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Fine-structure spectrum of $O_2$–rare gas van der Waals molecules

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A simple analytically solvable model is presented for the rotation-vibration-spin states in $O_2$–rare gas atom complexes, which predicts the form of the fine-structure spectrum. It is shown that this spectrum looks basically different from the pure $O_2$ spectrum, due to the partial quenching of the $O_2$ angular momentum by the anisotropic $O_2$–rare gas interaction potential. The model contains two properties of the $O_2$–X complex as parameters: the ground state average of the anisotropic potential $\langle V(R)\rangle_0$ and the end-over-end rotational constant $\langle R^{-2}\rangle_0$, where $R$ is the $O_2$–X distance. Adjusting these parameters yields quantitative agreement with the spectra that have recently been obtained from two different empirical potentials via accurate dynamical calculations. The model can be used for interpreting the experimental fine-structure spectrum of $O_2$Ar which is currently being measured.

INTRODUCTION

In a recent paper, Tennyson and Mettes report accurate dynamical calculations of the rotation-vibration-electron spin states in $O_2$Ar. From these calculations, they obtain the fine-structure transition frequencies and intensities. Two features are especially noteworthy.

First, their spectrum of $O_2$Ar looks very different from the pure $O_2$ spectrum. This is not only of practical interest in view of the measurements (where to find lines in the microwave or radiofrequency beam resonance experiments which are now carried out?), but it is also interesting since the deviation from the pure $O_2$ spectrum is expected to be a measure of the anisotropy in the $O_2$–Ar interaction potential (if $O_2$Ar were bound by a purely isotropic interaction, its fine-structure spectrum would be identical to the $O_2$ spectrum). On the other hand, they found that two rather different empirical $O_2$–Ar potentials yield strikingly similar fine-structure spectra (changing the anisotropy in one of the potentials by a factor of 2 did affect the frequencies, however).

In view of these numerical results and the interpretation of the measurements which are in progress, it is important to understand why the spectrum of $O_2$Ar differs from $O_2$, how the differences depend explicitly on the anisotropy of the potential, and which transitions yield the most accurate information about the potential and other properties of the complex. In the present paper, it is shown how these questions can be answered by adopting a simple, but realistic, model for the rotation-vibration-electron spin states of $O_2$Ar (and other $O_2$X complexes, $X =$ rare gas atom) which can be solved analytically.

ROTATION-VIBRATION-SPIN STATES OF $O_2$X COMPLEXES

The relevant Hamiltonian can be written as

$$\hat{H} = \hat{H}_{\text{rot-vib}} + \hat{H}_{\text{fine}},$$

where $\hat{H}_{\text{rot-vib}}$ is the usual rotation-vibration Hamiltonian for an atom–rigid diatom complex

$$\hat{H}_{\text{rot-vib}} = -\frac{\hbar^2}{2\mu R} \frac{\partial^2}{\partial R^2} R + B(R) \hat{L}_z + b \hat{N}_z + V(R, \theta).$$

The vector $R = (r, \beta, \alpha)$ connects the $O_2$ mass center with the rare gas atom $X$, the vector $r = (r_0, \delta, \gamma)$ describes the (fixed) $O_2$ bond length $r_0$ and orientation and the angular momenta $\hat{L}$ and $\hat{N}$ are associated with the polar angles $(\beta, \alpha)$ and $(\delta, \gamma)$, respectively. All these angles are defined relative to an arbitrary space-fixed (SF) coordinate frame.

The constant $\mu$ denotes the reduced mass:

$$\mu = m_{X} m_{O_2}/(m_{X} + m_{O_2}),$$

$B(R)$ the end-over-end rotational constant of $O_2X$: $B(R) = (2\mu R^2)^{-1}$, and $b$ the $O_2$ rotational constant: $b = (m_{O_2} \delta^2)^{-1} = 43.1$ GHz. The potential $V(R, \theta)$ is conveniently expressed in Legendre polynomials in $(\cos \theta)$, where $\theta$ is the angle between $r$ and $R$:

$$V(R, \theta) = \sum_{\chi} V_{\chi}(R) P_{\chi}(\cos \theta).$$

For a homonuclear diatomic such as $O_2$ only terms with even $\chi$ occur. In addition to the isotropic potential $V_0(R)$, both the empirical $O_2$Ar potentials yield the dynamical calculations include only the anisotropic $V_\alpha(R)$ term.

The $O_2$ molecule is considered to stay in the electronic ground state $^2\Sigma^+_2$. Its electronic orbital momentum is zero and the dominant effective spin coupling term is given by $\lambda_{0} S_z^2$.

$$\hat{H}_{\text{fine}} = \frac{3}{2} \lambda_{0} (S_z^2 - \hat{S}^2)$$

with $\lambda_{0} = 59.5$ GHz, $\hat{S}$ denoting the electron spin momentum and $S_z$ its projection on the $O_2$ axis $r$. The $\mu_{0} \hat{N} \cdot \hat{S}$ term included in Ref. 1, and other terms, have been omitted here, since they are of minor importance.

Tennyson and Mettes have calculated the rotation-vibration-electron spin states of $O_2$Ar by diagonalizing the matrix of the Hamiltonian (1) over the following basis:

$$X_{\chi}(R) \left| (NS)JL JM_F \right>,$$

where $X_{\chi}(R)$ denotes numerical radial basis functions. The angular momentum functions are products of spherical harmonics $Y_{k_{m}}(\delta, \gamma)$ and electron spin functions.
\(b_{F,N}^{(2)}\) coupled via Clebsch-Gordan coefficients to get basis functions \(J_{L,M_J}\) which are then coupled to spherical harmonics \(Y_{L,M_L}(\beta, \alpha)\), in order to obtain eigenfunctions of the total angular momentum operators \(\hat{F}_{x}\) and \(\hat{F}_{z}\), which represent the exact angular quantum numbers of the system. Only basis functions with odd \(M_N\) have to be included, since the O\(_2\) nuclei have spin zero and the electronic ground state wave function is odd with respect to inversion (remember that the term symbol \(3\Sigma^{e}_{+}\) refers to a molecular frame lying along the O\(_2\) axis).

The electron spin basis is restricted to the ground state spin multiplet \(S = 1\). Convergence of the eigenvalues to within 0.3 GHz was reached for \(\theta \leq 4\) and \(\eta \leq 7\).

So far, all the terms in the Hamiltonian (2) and (4), as well as the basis (5), have been expressed relative to a space-fixed frame (SF). Actually, it is more convenient to use a body-fixed frame (BF) with the \(z\) axis lying along the O\(_2\)-X axis \(R\). This can be achieved by a rotation over two Euler angles \((\alpha, \beta)\) which are the polar angles of \(R\) in the SF frame. The Hamiltonian, after this rotation, can be written as

\[
\hat{H}_{\text{rot-vib}} = -\frac{b}{2\mu R} \frac{\hat{F}_{x}^{2}}{\hat{r}^{2}} R + B(R) [\hat{F} - \hat{J}]^{2} + b \hat{N}_{e}^{2} + V(R, \theta, \eta) \tag{6}
\]

and

\[
\hat{H}_{\text{fine}} = \frac{3}{2} \lambda_{0} [3\Sigma_{+}^{e} - \hat{S}^{2}]^{2}, \tag{7}
\]

where the operators \(\hat{N}, \hat{S}, \hat{J}, \) and \(\hat{F}\) are now expressed in body-fixed components \((\hat{F}^B = 3\Sigma^B_{+} = \hat{N}^B_{e} + \hat{S}^{2} \hat{B} + \hat{F}^B_{2}, \hat{F}^B_{2}\) since \(\hat{F}^B_{2} = 0\) and the second term in \(\hat{H}_{\text{rot-vib}}\) is most conveniently expanded as

\[
b(R) [\hat{F} - \hat{J}]^{2} = b(R) [\hat{F}_{x}^{2} + \hat{N}_{e}^{2} + \hat{S}^{2} - 2(\hat{N}_{x} \cdot \hat{S}_{z} + 2\hat{N}_{x} \hat{S}_{z}) + 2\hat{N}_{y} \hat{S}_{z}] = (\hat{N}_{x} \hat{F}_{x} + \hat{N}_{y} \hat{F}_{y} + \hat{S}_{x} \hat{F}_{z} + \hat{S}_{y} \hat{F}_{z}) + (\hat{N}_{x} \hat{S}_{x} + \hat{N}_{y} \hat{S}_{y}) \tag{8}
\]

This transformation of the Hamiltonian is an extension of the spin-free case.\(^{7-10}\) The rotation over two Euler angles \((\alpha, \beta)\) rather than three leads to an unusual form for the components of \(\hat{F}\) (cf. Refs. 8-10); also, they do not commute with \(\hat{N}\) and \(\hat{S}\). The step-up/down operators are defined as \(\hat{N}_{x} = \hat{N}_{x} \pm i\hat{N}_{y}, \hat{S}_{x} = \hat{S}_{x} \pm i\hat{S}_{y},\) and \(\hat{F}_{x} = \hat{F}_{x} \pm i\hat{F}_{y}\).

The basis (5) transforms into:

\[
\chi_{\alpha}(R) \sum_{\kappa} |(NS)J_{L}JK\rangle D_{\mu_{\kappa}}^{(F)}(\alpha, \beta, 0), \tag{9}
\]

where the angular functions in the ket are now expressed in BF angles and the functions \(D_{\mu_{\kappa}}^{(F)}\) are rotation matrix elements.\(^{11}\) Remembering that the polar angles of \(R\) are zero in the body-fixed frame and substituting the relation\(^{11}\)

\[
Y_{L,M_{L}}(0,0) = \left(\frac{2L+1}{4\pi}\right)^{1/2} \delta_{M_{L},0}, \tag{10}
\]

so that \(M_{J} = K\), one can replace Eq. (9) by an equivalent basis

\[
\chi_{\alpha}(R) |(NS)JK\rangle D_{m_{\kappa}}^{(F)}(\alpha, \beta, 0), \tag{10}
\]

The latter basis corresponds to the intermediate quantum numbers \(N, S, J, \) and \(K\), in addition to the exact quantum numbers \(F\) and \(m_{\kappa}\), while the basis (5) or (9) corresponds to \(N, S, J, \) and \(L\). The basis of Eqs. (5) and (9) would be most appropriate when the anisotropy in the potential is very weak, as it is in \(H_{2}X\) complexes.\(^{7}\)

The basis (10) is still not the most efficient one for our problem, however, since the anisotropic \((\lambda \neq 0)\) terms in the potential (3) will split the energy levels of different \(M_{N}\) states. Basis functions with \(N = 1\), for instance, will be split by the \(\lambda = 2\) term in the potential into levels \((V_{3}(R)) - \frac{1}{2} (V_{3}(R))\) for \(M_{N} = \pm 1\) and levels \((V_{3}(R)) + \frac{1}{2} (V_{3}(R))\) for \(M_{N} = 0\). So, if \((V_{3}(R))\) is positive, which corresponds to a \(T\)-shaped \(O_{2}X\) complex, and sufficiently large, then the functions with \(M_{N} = 0\) will be raised in energy to such an extent that they will hardly mix into the lower states of the complex (see next section). This destroys \(J\) as a good intermediate quantum number. A basis which reflects this splitting is the uncoupled product basis

\[
\chi_{\alpha}(R) Y_{N,M_{N}}(\theta, \phi) \Theta_{s,m_{S}} D_{m_{\kappa}}^{(F)}(\alpha, \beta, 0), \tag{11}
\]

where \((\theta, \phi)\) are the polar angles of \(r\) in the BF system and also the components \((m_{S})\) of the spin functions \(\Theta_{s,m_{S}}\) are expressed relative to this system. The elements of this basis are eigenfunctions of the operators \(\hat{N}_{e}^{2}, \hat{N}_{e}, \hat{S}_{e}^{2}, \hat{S}_{e}, \hat{F}_{e}^{2}, \hat{F}_{e}, \) and \(\hat{F}_{e}^{2}\) with eigenvalues \(N(N+1), M_{S}, s(s+1), M_{S}, K, F(F+1), \) and \(M_{F}\), respectively, \(^{11}\) and \(K = M_{N} + M_{S}\).

Finally, it is useful to consider the behavior of the bases under inversion. The SF basis (5), including the electronic wave function, has parity \((\lambda + s + l + 1)\). The BF basis (11) for \((M_{N}, M_{S})(0,0)\) has to be adapted to inversion:

\[
\frac{1}{\sqrt{2}} \chi_{\alpha}(R) Y_{N,M_{N}}(\theta, \phi) \Theta_{s,m_{S}} D_{m_{\kappa}}^{(F)}(\alpha, \beta, 0) \tag{12}
\]

Then, again including the odd parity electronic \(3\Sigma^{e}_{+}\) wave function, the total parity becomes \((\alpha + \mu + 1)\).

**THE MODEL**

**First order model**

Starting from the product basis (11) in a BF frame, one can make a number of simplifying assumptions regarding the lower rotation-vibration-spin states in \(O_{2}X\) complexes. It has been observed already that the \(O_{2}\) molecule can be considered to remain in its electronic ground state, which corresponds to a triplet spin function \(S = 1, M_{S} = -1, 0, 1\). Actually, the admixture of electronically excited states via spin-orbit coupling is already taken into account\(^{12,16}\) in the effective spin Hamiltonian (7). Basis functions with \(N = 1\) are lowest in energy, while basis functions with the next higher \(O_{2}\) rotational quantum number, \(N = 3\), are raised by the term \(b \hat{S}^{2}\) in the Hamiltonian (6) to an energy that is 100-431 GHz higher. The rotation barrier \(\Delta\) in \(O_{2}Ar\) from the \(T\)-shaped equilibrium structure to the linear structure is about 30 cm\(^{-1}\),\(^{12}\) which corresponds to an anisotropic potential \(V_{3}(R) = \frac{3}{2} \Delta \simeq 20 \text{ cm}^{-1} \simeq 600 \text{ GHz}\) in the range of the van der Waals minimum \(R \simeq R_{e}\). It is mentioned already in the previous section that this anisotropy raises the energy of the \(N = 1, M_{N} = 0\) states.
relative to the $N=1$, $M_X = \pm 1$ states by $\frac{2}{3} V_d(R) \approx 360$ GHz. 
Finally, one has to consider the radial (stretching) motion of the O$_2$–X complex. A reasonable estimate for the fundamental vibrational excitation energy in O$_2$Ar is $30 \text{ cm}^{-1} \approx 900$ GHz (cf. the Ar$_2$ value of 28 cm$^{-1}$).\textsuperscript{13} 

Given all these energy differences, one might assert that the lower rotation-vibration-spin states of O$_2$Ar (and other O$_2$X complexes) within, say, 200 GHz from the ground state are mainly composed of basis functions 

$$\phi_0(R) Y_{N,M}(\theta, \phi) \Theta_{S,M,S} D^{(F)}_{\alpha, \beta, 0}(R)$$

with:

$$N = 1, \quad M_X = \pm 1, \quad S = 1, \quad \text{and} \quad M_S = 0, \pm 1,$$

where $\phi_0(R)$ is the stretch ground state wave function ($\nu_a = 0$), which could be obtained, numerically or as a linear combination of functions $\chi_k(R)$ (cf., the basis (11)), from a radial (one-dimensional) equation with the effective potential $V_d(R) - \frac{2}{3} V_d(R)$. This effective potential corresponds exactly with the complete anisotropic potential\textsuperscript{14} if one can indeed restrict the ground state basis to $N = 1$, $M_X = \pm 1$.

The first order model proposed consists of diagonalizing the full rotation-vibration-spin Hamiltonian [Eqs. (6) and (7)], in a zero order BF basis (13) which is degenerate with respect to the "unperturbed" Hamiltonian 

$$\tilde{H}_0 = -\frac{\mu}{2R} \frac{\partial^2}{\partial R^2} R + b \tilde{N}^2 + \sum_\lambda \lambda_\nu_\lambda \langle V_\lambda(R) \rangle P_\lambda(\cos \theta)$$

with eigenvalue 

$$E_0 = \left\langle \left( - \frac{\mu}{2R} \frac{\partial^2}{\partial R^2} R \right) \right\rangle_0 + 2b + \langle V_d(R) \rangle_0 - \frac{1}{2} \langle V_d(R) \rangle_0 = \epsilon_0 + 2b,$$

where $\langle \_ \rangle_0$ denotes the radial ground state expectation value over $\phi_0(R)$.

The perturbation matrix elements are, using Eq. (8), with $B = \langle B(R) \rangle_0 = \langle R^2 \rangle_0/2\mu$:

$$\langle N\prime | M\prime | N \rangle = -(-1)^M [2S(M+1)(2S+1)]^{1/2} \begin{pmatrix} N^\prime & 2 & N \cr 0 & 2 & 0 \cr \end{pmatrix} \begin{pmatrix} S & 2 & S \cr 0 & M_S & 0 \cr \end{pmatrix} \begin{pmatrix} M_S & 0 & \pm 2 \cr \end{pmatrix} \begin{pmatrix} M_S \pm 1 & 0 & M_S \cr \end{pmatrix}$$

The latter matrix elements can be derived by expanding the BF spin Hamiltonian 

$$3J_S^2 = \sum_\lambda (-1)^\lambda C_{\lambda, \lambda}(\theta, \phi) U_{\lambda, \lambda}(\tilde{S})$$

in terms of second rank tensors\textsuperscript{5} and using the Wigner–Eckart theorem.\textsuperscript{11} The reduced matrix elements are

$$\langle N\prime || C_\lambda || N \rangle = (-1)^{M} [(2N\prime + 1)(2N+1)]^{1/2} \begin{pmatrix} N^\prime & 2 & N \cr 0 & 0 & 0 \cr \end{pmatrix}$$

and

$$\langle S || U_{\lambda} || S \rangle = [S(S+1)(2S+1)(2S+3)]^{1/2}.$$

The larger round brackets denote 3-$j$ symbols.\textsuperscript{11} 

Thus, the (first order) secular matrix for the six-dimensional zeroth order space (13) can be calculated. All the terms are diagonal in $K(K' = K)$ except for the "Coriolis" terms [Eq. (16b)]. In the first instance, I shall neglect these terms, making $K$ a good quantum number and the secular matrix diagonal, except for the

\begin{table}[h]
\centering
\caption{Results of the first order model.}
\begin{tabular}{|c|c|c|c|c|}
\hline
$i$ & \text{Eigenvectors} $|N, M_N, S, M_S, K, F \rangle$ & $|K|$ & $(-1)^F$ & \text{Total parity} \\
\hline
& \text{(multiplicity 2$^F$ + 1)} & & & \\
1 & $\frac{1}{\sqrt{2}} \left( |1,1; 1, 0, F \rangle + |1, 1; 1, 0, F \rangle \right)$ & 0 & + & $-(-1)^F$ & \text{BF}(F + 1) \\
2 & $\frac{1}{\sqrt{2}} \left( |1,1; 1, 2, F \rangle + |1, 1, -1, 2, F \rangle \right)$ & 2 & $\pm (-1)^F$ & $\frac{1}{2} \lambda_0 - 4B + BF(F + 1)$ \\
3 & $\frac{1}{\sqrt{2}} \left( |1,1; 1, 0; F \rangle + |1, 1, 0; -1, F \rangle \right)$ & 1 & $\pm (-1)^F$ & $\frac{1}{2} \lambda_0 + BF(F + 1)$ \\
4 & $\frac{1}{\sqrt{2}} \left( |1,1; 1, -1, 0, F \rangle - |1, 1, 1, 0, F \rangle \right)$ & 0 & $- (-1)^F$ & $\frac{1}{2} \lambda_0 + BF(F + 1)$ \\
\hline
\end{tabular}
\end{table}

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The secular matrix becomes completely diagonal. This model predicts the complete structure of the low energy region consists of four rotational ladders: \( \epsilon_k = B(F+1) \), \( i = 1, 2, 3, 4 \) with \( B = (B(R))_0 \) being the \( O_2X \) end-over-end rotational constant. Each ladder \( (i) \) corresponds with a definite \( (|K|, |p|) \) quantum number and the ladders start at different rungs, since the quantum numbers \( F \) labeling the "rotational" levels, must satisfy the relation \( F \geq |K| \). The lowest \( (i=1) \) and the highest \( (i=4) \) ladder, both with \( K=0 \), have levels of definite parity, alternating with \( F \), while the rungs of the middle two ladders \( (i=2, 3) \), \( |K|=2 \) and \( |K|=1 \), are doublets of both \( + \) and \( - \) parity.

Actually, these doublets will be split by the off-diagonal Coriolis terms [Eq. (16b)] which I have neglected so far. For the \( |K|=2 \) ladder this splitting will be very small as there is only direct coupling with the \( |K|=1 \) states, which yields equal shifts of the \( + \) and \( - \) levels. The \( |K|=1 \) states mix with \( K=0 \) states (of the same \( F \) and parity) and since the \( + \) and \( - \) states of the latter (for a given \( F \)) belong to the two different \( K=0 \) ladders, one obtains a splitting of order \( B^2(F+1)S(S+1)|[(\epsilon_3 - \epsilon_1)^2 - (\epsilon_2 - \epsilon_4)^2]| \) (the sign of this splitting alternates with \( F \)).

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The fine-structure transition frequencies can be obtained from the differences between these eigenvalues and the (dipole) selection rules:

\[ \Delta \nu = 0 \text{ or } \pm 1, \pm \pm \pm \text{ for magnetic dipoles} \pm \pm \pm \text{ for electric dipoles}. \]

Looking at the results of Tennyson and Mettes, one can observe that, indeed, accurate numerical calculations for O₂Ar yield a spectrum of this shape for both empirical potentials. This is clearly shown in Fig. 1. Table I of Ref. 1 contains the frequencies of transitions between the different ladders as well as transitions within the same ladders. From the splittings within the ladders one can deduce that \( B = (\beta(R))_0 \) equals 1.97 GHz for the PV potential and 2.04 GHz for the MG potential, which corresponds with an average O₂–Ar distance of \( \langle R^2 \rangle^{1/2} \approx 3.78 \) and 3.71 Å, respectively. The splittings between the ladders are found to be: \( \epsilon_1 = 39.6 \text{ GHz} \), \( \epsilon_2 = 99.6 \text{ GHz} \), and \( \epsilon_4 = 111.8 \text{ GHz} \) for the PV potential and \( \epsilon_3 = 39.4 \text{ GHz} \), \( \epsilon_3 = 101.3 \text{ GHz} \), and \( \epsilon_6 = 112.3 \text{ GHz} \) for the MG potential, whereas the first order model predicts \( \epsilon_5 = 39.7 \text{ GHz} \), \( \epsilon_5 = 71.4 \text{ GHz} \), and \( \epsilon_6 = 95.2 \text{ GHz} \), independently of the potential [provided that \( (V_z(R))_0 \) is sufficiently large to make Eq. (13) a good zeroth order basis]. Although the agreement is not unsatisfactory, considering the crudeness of the model, it can still be improved significantly via simple second order corrections.

\[
\langle N' M' S' J' M' S J | V_z(R) P_J(\cos \theta) | N M S J M S J \rangle = \langle N' M' S | (V_z(R))_0 | N M S J \rangle \delta_{M', M} \delta_{S', S} (-1)^{N' - N} \left( \begin{array}{ccc} N' & 2 & N \cr -M' & 0 & M \end{array} \right) \langle C_2 \parallel N \rangle \tag{20}
\]

and

\[
\langle N' M' S' J' M' S J | \hat{H}_{\text{fine}} | N M S J M S J \rangle = (-1)^{N' - S - M - S'} \delta_{M', M} \delta_{S', S} \left( \begin{array}{ccc} N' & 2 & N \\ -M' & M' & M \\ -M & M & M \end{array} \right) \langle N' \parallel C_2 \parallel N \rangle \langle S \parallel U_2 \parallel S \rangle \tag{21}
\]

with the reduced matrix elements given by Eq. (19).

The same correction procedure can be used for pure O₂. The first order model (in this case Hund’s coupling case b⁶) corresponds to taking a basis composed of spherical harmonics \( Y_{NM} \) with \( N = 1 \) and spin functions \( \Theta_{S,M} \) with \( S = 1 \), coupled to \( |M_J \rangle \) with \( J = 0, 1, 2 \), and calculating the expectation values of \( \hat{H}_{\text{fine}} \) [Eq. (7)]. The second order energy corrects for the admixture (also via \( \hat{H}_{\text{fine}} \)) of \( N = 3 \) functions, again coupled with \( S = 1 \). This affects only the \( J = 2 \) level; the correction is usually done by solving a two-dimensional secular problem. From the results given in Table III, it is evident that second order perturbation theory gives quite accurate results too.

For O₂X, the results are shown in Table IV. Substituting reasonable values for the anisotropy parameter \( V_z = (V_z(R))_0 \) in O₂Ar into the expressions of Table II yields quantitative agreement between the second order model splittings and the accurate numerical spectra calculated from the empirical potentials.

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**Second order model**

In order to obtain not just qualitative, but also quantitative, agreement with the accurate calculations by Tennyson and Mettes for the splittings between the four ladders, the first order model should be extended. Moreover, this will tell us how sensitive these splittings are to the anisotropy of the potential.

The zeroth order eigenstates and the first order eigenvalues (Table I) can be improved by the admixture of higher unperturbed states. The dominant excited states are probably the states with \( N = 1, M = 0 \), which lie above the ground state by \( \frac{1}{3} (V_z(R))_0 \approx 360 \text{ GHz} \) (see preceding section), and the \( N = 3 \) states which are higher than the \( N = 1 \) states by \( 10b = 431 \text{ GHz} \). The next higher \( N = 5 \) states correspond with an excitation energy \( 28b = 1207 \text{ GHz} \), which is considerably higher again. Moreover, the \( N = 5 \) states are not directly coupled to the ground \( (N = 1) \) state.

Both the \( N = 1, M = 0 \), and the \( N = 3, M = 0, \pm 1, \pm 2, \pm 3 \) excited states \( (M = 0, \pm 1) \) are coupled to the ground state by the spin terms \( \hat{H}_{\text{fine}} \) [Eq. (7)], while the \( N = 3, M = 0, \pm 1 \) states are coupled by the anisotropic potential \( V_z(R) P_2(\cos \theta) \) as well. Using first order perturbation theory for the wave functions and second order expressions for the energy levels, the corrections can still be done analytically (see Table II). The coupling matrix elements are

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**TABLE III. Second order model results for O₂.**

| \( \epsilon^{(1)} \) | \( \epsilon^{(2)} \) | \( \epsilon^{(1)} + \epsilon^{(2)} \) | Exact splittings from \( \hat{H}_{\text{fine}} \) | Experimental
<table>
<thead>
<tr>
<th></th>
<th></th>
<th></th>
<th></th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td>( \epsilon(J = 2) - \epsilon(J = 0) ): ( \frac{3}{4} \lambda_0 = 71.4 \text{ GHz} )</td>
<td>( -\frac{16}{5} \frac{a^2}{b^2} \lambda_0 = -7.9 \text{ GHz} )</td>
<td>63.5 GHz</td>
<td>63.2 GHz</td>
<td>62.5 GHz</td>
</tr>
<tr>
<td>( \epsilon(J = 1) - \epsilon(J = 0) ): ( 2 \lambda_0 = 119.0 \text{ GHz} )</td>
<td>0</td>
<td>119.0 GHz</td>
<td>119.0 GHz</td>
<td>118.8 GHz</td>
</tr>
</tbody>
</table>

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*Reference 5.*

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TABLE IV. Second order model results for $O_2Ar$ (splittings between the four ladders in GHz).

<table>
<thead>
<tr>
<th>$\epsilon^{(1)} - \epsilon^{(1)}$</th>
<th>$\epsilon^{(1)} + \epsilon^{(2)}$ for</th>
<th>Accurate dynamical calculations$^b$</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>$V_2=450,\text{GHz}$</td>
<td>$V_2=600,\text{GHz}$</td>
</tr>
<tr>
<td>$\epsilon_1 - \epsilon_1$</td>
<td>39.7/39.4</td>
<td>41.7/41.4</td>
</tr>
<tr>
<td>$\epsilon_2 - \epsilon_1$</td>
<td>71.4</td>
<td>92.3</td>
</tr>
<tr>
<td>$\epsilon_4 - \epsilon_1$</td>
<td>95.2</td>
<td>110.5</td>
</tr>
</tbody>
</table>

$^a$Calculated with $B=1.97$ and 2.04 GHz for the PV and MG potentials, respectively.
$^b$Reference 1.
$^c$Reference 4.
$^d$Reference 3.

CONCLUSION

From a very simple, first order model (see Table I), I have derived the general structure of the fine-structure spectrum in $O_2Ar$ (see Fig. 1). Although the $O_2$-$Ar$ interaction is a weak van der Waals bond, this spectrum is fundamentally different from the pure $O_2$ spectrum (cf. Table III). The differences are shown to be caused by the partial quenching of the free $O_2$ rotations by the anisotropic $O_2Ar$ interaction potential. This anisotropy makes the projection $|K|=|M_N + M_S|$ of the $O_2$ angular momentum $J=N+S$ on the $O_2Ar$ axis a (nearly) good quantum number, rather than the total diatom angular momentum $J$. The fine-structure spectrum thus obtained is typical for a T-shaped $O_2X$ ($X=$ rare gas atom) complex. For the linear case, if it exists, one can easily work out a similar model.

Adding (still analytical) second order corrections (Table II) to the energy level splittings yields quantitative agreement with the data from accurate dynamical calculations$^1$, which have started from two different empirical anisotropic $O_2Ar$ potentials.$^3,4$ The model shows explicitly how the transition frequencies depend on the strength of the anisotropic potential $V_2(R)$ and the value of the end-over-end rotational constant $B = \langle B(R) \rangle_0 = \langle R^2 \rangle_0 / 2 \mu$. This will be useful for interpreting the experimental $O_2Ar$ fine-structure spectrum which is currently being experimentally studied.$^2$ If one wishes to exploit the full precision of the experimental beam resonance data, one should still perform accurate numerical calculations, such as those by Tennyson and Mettes.$^1$ However, it will probably be necessary also to improve the existing empirical potentials, for instance, by the inclusion of higher anisotropic $V_4$ terms. The secular problem to be solved is simplified and convergence can be accelerated by using a body-fixed basis of the type (13), including higher rotational $N = 3, 5, \ldots$ and stretch vibrational ($\phi_2(R)$, with $\nu_2 = 1, 2, \ldots$) components [rather than the space-fixed basis (5) with stretch functions $\chi_\nu(R)$ derived from the isotropic potential$^1$].

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$^2$J. Mettes, D. Laine, and J. Reuss (private communication).