

NOTES

Combined Fitting of Optical and Millimeter Wave Data: The Linked $A^2\Pi-X^2\Sigma^+$ and $B^2\Sigma^+-X^2\Sigma^+$ Systems of Ca^{79}Br and Ca^{81}Br

In this note we illustrate the effects of combining, in a statistically rigorous procedure (1, 2), two large and highly precise data sets from millimeter wave (3) and laser excitation spectroscopy (4). The former set consists of 40 lines, at 40-kHz accuracy ($1.3 \times 10^{-6} \text{ cm}^{-1}$), from the $N \sim 15$ and $N \sim 50$ regions of $X^2\Sigma^+$, $v = 0-2$, for both $^{40}\text{Ca}^{79}\text{Br}$ and $^{40}\text{Ca}^{81}\text{Br}$; the latter, consists of more than 2000 lines, at 0.003-cm^{-1} accuracy, from the 0-0, 1-1, and 2-2 bands of the $B^2\Sigma^+-X^2\Sigma^+$ and 0-0 and 1-1 bands of the $A^2\Pi-X^2\Sigma^+$ electronic transitions for $0 < N < 117$ of both isotopic species.

Our reasons for illustrating what should by now be an obvious result are:

(1) The extent and precision of the optical data set are unusual. Inclusion of two linked electronic transitions with totally distinct branch structure would be expected to reduce correlations between upper- and lower-state parameters.

(2) The extent and precision of the millimeter wave data set are remarkable, but the transitions sampled do not span a continuous range of N levels. Such disjoint sampling can lead to artifacts in fitted, high-order constants.

(3) A large number of small and highly correlated parameters are required to fit the energy levels of $^2\Pi$ and $^2\Sigma^+$ states, in marked contrast to the situation for $^1\Sigma$ states.

(4) Two useful internal consistency tests were available to us, isotope relations and predictions of lines in $\Delta v \neq 0$ bands using rotational constants derived from $\Delta v = 0$ bands.

Table I displays several correlations between parameters and the effects of adding first the $A-X$ optical and then the X state mm-wave data to the $B-X$ data set. It is well known that correlation between upper- and lower-state parameters is one of the main factors that limits the precision of molecular constants obtained from electronic band spectra (2). Some of these correlations may be reduced by fitting simultaneously two electronic transitions which share a common state. For instance, our fit to the 0-0 bands of the $\text{CaBr } A-X$ and $B-X$ systems reduced the correlation coefficient between spin-rotation constants (γ) for the B and X states from 0.999 (separate $B-X$ fit) to 0.35 (combined fit). However, the (B'_0, B''_0) , (D'_0, D''_0) , and (B''_0, D''_0) correlation coefficients decrease only slightly. Introduction of the mm-wave data (with inverse-uncertainty-squared relative weighting) greatly reduces the remaining upper state-lower state correlations: (B'_0, B''_0) and (D'_0, D''_0) both decrease to 0.02, but the (B''_0, D''_0) correlation within $X^2\Sigma^+$ increases from 0.79 to 0.989, which is identical to that found for the mm-wave data set alone. The failure of the optical data to reduce the (B''_0, D''_0) correlation reflects the 10^2 greater sensitivity of B''_0 and D''_0 to the millimeter wave data. Because D''_0 is 2×10^6 smaller than B''_0 , the large (B''_0, D''_0) correlation allows a larger fractional error in the value of D''_0 than in B''_0 .

The B''_0 values from mm-wave alone and combined $B-X$, $A-X$ optical data differ by six times the standard deviation for the optical value. This is an example of small systematic errors resulting from nonrandom sampling within two distinct data sets. The X state B , D , and γ values obtained from mm-wave alone and from $B-X$, $A-X$, mm-wave combined data are identical, but with two to three times smaller uncertainties for those from the combined fit. This is simply a reflection of the larger number of degrees of freedom (data points) in the combined fit, despite the fact that each optical transition is weighted 10^{-6} as heavily as a mm-wave transition. The agreement between the mm-wave only and combined fits shows that no artifacts result from the disjoint nature of the mm-wave data set. B''_0 and D''_0 constants for the $B^2\Sigma^+$ state are changed by 6σ when the mm-wave data are added to the $A-X$, $B-X$ set, and these constants remain about 10 times less precisely determined than those of $X^2\Sigma^+$. Only part of the mm-wave precision is propagated into the upper states of the electronic transitions. Note that, as expected, ΔB changes by less than $6 \times 10^{-7} \text{ cm}^{-1}$ for the three fits.

TABLE I

Summary of Parameter Values and Correlation Coefficients for $\text{Ca}^{79}\text{Br } B^2\Sigma^+ - X^2\Sigma^+$, $v' = v'' = 0$

	mm-wave	$B^2\Sigma^+ - X^2\Sigma^+$ only	$B^2\Sigma^+ - X^2\Sigma^+$ and $A^2\Pi - X^2\Sigma^+$	Combined B-X, A-X and mm-wave
$X^2\Sigma^+$				
$B_0'' \times 10^2 \text{ cm}^{-1}$	9.426 448 8(44) [9.426 456 6(47)] ^a	9.424 86(131)	9.424 36(33)	9.426 448 8(18)
$D_0'' \times 10^8 \text{ cm}^{-1}$	4.130 28(91) [4.131 87(96)] ^b	4.206(220)	3.971(30)	4.130 28(38)
$\gamma_0'' \times 10^3 \text{ cm}^{-1}$	3.003 42(118) [3.003 31(105)] ^b	2.902(976)	3.024(11)	3.003 55(49) ^c
$B^2\Sigma^+$				
$\nu_{00} \text{ cm}^{-1}$	----	16 383.115(11)	16 383.108(11)	16 383.114(11)
$B_0' \times 10^2 \text{ cm}^{-1}$	----	9.627 46(128)	9.627 01(33)	9.629 057(71)
$D_0' \times 10^8 \text{ cm}^{-1}$	----	4.458(209)	4.241(33)	4.398(15)
$\gamma_0' \times 10^2 \text{ cm}^{-1}$	----	-6.9! 3 5(955)	-6.900 5(39)	-6.898 8(38)
$\gamma_{D_0} \times 10^7 \text{ cm}^{-1}$	----	2.80(14)	2.72(14)	2.58(14)
(B_0', B_0'')	----	0.999	0.978	0.025
(D_0', D_0'')	----	0.997	0.882	0.023
(B_0'', D_0'')	0.989	0.927	0.793	0.989
(γ_0', γ_0'')	----	0.999	0.352	0.013
(D_0'', γ_0'')	0.8×10^{-7}	-0.749	0.109	-0.0004
Degrees of Freedom	7	141	613	623
Variance	2.0	0.31	0.32	0.34

a. From a three-term Dunham expansion. c. Uncertainty should be increased by a factor of 50 due to a neglected hfs effect.
b. From a two-term Dunham expansion.

The effects of (B', B'') correlations in the optical data are manifest when rotational constants determined from fits to 0-0 and 1-1 bands were used in limited fits to a few high and low N lines of 1-0 and 0-1 bands. When lines were fitted by varying only the band origin, systematic residuals were observed. These residuals became random when, instead, fixed values of the rotational constants obtained from the combined mm-wave, optical fits were used.

Use of combined fit parameters also eliminated a systematic but trivial misassignment of the $\text{Ca}^{79}\text{Br } B-X$ 0-1 band P_1 branch near its bandhead. High and low N lines overlap to within their Doppler width near the head. These lines were resolved using intermodulated fluorescence spectroscopy (6), but the correct high vs low N assignment of each high- N , low- N pair was not obvious. When the combined mm-wave, A-X, B-X constants were used, these line pairs could be unambiguously assigned and the residuals from $N = 27$ to 66 were smaller than 0.001 cm^{-1} in a fit with the band origin as the only variable parameter.

Satisfaction of the usual isotope relationships (7, 8) between small parameters is the final, and perhaps most stringent test of the fits to various data sets. Table II gives the percentage agreement [(exp. ratio - calc. ratio)/calc. ratio $\times 100$] between experimental and theoretical isotopic ratios. The agreement for the small parameters of the optical data fitted alone is rather poor, but falls within the estimated experimental uncertainty. The addition of mm-wave data dramatically improves the agreement between experiment and theory. This implies that the combined optical-mm-wave fitted constants are superior estimates of the "true" molecular parameters.

After this work was completed, we learned of a molecular beam, rf-optical double-resonance study of CaBr by Childs *et al.* (9). The $X^2\Sigma^+$ hyperfine and spin-rotation splittings were measured

TABLE II
Ca⁸¹Br/Ca⁷⁹Br Isotope Ratios for B²Σ⁺ and X²Σ⁺ States

Parameter	Percentage Deviation from Theoretical Ratio		
	mm-wave	A-X and B-X Optical Data	Combined Optical and mm-wave data
B _e (X ² Σ ⁺)	-0.000068(106)%	0.014(10)%	-0.000068(106)
B _e (B ² Σ ⁺)		0.016(10)	0.0028(31)
α _e (X)	+0.0074(260)	-1.8(20)	-0.010(30)
α _e (B)		-1.7(20)	0.22(50)
D _e (X)	-0.014(49)	2.4(15)	0.013(17)
D _e (B)		3.8(16)	1.4(8)
γ _e (X) ^a	-0.042(93)	0.17(67)	0.041(58)
γ _e (B) ^a		-0.17(35)	-0.12(18)
γ _D (B)		-9.2(11)	-5.4(12)

σ uncertainties are in parentheses.

a. Spin-rotation constant.

at an accuracy of a few kHz. The new value of γ₀⁹ (9) disagreed significantly (45σ) with the mm-wave and the combined optical and mm-wave values, but not with the value obtained from optical data alone (Table I). This discrepancy resulted from neglect of unresolved hyperfine effects in the N ~ 15 mm-wave data. As a result, the substantial N dependence of γ₀⁹ found by Childs *et al.* was masked, and the combined fits produced a value of γ_{effective} appropriate for N ~ 50. This systematic error (neglect of both hfs and centrifugal distortion of γ₀⁹) increases the uncertainty in γ₀⁹ by a factor of 50 beyond that cited in Table I but has a negligible effect on all other constants. This illustrates once again the ubiquity of model dependent systematic errors.

ACKNOWLEDGMENTS

P.F.B. was supported, in part, by a Natural Sciences and Engineering Research Council of Canada Postgraduate Scholarship. The MIT portion of this research was supported by Grants AFOSR-76-3056, NSF CHE-78-18427, CHE-78-10178, and NATO 1177.

REFERENCES

1. R. N. ZARE, A. L. SCHMELTEKOPF, W. J. HARROP, AND D. L. ALBRITTON, *J. Mol. Spectrosc.* **46**, 37-66 (1973).
2. D. L. ALBRITTON, A. L. SCHMELTEKOPF, AND R. N. ZARE, in "Modern Spectroscopy, Modern Research" (K. Narahari Rao, Ed.), Vol. 2, pp. 1-67, Academic Press, New York, 1976.
3. K. MÖLLER AND T. TÖRRING, unpublished.
4. P. F. BERNATH, R. W. FIELD, B. PINCHEMEL, Y. LEFEBVRE, AND J. SCHAMPS, *J. Mol. Spectrosc.* **88**, 175-193 (1981).
5. D. L. ALBRITTON, W. J. HARROP, A. L. SCHMELTEKOPF, AND R. N. ZARE, *J. Mol. Spectrosc.* **46**, 103-18 (1973).
6. P. F. BERNATH AND B. PINCHEMEL, unpublished.

7. G. HERZBERG, "Spectra of Diatomic Molecules," Van Nostrand, New York, 1950.
8. J. M. BROWN AND J. K. G. WATSON, *J. Mol. Spectrosc.* **65**, 65-74 (1977).
9. W. J. CHILDS, D. R. COK, G. L. GOODMAN, AND L. S. GOODMAN, *J. Chem. Phys.*, in press.

P. F. BERNATH¹
B. PINCHEMEL²
R. W. FIELD

*Department of Chemistry and Spectroscopy Laboratory
Massachusetts Institute of Technology
Cambridge, Massachusetts 02139*

K. MÖLLER
T. TÖRRING

*Institut für Molekül Physik
Fachbereich Physik
Freie Universität Berlin
1000 Berlin 33, West Germany*

Received December 30, 1980

¹ Present address: Herzberg Institute of Astrophysics, National Research Council of Canada, K1A 0R6, Ottawa, Ontario, Canada.

² Visiting scientist at MIT. Present address: Laboratoire de Spectroscopie des Molécules Diatomiques, E.R.A. 303, Université des Sciences et Techniques de Lille, Bât. P5, 59655 Villeneuve d'Ascq, France.