The Radial Dependence of Non-mechanical Properties of Diatomic Molecules

J. F. Ogilvie

Contribution from Department of Chemistry, National Tsing Hua University, Hsinchu, Taiwan 30043

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Résumé

Une procédure est suggérée pour déterminer la dépendance radiale des interactions spin-spin et spin-rotation de molécules diatomiques dont les états électroniques sont $^3\Sigma$. La méthode est appliquée à O_2 X $^3\Sigma_g^-$, et les résultats sont valides dans les limites des distances internucléaires $1.12 < R/10^{-10}$ m<1.31.

Abstract

A procedure is presented for the determination of the radial dependence of the spin-spin and spin-rotational interactions of diatomic molecules in $^3\Sigma$ electronic states. The method is applied to O_2 X $^3\Sigma_g^-$, and the results are valid in the range of internuclear separation $1.12<R/10^{-10}$ m<1.31.

Introduction

In a previous report (1), we suggested a further application of the formula

$$Y_{kl} = U_{kl}\,\mu^{-(k+2l)/2}[1 + m_e(\Delta^a_{kl}/M_a + \Delta^b_{kl}/M_b)] \qquad [1]$$

developed by Ross *et al.* (2) for the correction of isotopic mass effects on the mechanical properties of diatomic molecules, specifically the coefficients Y_{kl} in the formula for the vibration-rotational energies

$$E(v,J) = \sum_{k=0}\sum_{l=0} Y_{kl}\,(v+1/2^k\,[J(J+1)]^l \qquad [2]$$

according to the formulation of Dunham (3). Our application was to the non-mechanical properties, namely the spin-spin interaction parameter, λ, and the spin-rotational interaction parameter, γ, of homonuclear diatomic molecules in $^3\Sigma$ electronic states, in particular O_2 in its ground state. Tiemann had previously made a similar application to a heteronuclear molecule, SO(4). Recently, we have developed a method to determine the radial dependence of the adiabatic and nonadiabatic corrections to the vibration-rotational energy coefficients (5). These corrections are primarily determined as the spectral parameters $\Delta^{a,b}_{kl}$ appearing in eq. 1, but they may be transformed to the form Z_{kl} in the extended term equation

$$E(v,J) = \sum_{k=0}\sum_{l=0} (Y_{kl} + Z^a_{kl} + Z^b_{kl})\,(v+1/2)^k[J(J+1)]^l \qquad [3]$$

In that work, we presented a set of relations for Z_{kl} in terms of both the parameters c_j in the potential-energy function (6)

$$V(z) = c_0\,z^2\,(1 + \sum_{j=1} c_j\,z^j) \qquad [4]$$

in which the internuclear displacement variable is defined as

$$z = 2\,(R - R_e)\,/\,(R + R_e) \qquad [5]$$

in terms of the instantaneous R and equilibrium R_e distances, and the parameters h_j in the additional radial function

$$K(z) = \sum_{j=0} h_j\,z^j \qquad [6]$$

to take into account the adiabatic and nonadiabatic effects collectively. In this paper, we apply a similar formalism to determine the radial dependence of the spin-spin and spin-rotational interactions of $^{16}O_2$ × $^3\Sigma_g$ for which the available spectral information permits such a demonstration of the general method.

Table 1. Basic Data for O_2 X $^3\Sigma_g$ Required for the Analysis.

		$^{16}O_2$	$^{18}O_2$
λ_e	$Z_{0,0}/m^{-1}$	198.233739±6.7×10^{-5}	198.233526±2.0×10^{-5}
α_λ	$Z_{1,0}/m^{-1}$	0.482777±6.7×10^{-5}	0.452093±1.7×10^{-5}
λ_D	$Z_{0,1}/10^{-4}\ m^{-1}$	1.8623 ±0.0033	1.6528 ±0.0020
λ_D	$Z_{0,2}/10^{-9}\ m^{-1}$	1.134 ±0.50	0.647 ±0.17
$\alpha_{\lambda D}$	$Z_{1,1}/10^{-5}\ m^{-1}$	1.651 ±0.020	1.347 ±0.013
$\alpha_{\lambda DD}$	$Z_{1,2}/10^{-10}\ m^{-1}$	6.00 ±5.0	4.20 ±1.0
γ_e	$Z_{0,0}/m^{-1}$	-0.841528±6.7×10^{-5}	-0.747798±1.0×10^{-5}
α_γ	$Z_{1,0}/10^{-3}\ m^{-1}$	-2.0207 ±0.0067	-1.714 ±0.010
γ_D	$Z_{0,1}/10^{-7}\ m^{-1}$	-8.046 ±0.067	-6.47 ±0.13
$\alpha_{\gamma D}$	$Z_{1,1}/10^{-9}\ m^{-1}$	-27.0 ±13.	-4.0 ±13.
	B_e/m^{-1}	144.55827 ±0.00013	128.463315±0.00017
	$\gamma_p/10^{-3}$	1.82990317±2.5×10^{-6}	1.72504112±3.3×10^{-6}
	c_1	-2.01021±0.0087	
	c_2	2.11429±0.0024	
	c_3	-0.13343±0.037	

Treatment and Results

Analysis of the data from experimental measurements of the far-infrared and laser-magnetic-resonance spectra of $^{16}O_2$ and $^{18}O_2$ in two vibrational states $v=0$ and $v=1$ enabled the determination of significant values of equilibrium parameters of the spin-spin and spin-rotational interactions and of their dependence on isotopic mass (7). In Table I, we list the values of these parameters for $^{16}O_2$ and $^{18}O_2$ and the designation of the equivalent parameters Z^λ_{k1} and Z^γ_{k1}, and also the values of the potential-energy coefficients c_j and of other parameters (including $\gamma_p = 2\ B_e/\omega_e$) required for our analysis.

When we applied serially the relations for Z^λ_{k1} (5) including a correction term for $Z^\lambda_{0,0}$ (8) to the data for the spin-spin interaction (7), we obtained the values of the coefficients H^λ_j (h^λ_1 from $Z^\lambda_{0,1}$, h^λ_2 from $Z^\lambda_{1,0}$, *etc.*). In order to obtain a value for h^λ_4 we required an additional expression, $Z_{1,2}$, beyond those already published (5,8):

$$\begin{aligned} Z_{1,2} = \gamma^5\,[&h_1\,(-405/8\ c_1^2 - 567/\ 16\ c_1^3 + 99/2\ c_1c_2 \\ &- 243/8\ c_1 + 33/2\ c_2 - 15\ c_3 - 39/4) \\ &+ h_2\,(189/8\ c_1^2 + 45/2\ c_1 - 15\ c_2 + 9/2) \\ &+ h_3\,(-27/2\ c_1 - 9) + 6\ h_4] \end{aligned} \qquad [7]$$

The values presented in Table II represent the results from the analysis of both the statistically weighted data for $^{16}O_2$ and $^{18}O_2$, together. Because values of $Z^\lambda_{0,2}$ are also available, an alternative but less accurate value $h^\lambda_2 = (19.5 \pm 19)\ m^{-1}$ may also be derived. The stated uncertainties indicate one standard error propagated ultimately from the experimental measurements of transition frequencies.

Table II. Values of the Coefficients of the Radial Functions for the Spin-spin and Spin-rotational Interactions of O_2 X $^3\Sigma_g$.

j	h^λ_j/m^{-1}	$h^\gamma_j/10^{-3}$
0	198.2290 ± 0.0027	-5.821377 ± 8x10^{-5}
1	55.56 ± 0.06	-1.668 ± 0.35
2	39.08 ± 0.42	-0.970 ± 0.090
3	647.8 ± 9.3	0.33 ± 2.3
4	2526 ± 1250	

We proceeded analogously in the treatment of the data for the spin-rotational interaction (7) except that, because the data are fewer than for the spin-spin interaction, no correction term for $Z^\gamma_{0,0}$ was applicable. A further distinction from the case of the spin-spin interaction is that, because the spin-rotational parameter $\gamma_e = Z^\gamma_{0,0}$ depends on mass (for isotopic molecules), an additional factor, B_e (the equilibrium rotational parameter), was incorporated into each expression for Z^γ_{k1}. In this case, the derived values of the coefficients h^γ_j are dimensionless. These results for h^γ_j are also listed in Table II.

The range of validity of these radial functions $K^\lambda(z)$ and $K^\gamma(z)$ should be approximately between the classical vibrational turning points of the state with the greatest value of the vibrational quantum number v for which the data have been used in the analyses. Because, for the available data, the highest vibrational state has $v=1$, the range of validity is therefore $1.12 < R/10^{-10}\ m < 1.31$.

Discussion

To the author's knowledge, this work presents the first determination of the radial dependence of these spin-spin and spin-rotational interactions primarily from experimental data for molecules in $^3\Sigma$ states. The method is of course applicable to other Σ states of greater multiplicity. A fundamental assumption of this procedure is that the measured values of the parameters Z_{k1} with $1>0$ reflect essentially only the centrifugal effects on the interaction and therefore include negligible contributions form nonadiabatic effects. Perhaps in the case of the spin-spin interaction, a rough test of this assumption is possible because the value of h^λ_2 obtained from $Z^\lambda_{0,2}$ is in satisfactory agreement (within about one standard error) with that obtained from the purely vibrational effect in $Z^\lambda_{1,0}$. On the other hand, the small but significant deviations from the mass scaling law in a few parameters (5,7), notably $Z^\lambda_{0,0}$ and $Z^\lambda_{1,0}$, indicate that interference from non-adiabatic effects may not be entirely negligible.

Although in the case of the spin-rotational interaction, the above test is not possible because of a lack of an experimental value of $Z^{\gamma}_{0,2}$, one can, however, estimate such a value by means of the known expression for $Z^{\gamma}_{0,2}$ and the values of h^{γ}_{1} and h^{γ}_{2} in Table II. The result predicted for $^{16}O_2$ is $Z^{\gamma}_{0,2} = -4{,}3 \times 10^{-12}\ m^{-1}$.

The advantage of using the functional dependence in terms of the variable z is that additional terms in the representations of $K^{\lambda}(z)$ and $K^{\gamma}(z)$ as power series may be generated, by means of analytic continuation from the known dependence of the spin-spin and spin-rotational interactions on distance in the approaches to the separate atoms at large R and to the united atom at small R (9). Because the available spectral data dictate only a relatively small range of the validity of the generated functions $K^{\lambda}(z)$ and $K^{\gamma}(z)$, it seems premature to extend the present functions by means of such asymptotic conditions.

The accuracy of the results depends both on the accuracy of the frequency measurements (7), and on the model used in the interpretation of these observations. Because data were available only for the two vibrational states $v=0$ and $v=1$, a linear model had to be used in the analysis (7). Thus, the precision of the resulting parameters may exceed their accuracy (5). For the same reason, not taking into account the non-adiabatic effects (5,7) may also lead to some inaccuracy to the radial functions. Despite these limitations, until data from other vibrational states become available, the present results may be useful as a test of theoretical predictions (for instance, from *ab initio* quantum computations).

In summary, the spectral data for the spin-spin and spin-rotational interactions of O_2 have been inverted to produce the corresponding radial functions within a range near the equilibrium internuclear separation. The method may be extended to other molecules in $^3\Sigma$ states, such as the ground electronic state of SO, or to molecules with Σ electronic states of greater multiplicity, provided that spectral data enable the determination of parameters reflecting the vibrational and rotational dependence of each interaction.

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