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# Hartree-Fock Functions and Spectral Isotope Shift for Excited States of Carbon and Oxygen*

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Hartree-Fock type atomic wave functions have been calculated for the $3s\ {}^5S$ and $3p\ {}^5P$ terms of oxygen and for the $2p3s\ {}^1P$ term of carbon. The calculations were carried out on an IBM card programmed calculator. A simple rapidly-converging method for determining the eigenvalues was developed.

Spectral isotope shifts were computed for the $3s\ {}^5S-3p\ {}^5P$ and other transitions of oxygen and for the $2p^2\ {}^1S-2p3s\ {}^1P$ transition of carbon. The results are compared with values previously reported by the authors, computed with wave functions without exchange. A comparison is made between these calculated values and the experimental determinations. For oxygen, the values of the specific shifts computed with exchange agree with measured values to within experimental error and are much better than the results obtained without exchange. For carbon, the isotope shift value using exchange shows no improvement on the value without exchange, both calculations disagreeing slightly with experimental results. A possible reason for the difference in behavior between the results for oxygen and carbon is postulated, based on the relative magnitudes of factors making up the formula for isotope shift.

## INTRODUCTION

ALTHOUGH spectral isotope shifts have been accurately measured in most of the light elements, theoretical calculations have been limited by a lack of accurate wave functions for excited configurations of these elements. Hartree self-consistent wave functions and Morse-Young-Haurwitz[1] analytic wave functions have been used for calculations in many of the light elements but in no case have wave functions been available which include exchange for both the upper and lower energy levels of a transition for which the isotope shift has been measured. The results of the calculations that have been performed are not, in general, in good agreement with the measured value of the isotope shift. It has been pointed out that the calculated values of the isotope shift of atomic energy levels are quite strongly dependent on the type of wave function used in the calculation. In particular, the use of Hartree-Fock functions in the calculation of the isotope shift in the ground level of carbon gave a result which differed from the Hartree calculation by more than 0.1 cm$^{-1}$, which is greater than the usual disagreement between theory and experiments in the light elements. Thus, it was felt that the use of Hartree-Fock wave functions in the isotope shift calculations might improve the results considerably. Primarily to check this point, Hartree-Fock wave functions were calculated for the $2p3s\ {}^1P$ level of carbon (J.N.) and for the $2p^33s\ {}^5S$ and $2p^33p\ {}^5P$ levels of oxygen (C.T.). The isotope shifts were calculated for the optical transitions and compared with those calculated from Hartree functions.

## HARTREE-FOCK EQUATIONS

The Hartree-Fock equations for one-electron wave functions can be derived from the general variational theorem by writing the atomic wave function as a determinant of one-electron product functions and employing the hydrogen-like solutions for the angular dependence. This derivation is given, for instance, by Hartree and Hartree.[2] The result is that for each electron of the atom one obtains a radial differential equation of the form

$$\frac{d^2P(nl/r)}{dr^2}+\left[2V(nl/r)-\frac{l(l+1)}{r^2}-\epsilon_{nl,\,nl}\right]P(nl/r)+T(nl/r)+\sum_{n'\neq n}\epsilon_{nl,\,n'l}P(n'l/r)=0, \quad (1)$$

where $r$ is the radial distance in units of the Bohr radius and $P(nl/r)$ is $r$ times the one-electron radial wave function for the electron with quantum numbers $n$ and $l$. $V(nl/r)$ is equal to the average electrostatic potential felt by the $nl$ electron (in units of twice the ionization energy of hydrogen) and $T(nl/r)$ is an exchange term peculiar to the Hartree-Fock formulation. In the last term the coefficients $\epsilon_{nl,\,n'l}$ are adjustable, and so are chosen to make $P(nl/r)$ orthogonal to $P(n'l/r)$ for all values of $n'\neq n$. This insures that all the one-electron functions will be orthogonal, since for electrons with different $l$ values the orthogonality of the one electron wave functions is brought about by the orthogonality of the angular wave functions. It is also required that the functions $P(nl/r)$ be normalized, so that $\int_0^\infty P^2(nl/r)dr=1$.

For the states investigated in this work, $V(nl/r)$ and $T(nl/r)$ can be written

$$V(nl/r)=\frac{Z}{r}+X_0(nl,nl/r)-\sum_{\text{all electrons}}X_0(n'l',n'l'/r), \quad (2)$$

$$T(nl/r)=\sum_{k=0}^{2}\sum_{\text{all } n',l'}\alpha_k(nl,n'l')\times X_k(nl,n'l'/r)P(n'l'/r), \quad (3)$$

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* Taken from dissertations submitted by the authors in partial fulfillment of degrees of Doctor of Philosophy at the University of Buffalo.

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[1] Morse, Young, and Haurwitz, Phys. Rev. 48, 948 (1935).

[2] D. R. Hartree and W. Hartree, Proc. Roy. Soc. (London) A143, 588 (1936).

where the values $\alpha_k(nl,n'l')$ are given in Table I and $X_k(n'l',nl/r)$ is given by

$$X_k(n'l',nl/r)=r^{-(k+1)}\int_0^r x^kP(nl/x)P(n'l'/x)dx \\ +r^k\int_r^\infty x^{-(k+1)}P(nl/x)P(n'l'/x)dx. \quad (4)$$

For each of the energy states discussed herein, a numerical solution was obtained for a set of simultaneous integro-differential equations (1) through (4), with $n$, $l$ taking on the values required for the particular configuration. The method of solution is discussed in a later section. The Hartree equations (without exchange) can be obtained by setting $T(nl/r)=0$ and $\epsilon_{nl,\,n'l'}=0$ in Eq. (1).

### SPECTRAL ISOTOPE SHIFT

It has been shown by Hughes and Eckart[3] that the assumption of a finite nuclear mass adds a term to the Hamiltonian of an atom with $\nu$ electrons equal to

$$(2M)^{-1}(\sum_{i=1}^{\nu}\mathbf{p}_i)^2, \quad (5)$$

where $\mathbf{p}_l$ is the linear momentum of the $i$th electron relative to the nucleus and $M$ is the nuclear mass. This term can be expressed as the sum of two terms,

$$N=(2M)^{-1}\sum_{i=1}^{\nu}(\mathbf{p}_i)^2 \quad \text{and} \quad \sigma=M^{-1}\sum_{i>j}\sum \mathbf{p}_i\cdot\mathbf{p}_j. \quad (6)$$

The quantity $N$ is customarily called the "normal" shift. It can be shown that its effect is to add a term $-(m/M)E$ to the unperturbed energy, where $E$ is the observed total energy and $m$ is the electron mass. This is equivalent to assuming a reduced mass for the electrons as is done in the case of the hydrogen atom. The second term is customarily called the "specific" shift. Its effect cannot be evaluated exactly but since it is small compared to the energy of the atom, first-order perturbation theory can be applied. In the experimental comparisons made later in this paper, the calculated value of the specific shift is compared with the experimental value minus the normal shift. This difference is called the "experimental specific shift."

TABLE I. Coefficients $\alpha_k(nl,n'l')$ in expression for $T(nl/r)$.[a]

| | | | Oxygen | | Carbon |
|---|---|---|---|---|---|
| $k$ | $nl$ | $n'l'$ | $3s\ ^5S$ | $3p\ ^5P$ | $2p3s\ ^1P$ |
| 0 | $1s$ | $2s$ | 2 | 2 | 2 |
| | | $3s$ | 1 | ... | 1 |
| | $2s$ | $1s$ | 2 | 2 | 2 |
| | | $3s$ | 1 | ... | 1 |
| | $3s$ | $1s$ | 2 | ... | 2 |
| | | $2s$ | 2 | ... | 2 |
| | $2p$ | $3p$ | ... | $\frac{2}{3}$ | ... |
| | $3p$ | $2p$ | ... | 2 | ... |
| 1 | $1s$ | $2p$ | 1 | 1 | $\frac{1}{3}$ |
| | | $3p$ | ... | $\frac{1}{3}$ | ... |
| | $2s$ | $2p$ | 1 | 1 | $\frac{1}{3}$ |
| | | $3p$ | ... | $\frac{1}{3}$ | ... |
| | $3s$ | $2p$ | 2 | ... | $-\frac{2}{3}$ |
| | $2p$ | $1s$ | $\frac{2}{3}$ | $\frac{2}{3}$ | $\frac{2}{3}$ |
| | | $2s$ | $\frac{2}{3}$ | $\frac{2}{3}$ | $\frac{2}{3}$ |
| | | $3s$ | $\frac{2}{3}$ | ... | $-\frac{2}{3}$ |
| | $3p$ | $1s$ | ... | $\frac{2}{3}$ | ... |
| | | $2s$ | ... | $\frac{2}{3}$ | ... |
| 2 | $2p$ | $2p$ | $\frac{4}{5}$ | $\frac{4}{5}$ | ... |
| | | $3p$ | ... | $\frac{4}{15}$ | ... |
| | $3p$ | $2p$ | ... | $\frac{4}{5}$ | ... |

[a] Coefficients not listed are equal to zero.

Assuming a determinental wave function formed from an orthonormal set of one-electron functions, a general expression can be derived[4,5] for the specific shift of an atomic energy level by evaluating the expectation value of $\sigma$. For a transition between two such levels, the shift in the spectral line can be obtained by taking the difference in the shifts of the two levels. For the energy levels of interest in this discussion the formulas for the specific shifts of the heavier isotope relative to the lighter are given by:

*$2p^33s$ configuration of oxygen*

$$\bar{\sigma}(^5S)=3A+3B,\quad \bar{\sigma}(^3S)=3A-3B,\quad \bar{\sigma}(^3P)=3A+2B,$$
$$\bar{\sigma}(^1P)=3A,\quad \bar{\sigma}(^3D)=3A+2B,\quad \bar{\sigma}(^1D)=3A;$$

*$2p^33p$ configuration of oxygen*

$$\bar{\sigma}\ (\text{all states})=3A'+C'; \quad (7)$$

*$2p^2$ configuration of carbon*

$$\bar{\sigma}(^1S)=2A;$$

*$2p3s$ configuration of carbon*

$$\bar{\sigma}(^1P)=A'-B',$$

where the constants $A$, $B$, and $C$ are defined by

$$A=(M_L^{-1}-M_H^{-1})(\tfrac{2}{3}m\ \text{ry})[J^2(2p,2s)+J^2(2p,1s)],$$
$$B=(M_L^{-1}-M_H^{-1})(\tfrac{2}{3}m\ \text{ry})[J^2(2p,3s)], \quad (8)$$
$$C=(M_L^{-1}-M_H^{-1})(\tfrac{2}{3}m\ \text{ry})[J^2(3p,2s)+J^2(3p,1s)],$$

and

$$J(n,l,n',l-1)=\int_0^\infty P(nl/r) \\ \times\left[\frac{dP(n',l-1/r)}{dr}-\frac{l}{r}P(n',l-1/r)\right]dr. \quad (9)$$

$M_L$ is the mass of the lighter nucleus and $M_H$ that of the heavier; $m$ is the electron mass, and ry the Rydberg constant. If $\bar{\sigma}$ is expressed in cm$^{-1}$ and $r$ in units of the Bohr radius, the constants for $O^{18}-O^{16}$ shifts have the value

$$(M_{16}^{-1}-M_{18}^{-1})(\tfrac{2}{3}m\ \text{ry})=0.2767,$$

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[3] D. S. Hughes and C. E. Eckart, Phys. Rev. **36**, 694 (1930).

[4] J. H. Bartlett and J. J. Gibbons, Phys. Rev. **44**, 538 (1933).

[5] J. P. Vinti, Phys. Rev. **56**, 1120 (1939).

and for carbon

$$(M_{12}{}^{-1}-M_{14}{}^{-1})(\tfrac{2}{3}m\text{ ry})=0.4740,$$

$$(M_{12}{}^{-1}-M_{13}{}^{-1})(\tfrac{2}{3}m\text{ ry})=0.2552.$$

In formula (7), primes have been used to indicate the higher energy state.

## METHOD OF CALCULATION

The iterative calculation of the Hartree-Fock wave functions was carried out using IBM card-programmed calculators. These computers are equipped with floating-point routine and carry eight significant figures in all calculations. The storage is limited to 72 words, so that intermediate results were carried on punched cards.

Hartree wave functions, available from previous calculations,[6,7] were used as the starting point for the Hartree-Fock calculation.[8] The functions $V(nl/r)$ and $T(nl/r)$ for a particular $nl$ electron were formed from these wave functions by using Eqs. (2), (3), and (4) and employing Simpson's rule of numerical integration. Equation (1) was then solved by Milne's method. This procedure was followed for each of the electrons and then the cycle was repeated until, for two successive iterations, the change in the integral

$$\int_0^r P^2(nl/r)dr$$

was less than 0.001 for any value of $r$, and the value of $\int_0^\infty P^2(nl/r)dr$ was equal to 1.0000. Also, it was required that

$$\int_0^\infty P(nl/r)P(n'l/r)dr,\quad n\neq n'$$

be less than 0.001. These results were then taken as the Hartree-Fock self-consistent solutions.

In the solution of Eq. (1) the eigenvalue $\epsilon_{nl,\,nl}$ was adjusted until the function $P(nl/r)\longrightarrow 0$ as $r\longrightarrow\infty$. A procedure was found which greatly simplified the process of making successive adjustments of $\epsilon_{nl,\,nl}$. First, a large value of $r$ was chosen for which it would be expected that $P(nl/r)$ would be equal to zero within the accuracy of the calculation. The numerical integration of Eq. (1) was continued until this value of $r$ was reached. The value of $\epsilon_{nl,\,nl}$ was then changed in linear proportion to the value of $P(nl/r)$ at this point. The proportionality constant to be used can be determined from the first two integrations and it was found that this constant changed by a negligible amount between successive calculations. In general, successive changes in $\epsilon_{nl,\,nl}$ decreased by a factor of 10 or better.

Wave functions[9] were calculated for the $2p^33s\ {}^5S$ and $2p^33p\ {}^5P$ states of oxygen and for the $2p3s\ {}^1P$ state of carbon. The functions for the $2p^2\ {}^1S$ state of carbon were available from calculations by Jucys.[10] However, one iteration was performed for the ${}^1S$ state using Jucys' functions to check that the different methods of calculation did not affect the results. It was found that the changes were negligible.

To determine the isotope shift, it was necessary to calculate the $J$ integrals of the form of Eq. (9). The function $dP(nl/r)/dr$ was obtained by numerical integration of $d^2P(nl/r)/dr^2$, this latter function being calculated from the differential equation and the known wave functions. The $J$ integrals were then calculated by using Simpson's rule. Additional calculations of these integrals were made using the next to last set of wave functions obtained in the self-consistent process and it was found that the last iteration would not affect the calculated isotope shift by a measurable amount. The results of these calculations are given in the next section.

## RESULTS AND DISCUSSION

### I. Oxygen

The values of the $J$ integrals (see formula 9) are given in Table II. Results are tabulated for calculations with the Hartree and Hartree-Fock wave functions. Table IV includes the $A$, $B$, and $C$ factors, obtained from the $J$ integrals by using formulas 8. If one makes the assumption (implicit in the Hartree approach) that the various states of the configuration can be represented by the same one-electron wave functions, these constants can be used in simple combinations[11] to obtain the specific isotope shift in all the members of the multiplet corresponding to the transition $2p^33p-2p^33s$. This multiplet contains nine spectral lines. The formulas for the specific shift for these nine lines, along

TABLE II. Square of the $J$ integrals for oxygen.

| Term | Integral | Hartree (orthogonalized) | Hartree-Fock |
|---|---|---|---|
| $2p^33s\ {}^5S$ | $J^2(2p,1s)$ | 4.3143 | 4.7781 |
| | $J^2(2p,2s)$ | 0.3768 | 0.3584 |
| | $J^2(2p,3s)$ | 0.0326 | 0.0599 |
| $2p^33p\ {}^5P$ | $J^2(2p',1s')$ | 4.2936 | 4.8264 |
| | $J^2(2p',2s')$ | 0.4682 | 0.3594 |
| | $J^2(3p',1s')$ | 0.0136 | 0.0849 |
| | $J^2(3p',2s')$ | 0.0008 | 0.0134 |

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[6] J. P. Nicklas, Phys. Rev. **95**, 1469 (1954).

[7] C. E. Treanor, Phys. Rev. **95**, 1472 (1954).

[8] An interval of 0.01 in $r$ was used from $r=0$ to $r=0.1$. The interval was then doubled for the next 10 points, doubled again for the next 10 points, etc. For wave functions with $n=3$, it was necessary to use slightly over 80 points.

[9] These tabulated functions are available on request from the authors. They have also been deposited as Document No. 5531 with the ADI Auxiliary Publications Project, Photoduplication Service, Library of Congress, Washington 25, D. C. A copy may be secured by citing the Document number and by remitting \$2.50 for photoprints of \$1.75 for 35-mm microfilm. Advance payment is required. Make checks or money orders payable to: Chief, Photoduplication Service, Library of Congress.

[10] A. Jucys, Proc. Roy. Soc. (London) **173**, 59 (1939).

[11] E. U. Condon and G. H. Shortley, *The Theory of Atomic Spectra* (Cambridge University Press, New York, 1951), second edition, p. 419.

TABLE III. Specific shifts in transitions between the first two excited configurations of oxygen ($cm^{-1}$).

| Formula for shift | λ (A) | Transition | Experimental specific shifts (Parker and Holmes[a]) | Calculated specific shifts (Hartree fns.) | Calculated specific shifts (Hartree-Fock fns.) |
|---|---|---|---|---|---|
| $3(A'-A)+C'-3B$ | 7772 | $3s\,{}^5S-3p\,{}^5P$ | $0.013 \rightarrow 0.019$ | $-0.0382$ | 0.0184 |
| $3(A'-A)+C'$ | 8820 | $3s\,{}^1D-3p\,{}^1F$ | $0.064 \rightarrow 0.068$ | $-0.0112$ | (0.0682) |
| $3(A'-A)+C'+B$ | 8446 | $3s\,{}^3S-3p\,{}^3P$ | $0.08 \rightarrow 0.10$ | $-0.0022$ | (0.0848) |
| $-3(A'-A)-C'+2B$ | 3955 | $3p\,{}^3P-3s\,{}^3P$ | $0.0 \rightarrow -0.2$ | 0.0292 | $(-0.0350)$ |
| $3(A'-A)+C'-2B$ | 8222 | $3s\,{}^3D-3p\,{}^3D$ | $0.034 \rightarrow 0.040$ | $-0.0292$ | (0.0350) |
| $3(A'-A)+C'-2B$ | 3823 | $3s\,{}^3D-3p\,{}^3D$ | $0.03 \rightarrow 0.05$ | $-0.0292$ | (0.0350) |
| $3(A'-A)+C'$ | 7157 | $3s\,{}^1D-3p\,{}^1D$ | $0.05 \rightarrow 0.07$ | $-0.0112$ | (0.0682) |
| $-3(A'-A)-C'+2B$ | 7995 | $3p\,{}^3P-3s\,{}^3D$ | $-0.06 \rightarrow -0.07$ | 0.0292 | $(-0.0352)$ |
| $3(A'-A)+C'-2B$ | 7476 | $3s\,{}^3P-3p\,{}^3D$ | $-0.04 \rightarrow -0.06$ | $-0.0292$ | (0.0352) |

[a] See reference 12.

with the measured and calculated values of the shift, are given in Table III. The experimental results are taken from the work of Parker and Holmes.[12] The normal shift has been subtracted from each of the measured values to obtain the specific shift. All shifts are those of isotope 18 relative to 16. It should be pointed out that the calculated value obtained with the Hartree-Fock functions strictly applies only to the $3s\,{}^5S-3p\,{}^5P$ transition, but it is felt that the small changes in the wave functions for other states would contribute little to the isotope shift integrals. However, the Hartree-Fock results for the other transitions are entered in parentheses in Table III.

Inspection of Table III shows that the Hartree-Fock functions give calculated shifts in good over-all agreement with the experimental values. Only two of the lines (λ 7995 and λ 7476) are reasonably outside the experimental limits of error. Parker and Holmes[12] have pointed out that the measured shift in λ 7476 is not consistent with the shifts in other lines, using the fact that the shift in λ 7476($3s\,{}^3P-3p\,{}^3D$) should be equal to the shifts in λ 3823($3s\,{}^3D-3p\,{}^3D$)+λ 7995($3p\,{}^3P-3s\,{}^3D$) −λ 3995($3p\,{}^3P-3s\,{}^3P$). In addition, this line should be a triplet, but only one component was observed. They suggest that the line may be incorrectly classified.

Parker and Holmes have shown that the first seven lines of Table IV show shifts consistent with the assumption that $3(A'-A)=0$, $B=0.0165\pm0.0015$ $cm^{-1}$, and $C'=0.006\pm0.002$ $cm^{-1}$. Since $A$, $A'$ and $C'$ are involved in the calculation only the combination $3(A'-A)+C'$, it is not necessary to make separate assumptions about these variables, but only about the combination. Parker and Holmes' experimental values are compared with the calculated values in Table IV. It is seen that although the separate assumptions about $3(A'-A)$ and $C'$ are not justified, the Hartree-Fock functions give good agreement with the experimental values of $3(A'-A)+C'$ and $B$.

TABLE IV. Comparison of experimental and calculated values of the isotope shift parameters ($cm^{-1}$).

| Isotope shift parameter | Values suggested by Parker and Holmes | Values obtained with Hartree functions | Values obtained with Hartree-Fock functions |
|---|---|---|---|
| $A$ | ... | 1.2634 | 1.4212 |
| $A'$ | ... | 1.2583 | 1.4349 |
| $3(A'-A)$ | 0 | $-0.0153$ | 0.0410 |
| $C'$ | $0.066\pm0.002$ | 0.0041 | 0.0272 |
| $B$ | $0.0165\pm0.0015$ | 0.0090 | 0.0166 |
| $3(A'-A)+C'$ | $0.066\pm0.002$ | $-0.0112$ | 0.0682 |

The similarity between the quantities discussed in the previous paragraph and those involved in the isotope shift for neon, $2p^53s-2p^53p$, permits a direct comparison with work that has been done with that element. For the $2p^53s$ configuration there are two energy levels. The formulas for the isotope shifts are

$$\text{neon:}\quad \bar{\sigma}({}^3P)=5A+3B,$$

$$\text{neon:}\quad \bar{\sigma}({}^1P)=5A+B.$$

For the $2p^53p$ levels all shifts are the same; namely,

$$\text{neon:}\quad \bar{\sigma}(\text{all } 2p^53p \text{ levels})=5A'+C'.$$

The quantities $A$, $B$, $A'$, and $C'$ are defined in the same way as for oxygen.

Isotope shifts have been measured[13] in spectral lines representing the transitions $3s\,{}^1P-3p$ and $3s\,{}^3P-3p$. The shifts have been calculated by Bartlett and Gibbons,[4] using Hartree wave functions. Since the $1s$, $2s$, and $2p$ functions change very little between the $2p^53s$ and $2p^53p$ configurations, it was assumed that $5(A'-A)=0$. Although these changes are small, for calculation of the isotope shift small changes in the $2p$ wave function can make a significant change in the $J(2p,1s)$ integral, so that $(A'-A)$ cannot be taken equal to zero. For oxygen, this fact is clearly brought out in Table IV. The pertinent factors for neon are presented in Table V. The difference in the shifts for the two spectral lines is 0.017 $cm^{-1}$. The calculated value for this difference is in good agreement (0.0195), as pointed out by Bartlett and Gibbons. It is seen from Table V that the formula for the difference in shifts does not depend on $5(A'-A)+C'$, so that the calculated value of $B$ is evidently good to within 0.0015 $cm^{-1}$.

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[12] L. W. Parker and J. R. Holmes, J. Opt. Soc. Am. **43**, 103 (1953).

[13] H. Nagaoka and T. Mishima, Sci. Papers Inst. Phys. Chem. Research Tokyo **13**, 293 (1930).

TABLE V. Specific shifts in transitions between the first two excited configurations of neon.

| Neon transition | Experimental[a] specific shift ($\text{cm}^{-1}$) | Calculated[b] specific shift ($\text{cm}^{-1}$) | Formula for specific shift |
|---|---|---|---|
| $3s\,^3P-3p$ | 0.016 | $-0.0157$ | $5(A'-A)+C'-3B$ |
| $3s\,^1P-3p$ | 0.033 | 0.0038 | $5(A'-A)+C'-B$ |

[a] See reference 13.
[b] See reference 4.

TABLE VI. Squares of the $J$ integrals for carbon.

| Term | Integral | Hartree functions (orthogonalized) | Hartree-Fock functions |
|---|---|---|---|
| $2p^2\,^1S$ | $J^2(2p,1s)$ | 1.5131 | 1.6466 |
| | $J^2(2p,2s)$ | 0.2657 | 0.2786 |
| $2p3s\,^1P$ | $J^2(2p,1s)$ | 2.1196 | 2.3917 |
| | $J^2(2p,2s)$ | 0.2223 | 0.2296 |
| | $J^2(2p,3s)$ | 0.0251 | 0.0333 |

Going through a differencing procedure for the shifts in the oxygen lines gives the value of $B$ suggested by Parker and Holmes ($0.0165\pm0.0015$). The Hartree functions for oxygen give a value of $B$ which disagrees with this by $0.0075\pm0.0015$. However, the important feature in causing disagreement in the line shifts (Table IV) is clearly the disagreement of the term $3(A'-A)+C'$. This factor agrees very well in the Hartree-Fock calculations.

## II. Carbon

The values of the $J$ integrals for carbon are given in Table VI. The computed values of constants $A$, $A'$, and $B'$ are listed in Table VII.

In contrast to oxygen, investigators[14,15] have measured the shift of only one transition in carbon. Measurements have been made, however, of both the $C^{14}-C^{12}$ and $C^{13}-C^{12}$ shifts of the transition $2p^2\,^1S-2p\,3s\,^1P$ ($\lambda=2478.5$ A). The formula for the shift in terms of the $A$, $A'$, and $B'$ is $\bar{\sigma}=A'-B'-2A$. A comparison of the computed and experimental values of the isotope shift is given in Table VIII.

For the shift of $C^{14}$ relative to $C^{12}$, the discrepancy between experimental and theoretical values is 0.033 $\text{cm}^{-1}$ with Hartree functions and 0.043 $\text{cm}^{-1}$ with Hartree-Fock functions. Both of these discrepancies are less than 10% of the experimental value. However, they are much larger than the experimental error of $\pm0.002$ $\text{cm}^{-1}$. The difference between the specific shifts computed with Hartree and Hartree-Fock functions is 0.010 $\text{cm}^{-1}$ in a direction so as to make the agreement with experiment poorer for the latter.

There is an important difference between the carbon and oxygen isotope shifts. The spectral lines measured in carbon involve the transition of a $2p$ electron, while those measured in oxygen do not. As a result the carbon isotope shift depends on the actual magnitude of the factor $A$, while the oxygen shifts depend only on $(A'-A)$. This is the reason that the isotope shift in carbon is much greater than that in oxygen. It can be seen from Tables IV and VII that the values of $A$ and $A'$ are strongly influenced by the type of wave functions used in the calculation, while the difference $A-A'$ is not affected nearly as much. It is possible that the relative accuracy of $A$ and $A'$ is better for both the carbon and oxygen calculations with Hartree-Fock functions, and that it shows up as a distinct improvement in the oxygen results while it is masked by the large contribution of the absolute value of $A$ to the isotope shift in carbon.

From the oxygen results, it appears that in the cases where the number of $A$ and $A'$ is the same in the isotope shift formula, the calculated shift might be improved by using Hartree-Fock functions because of the improved relative accuracy of $A$ and $A'$. A case where this might be checked is in the neon transition that has been cited previously. If the postulated behavior of $A$ and $A'$ is correct, then a calculation of the isotope shift for neon with Hartree-Fock functions should yield results equally as good as those reported here for oxygen.

TABLE VII. Calculated isotope shift parameters for carbon ($\text{cm}^{-1}$).

| Isotopes | Parameter | Hartree functions (orthogonalized) | Hartree-Fock functions |
|---|---|---|---|
| $C^{13}-C^{12}$ | $A$ | 0.4540 | 0.4913 |
| | $A'$ | 0.5977 | 0.6689 |
| | $B'$ | 0.0064 | 0.0085 |
| $C^{14}-C^{12}$ | $A$ | 0.8432 | 0.9126 |
| | $A'$ | 1.1101 | 1.2424 |
| | $B'$ | 0.0119 | 0.0158 |

TABLE VIII. Comparison of experimental and calculated shifts for the transition $2p^2\,^1S-2p3s\,^1P$ ($\lambda=2478.5$ A) in $\text{cm}^{-1}$.

| | $C^{13}$ relative to $C^{12}$ | $C^{14}$ relative to $C^{12}$ |
|---|---|---|
| Experimental specific shift[a] | $-0.297\pm0.002$ | $-0.555\pm0.002$ |
| Calculated specific shift (Hartree) | $-0.317$ | $-0.588$ |
| Calculated specific shift (Hartree-Fock) | $-0.323$ | $-0.598$ |

[a] See reference 14 and 15.

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