PHYSICAL REVIEW A VOLUME 30, NUMBER 4 OCTOBER 1984

# Radiofrequency resonance measurements of Na $d$-$f$ intervals

N. H. Tran, H. B. van Linden van den Heuvell, R. Kachru, and T. F. Gallagher
*Molecular Physics Department, SRI International,*
*Menlo Park, California 94025*

(Received 12 June 1984)

Using microwave resonance techniques, we have measured Na $d$-$f$ intervals from $n=9$–$12$ at frequencies of up to 116 GHz. The measured intervals are an order of magnitude more precise than previous $d$-$f$ interval measurements, with typical uncertainties of 100 kHz. These measurements are a necessary part of improved quantum-defect measurements in Na and determine the $nd$ fine-structure intervals a factor of 5 more accurately than the previous work. Finally the $nf$ fine-structure intervals are determined to be 3%–4% less than the hydrogenic interval for $n$ as low as 9.

The fine-structure intervals of alkali-metal atoms are one of the more evident indications of the presence or absence of core penetration by the valence electron. In a series such as the Na $nd$ series, in which the penetration energy shift is appreciable, more than 10% of the polarization energy shift, the fine structure is frequently inverted due to the pènetration.[1] In the next-higher-$l$ series of states, such as the Na $nf$ states, in which penetration effects are nearly negligible, $<1\%$, the fine-structure intervals are nearly hydrogenic. Such a pair of series is thus rather interesting as it provides useful benchmarks for atomic structure calculations. Of the pair of Na $nd$ and $nf$ series it is particularly interesting to observe the Na $nf$ fine-structure intervals as they may at present be calculated with more confidence.

Sternheimer, Rodgers, and Das[1] have made extensive calculations of the Na $nf$ intervals and have found that they slowly decrease from 3% less than the hydrogenic interval at $n=4$ to 7% less at $n>10$. These calculations are to be compared to a laser spectroscopy measurement of the Na $4f$ state which indicates that the fine-structure interval is hydrogenic to within 1% (Ref. 2) and microwave resonance measurements for $n=11$–$14$ which show that the Na $nf$ fine-structure interval is 5% less than the hydrogenic interval.[3] In an effort to fill the experimental gap between $n=4$ and $n=11$ we have extended the microwave resonance measurements to lower $n$.

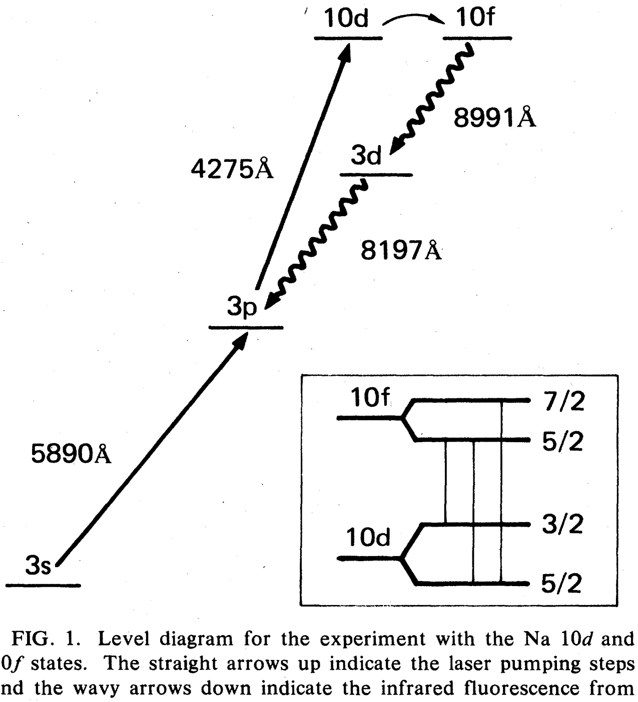

FIG. 1. Level diagram for the experiment with the Na $10d$ and $10f$ states. The straight arrows up indicate the laser pumping steps and the wavy arrows down indicate the infrared fluorescence from the $10f$ state.

The experimental apparatus and procedures are extensions of those described previously.[3,4] Figure 1 shows the basic laser pumping scheme for the $n=10$ level in Na. Two dye laser pulses of $\sim 5$-nsec pulse duration are used to pump the Na atoms first from the $3s_{1/2}$ level to the $3p_{1/2}$ level and then to the $10d_{5/2}$ state. (By choosing $3p_{1/2}$ as intermediate state we can selectively populate the $10d_{3/2}$ state.) A microwave field is then applied to drive the $10d_{3/2}$-$10f_{5/2}$ transition, which is detected by observing the infrared, 8200 Å, $3d$-$3p$ fluorescence. When the microwave frequency does not correspond to one of the $10d$-$10f$ transitions shown in the inset of Fig. 1, little infrared fluorescence is observed, but as the microwave frequency is swept through the resonant frequencies of these transitions, sharp increases in the infrared fluorescence are detected, as shown in Fig. 2.

The experimental apparatus has been described elsewhere,[3,4] so only its salient features are recalled here. The Na vapor is contained in a cylindrical Pyrex cell, 10 cm long and 2.5 cm in diameter which is typically kept at a temperature of 150 °C, producing a Na vapor pressure of $8\times10^{-6}$ Torr, whereas the background gas pressure is $\sim 10^{-7}$ Torr. The exciting laser beams pass along the axis of the cell and

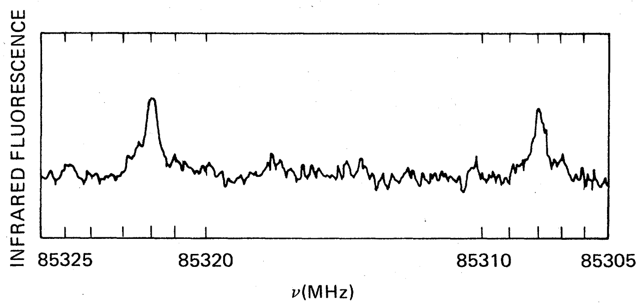

FIG. 2. The Na $10d_{5/2}$-$10f_{5/2}$ and $10d_{5/2}$-$10f_{7/2}$ transitions observed on a sweep of decreasing frequency. The microwave power of the 8.53-GHz source was increased by 6 dB between the two resonances.

TABLE I. Observed Na $d$-$f$ transitions.

| Transitions | Harmonic | Frequency (MHz) |
|---|---|---|
| $9d_{3/2}$-$9f_{5/2}$ | 11 | 116 166.10(7) |
| $9d_{5/2}$-$9f_{5/2}$ | 11 | 116 292.50(20) |
| $9d_{5/2}$-$9f_{7/2}$ | 11 | 116 311.66(17) |
| $10d_{3/2}$-$10f_{5/2}$ | 10 | 85 215.05(15) |
| $10d_{5/2}$-$10f_{5/2}$ | 10 | 85 308.01(10) |
| $10d_{5/2}$-$10f_{7/2}$ | 10 | 85 322.14(9) |
| $11d_{3/2}$-$11f_{5/2}$ | 8 | 64 316.27(5) |
| $11d_{5/2}$-$11f_{5/2}$ | 8 | 64 386.67(8) |
| $11d_{5/2}$-$11f_{7/2}$ | 8 | 64 397.28(5) |
| $12d_{3/2}$-$12f_{5/2}$ | 6 | 49 710.47(10) |
| $12d_{5/2}$-$12f_{5/2}$ | 6 | 49 765.20(14) |
| $12d_{5/2}$-$12f_{7/2}$ | 6 | 49 773.28(9) |

excite a cylindrical volume of atoms ~4 mm wide. If the lasers are collimated more tightly, superradiance is inferred to occur[5] as evidenced by the broader microwave resonances and a spectral distribution of radiation which is not consistent with the branching ratios.[6] The infrared fluorescence is observed in the direction perpendicular to the cell axis by a Hammamatsu R666 photomultiplier with a Wrattan 87 filter. The microwave radiation is introduced from a microwave horn on the opposite side of the cell. In order to observe microwave resonances ~0.5 MHz wide we observe only the fluorescence which is emitted during a 0.5-$\mu$s period centered 1.75 $\mu$s after the laser excitation. Thus with the optimum microwave power we should see the maximum signal with a 0.6-MHz linewidth.[7] The 1.75-$\mu$s delay time represents a compromise between a desire for narrow linewidths, decreasing inversely with delay time, and a desire for fluorescence signal strength, which decays exponentially with a time constant of 1 to 2 $\mu$s corresponding to the lifetimes of these $d$ and $f$ states.[8,9] Finally, the Na cell is shielded from ambient magnetic fields by enclosing it in a double magnetic shield consisting of an inner shell made of 0.010-in.-thick Co-netic, and an outer shield made of 0.030-in.-thick mild steel. Evidently Zeeman and pressure broadening are negligible, < 0.1 MHz, as evidenced by the uncertainty principle limited linewidths of ~0.6 MHz as shown in Fig. 2.

There are two important changes in these experiments as compared to the previous ones.[3,4] The first is the use of a Hewlett Packard 5343A frequency counter to directly measure the frequency of the microwave sweep oscillator. This, coupled to the large number of measurements made (typically 15 sweeps of increasing and decreasing microwave frequency for each transition) results in an increase of a factor of ~10 in the accuracy of the absolute frequency measurements.

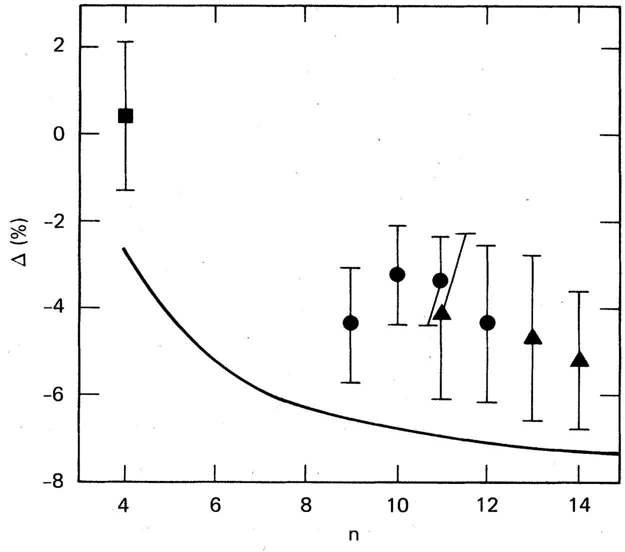

FIG. 3. The percent difference Δ in the Na and H fine-structure intervals vs $n$. Experimental (■) Liao and Bjorkholm (Ref. 2), (▲) Gallagher, Cooke, Edelstein, and Hill (Ref. 3), (●) this work. Theoretical (——) Sternheimer, Rodgers, and Das (Ref. 1).

The second change is method of generation of the microwave radiation. In the previous experiments[3,4] on the $n=11$ to 17 levels of Na microwave frequencies of up to 64 GHz were required. To drive the transitions reported here necessitates the generation of microwave frequencies of up to 116 GHz. In order to achieve this, a harmonic mixer is employed to generate high harmonics of the output of a Hewlett Packard 8694A 7–11-GHz sweep oscillator.

In Table I we list the observed frequencies for the Na $nd$-$nf$ transitions for $n=9$ to 12. The errors in parentheses represent statistical fluctuations in the data. Table II gives the fine-structure intervals of the $f$ states in Na deduced from these measurements and other measurements as well as the hydrogenic intervals.[10] To compare these results with

TABLE II. Na $f$ fine-structure intervals.

| $n$ | Na $f$-$fs$ interval (MHz) | H $fs$ interval[a] (MHz) | Difference (MHz) | % Difference |
|---|---|---|---|---|
| 4[b] | 229(4) | 228 | +1(4) | +0.4(17) |
| 9 | 19.16(26) | 20.04 | −0.88(26) | −4.4(13) |
| 10 | 14.13(15) | 14.61 | −0.48(15) | −3.3(11) |
| 11 | 10.61(10) | 10.98 | −0.37(10) | −3.4(10) |
| 11[c] | 10.52(21) | 10.98 | −0.46(21) | −4.2(19) |
| 12 | 8.08(15) | 8.45 | −0.37(15) | −4.4(18) |
| 13[c] | 6.34(12) | 6.65 | · · · | −4.7(19) |
| 14[c] | 5.02(8) | 5.35 | · · · | −5.2(16) |

[a] Reference 10.
[b] Reference 2.
[c] Reference 3.

TABLE III. Na *nd* fine-structure intervals.

| *nd* | This work (MHz) | Fabre *et al.*[a] (MHz) |
|---|---|---|
| 9 | −126.40(21) | −124.5(15) |
| 10 | −92.96(18) | −91.5(10) |
| 11 | −70.40(10) | −70.0(7) |
| 12 | −54.73(17) | −54.0(5) |

[a] See Ref. 11.

the calculations of Sternheimer *et al.*,[1] we have plotted the percent difference Δ, defined by $\Delta=(F_{\rm Na}-F_{\rm H})/F_{\rm H}$ in Fig. 3 with that calculated by Sternheimer *et al.*[1] Here $F_{\rm Na}$ and $F_{\rm H}$ are the Na and H *nf* fine-structure intervals. As shown by Fig. 3 the calculated values of Δ appear to have a constant offset of −0.024 from the experimental values, but both curves have the same shape. Why this is true is not apparent to us.

Although our primary goal was the measurement of the Na *f* fine-structure intervals we have also obtained values for the *nd* fine-structure intervals, $D_{\rm Na}$ which are an order of magnitude more precise than the best previous values, obtained by quantum beat spectroscopy.[11] Both sets are given in Table III. In Fig. 4 we show a plot of $-n^3D_{\rm Na}$ vs $1/n^2$ to show the energy dependence of the *nd* fine-structure intervals. As shown by Fig. 4 our values are consistently ~1% higher than the values of Fabre, Gross, and Haroche,[11] but the source of this systematic discrepancy is not evident. Assuming the linear energy dependence of the *nd* fine-structure intervals the values of $D_{\rm Na}$ in Table III may be represented by

$$D_{\rm Na}=-an^3+bn^{-5}\ , \tag{1}$$

where $a=97.12(44)$ GHz and $b=408(4)$ GHz. As the calculations of Sternheimer *et al.*[1] give Na *nd-fs* intervals which are also inverted but ~30% too small it is apparent that these intervals still remain a theoretical challenge.

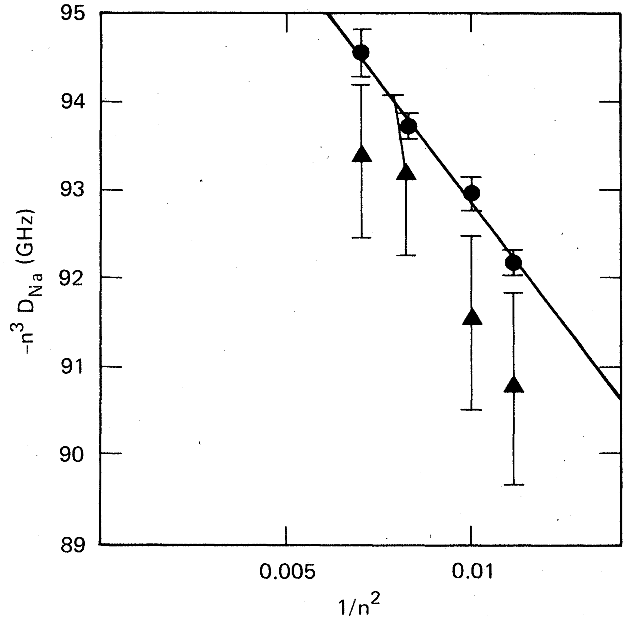

FIG. 4. Plot of $-n^3D_{\rm Na}$ vs $1/n^2$ to show the linear energy dependence of the *nd* fine-structure intervals, (▲) Fabre, Gross, and Haroche (Ref. 11), (●) this work. The line represents the fit of Eq. (1).

Finally we note that these data are an order of magnitude more precise than the previous Na *d-f* intervals and are thus the first step in making substantially more accurate quantum-defect measurements in Na.

We acknowledge useful suggestions of Clarence Arnow and John Watjen in the course of this work, which was supported by the U.S. Air Force Office of Scientific Research under Contract No. F49620-79-C-0212.

---

[1] R. M. Sternheimer, J. E. Rodgers, and T. P. Das, Phys. Rev. A **17**, 505 (1978).
[2] P. F. Liao and J. E. Bjorkholm, Phys. Rev. Lett. **36**, 1543 (1976).
[3] T. F. Gallagher, W. E. Cooke, S. A. Edelstein, and R. M. Hill, Phys. Rev. A **16**, 273 (1977).
[4] T. F. Gallagher, R. M. Hill, and S. A. Edelstein, Phys. Rev. A **13**, 1448 (1976).
[5] M. Gross, C. Fabre, P. Pillet, and S. Haroche, Phys. Rev. Lett. **36**, 1035 (1976).
[6] T. F. Gallagher and W. E. Cooke (unpublished).
[7] N. F. Ramsey, *Molecular Beams* (Oxford Univ., London, 1956).
[8] T. F. Gallagher, S. A. Edelstein, and R. M. Hill, Phys. Rev. A **11**, 1504 (1975).
[9] T. F. Gallagher, W. E. Cooke, and S. A. Edelstein, Phys. Rev. A **17**, 904 (1978).
[10] H. A. Bethe and E. A. Salpeter, *Quantum Mechanics of One- and Two-Electron Atoms* (Academic, New York, 1975).
[11] C. M. Fabre, M. Gross, and S. Haroche, Opt. Commun. **13**, 393 (1975).