Radial Functions from the Hyperfine Spectrum of NaBr

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By means of the analytic procedure previously reported, the radial dependences describing various hyperfine interactions have been calculated from the data from measurements on molecular beams of ²³Na⁷⁹Br and ²³Na⁸¹Br by Cederberg *et al.* (*J. Mol. Spectrosc.* **122**, 171–181 (1987)). © 1988 Academic Press, Inc.

Recently Cederberg *et al.* (1) presented some results from experiments by the technique of electric resonance on molecular beams of ²³Na⁷⁹Br and ²³Na⁸¹Br in a few vibrational ($0 \le v \le 5$) and rotational ($2 \le J \le 6$) states. In fitting their measured frequencies, they allowed for several interactions, specifically the electric quadrupole moment of each nucleus with the gradient of the molecular electric field (quad), the intrinsic angular momentum of each nucleus with the angular momentum of the nuclei rotating about the center of molecular mass (s-r), the spin of one nucleus with the spin of the other nucleus in both scalar (s-s s) and tensor (s-s t) forms, and even an interaction involving the electric octupolar moment of each nucleus (oct). In the discussion of their results, they mentioned the possible determination of the effective radial functions related to these phenomena, but made no actual calculations of these functions. The purpose of this note is to demonstrate how easily these functions can in fact be generated from the available data, according to a general analytic procedure (2).

Cederberg *et al.* (1) have given in their Table II the necessary data in precisely the appropriate form. Thus one can directly associate their listed coefficients of $(v + \frac{1}{2})^k [J(J+1)]^l$ with the parameters Z_{kl} that have been in turn expressed (2) in terms of the potential-energy coefficients c_j , defined in the general analytic function with the variable $z = 2(R - R_e)/(R + R_e)$ for the reduced internuclear displacement,

$$V(z) = c_0 z^2 (1 + \sum_{j=1}^{n} c_j z^j),$$

the coefficients h_i of the particular radial function

$$K(z)=\sum_{j=0}h_jz^j,$$

and the expansion parameter $\gamma \equiv 2B_e/\omega_e$. In order to apply this procedure to the data available for NaBr, one requires values of the potential-energy coefficients; these values have of necessity been derived from the pure rotational spectra (3) due to the lack of vibration-rotation data. Therefore the published values of $Y_{0,1}$, $Y_{1,1}$, $Y_{2,1}$, $Y_{0,2}$, and $Y_{1,2}$ were used to obtain values of $Y_{1,0}$ and c_j , $1 \le j \le 3$, according to the analytic

formulae (4); the distinctions between B_e and $Y_{0,1}$ and between ω_e and $Y_{1,0}$ were neglected because of both the relatively small value of the expansion coefficient γ , $\sim 10^{-3}$, and the other and more important sources of error. The data for ²³Na⁷⁹Br and ²³Na⁸¹Br were treated independently. The published equations for Z_{kl} were used directly except that for the spin-rotation data a factor B_e was incorporated into each equation; for this reason also the corresponding values of h_j are dimensionless. The results are listed in Table I, in which the abbreviations used in the headings correspond to the terms defined above. These results have been expressed in wavenumber units (m⁻¹) for ease of comparison with previous results ((2) and elsewhere).

No attempt has been made to assign uncertainties to the values of the parameters in Table I for two reasons. First, the rigorous procedure to accomplish this objective requires knowledge of the values of the correlation coefficients (off-diagonal elements in the variance-covariance matrix) between at least the various elements within each set of Y_{kl} and Z_{kl} coefficients. Second, that the values of X^2 obtained in the analyses of the previous data differed significantly for the two different isotopic species, processed at different times during the project (1), was supposed to indicate either a small unidentified systematic error or a remaining unidentified interaction. Furthermore, within the limited range of the variation of the rotational quantum number and by the nature of the much smaller sensitivity of the effects to variation of rotational rather than to vibrational quantum numbers, the relatively inaccurate values of $Z_{k,1}$ are to be expected. Then the inaccuracy of the values of h_1 derived therefrom is unavoidably propagated to values of h_i further in the course of their determination.

			² ³ Na ⁷⁹ Br		
	B _e /m ^{−1}	15.1253	c	1 -2.04613	
	∉_∕_m⁻¹	29848.7	c	2 2.6669	
	c ₀ /m ⁻¹	1.4726×107	c	₃ -2.916	
	Br quad /m ⁻¹	Na quad /m ⁻¹	Br s-r	Na s-r	s-s (t) ∕m ⁻¹
ho	191.76	33 -16.4003	6.826×10 ⁻⁵	1.513×10 ⁻⁴	0.00131
hi	1453.6	-19.5	0.0365	-0.085	0.455
h ₂	-2094.5	79.3	-0.147	0.35	-1.85
h ₃	-2356.2	17940			
h4	8741.1	-1.11×10	^j		
h ₀ /m	⁻¹ s-s (s) 2.60×10 ⁻⁴	Br oct 6.7×1	0 ⁻⁷ Na oct	-2.7×10 ⁻⁷
			²³ Na ⁸¹ Br		
	B_/m ⁻¹	15.0411	c	-2.04814	
	∉ັ∕m ^{−1}	29799.9	c	2.4596	
	c ₀ /m ⁻¹	1.4760×10 ⁷	c	3 -1.203	
	Br quad /m ⁻¹	Na quad /m ⁻¹	Br s-r	Na s-r	s-s (t) /m ⁻¹
ho	160.19	69 -16.4455	7.394×10 ⁻⁵	1.552×10 ⁻⁴	0.00142
hi	1221.3	-29.5	0.0305	-0.3917	-0.687
h ₂	-1777.9	264.	-0.123	1.59	2.79
h ₃	-2123.0	2265.			
h4	10402	-1.69×104			
h ₀ /m	⁻¹ s-s (s) 2.87×10 ⁻⁴	Br oct 1.2×1	0 ⁻⁶ Na oct	1.6×10 ⁻⁶

TABLE	l
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On the other hand, the apparent discord between the values of the coefficients h_i for the quadrupolar and spin-rotational interactions of Br is to be expected from the nature of the two distinct Br nuclei; the measured interaction qQ represents the expectation value, within a particular vibration-rotational state, of the product of the intrinsic electric quadrupole moment O of the Br nucleus and the gradient q at that nucleus of the internal molecular electric field of this polar molecule. The ratios for the two isotopic species ²³Na⁷⁹Br and ²³Na⁸¹Br of the values of the quotients h_i/h_0 , $1 \le i \le 4$, for the quadrupole interaction differ from unity by 0.57, 1.6, 7.8, and 42%, respectively; these values indicate not only the limits of the reliability of the data but also the physical significance of this radial function. The ratio of the intrinsic electric quadrupole moments of the ⁷⁹Br and ⁸¹Br nuclei should be given as 1.19704773, calculated from the ratio of the corresponding values of h_0 rather than from the ratio (1) of the $Z_{0,0}$ values in which a significant mass effect remains (i.e., the correction term (2) containing a factor γ^2). In contrast, no such scaling effect applies to the values of the coefficients of the radial functions for the spin-rotational interaction of the Br nuclei, for which there is no apparent explanation of the large discrepancies of the h_0 coefficients between ²³Na⁷⁹Br and ²³Na⁸¹Br.

At least until more extensive and accurate values of the potential-energy coefficients c_j may be determined from spectroscopic data, it seems unlikely that the validity of the Born-Oppenheimer approximation can be tested by the results determined by Cederberg *et al.* (1). Moreover, as demonstrated previously (2), even when the isotopic effects are most pronounced (as in the case of replacement of ¹H by ²H), extremely great precision is required to transcend the effects regularly encompassed within the appropriate terms of higher order in the various expressions for Z_{kl} .

In conclusion, we have demonstrated how data from experiments on molecular beams of diatomic molecules in which dependences on both rotational and vibrational quantum numbers are measurable can be used to generate the associated radial functions. These functions should have approximate validity within the range $2.27 \le R/10^{-10} m \le 2.8$, between the classical vibrational turning points of the state v = 5.

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