

 Open access • Journal Article • DOI:10.1063/1.453654

The O₂–O₂ dimer: Magnetic coupling and spectrum — [Source link](#)

A. van der Avoird, Geert Brocks

Published on: 01 Nov 1987 - Journal of Chemical Physics (American Institute of PhysicsAIP)

Topics: Magnetic dipole, van der Waals force, Intermolecular force, Exchange interaction and Ground state

Related papers:

- [A van der Waals intermolecular potential for \(O₂\)₂](#)
- [\(Heisenberg\) exchange and electrostatic interactions between O₂ molecules: An ab initio study](#)
- [Structure and energy transfer within isolated \(O₂\)₂ dimers via high resolution electronic spectroscopy](#)
- [Spectroscopic investigation of van der Waals molecules. I. The infrared and visible spectra of \(O₂\)₂](#)
- [Rotational excitation in H₂–H₂ collisions: Close-coupling calculations](#)

Share this paper:    

View more about this paper here: <https://typeset.io/papers/the-o2-o2-dimer-magnetic-coupling-and-spectrum-57sw8mu9hl>

PDF hosted at the Radboud Repository of the Radboud University Nijmegen

The following full text is a publisher's version.

For additional information about this publication click this link.

<http://hdl.handle.net/2066/16160>

Please be advised that this information was generated on 2022-05-31 and may be subject to change.

The O₂-O₂ dimer: Magnetic coupling and spectrum

A. van der Avoird and G. Brocks

Institute of Theoretical Chemistry, University of Nijmegen, Toernooiveld, 6525 ED Nijmegen, The Netherlands

(Received 6 May 1987; accepted 7 July 1987)

A theoretical analysis has been made of the van der Waals vibration-rotation-electron spin states of the O₂-O₂ dimer in its $^3\Sigma_g^- - ^3\Sigma_g^-$ electronic ground state. This analysis is based on a Hamiltonian that includes a spin-dependent O₂-O₂ interaction potential and it involves also the permutation-inversion symmetry of the system. We have constructed some hindered internal rotor models for the vibrational states of the O₂-O₂ dimer which correspond with different equilibrium geometries, and for each of these models we have numerically calculated the spin-rotation fine structure. This fine structure appears to be determined not only by the Heisenberg exchange interaction between the O₂ monomer triplet states, but also by intramolecular spin-orbit and spin-spin coupling and, to a smaller extent, by the intermolecular spin-spin (magnetic dipole) interaction and by the Coriolis terms in the kinetic energy. The resulting fine-structure spectrum is very complex, and very sensitive to the geometry of the O₂-O₂ dimer, to the nature of its internal motions and to the various magnetic couplings. This implies that detailed measurements of this spectrum, which can be interpreted with the help of the theory presented here, will yield interesting information on the properties of the O₂-O₂ dimer and, at the same time, verify our assumptions on the magnetic interactions between O₂ molecules which have important consequences for the properties of solid oxygen.

I. INTRODUCTION

It has been suggested by Lewis¹ that the O₂-O₂ dimer may be stabilized by a weak chemical bond between the open-shell O₂ molecules. Although this suggestion has not been confirmed by experimental evidence, and the O₂-O₂ interactions seem to be purely of van der Waals type, the O₂-O₂ dimer remains one of the most interesting van der Waals molecules. The triplet nature of the O₂ ground state, which is very unusual for a stable molecule, leads to magnetic coupling between the O₂ spin momenta or, in other words, to a spin-dependent O₂-O₂ potential. The knowledge of these magnetic interactions is crucial for the understanding of the properties of bulk O₂, which is a very interesting magnetic material.² The O₂-O₂ dimer is the most suitable system to investigate these interactions in detail. The study of the O₂-O₂ dimer is further relevant for gas phase reactions involving metastable excited O₂ molecules. The most efficient quenching of the metastable $^1\Delta_g$ and $^1\Sigma_g^+$ states of O₂ occurs via the formation of (collisional) O₂-O₂ dimers.^{3,4}

The most complete spectroscopic studies of the O₂-O₂ dimer have been made by Long and Ewing⁵ and by Goodman and Brus.⁶ Long and Ewing have observed O₂-O₂ dimers in the gas phase at 90 K, Goodman and Brus have studied such dimers in a solid neon matrix at 4.2 K. Both groups have measured the spectrum in the visible region, which corresponds with (simultaneous) monomer transitions between the $^3\Sigma_g^-$ ground states and the low-lying electronically excited $^1\Delta_g$ and $^1\Sigma_g^+$ states. Long and Ewing were mainly interested in the vibrational structure and they have also measured the dimer absorption spectrum in the infrared region around the O₂ fundamental stretch frequency. Goodman and Brus were particularly interested in the electronic and vibrational energy transfer between the O₂ monomers.

This energy transfer between monomer vibronic states is directly related to the exchange splittings between the dimer states that correlate with these monomer states. These splittings could be measured for various isotopic combinations with polarized high-resolution laser spectroscopy.

In spite of these beautiful and detailed investigations the properties of the O₂-O₂ dimer are still not well understood. Long and Ewing could not derive the equilibrium structure of the dimer from their interpretation of the visible and infrared spectra. Their assignment of the bands due to van der Waals vibrations is only tentative and it is not yet supported by calculations based on a potential surface. Goodman and Brus find a parallel D_{2h} geometry as the most probable, but they have only considered a limited set of *rigid* dimer structures. Calculations on similar van der Waals dimers, such as N₂-N₂,^{7,8} N₂-Ar,^{9,10} and O₂-Ar,¹¹⁻¹⁴ have taught us, however, that isolated van der Waals molecules of this type are rather floppy. It is possible, since the van der Waals interactions of the O₂ molecules with the neon atoms in the matrix are of similar strength as the O₂-O₂ interactions, and molecular crystals are generally less flexible than the corresponding dimers,¹⁵ that the O₂-O₂ dimer in a solid neon matrix is considerably more rigid than the isolated O₂-O₂ dimer. In this context, it is remarkable that Goodman and Brus have found the exchange interaction between $^3\Sigma_g^-$ ground state O₂ molecules in the dimer to be larger even than the same interaction between the nearest neighbors in solid α -O₂ (which have a parallel D_{2h} structure also). Furthermore, they have interpreted their results in terms of a model by Bhandari and Falicov¹⁶ that is based on a molecular orbital (MO) scheme. For weakly interacting open-shell species, such as O₂ molecules, the MO model is not appropriate, since the O₂-O₂ dimer does not dissociate into correct O₂ monomer states in this model.

So we think that it is worthwhile to revisit the O₂-O₂ dimer, especially from a theoretical point of view. Recently the exchange and multipole interactions between ³Σ_g⁻ ground state O₂ molecules have been calculated *ab initio* in our institute.¹⁷ The results, together with a semiempirical estimate for the (spin-independent) long-range dispersion interactions, have been expressed in the form of an analytical *spin-dependent* potential. A Heisenberg effective spin operator in this potential represents the exchange splittings between the singlet, triplet, and quintet states of the O₂-O₂ dimer, for any geometry. The coupling parameter *J* in this operator depends not only on the intermolecular distance, but it also appears to be a strongly varying function of the molecular orientations. The Heisenberg exchange term is not the only spin-dependent term in the potential, however. It is well known from the spectroscopy on the free O₂ molecule¹⁸ that spin-orbit and spin-spin interactions couple the molecular spin-momentum to the direction of the molecular axis. In the O₂-O₂ dimer, such intramolecular coupling terms have to be included for each monomer. Moreover, there is of course the magnetic dipole-dipole coupling between the O₂ monomer triplet spin momenta. With all these terms taken into account in the spin-dependent O₂-O₂ potential, several of the properties of solid α and β oxygen, as well as some phenomena occurring at the magnetoelastic α-β phase transition, could be understood completely from first principles^{19,20} (with the aid of lattice dynamics and spin-wave calculations).

In the present paper we evaluate the effects of the same spin-dependent interactions on the properties of the O₂-O₂ dimer. We make a theoretical and computational study of the dimer states which derive from the ³Σ_g⁻ rovibronic ground states monomers. Since the long-range dispersion contribution to the intermolecular potential is not known accurately and, therefore, the O₂-O₂ equilibrium structure is not known either, we have refrained from detailed computations of the dimer states. Instead, we try to predict how the splittings between these states depend on the structure of the O₂-O₂ dimer or rather, since this dimer is expected to be fairly "floppy," on the character of its van der Waals vibrational states. For the much simpler case of O₂-rare gas atom dimers this has been done in our institute earlier.¹¹⁻¹³ In that case, the calculated Zeeman spectrum has been quantitatively confirmed by radio frequency measurements on O₂-Ar and O₂-Ne dimers in a molecular beam.^{14,21} Also, O₂-O₂ dimers have been observed in molecular beams,^{22,23} and we think that, with present day technology, it is possible to measure their high-resolution visible, infrared, microwave, or radio frequency spectra. Our calculations can be used to interpret such measurements and to understand the experimental results in terms of the basic O₂-O₂ interactions. On the other hand, the measurements will verify the spin-dependent O₂-O₂ interaction potential that has been used in the calculations on solid O₂^{19,20} and in the present calculations.

II. PERMUTATION-INVERSION SYMMETRY

Goodman and Brus⁶ have assumed that the O₂-O₂ dimer, in their solid neon matrix, is rigid with some point

group, probably *D*_{2h}, symmetry. In their interpretation of the visible spectra they have used the selection rules pertaining to this point group. Since we expect that the, isolated, O₂-O₂ dimer is rather floppy, we use the permutation-inversion (PI) group. Usually, when one considers the rovibrational states, the molecular symmetry group²⁴ contains all those permutations of identical nuclei which may be called *feasible*²⁵ in the case of interest, possibly combined with space inversion. In the standard treatment of nearly rigid molecules, which involves an Eckart molecular frame, the group of feasible PIs maps onto the point group of the molecule, as far as the vibrational coordinates are concerned. The PI group is more generally valid, however, and can also be applied to floppy molecules.

For the van der Waals molecule N₂-N₂,^{7,8} which is geometrically similar to O₂-O₂ (see Fig. 1), this group *G* 16 is generated by the permutations *P*₁₂, *P*₃₄, and *P*₁₃*P*₂₄ and by space inversion *E*^{*} and it contains all permutations of the nuclei which do not involve the breaking of the strong chemical N≡N bonds. The case of O₂-O₂ is different, however, because one has to treat the rovibrational states in combination with the electron spin states. As one shall see in Sec. III, the spin-dependent potential which we use in this treatment is not invariant under the pure nuclear permutation *P*₁₃*P*₂₄. A proper symmetry operation is obtained, however, if we combine the permutation *P*₁₃*P*₂₄, that interchanges the nuclei 1 and 2 in molecule A with the nuclei 3 and 4 in molecule B, with a simultaneous permutation of all the electrons *i* = 5, ..., 20 in molecule A with all the electrons *j* = 21, ..., 36 in molecule B. Such a permutation of all the particles in molecule A with all the particles in molecule B we call *P*_{AB}:

$$P_{AB} = P_{13}P_{24} \prod_{i=5}^{20} P_{i,i+16}. \quad (1)$$

In order to understand this problem, which is essential in the treatment of O₂-O₂, we have to define various coordi-

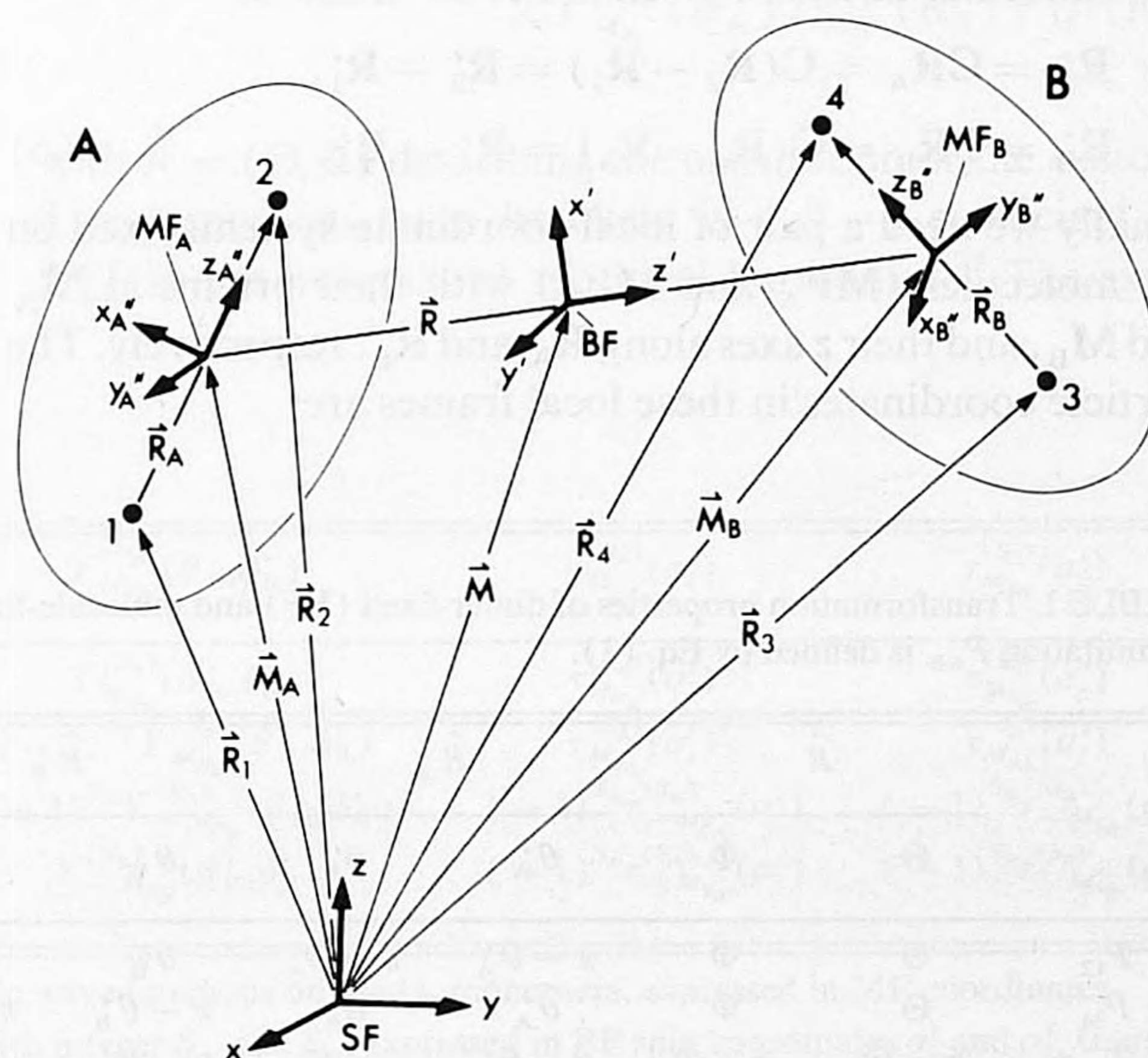


FIG. 1. Coordinate systems used in the O₂-O₂ dimer.

nate systems (see Fig. 1). We assume that all the oxygen nuclei are identical; the case of mixed isotopes is simpler from the permutational symmetry point of view. Let us begin with an arbitrary space-fixed (SF) coordinate frame. The nuclear coordinates with respect to this frame are called $\mathbf{R}_1, \mathbf{R}_2, \mathbf{R}_3,$ and \mathbf{R}_4 and the electron coordinates $\{\mathbf{r}_i | i = 5, \dots, 20\}$ and $\{\mathbf{r}_j | j = 21, \dots, 36\}$. The next coordinate system, which we shall use in Secs. III, IV, and V, is a dimer body-fixed (BF) frame, with its origin in the dimer center of mass \mathbf{M} and its z axis along the vector $\mathbf{R} = \mathbf{M}_B - \mathbf{M}_A$ that connects the monomer centers of mass \mathbf{M}_A and \mathbf{M}_B . The coordinates of the particles with respect to this frame are defined as:

$$\begin{aligned} \mathbf{R}'_I &= C(\mathbf{R}_I - \mathbf{M}) \quad \text{for the nuclei } I = 1, \dots, 4, \\ \mathbf{r}'_i &= C(\mathbf{r}_i - \mathbf{M}) \quad \text{for the electrons } i = 5, \dots, 20, \\ \mathbf{r}'_j &= C(\mathbf{r}_j - \mathbf{M}) \quad \text{for the electrons } j = 21, \dots, 36, \end{aligned} \quad (2)$$

with

$$\begin{aligned} \mathbf{M}_A &= \frac{1}{2}(\mathbf{R}_1 + \mathbf{R}_2), \\ \mathbf{M}_B &= \frac{1}{2}(\mathbf{R}_3 + \mathbf{R}_4), \\ \mathbf{M} &= \frac{1}{2}(\mathbf{M}_A + \mathbf{M}_B), \\ \mathbf{R} &= \mathbf{M}_B - \mathbf{M}_A \end{aligned} \quad (3)$$

and the rotation matrix

$$C = \begin{pmatrix} \cos \Theta \cos \Phi & \cos \Theta \sin \Phi & -\sin \Theta \\ -\sin \Phi & \cos \Phi & 0 \\ \sin \Theta \cos \Phi & \sin \Theta \sin \Phi & \cos \Theta \end{pmatrix}. \quad (4)$$

The angles Θ and Φ are the polar angles of the vector \mathbf{R} with respect to the SF frame and it is easy to verify, using Eqs. (1)–(3), that in the BF frame:

$$\begin{aligned} \mathbf{R}' &= C\mathbf{R} = (0, 0, R), \\ \mathbf{M}'_A &= C(\mathbf{M}_A - \mathbf{M}) = -\frac{1}{2}C\mathbf{R} = (0, 0, -R/2), \\ \mathbf{M}'_B &= C(\mathbf{M}_B - \mathbf{M}) = \frac{1}{2}C\mathbf{R} = (0, 0, R/2). \end{aligned} \quad (5)$$

The vectors \mathbf{R}_A and \mathbf{R}_B which describe the orientations of the molecular axes, are given in the BF frame as

$$\begin{aligned} \mathbf{R}'_A &= C\mathbf{R}_A = C(\mathbf{R}_2 - \mathbf{R}_1) = \mathbf{R}'_2 - \mathbf{R}'_1, \\ \mathbf{R}'_B &= C\mathbf{R}_B = C(\mathbf{R}_4 - \mathbf{R}_3) = \mathbf{R}'_4 - \mathbf{R}'_3. \end{aligned} \quad (6)$$

Finally we need a pair of local coordinate systems fixed on the molecules (MF_A and MF_B) with their origins at \mathbf{M}'_A and \mathbf{M}'_B , and their z axes along \mathbf{R}'_A and \mathbf{R}'_B , respectively. The particle coordinates in these local frames are

$$\begin{aligned} \mathbf{R}''_1 &= C_A(\mathbf{R}'_1 - \mathbf{M}'_A) = -\frac{1}{2}C_A\mathbf{R}'_A = (0, 0, -R_A/2), \\ \mathbf{R}''_2 &= C_A(\mathbf{R}'_2 - \mathbf{M}'_A) = \frac{1}{2}C_A\mathbf{R}'_A = (0, 0, R_A/2), \\ \mathbf{r}''_i &= C_A(\mathbf{r}'_i - \mathbf{M}'_A) = C_A C(\mathbf{r}_i - \mathbf{M}_A) \end{aligned} \quad \text{for } i = 5, \dots, 20,$$

and

$$\begin{aligned} \mathbf{R}''_3 &= C_B(\mathbf{R}'_3 - \mathbf{M}'_B) = (0, 0, -R_B/2), \\ \mathbf{R}''_4 &= C_B(\mathbf{R}'_4 - \mathbf{M}'_B) = (0, 0, R_B/2), \\ \mathbf{r}''_j &= C_B(\mathbf{r}'_j - \mathbf{M}'_B) = C_B C(\mathbf{r}_j - \mathbf{M}_B) \end{aligned} \quad (7) \quad \text{for } j = 21, \dots, 36.$$

The rotation matrices C_A and C_B have the same form as the matrix C in Eq. (4), but they contain the polar angles (θ'_A, ϕ'_A) and (θ'_B, ϕ'_B) of the vectors \mathbf{R}'_A and \mathbf{R}'_B in the BF frame.

The action of the permutations in the SF frame is trivial; they simply interchange the labels of the vectors $\mathbf{R}_1, \dots, \mathbf{R}_4$ and those of $\{\mathbf{r}_i | i = 5, \dots, 20\}$ and $\{\mathbf{r}_j | j = 21, \dots, 36\}$. Also, the action of space-inversion E^* is simple; it replaces every vector \mathbf{r} by $-\mathbf{r}$. The transformations in the dimer- and molecule-fixed coordinates induced by these operations are not so trivial, however, because the coordinate frames themselves are affected by the operations as well. One has to make explicit use of the formulas in Eqs. (2) and (7). So one finds, for example, that the permutation P_{12} leaves the vector \mathbf{R} invariant and simply transforms the vector \mathbf{R}'_A into $-\mathbf{R}'_A$, but that it acts as twofold rotation about the x axis on the local coordinates \mathbf{r}''_i in the molecule-fixed frame MF_A . The relevant results are summarized in Table I.

Now we can discuss why the different coordinate frames are essential to our treatment of the O₂-O₂ dimer. The BF frame will be used in the rovibrational-spin calculations. In particular, the basis functions introduced in Sec. IV will be expressed in BF coordinates, because this is convenient and physically meaningful (see Secs. IV and V). The transformations given in Table I can be applied to adapt this basis to the permutation-inversion symmetry, which simplifies the calculations and directly yields the selection rules.

The MF frames are not explicitly used in our calculations, but they are essential to define our model. We consider those electronic states of the O₂-O₂ dimer that correlate with the $^3\Sigma_g^-$ ground states of the monomers. These states can be obtained from the monomer states by vector coupling of the triplet spin momenta and antisymmetrization in the electron coordinates. The spatial parts of the electronic wave func-

TABLE I. Transformation properties of dimer-fixed (BF) and molecule-fixed (MF) coordinates, under the generating elements of the PI group G_{16} . The permutation P_{AB} is defined by Eq. (1).

	\hat{R}		\hat{R}'_A		\hat{R}'_B		\mathbf{r}''_i			\mathbf{r}''_j		
	Θ	Φ	θ'_A	ϕ'_A	θ'_B	ϕ'_B	x''_i	y''_i	z''_i	x''_j	y''_j	z''_j
P_{12}	Θ	Φ	$\pi - \theta'_A$	$\pi + \phi'_A$	θ'_B	ϕ'_B	x''_i	$-y''_i$	$-z''_i$	x''_j	y''_j	z''_j
P_{34}	Θ	Φ	θ'_A	ϕ'_A	$\pi - \theta'_B$	$\pi + \phi'_B$	x''_i	y''_i	z''_i	x''_j	$-y''_j$	$-z''_j$
P_{AB}	$\pi - \Theta$	$\pi + \Phi$	$\pi - \theta'_B$	$-\phi'_B$	$\pi - \theta'_A$	$-\phi'_A$	$-x''_j$	$-y''_j$	z''_j	$-x''_i$	$-y''_i$	z''_i
E^*	$\pi - \Theta$	$\pi + \Phi$	θ'_A	$\pi - \phi'_A$	θ'_B	$\pi - \phi'_B$	x''_i	$-y''_i$	z''_i	x''_j	$-y''_j$	z''_j

tions do not enter into our calculation—the spin parts do—but the coupling constants in the spin-dependent potential of Sec. III are actually integrals over these wave functions for the given electronic states. In order to use in our dimer calculations those rovibrational–spin functions that have the correct symmetry, we have to include also the symmetry of the electronic states. The latter symmetry becomes evident only when the monomer electronic wave functions are expressed in the local MF coordinates \mathbf{r}_i'' and \mathbf{r}_j'' . For instance, the Σ_g^- symmetry of the monomer ground states is defined with respect to the local MF frames. Also the property that the ${}^3\Sigma_g^-$ functions on the monomers A and B have an identical form is only visible when these functions are expressed in terms of the local coordinates \mathbf{r}_i'' and \mathbf{r}_j'' . From the observation that these local coordinates depend both on the electronic and on the nuclear positions [see Eq. (7)] it follows then that the combined nuclear and electronic permutation P_{AB} [see Eq. (1)] is a symmetry operation, whereas the pure nuclear permutation $P_{13}P_{24}$ is not. The complete transformation properties of the monomer wave functions are given in Table II. The antisymmetry of the ${}^3\Sigma_g^-$ electronic states on the monomers A and B under the local nuclear permutations P_{12} and P_{34} leads for ${}^{16}\text{O}$ nuclei, which are bosons with zero nuclear spin, to the result that only the spherical harmonics with odd values of N_A and N_B will be allowed in the rovibrational basis of Sec. IV. This can directly be read from Table II. Although we discuss only those dimer states that dissociate into two ${}^3\Sigma_g^-$ ground state monomers, this reasoning can be rather easily extended to the excited electronic states.

III. SPIN-DEPENDENT POTENTIAL AND HAMILTONIAN OF O₂-O₂

The interactions between O₂ molecules in their ${}^3\Sigma_g^-$ ground states depend on the coupling between their triplet electronic spin momenta. In the O₂-O₂ dimer, the two triplets, $S_A = 1$ and $S_B = 1$, can couple to a singlet, a triplet, or a quintet ($S = 0, 1$, or 2). If we neglect, in first instance, the spin-orbit and spin-spin (magnetic dipole) interactions, the total spin S of the dimer is a good quantum number and each of the three total spin states has its own potential surface. The difference between these surfaces is caused by electron exchange interactions, since the total electron spin quantum number is directly related with the permutational symmetry

of the electronic wave function.²⁶ It is in fact by an explicit *ab initio* calculation of these exchange interactions for the three different total spin states of the O₂-O₂ dimer that the leading terms in the spin-dependent O₂-O₂ potential have been obtained.¹⁷ The interaction potential for each of the three spin states, $S = 0, 1$, and 2 , can be accurately represented, in the most general SF frame, as follows:

$$V_S(\hat{R}_A, \hat{R}_B, \mathbf{R}) = V_{av}(\hat{R}_A, \hat{R}_B, \mathbf{R}) - 2J(\hat{R}_A, \hat{R}_B, \mathbf{R})\mathbf{S}_A \cdot \mathbf{S}_B. \quad (8)$$

The symbols \hat{R}_A and \hat{R}_B denote unit vectors along the monomer axes \mathbf{R}_A and \mathbf{R}_B which determine the orientations (θ_A, ϕ_A) and (θ_B, ϕ_B) of these axes; \mathbf{S}_A and \mathbf{S}_B are the monomer electron spin operators. The first, spin-independent, potential is the (multiplicity weighted) average of the singlet, triplet, and quintet surfaces. The second, Heisenberg, term describes the splitting between these surfaces. The latter implies that the quintet–triplet splitting is exactly twice the triplet–singlet splitting, for any geometry of the O₂-O₂ dimer. In the *ab initio* calculations, this was found to be very nearly so.¹⁷

Just as the spin-independent potential V_{av} , the Heisenberg coupling parameter J depends on the distance R between the O₂ monomers and on their orientations \hat{R}_A and \hat{R}_B . The orientational dependence of these quantities can be explicitly expressed by the expansions²⁷:

$$V_{av}(\hat{R}_A, \hat{R}_B, \mathbf{R}) = (4\pi)^{3/2} \sum_{L_A, L_B, L} v_{L_A, L_B, L}(R) \times A_{L_A, L_B, L}(\hat{R}_A, \hat{R}_B, \hat{R}), \quad (9)$$

$$J(\hat{R}_A, \hat{R}_B, \mathbf{R}) = (4\pi)^{3/2} \sum_{L_A, L_B, L} j_{L_A, L_B, L}(R) \times A_{L_A, L_B, L}(\hat{R}_A, \hat{R}_B, \hat{R}) \quad (10)$$

in the complete orthonormal set of angular functions

$$A_{L_A, L_B, L}(\hat{R}_A, \hat{R}_B, \hat{R}) = \sum_{M_A, M_B, M} \begin{pmatrix} L_A & L_B & L \\ M_A & M_B & M \end{pmatrix} \times Y_{M_A}^{(L_A)}(\hat{R}_A) Y_{M_B}^{(L_B)}(\hat{R}_B) Y_M^{(L)}(\hat{R}), \quad (11)$$

with $\hat{R} = (\Theta, \Phi)$ describing the orientation of the vector \mathbf{R} . The symbol in large brackets is a 3- j coefficient and $Y_m^{(l)}(\hat{r})$ are normalized spherical harmonics.²⁸ The expan-

TABLE II. Transformation properties of the relevant basis functions.^a

	$\Phi_A(\mathbf{r}_i'')$	$\Phi_B(\mathbf{r}_j'')$	$Y_{M_{N_A}}^{(N_A)}(\theta'_A, \phi'_A)$	$Y_{M_{N_B}}^{(N_B)}(\theta'_B, \phi'_B)$	$\tau_{M_{S_A}}^{(S_A)}(\sigma'_i)$	$\tau_{M_{S_B}}^{(S_B)}(\sigma'_j)$
P_{12}	$-\Phi_A(\mathbf{r}_i'')$	$\Phi_B(\mathbf{r}_j'')$	$(-1)^{N_A} Y_{M_{N_A}}^{(N_A)}(\theta'_A, \phi'_A)$	$Y_{M_{N_B}}^{(N_B)}(\theta'_B, \phi'_B)$	$\tau_{M_{S_A}}^{(S_A)}(\sigma'_i)$	$\tau_{M_{S_B}}^{(S_B)}(\sigma'_j)$
P_{34}	$\Phi_A(\mathbf{r}_i'')$	$-\Phi_B(\mathbf{r}_j'')$	$Y_{M_{N_A}}^{(N_A)}(\theta'_A, \phi'_A)$	$(-1)^{N_B} Y_{M_{N_B}}^{(N_B)}(\theta'_B, \phi'_B)$	$\tau_{M_{S_A}}^{(S_A)}(\sigma'_i)$	$\tau_{M_{S_B}}^{(S_B)}(\sigma'_j)$
P_{AB}	$\Phi_B(\mathbf{r}_j'')$	$\Phi_A(\mathbf{r}_i'')$	$(-1)^{N_A} Y_{-M_{N_A}}^{(N_A)}(\theta'_A, \phi'_A)$	$(-1)^{N_B} Y_{-M_{N_B}}^{(N_B)}(\theta'_B, \phi'_B)$	$(-1)^{S_A} \tau_{-M_{S_A}}^{(S_A)}(\sigma'_i)$	$(-1)^{S_B} \tau_{-M_{S_B}}^{(S_B)}(\sigma'_j)$
E^*	$-\Phi_A(\mathbf{r}_i'')$	$-\Phi_B(\mathbf{r}_j'')$	$Y_{-M_{N_A}}^{(N_A)}(\theta'_A, \phi'_A)$	$Y_{-M_{N_B}}^{(N_B)}(\theta'_B, \phi'_B)$	$(-1)^{S_A} \tau_{-M_{S_A}}^{(S_A)}(\sigma'_i)$	$(-1)^{S_B} \tau_{-M_{S_B}}^{(S_B)}(\sigma'_j)$

^aThe functions $\Phi_A(\mathbf{r}_i'')$ and $\Phi_B(\mathbf{r}_j'')$ are the spatial parts of the ${}^3\Sigma_g^-$ electronic wave functions on the O₂ monomers, expressed in MF coordinates. We have used the property that the spin functions $\tau_{M_{S_A}}^{(S_A)}(\sigma'_i)$ and $\tau_{M_{S_B}}^{(S_B)}(\sigma'_j)$ with integer S_A and S_B , expressed in BF spin coordinates σ'_i and σ'_j , transform analogously to the spherical harmonics $Y_{M_{N_A}}^{(N_A)}(\theta'_A, \phi'_A)$ and $Y_{M_{N_B}}^{(N_B)}(\theta'_B, \phi'_B)$ under rotations, but that they are invariant under inversion. The spin operators S'_A and S'_B transform just as the spin functions with $S_A = 1$ and $S_B = 1$.

sion in Eq. (10) converges more slowly than that in Eq. (9), because J is considerably more anisotropic even than the most anisotropic contributions to V_{av} . A positive sign of J implies ferromagnetic coupling between the O₂ triplets; negative J means antiferromagnetic coupling. Both these cases actually occur for various orientations of the O₂ monomers and specific distances R . This is related to the nodal character of the antibonding π_g orbitals in the O₂ monomers, which contain the unpaired electrons.

The expansion coefficients of the spin-independent potential V_{av} have been written^{17,20} as follows:

$$v_{L_A, L_B, L}(R) = C_{L_A, L_B, L}^{(\text{exp})} \exp(-\alpha_{L_A, L_B, L} R - \beta_{L_A, L_B, L} R^2) + C_{L_A, L_B, L}^{(\text{mult})} R^{-L_A - L_B - 1} + C_{L_A, L_B, L}^{(6)} R^{-6} + C_{L_A, L_B, L}^{(8)} R^{-8} + C_{L_A, L_B, L}^{(10)} R^{-10}. \quad (12)$$

The first, exponential, contribution is due to overlap (exchange and charge penetration) effects, the second term corresponds with the electrostatic multipole-multipole interactions and the last three terms arise from dispersion interactions. The coefficients and exponents in the first two terms have been calculated *ab initio* in Ref. 17, the coefficients in the dispersion terms have been estimated semiempirically in Ref. 20. The Heisenberg coupling parameter J contains exponential contributions only:

$$j_{L_A, L_B, L}(R) = C_{L_A, L_B, L}'^{(\text{exp})} \exp(-\alpha'_{L_A, L_B, L} R - \beta'_{L_A, L_B, L} R^2) \quad (13)$$

because it originates merely from exchange effects. Also the coefficients and exponents in Eq. (13) have been calculated *ab initio*.¹⁷

Now, we consider the spin-orbit and spin-spin coupling. In the *free* O₂ molecule in its electronic $^3\Sigma_g^-$ ground state, the effects of spin-orbit and spin-spin coupling can be represented,¹⁸ in spherical tensor form,²⁸ by the following operator:

$$\frac{1}{3} \sqrt{6} A \sum_m (-1)^m C_m^{(2)}(\theta, \phi) [\mathbf{S} \otimes \mathbf{S}]_{-m}^{(2)}, \quad (14)$$

where the angles (θ, ϕ) describe the orientation of the molecular axis and $C_m^{(2)}(\theta, \phi)$ is a Racah spherical harmonic. The tensor product of the spin vector \mathbf{S} with itself is given by the following, more general, definition for two arbitrary tensors $\mathsf{T}^{(l_1)} = \{T_{m_1}^{(l_1)} | m_1 = -l_1, \dots, l_1\}$ and $\mathsf{T}^{(l_2)} = \{T_{m_2}^{(l_2)} | m_2 = -l_2, \dots, l_2\}$:

$$[\mathsf{T}^{(l_1)} \otimes \mathsf{T}^{(l_2)}]_m^{(l)} = \sum_{m_1, m_2} T_{m_1}^{(l_1)} T_{m_2}^{(l_2)} (l_1, m_1; l_2, m_2 | l, m). \quad (15)$$

The coefficients are Clebsch-Gordan coefficients.²⁸ The coupling constant $A = 3.96 \text{ cm}^{-1} = 5.712 \text{ K}$ is positive,¹⁸ from which it follows that the triplet spin momentum of the O₂ molecule prefers to be perpendicular to the molecular axis.

In the O₂-O₂ dimer, we assume that the electronic charge distribution of the monomers, and consequently also the intramolecular spin-orbit and spin-spin couplings, are

not much perturbed by the weak intermolecular van der Waals interactions. The same assumption has been made for O₂-rare gas dimers¹¹⁻¹³ and it appears to explain their experimental Zeeman spectra^{14,21} very well. We then obtain the following contribution to the spin-dependent potential for the O₂-O₂ dimer:

$$V_{\text{intra}}(\hat{R}_A, \mathbf{S}_A; \hat{R}'_B, \mathbf{S}_B) = \frac{1}{3} \sqrt{6} A \sum_m (-1)^m \{ C_m^{(2)}(\hat{R}_A) [\mathbf{S}_A \otimes \mathbf{S}_A]_{-m}^{(2)} + C_m^{(2)}(\hat{R}_B) [\mathbf{S}_B \otimes \mathbf{S}_B]_{-m}^{(2)} \}. \quad (16)$$

Finally, we include the intermolecular spin-spin (magnetic dipole) interactions between the monomer triplets. If the triplet spin momenta are considered as magnetic point dipoles $g_e \mu_B \mathbf{S}_A$ and $g_e \mu_B \mathbf{S}_B$, with $g_e = 2.0023$ and μ_B being the Bohr magneton, which are located on the monomer centers of mass \mathbf{M}_A and \mathbf{M}_B , then we can write for the dipole-dipole interaction, in spherical tensor form:

$$V_{dd}(\mathbf{R}, \mathbf{S}_A, \mathbf{S}_B) = -\sqrt{6} g_e^2 \mu_B^2 R^{-3} \sum_m (-1)^m C_m^2(\hat{R}) \times [\mathbf{S}_A \otimes \mathbf{S}_B]_{-m}^{(2)}. \quad (17)$$

Herewith, the most important contributions to the spin-dependent O₂-O₂ potential are completely characterized. Summarizing, we write this potential as

$$V(\hat{R}_A, \hat{R}_B, \mathbf{R}, \mathbf{S}_A, \mathbf{S}_B) = V_{av}(\hat{R}_A, \hat{R}_B, \mathbf{R}) + V_{\text{Heis}}(\hat{R}_A, \hat{R}_B, \mathbf{R}, \mathbf{S}_A, \mathbf{S}_B) + V_{\text{intra}}(\hat{R}_A, \mathbf{S}_A; \hat{R}_B, \mathbf{S}_B) + V_{dd}(\mathbf{R}, \mathbf{S}_A, \mathbf{S}_B), \quad (18)$$

where the spin-independent contribution V_{av} and the Heisenberg term V_{Heis} are given by Eq. (8), with the expansions (9) to (13), and the latter two terms are given by Eqs. (16) and (17). Note that this potential is anisotropic, both with respect to the orientations of the molecular axes and with respect to the orientations of the molecular spin momenta. Thus, there will be a coupling between the rotational vibrations or hindered rotations of the O₂ monomers in the dimer and their spin states.

The same potential has been used in recent lattice dynamics and spin wave calculations on solid α and β oxygen,^{19,20} where it replaces a much cruder phenomenological model that cannot be reduced to the molecular level. It appears that the coupling between the orientational vibrations (or librations) and the spin states, which was not included in the earlier treatments, is essential in the solid for understanding its elastic and magnetic properties and, in particular, the nature of the α - β phase transition.

So far, we have expressed all terms in the interaction potential in the most general SF frame. Since the potential is invariant under overall rotations of the dimer, it is convenient to take out the "external" rotation angles. We prefer to remove only two of these angles, however, and not three, because then the full symmetry of the dimer remains explicitly visible.²⁹ This is simply performed by substituting $\hat{R} = (\Theta, \Phi) = (0, 0)$ and replacing all the quantities $\hat{R}_A = (\theta_A, \phi_A)$, $\hat{R}_B = (\theta_B, \phi_B)$, \mathbf{S}_A and \mathbf{S}_B by their primed

equivalents which are defined with respect to the BF frame, see Eqs. (2) to (6). Although the angles ϕ'_A and ϕ'_B are both kept as "internal" angles in this way, the potential depends only on the difference ($\phi'_A - \phi'_B$). Simplifications of Eqs. (11) and (17), in particular, can be obtained after substitution of the relation²⁸

$$C_m^{(l)}(0,0) = \left(\frac{4\pi}{2l+1}\right)^{1/2} Y_m^{(l)}(0,0) = \delta_{m,0}. \quad (19)$$

Given the complete spin-dependent potential, it is easy to write the Hamiltonian for the rotation-vibration-spin states of the O₂-O₂ dimer. One has just to add the kinetic energy terms. Since there is no kinetic energy associated with the spin "motions," the kinetic energy operator is the same as for the N₂-N₂ dimer.^{7,8} We write it in somewhat different form, however, because the operator **J**, which is the total angular momentum in N₂-N₂, is not a constant of the motion in O₂-O₂. In the latter case, one has to add the spin momentum **S** = **S**_A + **S**_B in order to obtain the total angular momentum **F** = **J** + **S**. In the BF coordinates introduced in Sec. II, the total Hamiltonian then reads

$$H = b_0 N_A^2 + b_0 N_B^2 - \frac{\hbar^2}{2\mu R} \frac{\partial^2}{\partial R^2} R + \frac{1}{2\mu R^2} \times (F^2 + N^2 + S^2 - 2\mathbf{S}\cdot\mathbf{F} - 2\mathbf{N}\cdot\mathbf{F} + 2\mathbf{N}\cdot\mathbf{S}) + V(\hat{R}'_A, \hat{R}'_B, R, \mathbf{S}'_A, \mathbf{S}'_B). \quad (20)$$

The operators **N**_A and **N**_B are the angular momenta associated with the monomer rotations, in the BF coordinates (θ'_A, ϕ'_A) and (θ'_B, ϕ'_B), and **N** = **N**_A + **N**_B is their vector sum. The constant b_0 is the monomer rotational constant, $b_0 = 1.438 \text{ cm}^{-1}$ for ¹⁶O₂, and $\mu = 16 \text{ amu}$ is the dimer reduced mass. With respect to the SF frame, the total angular momentum operator **F** can be written as **F** = **J** + **S** = **L** + **N** + **S**, where **L** is the angular momentum associated with the rotation of the vector **R**, expressed in the angles $\hat{R} = (\Theta, \Phi)$. In the (partially) BF frame of Sec. II, it looks as if **L** has simply been replaced by **F** - **N** - **S**, but one must realize that actually some problems are connected with this substitution.²⁹ For instance, the operators **N** and **F** do not commute. The action of the kinetic energy operators in Eq. (20) on the BF basis introduced in the next section is fairly simple, however, as it has been shown in Ref. 29 for general dimers without a net electron spin momentum.

It is easy to check in either frame, SF or BF, that the individual terms in the Hamiltonian (20) with the spin-dependent potential of Eq. (18) are all invariant under the permutation-inversion group, of which the generating elements are given in Tables I and II. Whereas the exact electronic and nuclear Hamiltonian of the O₂-O₂ dimer is invariant only under simultaneous inversion E^* of the electron and nuclear coordinates, the Hamiltonian in Eq. (20) is also invariant under inversion of the nuclear coordinates. This is related to the fact that Eq. (20) actually defines an effective Hamiltonian in which the coupling constants have been obtained by integration over the spatial electronic coordinates.

IV. BASIS FUNCTIONS AND THEIR SYMMETRY: MATRIX ELEMENTS

A convenient basis for the expansion of the vibration-rotation-spin eigenstates of the Hamiltonian (20) is the following:

$$\chi_n(R) \mathcal{Y}_{M_N}^{(N)N_A, N_B}(\theta'_A, \phi'_A, \theta'_B, \phi'_B) \tau_{M_S}^{(S)S_A, S_B} D_{M_F, K}^{(F)*}(\Phi, \Theta, 0), \quad (21)$$

which is expressed in the BF coordinates. The radial functions $\chi_n(R)$ can be defined either numerically or analytically.²⁹ The internal angular functions are monomer rotation functions (spherical harmonics), coupled via Eq. (15):

$$\mathcal{Y}_{M_N}^{(N)N_A, N_B} = [Y^{(N_A)}(\theta'_A, \phi'_A) \otimes Y^{(N_B)}(\theta'_B, \phi'_B)]_{M_N}^{(N)} \quad (22)$$

and the spin functions are coupled monomer (triplet) spin states:

$$\tau_{M_S}^{(S)S_A, S_B} = [\tau^{(S_A)} \otimes \tau^{(S_B)}]_{M_S}^{(S)}. \quad (23)$$

Although the vector coupling in Eqs. (22) and (23) does not provide eigenstates of the Hamiltonian (20), it can still yield physical insight because N and S may be approximate quantum numbers. So we can observe, for instance, the mixing between the dimer singlet, triplet, and quintet spin states which is caused by the intramolecular spin-orbit and spin-spin coupling operator (16). Moreover, the vector coupling is convenient, because it facilitates the calculation of the matrix elements. The last factors

$$D_{M_F, K}^{(F)*}(\Phi, \Theta, 0)$$

in the basis are normalized Wigner rotation matrix elements in the convention of Ref. 28. The (exact) quantum number M_F is the projection of **F** on the space-fixed z axis and the (approximate) quantum number $K = M_N + M_S$ is the projection of **F** on the body-fixed z axis. The basis (21) in the BF coordinates can be obtained from a SF basis in the same way as for the simpler cases of N₂-N₂ and O₂-X treated in Refs. 7 and 12.

It follows directly from Tables I and II that the basis of Eq. (21) is already symmetry adapted with respect to the nuclear permutations P_{12} and P_{34} . Its parity under these permutations is $(-1)^{N_A}$ and $(-1)^{N_B}$, respectively. The electronic ${}^3\Sigma_g^-$ wave functions are odd under these permutations, see Sec. II. So, if we consider the most abundant ¹⁶O isotopes, which have zero nuclear spin, only basis functions with odd N_A and N_B are allowed.

The basis of Eq. (21) is not yet symmetry adapted with respect to the permutation P_{AB} . The nuclear permutation $P_{13}P_{24}$ which is contained in P_{AB} , see Eq. (1), reverses the BF z axis and P_{AB} acts on the BF coordinates as a twofold rotation about the BF x axis (including the interchange of the labels of the particles in molecule A with those in molecule B). Using the symmetry properties of Clebsch-Gordan coefficients and rotation matrix elements,²⁸ it follows that P_{AB} has the following effect on a general basis function of the type (21):

$$P_{AB} \mathcal{Y}_{M_N}^{(N)N_A, N_B} \tau_{M_S}^{(S)S_A, S_B} D_{M_F, K}^{(F)*} = (-1)^{N_A + N_B + S_A + S_B + F} \mathcal{Y}_{-M_N}^{(N)N_B, N_A} \tau_{-M_S}^{(S)S_B, S_A} D_{M_F, -K}^{(F)*}. \quad (24)$$

Analogously, one derives for the inversion operator E^* , which acts on the BF coordinates as a reflection with respect to the BF yz plane, that

$$E^* \mathcal{Y}_{M_N}^{(N)N_A, N_B} \tau_{M_S}^{(S)S_A, S_B} D_{M_F, K}^{(F)*} = (-1)^{N_A + N_B + N + S + F} \mathcal{Y}_{-M_N}^{(N)N_A, N_B} \tau_{-M_S}^{(S)S_A, S_B} D_{M_F, -K}^{(F)*} \quad (25)$$

In the sequel of this paper we shall restrict ourselves to the electronic triplet ground states of the monomers, i.e., to $S_A = 1$ and $S_B = 1$, and also to their rotational ground states, i.e., to $N_A = 1$ and $N_B = 1$ for ¹⁶O₂ molecules. A symmetry adapted basis for that case is given by

$$\psi_{M_N, M_S, K, M_F}^{N, S, \kappa, F} = \frac{1}{\sqrt{2}} \left[\mathcal{Y}_{M_N}^{(N)} \tau_{M_S}^{(S)} D_{M_F, K}^{(F)*} + (-1)^{\kappa} \mathcal{Y}_{-M_N}^{(N)} \tau_{-M_S}^{(S)} D_{M_F, -K}^{(F)*} \right] \quad (26)$$

and the irreducible representations of the permutation-inversion group G_{16} which are carried by this basis are listed in Table III. The symmetry of the spatial electronic wave function does not interfere with the symmetry adaptation, since this function is invariant under P_{AB} and E^* as long as both monomers remain in their ³Σ_g⁻ ground states. [The exchange symmetry of the electronic wave function required by the exclusion principle, i.e., the permutation symmetry with respect to all electron permutations, not just P_{AB} , has been taken into account already in the electronic structure calculations¹⁷ which led to the exchange coupling parameter J in Eq. (8).] Again considering ¹⁶O nuclei only, which are bosons with zero nuclear spins, it follows that only functions even under $P_{13}P_{24}$, and thus even under P_{AB} , are physically allowed. In Table III this leaves the possibilities A_1^+ and B_1^- . Note that the parity of these functions is determined by $N + S$. M_N takes values from 0 to N ; if $M_N > 0$ then M_S takes values from $-S$ to S and if $M_N = 0$ then M_S takes values

TABLE III. Symmetry of the basis (26) with $N_A = N_B = 1$ and $S_A = S_B = 1$, together with the spatial electronic wave functions, with respect to the PI group G_{16} .

$(N + S)$	$(\kappa + F)$	P_{12}	P_{34}	P_{AB}	E^*	G_{16} irrep.
even	even	+	+	+	+	A_1^+
even	odd	+	+	-	-	A_2^-
odd	even	+	+	+	-	B_1^-
odd	odd	+	+	-	+	B_2^+

from 0 to S . In the case that $M_N = M_S = 0$, we have only even F states.

The Hamiltonian in Eq. (20) has been written in such a form that the calculation of its matrix elements with respect to the basis (21) in the BF frame becomes easy. The radial integrals in these matrix elements are straightforward and they could be calculated by numerical or (partly) by analytic integration methods.²⁹ In our analysis in Sec. V we shall keep the distance R fixed, however, and so we write here only the angular and spin matrix elements. The complete Hamiltonian is diagonal in the exact quantum numbers F and M_F ; in the absence of an external magnetic field the energy of its eigenstates does not depend on M_F . The kinetic energy operator in Eq. (20) has terms which are diagonal in the approximate quantum numbers $N_A, N_B, N, M_N, S_A, S_B, S, M_S$, and $K = M_N + M_S$:

$$b_0 N_A (N_A + 1) + b_0 N_B (N_B + 1) + (2\mu R^2)^{-1} [F(F + 1) + N(N + 1) + S(S + 1) - 2K^2 + 2M_N M_S] \quad (27)$$

and also some off-diagonal terms:

$$\begin{aligned} & - (2\mu R^2)^{-1} [F(F + 1) - K(K \pm 1)]^{1/2} [N(N + 1) - M_N(M_N \pm 1)]^{1/2} \\ & \quad \text{for } \Delta M_N = \pm 1, \Delta M_S = 0, \text{ and } \Delta K = \pm 1, \\ & - (2\mu R^2)^{-1} [F(F + 1) - K(K \pm 1)]^{1/2} [S(S + 1) - M_S(M_S \pm 1)]^{1/2} \\ & \quad \text{for } \Delta M_N = 0, \Delta M_S = \pm 1, \text{ and } \Delta K = \pm 1, \\ & - (2\mu R^2)^{-1} [N(N + 1) - M_N(M_N \pm 1)]^{1/2} [S(S + 1) - M_S(M_S \mp 1)]^{1/2} \\ & \quad \text{for } \Delta M_N = \pm 1, \Delta M_S = \mp 1, \text{ and } \Delta K = 0. \end{aligned} \quad (28)$$

The potential energy terms, expressed in the BF frame, do not depend on the external rotation angles (Θ, Φ) . So, one can directly integrate the Wigner rotation functions in the basis (21) over these angles. Expressing the angular functions (11) occurring in Eqs. (9) and (10) in the BF coordinates $\hat{R}'_A = (\theta'_A, \phi'_A)$, $\hat{R}'_B = (\theta'_B, \phi'_B)$, and $\hat{R}' = (0, 0)$ results in the following integrals:

$$\begin{aligned} (4\pi)^{3/2} \langle \mathcal{Y}_{M'_N}^{(N')N'_A, N'_B} | A_{L_A, L_B, L} | \mathcal{Y}_{M_N}^{(N)N_A, N_B} \rangle &= \delta_{M'_N, M_N} (-1)^{N + N_A + N_B - M_N} [(2L_A + 1)(2L_B + 1)(2L + 1)]^{1/2} \\ & \times [(2N' + 1)(2N'_A + 1)(2N'_B + 1)(2N + 1)(2N_A + 1)(2N_B + 1)]^{1/2} \\ & \times \begin{pmatrix} N'_A & L_A & N_A \\ 0 & 0 & 0 \end{pmatrix} \begin{pmatrix} N'_B & L_B & N_B \\ 0 & 0 & 0 \end{pmatrix} \begin{pmatrix} N' & L & N \\ -M_N & 0 & M_N \end{pmatrix} \\ & \times \begin{Bmatrix} N'_A & N_A & L_A \\ N'_B & N_B & L_B \\ N' & N & L \end{Bmatrix}. \end{aligned} \quad (29)$$

In addition, the spin operator in the Heisenberg exchange coupling term in Eq. (8) yields

$$\langle \tau_{M'_S}^{(S')S_A, S_B} | -2\mathbf{S}'_A \cdot \mathbf{S}'_B | \tau_{M_S}^{(S)S_A, S_B} \rangle = \delta_{S', S} \delta_{M'_S, M_S} [S_A(S_A + 1) + S_B(S_B + 1) - S(S + 1)]. \quad (30)$$

The operator V_{intra} , Eq. (16), leads to

$$\begin{aligned} & \langle \mathcal{Y}_{M'_N}^{(N')N'_A, N'_B} \tau_{M'_S}^{(S')S_A, S_B} | V_{\text{intra}} | \mathcal{Y}_{M_N}^{(N)N_A, N_B} \tau_{M_S}^{(S)S_A, S_B} \rangle \\ &= \frac{1}{3} A (-1)^{S_A + S_B + M'_N + M_S} [(2N' + 1)(2N + 1)(2S' + 1)(2S + 1)]^{1/2} \\ & \times \left[\sum_m \begin{pmatrix} N' & 2 & N \\ -M'_N & m & M_N \end{pmatrix} \begin{pmatrix} S' & 2 & S \\ -M'_S & -m & M_S \end{pmatrix} \right] \\ & \times [(-1)^{N' + N + S' + S} (-1)^{N'_B} \delta_{N'_B, N_B} [(2N'_A + 1)(2N_A + 1)]^{1/2} \\ & \times [S_A(S_A + 1)(2S_A - 1)(2S_A + 1)(2S_A + 3)]^{1/2} \begin{pmatrix} N'_A & 2 & N_A \\ 0 & 0 & 0 \end{pmatrix} \begin{Bmatrix} N' & N & 2 \\ N_A & N'_A & N_B \end{Bmatrix} \begin{Bmatrix} S' & S & 2 \\ S_A & S_A & S_B \end{Bmatrix} \\ & + (-1)^{N'_A} \delta_{N'_A, N_A} [(2N'_B + 1)(2N_B + 1)]^{1/2} \\ & \times [S_B(S_B + 1)(2S_B - 1)(2S_B + 1)(2S_B + 3)]^{1/2} \begin{pmatrix} N'_B & 2 & N_B \\ 0 & 0 & 0 \end{pmatrix} \begin{Bmatrix} N' & N & 2 \\ N_B & N'_B & N_A \end{Bmatrix} \begin{Bmatrix} S' & S & 2 \\ S_B & S_B & S_A \end{Bmatrix}] \quad (31) \end{aligned}$$

and the magnetic dipole-dipole coupling operator V_{dd} , Eq. (17), to

$$\begin{aligned} & \langle \mathcal{Y}_{M'_N}^{(N')N'_A, N'_B} \tau_{M'_S}^{(S')S_A, S_B} | V_{dd} | \mathcal{Y}_{M_N}^{(N)N_A, N_B} \tau_{M_S}^{(S)S_A, S_B} \rangle \\ &= -\sqrt{30} g_e^2 \mu_B^2 R^{-3} \delta_{N'_A, N_A} \delta_{N'_B, N_B} \delta_{N', N} \delta_{M'_N, N} \delta_{M'_S, M_S} (-1)^{S' - M_S} \\ & \times [(2S' + 1)(2S + 1)S_A(S_A + 1)S_B(S_B + 1)(2S_A + 1)(2S_B + 1)]^{1/2} \\ & \times \begin{pmatrix} S' & 2 & S \\ -M'_S & 0 & M_S \end{pmatrix} \begin{Bmatrix} S_A & S_A & 1 \\ S_B & S_B & 1 \\ S' & S & 2 \end{Bmatrix}. \quad (32) \end{aligned}$$

The symbols in large round brackets are 3- j coefficients and those in curly braces are 6- j and 9- j coefficients.²⁸ Note that expression (31) vanishes in the case that $N'_A = N'_B$, $N_A = N_B$, and $S_A = S_B$, when the parity of $(N' + S')$ is different from the parity of $(N + S)$. This reflects the symmetry of the basis under the permutation-inversion operation E^*P_{AB} , see Eqs. (24) and (25).

Using the expressions (29) to (32), one can evaluate the individual contributions, Eqs. (8), (16), and (17), to the spin-dependent O₂-O₂ potential, Eq. (18). All these contributions are diagonal in the approximate quantum number $K = M_N + M_S$. This completes the calculation of the Hamiltonian matrix elements in the basis (21). Transformation to the symmetry adapted basis (26) is straightforward. This leads to a separate secular problem of each physically allowed irreducible representation of the permutation-inversion group.

V. VIBRATIONAL STATES OF THE O₂-O₂ DIMER: ROTATIONAL AND FINE STRUCTURE

With the spin-dependent Hamiltonian from Sec. III and the basis from Sec. IV it is possible, in principle, to calculate all the bound vibrational-rotational-spin states of the O₂-O₂ dimer by diagonalizing the secular matrix. Although the Heisenberg term is strongly anisotropic with respect to the monomer orientations, which leads to very interesting ef-

fects in solid oxygen,^{19,20} it is still the spin-independent term $V_{\text{av}}(\hat{R}_A, \hat{R}_B, \mathbf{R})$ in Eq. (8) that dominates the anisotropy of the potential, in the absolute sense. Therefore, it is mainly this term which determines the equilibrium geometry and the nature of the vibrational states of the O₂-O₂ complex. The problem is, however, that the attractive dispersion contributions to the spin-independent potential [see Eq. (12)] have only been estimated crudely, whereas the other contributions have been obtained from fairly accurate *ab initio* calculations.¹⁷ Since we know from our studies on the N₂-N₂ dimer⁷⁻⁹ that the equilibrium geometry depends on a subtle balance between the attractive and repulsive forces, we must conclude at this stage that we do not know the equilibrium geometry of the O₂-O₂ dimer. Also, from experiment,^{5,6} the O₂-O₂ dimer structure is not known, except perhaps in a solid neon matrix. So in our present studies we retain various possible equilibrium geometries.

The second question which is relevant for this study concerns the nature of the van der Waals vibrations. Because of the uncertainty in the spin-independent potential we have to make some assumptions about this matter also. One extreme would be a nearly rigid dimer with small amplitude vibrations about the equilibrium geometry; another extreme would be a dimer with freely rotating monomers. In the N₂-N₂ dimer the situation is intermediate between these two extremes; the vibrations of the monomers about the equilibrium geometry are characterized by large amplitudes, even in the vibrational ground state. Also in the cases of N₂-Ar^{9,10}

and O₂-Ar¹¹⁻¹⁴ one has found such large amplitude oscillations, or hindered rotations, of the N₂ and O₂ molecules about the T-shaped equilibrium geometries.

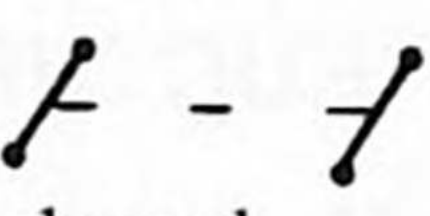
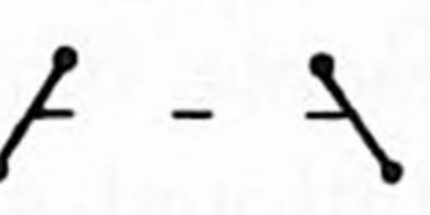
Let us briefly consider the O₂-Ar complex, because this dimer displays fine structure, just as O₂-O₂, although much simpler. The fine structure in the vibrational ground state of the O₂-Ar complex can be completely understood from a hindered internal rotor model.¹¹⁻¹⁴ It can be described by assuming that only the O₂ rotational functions $|N, M_N\rangle = |1, \pm 1\rangle$ are of importance, where M_N is the quantum number associated with the projection of **N** on the BF *z* axis. The functions $Y_{\pm 1}^{(1)}(\theta', \phi')$ have their maximum amplitude at $\theta' = 90^\circ$, so that this situation corresponds with a floppy T-shaped structure. The anisotropy of the spin-independent part of the O₂-Ar potential separates these states from the state $|N, M_N\rangle = |1, 0\rangle$ which has its maximum amplitude at $\theta' = 0^\circ$. On the other hand, this anisotropy is not sufficiently large to strongly admix the rotational functions with higher N (i.e., $N = 3, 5, \dots$) into the vibrational ground state. The fine structure can be calculated by treating the spin-dependent contribution to the potential as a perturbation. In first-order perturbation theory, one obtains the complete qualitative picture with inaccuracies in the splittings that are less than 20%. In order to obtain better quantitative agreement, second-order corrections have to be added.

We adopt a model for the vibrational ground state of the O₂-O₂ dimer which is a generalization of the O₂-Ar model just described. In O₂-Ar, the hindered rotor functions $Y_{\pm 1}^{(1)}(\theta', \phi')$ correspond with a floppy T-shaped structure, while the function $Y_0^{(1)}(\theta', \phi')$ corresponds with a floppy linear structure. For the free O₂-O₂ dimer, where the equilibrium structure is not known, we take both possibilities $Y_{\pm 1}^{(1)}(\theta', \phi')$ and $Y_0^{(1)}(\theta', \phi')$ for each of the O₂ monomers and we

combine these functions in all nine possible ways into symmetrized products, six of which are essentially different, see Table IV. As indicated in this table, these symmetrized products are simply related to the coupled functions of Eq. (22). Also, the various floppy O₂-O₂ structures which are represented by these model functions are described in Table IV. We assume that each of these vibrational model states could be "prepared" by the anisotropic spin-independent potential $V_{av}(\hat{R}'_A, \hat{R}'_B, R)$. The anisotropic potential separates the model states, but we do not know which of these states actually corresponds to the vibrational ground state of O₂-O₂, because of the uncertainty in the long-range dispersion contributions to the potential. The van der Waals bond length R is varied within reasonable limits. As a lower limit we take the nearest neighbor distance $R = 3.2 \text{ \AA}$ in solid α -oxygen and we study the range up to $R = 4 \text{ \AA}$. For each of these model states we calculate the fine structure which is due to the spin-dependent terms in the Hamiltonian. We multiply each vibrational wave function with all the nine spin states that are obtained by coupling the monomer triplet functions, cf. Eq. (23) with $S_A = S_B = 1$, and with the overall rotation functions, cf. the basis in Eq. (21). This provides a basis for each of the vibrational model states in which the Hamiltonian with the spin-dependent coupling terms V_{Heis} , V_{intra} , and V_{dd} can be diagonalized. The result is a first-order picture of the fine structure in each of the model states. The eigenstates of the Hamiltonian will be automatically adapted to the permutation-inversion symmetry, but it is convenient to adapt the basis functions first, using Eq. (26).

The final results for the fine structures are very complex, so we shall explain them by treating the different coupling terms in the Hamiltonian successively. We wish to start with the largest one, but we find that this can be either V_{Heis} or

TABLE IV. Model states for the van der Waals vibrations in O₂-O₂.

State	Hindered rotor wave function			
I	$Y_{\pm 1}^{(1)}(\theta'_A, \phi'_A) Y_{\pm 1}^{(1)}(\theta'_B, \phi'_B)$		=	$\mathcal{Y}_{\pm 2}^{(2)}(\theta'_A, \phi'_A, \theta'_B, \phi'_B)$
II	$\frac{1}{\sqrt{2}} [Y_{\pm 1}^{(1)}(\theta'_A, \phi'_A) Y_0^{(1)}(\theta'_B, \phi'_B) + Y_0^{(1)}(\theta'_A, \phi'_A) Y_{\pm 1}^{(1)}(\theta'_B, \phi'_B)]$		=	$\mathcal{Y}_{\pm 1}^{(2)}(\theta'_A, \phi'_A, \theta'_B, \phi'_B)$
III	$\frac{1}{\sqrt{2}} [Y_{\pm 1}^{(1)}(\theta'_A, \phi'_A) Y_0^{(1)}(\theta'_B, \phi'_B) - Y_0^{(1)}(\theta'_A, \phi'_A) Y_{\pm 1}^{(1)}(\theta'_B, \phi'_B)]$		=	$\mathcal{Y}_{\pm 1}^{(1)}(\theta'_A, \phi'_A, \theta'_B, \phi'_B)$
IV	$\frac{1}{\sqrt{2}} [Y_1^{(1)}(\theta'_A, \phi'_A) Y_{-1}^{(1)}(\theta'_B, \phi'_B) + Y_{-1}^{(1)}(\theta'_A, \phi'_A) Y_1^{(1)}(\theta'_B, \phi'_B)]$		=	$\frac{1}{\sqrt{3}} [\sqrt{2} \mathcal{Y}_0^{(0)}(\theta'_A, \phi'_A, \theta'_B, \phi'_B) + \mathcal{Y}_0^{(2)}(\theta'_A, \phi'_A, \theta'_B, \phi'_B)]$
V	$\frac{1}{\sqrt{2}} [Y_1^{(1)}(\theta'_A, \phi'_A) Y_{-1}^{(1)}(\theta'_B, \phi'_B) - Y_{-1}^{(1)}(\theta'_A, \phi'_A) Y_1^{(1)}(\theta'_B, \phi'_B)]$		=	$\mathcal{Y}_0^{(1)}(\theta'_A, \phi'_A, \theta'_B, \phi'_B)$
VI	$Y_0^{(1)}(\theta'_A, \phi'_A) Y_0^{(1)}(\theta'_B, \phi'_B)$		=	$\frac{1}{\sqrt{3}} [\mathcal{Y}_0^{(0)}(\theta'_A, \phi'_A, \theta'_B, \phi'_B) - \sqrt{2} \mathcal{Y}_0^{(2)}(\theta'_A, \phi'_A, \theta'_B, \phi'_B)]$
State	θ'_A	θ'_B	$\phi'_A - \phi'_B$	Dimer "structure"
I	$\approx 90^\circ$	$\approx 90^\circ$...	free torsional rotation
II	$\approx 90^\circ/0^\circ$	$\approx 0^\circ/90^\circ$	$\approx 0^\circ$	symmetrized T-shaped, tunneling via 
III	$\approx 90^\circ/0^\circ$	$\approx 0^\circ/90^\circ$	$\approx 180^\circ$	symmetrized T-shaped, tunneling via 
IV	$\approx 90^\circ$	$\approx 90^\circ$	$\approx 0^\circ/180^\circ$	H-shaped (D_{2h})
V	$\approx 90^\circ$	$\approx 90^\circ$	$\approx 90^\circ/270^\circ$	crossed (D_{2d})
VI	$\approx 0^\circ$	$\approx 0^\circ$...	linear

V_{intra} , depending on the vibrational model state considered and on the distance R .

The Heisenberg exchange interaction splits every state that is derived from the two triplet O₂ monomers into a singlet, a triplet, and a quintet ($S = 0, 1$, and 2). The singlet-triplet splitting is $2\langle J(R) \rangle$ and the triplet-quintet splitting is $4\langle J(R) \rangle$, where $\langle J(R) \rangle$ is the expectation value of the Heisenberg coupling parameter $J(\hat{R}'_A, \hat{R}'_B, R)$ over the given vibrational model state from Table IV, which is a function of $\hat{R}'_A = (\theta'_A, \phi'_A)$ and $\hat{R}'_B = (\theta'_B, \phi'_B)$. Since this coupling parameter J is an extremely anisotropic function of the molecular orientations (see Sec. III) it is not surprising that the expectation value $\langle J(R) \rangle$ is very different for the various vibrational model states. In some of the states we find a negative $\langle J(R) \rangle$, which means antiferromagnetic coupling (i.e., the singlet state is lowest), whereas in other states $\langle J(R) \rangle$ is positive and the coupling is ferromagnetic (i.e., the quintet is lowest in energy). Moreover, $\langle J(R) \rangle$ decreases steeply in absolute value with increasing R (in fact, exponentially, with exponents varying from 3.6 to 4.2 Å⁻¹ for different orientations, see Refs. 17 and 30). In some cases it changes sign at a certain distance R and the order of the dimer spin states is reversed. Illustrative examples are shown in Figs. 2, 3, and 4, where the splittings due to the Heisenberg exchange interaction are shown in the left-hand column.

The intramolecular spin-orbit and spin-spin coupling represented by V_{intra} is the sum of two monomer terms and so it does not depend on the distance between the monomers. In order to explain the level structure which results from this term only, it is convenient to use (symmetrized) products of monomer spin and rotation functions, as in the analysis of the fine structure in O₂-Ar.¹² In fact, for the rotations of the monomers we have already done this by using the functions of Table IV. The spin functions can be chosen in exactly the same way:

$$|M_{S_A}, M_{S_B}\rangle^\pm = \frac{1}{\sqrt{2}} [|M_{S_A}, M_{S_B}\rangle \pm |M_{S_B}, M_{S_A}\rangle]. \quad (33)$$

As mentioned before, there is a trivial correspondence between these symmetrized product states and the $|S, M_S\rangle$ states (see Table IV) which leaves the expression for the model states, cf. Eq. (26), practically unaltered.

In order to understand the spin structure of these model states, let us start with one monomer A in a certain M_{N_A} state. This corresponds with the situation in O₂-Ar. There we find that for $M_{N_A} = 0$, the $M_{S_A} = 0$ level lies at $-\frac{4}{15}A$ and the $|M_{S_A}| = 1$ level at $\frac{2}{15}A$, where A is the coupling constant of Eq. (14). For $M_{N_A} = 1$, we find $M_{S_A} = 1$ at $-\frac{1}{15}A$ and $M_{S_A} = 0$ at $\frac{2}{15}A$. All these levels are determined by the "diagonal" term of the spin-orbit coupling.^{12,13} This diagonal term alone would make $M_{S_A} = -1$ degenerate with $M_{S_A} = 1$. However, the "off-diagonal" term of the spin-orbit coupling can split the states $|M_{N_A}, M_{S_A}\rangle$ which are symmetrized with respect to inversion, but this term is nonzero only if $M_{N_A} + M_{S_A} = 0$. This results in $M_{S_A} = -1$ levels at $(\frac{1}{15} \pm \frac{2}{5})A$ for $\mp (-)^F$ parity, respectively. A detailed explanation can be found in Refs. 12 and 13.

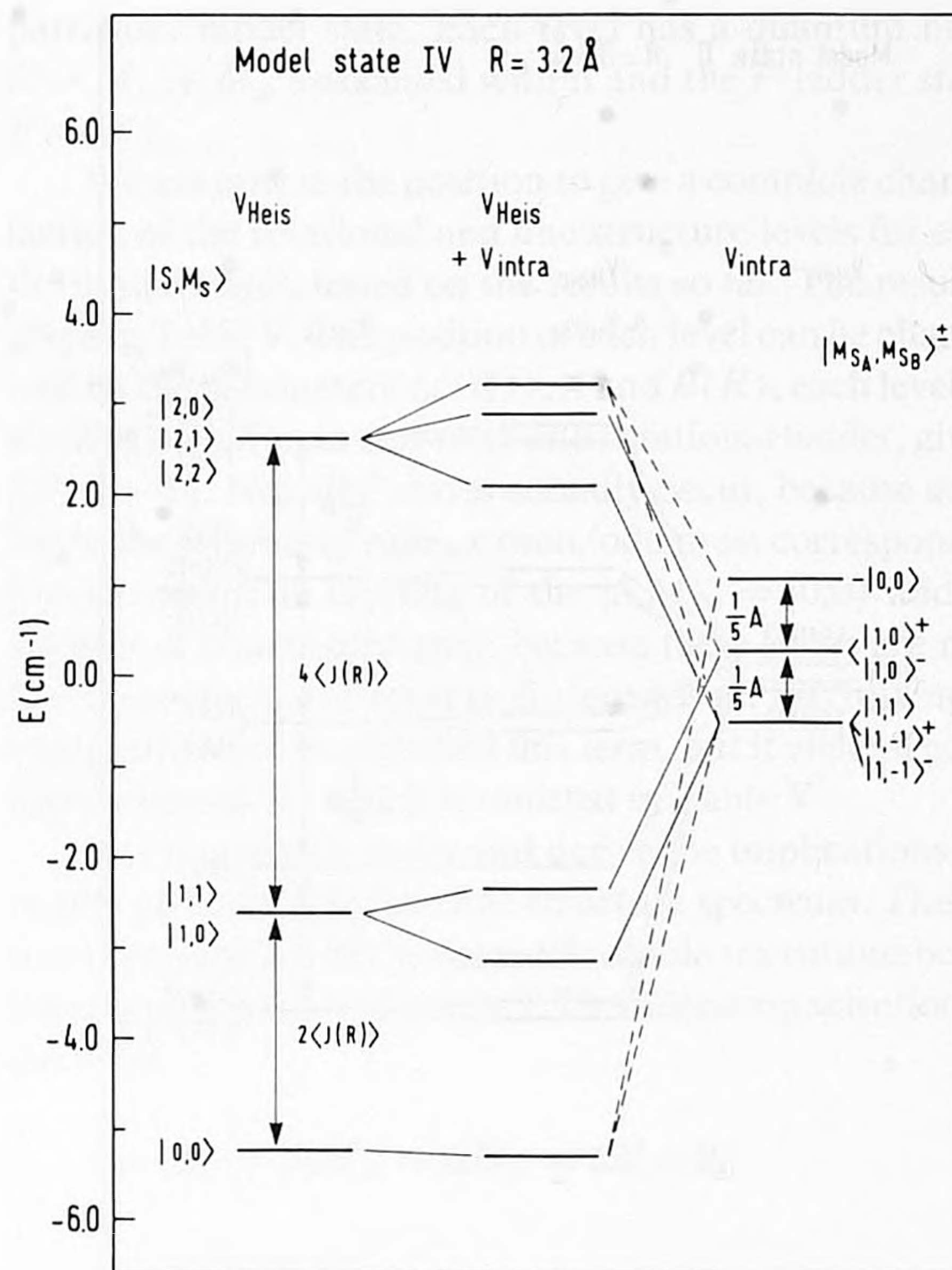


FIG. 2. Spin levels in the O₂-O₂ dimer, vibrational model state IV at $R = 3.2$ Å, derived from the Heisenberg exchange interaction (left column), from the intramolecular spin-coupling terms (right column), and from the combined effect of these interactions (middle column). This is a typical case where the exchange splitting $2\langle J(R) \rangle$ is larger than the intramolecular zero-field splittings $\frac{1}{5}A$.

In most cases, the spin structure of the O₂-O₂ dimer due to V_{intra} only can be understood by summation of these monomer results, but we must keep in mind that the complete vibrational-rotational-spin state must be symmetrized according to Eq. (26). For the moment we disregard the overall rotational quantum numbers F and M_F . Using the model states of Table IV and the spin functions of Eq. (33), a complete state is then characterized by $|M_{N_A}, M_{N_B}\rangle^\pm |M_{S_A}, M_{S_B}\rangle^\pm |\kappa\rangle$. A complete set of states is given by $M_{N_A}, M_{N_B}, M_{S_A}, M_{S_B} = 0, \pm 1$ and $\kappa = 0, 1$, with $M_N = M_{N_A} + M_{N_B} \geq 0$ and the restrictions that if $M_N = 0$ then $M_S = M_{S_A} + M_{S_B} > 0$ and if $M_N = M_S = 0$ then $\kappa = 0$. Using these conditions, the spin structure of the dimer due to V_{intra} can be derived from the O₂-Ar results. For $|M_{N_A}, M_{N_B}\rangle = |0,0\rangle$ (state VI in Table IV) one can simply sum the results of the monomers, which gives a $|M_{S_A}, M_{S_B}\rangle = |0,0\rangle$ level at $-\frac{8}{15}A$, a twofold degenerate level at $-\frac{2}{15}A$ for $|M_{S_A}, M_{S_B}\rangle = |1,0\rangle^\pm$ [see Eq. (33)] and a level at $\frac{4}{15}A$ for $|M_{S_A}, M_{S_B}\rangle = |1,1\rangle$, all these for both $\kappa = 0$ and $\kappa = 1$. For $\kappa = 0$ we have two more levels at $\frac{4}{15}A$ for $|M_{S_A}, M_{S_B}\rangle = |1, -1\rangle^\pm$. Also for $|M_{N_A}, M_{N_B}\rangle = |1,1\rangle$, i.e., in state I in Table IV, we can simply sum the monomer results. The only difference is that the off-diagonal spin-orbit term is not involved here, because of the symmetry. This leads to a fourfold degenerate level at $-\frac{2}{15}A$ for $||M_{S_A}|, |M_{S_B}|\rangle = |1,1\rangle^\pm$, a fourfold degenerate

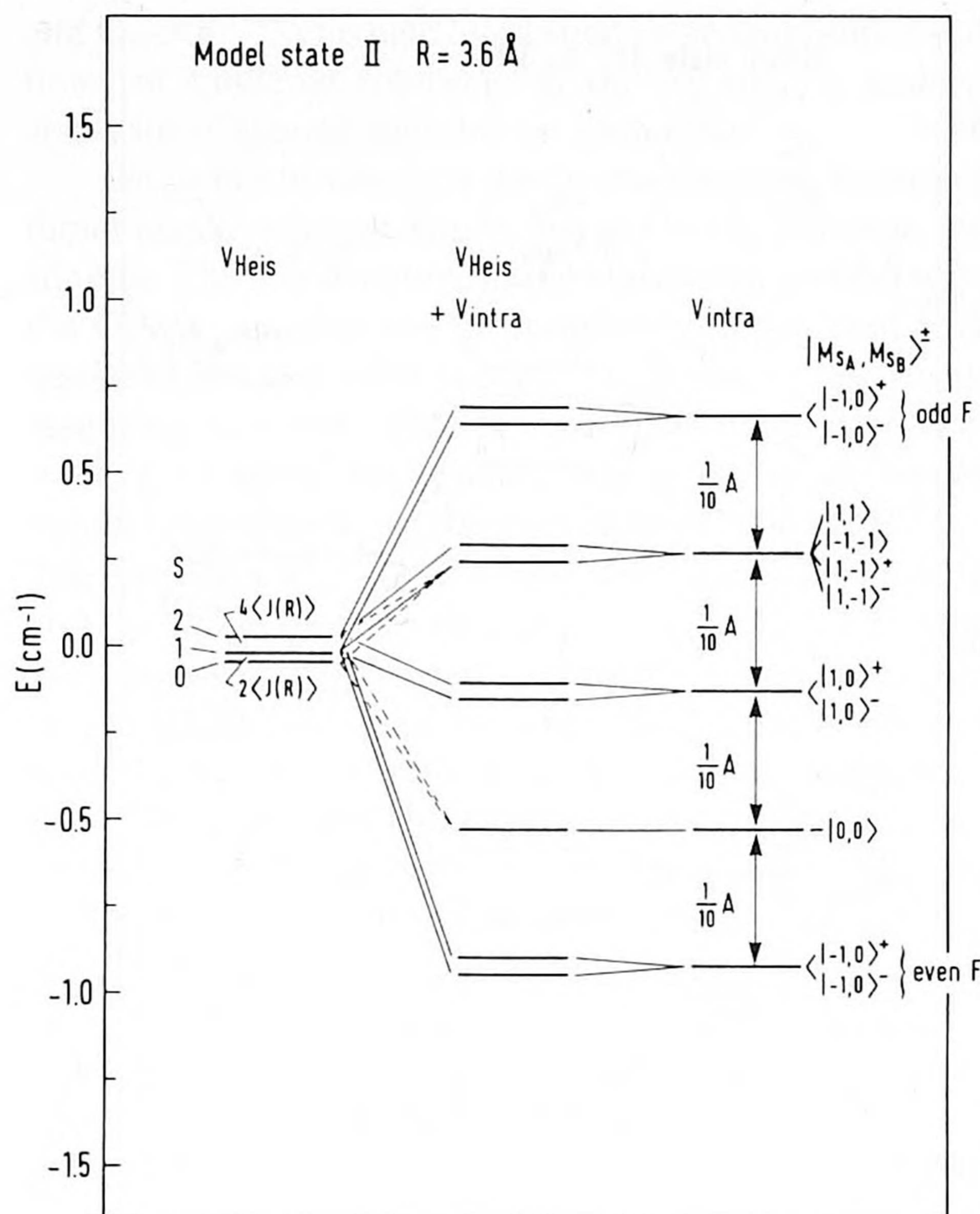


FIG. 3. Spin levels for vibrational model state II at $R = 3.6 \text{ \AA}$, derived from the Heisenberg exchange interaction and the intramolecular spin-coupling terms, as in Fig. 2. $\langle J(R) \rangle$ is much smaller than A in this case, because in model state II there is a sign change in $\langle J(R) \rangle$ for R slightly larger than 3.6 \AA .

level at $\frac{1}{15}A$ for $||M_{S_A}, |M_{S_B}\rangle = |1,0\rangle^\pm$ and a single level at $\frac{4}{15}A$ for $|M_{S_A}, M_{S_B}\rangle = |0,0\rangle$ all these for $\kappa = 0$ and $\kappa = 1$. For $|M_{N_A}, M_{N_B}\rangle = |1, -1\rangle^\pm$, i.e., states IV and V of Table IV, the results are similar. We have a level $|M_{S_A}, M_{S_B}\rangle = |1,1\rangle$ at $-\frac{2}{15}A$, for $\kappa = 0$ and $\kappa = 1$, and two more levels at this energy for $|M_{S_A}, M_{S_B}\rangle = |1, -1\rangle^+$ only for $\kappa = 0$. A twofold degenerate level occurs at $\frac{1}{15}A$ for $|M_{S_A}, M_{S_B}\rangle = |1,0\rangle^\pm$ for $\kappa = 0$ and 1 and a single level at $\frac{4}{15}A$ for $|M_{S_A}, M_{S_B}\rangle = |0,0\rangle$ only for $\kappa = 0$.

The results for $|M_{N_A}, M_{N_B}\rangle = |1,0\rangle^\pm$, i.e., states II and II in Table IV, can be understood by averaging the results of the cases $|0,0\rangle$ and $|1,1\rangle$. In other words, we can assume one monomer in an $M_{N_A} = 1$ and the other in an $M_{N_B} = 0$ state. This leads to a single level at $-\frac{2}{15}A$ for $|M_{S_A}, M_{S_B}\rangle = |0,0\rangle$, a twofold degenerate level at $-\frac{1}{30}A$ for $|M_{S_A}, M_{S_B}\rangle = |1,0\rangle^\pm$, and a fourfold degenerate level at $\frac{1}{15}A$ for $||M_{S_A}, |M_{S_B}\rangle = |1,1\rangle^\pm$, all for $\kappa = 0$ and 1 . For the $|M_{S_A}, M_{S_B}\rangle = |-1,0\rangle^\pm$ states, the off-diagonal spin-orbit terms are nonzero now. These result in a splitting which is half the size of the splitting in the monomer case. We find the $|-1,0\rangle^\pm$ states at $[-\frac{1}{30} + (-)^{\kappa} \frac{1}{5}]A$ for $\kappa = 0$ and $\kappa = 1$, respectively. We have now explained the spin structure of the dimer when only V_{intra} is important. Examples are shown in the right-hand column of Figs. 2, 3, and 4. We conclude this discussion by stressing that the effect of V_{intra} is based on a

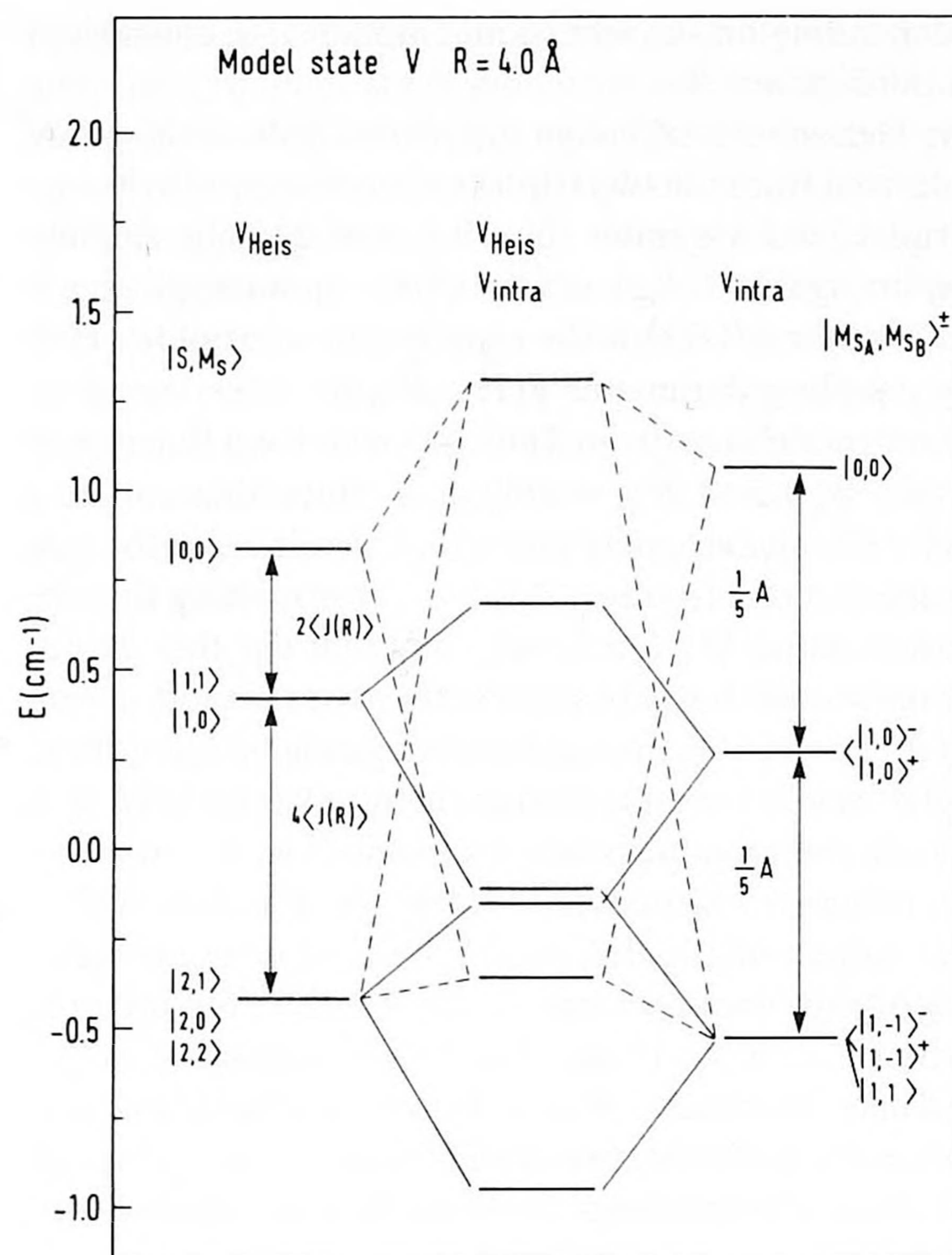


FIG. 4. Spin levels for vibrational model state V at $R = 4.0 \text{ \AA}$, as in Figs. 2 and 3. This is a typical example where the splittings originating from the Heisenberg exchange interaction are comparable in size with the splittings resulting from the intramolecular spin-coupling terms.

first-order analysis only. Just as in O₂-Ar, higher-order effects which introduce the coupling with higher $|N_A, N_B\rangle$ states, may alter the various splittings quantitatively. Although the first-order model is expected to give reasonable results, the quantum labels which are used are only approximate. This is in contrast with the spin labels for the Heisenberg term, which are valid to any order.

The picture which emerges from the combined effect of V_{Heis} and V_{intra} depends on the actual size of $\langle J(R) \rangle$ for a given dimer model state and distance R , relative to the size of the constant A . In Fig. 2, where $\langle J(R) \rangle$ is dominant, the fine-structure states can be characterized as three separate multiplets for $S = 0, 1$, and 2 . The individual levels of the multiplets can be characterized by M_S . One reason for this simple result is that the product spin states of Eq. (33) have a one-to-one correspondence with the $|S, M_S\rangle$ states, except for $|0,0\rangle$ and $|2,0\rangle$, which are mixed. This correspondence is the same as for the monomer rotation functions, cf. Table IV. So the splittings in the individual multiplets, which are a result of V_{intra} , are as described above. The only exceptions are $|M_{S_A}, M_{S_B}\rangle = |0,0\rangle$ and $|1, -1\rangle^+$ which are mixed and recoupled to yield approximately $|S, M_S\rangle = |0,0\rangle$ and $|2,0\rangle$ states.

Figure 4 illustrates a situation where $\langle J(R) \rangle$ and A are comparable in size. Although the resulting picture seems rather complicated, the underlying structure is in fact simple. Because of the one-to-one correspondence between

product spin states $|M_{S_A}, M_{S_B}\rangle^\pm$ and the coupled spin states $|S, M_S\rangle$, we can sum the level energies as obtained from the Heisenberg and the spin-orbit terms separately. As mentioned, the only exception to this rule are the quintet and singlet $M_S = 0$ states, which are mixed depending on the relative size of $\langle J(R) \rangle$ and A .

Next, we add the diagonal spin- (dimer and monomer) rotation coupling terms, which result from the kinetic energy. This introduces a shift of the states $|N, M_N, S, M_S\rangle$, which can be derived from Eq. (27) and is given by

$$B(R) [N(N+1) + S(S+1) - 2M_N^2 - 2M_S(M_N + M_S)]. \quad (34)$$

The size of this shift is determined by the magnitude of the end-over-end rotational constant $B(R) = \hbar^2 / (2\mu R^2)$, which is typically 0.086 cm^{-1} for $R = 3.5 \text{ \AA}$. This is shown in the middle column of Fig. 5.

The last term to be added is the magnetic dipole-dipole interaction, which is typically 0.040 cm^{-1} for $R = 3.5 \text{ \AA}$. The effect of this term is shown in the last column of Fig. 5. It is small enough to be neglected for the analysis concerning the O₂-O₂ dimer.

Also the dependence of the energy levels on the overall angular momentum F can be derived from Eq. (27). According to the diagonal kinetic energy contributions, an end-over-end rotational ladder with rungs at the energies $B(R)F(F+1)$ is put onto each of the nine spin levels for a

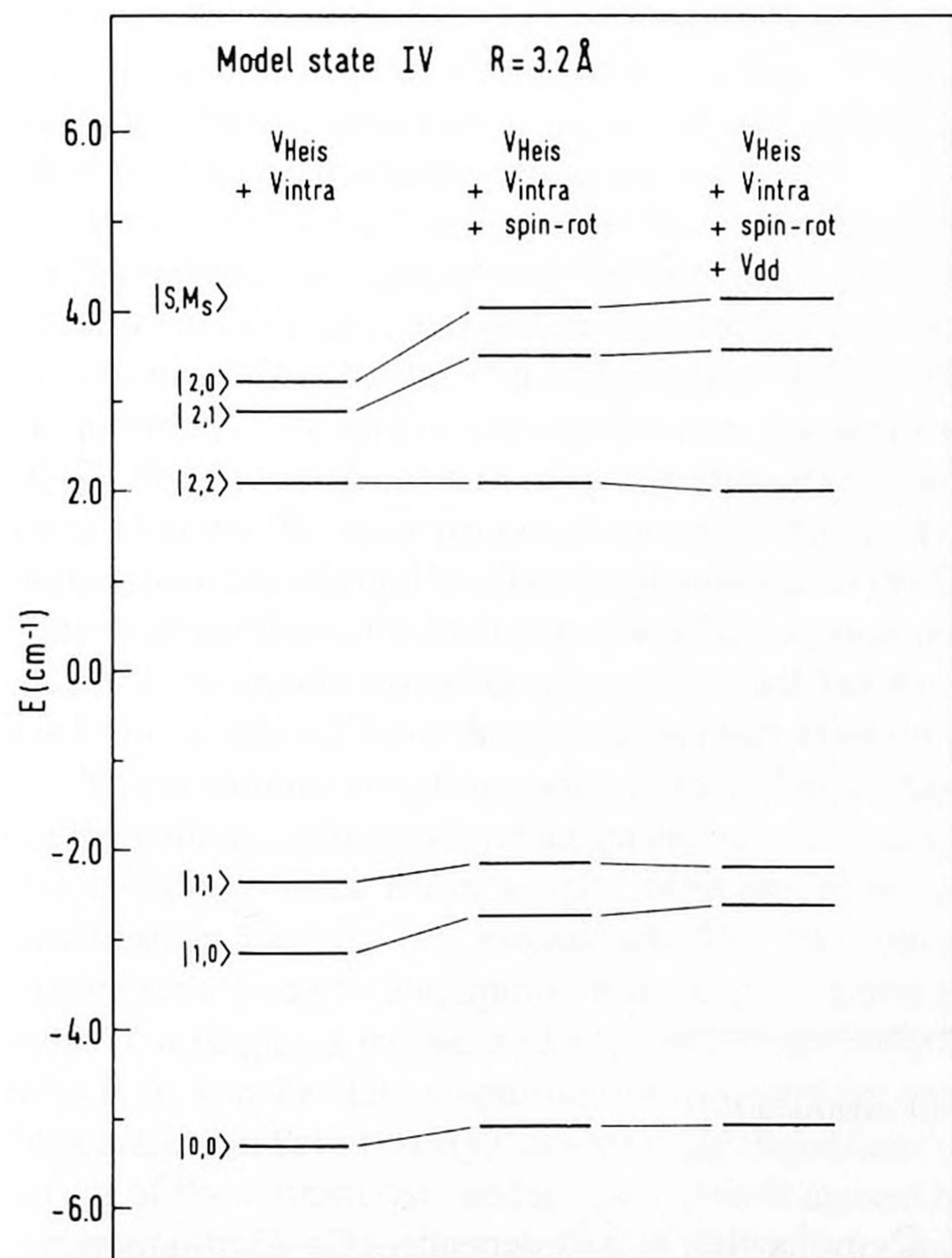


FIG. 5. Effects of the diagonal spin-rotation (kinetic energy) terms and the magnetic dipole-dipole interaction on the spin levels in model state IV at $R = 3.2 \text{ \AA}$, as an example (cf. Fig. 2, middle column).

particular model state. Each level has a quantum number $K = M_N + M_S$ associated with it and the F ladder starts at $F = |K|$.

We are now in the position to give a complete characterization of the rotational and fine structure levels for each of the model states, based on the results so far. The results are given in Table V. The position of each level can be characterized by the parameters $\langle J(R) \rangle$, A and $B(R)$; each level is the starting point for an end-over-end rotational ladder, given by $BF(F+1)$. Not all F states actually occur, because according to the symmetry rules, κ even/odd must correspond with F even/odd. The labeling of the $|S, M_S\rangle = |0,0\rangle$ and $|2,0\rangle$ states is of course arbitrary, because these states are mixed. For these states, the term in B depends on this mixing. It is straightforward to calculate this term, but it yields a complicated expression, which is omitted in Table V.

It is interesting to try and derive the implications of the results of Table V for the fine structure spectrum. This spectrum corresponds to the magnetic dipole transitions between the spin fine structure levels.¹¹ The following selection rules are valid:

- $\Delta N = \Delta M_N = \Delta M_F = \Delta S = 0$,
- $\Delta M_S = 0, \pm 1$,
- $\Delta F = 0, \pm 1$.

A number of conclusions can be made from these selection rules. Because only transitions within one S multiplet are allowed, most of these are independent of $\langle J(R) \rangle$. The only exceptions to this are the mixed $|S, M_S\rangle = |0,0\rangle$ and $|2,0\rangle$ states. Transitions from/to these states thus contain the complete J dependence of the spectrum. The dependence of the fine structure levels on A results in three groups of different spectra for the model states, namely (I, IV, V), (II, III), and VI. In the simple terms of Table IV, this distinguishes between parallel, T-shaped, and linear structures. A distinction between the model states of one group based on the fine structure spectrum, is more subtle.

Until now, we have neglected the off-diagonal spin- (dimer and monomer) rotation coupling terms (also called Coriolis terms¹²) of Eq. (27). These couple the states M_S and $M_S \pm 1$ within one S multiplet. [The other off-diagonal terms of Eq. (27) are zero, because the model assumes that M_N is a good quantum number.] In principle, the splittings within one S multiplet are determined by V_{intra} , so the effect of these off-diagonal terms is not very different from that in O₂-Ar. An exception may be the $|N, |M_N|\rangle = |2,1\rangle$ and $|1,1\rangle$ states (cf. Table IV) where the splitting between the M_S states is halved as compared to O₂-Ar. The effect of the off-diagonal terms is relatively larger in this case. This simple scheme is perturbed of course in case of the $|S, M_S\rangle = |0,0\rangle$ and $|2,0\rangle$ states, which are mixed. Also the effect of the off-diagonal coupling terms thus depends on this mixing.

A complete example of the resulting levels is given in Fig. 6. Note that each F ladder starts at $F = |K| = |M_S + M_N|$. Furthermore, in the case that $M_S = M_N = 0$, we have only even F states.

TABLE V. Fine structure in the various vibrational model states, arising from the dominant terms in the spin-dependent Hamiltonian. The averaged Heisenberg coupling parameter $J = \langle J(R) \rangle$, the intramolecular spin-coupling constant A , and the end-over-end rotational constant $B = B(R)$ are defined in the text.

Model state ^a $ M_{N_A}, M_{N_B}\rangle^\pm$	$ S, M_S\rangle$	b (-) [*]	Energy
I $ 1,1\rangle$	$ 2,2\rangle$	\pm	$-2J - \frac{2}{15}A - 12B$
	$ 2, -2\rangle$	\pm	$-2J - \frac{2}{15}A + 4B$
	$ 2,1\rangle$	\pm	$-2J + \frac{1}{15}A - 2B$
	$ 2, -1\rangle$	\pm	$-2J + \frac{1}{15}A + 6B$
	$ 2,0\rangle^c$	\pm	$J + \frac{1}{15}A - (9J^2 + \frac{1}{25}A^2 - \frac{2}{5}JA)^{1/2}$
	$ 1,1\rangle$	\pm	$2J + \frac{1}{15}A - 6B$
	$ 1, -1\rangle$	\pm	$2J + \frac{1}{15}A + 2B$
	$ 1,0\rangle$	\pm	$2J - \frac{2}{15}A$
II $ 1,0\rangle^+$	$ 0,0\rangle^c$	\pm	$J + \frac{1}{15}A + (9J^2 + \frac{1}{25}A^2 - \frac{2}{5}JA)^{1/2}$
	$ 2,2\rangle$	\pm	$-2J + \frac{1}{15}A - 2B$
	$ 2, -2\rangle$	\pm	$-2J + \frac{1}{15}A + 6B$
	$ 2,1\rangle$	\pm	$-2J - \frac{1}{30}A + 6B$
	$ 2, -1\rangle$	\pm	$-2J - (\frac{1}{30} \mp \frac{1}{3})A + 10B$
	$ 2,0\rangle^c$	\pm	$J - \frac{1}{30}A - (9J^2 + \frac{1}{100}A^2 + \frac{1}{5}JA)^{1/2}$
	$ 1,1\rangle$	\pm	$2J - \frac{1}{30}A + 2B$
	$ 1, -1\rangle$	\pm	$2J - (\frac{1}{30} \mp \frac{1}{3})A + 6B$
III $ 1,0\rangle^-$	$ 1,0\rangle$	\pm	$2J + \frac{1}{15}A + 6B$
	$ 0,0\rangle^c$	\pm	$J - \frac{1}{30}A + (9J^2 + \frac{1}{100}A^2 + \frac{1}{5}JA)^{1/2}$
	$ 2,2\rangle$	\pm	$-2J + \frac{1}{15}A - 6B$
	$ 2, -2\rangle$	\pm	$-2J + \frac{1}{15}A + 2B$
	$ 2,1\rangle$	\pm	$-2J - \frac{1}{30}A + 2B$
	$ 2, -1\rangle$	\pm	$-2J - (\frac{1}{30} \mp \frac{1}{3})A + 6B$
	$ 2,0\rangle^c$	\pm	$J - \frac{1}{30}A - (9J^2 + \frac{1}{100}A^2 + \frac{1}{5}JA)^{1/2}$
	$ 1,1\rangle$	\pm	$2J - \frac{1}{30}A - 2B$
IV $ 1, -1\rangle^+$	$ 1, -1\rangle$	\pm	$2J - (\frac{1}{30} \mp \frac{1}{3})A + 2B$
	$ 1,0\rangle$	\pm	$2J + \frac{1}{15}A + 2B$
	$ 0,0\rangle^c$	\pm	$J - \frac{1}{30}A + (9J^2 + \frac{1}{100}A^2 + \frac{1}{5}JA)^{1/2}$
	$ 2,2\rangle$	\pm	$-2J - \frac{2}{15}A$
	$ 2,1\rangle$	\pm	$-2J + \frac{1}{15}A + 6B$
	$ 2,0\rangle^c$	$+$	$J + \frac{1}{15}A - (9J^2 + \frac{1}{25}A^2 - \frac{2}{5}JA)^{1/2}$
V $ 1, -1\rangle^-$	$ 1,1\rangle$	\pm	$2J + \frac{1}{15}A + 2B$
	$ 1,0\rangle$	$+$	$2J - \frac{2}{15}A + 4B$
	$ 0,0\rangle^c$	$+$	$J + \frac{1}{15}A + (9J^2 + \frac{1}{25}A^2 - \frac{2}{5}JA)^{1/2}$
	$ 2,2\rangle$	\pm	$-2J - \frac{2}{15}A$
	$ 2,1\rangle$	\pm	$-2J + \frac{1}{15}A + 6B$
	$ 2,0\rangle^c$	$+$	$J + \frac{1}{15}A - (9J^2 + \frac{1}{25}A^2 - \frac{2}{5}JA)^{1/2}$
VI $ 0,0\rangle$	$ 1,1\rangle$	\pm	$2J + \frac{1}{15}A + 2B$
	$ 1,0\rangle$	$+$	$2J - \frac{2}{15}A + 4B$
	$ 0,0\rangle^c$	$+$	$J + \frac{1}{15}A + (9J^2 + \frac{1}{25}A^2 - \frac{2}{5}JA)^{1/2}$
	$ 2,2\rangle$	\pm	$-2J + \frac{4}{15}A + 2B$
	$ 2,1\rangle$	\pm	$-2J - \frac{2}{15}A + 8B$
	$ 2,0\rangle^c$	$+$	$J - \frac{2}{15}A - (9J^2 + \frac{4}{25}A^2 + \frac{4}{5}JA)^{1/2}$

^a Cf. Table IV.

^b The states are symmetrized according to Eq. (26). Note that even/odd κ corresponds with even/odd F .

^c These states are mixed.

VI. CONCLUSIONS

We have made a theoretical study of the vibrational-rotational-spin states of the O₂-O₂ dimer in its electronic ground state, which corresponds with two weakly interact-

ing ³Σ_g⁻ O₂ molecules. A spin-dependent O₂-O₂ interaction potential has been derived from earlier *ab initio* calculations¹⁷ and from the O₂ monomer properties and the complete vibrational-rotational-spin Hamiltonian has been constructed. We have discussed the permutation-inversion

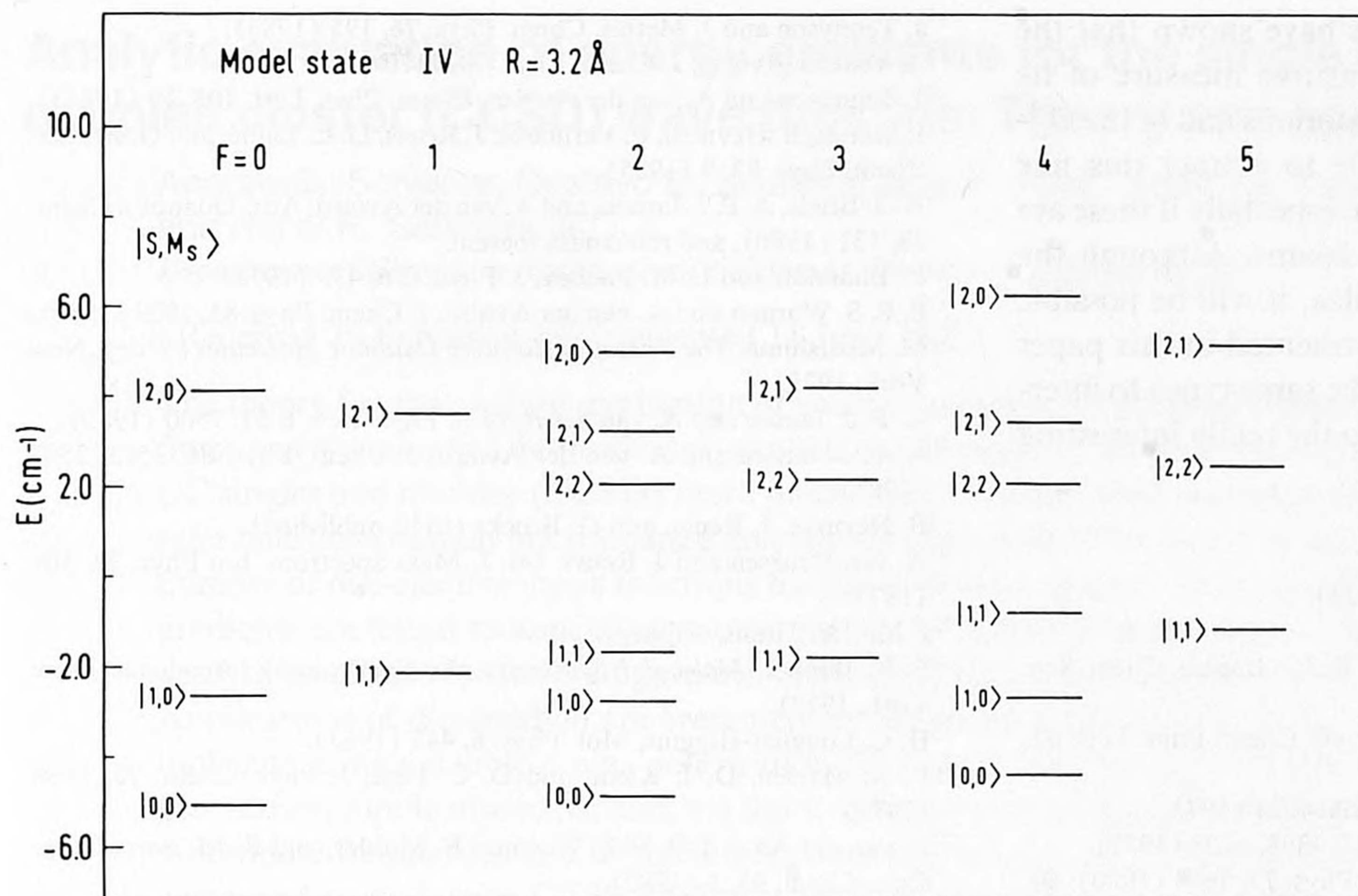


FIG. 6. Spin-rotation levels for model state IV at $R = 3.2 \text{ \AA}$. These levels have been obtained from the right column of Fig. 5 by adding the rotational energy $B(R)F(F+1)$ with $F \geq |K| = |M_N + M_S|$ and the off-diagonal kinetic energy (Coriolis) terms.

symmetry of the system, in the various coordinate systems which are relevant to this problem. Because of the open-shell character of the O₂ monomer and the explicit dependence of the interaction potential on the electronic spin momenta, this symmetry differs from the usual symmetry associated with the nuclear motions in nonrigid molecules or complexes. This study further involves the construction of a convenient basis for the van der Waals vibrations, rotations, and spin states of the O₂-O₂ dimer, which reflects all the exact and approximate quantum numbers of the system and is adapted to its permutation-inversion symmetry.

We have also made some numerical calculations, in order to predict semiquantitatively the spin and rotational fine structure in the vibrational ground state of the complex. Due to the uncertainty in the spin-independent contribution to the interaction potential, the equilibrium geometry of the O₂-O₂ dimer and the nature of its vibrational ground state are not known. We have proposed several vibrational model states which correspond to different geometries of the O₂-O₂ dimer with hindered internal rotations of the monomers. For each of these model states the spin-rotational fine structure has been calculated from the spin-dependent Hamiltonian.

The dominant coupling terms in this Hamiltonian are the Heisenberg exchange interaction and the intramolecular spin-coupling, which is due to spin-orbit and spin-spin interactions in the $^3\Sigma_g^-$ O₂ monomers. The Heisenberg exchange term leads to a coupling of the O₂ monomer triplet states to a singlet, a triplet, and a quintet state of the dimer ($S = 0, 1$, and 2). The magnitude of the splitting between these states, and even its sign, are strongly dependent on the nature of the vibrational model state. This is caused by the extremely strong anisotropy and steep distance dependence of the Heisenberg coupling parameter J , which is known from the *ab initio* calculations.¹⁷ In most cases, the intramolecular spin-coupling term is of comparable size, however, and if the van der Waals bond length R is not too short, this

coupling is even stronger than the Heisenberg exchange interaction. In that case, the fine structure displays a completely different picture. When the intramolecular spin coupling is dominant, the spin levels in the O₂-O₂ dimer can be constructed from the O₂ monomer levels which occur in a hindered rotor case such as O₂-Ar.¹² In any case, the intramolecular spin-coupling terms cause a considerable splitting of the triplet and quintet states, and mixing of the singlet state with the $M_S = 0$ quintet state. Although the resulting level scheme looks rather complex, actually it can still be explained by a simple analytical model containing two parameters: $\langle J(R) \rangle$, the expectation value of the Heisenberg exchange coupling parameter J , and A , the intramolecular spin-coupling (zero-field splitting) constant.

The gross picture originating from these two dominant terms in the spin-dependent Hamiltonian is refined by the smaller terms. The diagonal kinetic energy terms shift the levels by multiples of the end-over-end rotational constant $B(R) = \hbar^2 / (2\mu R^2)$. Moreover, they add to each spin level a rotational ladder with energies $B(R)F(F+1)$, where F is the overall spin and rotation angular momentum. The intermolecular spin-spin (magnetic dipole) interaction leads to additional shifts which are still smaller. Finally, the off-diagonal Coriolis terms split and shift the rungs in the rotational ladders even further. Illustrative examples have been shown in the figures.

So, on the whole we must conclude from these calculations that the spin-rotational fine structure in the O₂-O₂ dimer is very complex. It is certainly not determined by the Heisenberg exchange coupling between the monomer triplets alone. It depends strongly on the equilibrium geometry of the O₂-O₂ dimer and on the nature of its van der Waals vibrations, as modeled in our calculations. Further calculations can be easily performed now, also in the presence of an external magnetic field which will yield the Zeeman splittings. We think, however, that the next move should be made

by experimentalists. Our calculations have shown that the fine structure in O₂-O₂ is a very sensitive measure of its structure, of the nature of its internal motions and of the O₂-O₂ interactions. It should be possible to extract this fine structure from high resolution spectra, especially if these are taken in low-temperature molecular beams. Although the spectra will probably be rather complex, it will be possible via the theory and the calculations presented in this paper (and possibly further calculations of the same type) to interpret these spectra and to gain access to the really interesting properties of O₂-O₂.

¹G. N. Lewis, *J. Am. Chem. Soc.* **46**, 2031 (1924).

²G. C. de Fotis, *Phys. Rev. B* **23**, 4714 (1981).

³R. Boodaghians, P. M. Borrell, P. Borrell, and K. R. Grant, *J. Chem. Soc. Faraday Trans. 2* **78**, 1195 (1982).

⁴R. B. Boodaghians, P. M. Borrell, and P. Borrell, *Chem. Phys. Lett.* **97**, 193 (1983).

⁵C. A. Long and G. E. Ewing, *J. Chem. Phys.* **58**, 4824 (1973).

⁶J. Goodman and L. E. Brus, *J. Chem. Phys.* **67**, 4398, 4408 (1977).

⁷J. Tennyson and A. van der Avoird, *J. Chem. Phys.* **77**, 5664 (1980); **80**, 2986 (1984).

⁸G. Brocks and A. van der Avoird, *Mol. Phys.* **55**, 11 (1985).

⁹G. Brocks and A. van der Avoird, *Proceedings NATO ARW Structure and Dynamics of Weakly Bound Molecular Complexes* (Reidel, Dordrecht, 1987).

¹⁰G. Brocks, *J. Chem. Phys.* (to be published).

¹¹J. Tennyson and J. Mettes, *Chem. Phys.* **76**, 195 (1983).

¹²A. van der Avoird, *J. Chem. Phys.* **79**, 1170 (1983).

¹³J. Tennyson and A. van der Avoird, *Chem. Phys. Lett.* **105**, 49 (1984).

¹⁴J. Mettes, B. Heymen, P. Verhoeve, J. Reuss, D. C. Lainé, and G. Brocks, *Chem. Phys.* **92**, 9 (1985).

¹⁵W. J. Briels, A. P. J. Jansen, and A. van der Avoird, *Adv. Quantum Chem.* **18**, 131 (1986), and references therein.

¹⁶R. Bhandari and L. M. Falicov, *J. Phys. C* **6**, 479 (1973).

¹⁷P. E. S. Wormer and A. van der Avoird, *J. Chem. Phys.* **81**, 1929 (1984).

¹⁸M. Mizushima, *The Theory of Rotating Diatomic Molecules* (Wiley, New York, 1975).

¹⁹A. P. J. Jansen and A. van der Avoird, *Phys. Rev. B* **31**, 7500 (1985).

²⁰A. P. J. Jansen and A. van der Avoird, *J. Chem. Phys.* **86**, 3583, 3597 (1987).

²¹B. Heymen, J. Reuss, and G. Brocks (to be published).

²²A. van Deursen and J. Reuss, *Int. J. Mass Spectrom. Ion Phys.* **23**, 109 (1977).

²³J. Mettes, Thesis, Nijmegen, 1984.

²⁴P. R. Bunker, *Molecular Symmetry and Spectroscopy* (Academic, New York, 1979).

²⁵H. C. Longuet-Higgins, *Mol. Phys.* **6**, 445 (1963).

²⁶F. A. Matsen, D. J. Klein, and D. C. Foyt, *J. Phys. Chem.* **75**, 1866 (1971).

²⁷A. van der Avoird, P. E. S. Wormer, F. Mulder, and R. M. Berns, *Top. Curr. Chem.* **93**, 1 (1980).

²⁸D. M. Brink and G. R. Satchler, *Angular Momentum* (Clarendon, Oxford, 1968).

²⁹G. Brocks, A. van der Avoird, B. T. Sutcliffe, and J. Tennyson, *Mol. Phys.* **50**, 1025 (1983).

³⁰M. C. van Hemert, P. E. S. Wormer, and A. van der Avoird, *Phys. Rev. Lett.* **51**, 1167 (1983).