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Isotope Shift in Neutral Oxygen*

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Isotope shifts in levels of the first and second excited configurations of oxygen were calculated using Hartree one-electron wave functions, computed for $1s^22s^22p^33s$ and $1s^22s^22p^33p$. The suitability of the wave functions for this type of calculation can be checked with recent experiments in nine spectral lines of neutral oxygen. The discrepancies between calculated and observed shifts are from -0.09 cm^{-1} to $+0.09$ cm^{-1} for the shift between O^{18} and O^{16}. It appears that better one-electron wave functions (e.g., Hartree-Fock functions including exchange) could account for these discrepancies.

INTRODUCTION

RECENT spectroscopic measurements with oxygen enriched in O^{18} have resulted in the determination of the isotope shift in 20 lines of neutral oxygen.[1] Nine of these lines are transitions between the configurations $1s^22s^22p^33s$ and $1s^22s^22p^33p$, the first and second excited configurations. Parker and Holmes,[1] using the first order theory of Bartlett and Gibbons,[2] have shown that the shifts of the various states can be made consistent with the assumption that they are caused by nuclear motion. They fixed two parameters in the theory by using the experimental data from two lines (λ7772 and λ8820), assumed a third parameter to be negligibly small, and found that most remaining shifts could be calculated correctly from this. In the present paper Hartree one-electron wave functions without exchange were computed and used to calculate the isotope shift for these configurations.

The general theory required for calculation of the isotope shift due to nuclear motion is reviewed in the paper preceding this.[3] The same notation will be used here. The isotope shift of an energy level is divided into the "normal" shift ($\bar{N}$) and the "specific" shift ($\bar{\sigma}$). We will be concerned only with the specific shift, since the normal shift can be determined without knowledge of the wave functions.

FORMULAS FOR THE SPECIFIC SHIFT IN NEUTRAL OXYGEN

The first excited configuration of neutral oxygen' $1s^22s^22p^33s$, gives rise to 6 Russell-Saunders terms. The formulas for the specific shift for these terms can be obtained by using the diagonal sum rule, as described in the preceding paper on carbon.[3] The formulas listed below describe the shift of O^{18} relative to O^{16}.

$$\begin{aligned} &\bar{\sigma}(^5S)=3A+3B, && \bar{\sigma}(^1P)=3A \\ &\bar{\sigma}(^3S)=3A-B, && \bar{\sigma}(^3D)=3A+2B, \\ &\bar{\sigma}(^3P)=3A+2B, && \bar{\sigma}(^1D)=3A. \end{aligned} \tag{1}$$

The abbreviations introduced are

$$\begin{aligned} A&=(M_{16}{}^{-1}-M_{18}{}^{-1})(\tfrac{2}{3}mRy)[J^2(2p,2s)+J^2(2p,1s)] \\ B&=(M_{16}{}^{-1}-M_{18}{}^{-1})(\tfrac{2}{3}mRy)[J^2(2p,3s)] \end{aligned} \tag{2}$$

and, for example,

$$J(2p,3s)=\int_0^\infty R(2p)\frac{d}{dr}R(3s)r^2dr.$$

$\bar{\sigma}$ is expressed in cm^{-1}, while r is in units of the Bohr radius. The quantity $(M_{16}{}^{-1}-M_{18}{}^{-1})(\tfrac{2}{3}mRy)=0.2767$.

In the case of the $2p^33p$ configuration, the shifts are the same for all states of the configuration, namely $\bar{\sigma}$ (all $2p^33p$ states) $=3A'+C'$, with

$$\begin{aligned} A'&=(M_{16}{}^{-1}-M_{18}{}^{-1})(\tfrac{2}{3}mRy) \\ &\qquad\times[J^2(2p',2s')+J^2(2p',1s')] \\ C'&=(M_{16}{}^{-1}-M_{18}{}^{-1})(\tfrac{2}{3}mRy) \\ &\qquad\times[J^2(3p',2s')+J^2(3p',1s')]. \end{aligned} \tag{3}$$

The primes indicate the second excited configurations.

The shift in a spectral line of O^{18} relative to O^{16} is then obtained by subtracting the shift in the lower level from that of the upper level.

NUMERICAL CALCULATIONS

The formulas (1) for the quantities $\bar{\sigma}$ assume that the one-electron wave functions are orthogonal. Although this is not satisfied by Hartree wave functions with the same l but different n, the difficulty can be circumvented by using linear combinations of the original functions. The orthonormal combinations used in this calculation are

$$\begin{aligned} &R_0(1s)=R(1s), \\ &R_0(2s)=(1.0004)R(1s)-(0.0270)R(1s), \\ &R_0(3s)=(1.0052)R(3s)-(0.0723)R(2s)-(0.0038)R(1s), \\ &R_0(2p)=R(2p), \\ &R_0(3p)=(1.0123)R(3p)-(0.1571)R(2p), \end{aligned}$$

$$\int_0^\infty R_0(n,l)R_0(n',l)r^2dr=\delta_{n,n'}.$$

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

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

[3] J. P. Nicklas, preceding paper [Phys. Rev. **95**, 1469 (1954)].

TABLE I. Specific shift of O^{18} relative to O^{16} in cm^{-1}.

λ	Transition	Formula for shift	Calculated specific shift	Experimental specific shift	Experimental minus calculated
7772	$3s\,{}^5S-3p\,{}^5P$	$3(A'-A)+C'-3B$	-0.0382	$0.015\rightarrow0.018$	$+0.055$
8820	$3s\,{}^1D-3p\,{}^1F$	$3(A'-A)+C'$	-0.0194	$0.064\rightarrow0.068$	$+0.085$
8446	$3s\,{}^3S-3p\,{}^3P$	$3(A'-A)+C'+B$	-0.0022	$0.08\rightarrow0.10$	$+0.09$
3955	$3p\,{}^3P-3s\,{}^3P$	$3(A-A')-C'+2B$	$+0.0292$	$0.0\rightarrow-0.2$	...
8222	$3s\,{}^3D-3p\,{}^3D$	$3(A'-A)+C'-2B$	-0.0292	$0.034\rightarrow0.040$	$+0.066$
3823	$3s\,{}^3D-3p\,{}^3D$	$3(A'-A)+C'-2B$	-0.0292	$0.03\rightarrow0.05$	$+0.07$
7157	$3s\,{}^1D-3p\,{}^1D$	$3(A'-A)+C'$	-0.0112	$0.05\rightarrow0.07$	$+0.07$
7995	$3p\,{}^3P-3s\,{}^3D$	$3(A-A')-C'+2B$	$+0.0292$	$-0.06\rightarrow-0.07$	-0.09
7476	$3s\,{}^3P-3p\,{}^3D$	$3(A'-A)+C'-2B$	-0.0292	$-0.04\rightarrow-0.06$	-0.02

The required J integrals, calculated with these orthogonal wave functions, are

$$J(2p,1s)=-2.0771,\quad J(2p',1s')=-2.0721,$$
$$J(2p,2s)=0.6138,\quad J(2p',2s')=0.6160,$$
$$J(2p,3s)=0.1806,\quad J(3p',1s')=0.1253,$$
$$J(3p',2s')=0.0282,$$

so that the quantities defined by Eqs. (2) and (3) become

$$A=1.2634\ \text{cm}^{-1},\quad A'=1.2583\ \text{cm}^{-1},$$
$$B=0.0090\ \text{cm}^{-1},\quad C'=0.0041\ \text{cm}^{-1}.$$

The corresponding shifts in nine spectral lines were calculated from these and are given in Table I. Also listed are the experimental shifts observed by Parker and Holmes.

Parker and Holmes[1] have shown that all but two of the lines (λ7995 and λ7476) have shifts consistent with the assumption that $3(A'-A)=0$, $B=0.0165\pm0.0015$ cm^{-1}, and $C'=0.066\pm0.002$ cm^{-1}. They point out that λ7476 may be incorrectly classified. The only comparisons available for transitions between two excited levels are calculations in neon, where the configurations are the same as for oxygen (except for two more $2p$ electrons), and a single transition in ionized boron, where Morse, Young, Haurwitz (M.Y.H.) functions were used. In the case of ionized boron, the discrepancy is 0.168 cm^{-1}. In the calculation for neon, where Hartree wave functions were used, four transitions could be checked. The value of $5(A'-A)$ was assumed negligibly small, and experimental comparison indicates that the calculated value of C' is too small by about 0.03 cm^{-1}, which is in the same direction (and about half as large) as the discrepancy in oxygen. Although configuration interaction is certainly important in many of the levels of oxygen, it could be expected that the effect on λ7772 ($3s\,{}^5S-3p\,{}^5P$) would be small. The error of 0.055 cm^{-1} in this line is as bad as that in some of the other lines.

The effect on the isotope shift of including exchange in the one-electron wave functions has been investigated in a preliminary way in carbon.[3] Calculations show that the shift of the ground level is changed 0.170 cm^{-1} for ${}^1S$ and 0.290 cm^{-1} for ${}^3P(\Delta M=2)$ by including the effects of exchange in the calculation of the wave functions. The Hartree wave functions give equal shifts for the two levels, while Hartree-Fock wave functions give a difference of 0.120 cm^{-1}. It seems plausible then that the neglect of exchange could explain the discrepancy in λ7772. In fact, a discrepancy of the same magnitude in neutral boron (transition from first excited configuration to ground configuration) was removed by using M.Y.H. wave functions in place of Hartree functions.[4] To investigate this and other problems in neutral oxygen, it is planned to calculate the wave functions including exchange for the $3s\,{}^5S$ and $3p\,{}^5P$ configurations.

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[4] J. P. Vinti, Phys. Rev. **58**, 879 (1940).