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Higher-Order Fine Structure of the $a^4\Pi_u$ State of O_2^+

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It is shown that the quality of the fit of frequencies for the (4, 4) band of the $b^4\Sigma_g^- - a^4\Pi_u$ transition of O_2^+, obtained in an ion-beam experiment, can be significantly improved by the inclusion of a fine structure term of the form $L_z S_z^3$ in the effective Hamiltonian for the $a^4\Pi_u$ state, where L_z and S_z are respectively the components of the total orbital and spin angular momenta along the internuclear axis. The various contributions to this term in the Hamiltonian are assessed from a general standpoint by the use of a new order-of-magnitude scheme. The separate contributions to the parameter involved, η, are then considered in detail by means of a perturbation treatment of the spin–orbit and spin–spin interactions through third order. Attempts to interpret the parameter values determined for the $a^4\Pi_u$ state of O_2^+ are severely limited by the present lack of detailed knowledge of the properties of the various electronic states of O_2^+.

1. INTRODUCTION

Recent high-resolution studies (*1–3*) of the $b^4\Sigma_g^- - a^4\Pi_u$ transition of O_2^+ have led to a notable improvement in the molecular constants of the states involved. In the fitting of the data, however, there remained small but systematic residuals correlated with the components of the $a^4\Pi_u$ state, the mean residuals being -0.0018, $+0.0122$, -0.0269, and $+0.0047$ cm^{-1} for the F_1'', F_2'', F_3'', and F_4'' components, respectively (*2*). The F_2'' and F_3'' residuals in particular are quite significant compared with the estimated experimental precision of 0.0028 cm^{-1}.

Since the $a^4\Pi_u$ state is a good case (*a*) state with $A/B \simeq -47$, the absence of an

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observed correlation with J'' indicates that the residuals are due to a rotation-independent term in the molecular Hamiltonian. In the fit, the parameters describing the three intervals between the $^4\Pi$ components of the nonrotating molecule were the spin–orbit coupling constant A_{nv} and the spin–spin coupling constant λ_{nv} (or $\epsilon_{nv} = 2\lambda_{nv}/3$), where the subscripts refer to the vibrational state v of electronic state n. These correspond to terms respectively linear and quadratic in the operator S_z, the former having a factor L_z as required by time-reversal and other symmetry requirements. The next term, which is cubic in S_z, we take in the (unnormalized) tensor form,

$$\eta_{nv} L_z S_z [S_z^2 - (1/5)(3\mathbf{S}^2 - 1)], \tag{1}$$

where the new molecular constant η_{nv} is a higher-order fine structure constant. The theoretical interpretation of η_{nv} requires third-order perturbation theory, discussed in Section 4. First, in Section 2, we confirm that the introduction of the term (1) removes the systematic residuals found previously.

2. DATA FITTING

The general Hamiltonian for diatomic molecules has been discussed extensively in the literature, for example, by Zare *et al.* (*4*), by Mizushima (*5*), and by Brown *et al.* (*6*). The specific case of $^4\Pi$ states has been considered by Veseth (*7*). The present treatment and notation follow Brown *et al.* (*6*) and Brown and Merer (*8*). The introduction of term (1) into Eq. (18) of Ref. (*6*) gives for the rotation–spin Hamiltonian of the vibronic state nv

$$\begin{aligned} H_{nv}/hc = {} & T_{nv} + B_{nv}\mathbf{N}^2 - D_{nv}\mathbf{N}^4 + (1/2)[A_{nv} + A_{nDv}\mathbf{N}^2, L_z S_z]_+ + \gamma_{nv}\mathbf{N}^2\mathbf{N}\cdot\mathbf{S} \\ & + 2\lambda_{nv}(S_z^2 - (1/3)\mathbf{S}^2) + \eta_{nv} L_z S_z [S_z^2 - (1/5)(3\mathbf{S}^2 - 1)] \\ & - (1/2)o_{nv}(\Lambda_+^2 S_-^2 + \Lambda_-^2 S_+^2) + (1/2)p_{nv}(\Lambda_+^2 S_- N_- + \Lambda_-^2 S_+ N_+) \\ & - (1/2)q_{nv}(\Lambda_+^2 N_-^2 + \Lambda_-^2 N_+^2), \end{aligned} \tag{2}$$

when $[\ ,\ ]_+$ indicates an anticommutator and the higher-order terms γ_{nDv}, λ_{nDv}, o_{nDv}, p_{nDv}, and q_{nDv} are omitted. The matrix elements of this Hamiltonian were evaluated in a parity-projected case (a) basis set, as in Table II of Ref. (*8*). The resulting matrices (of dimension 4×4 except for $J < 5/2$) were diagonalized numerically to yield the set of term values.

The experimental data come from the very precise measurements by Cosby *et al.* (*2*) of Doppler-tuned laser absorption by an O_2^+ beam. Many lines in four different vibrational bands of the $b^4\Sigma_g^- - a^4\Pi_u$ system were measured, of which the (4, 4) band is the most extensive. Cosby *et al.* published the results of a least-squares fit of 201 lines of this band, employing the Hamiltonian of Zare *et al.* (*4*) and Albritton *et al.* (*9*). The parameter values they obtained are given in the first column of Table I. The standard deviation, 0.0136 cm^{-1}, is significantly larger than the estimated experimental precision, 0.0028 cm^{-1}.

We have performed two unweighted fits of the same 201 lines with the Hamiltonian of Eq. (2). In the first η_{nv} was constrained to zero and the Hamiltonian was essentially equivalent to that employed by Cosby *et al.* (*2*), the differences

TABLE I

Some Results from Least-Squares Fits of Data from the (4, 4) Band of the $b^4\Sigma_g^+ - a^4\Pi_u$ System of O_2^+

	Cosby *et al*[a]	Present work Fit 1	Present work Fit 2
ν_o	17177.085(12)[b]	17178.175(8)	17178.159(3)
B'	1.186523(82)	1.186527(82)	1.186414(26)
$10^6\ D'$	6.662(110)	6.66(11)	6.513(34)
$10^3\ \gamma'$	-1.338(110)	-1.35(11)	-1.337(35)
λ'	0.2088(10)	0.2088(10)	0.20854(32)
A''	-47.6925(45)	-47.6706(30)	-47.68131(99)
$10^4\ A_D''$	1.90(130)	2.1(13)	0.32(41)
B''	1.034982(77)	1.034989(76)	1.034861(24)
$10^6\ D''$	5.222(100)	5.22(10)	5.081(32)
$10^2\ \gamma''$	-0.78(31)	-1.00(30)	-0.537(95)
λ''	0.9425(33)	0.9537(26)	0.94675(84)
o''	-0.02177[c,d]	0.1514(20)	0.14950(63)
$10^3\ p''$	3.78(37)	3.73(37)	3.90(12)
$10^5\ q''$	-1.4(23)	-1.6(23)	-2.33(72)
α''	0.1949(47)	—[e]	—[e]
$10^2\ \eta''$	0.0[c]	0.0[c]	5.60(13)
σ_{fit}[f]	0.0136	0.01365	0.0043

[a] Taken from ref. (2). The parameters determined in the fit are defined in refs. (4) and (9); they differ slightly from those used in the present work, which are defined in ref. (6).

[b] Parameter values quoted in cm^{-1}. The figures in parenthesis are one standard deviation of the least-squares fit, in units of the last quoted decimal place.

[c] Parameter constrained to this value in the fit.

[d] This is a calculated value, derived from $o = \frac{1}{8}(A/B)p$. Note however that this formula, which is based on a unique perturber model, is actually the second order correction to the spin orbit coupling constant, $A^{(2)}$ (6).

[e] There is no equivalent to the parameter α in the model used in this work. The quantity $(2\alpha + 2o)$ used by Albritton *et al* (9) corresponds to our lambda doubling parameter o.

[f] The standard deviation of fit of 201 data points of equal weight.

being mainly in the definitions of the parameters. The results, collected in column 2 of Table I, show that the standard deviation, 0.01365 cm^{-1}, is essentially the same as in column 1. Furthermore, the pattern of residuals was identical in the two fits. In our second fit the parameter η_{nv} was freed, with the results shown in column 3 of Table I. The standard deviation, 0.0043 cm^{-1}, is greatly reduced and

is now comparable to the estimated experimental precision. The mean residuals for the F_1'', F_2'', F_3'', and F_4'' components are -0.00018, 0.00056, -0.00112, 0.00026 cm^{-1}, respectively, indicating that the previous systematic pattern of residuals has been almost entirely removed.

Without exception, the standard deviations of individual parameters are reduced in the second fit. This applies both to the parameters A_{nv}'' and λ_{nv}'' associated with the quartet splitting in the nonrotating molecule and to parameters such as A_{nDv}'', γ_{nv}'', and q_{nv}'' associated with rotation. The standard deviation of q_{nv}'' is now less than the parameter value. Of particular interest is the fact that both A_{nDv}'' and γ_{nv}'' are determined in these fits. Thus indeterminacies of the type discussed for $^2\Pi$ states by Brown *et al.* (*6*) do not occur in the $^4\Pi$ Hamiltonian in Eq. (2).

These fits show that the introduction of term (1) accounts satisfactorily for the pattern of residuals found previously. The high precision of the ion-beam experiment, which is largely a result of the kinematic compression of the velocity distribution for large Doppler tuning, has therefore led to the determination of a new molecular parameter, η_{nv}. In the following sections we consider the theoretical interpretation of this and other parameters.

3. ORDER-OF-MAGNITUDE CONSIDERATIONS

The calculation of a theoretical formula for η requires the use of third-order perturbation theory. As in all applications of higher-order perturbation theory, it is convenient to have a general picture of the relative orders of magnitude of the energy contributions of different terms. For example, the spin–rotation constant γ is usually dominated by the second-order contribution $\gamma^{(2)}$ (*6*, *10*). What is desired is some general scheme that makes the relative sizes of different contributions, such as $\gamma^{(1)}$ and $\gamma^{(2)}$, readily intelligible.

(i) Dependence on α

The first step consists essentially of expressing the various terms in the Hamiltonian in atomic units. Relative to an atomic unit of energy, which we take as the Rydberg R_H, each term depends on some power of the dimensionless fine structure constant $\alpha \simeq 0.007297$. For example, the spin–orbit and spin–spin coupling operators are of order $\alpha^2 R_H$ in this classification.

(ii) Dependence on κ

Consideration of the nuclear motion introduces the nuclear masses, of order m_n. The orders of magnitude can be expressed in terms of the Born–Oppenheimer parameter $\kappa = (m_e/m_n)^{1/4}$. For example, if the equilibrium bond length r_e is of the order of the Bohr radius a_0, the rotational constant B_e is of order $(m_e/m_n)R_H = \kappa^4 R_H$. If nuclear displacements are measured in units of a_0, the nuclear kinetic energy is of order $\kappa^4 R_H$ and the harmonic potential of order R_H. The usual harmonic oscillator solution then gives vibrational energy levels whose order of magnitude is the geometric mean of these quantities, $\kappa^2 R_H$, and typical vibrational displacements of order κa_0. The vibrational matrix elements of the cubic, quartic, . . . poten-

tials are then of order $\kappa^3 R_H$, $\kappa^4 R_H$, . . . , respectively. Similar results can be applied to the matrix elements of the expansions of other operators, such as the electric dipole moment or the spin–orbit coupling operator, in powers of the nuclear displacement.

(iii) Dependence on Z

The dependence on atomic number Z is more difficult to estimate. For example, the total electronic energy increases rapidly with Z but the quantity of interest is usually the separation between low-lying electronic states, which is largely independent of Z and therefore to be classified of order R_H.

The dependence of the spin–orbit coupling on Z is responsible in atoms for the change from typical LS coupling at low Z to jj coupling at higher Z, and in molecules for the change from case (b) at low Z to case (a) at intermediate Z and case (c) at higher Z. The quantitative representation of this trend is discussed by Landau and Lifshitz (*11*). The relevant part of the spin–orbit constant is a sum over terms proportional to $Z_\alpha \langle r_{i\alpha}^{-3} \rangle$, where $r_{i\alpha}$ is the distance between unpaired electron i and nucleus α. Integrals of the type $\langle r_{i\alpha}^{-n} \rangle$ can be regarded as consisting of a contribution from the immediate vicinity of nucleus α and a contribution from the remainder of space. Since an unpaired electron is generally in an outer orbital of approximate radius a_0, independent of Z, the latter contribution is of order a_0^{-n}. Near the nucleus, the nucleus is almost unscreened and the former contribution consists of the unscreened integral ($\simeq Z_\alpha^n a_0^{-n}$) multiplied by the relative probability (Z_α^{-2}) of finding an outer electron in the vicinity of the nucleus. Thus the two contributions are of order $Z_\alpha^{n-2} a_0^{-n}$ and a_0^{-n}, respectively. For $n = 3$ the former contribution $Z_\alpha a_0^{-3}$ is dominant while for $n = 1$ the latter contribution a_0^{-1} is dominant (assuming $Z_\alpha > 1$). For $n = 2$ the two contributions are comparable, a_0^{-2}. Curl (*10*) has drawn attention to this distinction by stating that $\langle r_{i\alpha}^{-3} \rangle$ is a property of the wavefunction in the immediate neighborhood of nucleus α, $\langle r_{i\alpha}^{-2} \rangle$ is a property of the wavefunction of atom α, and $\langle r_{i\alpha}^{-1} \rangle$ is a property of the wavefunction of the whole molecule.

(iv) General

From the above considerations the first-order spin–orbit coupling function $A^{(1)}(r)$ is of order $Z^2\alpha^2 R_H$, where Z is normally the atomic number of the heavier nucleus (unless the unpaired electrons are localized on the lighter nucleus). For most functions of internuclear distance it can be assumed that the derivative with respect to $\xi = (r - r_e)/r_e$ is of the same order as the function itself. However, special considerations arise for $dA^{(1)}/d\xi$ because $A^{(1)}$ is dominated by the behavior of the electronic wavefunction in the vicinity of the nucleus, and this varies less rapidly with ξ than for typical functions. The variable part of $A^{(1)}$ is the "molecular" contribution, which is of order $Z\alpha^2 R_H$ rather than $Z^2\alpha^2 R_H$.

The second-order part $A^{(2)}$ is of order $[A^{(1)}]^2/\Delta T_e \simeq Z^4\alpha^4 R_H$. The derivative $dA^{(2)}/d\xi$ then has contributions of order $Z^3\alpha^4 R_H$ and $Z^4\alpha^4 R_H$ from differentiation of the numerator and denominator, respectively. The latter will be dominant at high Z. Also, while $A^{(2)}/A^{(1)} \sim Z^2\alpha^2$ is generally small, the derivative of $A^{(2)}$ becomes relatively more important, $A^{(2)\prime}/A^{(1)\prime} \sim Z^3\alpha^2$.

TABLE II

Orders of Magnitude[a]

Matrix Elements			
$\langle n\|H_{so}^{(e)}\|n'\rangle$	$\approx Z^2\alpha^2 R_H$	$\langle n\|H_{so}^{(n)}\|n'\rangle$	$\approx Z\alpha^2\kappa^4 R_H$
$\langle n\|H_{ss}\|n'\rangle$	$\approx \alpha^2 R_H$	$\langle n\|H_{rot}\|n'\rangle$	$\approx \kappa^4 R_H$

Parameters			
$A^{(1)}$	$Z^2\alpha^2 R_H$	$\eta^{(1)}$	?
$A^{(2)}$	$Z^4\alpha^4 R_H$	$\eta^{(2)}$	$Z^2\alpha^4 R_H$
B	$\kappa^4 R_H$	$\eta^{(3)}$	$Z^6\alpha^6 R_H$
D	$\kappa^8 R_H$	$o^{(1)}$	$\alpha^2 R_H$
$\lambda^{(1)}$	$\alpha^2 R_H$	$o^{(2)}$	$Z^4\alpha^4 R_H$
$\lambda^{(2)}$	$Z^4\alpha^4 R_H$	p	$Z^2\alpha^2\kappa^4 R_H$
$\gamma^{(1)}$	$Z\alpha^2\kappa^4 R_H$	q	$\kappa^8 R_H$
$\gamma^{(2)}$	$Z^2\alpha^2\kappa^4 R_H$		

[a]Notation: R_H = Rydberg constant.
Z = atomic number, usually of heavier atom.
α = fine-structure constant ≈ 0.007297.
κ = Born-Oppenheimer parameter ≈ 0.1.

The above considerations have been applied to matrix elements of various terms in the Hamiltonian, and the proposed orders of magnitude are presented in Table II. Since the terms also contain numerical factors that are not necessarily close to 1, it should be appreciated that the expressions do not have absolute quantitative significance but indicate general trends. For example, returning to the problem of $\gamma = \gamma^{(1)} + \gamma^{(2)}$, we see from Table II that $\gamma^{(2)}/\gamma^{(1)} \sim Z$, and therefore the dominance of $\gamma^{(2)}$ increases with increasing Z.

4. PERTURBATION CONTRIBUTIONS TO η_{nv}

The parameter η_{nv} is the effective coefficient for the vibrational level v of electronic state n of the operator in Eq. (1). As discussed previously for other operators (*6*), the dependence on v can be obtained by a vibrational perturbation treatment of terms in the effective Hamiltonian H_n for electronic state n [cf. Eq. (10) of Ref. (*6*)].

There is a first-order contribution,

$$\eta_{nv}^{(v1)} = \langle v | \eta_n(r) | v \rangle \tag{3}$$

from the operator $\eta_n(r)$ to be discussed below. There is also a second-order contribution

$$\eta_{nv}^{(v2)} = 4Re \sum_{v'}{}' \langle v | A_n(r) | v' \rangle \langle v' | \lambda_n(r) | v \rangle / (G_v - G_{v'}) \tag{4}$$

involving the operators $A_n(r)$ and $\lambda_n(r)$ given previously (*6*). From Eq. (4), the equilibrium value $\eta_{ne}^{(v2)}$ is found to be

$$\eta_{ne}^{(v2)} = -\frac{4A'_{ne}\lambda'_{ne}B_{ne}}{\omega_{ne}^2}, \tag{5}$$

where A'_{ne} and λ'_{ne} are the derivatives $(dA_n/d\xi)_{ne}$ and $(d\lambda_n/d\xi)_{ne}$, respectively. From Section 3, $\eta_{ne}^{(v2)}$ contains principal contributions of order $Z\alpha^4 R_H$ and $Z^5\alpha^6 R_H$.

The operator $\eta_n(r)$ in Eq. (3) is obtained from a purely electronic perturbation calculation. The contributions to $\eta_n(r)$ are considered below according to the different orders of perturbation theory,

$$\eta_n(r) = \eta_n^{(1)}(r) + \eta_n^{(2)}(r) + \eta_n^{(3)}(r). \tag{6}$$

(1) First Order

The fundamental Hamiltonian employed previously,

$$H = H_{\text{elec}} + \frac{1}{2\mu} P_r^2 + hcB(r)(\mathbf{N} - \mathbf{L})^2 + \frac{1}{2M} \mathbf{P}^2 + H_{\text{so}}^{(e)} + H_{\text{so}}^{(n)} + H_{\text{ss}}^{(s)} + H_{\text{ss}}^{(t)}, \tag{7}$$

contains terms up to quadratic in the spins. (See Ref. (*6*) for definitions of the terms). This Hamiltonian therefore does not provide a first-order contribution cubic in the spins, as required for $\eta_n^{(1)}(r)$. However, this Hamiltonian consists merely of the early terms of a nonrelativistic expansion, and is only an approximation to the "true" molecular Hamiltonian, if such a thing exists. Further terms will be obtained by a higher-order treatment of the radiative corrections. This would be an extension of the calculation of the spin–spin terms in Eq. (7) which come from the Breit operator, which is itself obtained by a perturbation treatment of the radiative terms (*12*, *13*). Higher-order radiative corrections may be expected to yield, among others, a term with the form of Eq. (1). The expectation value of this for the electronic state n gives the first-order contribution $\eta_n^{(1)}(r)$. The detailed form of these higher radiative corrections does not appear to have been considered in the literature, and it is difficult to estimate the order of magnitude of $\eta_n^{(1)}(r)$. Clearly, however, a quantitative treatment of small effects like $\eta_n(r)$ which can now be measured experimentally would require an extension of the basic molecular Hamiltonian to include higher terms.

(2) Second Order

In second order the Hamiltonian (7) can produce terms cubic in the spins from the cross-terms between the spin–orbit and spin–spin coupling terms. The largest

spin–orbit effects are associated with $H_{so}^{(e)}$, the part depending on the electronic velocities. This is a first-rank tensor in the spins. In order to generate a third-rank tensor overall, we must use $H_{ss}^{(t)}$, the second-rank tensor part of the spin–spin coupling. The contribution $\eta_n^{(2)}(r)$ is therefore contained in

$$2Re \sum_{n'\Lambda'\Sigma}{}' \langle n\Lambda(S)\Sigma|H_{so}^{(e)}|n'\Lambda'(S')\Sigma'\rangle\langle n'\Lambda'(S')\Sigma'|H_{ss}^{(t)}|n\Lambda(S)\Sigma\rangle \div (V_n - V_{n'}), \quad (8)$$

where the factors are all functions of r.

To isolate the third-rank tensor part of (8) we use a projection technique to eliminate the first- and second-rank tensor parts. From angular momentum theory (*14*) the right side of (8) contains terms proportional to the $3j$ symbols $\begin{pmatrix} S & k & S \\ -\Sigma & 0 & \Sigma \end{pmatrix}$ with $k = 1, 2, 3$. By multiplication by $\begin{pmatrix} S & 3 & S \\ -\Sigma & 0 & \Sigma \end{pmatrix}$ and use of the orthogonality relation (Ref. (*14*, p. 136))

$$\sum_{\Sigma} \begin{pmatrix} S & k & S \\ -\Sigma & 0 & \Sigma \end{pmatrix}\begin{pmatrix} S & 3 & S \\ -\Sigma & 0 & \Sigma \end{pmatrix} = \frac{1}{7}\delta_{k3}$$

we can isolate the $k = 3$ part. The explicit $3j$ symbol required here is

$$\begin{pmatrix} S & 3 & S \\ -\Sigma & 0 & \Sigma \end{pmatrix} = \frac{(-)^{S-\Sigma+1}20[\Sigma^3 - (1/5)(3S^2 + 3S - 1)\Sigma]}{[(2S + 4)!/(2S - 3)!]^{1/2}}. \quad (9)$$

The projected result gives

$$\eta_n^{(2)}(r) = \frac{2800}{hc\Lambda}\frac{(2S - 3)!}{(2S + 4)!}\sum_{\Sigma}\left[\Sigma^3 - \frac{1}{5}(3S^2 + 3S - 1)\Sigma\right]$$
$$\times \{2Re \sum_{n'\Lambda'\Sigma'}{}' \langle n\Lambda(S)\Sigma|H_{so}^{(e)}|n'\Lambda'(S')\Sigma'\rangle$$
$$\times \langle n'\Lambda'(S')\Sigma'|H_{ss}^{(t)}|n\Lambda(S)\Sigma\rangle/(V_n - V_{n'})\}. \quad (10)$$

The intermediate states n' in this formula can have $S' = S$, $S \pm 1$ and $\Lambda' = \Lambda$, $\Lambda \pm 1$. Thus if n is a $^4\Pi$ state the perturbing states can be $^{2,4,6}\Sigma^{\pm}$, $^{2,4,6}\Pi$ and $^{2,4,6}\Delta$, and the perturbation is summed over *all* such states. The order of magnitude of $\eta_n^{(2)}(r)$ is $Z^2\alpha^4 R_H$.

(3) Third Order

The linear terms $H_{so}^{(e)}$ can produce in third order a contribution cubic in the spins, of order $Z^6\alpha^6 R_H$. With the projection technique described above, the expression obtained for $\eta_n^{(3)}(r)$ is

$$\eta_n^{(3)}(r) = \frac{2800(2S - 3)!}{hc\Lambda(2S + 4)!}\sum_{\Sigma}\left[\Sigma^3 - \frac{1}{5}(3S^2 + 3S - 1)\Sigma\right]$$
$$\times \{\sum_{\substack{n'\Lambda'\Sigma' \\ n''\Lambda''\Sigma''}}{}' \langle n\Lambda(S)\Sigma|H_{so}^{(e)}|n'\Lambda'(S')\Sigma'\rangle\langle n'\Lambda'(S')\Sigma'|H_{so}^{(e)}|n''\Lambda''(S'')\Sigma''\rangle$$
$$\times \langle n''\Lambda''(S'')\Sigma''|H_{so}^{(e)}|n\Lambda(S)\Sigma\rangle/(V_n - V_{n'})(V_n - V_{n''})$$

$$- Re \sum_{\substack{\Lambda'\Sigma' \\ n''\Lambda''\Sigma''}}{}' \langle n\Lambda(S)\Sigma|H_{so}^{(e)}|n\Lambda'(S)\Sigma'\rangle\langle n\Lambda'(S)\Sigma'|H_{so}^{(e)}|n''\Lambda''(S'')\Sigma''\rangle$$

$$\times \langle n''\Lambda''(S'')\Sigma''|H_{so}^{(e)}|n\Lambda(S)\Sigma\rangle/(V_n - V_{n''})^2\}, \quad (11)$$

where the first sum in the braces is restricted by $n' \neq n$, $n'' \neq n$ and the second sum by $n'' \neq n$. Each matrix element must satisfy the spin–orbit selection rules

$$\Delta S = 0, \pm 1,$$

$$\Delta\Lambda = -\Delta\Sigma = 0, \pm 1. \quad (12)$$

Obviously a large number of different sets of intermediate states are allowed by these rules.

5. DISCUSSION OF THE $a^4\Pi_u$ STATE OF O_2^+

The recent measurements of the $b^4\Sigma_g^- - a^4\Pi_u$ system of O_2^+ by the laser-ion-beam technique (*1–3*) have provided detailed information on the rotational structure of the $a^4\Pi_u$ state, which is accurately fitted by the present parameters. These parameters are of interest both on their own account and in relation to the important isoelectronic molecule NO, for which the quartet states are less well characterized.

In general, each effective parameter consists of a first-order part determined purely by the $a^4\Pi_u$ wavefunction, and second- and higher-order parts produced by interactions with other electronic states. For some parameters (e.g., p, q) the first-order part vanishes. A qualitative discussion of the effective parameters therefore requires some information on the perturbing electronic states. Unfortunately the experimental knowledge of the other states is limited at present (*15*). Although ab initio potentials of many states have been computed (*16*), the required matrix elements of the interactions are almost entirely unknown. A simplifying feature for O_2^+ compared to NO is the center of symmetry, which means that $a^4\Pi_u$ is only perturbed by other u states.

The various parameters differ in the degree of complexity of the perturbations, and it is appropriate to consider them in order of increasing complexity:

(*i*) A. The ordinary spin–orbit coupling constant A is dominated by the first-order part $A^{(1)}$. The single configuration . . . $(1\pi_u)^3(1\pi_g)^2$ probably provides a good representation of this state, and gives

$$A^{(1)}(a^4\Pi_u) = -(1/3)a(1\pi_u),$$

where $a(1\pi_u)$ is the contribution for the single orbital $1\pi_u$. The observed value, $A = -47.68$ cm^{-1}, is reasonably consistent with the ab initio estimate $a(1\pi_u) = 126$ cm^{-1} (*17*).

The part $A^{(2)}$ results from spin–orbit interactions with other states. From the expressions in Ref. (*6*) it can be shown that

$$A_n^{(2)} = \frac{1}{4\Lambda S(S+1)(2S+1)} \sum_{n'\Lambda'}{}' \frac{|\langle n\Lambda(S)\|H_{so}^{(e)}\|n'\Lambda'(S')\rangle|^2(\Lambda' - \Lambda)}{(V_n - V_{n'})}$$

$$\times [S(S+1) - S'(S'+1) + 2], \quad (13)$$

where the partially reduced matrix elements are defined by

$$\langle n\Lambda(S)\Sigma|H_{so}^{(e)}|n'\Lambda'(S')\Sigma'\rangle = (-)^{S-\Sigma}\begin{pmatrix} S & 1 & S' \\ -\Sigma & \Lambda' - \Lambda & \Sigma' \end{pmatrix}\langle n\Lambda(S)\|H_{so}^{(e)}\|n'\Lambda'(S')\rangle. \quad (14)$$

Note that the partially reduced matrix elements still depend on the component quantum numbers Λ, Λ'. From Eq. (13) it is seen that, because of the factor $(\Lambda' - \Lambda)$, perturbing states with the same value of Λ do not contribute to $A_n^{(2)}$. This is important for $a^4\Pi_u$ of O_2^+, since the nearest possible perturber is $A^2\Pi_u$. The above selection rule means that $A^2\Pi_u$ does not contribute to $A^{(2)}(a^4\Pi_u)$. From a rough estimate of the effects of the $^{2,4,6}\Sigma_u^\pm$ and $^{2,4,6}\Delta_u$ states, the probable order of magnitude of $A^{(2)}$ is 0.1 cm^{-1}, negligible compared to $A^{(1)}$, although large compared to the experimental uncertainty.

The observed value of A_D could provide the derivative $dA/d\xi$, but is at present not significantly determined.

(ii) q. The Λ-doubling constant q is purely second order, due to $^4\Sigma_u^\pm$ states. On the assumption that all such states are above the $a^4\Pi_u$ state, the sign of q indicates that the $^4\Sigma_u^+$ states predominate over the $^4\Sigma_u^-$ states. The ab initio potential curves (*16*) show that at this bond length the lowest $^4\Sigma_u$ state is a repulsive $^4\Sigma_u^+$ state. Several other $^4\Sigma_u$ states, both $^4\Sigma_u^+$ and $^4\Sigma_u^-$, have slightly higher energies. On the simplest assumption, that the repulsive $^4\Sigma_u^+$ state is responsible for q, the orbital matrix element obtained is

$$|\langle a^4\Pi_u|L_+|^4\Sigma_u^+\rangle| \simeq 0.66.$$

The order of magnitude seems reasonable. The most one can conclude, however, is that the q value does not appear to be anomalous.

(iii) p and γ. The Λ-doubling constant p is also entirely due to the second-order effects of $^4\Sigma_u^\pm$ states. The spin–rotation constant γ has first- and second-order parts. The first-order part $\gamma^{(1)}$ is an "atomic" property in Curl's terminology (*10*). An approximate estimate by the method of Ref. (*18*) suggests that $\gamma^{(1)}$ is much smaller than the observed γ, which can therefore be regarded as $\gamma^{(2)}$.

There are three contributions to $\gamma^{(2)}$,

$$\gamma^{(2)} = \gamma^{(2)}(^4\Sigma_u^+) + \gamma^{(2)}(^4\Sigma_u^-) + \gamma^{(2)}(^4\Delta_u) \quad (15)$$

while p is given by

$$p = -2\gamma^{(2)}(^4\Sigma_u^+) + 2\gamma^{(2)}(^4\Sigma_u^-). \quad (16)$$

Here the states in parentheses are the perturbing states, and each contribution is summed over all states of the indicated type. The observed relationship $\gamma/p \simeq -1.38$ is not consistent with a unique type being dominant. Examination of the ab initio potential curves (*16*) suggests that $^4\Sigma_u^+$ and $^4\Delta_u$ may dominate $^4\Sigma_u^-$. Neglecting the effects of the latter completely, we obtain

$$\gamma^{(2)}(^4\Sigma_u^+) = -1.95 \times 10^{-3}\ cm^{-1}, \quad (17)$$

$$\gamma^{(2)}(^4\Delta_u) = -3.42 \times 10^{-3}\ cm^{-1}. \quad (18)$$

On the unique perturber approximation for $\gamma^{(2)}(^4\Sigma_u^+)$, using the previous orbital matrix element, the off-diagonal spin–orbit matrix element obtained is

$$\left|\langle {}^4\Sigma^+_{u1/2}\left|H_{so}^{(e)}\right|a^4\Pi_{u1/2}\rangle\right| \simeq 57 \text{ cm}^{-1}. \tag{19}$$

This is of the same order as $A(a^4\Pi_u)$. It is difficult to proceed further with $\gamma^{(2)}(^4\Delta_u)$, since neither the orbital nor the spin–orbit matrix elements are known. However, the fact that the $^4\Delta_u$ contribution is of similar magnitude to the $^4\Sigma_u^+$ contribution is consistent with the fact that the lowest $^4\Delta_u$ and $^4\Sigma_u^+$ states have similar energies.

(*iv*) o. The Λ-doubling constant o has first- and second-order parts. The latter is due to $^{2,4,6}\Sigma_u^+$ states. Of these, the lowest at this bond length are $^2\Sigma_u^+$ and $^6\Sigma_u^+$. It is likely that $o^{(1)}$ and $o^{(2)}$ are comparable in magnitude, and it is therefore difficult to make any useful comments. However, an ab initio calculation of $o^{(1)}$ would obviously be of great interest.

(*v*) λ. The spin–spin constant λ is even more complicated, since the second-order contributions are due to $^{2,4,6}\Sigma_u^\pm$, $^{2,4,6}\Pi_u$, and $^{2,4,6}\Delta_u$ states. Of these, easily the closest is the $A^2\Pi_u$ state. The ab initio matrix element

$$\left|\langle A^2\Pi_{u3/2}\left|H_{so}\right|a^4\Pi_{u3/2}\rangle\right| = 72 \text{ cm}^{-1} \tag{20}$$

has been estimated by Roche (*17*). From this, the contribution of the A state to $\lambda^{(2)}$ is

$$\frac{\left|\langle A\left|H_{so}\right|a\rangle\right|^2}{4(V_A - V_a)} = +0.17 \text{ cm}^{-1}. \tag{21}$$

The second-order effects of other states are probably much smaller. By subtraction, the value of $\lambda^{(1)}$ is

$$\lambda^{(1)} \simeq 0.78 \text{ cm}^{-1}. \tag{22}$$

For comparison, the ab initio value of $\lambda^{(1)}$ for the $X^3\Sigma_g^-$ state of O_2 is 0.7079 cm^{-1} (*19*). The value for $\lambda^{(1)}$ for O_2^+ can be estimated from semiempirical formulas given by Field and Lefebvre-Brion (*20*). For a homonuclear molecule in a $^4\Pi$ state arising from a $\pi^3\pi'^2$ configuration, $\lambda^{(1)} = 2\eta_A$, where η_A is an atomic spin–spin parameter (for atom A), not to be confused with the spin–orbit parameter η_{nv} introduced in this paper. Using the values for η_O of 0.250 cm^{-1} and for η_{O^+} of 0.372 cm^{-1} calculated by Yamanouchi and Horie (*21*), the value for $\lambda^{(1)}$ is 0.62 cm^{-1} which is slightly smaller than the value given in Eq. (22). Nevertheless, it suggests that our interpretation is reasonable.

(*vi*) η. From Eq. (4), the second-order vibrational contribution $\eta^{(v2)}$ is estimated to be of order 10^{-4} cm^{-1}, and therefore negligible compared to the observed η. If the unknown $\eta^{(1)}$ is also ignored, the new constant η consists of second- and third-order parts due to perturbations by $^{2,4,6}\Sigma_u^\pm$, $^{2,4,6}\Pi_u$, and $^{2,4,6}\Delta_u$ states. It is probable that $A^2\Pi_u$ is the dominant state. The unique perturber approximation gives

$$\eta^{(3)} \simeq \left\{\frac{\langle A\left|H_{so}^{(e)}\right|a\rangle}{(V_A - V_a)}\right\}^2 (A_a - A_A) \simeq -3.8 \times 10^{-3} \text{ cm}^{-1}. \tag{23}$$

Here A_a and A_A are the spin–orbit constants of the a and A states. Since this is an order of magnitude smaller than the observed η, it seems likely that η is dominated

by $\eta^{(2)}$. This is consistent with the relative order of magnitudes of $\eta^{(2)}$ and $\eta^{(3)}$, Table II. For the unique perturber approximation, we have

$$\eta^{(2)} = -\frac{2}{(V_A - V_a)} \langle a | H_{so}^{(e)} | A \rangle \langle A | H_{ss}^{(t)} | a \rangle. \tag{24}$$

Setting this equal to the observed η implies

$$|\langle A^2\Pi_{u3/2} | H_{ss}^{(t)} | a^4\Pi_{u3/2} \rangle| \simeq 2.8 \text{ cm}^{-1}. \tag{25}$$

This off-diagonal spin–spin matrix element is somewhat larger than the diagonal matrix element

$$\langle a^4\Pi_{u3/2} | H_{ss}^{(t)} | a^4\Pi_{u3/2} \rangle = -2\lambda^{(1)} \simeq -1.56 \text{ cm}^{-1}, \tag{26}$$

but may not be unreasonable. The values for the matrix elements in Eqs. (25) and (26) have been estimated ab initio by Lefebvre-Brion and Roche (*17*) as 1.11 cm^{-1} and -1.16 cm^{-1}, respectively. The calculation was performed at the single configuration SCF level with neglect of two-center spin–spin integrals.

6. SUMMARY

The above discussion of the properties of the $a^4\Pi_u$ state of O_2^+ is largely speculative, and serves mainly to indicate the lines along which progress may be made. Clearly, ab initio computations of the off-diagonal matrix elements of the spin–orbit and spin–spin operators with neighboring electronic states would be valuable. Also, an extension of the fundamental molecular Hamiltonian to higher-order terms such as $\eta^{(1)}$ is desirable.

The inclusion of the η term has led to an improved fit of the data, the standard deviation being comparable with the experimental error. This in turn has resulted in improved precision of the other parameters. The values of the parameters appear consistent with the present, rather limited, knowledge of the various other states and their interactions with the $a^4\Pi_u$ state.

In fitting the data for a state such as the $a^4\Pi_u$ state of O_2^+, with a rather complex set of possible perturbing states, it is obviously impractical to employ the full Hamiltonian matrix between these states, particularly considering the shortage of data for the other states. The present results demonstrate how the effective Hamiltonian method satisfactorily overcomes this difficulty. The practical fitting of the spectrum is achieved in terms of a set of effective parameters, without assumptions regarding the perturbing states. These parameters can then be interpreted according to existing theories of the electronic structure of the molecule.

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