

Hyperfine Structure of Sodium Iodide*

CARL E. MILLER

Physics Department, Mankato State College, Mankato, Minnesota 56001

AND

JENS C. ZORN

Randall Laboratory of Physics, University of Michigan, Ann Arbor, Michigan 48104

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A molecular-beam electric resonance spectrometer has been used to study radio-frequency transitions between the hyperfine-structure sublevels of the $J=1$ state of $^{23}\text{Na}^{127}\text{I}$. Transitions for the first four vibrational states have been observed in very weak electric field and near zero magnetic field. The intramolecular interaction constants obtained for the ground vibrational state are: $(eqQ)_{\text{sodium}} = -4073.0(10)$ kHz; $(eqQ)_{\text{iodine}} = -262\,140.7(10)$ kHz; $c_{\text{sodium}} = 0.74(8)$ kHz; $c_{\text{iodine}} = 0.28(4)$ kHz; $c_3 = 0.17(8)$ kHz, $c_4 = -0.27(8)$ kHz. The numbers in parentheses are the uncertainties in units of the last quoted digit. Constants for the excited vibrational states have been determined with less precision because fewer transitions were observed.

I. INTRODUCTION

A molecular-beam electric resonance (MBER) spectrometer has been used to investigate the hyperfine structure of $^{23}\text{Na}^{127}\text{I}$. The present work¹ on sodium iodide and the study of potassium chloride by van Wachem and Dymanus² are the first spectroscopic measurements on molecules containing two nuclei with quadrupole moments in which it has been possible to resolve both the electric quadrupole and nuclear magnetic dipole contributions to the hyperfine structure. Our investigation of radio-frequency transitions between hyperfine sublevels of the $J=1$ state of $^{23}\text{Na}^{127}\text{I}$ yielded values of the sodium and iodine quadrupole coupling constants for the first few vibrational states, values of the sodium and iodine spin-rotation interaction constants, and values for the constants which characterize the scalar and tensor parts of the nuclear magnetic dipole-dipole interaction.

The sodium quadrupole and spin-rotation coupling constants in $^{23}\text{Na}^{127}\text{I}$ have been measured by molecular-beam magnetic resonance experiments.³⁻⁵ The state selection in the magnetic resonance beam spectrometer permitted contributions from many rotational and vibrational states, so the values of the sodium hyperfine coupling constants could be obtained only after a complicated analysis of the spectrum; moreover, the spectrum associated with the interactions of the iodine nucleus was so broad that no measurement of the iodine quadrupole coupling constant was possible.⁵

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¹ A preliminary report of this work has been given: C. E. Miller and J. C. Zorn, 22nd Symposium on Molecular Structure and Spectroscopy, Ohio State University, Columbus, Ohio, September, 1967, p. 58.

² R. van Wachem and A. Dymanus, *J. Chem. Phys.* **46**, 3749 (1967).

³ W. A. Nierenberg and N. F. Ramsey, *Phys. Rev.* **72**, 1075 (1947).

⁴ R. A. Logan, R. E. Coté, and P. Kusch, *Phys. Rev.* **86**, 280 (1952).

⁵ R. E. Coté and P. Kusch, *Phys. Rev.* **90**, 103 (1953).

The iodine quadrupole interaction in sodium iodide was first measured in a microwave absorption experiment by Honig, Mandel, Stitch, and Townes⁶; they were able to make observations on the first four vibrational states, but their spectrometer was not capable of resolving any of the other hyperfine interactions.

II. THEORY

The Hamiltonian used to explain the observed radio-frequency spectra is^{7,8}

$$H = \sum_{i=1}^2 [(Q \cdot V)_i + c_i(I_i \cdot J)] + c_3 I_1 \cdot d(J) \cdot I_2 + c_4 I_1 \cdot I_2, \quad (1)$$

where the subscript 1 refers to the ^{127}I nucleus and subscript 2 refers to the ^{23}Na nucleus. The operators $(Q \cdot V)_i$ and $c_i(I_i \cdot J)$ represent the electric quadrupole and nuclear-spin-molecular-rotation interactions of the i th nucleus; the remaining terms describe the tensor and scalar parts of the nuclear magnetic dipole-dipole interaction. Since the transitions between the $J=1$ hyperfine levels were examined under conditions of very weak electric field (<3 V/cm) and near zero (<50 mG) magnetic field, the Stark and Zeeman operators need not be included in the Hamiltonian.

The earlier investigations of this molecule show that the quadrupole interaction of the iodine nucleus is much larger than the quadrupole interaction of the sodium. As a result, the most useful representation for the very weak field situation is $|\alpha I_1 J F_1 I_2 F\rangle$, conveniently abbreviated as $|F_1 F\rangle$, which corresponds to the coupling scheme $F_1 = I_1 + J$, $F = F_1 + I_2$. The vectors I_1 and I_2 refer to the nuclear spins of iodine and sodium; J is the rotational angular momentum of the molecule;

⁶ A. Honig, M. Mandel, M. L. Stitch, and C. H. Townes, *Phys. Rev.* **96**, 629 (1954).

⁷ K. V. Svidzinskii, *Soviet Maser Research* (Consultants Bureau Enterprises, Inc., New York 1964).

⁸ J. Bardeen and C. H. Townes, *Phys. Rev.* **73**, 627 (1948).

TABLE I. The hfs constants^a for the $J=1$ state of NaI.

Quantity	$v=0$	$v=1$	$v=2$	$v=3$
Present experiment				
$(eqQ)_{Na}$	-4 073.0(10)	-4 039.6(20)	-3 997.8(40)	-3 955.0(80)
$(eqQ)_I$	-262 140.7(10)	-265 523.3(20)	-268 841.4(40)	-272 090.0(80)
c_{Na}	0.74(8)	0.80(12)		
c_I	0.28(4)	0.21(6)		
c_3	0.17(8)	0.16(10)		
c_4	-0.27(8)	-0.25(10)		
Other results				
	Ref.			
$(eqQ)_{Na}$	b	-3 960		
	c	-4 100(50)	-4 050(50)	-3 980(50)
$(eqQ)_I$	d	-259 870(600)	-264 520(650)	-267 590(400)
	c	-262 000(500)	-265 430(500)	-268 800(500)
$ c_{Na} $	b	0.69		

^a All the constants are given in kilohertz; uncertainties, in parentheses, are in units of the last digit given.

^b Molecular-beam magnetic resonance; see Ref. 5.

^c Molecular beam electric resonance; F. J. Lovas, University of California Radiation Laboratory Rept. UCRL-17909, November, 1967.

^d Microwave absorption spectroscopy; see Ref. 6.

and α denotes the remaining quantum numbers which are necessary to complete the representation.

The energy of each hfs level, relative to a particular vibration-rotational energy state, is

$$\begin{aligned}
 E_{F_1, F} = & \langle F_1 F | \sum_{i=1}^2 [(Q \cdot V)_i + c_i (I_i \cdot J)] | F_1 F \rangle \\
 & + \sum_{J'} \frac{|\langle \alpha I_1 J' F_1 I_2 F | (Q \cdot V)_1 | \alpha I_1 J F_1 I_2 F \rangle|^2}{E_J - E_{J'}} \\
 & + \sum_{F_1'} \frac{|\langle F_1' F | (Q \cdot V)_2 | F_1 F \rangle|^2}{E_{F_1'} - E_{F_1}} \\
 & + \langle F_1 F | c_3 I_1 \cdot d(J) \cdot I_2 + c_4 I_1 \cdot I_2 | F_1 F \rangle, \quad (2)
 \end{aligned}$$

where $E_{F_1} = \langle F_1 F | (Q \cdot V)_1 | F_1 F \rangle$, $E_J = B_v J(J+1)$, and B_v is the rotational constant of the molecule.

The interactions of the nuclear magnetic dipole moments are small enough so that first-order perturbation theory is sufficient to calculate their effects on the energy levels of the molecule. The large quadrupole interaction of the iodine causes an appreciable mixing of the rotational states, however, and the sodium quadrupole interaction energy is not negligible compared to the separation between the F_1 levels of the $J=1$ state; so, the contributions of both nuclear quadrupole interactions to the energy levels must be calculated to second order in the perturbation theory. Contributions in higher orders of perturbation theory have been calculated for all the hfs interactions but they are small enough to be neglected in the present experiment.

III. EXPERIMENT

The MBER spectrometer used for these investigations⁹ is similar to those which have been described in the literature.^{2,10} The beam is produced in an oven made of nickel, and the beam molecules are detected with a surface ionizer. The four-pole A and B fields which provide state selection are each 25 cm long. The detected signal from the total molecular beam was typically 8×10^{-11} A; the signal from state selected molecules was 8×10^{-12} A on a background of 1.5×10^{-12} A.

The transitions $(F_1 = \frac{3}{2}, F = 2) \rightarrow (F_1 = \frac{1}{2}, F = 4)$ at 23.9002 MHz and $(F_1 = \frac{3}{2}, F = 3) \rightarrow (F_1 = \frac{1}{2}, F = 4)$ at 78.9744 MHz were the largest observed; they were seen with a signal-to-noise ratio of about 10/1 as a change of 2.5×10^{-14} A in the detector current. The rf was applied over a 17 cm long portion of the C field, and the observed linewidth was 2.6 kHz.

For $^{23}\text{Na}^{127}\text{I}$ in the $J=1$ rotational state, a total of 23 hyperfine transitions for $|\Delta F_1| = 1, 2$ within each vibrational state satisfy both the selection rules and the criterion for observability in an MBER spectrometer. In this experiment, 16 lines were seen for $v=0$, nine for $v=1$, four in $v=2$, and two in $v=3$.

IV. RESULTS

A least-squares analysis of the data was made to determine the hfs constants. Subjective estimates of the quality of the spectral lines were used to assign weights to the observation equations. Since the observation equations are nonlinear functions of the hfs con-

⁹ C. E. Miller, Ph.D. dissertation, University of Michigan, University Microfilms, Ann Arbor, Michigan, 1967.

¹⁰ C. Schlier, Z. Physik **147**, 600 (1957).

stants, there is no simple way to calculate the uncertainties in the final values of these constants. Therefore, the uncertainties were estimated by seeing how the output values of the hfs constants changed when one or more input values of the transition frequencies were slightly altered.

Enough data are available for independent determinations of all the hfs constants in $v=0$ and $v=1$. Since the spin-rotation and dipole-dipole interaction constants in $v=0$ and $v=1$ are the same to within the accuracy of our measurements, we use the $v=1$ values of c_{Na} , c_{I} , c_3 , and c_4 to extract from the $v=2$ and $v=3$ spectrum values of the quadrupole interactions in these higher vibrational states.

Our measured values for the hyperfine interaction constants are given in Table I.

If we express the quadrupole interaction constants in a power series of the form

$$eqQ = a + b(v + \frac{1}{2}) + c(v + \frac{1}{2})^2, \quad (3)$$

the iodine quadrupole interaction can be described by $a = -260\,425.0$ kHz, $b = -3447.5$ kHz, and $c = 32.4$ kHz. The sodium quadrupole interaction can be described by the coefficients: $a = -4086.6$ kHz, $b = 25$ kHz, and $c = 4.2$ kHz. These coefficients were calculated from the $v=0, 1, 2$ data because of the large uncertainties in the values of the $v=3$ coupling constants. The predictions made by using the a, b , and c coefficients in Eq. (3), however, agree with our measured values of the quadrupole coupling constants in the $v=3$ state.

As can be seen from Table I, the iodine quadrupole coupling constants in the $v=0, 1, 2, 3$ states of $^{23}\text{Na}^{127}\text{I}$ measured by microwave absorption⁶ differ from the MBER values by more than three times the sum of the quoted errors. The reason for this discrepancy is not understood.

The magnitude of the sodium spin-rotation interaction constant measured by Coté and Kusch⁵ is in good agreement with our result. Their value for the sodium quadrupole interaction constant differs by several percent from ours, but at least part of this difference could be attributed to the difficulty in analyzing all the rotational-state contributions to the magnetic resonance spectrum.

V. DISCUSSION

It has been shown by several workers^{11,12} how a knowledge of the vibrational state dependence of

¹¹ H. W. deWijn, *J. Chem. Phys.* **44**, 810 (1966).

¹² C. H. Townes and B. P. Dailey, *J. Chem. Phys.* **17**, 782 (1949).

quadrupole coupling constants helps to understand the nature of the chemical bond. Microwave absorption and molecular-beam experiments have given values for the hyperfine coupling constants in many of the alkali halides, but most of these experiments have given accurate values for only one of the quadrupole interactions in any given molecule. Measurements which fully resolve the hyperfine structure of the alkali chlorides, bromides, and iodides are therefore useful to test those theories which predict how both the alkali and the halogen quadrupole interaction should change as a function of the molecule's vibrational state.

For example, deWijn¹¹ has proposed that the simple ionic model of a polar diatomic molecule should be modified to include not only the mutual polarization of the ions and the antishielding effects, but also the quenching of the ion polarizations by the repulsive forces between the ions. The different electron configurations of the two ions then leads to a different predicted dependence on vibrational state for the alkali and halogen nuclear quadrupole interactions.

For (eqQ) (halogen) in the deWijn model, the antishielding effects are small compared to the polarization of the halogen ion's orbitals; the electric field gradient at the iodine nucleus is predicted to change by 32×10^{12} esu/cm² per vibrational state, while our experiment indicates that the change is 61×10^{12} esu/cm².

For (eqQ) (alkali), the deWijn model predicts an enhancement of the antishielding by the mutual polarization of the ions; the change in the electric field gradient at the sodium nucleus is predicted to be 2.2×10^{12} esu/cm² per vibrational state, while the experiment gives a value of 3.4×10^{12} esu/cm².

The qualitative agreement between experiment and theory suggests that progress is being made toward the understanding of the nature of the bond in polar molecules.

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