

Critical Evaluation of Transition Probabilities of Na-Ca (Z=11 - 20)

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NIST is in the process of critically evaluating and compiling transition probabilities of H-Ca (Z=1-20). These elements were covered about 30 years ago in Vols. I and II of "Atomic Transition Probabilities" by W. L. Wiese et al. Much work has been done since then, mostly theoretical, with by far the most extensive results being provided by members of the "Opacity Project" (OP). In 1996, "Atomic Transition Probabilities of Carbon, Nitrogen, and Oxygen" was published by W. L. Wiese, J. R. Fuhr, and T. M. Deters [1]. Work on updating the other elements is continuing, and revision of Vol. II is currently focused on Na, Mg, Al, and Si (Z=11-14). For many spectra, our new compilations contain about an order of magnitude more transitions than the earlier ones.

Our new compilations rely heavily on OP results because they are so extensive and because they appear to be reasonably accurate in many cases. Accurate experiments (and high precision computational results) are also essential, primarily for reference values in critical evaluation and for benchmark values in their own right. OP calculations cover an extensive range of allowed transitions, essentially comprehensive up to $n=10$ and $\ell=3,4$. OP values have been made electronically available for all stages of H-Ca, except P, Cl, and K, which are planned for future work. Currently available OP calculations do not, however, include the effects of the spin-orbit interaction, and only average-multiplet values are reported. We decompose the LS multiplet averages into their LSJ fine structure components using the following LS coupling rule:

$$\mathbf{S}_{LSJ^{-}LS'J'} = \mathbf{S}_{LS^{-}LS'} (2J+1)(2J'+1) \left\{ \begin{matrix} L & S & J \\ J' & 1 & L' \end{matrix} \right\}^2,$$

where \mathbf{S} is the line strength, and the curly brackets indicate a 6- J symbol. We consider only those transitions for which experimental energies are tabulated in NIST energy level tables for both the lower and upper level. We take only the line strengths from the Opacity Project, using experimental energies to derive wavelengths and to convert line strengths to oscillator strengths and transition probabilities.

For the stronger transitions of most spectra, reasonably good agreement is found between the Opacity Project on the one hand, and experiments and accurate calculations which include spin-orbit effects on the other. Large spin-orbit effects such as those in noble-gas-like spectra can probably account for large differences observed in such spectra. However, the origin of large discrepancies in all but the strongest transitions in some other spectra is not yet understood. Note, for example, the comparison of line strengths for OP [2] and CIV-3 [3] in fluorine-like spectra of Na III and Si VI in Figures 1 and 2. Comparisons in the figures only include transitions for which the outermost electron of the upper level is in an $n=3$ principal quantum number, because only these are listed in [3].

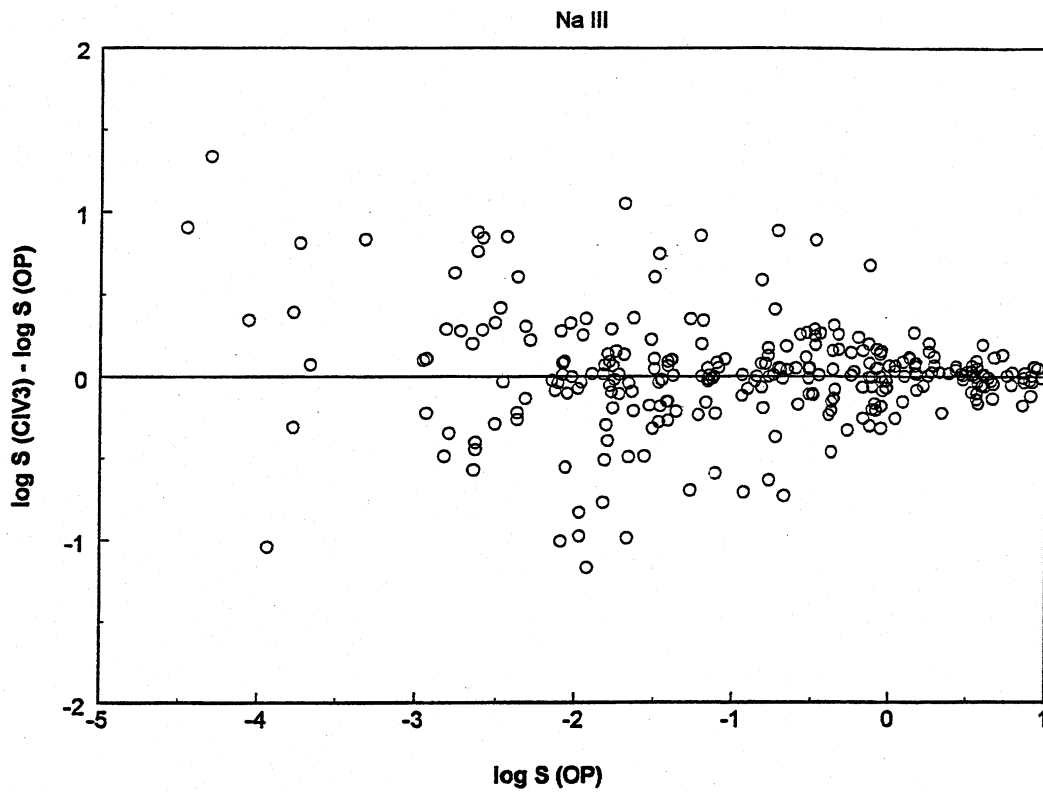


Figure 1: Logarithms of the ratios of line strengths $S(\text{CIV-3})/S(\text{OP})$ are plotted vs. $\log S(\text{OP})$ for fluorine-like Na III. All transitions involve $2s^2 2p^4 3l$ upper levels.

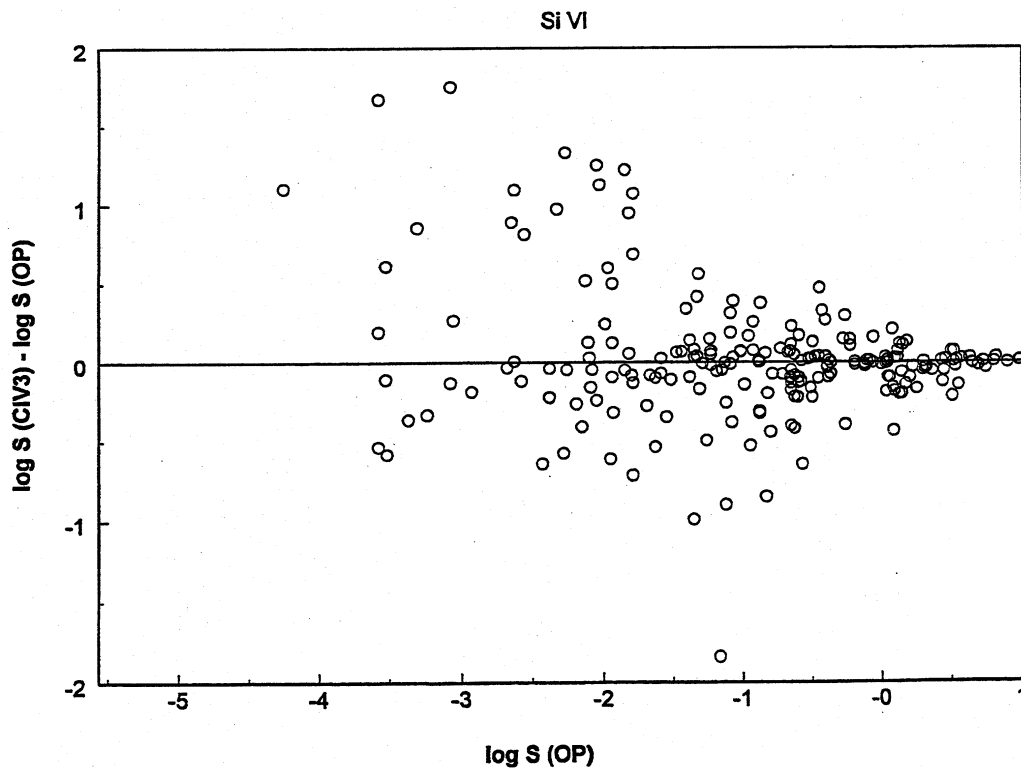


Figure 2: Logarithms of the ratios of line strengths $S(\text{CIV-3})/S(\text{OP})$ are plotted vs. $\log S(\text{OP})$ for fluorine-like Si VI. All transitions involve $2s^2 2p^4 3l$ upper levels.

The discrepancy in line-strengths for fluorine-like spectra between OP and CIV-3 results deserves special attention. These methods represent two of the most important methods to-date for large scale line strength calculations. The OP method relies on CIV-3 (or the similar "Superstructure" approach) for its core state correlations, as discussed below. All but the lowest three bound levels of Na III have configurations of the type $2s^2 2p^4(n)\ell$, where the parentheses indicate a parent term of either 1S , 3P , or 1D . Bound interloper levels, such as the $2s5pn\ell$ levels, exist only for the more highly ionized members of the isoelectronic series. The three parent configurations cited above lie sufficiently close in energy that both intermediate coupling and configuration interaction occur at noticeable and frequently comparable levels throughout the bound spectrum. Relative Landé intervals of the quartet states (relative intervals for doublets cannot be derived from level energies) are typically far from those expected for LS coupling.

The OP uses a close-coupling expansion (CC) approximation that represents the total wavefunction as a superposition of ionic core and valence-electron wavefunctions. The ionic core (without the valence electron) is described by a configuration-interaction method, using either CIV-3 (Slater-type Orbitals) or superstructure (effective-charge statistical-model potentials). The R-matrix method is used to solve the core plus valence electron problem in the inner region. It divides the problem into two regions of space: the "inner" and "outer" regions, and requires that the wavefunctions in these two regions and their radial derivatives match at an intermediate boundary. The outer-region wavefunction approaches a "Coulomb" solution asymptotically. It is usually evaluated by integrating the asymptotic solutions inward. The *ab initio* CC expansion method is similar in spirit to, but considerably more sophisticated than, such semi-empirical methods as the Coulomb approximation, quantum defect theory, or core polarization models. Even the latter, for example, must use a short-range cut-off of the potential to simulate the effect of exchange between the excited and core electrons. The CC approach is generally more efficient than variational methods for large-sweep calculations of transitions involving more highly excited levels. In principle at least, the assumptions of the CC model become increasingly valid for more highly excited states. (One caveat is that the CC model must be built on an intermediate-coupled core, if intermediate coupling is significant.) This advantage tends to offset the intrinsic fact that binding energies are smaller for more highly excited states. Thus, a fixed absolute error yields a larger relative error, as well as the fact that more basis states often need to be included to obtain the same level of absolute accuracy. Some authors argue that the CC method becomes more accurate than variational methods for more highly excited states because it builds in the effect of highly excited states and the continuum; as a practical matter, it may prove difficult to expand the basis set sufficiently as n and ℓ increase. The CC method, however, usually cannot practically build-in as much correlation between the core and low-excited electron as can full-blown multi-configurational variational methods. Thus the latter can be superior for calculating transitions involving the lowest-excited levels, for transitions whose strengths are sensitive to cancellations in the dipole matrix elements, and, of course, for calculating wavefunctions for the ion core used in CC calculations.

Recently, the Opacity Project group in Belfast has gained the capability to include intermediate coupling via inclusion of the Breit Pauli (BP) interaction in their CC calculations. This is an important new development. NIST has received the Na III (F-like) energy levels of and the transition strengths between the odd $J=1/2$, $J=3/2$, and even $J=1/2$ states [4]. The energies agree with experimental values to within 0.8% or better, and the agreement between the length and velocity values for the electric dipole matrix element is encouraging. The agreement between the CIV-3 and CC with BP, however, is not much improved compared to CIV-3 vs. OP results. The origin of these discrepancies is not understood and is presently under study. It will thus be

interesting to compare CIV-3 and forthcoming CC/BP calculations of transition strengths with experimental results available for other spectra, particularly for weaker transitions.

Because it overcomes the primary limitation of OP calculations, this extended CC/BP version may offer the potential for mass production of accurate transition probabilities of all spectra, at least for $Z < \sim 36$ and for transition strengths whose values are not dominated by cancellation effects. Only time will tell, however, if the extended method is capable of generating reasonably accurate line strengths for values significantly less than one.

References

- [1] W. L. Wiese, J. R. Fuhr, and T. M. Deters, "Atomic Transition Probabilities of Carbon, Nitrogen, and Oxygen" *J. Phys. Chem. Ref. Data, Monograph 7* (1996)
- [2] K. Butler and C. J. Zeippen, *Opacity Project, to be published* (data is available on the internet via "topbase")
- [3] H. M. S. Blackford and A. Hibbert, *At. Data Nucl. Data Tables* **58**, 101 (1994)
- [4] K. Berrington, *private communication*