Electric Polarity ⁺BrCl⁻ and Rotational *g* Factor from Analysis of Frequencies of Pure Rotational and Vibration–Rotational Spectra

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The electric dipole moment and rotational g factor of BrCl have been estimated by relating non-adiabatic effects, evaluated from analysis of the frequencies of pure rotational and vibration-rotational transitions of BrCl (electronic state X 0⁺) in its four isotopic variants, to electric and magnetic properties; the electric polarity is ⁺BrCl⁻ and g_J of ⁷⁹Br ³⁵Cl is -0.02509 ± 0.00070 . Among ten parameters used to reproduce quantitatively 883 frequencies of transitions of four isotopic variants in vibration states up to v = 3, six parameters serve to define the function for potential energy in the range $2.0 < (R/10^{-10} \text{ m}) < 2.3; R_e = (2.1370376 \pm 0.0000018) \times 10^{-10} \text{ m}.$

The polarity of simple molecules in relation to qualitative descriptions and theories of molecular binding retains chemical interest. Isotopic dependence of the rotational g factor¹ was the original experimental method used to enable deduction of this polarity. Possession of rotational angular momentum by an otherwise diamagnetic diatomic molecule (such as in an electronic state 0⁺) bestows a magnetic dipole moment; the ratio of this moment to the rotational angular momentum is the product of the rotational g factor and the nuclear magneton (to carry units). Splitting of lines in the pure rotational spectrum when a dilute gaseous sample is exposed to an appropriately aligned magnetic field, yields the magnitude of g_J . Various techniques, such as the use of circularly polarised microwave radiation at the frequency of a rotational transition,¹ allow establishment of the sign of g_J .

First experiments² to determine the sense of the electric moment of CIF yielded a questionable polarity ⁻CIF⁺, later revised to the opposite polarity ⁺ClF^{-,3} As during that period computations of molecular electronic structure were still unreliable,² such experiments were important: empirical results were essential to guide the development of computational methods to generate molecular properties of increased accuracy. Since 1980, few measurements of g_J have been reported and methods to determine the sign of g_J are generally indirect. The reason is that the Zeeman effect is applied less commonly than the Stark effect and is considered experimentally less convenient. In currently practised microwave spectroscopy in which a spectrum is derived from the Fourier transform of the total spectral emission from a sample, typically in a supersonic jet, even the Stark effect is difficult to apply. Consequently, development of other methods is required to derive fundamental electric and magnetic properties of simple molecules to overcome such obstacles of applying well defined external electric and magnetic fields.

Within an exploration of adiabatic and non-adiabatic effects discernible in pure rotational and vibration-rotational spectra of isotopically varied diatomic molecules,⁴ we presented a method to evaluate both the electric dipole moment and the rotational g factor from spectra measured in the absence of electric and magnetic fields.⁵ This novel approach has been applied to estimate the rotational g factor of BrCl and the sense of electric polarity of this molecule. For motion of nuclei separated by a distance R in an electronic state 0^+ , an effective Hamiltonian has the form⁶

$$\mathcal{H}_{\rm eff}(R) = \hat{p}[1 + \beta(R)]\hat{p}/2\mu + V(R) + V'(R) + hcB_{\rm e}[1 + \alpha(R)]J(J + 1)R_{\rm e}^2/R^2$$
(1)

in which R_e is the equilibrium internuclear separation, B_e the rotational parameter, and \hat{p} the operator for linear momentum of the nuclei; explanations of other quantities follow.

Unlike the internuclear distance R, the reduced displacement variable⁷

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$$z = 2(R - R_e)/(R + R_e)$$
 (2)

possesses a valuable property of remaining finite throughout the range of molecular existence: for $0 \le R < \infty$, $-2 \le z < 2.^{7.8}$ The potential energy V(R), independent of nuclear mass, has the form⁴

$$V(z) = c_0 z^2 \left(1 + \sum_{j=1}^{n} c_j x^j \right)$$
(3)

For a diatomic molecule AB having nuclei of unlike protonic numbers and reduced mass μ , other functions dependent on individual nuclear masses M_a and M_b become expansions separate for the atomic centre of each type A and B. In the final term of eqn. (1) that represents centrifugal motion of nuclei and their associated electrons, a function $\alpha(R)$ of nonadiabatic rotational effects takes into account that electrons follow nuclei imperfectly in their rotation about the centre of mass,⁴

$$\alpha(R) \to \alpha(z) = m_{\rm e} \left(\sum_{j=0} t_j^{\rm a} z^j / M_{\rm a} + \sum_{j=0} t_j^{\rm b} z^j / M_{\rm b} \right) \tag{4}$$

For non-adiabatic vibrational effects that analogously pertain to vibrational inertia of electrons with respect to nuclear motion, the first term in eqn. (1) for nuclear kinetic energy of motion along the internuclear axis contains a function⁴

$$\beta(R) \rightarrow \beta(z) = m_{\rm e} \left(\sum_{j=0} s_j^{\rm a} z^j / M_{\rm a} + \sum_{j=0} s_j^{\rm b} z^j / M_{\rm b} \right)$$
(5)

For adiabatic effects according to which the true internuclear potential energy [i.e. V(R) + V'(R)] depends in general not only on internuclear distance as V(R) independent of mass but also slightly on relative momenta of nuclei and hence on their masses. The correction term is⁴

$$V'(R) \rightarrow V'(z) = m_{\rm e} \left(\sum_{j=1} u_j^{\rm a} z^j / M_{\rm a} + \sum_{j=1} u_j^{\rm b} z^j / M_{\rm b} \right) \qquad (6)$$

Molecular energies within a particular electronic state, or vibration-rotational terms (unit: m^{-1}), are expressed in the form⁴

$$\tilde{E}_{vJ} = \sum_{k=0}^{N} \sum_{l=0}^{N} (Y_{kl} + Z_{kl}^{r,a} + Z_{kl}^{r,b} + Z_{kl}^{v,a} + Z_{kl}^{v,b}) \times (v + \frac{1}{2})^{k} (J^{2} + J)^{l}$$
(7)

in which explicit isotopic dependence of term coefficients Y_{kl} and various Z_{kl} is suppressed; dependence of these term coefficients on radial coefficients, c_j , $s_j^{a,b}$, $t_j^{a,b}$ and $u_j^{a,b}$ according to analytic relations is explained elsewhere.⁴

Frequency data of BrCl in the electronic ground state X 0⁺ input to the program RADIATOM⁴ consist of eight pure

rotational transitions, $J = 1 \leftarrow J = 0$ of each isotopic variant ⁷⁹Br ³⁵Cl, ⁷⁹Br ³⁷Cl, ⁸¹Br ³⁵Cl and ⁸¹Br ³⁷Cl in vibrational states v = 0 and v = 1,⁹ 33 further transitions up to v = 3 and J = 34¹⁰ and 842 vibration-rotational transitions of the same four species involving states up to v = 3 and J = 85.¹¹ Uncertainties associated with measurement of microwave frequencies are assigned according to standard deviations indicated by the original authors.^{9,10} Most IR lines are assigned an uncertainty 0.015 m^{-1} consistent with the standard deviation of a fit of these data to spectral parameters,¹¹ with other lines, blended or overlapped, being assigned uncertainties large enough that their presence in the data set failed to affect the quality of the fit. During simultaneous inversion of all spectral data directly to radial coefficients according to the criterion of least-sum of weighted squares of residuals, the weight of each datum is the reciprocal square of the corresponding uncertainty.

According to an unbiased criterion of maximum value of the F statistic to select the model,⁴ the best fit of 883 lines requires only ten adjustable parameters, with values of all other possible parameters set to zero (Table 1). These parameters include the equilibrium internuclear distance R_e , equilibrium force coefficient k_e , four coefficients c_j with $1 \le j \le 4$ of function V(z) to represent potential energy [eqn. (3)], two coefficients $t_0^{\text{Br}, \text{Cl}}$ in a function $\alpha(z)$ to represent non-adiabatic rotational effects [eqn. (4)], and two coefficients $s_0^{\text{Br}, \text{Cl}}$ in a function $\beta(z)$ to represent non-adiabatic vibrational effects [eqn. (5)]. The normalised standard deviation $\hat{\sigma}$ of this fit is 0.934, equivalent to that attained in a fit of the same IR lines excluding microwave lines to eight other parameters.¹¹ Without microwave data,^{9,10} the fits require only eight parameters. The maximum range of validity of radial functions in the table is $2.0 \le (R/10^{-10} \text{ m}) \le 2.3$.

Parameters $t_0^{a,b}$ of atomic centres A and B in a diatomic molecule ${}^{+}AB^{-}$ of this polarity are related to electric dipolar moment, μ^{e} , and rotational g-factor, g_J , according to relations⁵

$$\boldsymbol{\mu}^{\mathbf{c}} \approx \frac{1}{2} e R_{\mathbf{e}} (t_0^{\mathbf{a}} - t_0^{\mathbf{b}}) \tag{8}$$

$$g_J \approx m_{\rm p} (t_0^{\rm a}/M_{\rm a} + t_0^{\rm b}/M_{\rm b}) \tag{9}$$

in which e and m_p are protonic charge and mass, and M_a and M_b are rest masses of neutral atoms into which the diatomic molecule dissociates. Thereby values of μ^e and g_J appear in Table 1. Values of t_0^{Br} and t_0^{Cl} are consistent with the polarity ⁺BrCl⁻.

Measurements of the Stark effect on pure rotational transitions $J = 1 \leftarrow J = 0$ of both ⁷⁹Br ³⁵Cl and ⁸¹Br ³⁵Cl in

Table 1 Results of analysis of spectra of BrCl in the electronic ground state X 0^+

property	fitted value ^a
$k_{e}/N \mathrm{m}^{-1}$	281.77511 ± 0.00059
$R_{e}/10^{-10}$ m	2.1370376 ± 0.0000018
<i>c</i> ₁	-2.458127 ± 0.000016
<i>c</i> ₂	2.462864 ± 0.000134
<i>c</i> ₃	-2.8577 ± 0.0037
<i>c</i> ₄	4.042 ± 0.038
S ^{Br}	1.70 ± 0.26
$s_0^{C_1}$	0.846 ± 0.058
t_0^{Br}	-0.5073 ± 0.054
t_0^{Cl}	-0.6463 ± 0.0108
$\tilde{\mu^{e}}/10^{-30}$ C m	2.38 ± 0.78
g_1^{b}	-0.02509 ± 0.00070
$\hat{\sigma}_{\epsilon_{i}}$	0.946
<i>F</i> /10 ¹⁵	5.6

^a Specified uncertainties signify single estimated standard errors; errors of values of k_e and R_e take into account the errors of pertinent fundamental constants h and N_A . SI units are used consistently. ^b Parameters are independent of mass except g_J that applies specifically to ⁷⁹Br ³⁵Cl.

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vibrational state v = 0 yielded only a (mean) magnitude of electric dipole moment, (1.732 \pm 0.007) × 10⁻³⁰ \breve{C} m.¹² No measurement of Zeeman effect on BrCl is available. The distinction between equilibrium properties μ^{e} and g_{J} in eqn. (8) and (9) and their expectation values that correspond to physical measurements is negligible with respect to estimated standard errors of these quantities. The rough value of μ^e confirms only the magnitude measured more precisely by means of the Stark effect,¹² but the sign has also been determined with respect to the internuclear axis. As eqn. (8) shows, the value of μ^{e} results from a relatively small difference between two numbers of only moderate magnitudes; the error of μ^{e} is relatively large because the value of μ^{e} is small and because the error of t_0^{Br} is comparable with the difference between t_0^{Br} and t_0^{Cl} . Being within the nominal standard error, agreement between the value of μ^{e} and that determined with the Stark effect is satisfactory. According to results for SiS and other molecules,13 genuinely adiabatic effects appear negligible for these massive nuclides; hence coefficients $u_i^{\text{Br, Cl}}$ were excluded from parameters in tested sets. The procedure implies separate treatment of electronic and nuclear motions, but explicit account of non-adiabatic (and, if necessary, adiabatic) effects signifies that results transcend nominal limitations of this approximation.

According to the present work with data of only transition frequencies, (neither intensity data nor frequency shifts due to Stark and Zeeman effects were included), the sense +BrCl- of electric polarity of this diatomic molecular species is that expected according to conventional periodic trends, unlike the original deduction for CIF.² The method requires precise data for its success. With only IR data, neither t_0^{Br} nor t_0^{Cl} was evaluated significantly. Although the relative precision of the wavenumbers of most IR lines of BrCl is one part in 3×10^6 ,¹¹ that of microwave lines is one part in (0.3-2) $\times 10^{7.9,10}$ This improvement enables significant evaluation of t_0^{Br} and t_0^{Cl} , hence the rotational g factor and electric dipole moment. Almost all microwave data9,10 were reproduced within 0.9 times their nominal uncertainties. Applications of this method to other diatomic molecular species having sufficient isotopic variants, including molecular ions for which application of Stark and Zeeman effects is troublesome, are expected to yield corresponding results of chemical interest and quantitative estimates of fundamental molecular properties.

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References

- C. H. Townes and A. L. Schawlow, Microwave Spectroscopy, McGraw-Hill, New York, USA, 1955.
- 2 J. J. Ewing, H. L. Tigelaar and W. H. Flygare, J. Chem. Phys., 1972, 56, 1957.
- 3 K. C. Janda, W. Klemperer and S. E. Novick, J. Chem. Phys., 1976, 64, 2698.
- 4 J. F. Ogilvie, J. Phys., B: At. Mol. Phys., 1994, 27, 47.
- 5 J. F. Ogilvie and S. C. Liao, Chem. Phys. Lett., 1994, 226, 281.
- 6 F. M. Fernandez and J. F. Ogilvie, Chin. J. Phys., 1992, 30, 177; 599.
- 7 J. F. Ogilvie, Proc. R. Soc. London, A, 1981, **378**, 287; 1982, **381**, 479.
- 8 J. F. Ogilvie, J. Chem. Phys., 1988, 88, 2804.
- 9 A. C. Legon and J. C. Thorn, Chem. Phys. Lett., 1993, 215, 554.
- R. E. Willis, Ph.D. Thesis, Duke University, USA, 1979; R. E.
 Willis and W. W. Clark, J. Chem. Phys., 1980, 72, 4946.
- 11 H. Uehara, T. Konno, Y. Ozaki, K. Horiai, K. Nakagawa and J. W. C. Johns, *Can. J. Phys.*, 1994, 72, 1145.
- 12 K. P. R. Nair, J. Hoeft and E. Tiemann, Chem. Phys. Lett., 1978, 58, 153.
- 13 J. F. Ogilvie and S. C. Liao, Acta Phys. Hung., 1994, 74, 365.
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