J-DEPENDENT LIFETIMES OF QUINTET LEVELS IN NEUTRAL CARBON

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Beam–foil measurements and configuration interaction calculations are reported for the lifetimes of the individual levels of the $2s2p^2 3s\,^5P_J$ term in C I. The experimental lifetimes show a strong J-dependence, with $\tau(J=3)=2.5\pm0.5$ ns and $\tau(J=1,2)=0.3\pm0.1$ ns. These results are in close agreement with theoretical predictions and indicate that autoionisation strongly affects the $J=1$ and 2 levels.

Although the singlet and triplet spectra of the neutral carbon atom have been comprehensively studied [1–3], only two terms, $2s2p^3\,^5S^o_2$ and $2s2p^2(^4P)3s\,^5P_{1,2,3}$, have been established [4,5] of the displaced or doubly excited terms (2s vacancy) of the quintet system. The positions of these levels relative to the triplets and singlets cause them to have interesting decay properties. The $2s2p^3\,^5S_2$ level lies about 4.18 eV above the $2s^22p^2\,^3P$ ground term of C I, and it decays by intercombination transitions. The $2s2p^2(^4P)3s\,^5P_{1,2,3}$ levels lie 12.84 eV above the C I ground term which places them 1.58 eV above the first $(2s^22p\,^2P)$ ionisation limit of C I, but well below (by 3.75 eV) the $2s2p^2\,^4P$ parent term of C II [2]. Autoionisation of the $3s\,^5P$ levels into the $2s^22p(^2P)\epsilon l$ triplet continuum is energetically possible, but the fast Coulomb autoionisation mode is ruled out (in the case of LS coupling) by the $\Delta S=0$ selection rule. However, intermediate coupling opens autoionisation channels to the $(^2P)\epsilon l$ continuum through mixing of $3s\,^5P$ levels with autoionising triplet levels of the same configuration. There occurs mixing of $^5P_3$ with $^3D_3$, of $^5P_2$ with $^3D_2$, $^3P_2$, and of $^5P_1$ with $^3D_1$, $^3P_1$, $^3S_1$. Radiative decay rates for the $^5S_2$–$^5P_{1,2,3}$ lines have been measured [6] by intensity calibrated wall stabilised arc emission methods, and they exhibit only a very weak dependence on J. However, the variations in quintet–triplet mixing and subsequent autoionisation, as noted above, can lead to level lifetimes that are strongly J-dependent. Lifetime measurements of the individual J components can quantitatively reveal the autoionisation rates.

In order to investigate these radiative and autoionisation effects, we have undertaken a combined theoretical and experimental study of the lifetimes of the individual fine structure levels of the $2s2p^2 3s\,^5P_J$ term in C I. The experimental portion was carried out by beam–foil excitation methods, and the theoretical calculations were made using the multiconfiguration Hartree–Fock program developed by Cowan [7], which includes both radiation and autoionisation. It is worth noting that beam–foil studies of similar states of O I have been reported some years ago [8,9]. An alternative approach, which utilised differential line widths to deduce autoionisation rates for doubly excited triplet states in Zn I, has been used by Martin and Kaufman [10].

Time resolved carbon spectra were obtained by directing beams of 100–200 keV C^+ ions from the University of Toledo 330 kV Danfysik heavy ion accelerator through a translatable 2 $\mu g/cm^2$ carbon foil. At these energies the beam loses approximately 3.5 keV in traversing the foil. The wavelength range 1150–1800 Å was studied, using an Acton 1 m normal incidence vacuum monochromator equipped with a solar blind EMI photomultiplier at the exit slit. The wavelength resolution used was 0.8 Å

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FWHM and the time window was set at 0.3 ns, values chosen to optimise the necessary compromises between resolution and signal intensity that are inherent in the beam–foil light source. Lifetimes were measured by recording the intensity of the spectral lines as a function of the distance from the foil. Many known lines from C I and C II were identified, and their relative intensities were used to select a beam energy that is well suited to the study of C I. Lifetime measurements of many of the singlet and triplet levels were also made. The results agreed well with earlier work, and served as an additional check of the determination of beam energy and energy loss in the foil. These results will be reported elsewhere [11].

The wavelengths of the $2s2p^3\ ^5S_2$–$2s2p^23s\ ^5P_{1,2,3}$ transitions are 1432.530, 1432.105 and 1431.597 Å [2], which creates special problems for fine structure resolved lifetime measurements. The beam–foil source copiously populates core-excited and displaced levels and is ideally suited to their production, but its tenuous density leads to low light levels that require fast optical systems, and its high velocity produces Doppler broadening. To obtain a high fraction of neutral atoms in the post foil beam, the beam energy must be kept low, which leads to Rutherford line broadening by the foil. We minimised the Doppler linewidths due to the longitudinal velocity of the beam by refocusing of the spectrometer to a moving source [12], and minimised Rutherford broadening by using the thinnest foils that could be reliably mounted. Stoner and Radziemski [13] have calculated the line broadening caused by scattering processes in the foil, and for 100 keV C ions through a 2 μg/cm^2 foil in this wavelength region their calculation yields a FWHM linewidth of 0.9 Å, in close agreement with our measured linewidths. Thus these lines are too closely spaced to be totally resolved by present beam foil technology. However, the decay curves exhibited a very pronounced variation across the broadened profile of this blend of lines, and we combined time and wavelength information to resolve the level lifetimes.

Since this spectral region was relatively free of backgrounds and blends from other lines, it was possible to determine the lifetimes of the individual fine structure levels by a three-dimensional intensity versus distance versus wavelength analysis. The intensity $I(\lambda, x)$ was measured at 17 equally spaced and accurately reproducible values for the wavelength λ over the profile of the line, and these measurements were repeated at each of 50 positions x downstream from the foil. This array of measurements was performed rapidly and repeatedly to minimise the effects of degradation of the foils. Each data set was separately analysed, and the results quoted represent the weighted combination of over forth individual measurements.

Fig. 1 displays two typical decay curves $I(\lambda, x)$ taken at fixed wavelength positions on the long and short wavelength sides of the line profile at flight times $t=x/v$ downstream from the foil. The fast exponential evident at the longer wavelength diminishes as the monochromator setting moves toward the shorter wavelength side of the line profile. Since the lifetime determinations were made by combining the results of the analyses of many such curves, fig. 1 is intended only to convey the sharp wavelength dependence of the decay. After a channel-by-channel subtraction of backgrounds (typically one

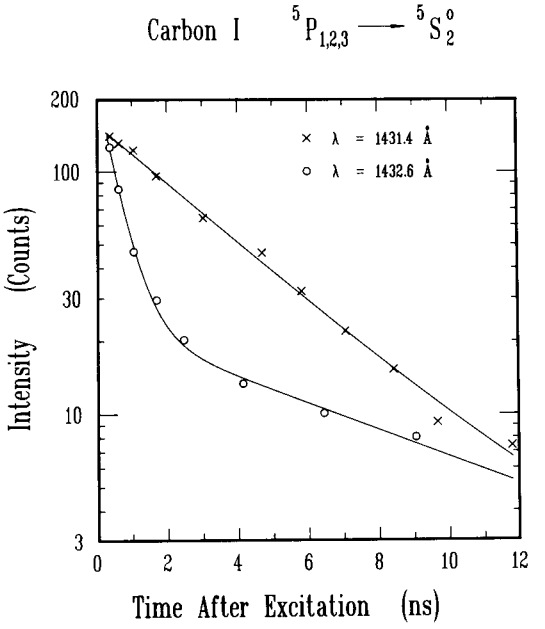

Fig. 1. Portions of sample intensity decay curves $I(\lambda, vt)$ versus time since excitation t for two different wavelength settings: (○) measured at 1432.6 Å and favours the $J=1$, 2 transitions; (×) measured at 1431.4 Å and favours the $J=3$ transition. Most of the blending observed at the line center has been separated and cascading effects appear to be small. The beam energy was 100 keV.

count per channel) the data have been binned in three-channel groups to trace trends, but the scatter in this isolated plot has no relevance to the uncertainties in the final determination.

The decay curves were analysed using the multiexponential fitting program DISCRETE [14]. This program was particularly useful in this application, because it generates its own initial values (through Fredholm transforms) for the nonlinear least squares optimisation, and automatically evaluates and tests various choices for the number of exponentials included in the fit. This avoids possible unconscious biases that can be introduced when the experimenter must steer the convergence of a fitting program.

The results of the analysis by DISCRETE indicated that all of the decay curves contain two exponential terms of dissimilar lifetime. The longer lifetime dominates on the short wavelength ($J=3$) side of the blended line, and the shorter lifetime dominates on the long wavelength ($J=1, 2$) side of the line. This indicates that the two-exponential behaviour arises mainly from blending, and that cascade repopulation is not a significant contribution. This confirms our CI calculations which indicate that, although quintet levels in the $2s2p^23p$ configuration do have infrared transitions to the ^5P levels of interest, these have very low ($<10^7$/s) radiative transition rates. Our theoretical calculations also indicate that the $J=1$ and $J=2$ lifetimes differ somewhat from each other, and both differ substantially from the $J=3$ lifetime. Because of the nonorthogonal nature of sums of decay exponentials, it is difficult to reliably extract three exponentials by curve fitting methods when two of the lifetimes differ by less than a factor of two. Thus, although there was some indication of the $J=1$ and $J=2$ lifetime difference in the data, we report the results of a two-exponential fit. If we assume statistical populations, then the shorter measured lifetime arises primarily from the $J=2$ level. From these fits, we conclude that the lifetimes are $\tau(J=3)=2.5\pm0.5$ ns and $\tau(J=1, 2)=0.3\pm0.1$ ns.

In order to provide the theoretical comparison, the Cowan suite of programs RCN-RCG [7] was used to compute the autoionisation rates of the ^5P levels. The calculation included interactions among eight even parity configurations ($2s^22p^2$, $2s2p^23s$, $2s2p^24s$, $2s^22p3p$, $2s^22p4p$, $2s2p^23d$, $2s2p^24d$, $2s^22p4f$) and seven odd parity configurations ($2s2p^3$, $2s^22p3s$, $2s^22p4s$, $2s2p^23p$, $2s2p^24p$, $2s^22p3d$, $2s^22p4d$). The autoionisation transition $2s2p^23s \rightarrow 2s^22p\epsilon p$ was calculated using an outgoing electron energy of 0.116 Ry, computed from the observed position of the $2s2p^23s\ ^5P$ term and the ionisation potential. The autoionisation rate is J-dependent because the spin–orbit mixing with nearby triplet levels is J-dependent. This mixing is determined by the spin–orbit interaction strength and by the energy intervals between the ^5P and the other $2s2p^23s$ terms with which it is mixed. The former can be determined empirically from the ^5P fine structure; however the latter cannot because the energies of the other terms are not known.

The results lend considerable support to our interpretation of the source of the J-dependent mean lives. The radiative decay rates are given in table 1 and compared with the corresponding values deduced assuming statistical populations in the intensity calibrated wall stabilised arc emission measurements by Boldt [6]. Although calculated values are about 50% larger than the emission measurements, both theory and experiment indicate that there is no strong J-dependence in the radiative rates.

For the autoionisation rates we report two theoretical values for comparison in table 1: HF/CI indicates the Hartree–Fock results, including the interactions among all the configurations listed above, but with the spin–orbit integral scaled (to 88% of its HF value) to give the correct fine structure in the ^5P term; HF/CI ADJUSTED indicates the same calculation but with the electrostatic integrals also adjusted to give the correct wavelengths for the ^5S–^5P lines and improved agreement with observed term intervals. These adjustments are not unique; an accurate calculation of small spin–orbit mixing effects requires either a major theoretical effort or accurate experimental knowledge of all the interacting energy levels, which is not available for the $2s2p^23s$ configuration. Nevertheless the results give substantial support to the experimental findings, also given in table 1.

In conclusion, we have made experimental and theoretical studies of radiative and autoionisation decays of the $2s2p^23s\ ^5P$ ($J=1, 2, 3$) levels in CI. Time dependences were used to deconvolute blended decay curves. The lifetime extraction indicated a strong variation of autoionisation with J, and little

Table 1

Level	λ (Å)	Decay rates (ns^{-1})						
		A (radiative)		A (Auger)		A (total)		
		theory [a,b]	expt (±) [c]	theory [a]	theory [b]	theory [a]	theory [b]	expt (±) [d]
$2s2p^23s\ ^5P_1$	1432.53	0.21	0.13(3)	1.17	1.81	1.4	2.0	3.3(9)
$2s2p^23s\ ^5P_2$	1432.11	0.21	0.14(4)	1.96	2.83	2.2	3.1	
$2s2p^23s\ ^5P_3$	1431.60	0.21	0.15(4)	0.08	0.29	0.3	0.5	0.40(8)

[a] This work, HF/CI Hartree–Fock configuration interaction calculation.
[b] This work, HF/CI ADJUSTED to yield measured intervals.
[c] Ref. [6], emission measurement.
[d] This work, beam–foil lifetime measurement.

cascading from higher levels. The theoretical studies have also provided estimates of the positions of other quintet levels.

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