

NOTE ON THE INTERPRETATION OF CERTAIN
 ${}^2\Delta$, ${}^2\Pi$ BANDS OF SiH

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ABSTRACT

It is shown that Jackson's ${}^2\Delta, {}^2\Pi$ SiH bands have a *regular* ${}^2\Pi$ state and thus are closely analogous to the $\lambda 4300$ bands of CH. The orbit-spin coupling coefficient A is determined for the ${}^2\Pi$ state of SiH and shown to agree closely with A of the 3P state of the Si atom, from which the ${}^2\Pi$ molecular state is supposed to be derived. This is a new example of a relation which seems to be universal. Another new example of the same relation, found in BeH, is also cited.—The coefficients A and B of the ${}^2\Delta$ state and B of the ${}^2\Pi$ state of SiH are also discussed.

C. V. JACKSON has obtained some SiH bands near $\lambda 4100$ and has shown by a skilful analysis that they have a structure corresponding to a ${}^2\Delta, {}^2\Pi$ transition.¹ Because of the analogy of Si to C, there is a very strong presumption that these bands are analogous to the ${}^2\Delta, {}^2\Pi$ bands of CH near $\lambda 4300$. In the case of CH the ${}^2\Delta$ doublet is very narrow and inverted ($A/B \sim -0.07$, $B = 14.57$), while the ${}^2\Pi$ is regular ($A/B = +2.0$, $B = 14.2$). According to Jackson, the ${}^2\Delta$ state of SiH is narrow and *regular*, but the ${}^2\Pi$ *inverted*, with $A/B \sim -10$, $B = 7.4$. From a consideration of electron configurations, however, it is clear that if the ${}^2\Pi$ state of SiH is inverted it cannot be at all analogous to that of CH, since in such simple molecules² an inverted Π state implies a group of three equivalent π electrons, whereas a regular Π state implies only a single π electron outside of closed shells. In the case of the ${}^2\Delta$ state, however, the existence of a reversed sign of A in SiH, while rather unexpected, has no such important implications. For the ${}^2\Delta$ state of CH is attributed to an electron configuration $\cdots \sigma\pi^2$, in which the small observed doubling can be ascribed to the small interaction of the spin of the σ electron with the orbital angular momenta of the two π electrons.² In similar cases in atomic spectra, we know that doublets of this kind may be either regular or inverted.

A study of Jackson's analysis shows that, while the fact that the ${}^2\Delta$ is regular is incontrovertible, the only evidence that the ${}^2\Pi$ is inverted comes from an application of Van Vleck's theoretical work³ on Λ -type doubling. [The question whether a given ${}^2\Pi$ level is regular or inverted can in general also be decided by determining the lowest J value in each of the two sets of levels supposed to be ${}^2\Pi_{1/2}$ and ${}^2\Pi_{1/2}$, but this method could not be used in the present instance because of the complexity of the band and the weakness of the lines having low J values.] Van Vleck's theory demands that in case a the Λ -type

¹ C. V. Jackson, Proc. Roy. Soc. **126A**, 373 (1930).

² R. S. Mulliken, Phys. Rev. **33**, 730 (1929).

³ J. H. Van Vleck, Phys. Rev. **33**, 496-7 (1929).

doublets shall be much wider in the ${}^2\Pi_{1/2}$ than in the ${}^2\Pi_{1\ 1/2}$ levels, and if we assume case *a*, this criterion applied to the experimental data indicates an inverted ${}^2\Pi$. This was the basis of Jackson's conclusions.

But, as is mentioned in another forthcoming paper,⁴ we have in the ${}^2\Pi$ of SiH a state which is case *a* for the lowest *J* values but goes over to case *b* with increasing *J*. In such a case the ${}^2\Pi_{1/2}$ Λ -type doublets, although they should at first be wider than those for ${}^2\Pi_{1\ 1/2}$, should soon get narrower again and their widths should pass through zero, while the ${}^2\Pi_{1\ 1/2}$ doublets should begin to widen rapidly under the influence of the approach to case *b*.³ This would give on the whole wider doublets for ${}^2\Pi_{1\ 1/2}$ than for ${}^2\Pi_{1/2}$, and would require that we reverse Jackson's conclusions and interpret the ${}^2\Pi$ state as regular. In order to prove that this interpretation is correct we should show that the Λ -type doublets change sign with increasing *J* in what is here considered to be the ${}^2\Pi_{1/2}$ state (Jackson's ${}^2\Pi_{1\ 1/2}$ state). Now according to Jackson, the levels which we call ${}^2\Pi_{1/2}$ show measurable doubling only beginning with *K* = 14, while in the ${}^2\Pi_{1\ 1/2}$ levels doubling becomes appreciable at *K* = 8. But Jackson remarks that lines going to the levels *K* = 5 and 6 of ${}^2\Pi_{1/2}$ also show a doubling, which he classifies as a perturbation. If, however, we suppose that the Λ -type doubling in the ${}^2\Pi_{1/2}$ state first increases to a maximum, which is just large enough to be measurable, at *K* = 5 or 6, then decreases again, passes through zero at about *K* = 11 or 12, and again increases with opposite sign until at *K* = 14 it is again large enough to be detected experimentally, all the observed relations are explained, and we have surely a regular ${}^2\Pi$ state. Table I, based on Jackson's Table VIII, gives the values of the Λ -type doublet separations.

TABLE I. Λ -type doublet widths (cm^{-1}) in ${}^2\Pi$ state of SiH.*

| <i>K</i> | ${}^2\Pi_{\frac{1}{2}}$ | ${}^2\Pi_{1\frac{1}{2}}$ | <i>K</i> | ${}^2\Pi_{\frac{1}{2}}$ | ${}^2\Pi_{1\frac{1}{2}}$ | <i>K</i> | ${}^2\Pi_{\frac{1}{2}}$ | ${}^2\Pi_{1\frac{1}{2}}$ |
|----------|-------------------------|--------------------------|----------|-------------------------|--------------------------|----------|-------------------------|--------------------------|
| 4 | — | — | 9 | — | 0.66 | 14 | 0.33 | 1.61 |
| 5 | -0.30 | — | 10 | — | 0.80 | 15 | 0.60 | 1.91 |
| 6 | -0.27 | — | 11 | — | 0.99 | 16 | 0.84 | 2.12 |
| 7 | — | — | 12 | — | 1.0 | 17 | 0.99 | 2.42 |
| 8 | — | 0.38 | 13 | — | 1.35 | 18 | 1.32 | — |

* Most of these values are weighted averages of values obtained from *P*, *Q*, and *R* branches as given by Jackson in his Table VIII. The negative signs for the low numbered *K* values of ${}^2\Pi_{\frac{1}{2}}$ and the positive signs for all other values are of only relative significance here, and furthermore are based only on the fact that according to Van Vleck's theory, the sign of the doubling should be the same in case *b* (high *K* values) for ${}^2\Pi_{\frac{1}{2}}$ as for ${}^2\Pi_{1\frac{1}{2}}$. Empirically there is no way of deciding, from data on Δ , Π bands, whether the T_a or the T_b levels of the Π state are higher. (In the case of a Π , Σ transition this *can* be decided empirically).

Thus we have a regular ${}^2\Delta$ and a regular ${}^2\Pi$ state in SiH, and there is every reason to believe that these are analogous to the similar states of CH. It is of interest to determine the magnitudes of the coefficients *A* of the coupling between Λ and *S* for the two states of SiH. The value of *A/B* for the ${}^2\Pi$ state can be estimated most accurately by fitting Hill and Van Vleck's formula⁵ for the general intermediate case between cases *a* and *b* to the data on

⁴ R. S. Mulliken and A. Christy, forthcoming Phys. Rev.

⁵ E. L. Hill and J. H. Vleck, Phys. Rev. **32**, 250 (1928).

the term *differences* between ${}^2\Pi_{1/2}$ and ${}^2\Pi_{1\ 1/2}$ states of the same K values (cf. Jackson's Table IX). This and a further use of Jackson's data on ΔF 's in order to determine B more accurately, give $A/B = +19.5$ and $B = 7.35$.⁶ [$A/B = -15.5$ would do equally well if we did not know from Van Vleck's theory of Λ -type doubling that $A > 0$.] In a similar way one obtains for the ${}^2\Delta$ state the values $A/B = +0.6$ and $B = 7.3$ [$A/B = +3.4$ would equally well explain the observed spectrum, but since we expect a very small A for a $\sigma\pi^2$ ${}^2\Delta$ state, and since $A/B \sim -0.07$ is very small in ${}^2\Delta$ of CH, the value $A/B = +0.6$ is the more probable].

We thus have $A = +4$ for the ${}^2\Delta$ state and $A = +143$ for the ${}^2\Pi$ state, which may be compared with the values $A = -1$ and $A = +28$ for the corresponding states of CH. In the case of CH there is an interesting relation between A in the ${}^2\Pi$ state of the molecule and A in the 3P state of the carbon atom from which the ${}^2\Pi$ of CH is supposed to be derived by the addition of a hydrogen atom.² For a $\cdot\cdot\cdot p^2$ 3P atomic state, we know that for normal coupling the over-all width of the triplet, i.e., ${}^3P_2 - {}^3P_0$, is $1\frac{1}{2}A$. For the normal state of carbon, ${}^3P_2 - {}^3P_0 = 42$ cm⁻¹, giving $A = +28$ in exact agreement with A as obtained from the ${}^2\Pi$ state of CH. [Similar, although usually less exact, agreements are found in many other hydrides. Usually the A from the molecule is somewhat *less* than that from the atom.²] A similar comparison is of interest for the normal 3P of the silicon atom and the ${}^2\Pi$ of SiH. For the atom, ${}^3P_2 - {}^3P_0 = 223$, giving $A = +149$, in excellent agreement with the value $A = +143$ from SiH. The significance of such agreements has been discussed in a previous paper.²

In connection with the comparison of A values of atoms and their hydrides, a recent result of Watson and Parker² is of interest. These authors find $A = +1.97$ for the presumably $1s\sigma^2 2s\sigma^2 2p\pi$, ${}^2\Pi$ state of BeH, which agrees well with the value $A = +2.08$ from the triplet separation (${}^3P_2 - {}^3P_0$, $\Delta\nu = 3.12$) of the $1s^2 2s 2p$, 3P state of the Be atom.

⁶ No attempt has been made to obtain very accurate values of A and B , but it is believed that the A value of the ${}^2\Pi$ state is fairly accurate, the calculations having been made by means of the Hill and Van Vleck formula in such a way as to make the best use of the experimental data.

⁷ W. W. Watson and A. E. Parker, Phys. Rev. **37**, 167 (1931).