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The Inversion of Spectral Data for the Spin–Orbital Interaction in the Hydroxyl Radical OH $X\,^2\Pi_i$

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Abstract

Experimental data for the spin–orbital interaction and Λ-doubling parameters of the OH radical in the ground electronic state $X\,^2\Pi_i$ are analysed in order to extract the radial dependence of the corresponding functions. The procedure is compared with those employed in previous work.

1. Introduction

According to Hund's case (a) of the coupling of various angular momenta of a diatomic molecule, an electronic state designated $^2\Pi$ consists of two electronic substates, $^2\Pi_{1/2}$ and $^2\Pi_{3/2}$, essentially differing only in their values of the total electronic angular momentum Ω. For a free molecule belonging to this case, an electronic transition from a state with a value of the vibrational quantum number v within one electronic substate to a state with the same value of the quantum number v in the other electronic substate is not directly observable if all the other quantum numbers have their minimum values, but the energies (expressed as wavenumbers) of such hypothetical transitions may be deduced by means of analysis of either the vibration-rotational spectra between the substates or rovibronic spectra involving a further electronic state. These transition energies are designated A_v, a parameter related to the interaction between the spin and orbital angular momenta in each substate.

Within the classical model of the diatomic molecule introduced into quantum mechanics by Born and Oppenheimer [1], the dependence of A_v upon the quantum number v reflects the dependence of a function of internuclear separation R, the spin–orbital interaction function $A(R)$. The vibrational dependence of such a function reflects some radial dependence because the vibrational amplitude, the region between the classical turning points, varies with the vibrational quantum number v according to the potential-energy function $V(R)$. The effective value of the spin–orbital interaction parameter A_v is then the expectation value of the radial function essentially over the range of the vibrational amplitude:

$$A_v = \langle v|A(R)|v\rangle. \tag{1}$$

Taking the equilibrium internuclear separation R_e as the expansion centre, we express the radial dependence in a power series of the argument x,

$$x \equiv (R - R_e)/R_e \tag{2}$$

the reduced displacement coordinate in the conventional theory due to Dunham [2, 3]; thus

$$A(x) = \sum_{j=0} A_j x^j. \tag{3}$$

The number of coefficients A_j in this radial function that are required to fit a given set of experimental data depends on the extent of the variation of A_v with v. We make an expansion A_v in a power series of argument $(v + 1/2)$:

$$A_v = \sum_{k=0} A^{(k)}(v + 1/2)^k. \tag{4}$$

The relationship between the parameters A_j and $A^{(k)}$ depends on the potential-energy function and therefore on the parameters a_j in the Dunham [2] equation:

$$V(x) = B_e\gamma_p^{-2}x^2\left(1 + \sum_{j=1} a_j x^j\right) \tag{5}$$

in which B_e is the equilibrium rotational parameter

$$B_e = h/(8\pi^2 c\mu R_e^2) \tag{6}$$

with μ the reduced mass and the expansion parameter $\gamma_p = 2B_e/\omega_e$ is the ratio of the limiting rotational and vibrational intervals.

In the case of the hydroxyl radical OH in the electronic ground state $X\,^2\Pi_i$, Coxon and Foster [4] found (and this result is confirmed) that a cubic function A_v, with $A^{(k)}$ up to $k = 3$, is required to fit the available spectral data within the range $0 \leqslant v \leqslant 10$ with statistical significance. Therefore if we retain all terms up to γ_p^3 in order to maintain consistency of order in the treatment of the data, we have the following expressions for $A^{(k)}$, taken from the expectation values [5] of x to the appropriate powers:

$$A_v = \sum_{k=0} A^{(k)}(v + 1/2)^k = \langle v|A(x)|v\rangle = \sum_{j=0} A_j\langle v|x^j|v\rangle \tag{7}$$

$$\begin{aligned}
A^{(0)} = {} & A_0 + \gamma_p^2[A_1(-21/32a_1^3 + 23/16a_1a_2 - 15/16a_3) \\
& + A_2(7/16a_1^2 - 3/8a_2) - 7/16a_1A_3 + 3/8A_4] \\
A^{(1)} = {} & \gamma_p[-3/2a_1A_1 + A_2] + \gamma_p^3[A_1(-31185/2048a_1^5 \\
& + 14259/256a_1^3a_2 - 5145/128a_1^3a_3 - 4677/128a_1a_2^2 \\
& + 795/32a_1a_4 + 715/32a_2a_3 - 175/16a_5) \\
& + A_2(10395/1024a_1^4 - 3213/128a_1^2a_2 + 475/32a_1a_3 \\
& + 335/64a_2^2 - 75/16a_4) + A_3(-1155/128a_1^3 \\
& + 459/32a_1a_2 - 95/16a_3) + A_4(459/64a_1^2 \\
& - 67/16a_2) - 95/16a_1A_5 + 25A_6] \\
A^{(2)} = {} & \gamma_p^2[A_1(-45/8a_1^3 + 39/4a_1a_2 - 15/4a_3) \\
& + A_2(15/4a_1^2 - 3/2a_2) - 15/4a_1A_3 + 3/2A_4] \\
A^{(3)} = {} & \gamma_p^3[A_1(-19035/512a_1^5 + 7545/64a_1^3a_2 - 2175/32a_1^2a_3 \\
& - 2055/32a_1a_2^2 + 255/8a_1a_4 + 225/8a_2a_3 - 35/4a_5) \\
& + A_2(6345/256a_1^4 - 1575/32a_1^2a_2 + 175/8a_1a_3
\end{aligned}$$

$$+ 85/16a_2^2 - 15/4a_4) + A_3(-705/32a_1^3 + 225/8a_1a_2 - 35/4a_3) + A_4(225/16a_1^2 - 17/4a_2) - 35/4a_1A_5 + 5/2A_6]. \qquad (8)$$

First of all, these equations make clear that the coefficients A_j with j up to 6 are required to express the radial dependence of A_v up to $v = 10$, because terms with $A^{(k)}$ up to $k = 3$ are required. Secondly, although $A^{(0)}$ is given by A_0 to a good approximation (because $\gamma_p \sim 10^{-2}$ for OH), each successive quantity $A^{(k)}$ involves two further coefficients A_j. Therefore these expectation values do not alone suffice to determine the coefficients A_j, because the successive pairs of coefficients A_{odd} and A_{even} are completely correlated with each other. This conclusion applies equally well to any attempt to determine the values of the coefficients A_j either through any analytic relations, such as those above, or by means of purely numerical methods, such as those based on the RKR procedure. The results in eqs. (8) constitute an analytic proof of Watson's [6] conjecture about their applicability to general radical functions.

In both previous attempts [4, 7] to determine the radial function $A(R)$ for the spin-orbital interaction of OH $X\,^2\Pi_i$ from experimental data, only the quantities A_v were employed. This procedure is entirely equivalent to the determination of the potential-energy function from only vibrational data, and is likewise unfounded and thus unreliable, for the reason stated above. The complementary information to the spin-orbital interaction parameter A_v is the parameter A_{Dv} that is customarily taken to describe the centrifugal distortion of the coupling of spin and orbital angular momenta. Although Coxon and Foster [8] were aware of the necessity of such A_{Dv} data in their original attempt to derive the radial function $A(R)$, they were unable to incorporate the applicable values of the latter quantities in their main results, but Amano [9] derived values of A_{Dv} for both OH and OD, for both $v = 0$ and $v = 1$, using the isotope effect and a careful analytical procedure. Here we use the more accurate data of Amano wherever possible. Furthermore there seems to be a systematic difference between the data of Coxon and Foster [4] and of Amano [9], also noted by Amano. In an attempt to take account of this discrepancy in order to combine the two sources of data for the analysis here, we subtract an amount 11.5 m^{-1} from the leading coefficient $A^{(0)}$ fitted from the data of Coxon and Foster [4].

2. Procedure

The basic data for our analysis are listed in Table I. These include the values of $A^{(k)}$ calculated from the data of Coxon and Foster [4], with $A^{(0)}$ corrected as noted above, and the values of $A_D^{(k)}$ fitted from the data of Amano [9]. Because the values of A_{Dv} are available [9] for only $v = 0$ and $v = 1$, and because these values differ significantly the one from the other, a linear fit was applied, yielding $A_D^{(0)}$ and $A_D^{(1)}$; however because Amano's definition of A_{Dv} differs from the conventional [4, 6] definitions, the requisite factor two was here applied.

To find the radial dependence of the spin-orbital interaction, we apply the general method described elsewhere [10]. Rather than use the potential-energy function $V(x)$ [2] which suffers from a finite radius of convergence, $|x| \leqslant 1$, due to the internuclear coulombic repulsion, we employ $V(z)$ [11],

$$V(z) = B_e\gamma_p^{-2}z^2\left(1 + \sum_{j=1} c_jz^j\right) \qquad (9)$$

with

$$z \equiv 2(R - R_e)/(R + R_e), \qquad (10)$$

for which the corresponding radius of convergence of z, $|z| < 2$, corresponds to the entire range of molecular existence, $0 \leqslant R < \infty$. With this potential-energy function, we write the vibration-rotational energies in the form (for $^1\Sigma$ states) [2]:

$$E(v, J) = \sum_{k=0}\sum_{l=0} Y_{kl}(v + 1/2)^k[J(J + 1)]^l \qquad (11)$$

in which the term coefficients Y_{kl} are functions of the parameters c_j, B_e and γ_p [12]. In terms of the same argument z, we write the radial function for the spin-orbital interaction

$$A(z) \equiv K^A(z) = \sum_{j=0} h_j^A z^j. \qquad (12)$$

Table I. *Basic data from spectral analyses of OH* $X\,^2\Pi_i$ *[4, 8] required for the present treatment*

Quantity	Value/m^{-1}	Quantity	Value
$A^{(0)}\ Z^A_{0,0}$	-13907.02 ± 1.6	B_e	1891.1399 m^{-1}
$A^{(1)}\ Z^A_{1,0}$	-18.47 ± 2.2	γ_p	0.01011798
$A^{(2)}\ Z^A_{2,0}$	-4.337 ± 0.67	c_1	-1.26255
$A^{(3)}\ Z^A_{3,0}$	0.6074 ± 0.050	c_2	0.75746
$A_D^{(0)}\ Z^A_{0,1}$	-0.04070 ± 0.014	c_3	-0.32631
$A_D^{(1)}\ Z^A_{1,1}$	-0.0160 ± 0.016	c_4	-0.14486
$p^{(0)}\ Z^p_{0,0}$	24.0735 ± 0.0048	c_5	-0.66991
$p^{(1)}\ Z^p_{1,0}$	-1.1402 ± 0.016		
$p^{(2)}\ Z^p_{2,0}$	0.0911 ± 0.017		
$p^{(3)}\ Z^p_{3,0}$	-0.0413 ± 0.0078		
$p_D^{(0)}\ Z^p_{0,1}$	$(-5.1780 \pm 0.0010) \times 10^{-3}$		
$p_D^{(1)}\ Z^p_{1,1}$	$(-0.0100 \pm 0.0005) \times 10^{-3}$		
$p_D^{(2)}\ Z^p_{2,1}$	$(0.0000 \pm 0.0001) \times 10^{-3}$		
$q^{(0)}\ Z^q_{0,0}$	$-3.955418 \pm 9.0 \times 10^{-5}$		
$q^{(1)}\ Z^q_{1,0}$	$0.17516 \pm 2.4 \times 10^{-4}$		
$q^{(2)}\ Z^q_{2,0}$	$-1.70 \times 10^{-4} \pm 1.5 \times 10^{-5}$		
$q^{(3)}\ Z^q_{3,0}$	$1.58 \times 10^{-4} \pm 2.5 \times 10^{-5}$		
$q_D^{(0)}\ Z^q_{0,1}$	$(1.488794 \pm 2.3 \times 10^{-5}) \times 10^{-3}$		
$q_D^{(1)}\ Z^q_{1,1}$	$(-3.0604 \times 10^{-2} \pm 2.5 \times 10^{-5}) \times 10^{-3}$		
$q_D^{(2)}\ Z^q_{2,1}$	$(2.0406 \times 10^{-3} \pm 4.8 \times 10^{-6}) \times 10^{-3}$		

Table II. *Coefficients in the radial functions for the spin–orbital interaction and for the* Λ*-doubling effects of OH X* $^2\Pi_i$ *and their ranges of validity*

j	h_j^A/m^{-1}	h_j^p	$h_j^q/10^{-6}$ m
0	-13906.37 ± 0.47	$0.0127180 \pm 7.7 \times 10^{-6}$	$-1.1062 \pm 2.0 \times 10^{-4}$
1	-397.6 ± 136	$-0.026745 \pm 5.1 \times 10^{-3}$	$4.0663 \pm 6.3 \times 10^{-2}$
2	-675.0 ± 218	0.017808 ± 0.0015	-6.927 ± 0.18
3	-3700.0 ± 2250	-0.024 ± 0.04	8.624 ± 0.28
4	-9600.0 ± 4400	0.3492 ± 0.06	-7.456 ± 0.54
5	–	-1.0607 ± 0.22	8.466 ± 2.5
6	–	-5.745 ± 1.8	-28.6 ± 16
$R_-/^{-10}$ m	0.80	0.74	0.74
$R_+/10^{-10}$ m	1.25	1.45	1.45

Then the corresponding effect on the energies is expressed in the extended equation for the energy terms

$$E(v, J, \Omega) = \sum_{k=0} \sum_{l=0} (Y_{kl} + Z_{kl})(v + 1/2)^k [J(J+1) - \Omega^2]^l. \tag{13}$$

Expressions for some of the additional coefficients Z_{kl}, being functions of the parameters c_j, h_j and γ_p, have already been published [10, 13].

We associate the parameters $A^{(k)}$ with $Z_{k,0}^A$ and the $A_D^{(k)}$ with $Z_{k,1}^A$. We apply the expressions for the parameters Z_{kl}^A serially to the available data, thus obtaining the values of the coefficients h_j^A given in Table II. The stated uncertainties of these values of h_j^A, each representing one estimated standard error, are propagated from the experimental error in the measurements of wavenumber [8] or frequency [9] through the intermediate quantities A_v, A_{Dv}, $A^{(k)}$, $A_D^{(k)}$ and hence Z_{kl}^A, estimated according to the Monte-Carlo method [14].

One can analogously attribute the vibrational dependence of the Λ-doubling parameters p_v and q_v, and their associated centrifugal parameters p_{Dv} and q_{Dv} respectively, to the radial dependence of appropriate functions $K^p(z)$ and $K^q(z)$, containing the coefficients h_j^p and h_j^q respectively. As one can, exactly analogously according to the procedure described above, associate the parameters $p^{(k)}$, $p_D^{(k)}$, $q^{(k)}$, and $q_D^{(k)}$ with the corresponding parameters Z_{kl}^p and Z_{kl}^q, one can hence derive values of the coefficients h_j^p and h_j^q. In this case Amano's accurate results [9] confirm those of Coxon and Foster [4], so the latter more extensive data are used here. Because of the isotopic mass dependence of the p and q parameters, factors of B_e and B_e^2 respectively are inserted into the expressions Z_{kl}^p and Z_{kl}^q so that the functions $K^p(z)$ and $K^q(z)$ remain independent of mass, according to the approach of Born and Oppenheimer [1]. In the case of both p and q, the spectral data [4] are sufficiently accurate and extensive to define meaningful values of $Z_{2,1}$ and $Z_{3,0}$ which can then yield values of coefficients h_5 and h_6 through the expressions (not previously reported) given in Table III.

The present results in Table II are valid within the ranges (from $\sim R_-$ to $\sim R_+$) of internuclear separation also specified in that table. These ranges are estimated from the classical turning points of the vibrational state with the maximum value of v for which the relevant data were used to determine the values of the various Z_{kl} parameters.

3. Discussion

The accuracy of the present results, listed in Table II, depends not only directly on the accuracy of the experimental data listed in Table I, but also on the condition that nonadiabatic contributions to the values of the centrifugal parameters $Z_{k,1}$ must be negligible. The latter condition, the lack of interference from perturbations or the elimination of their effects before applying the data, is implicit in any such inversion of spectral data. Whether this condition applies in the instance of a particular electronic state of a molecule of interest can be tested by theoretical computations and by the self-consistency of the values of the coefficients h_j determined by different combinations of the Z_{kl} coefficients. Unfortunately in the present case of the OH molecule, the lack of values of such coefficients as $Z_{0,2}$ precludes such a test [10] of the validity of the analysis of the experimental results. It should also be noted that the nominal uncertainties of the A_{Dv} data [9] reflect to some extent the correlations with the values of other parameters in Amano's treatment of his data; for this reason the stated uncertainties, and consequently the propagated uncertainties in the values of the coefficients h_j^A, may not entirely accurately reflect the statistical significance of the results.

Comparison of the function $K^A(z)$ can be made both with the results of Coxon and Foster [4], based on their own collection of spectral data, and with those of Bessis *et al.* [7] who used the same experimental data. In both these cases, as already noted, only the A_v or $Z_{k,0}^A$ data were used; for this reason the agreement of both these sets of results with not only the present results but also the theoretical results [15] must be regarded as largely fortuitous. Also, because no significant value of $Z_{2,1}^A$ is available from experiment, the datum $A^{(3)} = Z_{3,0}^A$ cannot be used; thus neither h_5^A nor h_6^A can

Table III. *Expressions for* $Z_{2,1}$ *and* $Z_{3,0}$ *required for the analysis*

$$\begin{aligned} Zz_{2,1} = {} & \gamma_p^4[h_1(33/8c_1 - 66c_1c_2 + 285/4c_1c_3 - 15/8c_2 + 15c_3 - 45/2c_4 \\ & + 63/4c_1^2 - 621/4c_1^2c_2 + 423/8c_1^3 + 135/2c_1^4 + 39c_2^2 + 3/32) \\ & + h_2(-3/4c_1 + 117/2c_1c_2 - 15c_3 - 81/4c_1^2 - 45c_1^3) + h_3(27/2c_1 \\ & - 39/2c_2 + 135/4c_1^2 + 3/8) - 39/2c_1h_4 + 15/2h_5] \end{aligned}$$

$$\begin{aligned} Z_{3,0} = {} & \gamma_p^3[h_1(-15/32c_1^2c_2 - 2175/32c_1^2c_3 - 15/32c_1^2 + 7545/64c_1^3c_2 \\ & + 1005/128c_1^3 - 855/256c_1^4 - 19035/512c_1^5 + 85/16c_2^2 \\ & - 2055/32c_1c_2^2 - 425/32c_1c_2 + 25/8c_1c_3 + 255/8c_1c_4 - 9/16c_1 \\ & + 225/8c_2c_3 + 13/8c_2 + 65/16c_3 - 15/4c_4 - 35/4c_5 + 1/8) \\ & + h_2(-1575/32c_1^2c_2 - 285/64c_1^2 - 105/32c_1^3 + 6345/256c_1^4 \\ & + 85/16c_2^2 + 85/8c_1c_2 + 175/8c_1c_3 + 3/2c_1 + 9/16c_2 - 15/4c_3 \\ & - 15/4c_4 - 1/8) + h_3(45/16c_1^2 - 705/32c_1^3 + 225/8c_1c_2 \\ & + 57/16c_1 - 17/4c_2 - 35/4c_3 - 1) + h_4(225/16c_1^2 - 17/4c_1 \\ & - 17/4c_2 - 3/8) + h_5(-35/4c_1 + 5/2) + 5/2h_6] \end{aligned}$$

be determined significantly from the available data. For this reason, related to the fact that the present analysis is based in part upon the more accurate but less extensive data of Amano [9], the stated ranged of validity of the results is less wide than that claimed in the earlier treatments of experimental data.

Comparisons of the functions $K^p(z)$ and $K^q(z)$ can also be made with the results of Coxon and Foster [4] and of Bessis *et al.* [7]. Because the mass dependence has been removed from these functions, and because of additional factors R^2 and $-R^4$ with these functions in relation to the theoretical results [16] (i.e. $R^2K^p(z)$ and $-R^4K^q(z)$ have the appropriate theoretical meaning), the necessary transformations should be applied before any such comparison with other data. The agreement among the various sets of results is satisfactory.

Finally, the use of the present results in Table II leads to predictions of the observable quantities for OD in satisfactory agreement with experimental values [9], necessarily so, because the same calculated dependences on reduced mass that Amano's results [9] obey, as he states, are incorporated within the expressions Z_{kl} through the factor γ_p. However the present results fail to predict satisfactorily the data of Amiot *et al.* [17] for OD to the extent, quite large for some quantities, that those data deviate from Amano's values [9]. For instance gross irregularities in the values of p_D and q_D as a function of vibrational quantum number v, $0 \leqslant v \leqslant 6$, are discernible in the data of Amiot *et al.* [17]. Nevertheless, their [17] measured value $(-1.52 \pm 0.12) \times 10^{-8}\,\mathrm{m}^{-1}$ of the quantity q_H for $v = 0$ of OD, the parameter with the smallest magnitude determined in that investigation, has the same sign and order of magnitude as the predicted value $-2.17 \times 10^{-8}\,\mathrm{m}^{-1}$ of $Z^q_{0,2}$ in this work.

4. Conclusions

The formalism and procedure presented in this work are applicable to the treatment of experimental data for the vibrational and rotational dependence of the spin–orbital interaction in order to extract the radial dependences of the corresponding functions. Previous procedures for the treatment of only the vibrational dependence of the spin–orbital interaction A_v lack theoretical foundation, and are hence inherently unreliable.

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