EFFECTS OF THE POTENTIAL ANISOTROPY ON THE CALCULATED FINE-STRUCTURE SPECTRUM OF O_2He

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Ro-vibrational-spin calculations are performed on the O_2He van der Waals molecule using a recent empirical potential-energy surface. All the bound states of the complex are presented, as are the fine-structure spectrum and weak-field Zeeman splittings of the low-lying states. The V_4 anisotropic term is sometimes found to have a significant ($\approx 10\%$) effect, whilst that of the higher anisotropic terms is negligible ($<1\%$).

1. Introduction

Recently Tennyson and Mettes [1] calculated the fine-structure spectrum and weak-field Zeeman splittings of the O_2Ar van der Waals molecule using two empirically motivated interaction potentials [2,3]. Both these potentials were expressed as Legendre series in cos θ:

$$V(R, \theta) = \sum_{\lambda=0}^{\Lambda} V_\lambda(R) P_\lambda(\cos\theta) , \qquad (1)$$

where R is the distance from O_2 mid-point to the rare gas atom and θ the angle R makes with the O_2 bond. Only terms even in λ contribute by symmetry. Tennyson and Mettes found that whilst the isotropic potential (V_0) left the fine-structure spectrum of O_2 unaltered by complex formation, the effect of the leading anisotropic term was to perturb greatly this spectrum. This perturbation was found to be so great that no direct comparison with the pure O_2 spectrum could be made. Van der Avoird [4] used these results to develop a simple analytic model for the low-lying rovibration-spin states of O_2X complexes (X = rare gas atom).

In view of the importance of the V_2 term, it is interesting to ask whether the neglect of higher anisotropic terms is valid. For O_2Ar there are no potentials available with $\Lambda > 2$. Faubel et al. [5] recently published an empirical He–O_2 anisotropic interaction potential which supplements the isotropic potential of Battaglia et al. [6]. This potential, which was obtained from a multiproperty fit to a variety of experimental data [5,6], contains terms up to $\Lambda = 8$.

In this work we apply the approach of Tennyson and Mettes [1] to the fine-structure spectrum and weak-field Zeeman splittings of O_2He, paying particular attention to the effect of truncating the potential expansion (1). In doing this we hope to assess the reliability of O_2Ar calculations, based as they are, on a truncated potential. This result is of practical interest in view of the problems of finding the lines in the beam resonance experiments currently in progress [7].

For O_2He the barrier to internal rotation is only 12 cm^{-1}, which, as we shall show, is less than the zero-point energy of the ground state. Therefore, the geometry of O_2He is not well defined, in contrast with, for instance, O_2Ar which is (probably) localised in the T-shaped potential well [8]. The model of van

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der Avoird [4] is, in principle, less appropriate for O_2He than for O_2Ar, because of the lower rotation barrier. We shall demonstrate, however, that the results of the present calculations on O_2He can be well understood on the basis of this model.

2. Calculations and results

For details of the method used the reader is referred to the paper of Tennyson and Mettes [1]. This method employs a coupled spherical harmonic basis for the angular coordinates that can be written $|((NS)\,jL)\,JM_J\rangle$. $|NM_N\rangle$ represents the O_2 rotations (by Bose–Einstein statistics N must be odd) and $|SM_S\rangle$ the angular momentum of the spin, for the ground ${}^3\Sigma_g^-$ state of oxygen ($S = 1$). These couple to $|jM_j\rangle$, the total angular momentum quantum numbers of pure O_2 [9]. In the dimer $|jM_j\rangle$ couples with $|LM_L\rangle$, the end-over-end rotations of the complex, to give $|JM_J\rangle$. J, M_J and the parity of $N + L$ are the only good quantum numbers of the complex.

The calculations on He–O_2 used all angular functions with $N \leqslant 7$ which couple to a particular $|JM_J\rangle$. For the R stretching coordinate eight numerical functions were used. These were the lowest functions generated by solving a model one-dimensional problem based on V_0 [10]. As V_0 itself only supports one bound state, it was found necessary to lower V_0 in the model problem by 0.004 E_h for all $R \leqslant 13\ a_0$. This approach was found to give only a small (0.008 cm^{-1}) error in the calculated energy of the lowest state of V_0, and proved a satisfactory method of generating a basis set.

Table 1 gives the energies of the 35 (36 when $\Lambda = 2$) bound states of O_2He obtained by these calculations. As the van der Waals minimum lies at 23.5 cm^{-1} [5], all the bound states of the system lie above half way to dissociation.

The levels calculated using the potential of Faubel et al. [5] truncated at $\Lambda = 4$ are very similar to those calculated with the full $\Lambda = 8$ potential. However, the levels with $\Lambda = 4$ are shifted by up to 0.4 cm^{-1} (12 GHz) in comparison with those computed with only the leading anisotropic term, $\Lambda = 2$.

The (relative) positions of *all* the bound-state levels, as listed in table 1, can be understood via van der Avoird's model [4]. This model is based on the observation that the $N = 1$ rotational ground state of pure O_2 is split into $|M_N| = 1$ levels, which are lowered by the anisotropic O_2–X potential, and $|M_N| = 0$ levels, which are raised (here M_N refers to the component of

Table 1
Calculated rotation-vibration-spin levels [a] for O_2–He in cm^{-1} as a function of the terms in the Legendre series (1)

J	Parity [b]	$\Lambda = 2$	$\Lambda = 4$	$\Lambda = 8$
0	e	−6.160	−5.757	−5.761
1	e	−9.621	−9.270	−9.273
		−6.708	−6.536	−6.533
		−4.529	−4.512	−4.508
		−3.086	−3.148	−3.143
2	e	−7.948	−7.545	−7.549
		−5.719	−5.378	−5.380
		−3.897	−3.771	−3.766
		−2.081	−2.055	−2.051
3	e	−7.465	−7.132	−7.135
		−6.265	−6.033	−6.033
		−4.147	−3.994	−3.994
		−1.860	−1.773	−1.771
4	e	−4.667	−4.372	−4.374
		−2.468	−2.235	−2.236
5	e	−4.064	−3.874	−3.874
		−1.163	−1.031	−1.030
0	o	−10.191	−9.842	−9.844
		−4.766	−4.729	−4.730
1	o	−6.620	−6.277	−6.278
		−5.417	−5.199	−5.196
		−3.614	−3.688	−3.681
2	o	−8.629	−8.255	−8.259
		−7.913	−7.586	−7.588
		−5.747	−5.604	−5.603
		−3.509	−3.445	−3.444
		−1.144	−1.147	−1.145
3	o	−6.580	−6.231	−6.233
		−4.347	−4.058	−4.060
		−1.720	−1.624	−1.620
4	o	−5.986	−5.730	−5.730
		−3.962	−3.780	−3.780
		−1.952	−1.786	−1.787
5	o	−2.233	−1.997	−1.996
		−0.095		
6	o	−1.689	−1.553	−1.552

[a] All energies relative to dissociated He and O_2 in its $j = 1$ state.
[b] e = even, o = odd.

N on the body-fixed z axis, lying along the vector $\boldsymbol{R}$). This splitting destroys the O_2 angular momentum $\boldsymbol{j} = \boldsymbol{N} + \boldsymbol{S}$ as a constant of the motion. However, the z component of $\boldsymbol{j}$ (which is the same as the z component of $\boldsymbol{J} = \boldsymbol{j} + \boldsymbol{L}$) remains an approximately good quantum number (K). The O_2X levels originating from the $|M_N| = 1$ states of O_2 can be ordered in four distinct ladders, each labelled by this quantum number K and a parity index p; the overall parity of the states is given by $(-1)^{p+J+1}$. Those four ladders comprise 27 of the 35 bound states of O_2He, while the remaining 8 states are shown to form two additional ladders, with $|K| = 0$ and $|K| = 1$, originating from the $|M_N| = 0$ states of O_2 (see fig. 1). According to the model [4], the positions of the rungs on the ladders are determined by the expression $BJ(J+1)$ where J is the overall angular momentum quantum number ($J \geqslant |K|$) and B is the end-over-end rotational constant of O_2X, $\langle (2\mu R^2)^{-1} \rangle$. For O_2He we find that $B \approx 7.5$ GHz, about 4 times larger than for O_2Ar; this is mainly the effect of the smaller reduced mass: $\mu_{O_2Ar}/\mu_{O_2He} = 5.0$. The ladders are less regular than they are for O_2Ar. Apparently the rotational constant B of O_2He varies more for the different $|K|$, p states, while the mixing between these states is also stronger than for O_2Ar.

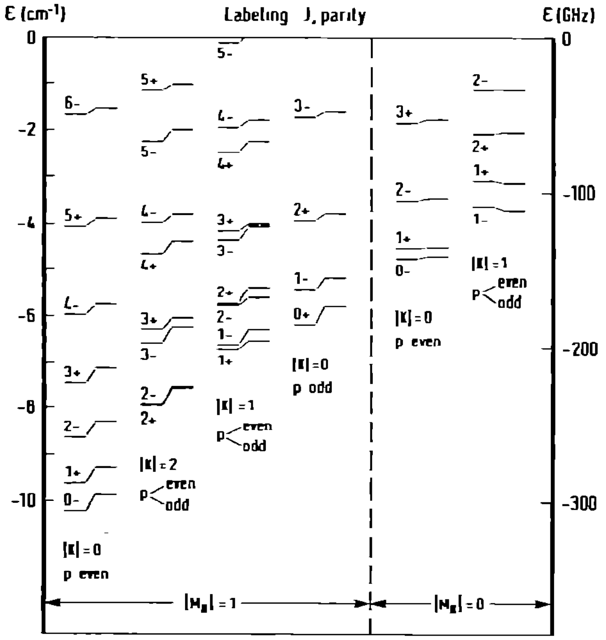

Fig. 1. Calculated rotation-vibration-spin levels for O_2–He ordered according to the model of van der Avoird [4], using the approximate quantum numbers $|M_N|$, $|K|$ and the parity p. The left-hand levels in each rotational ladder originate from the lowest, $\lambda \leqslant 2$, terms in the anisotropic potential (1), the right-hand levels result from the full, $\lambda \leqslant 8$, calculation; the shifts are mainly due to the $\lambda = 4$ term (cf. table 1).

The relative positions of the first four, $|M_N| = 1$, ladders are predicted by the model [4] (in first order) to be: $\epsilon_2 - \epsilon_1 = \frac{4}{5}\lambda_0 - 4B$, $\epsilon_3 - \epsilon_1 = \frac{6}{5}\lambda_0$ and $\epsilon_4 - \epsilon_1 = \frac{8}{5}\lambda_0$, with $\lambda_0 = 59.5$ GHz. In the case of O_2He these differences correspond with the values 17.6, 71.4 and 95.2 GHz, respectively, whereas the full calculations yield roughly 21, 87 and 123 GHz for the gaps between the ladders. According to the same first-order model the two extra $|M_N| = 0$ ladders with $|K| = 0$ and $|K| = 1$ should lie at $\epsilon_5 - \epsilon_1 = \frac{3}{5}V_2 + 2B + \frac{2}{5}\lambda_0$ and $\epsilon_6 - \epsilon_1 = \frac{3}{5}V_2 + \frac{6}{5}\lambda_0$, respectively, i.e. their gap should be $\epsilon_6 - \epsilon_5 = \frac{4}{5}\lambda_0 - 2B \approx 32.6$ GHz. The actual gap between those ladders in the calculated spectrum (fig. 1) is ≈ 36 GHz, while the value of $V_2 = \langle V_2(R) \rangle$ that can be deduced from the distance between the $|M_N| = 0$ and the $|M_N| = 1$ ladders is about 200 GHz ≈ 7 cm^{-1}, in fair agreement with the height of the rotation barrier: 12 cm^{-1} $\approx \frac{3}{2}V_2$. More quantitative agreement with the full calculations can be obtained when the model is extended by second-order corrections as in ref. [4]. The effect of the additional anisotropic terms in the potential, V_λ with $\lambda > 2$, is easily incorporated in these corrections; it does not occur in the first-order results.

Table 2 presents fine-structure transition frequencies for the low-lying states of O_2He. Whilst the spectra obtained with $\Lambda = 4$ and $\Lambda = 8$ are very similar, the transitions calculated with $\Lambda = 2$ are shifted. The sizes of these shifts seem rather irregular: some frequencies are hardly altered by the terms with $\lambda > 2$, other frequencies are shifted by as much as 10%. Looking at the shifts of the levels in fig. 1, however, we can observe the systematics. The (upward) shifts are largest for the $|M_N| = 1$ ladders; some of the $|M_N| = 0$ levels even shift downwards. Within the first group the shifts of the even p states in the $|K| = 2$ and $|K| = 1$ ladders are smaller. Moreover, they generally decrease for the higher levels.

In a magnetic field the $2J+1$ degeneracy of each state is lifted. To first order (or in a weak field), the splittings between the levels is given by $g_e\mu_B\langle S_z\rangle B_z$

Table 2
Frequency of the allowed ($\Delta J = 0, \pm 1$, parity conserved) fine-structure transitions in the low-lying states of O_2He as a function of the terms in the Legendre series (1). Energies of the lower state calculated with $\Lambda = 8$ are given for comparison

J		Parity	Transition frequency (GHz) [a]			Energy (cm^{-1})
$\lvert i\rangle$	$\lvert f\rangle$		$\Lambda = 2$	$\Lambda = 4$	$\Lambda = 8$	
2	2	o	21.47	20.05	20.10	−8.259
1	2	e	50.13	51.71	51.76	−9.273
2	1	o	60.24	59.30	59.37	−8.259
2	3	o	61.43	60.69	60.71	−8.259
2	2	o	86.40	79.46	79.61	−8.259
1	1	e	87.31	82.15	82.15	−9.273
2	1	o	96.30	91.63	91.82	−8.259
1	0	e	103.74	105.33	105.29	−9.273
0	1	o	107.06	106.88	106.92	−9.844
1	2	e	116.97	116.69	116.70	−9.273
2	3	o	128.37	125.82	125.88	−8.259
2	1	o	150.34	136.91	137.23	−8 259
0	1	o	132.12	139.20	139.37	−9 844
1	1	e	152.65	142.66	142.85	−9.273
2	2	o	153.49	144.19	144.33	−8.259
0	0	o	162 64	153.29	153.33	−9.844
1	2	e	171.60	164.85	165.08	−9.273
1	1	e	195.91	183.53	183.75	−9.273
0	1	o	197.15	184.49	184.78	−9.844

[a] 1 cm^{-1} = 29.97925 GHz.

if the z axis is taken as the direction of the magnetic field B. Table 3 gives $\langle S_z\rangle$ values for the low-lying states of O_2He. Again the splittings with $\Lambda = 4$ and $\Lambda = 8$ are very similar and those with $\Lambda = 2$ show occasional marked differences: 30–40% for the lowest two $J = 1$ (even) states.

Table 3
First-order (weak-field) Zeeman splittings of the low-lying states of O_2He calculated as a function of the terms in the Legendre series (1). The energy of the unperturbed state with $\Lambda = 8$ is given for comparison

J	Parity	Energy (cm^{-1})	$\langle S_z\rangle$		
			$\Lambda = 2$	$\Lambda = 4$	$\Lambda = 8$
1	e	9.273	0.0758	0.0579	0.0584
1	e	6.533	0.1498	0.2618	0.2590
2	e	7.549	0.4280	0.4275	0.4275
3	e	7.135	0.2737	0.2806	0.2803
1	o	6 278	0.4403	0.4176	0 4187
2	o	8.259	0.2209	0.1959	0.1964
2	o	7.588	0.2786	0.2975	0.2971
3	o	6.233	0.2726	0.2695	0.2696

3. Conclusions

The fine-structure spectrum and weak-field Zeeman splittings of O_2He have been calculated using different levels of anisotropy in the Legendre series. It has been shown that the calculated spectrum can be interpreted in terms of a simple model [4]. None of the results presented were sensitive to the $\lambda > 4$ terms in the Legendre expansion in line with the observation that the experimental data fitted by Faubel et al. [5] are insensitive to these higher anisotropic terms [11].

Neglecting the $\lambda = 4$ term made only a small (<2%) change to most of the calculated transition frequencies and Zeeman splittings. However, some of these results proved to be more sensitive (≈10%) to neglect of this term. This suggests firstly that if observations of fine structure of Zeeman spectra are to be based on this sort of ro-vibrational-spin calculation, then the V_4 term needs to be included for complete confidence in the results and, secondly, that experimental data on the bound states of O_2He could also yield information about V_4.

Finally, we consider the accuracy of these calculations Errors can arise from three sources. from incompleteness of the variational basis, from approximations in the hamiltonian and from inaccuracies in the potential. Convergence tests on our basis showed that the basis set used was well saturated so that this is unlikely to be a significant source of error.

The hamiltonian used contains two approximations above the usual Born–Oppenheimer approximation. Firstly the effects of the O_2 vibrations were neglected, an approximation which has been shown to be very good for the He–HF van der Waals molecule [12]. Secondly the fine-structure term was assumed to be the same as in the O_2 molecule [8]. This assumption is physically reasonable because of the weakness of the van der Waals interactions. It is expected to hold even in solid O_2, where the "molecular" fine-structure term is responsible for the dominant magnetic anisotropy in the antiferromagnetically ordered α-phase [13]. The analogous approximation was used successfully by Reuss and co-workers to fit the hyperfine levels of van der Waals complexes of H_2 [14]. However, final assessment of this assumption can only be made by direct comparison with experiment.

The potential-energy surface is usually the major source of error in ro-vibrational calculations. In this work we have used an empirical surface for which high accuracy is claimed – the position of the minimum to within 2% and the anisotropy in the well region to within 5% [5] – and it is thus hoped that the results presented reflect this accuracy.

References

[1] J. Tennyson and J. Mettes, Chem. Phys. 76 (1983) 195.
[2] V. Mingelgrin and R.G. Gordon, J. Chem. Phys. 70 (1979) 3828.
[3] F. Pirani and F. Vecchiocattivi, Chem. Phys. 59 (1981) 387.
[4] A. van der Avoird, J. Chem. Phys. 79 (1983) 1170.
[5] M. Faubel, K.H. Kohl, J.P. Toennies and F.A. Gianturco, J. Chem. Phys. 78 (1983) 5629.
[6] F. Battaglia, F.A. Gianturco, P. Casavecchia, F. Pirani and F. Vecchiocattivi, Faraday Discussions Chem. Soc. 73 (1982) 257.
[7] J. Mettes, D Lainé and J. Reuss, private communication.
[8] G. Henderson and G E. Ewing, J. Chem. Phys. 59 (1973) 2280.
[9] M. Mizushima, The theory of rotating diatomic molecules (Wiley, New York, 1975) ch. 9.
[10] G. Brocks and J. Tennyson, J. Mol. Spectry. 99 (1983) 263.
[11] M. Faubel, private communication.
[12] J Tennyson and B.T. Sutcliffe, J. Chem. Phys. 79 (1983) 43.
[13] G.C. DeFotis, Phys. Rev. B23 (1981) 4714.
[14] J. Verberne and J. Reuss, Chem. Phys. 50 (1980) 137; 54 (1981) 189;
M. Waaijer, M. Jacobs and J. Reuss, Chem. Phys. 63 (1981) 247, 257;
M. Waaijer and J. Reuss, Chem. Phys. 63 (1981) 263.