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HYPERFINE STRUCTURE IN THE VISIBLE MOLECULAR-IODINE ABSORPTION SPECTRUM*

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The observed hyperfine structure in the visible iodine absorption spectrum can be explained as a combination of a nuclear electric quadrupole interaction in both the ground and excited electronic states with a difference in coupling constants ($eQq' - eQq''$) = -958 ± 15 MHz (0.032 cm^{-1}) and a magnetic hyperfine interaction in the excited state with a coupling constant of 500 ± 100 MHz (0.017 cm^{-1}).

Recently there have appeared two descriptions of the use of the visible spectrum of iodine vapor to assist in the frequency stabilization of lasers. The experiment of Ezekiel and Weiss¹ detected the resonance fluorescence in a molecular beam of iodine excited by a $5145\text{-}\text{\AA}$ light from an argon-ion laser. The experiment of Hanes and Dahlstrom² detected saturated absorption in iodine vapor (~ 0.04 Torr) contained within the cavity of a He-Ne laser operating at 6328 \AA . Both of these experiments yielded what was interpreted to be hyperfine structure in this spectrum. In this Letter it will be shown that if one assumes a nuclear electric quadrupole (NEQ) interaction in both electronic states involved in the transition and a magnetic hyperfine interaction in the excited state, the 14 lines observed by Hanes and Dahlstrom can be calculated to within the experimental accuracy. Only the data of these workers will be discussed because they seem to result from a single value of the rotational quantum number J , namely, the $J'' = 127$ level of the ground-state vibrational level with quantum number $v'' = 5$. The data of Ezekiel and Weiss are at lower resolution and, in addition, may result from absorption at more than one value of J'' .

The 14 features observed by Hanes and Dahlstrom are listed in column 5 of Table I. As can

be seen they are arranged in alternating groups of 3 and 4 members with the groups separated by

Table I. Assignments of the observed transition $J' = 128 \leftarrow J'' = 127$.^a

	λ_{127} calc. as in ref. 7	F	ν_{calc} (MHz) NEQ only	ν_{obs} (MHz) ref. 2	ν_{calc} (MHz) NEQ + Magnetic
a	-0.4093	J+1	295.1	297.3	298.9
b	-0.4043	J	290.4	288.5	290.2
c	-0.3998	J-1	286.2	280.7	282.3
d	-0.2652	J+2	156.8	166.9	164.5
e	-0.2557	J+1	148.0	153.6	151.8
f	-0.2497	J-1	142.4	139.7	138.5
g	-0.2402	J-2	133.6	126.3	125.6
h	-0.1122	J+3	10.3	22.3	21.9
i	-0.1011	J	0.0	0.0	0.0
j	-0.09078	J-3	-9.6	-22.0	-21.3
k	+0.04572	J+3	-140.7	-129.3	-129.0
l	+0.05008	J+2	-144.8	-137.1	-137.0
m	+0.05128	J-2	-145.9	-152.3	-153.7
n	+0.05648	J-3	-150.8	-162.0	-162.4

^aThe frequencies in this table were calculated with $\Delta J = \Delta F = +1$, $\Delta \epsilon = 0$ (see Ref. 7). The seven remaining transitions are calculated to occur at -261.9 , -288.9 , -292.2 , -319.6 , -556.2 , -581.2 , and -606.2 MHz.

~150 MHz. Because the lines are observed in saturated absorption their widths are only ~2 MHz (the Doppler width in this case is ~370 MHz) and because of the NEQ interaction the lines are spread out over an interval greater than the Doppler width of a "single" line. The latter point was discovered independently by line-breadth measurements of the visible iodine absorption spectrum.³

The I^{127} nucleus has a spin $I_1 = \frac{5}{2}$ and a nonzero quadrupole moment Q . Because iodine is a homonuclear diatomic molecule the values of $\vec{I} = \vec{I}_1 + \vec{I}_2$ can take on only certain values for a given value of J . For the $^1\Sigma_g^+$ ground state the values $I = 5, 3, 1$ can combine only with odd values of J'' while the values of $I = 4, 2, 0$ can combine only with even values of J'' . For the excited state, $^3\Pi_{ou}^+$, the combinations are reversed because of the u character of the electronic wave function of the excited state. In the absence of perturbations dependent on I there are $2I + 1$ degenerate states associated with each value of I . In this case the even values of J'' will have a degeneracy of 15; the odd values, a degeneracy of 21. This causes an observable⁴ intensity alternation of $7(J'' \text{ odd}) : 5(J'' \text{ even})$ in the normal absorption spectrum of iodine.

The NEQ interaction will remove this degeneracy and since iodine is expected⁵ to have a large quadrupole coupling constant ($eQq'' \cong -2500$ MHz), the consequent splitting will be unusually large. Furthermore, the coupling constant is expected to be different in the two electronic states because of a difference in the electric field gradient q between the states. At high values of J the NEQ energy of a diatomic molecule having two nuclei with quadrupole moments can be approximated⁶ by the sum of two single-nucleus NEQ energies,

$$E_{\text{NEQ}} = l_i(eQq)_{\text{nuc1}} + l_j(eQq)_{\text{nuc2}} = \lambda eQq_1.$$

The second equality holds only for a homonuclear diatomic molecule. With a spin of $\frac{5}{2}$ the eigenvalues l_i and l_j can take on the values of $\frac{1}{4}$, $-1/20$, and $-\frac{1}{8}$. The eigenvalues of λ thus calculated, along with the number of states with the given eigenvalues, are presented in Table II. At high J a "single" line will be composed of six groups of lines. Four of these adjacent groups will be equally spaced with a separation $0.15(eQq' - eQq'') = 0.15\Delta eQq$; the final group will be separated by $0.30\Delta eQq$. Comparing Tables I and II it can be seen that the data of Hanes and Dahlstrom can be fitted only with $J''(\text{odd})$, $\Delta eQq \cong -1000$ MHz, and

with lines a , b , and c belonging to the eigenvalue -0.4 .

In the $I_1 I_2 I J F M_F$ representation, where

$$\vec{I}_1 + \vec{I}_2 = \vec{I}, \quad \vec{I} + \vec{J} = \vec{F},$$

and M_F is the projection of \vec{F} on a space-fixed axis, the first-order NEQ energy can be calculated exactly.⁷ With $I_1 = I_2 = \frac{5}{2}$ and $J = 127$ the eigenvalues in column 2 of Table I are calculated. With $\Delta eQq = -958$ MHz the transition frequencies in column 4 are obtained after setting the frequency of line i to be zero in order to agree with the convention of Hanes and Dahlstrom.

The overall agreement between columns 4 and 5 is fairly good, but the calculated and measured values of the lines h and j differ by about ten times the experimental error. The second-order NEQ energy⁵ does not seem to be large enough to explain these differences.⁸ If a magnetic hyperfine interaction of the form

$$E_{\text{mag}} = \frac{K(\vec{I}_1 \cdot \vec{J} + \vec{I}_2 \cdot \vec{J})}{J(J+1)} = \frac{KC}{J(J+1)},$$

where in the $I_1 I_2 I J F M_F$ representation⁶ $2C = F(F+1) - J(J+1) - I(I+1)$ is added to the diagonal terms of the NEQ matrix before diagonalization, a much improved set of values is obtained. With $K = 500$ MHz the values in column 6 of Table I are calculated. With the possible exception of lines d and e the calculated and observed values agree within the experimental error.

The seven unobserved lines predicted by this treatment are also included in Table I. Presumably they are not observed because the frequency scan of the laser does not extend over a great enough range. The error in ΔeQq is estimated to

Table II. Eigenvalues [λ of Eq. (1)] for NEQ interaction of a homonuclear diatomic molecule with nuclear spin $\frac{5}{2}$ at high J .

λ	$\Delta\lambda$	Number of states	
		J'' even	J'' odd
0.50		1	3
	0.30		
0.20		4	4
	0.15		
0.05		4	4
	0.15		
-0.10		1	3
	0.15		
-0.25		4	4
	0.15		
-0.40		1	3
		15	21
	Total	15	21

be ± 15 MHz; that of K , to be ± 100 MHz. It should be pointed out that this analysis has been facilitated by the large quadrupole coupling constant of iodine and the high value of J observed in this spectrum. At lower values of J the magnetic and NEQ interactions should become more nearly equal and the second-order NEQ interactions will become more significant. Thus, at low J the spectrum may be much more difficult to analyze.

This saturated absorption spectrum represents the highest resolving power (10^8) yet achieved in electronic spectroscopy. The technique should be applicable to other spectroscopic problems which require extremely high resolving power.

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⁸By assuming that the second-order NEQ energy can be approximated by the sum of the energies of two single nuclei the maximum corrections to the ground and excited states are calculated to be 0.55 and 1.36 MHz, respectively, with $eQq'' = -2500$ MHz and $eQq' = -3458$ MHz.

VACUUM-ULTRAVIOLET PHOTON PRODUCTION IN LOW-ENERGY COLLISIONS BETWEEN TWO NEUTRAL ARGON ATOMS*

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We describe the first observation of extreme-ultraviolet photons produced during collisions between two ground-state neutral argon atoms. The energy dependence of the relative cross section for photon production is found to exhibit structure at about 70 eV c.m. energy, similar to that observed in the cross section for ionization in argon collisions.

During an energetic collision between two neutral argon atoms, excitation may occur to a metastable level, or to a level which decays by emission of a photon. Photons from transitions of these excited states to the ground state, the argon resonance series, have wavelengths from 1067 to 778 Å, the ionization limit.¹ This Letter describes the first measurements made of the relative cross section for emission of photons of these wavelengths after an atom-atom encounter. The c.m. energies examined were from near threshold to 500 eV.

Ground-state argon ions formed in an electron-impact ion source were electrostatically accelerated and focused into a charge-transfer cell.² This cell contained a low-pressure hydrogen target which allowed the formation of argon neutral atoms entirely in the ground state for all incident ion energies below 230 eV. In this interval there is insufficient energy available in the c.m. system for excitation to occur during the charge-

transferring collision. This method of producing a neutral atomic beam with energies between 30 and 1000 eV in the laboratory system has been previously described.³ After passing through the charge-transfer cell, the ionic component of the beam was electrostatically removed from the beam by a parallel-plate repeller assembly and the neutral beam was allowed to pass into a target chamber. The incident argon-atom beam intensity was determined by measuring the current of slow hydrogen ions formed in the charge-transfer region and applying a measured correction for beam loss at the exit aperture of the charge-transfer cell and at the entrance aperture of the target chamber. The beam intensity was known to $\pm 30\%$.

The target chamber contained argon at a pressure of about 1×10^{-4} Torr and a Bendix magnetic electron multiplier (MEM). The 0.25-in.² cathode of the MEM is sensitive to photons of wavelength less than 1500 Å but greater than 2 Å,