Second-Order Corrections to Quadrupole Effects in Molecules

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ROTATIONAL lines of the molecules BrCN, ICl, and ICN occur at frequencies near 25,000 mc. Splittings of these lines due to nuclear quadrupole effects have been measured to an accuracy of about 0.1 mc, which is a considerable improvement on previous measurements[1] of BrCN and ICN. The rotational levels of these molecules are split by electrostatic quadrupole interactions between the nuclear and molecular charges. While the positions of the lines are in general agreement with the predictions of Casimir's formula,[2] small differences have been found which require the consideration of second-order effects.

The discrepancies are shown most clearly in the case of ICN. The spectrum is not complicated, as is that of ICl, by a second quadrupole interaction (the splitting due to N is of the order of 0.1 mc), and the splitting due to the halide quadrupole is larger in ICN than in BrCN. The energy levels are characterized by the total angular momentum, $\mathbf{F} = \mathbf{J} + \mathbf{I}$, obtained by combining the molecular rotation with the iodine nuclear spin. Absorption lines observed in ICN connect the rotational levels $J = 3$ and $J = 4$. We designate the lines by the F-values of the two levels, that for $J = 3$ coming first. The first column of Table I gives the measured frequencies relative to that of the strongest line at 25,823.1 mc which results from the transition $J = 3$, $F = 11/2$ to $J = 4$, $F = 13/2$. Corresponding theoretical values from Casimir's formula with an interaction constant $eqQ = -2420$ mc are given in the second column. Here Q is the usual quadrupole moment of the nucleus, and q is defined as the gradient of the electric field at the nucleus, $\partial^2 V / \partial Z^2$. Differences between the experimental values and those of the first-order

theory are listed in the third column. It has been found that these differences are adequately accounted for by second-order effects arising from matrix elements of the quadrupole interaction connecting different rotational levels.

Non-vanishing matrix elements connect states with the same F, M_F, but with different values of the rotational quantum number, J. They may be designated

$$(IJFM_F|H_Q|IJ'FM_F),$$

where H_Q is the quadrupole interaction. The second-order energy correction is given by the square of the matrix element divided by the energy difference between the rotational levels, summed over the various J' which connect with the given rotational level J. If this second-order effect is considered, the angular momentum due to molecular rotation is not a constant of the motion.

The required matrix elements applying to linear and symmetric top molecules have been evaluated by a method devised by Racah.[3] The quadrupole interaction contains as the pertinent factor $P_2(\cos\omega)$, where ω is the angle between a nuclear charge and a molecular charge, the angle being measured from the centroid of the nuclear charge. By the addition theorem, $P_2(\cos\omega)$ can be expressed as a scalar product of two spherical harmonics of the second order involving separately the nuclear and molecular coordinates. Racah has given a general formula[4] for the matrix element of the scalar product of two tensors which has been found convenient to use for this problem. The matrix element vanishes if J' differs from J by more than two. We need to give the formulas for $J' = J + 1$ and $J' = J + 2$ only, as the matrix element is symmetric in J

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[1] Townes, Holden, and Merritt, Phys. Rev. 71, 64 (1947); Gordy, Smith, Smith, and Ring, Phys. Rev. 72, 259 (1947).
[2] H. B. G. Casimir, *On the Interaction Between Atomic Nuclei and Electrons* (E. F. Bohn, Haarlem, 1936).
[3] G. Racah, Phys. Rev. 62, 438 (1942).
[4] Reference 3, Eq. (38).

and J'. The squares of the matrix elements are:

$$(IJFM_F|H_Q|IJ+1FM_F)^2$$

$$= \left(\frac{3eqQK}{8I(I-1)J(J+2)}\right)^2 \left(1-\frac{K^2}{(J+1)^2}\right)$$

$$\times \left(\frac{F(F+1)-I(I+1)-J(J+2)}{(2J+1)(2J+3)}\right)^2$$

$$\times (I+J+F+2)(J+F-I+1)$$

$$\times (I+F-J)(J+I-F+1). \quad (1)$$

$$(IJFM_F|H_Q|IJ+2FM_F)^2$$

$$= \left(\frac{3eqQ}{16I(2I-1)(2J+3)}\right)^2 \left(1-\frac{K^2}{(J+1)^2}\right)$$

$$\times \left(1-\frac{K^2}{(J+2)^2}\right)\frac{1}{(2J+1)(2J+3)}$$

$$\times (F+I+J+3)(F+I+J+2)(J+I-F+2)$$

$$\times (J+I-F+1)(J+F-I+2)(J+F-I+1)$$

$$\times (I+F-J)(I+F-J-1). \quad (2)$$

If any of the last four factors of (1) or of the

last eight factors of (2) is negative, the corresponding matrix element is zero. The quantum

number K refers to the spin about the molecular axis, either caused by rotation in a symmetric top molecule or by a transverse vibration in a linear molecule. In the latter case, $K=0$ for the lowest vibrational state. The matrix element with $J'=J+1$ vanishes when $K=0$, so only states for which J' differs from J by two need to be considered.

The lines of ICN listed in Table I refer to the lowest vibrational state, so we set $K=0$. Theoretical values of the second-order corrections to the lines are listed in column 4 of the table. It is seen that these corrections are in good agreement with the differences between the observed values and those derived from Casimir's first-order formula. Similar differences in ICl and smaller differences observed in BrCN are also accounted for very satisfactorily by these second-order corrections.

Lines produced by ICN molecules excited in the bending mode, for which $K=1$, have also been found and compared with theory. The observed positions, relative the the ground state transition $F=11/2\rightarrow13/2$, are listed in the first column of Table II. The lines are split by l-type doubling[1] into two components separated by about 21.5 mc. The upper lines for the transitions $F=5/2\rightarrow7/2$ and $3/2\rightarrow5/2$ were not observed, because both fall near strong lines of the ground state transitions. The first-order quadrupole fre-

quencies, as calculated from the symmetric top formula[5] with $eqQ=-2420$ mc, are listed in the

TABLE I. Quadrupole splitting of $J=3\rightarrow4$ line of ICN in ground vibrational state. Frequencies are given in megacycles relative to the strongest line, $F=11/2\rightarrow13/2$.

Transition	Experimental	First-order theory	Experiment minus first-order theory	Second-order theory
$11/2\rightarrow13/2$	0	0	0	0
$9/2\rightarrow11/2$	14.56	14.69	-0.13	-0.06
$7/2\rightarrow9/2$	-39.58	-37.17	-2.41	-2.35
$5/2\rightarrow7/2$	-94.31	-93.31	-1.00	-1.04
$3/2\rightarrow5/2$	-111.58	-111.65	$+0.07$	$+0.10$
$1/2\rightarrow3/2$	-70.43	-70.17	-0.26	-0.18
$11/2\rightarrow11/2$	-429.25	-428.98	-0.27	-0.45
$9/2\rightarrow9/2$	-33.23	-37.17	$+3.94$	$+3.97$
$7/2\rightarrow7/2$	131.28	132.54	-1.26	-1.38
$5/2\rightarrow5/2$	168.84	170.68	-1.84	-2.18
$3/2\rightarrow3/2$	146.50	147.62	-1.12	-1.15

TABLE II. Quadrupole splitting of $J=3\rightarrow4$ line of ICN in first vibrational state, $K=1$. Frequencies are given in megacycles relative to the strongest line, $F=11/2\rightarrow13/2$ of the ground vibrational state. Each line is split by l-type doubling into two components.

Transition	1 Experimental	2 First-order quadrupole effect	3 Theory plus freq. shift	4 Experiment minus first-order theory	5 Second-order theory
$11/2\rightarrow13/2$	104.58	35.75	103.65	$+0.93$	$+1.06$
	83.20		82.15	$+1.05$	$+1.06$
$9/2\rightarrow11/2$	70.69	3.85	71.75	-1.10	-1.27
	49.16		50.25	-1.09	-1.27
$7/2\rightarrow9/2$	27.70	-40.23	27.67	$+0.03$	-0.27
	6.23		6.17	$+0.06$	-0.27
$5/2\rightarrow7/2$	—	-65.36	2.54		
	-20.13		-18.96	-1.17	-0.75
$3/2\rightarrow5/2$	—	-52.73	17.17		
	-7.54		-6.33	-1.21	-1.00

[5] J. H. Van Vleck, Phys. Rev. 71, 468 (1947); D. K. Coles and W. E. Good, Phys. Rev. 70, 949 (1946).

second column of Table II. Empirical shifts of 67.9 mc for the upper component and of 46.4 mc for the lower component give the theoretical first-order frequencies relative to the ground state line $F=11/2{\rightarrow}13/2$ listed in the third column. Differences between the observed positions and those predicted by the first-order theory are given in the fourth column. These values are in fair agreement with the second-order corrections, as calculated from Eqs. (1) and (2) with $K=1$, given in the fifth column.

Matrix elements for $\Delta J = \pm 1$ as well as for $\Delta J = \pm 2$ contribute to the second-order energies.

The residual discrepancies, the differences between columns four and five of Table II, are larger than those for the ground state. The average is about 0.2 mc. The excited state lines are weaker than the ground state lines, and are thus subject to larger observational errors. The discrepancies are, however, somewhat larger than expected from experimental uncertainties, and may be real.