma_g^+$) and O_u^+ ($^3\Pi_g$) states involved in the avoided crossing.

around 0.9 nm. On the other hand the maximum of the lower O_g^+ [$^1\Sigma_g^+$] potential curve, quite possibily, will not appear in the spectrum, since the relevant oscillator strength suddenly decreases in the region around 0.9 nm of internuclear separation. It means that in the later case the spectral contribution to the interference pattern from the smaller internuclear separations will be negligible because of the rapidly decreasing oscillator strength and smaller value of the probability distribution function for the perturbing particles. In addition the corresponding maximum of the O_g^+ (1/2) falls in the region of the strong wing of the potassium first resonance doublet.

In conclusion we would like to mention that the present letter describes an attempt to interpret in a semiquantitative way the appearence of the two satellite bands in the far self-broadened wing of the potassium first resonance doublet. The interpretation is given in terms of calculated potential curves using either scaled ab initio configuration interaction calculations or asymptotic calculations. The existing theory of the satellite shape was employed only in the case of the pronounced triplet satellite band at 721.4 nm, since at present time there is no

theoretical description of a satellite band shape when the relevant oscillator strength changes its value appreciabely over the region of interest. We intend to observe and interpret the analogous satellite bands in rubidium and caesium spectra.

Acknowledgment

We would like to thank K. Niemax and Č. Vadla for the fruitful discussions that followed their independent observations of the satellite bands discussed in this letter. This work received support under a grant from the Self-management Community of Interest in Science of S. R. Croatia. Partial support from the National Bureau of Standards, Washington and a donation from Alexander von Humboldt Stiftung, W. Germany is gratefully acknowledged.

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SATELITI U PLAVOM KRILU KALIJEVOG PRVOG REZONANTNOG DUBLETA

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Originalni znanstveni rad

Promatrani su sateliti u dalekom kvazistatičkom plavom krilu kalijevog rezonantnog dubleta proširenog vlastitim pritiskom. Pored izraženog tripletnog satelita na 721.4 nm opažen je slabiji satelit na 748.5 nm. Tumačenje ovih pojava prikazano je pomoću interakcionih krivulja atoma kalija u $4P_{3/2,1/2}$ i $4S_{1\,2}$ stanju.