Vol. A54 (1978) *ACTA PHYSICA POLONICA* No 6

FAR-WING LINE BROADENING*

BY A. GALLAGHER

Joint Institute for Laboratory Astrophysics,
National Bureau of Standards and University of Colorado**

(Received April 24, 1978)

Some of the history and applications of the quasi-static theory of line broadening are discussed, as is its relationship to molecular radiation theory. Interaction potentials of alkali-noble gas diatomic pairs in the ground and first excited state, obtained from application of this theory, are given.

Atomic absorption and emission lines broaden, shift, and become asymmetric due to collisions with other gases. The impact theory of Lorentz [1] and Weisskopf [2] explained the broadening and shift at low pressures, for which the line width is less than τ_c^{-1} and τ_c is the characteristic collision time. In order to explain the asymmetry and the high-pressure shift, Kuhn [3] and Margenau [4] utilized a "statistical" or "quasi-static" approximation that had first been used by Holtzmark [5] to describe the line broadening due to ions in plasmas. Kuhn [3] also used this approximation, which considered the perturbers as static during the radiation process, to explain far-wing intensities and bands. However, considerable uncertainty and some controversy existed with regard to the interpretation of various wing intensities and far-wing diffuse bands. It was recognized that the Franck-Condon principle [6] should describe the overall intensity observed in the far line wings, but the exact connection to various observed features and the role of nuclear motion had not been clarified. These questions were definitively resolved and the quasi-static theory put on a solid foundation when Aleksander Jabłoński [7] derived the far-wing intensity as that due to molecular electronic transitions of the diatomic collision-complex. Jabłoński's treatment, based on the Born-Oppenheimer separation and the Frank-Condon principle, included perturber motion and unified the theories of collisional line broadening and molecular radiation.

The collision complex is a free vibrational state of a molecule, so Jabłoński considered free-free transitions and derived for them the classical approximation of constant inter-

---

* Dedicated to Professor Aleksander Jabłoński on the occasion of his 80th birthday.

** Address: Joint Institute for Laboratory Astrophysics, National Bureau of Standards and University of Colorado, Boulder, Colorado 80309, USA.

nuclear separation and nuclear kinetic energy during the electronic transition. This Classical Franck-Condon Principle was independently derived by Condon for the more customary bound-bound molecular transitions. This approximation leads to the familiar result that a photon radiated when the nuclei are at separation R will have energy $h\nu = V^*(R) - V(R)$, where $V^*(R)$ and $V(R)$ are the electronic energies of the upper and lower molecular adiabatic states respectively. The statistical theory had assumed this same relation, but without establishing that it was still a good approximation when nuclear motion is included. This classical approximation is a powerful interpretive tool that has had many important applications in molecular spectroscopy and in line broadening. It underlies virtually all interpretations of far-wing line-shape data.

Jabłoński's calculation of the free-free molecular transition probability utilized WKB wave functions and the random phase approximation. It thereby represented classical motion, and the calculated radiation intensity included the velocity factor of a curved classical orbit in the diatomic interaction potential. In essence, the radiation emitted during traversal of internuclear separation $R \to R+dR$ is proportional to the traversal time $dt = dR/v_R$ during the classical orbit, where v_R is the R component of velocity. When integrated over a thermal distribution of collision velocities [8], this leads to multiplicative Boltzmann factors $\exp\,[-V^*(R)/kT]$ in the emission intensity and $\exp\,[-V(R)/kT]$ for absorption. These Boltzmann factors represent the distribution of atoms and molecules in a thermal gas [9]. They yield consistency with thermodynamic radiation theory, and also provide a mechanism for analyzing line-broadening data to obtain the $V^*(R)$ and $V(R)$ responsible for the observed radiation. Since in this classical theory the photon frequency depends only on the difference $V^*(R) - V(R)$, either prior knowledge of one potential or some dependence on only one potential is necessary to determine the potentials from continuum intensity data. Thus these Boltzmann factors combined with the relation $h\nu = V^*(R) - V(R)$ provide a powerful mechanism for determining the potentials responsible for molecular continuum bands, or equivalently the far wings of collisionally broadened lines.

Accurate, quantitative intensity data as a function of temperature are necessary to take advantage of this potentially valuable interpretive scheme; consequently it has only been used relatively recently. The method has been utilized in our laboratory to determine the alkali-noble gas interaction potentials responsible for the far wings of the alkali resonance lines [10]. These diatomic pairs are very weakly bound, so that their interaction potentials were not known from traditional bound-bound molecular spectroscopy. In addition to explaining the general features of our line-wing data, these interaction potentials are also essential to understanding alkali excitation transfer due to inert gas collisions, another major topic in atomic collision theory.

As an example of this type of data and the resulting potentials [10] we show the Xe broadened Rb $5^2P_{3/2} - 5^2S_{1/2}$ resonance line, or equivalently the $A-X$ and $B-X$ bands of RbXe, in figure 1. The associated Rb$-$Xe interaction potentials are given in figure 2. The Rb interaction with several inert gases, deduced in this way, are also shown in figure 2 while the interactions of different alkalis [11] with Xe are given in figure 3. These potentials and their systematic behavior [12] can then be used to analyze the

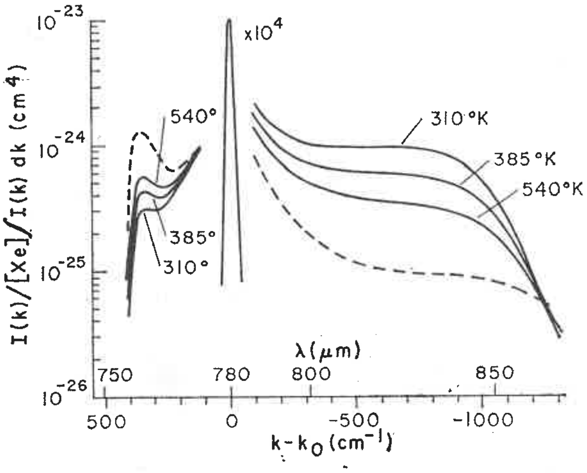

Fig. 1. Normalized Rb($5^2P_{3/2}$) spontaneous emission intensity $I(k)$ in the presence of Xe at a density [Xe] of $\sim 10^{19}$ cm^{-3}, from Ref. [10]. The gas temperature is indicated; the dashed line corresponds to the $T = \infty$ limit

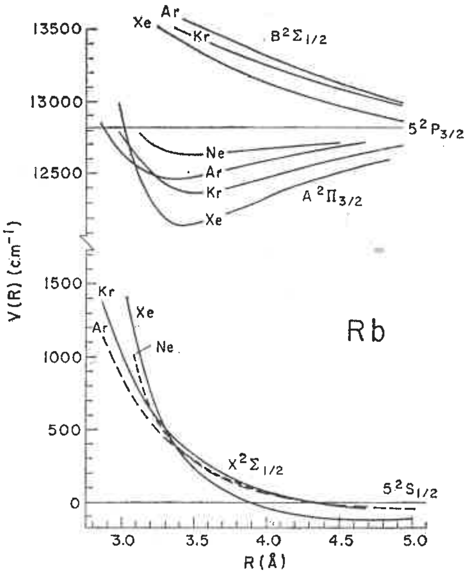

Fig. 2. Adiabatic potentials $V(R)$ for the $5^2S_{1/2}$ and $5^2P_{3/2}$ state of Rb interacting with the noble gases, from data in Ref. [8]

non-classical features of the band intensities and cross sections for excitation transfer. Thus application of the classical theory is the key first step in understanding the many non-classical aspects of the collisions as well as the general behavior of the far-wing intensities.

The theories of collisional line shapes have developed rapidly in recent years. Fully quantum mechanical calculations for the line center and far wings have been carried out, and many calculations of interatomic potential have become available. The range and accuracy of data is also advancing rapidly, and applications for this knowledge frequently appear. The quasi-static theory, as elucidated by Aleksander Jabłoński, still plays an essential and central role in this active field.

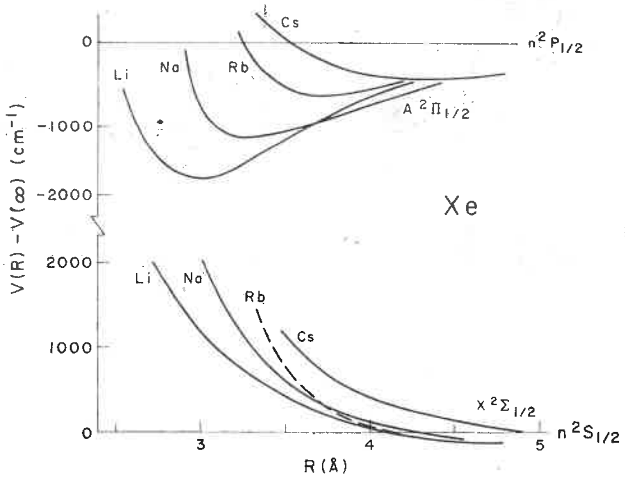

Fig. 3. Adiabatic potentials $V(R)$ for the ground ($n^2S_{1/2}$) and first excited ($n^2P_{1/2}$) states of the alkalis interacting with Xe, from data in Ref. [10]

REFERENCES

[1] H. A. Lorentz, *Proc. Acad. Sci. Amsterdam* **8**, 591 (1906).

[2] V. Weisskopf, *Phys. Z.* **34**, 1 (1933).

[3] H. Kuhn, *Z. Phys.* **63**, 458 (1930); *Philos. Mag.* **18**, 987 (1934); *Phys. Rev.* **52**, 133 (1937).

[4] H. Margenau, *Phys. Rev.* **40**, 387 (1932); **48**, 755 (1935).

[5] H. Holzmark, *Ann. Phys.* **58**, 577 (1917).

[6] J. Frank, *Z. Phys. Chem.* **120**, 144 (1926); E. U. Condon, *Phys. Rev.* **28**, 1132 (1926); **32**, 858 (1928).

[7] A. Jabłoński. *Acta Phys. Pol.* **6**, 371 (1937); **7**, 196 (1938).

[8] R. Hedges, D. Drummond, A. Gallagher, *Phys. Rev.* **A6**, 1519 (1972). The thermal distribution of free collision states reduces to the simple Boltzmann Factor only for a repulsive initial-state interaction potential. For attractive potentials a thermal distribution of bound states, as in a thermal gas, must also be included to obtain the Boltzmann factor.

[9] This Boltzmann factor was also included in the statistical theory (e.g. Ref. [4]), but for the wrong reason. In that theory the nuclei were assumed stationary so that the total nuclear energy reduced to the potential energy $V(R)$ in the initial state.

[10] R. Scheps, Ch. Ottinger, G. York, A. Gallagher, *J. Chem. Phys.* **63**, 2581 (1975) and references therein.

[11] The quasi-static theory is only applicable to isolated molecular states; those that are separated by $\hbar/\tau_c$ where τ_c is a characteristic collision time. Thus the classical analysis may require significant corrections at large R, where several states may converge to the same limit. The $A^2\Pi_{1/2}$ and $A^2\Pi_{3/2}$ fine-structure states are well isolated in the small R region of Figs. 2 and 3 for the Rb and Cs cases only. For Li and Na this fine-structure splitting is small enough to be ignored. The K case has not been studied in our laboratory since the levels are not well isolated, yet the splitting is not negligible.

[12] The general behavior of these excited-state potentials can be understood in terms of a molecular orbital model originally proposed by W. E. Baylis. In the $A^2\Pi$ state the alkali valence electron is far from the noble gas atom, in the plane perpendicular to R. The polarizable noble gas atom thus feels primarily the field of the alkali ion core, resulting in an R^{-4} attraction at large R. At small R, the overlap of the spherically symmetric noble gas and alkali ion core produces strong repulsion, at decreasing R for the lighter alkalis that have smaller ion cores. In essence, the $A^2\Pi$ state is Rydberg-like, following approximately the molecular ion potential shape. For the $B^2\Sigma$ state the alkali valence electron is along R, so it overlaps the inert gas at large R, causing a net repulsion. For $B^2\Sigma$ and $A^2\Pi$ the increasing polarizability of the heavier inert gases causes more attraction to the alkali ion core.