Erratum: Hyperfine structure of the BaI $X^2\Sigma^+$ and $C^2\Pi$ states [J. Chem. Phys. 85, 3735 (1986)]

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Erratum: Hyperfine structure of the BaI $X\,^2\Sigma^+$ and $C\,^2\Pi$ states [J. Chem. Phys. 85, 3735 (1986)]

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In simulating the hyperfine effects of the high-resolution BaI $C\,^2\Pi\!-\!X\,^2\Sigma^+$ spectra the paper by Ernst *et al.*[1] was reexamined. A new computer program was written for this simulation and used to fit the optical data in Table II.[1] The hyperfine interactions in the $X\,^2\Sigma^+$ state were calculated by diagonalizing a (2×2) matrix using the values of the hyperfine parameters in Table III.[1] These parameters, which had been determined from the optical-microwave double resonance experiment, were kept fixed during the fit. For the $C\,^2\Pi$ state the hyperfine interactions are as given in Eq. (12).[1] The $C\,^2\Pi$ hyperfine parameters were optimized by a nonlinear least squares fit of the simulated hyperfine effects in the $C\,^2\Pi\!-\!X\,^2\Sigma^+$ spectra to the experimental data in Table II.[1] The results are shown in Table I. Comparison with earlier results[1] shows that the value of d' changes by a factor of 2 and the value of $b'+c'$ is also different, although its uncertainty is large. These differences must be caused by an error in the original analysis. The frequencies calculated using the new hyperfine parameters (from Table I) reproduce the observed frequencies to the same accuracy as those given in Table II.[1] The overall standard deviation of the new fit is 7.1 MHz.

The hyperfine parameters were used by Ernst *et al.*[1] to discuss the bonding nature of BaI in the $C\,^2\Pi$ state. Although the values of $b'+c'$ and d' in Table I differ by up to a factor of 2 from the results published in Ref. 1, the conclusions remain the same. With the correctly determined values of a' and d', Eq. (21)[1] yields $c'=1173$ MHz instead of 889 MHz[1] and the same conclusion is valid; the spin and orbital angular momenta responsible for the hyperfine structure of the BaI $C\,^2\Pi$ state involve different electrons. Similarly, the assumption of a positive electron spin density at the iodine nucleus leads to the condition that $c'<-384$ MHz instead of -645 MHz,[1] again an

unreasonable value. Therefore, the conclusion remains that the electron spin density at the iodine nucleus must be negative and the bonding picture of a π-type Ba$^+$ orbital polarized toward I$^-$ is confirmed. If Eq. (26)[1] is applied to derive the Fermi contact term, b'_F, the result is now $b'_F=-131.3$ MHz instead of -307 MHz, again in agreement with the qualitative picture discussed.

It is also worth pointing out several misprints in the original paper. In the hyperfine Hamiltonians in Eqs. (4)[1] and (11)[1] the electric quadrupole interaction terms should read

$$eQq[3I_z^2-I(I+1)]/[4I(2I-1)].$$

Equation (15),[1] which is a term added to the energy levels of the $^2\Pi_{1/2}$ state to account for the effect of hyperfine structure on the Λ doublet, should read

$$\pm dC(F,I,J)(J+1/2)/[4J(J+1)],$$

where $C(F,I,J)=F(F+1)-I(I+1)-J(J+1)$, and the plus sign refers to e-parity states and the minus sign refers to f-parity states of the Λ doublet. Equation (17)[1] should read

$$b'=\frac{\mu_0\mu_I}{I}\left(\frac{16\pi}{3}|\Psi(0)|^2-\left[\frac{3\cos^2\theta-1}{r^3}\right]_{av}\right).$$

In addition, the F'' quantum numbers in Fig. 6[1] are mislabeled and should be in the reverse order, i.e., from 52 to 47, left to right.

TABLE I. Hyperfine parameters for the $C\,^2\Pi(v=0)$ states of BaI. The quantities in parentheses represent one standard deviation.

Parameter	Value (MHz)
a'	259(30)
$b'+c'$	$-256(59)$
d'	$-132(2)$
eQq'	$-217(7)$

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[1] W. E. Ernst, J. Kändler, C. Noda, J. S. McKillop, and R. N. Zare, J. Chem. Phys. 85, 3735 (1986).