ABSORPTION BANDS OF ALKALI ATOMS IN THE PRESENCE OF FOREIGN GASES: REMARKS ON CH'EN'S PAPER[1]

By Ta-You Wu (吳大猷)

Department of Physics, National University of Peking, Kunming

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ABSTRACT

The recent suggestion of Ch'en that the diffused bands appearing on the short wave-length side of the principal series lines of the alkali atoms in the presence of foreign gases are due to the increase in the energy of the optical electron in the upper state through collisions with a foreign atom is examined. Serious objections encountered in this theory are pointed out in this note.

It was found by Ny and Ch'en[2] that in the absorption spectra of the alkali metal atoms in the presence of foreign gases such as H, He, N, Ne, A, a narrow and structureless band appears on the short wave-length side of the second member of the principal series in the case of K, Rb, Cs and of the third member in the case of Na. A natural explanation of such bands seems to be that given by Oldenburg and Kuhn, namely, the bands arise from transitions in the alkali atom at the moment when it is perturbed by the close approach of a foreign atom[3]. Recently, after summarizing all the available observed data, Ch'en concludes that they do not support the theory of Oldenburg and Kuhn since the bands are found only in the neighborhood of the above-mentioned specific lines while the Oldenburg-Kuhn theory would lead one to expect such bands near other lines as well. Ch'en suggests that these bands are due to "the increase of the energy of

1. S. Y. Ch'en, Phys. Rev. *65*, 338, (1944).
2. Ny and Ch'en, Nature *138*, 1055, (1936).
3. Oldenburg, Zeits. f. Physik *47*, 184 (1928); *55*, 1 (1929); Kuhn and Oldenburg, Phys. Rev. *41*, 72, (1932).

the optical electron through the process of collision with the foreign gas atom when the electron reaches that energy level whose orbital radius is close to the distance of optical collision". On this picture, Ch'en explains the observed increase in the separation between the series line and the associated band with the decrease in the mass of the foreign gas atom as the consequent greater energy transfer from the foreign atom to the valence electron of the alkali atom. The observed increase in the width of the band with the decrease in the mass of the foreign atom is thought to be due to the greater energy spread of the lighter foreign atoms. The purpose of this note is to examine this proposed mechanism of the production of these bands.

(i) The contention that the energy of the optical electron in the upper state of the transition is raised by collision with a foreign atom so that the absorbed quantum corresponds to a higher frequency ν' than the ν of the series line leads to the following inconsistency: In order that the foreign atom may impart its kinetic energy to the excited alkali atom, the latter must first be in the excited state, i.e., it must first have absorbed the quantum $h\nu$ but not $h\nu'$. Granting that the electron of the alkali atom can now be raised to an energy state slightly above the ^2P states by collisions with foreign atoms, the alkali atom would then be already in that state (after absorbing the quantum $h\nu$ and receiving some K. E. from a foreign atom) and no further absorption of the quantum $h\nu'$ is possible. On the other hand, if the alkali atom does absorb the quantum $h\nu'$, then the atom would reach the upper final state by the absorption process alone, no additional K. E. from a foreign atom being necessary. It is not understandable how the alkali atom can absorb a quantum $h\nu'$ in anticipation of receiving a kick from a foreign atom; and in any case, the energy $h(\nu'-\nu)$ and the K. E. from a foreign atom would be redundant.

This absurdity does not arise in the theory of Kuhn and Oldenburg, according to which the bands arise from transitions in the alkali atom perturbed by the close collision with a foreign atom, or, what is the same thing, from transitions in the loosely bound molecule alkali atom + foreign atom.

(ii) If an impinging atom can impart its kinetic energy to the electron of an alkali atom, it would be necessary then to assume that the latter can exist in non-quantized states. This is at variance with the evidences from all other collision experiments (critical potential experiments).

(iii) Even granting the possibility of such an energy transfer from an atom to the electron of another atom, one meets with the difficulty that the amount of energy transferred would be only of the order m/M times the K. E. of the colliding atom, where m, M are the masses of the electron and the impinging atom respectively. Now the K. E. corresponding to 500 ° C, the temperature of the gas, is of the order 500 cm^{-1} and the energy transferred from H_2 will then be only of the order of a tenth of a cm^{-1}. This is far too small compared with the observed separations between the bands and the corresponding series lines, which are of the order 10^2 cm^{-1} in the case of Na and K.

Furthermore, since the electronic energy of an atom is very much greater than the thermal energy of the atoms at ordinary temperatures, collisions between the foreign atoms and the electrons of the alkali atoms would result in general in a decrease, instead of an increase, in the electron energy of the alkali atoms, even if we grant the possibility of such energy transfers that we do not admit according to (ii) above.

(iv) The cross-section or probability of a process in which the K. E. of a heavy particle (atom or molecule) is transferred into the energy of electronic excitation of an atom is known from the general theory to be extremely small unless the K. E. of the heavy particle is very large compared with the amount of the energy to be transferred. Hence, even if we grant the possibility of such a transfer in the present case (which we do not admit according to (ii) above), the probability of such transfers is exceedingly small.

(v) The suggested explanation fails to explain why such bands do not appear beside the series lines other than the second member in the case of K, Rb, Cs, and the third member in the case of Na. If the bands appear because the orbital radius of the proper P orbit is such that the impinging atom spends the major part of its time there, as is contended by Ch'en, then the same argument will lead one to expect bands to appear beside the higher series members (large P orbits) when the pressure is low, and beside the first series member when the pressure is sufficiently high. This is not observed to be the case.

Incidentally, the orbital radii given by Ch'en (Na 5p, 19A; K 5p, 19A; Rb 6p, 28A; Cs 7p, 38A) seem to have been calculated for H. In the alkalies, the radii would be very much smaller for the heavier ones because of the greater effective nuclear charge, as shown by the quantum defects (0.86 for ^2P of Na; 1.8

for ^2P of K; 2.7 for ^2P of Rb; etc.). Reference to an energy level diagram (such as given on p. 87 in White's *Introduction to Atomic Spectra*) shows in fact that the radii of the Na 4p, K 5p, Rb 6p, Cs 7p (all being the upper state for the second member of their principal series) are approximately the same. Similarly for Na 5p, K 6p, Rb 7p and Cs 8p. That the bands are observed near the third member in Na but the second member in the other alkalies shows that the orbital size of the upper state is not the only determining factor in the production of the bands.

(vi) Let us now consider Ch'en's objection against the theory of Kuhn and Oldenburg. Although the observed regularity regarding the width of the bands and their separations from the series lines in passing through the various alkali atoms and foreign gases cannot be given an a priori explanation on this theory, it may be remembered that the width of the band and its separation from the series line in each individual case can always be accounted for by suitably adjusting the potential curves for the system alkali atom + foreign atom. The non-appearance of bands near other series lines may be a matter of these potential curves. While it must be admitted that it seems rather queer that the potential curves are just such as to conform to the above mentioned observed regularities, it must also be admitted that there is nothing fundamentally impossible in it. Ch'en's objection to Kuhn-Oldenburg's theory is that it furnishes no explanation why bands are not observed near other lines; but as shown in (v) above, his suggested theory fails also at this point, not to mention the other difficulties (i), (ii) and (iii).

Editor's Note. Dr. Ch'en Shang-Yi has a reply to this critical essay which will appear later.