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ESR of matrix isolated bromine atoms produced in the H+Br₂ reaction ^{a)}

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The products of the H(D) + X_2 reaction, where X is Br, Cl, or F, have been trapped in solid argon at 4 °K and observed via ESR. With Br₂ as reactant the observed spectra are attributed to Br atoms electronically quenched in an axial crystal field. The spectra obtained using the other halogens were not clearly attributable to quenched atoms. The ESR of matrix-isolated Br atoms has not been observed previously, {While this paper was being reviewed, H. Muto and L. D. Kispert observed the ESR spectrum of partially quenched Br atoms in x-irradiated N-bromosuccinimide single crystals [J. Chem. Phys. 72, 2300 (1980)]} but their magnetic properties are similar to those recently observed by Iwasaki, Toriyama, and Muto for I atoms quenched in solid xenon. For Br: $g_{\perp} = 2.646(1)$, $g_{\parallel} = 1.55(1)$, $|A_{\perp}| = 1937(20)$ MHz, $|A_{\parallel}| = 423(10)$ MHz, and $Q_{\parallel} = 100(10)$ MHz. Comparison was made with crude axial crystal field predictions derived using the magnetic parameters of the gas-phase atoms.

I. INTRODUCTION

This research began as an exploratory attempt to observe the ESR spectra of radicals trapped at 4 °K during the reaction

 $H + X_2 - (HX_2) - HX + X ,$

where X is a halogen atom. Interest was principally in the possibility of observing the HX_2 radical in the vicinity of the saddle point. Many molecular beam studies¹⁻³ have been made of this reaction, and the geometry and electronic properties of the intermediate have been calculated or speculated on.⁴⁻⁷ Earlier, preliminary and inconclusive ESR matrix studies were attempted in this laboratory.⁸ From matrix IR spectra, Ault⁹ has found no evidence of the HF₂ radical and the formation of only a weakly bound complex between HF and Cl. His matrices were prepared by the photolysis of F₂ in the presence of either HCl or HF in argon at 14 °K.

The procedure used here involved the reaction of H (or D) atoms with the X_2 in a halogen-argon mixture during condensation of the gases onto a rod at 4 °K. For Br₂, but not for Cl₂ or F₂, it turned out that the spectrum could be clearly analyzed as that of electronically quenched atoms. This was unexpected in that the ESR spectra of halogen atoms had not previously been detected in matrices.¹⁰ However, while this paper was being prepared for publication, Iwasaki *et al.*¹¹ observed the ESR spectrum of quenched I atoms in xenon matrices, and a comparison with their parameters is of interest. For Cl₂ and F₂, although some lines were observed, they were not unequivocally assignable to quenched atoms.

The quenching of ${}^{2}P_{1/2}Al$, 12,13 Ga, 13 and B¹⁴ atoms in matrices has been studied earlier in this laboratory. Here we report on ${}^{2}P_{3/2}$ Br atoms observed in a similar, but different, manner than in previous matrix studies. Earlier preparations of halogen atoms in matrices utilized discharge or photolysis of X_2 molecules.¹⁰ The fact that these halogen atoms were not previously observed in ESR spectra was undoubtedly correctly explained by suggesting that matrix interactions with the orbital angular momentum of the atom caused severe magnetic anisotropy and broadening of the lines beyond detection.¹⁰ It is clear then that the site of the X atom here is quite different and, because of its mechanism of formation, it presumably lies adjacent to the HX molecule in the matrix.

II. EXPERIMENTAL

A 2% mixture of Br₂ (Reagent grade, Fisher Scientific Co., purified by successive applications of the freezepump-thaw technique) in argon gas (Airco, ultrapure grade) was codeposited with either H or D atoms produced by passing H_2 (Airco, 99.999% pure) or D_2 (Matheson, >99.5% pure) through a resistively heated (~2100 °C) tungsten tube onto a thin flat copper rod^{15} held at 4 °K. For Cl₂, a corresponding 2% mixture of Cl_2 (Airco 99.96% pure) in argon was used. F_2 (>99% pure) was kindly supplied by the Chemical Engineering Division of the Argonne National Laboratory. X-band ESR spectra were recorded using a Varian model 4500 spectrometer with superheterodyne detection.¹⁶ Details of the furnace and Dewar assemblies have been published previously.¹⁷ The weaker parallel lines in the spectra were signal averaged using a Nicolet 1074 instrument. Attempts to narrow the ESR lines by annealing the matrix were not successful since a slight increase in the temperature allowed the trapped H(D) atoms to diffuse and recombine, causing the matrix to vaporize.

III. ESR SPECTRA AND RESULTS

A. $H(D) + Br_2$

The ESR spectrum observed when D atoms were codeposited with Br_2/Ar is shown in Fig. 1. The spectra with $H + Br_2/Ar$ and with $D + Br_2/Ar$ were essentially the same and remained unchanged whether they were recorded with the flat surface of the rod oriented at either 0° or 90° with respect to the static magnetic field, thus indicating random orientation of the trapped radicals.

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FIG. 1. ESR spectrum of $D+Br_2$ reaction trapped in an argon matrix at 4 °K. D atoms were produced by dissociation of D_2 passing through a tungsten tube at ~2100 °C.

Spectra with $D + Br_2/Ar$ were used for analysis since those with $H + Br_2/Ar$ had a strong H atom signal overlapping with a perpendicular Br line, making an accurate determination of its line position difficult. The four strong broad [~130 G (FWHM)] lines are attributed to hyperfine structure (hfs) of the perpendicular transition of quenched Br atoms in an axial crystal field. There appear to be a few weak lines in between these which have not been assigned but may be due to some Br atoms trapped in a different matrix site. The two naturally occurring bromine isotopes, ⁷⁹Br and ⁸¹Br, both of spin $I = \frac{3}{2}$ and having very nearly the same magnetic moments (2.106 and 2.270 n.m.), contribute to the linewidth since they are also almost equally abundant. The parallel lines indicated in Fig. 1 are much less certain since it was necessary to use signal averaging to enhance their intensity.

The observed ESR spectrum could be fitted to an axially symmetric spin Hamiltonian of the form

$$\mathcal{H}_{spin} = g_{\parallel}\beta H_{x}S_{x} + g_{\perp}\beta (H_{x}S_{x} + H_{y}S_{y}) + A_{\parallel}S_{x}I_{x} + A_{\perp}(S_{x}I_{x} + S_{y}I_{y}) + Q_{\parallel}[I_{x}^{2} - \frac{1}{3}I(I+1)], \qquad (1)$$

where the symbols have their usual meaning.¹⁸ Computer diagonalization of this Hamiltonian yielded the magnetic parameters given in Table II, which provided the fit of the observed lines as indicated in Table I. The "parallel" parameters have a relatively high uncertainty,

TABLE I. Observed and calculated^a line positions for Br atoms trapped in an argon matrix at $4 \,^{\circ}$ K (spectrometer frequency = 9.4045 GHz).

Resonance	Perpendicul	ar component	Parallel component			
line M_I	Obs. (G)	Calc. (G)	Obs. (G)	Calc. (G)		
+ 32	1900(5)	1909	3836(15)	3832		
$+\frac{1}{2}$	2273(5)	2269	4055(15)	405 9		
$-\frac{1}{2}$	2680(5)	2684	4275(15)	4271		
- 32	3113(5)	3117	4522(20)	4530		

^aCalculated from the magnetic parameters in Table II.

TABLE II. Magnetic parameters for Br atoms trapped in an argon matrix at 4 °K.

g tensor	A tensor (MHz)	Q tensor (MHz)			
$g_{\parallel} = 1.55(1)$	$ A_{ } = 423(10)$	$Q_{ } = 100(10)$			
$g_1 = 2.646(1)$	$ A_{\perp} = 1937(20)$				
$\Delta g_{II} = -0.45$	$A_{1so} = 1433^{a}$				
$\Delta g_1 = 0.644$	$A_{dip} = -505^{a}$				

^aAssuming A_{\parallel} and A_{\perp} are positive.

but the second-order effect producing unequal spacing of the perpendicular lines¹⁹ indicates that the value of $|A_{\parallel}|$ given in Table II is of the correct order of magnitude.

B. $H+Cl_2$

The ESR spectrum of the $H + Cl_2$ reaction isolated in an argon matrix at 4 °K yielded only three very broad lines of rapidly decreasing intensity at 3067(5), 2797(5), and 2546(5) G [$\nu = 9.4050$ GHz]. It was considered possible that an even weaker fourth hyperfine line might lie at a lower field, but it was not detected. The breadth of the lines would have to be attributed to overlapping hyperfine features due to the ³⁵Cl and ³⁷Cl nuclei.

C. $H + F_2$

A number of experiments were performed in which F_2/Ar mixtures of $\frac{1}{100}$, $\frac{2}{100}$, and $\frac{5}{100}$ were used with H atoms produced by passing H₂ through a resistively heated tungsten cell or by forming H atoms using a microwave discharge. In some cases the liquid helium was vacuum pumped to reduce the temperature of the rod to ~2 °K. O₂F impurity signals may have appeared sometimes in the matrix spectra, but additional signals, not attributable to quenched F atoms, were observed but could not be analyzed.

IV. DISCUSSION

For a $p_x^2 p_y^2 p_z^1$, ${}^2P_{3/2}$ atom, as indicated by Ammeter and Schlosnagle (AS)¹³ (and Iwasaki *et al.*¹¹), the hole in the np^5 configuration may occupy the

$$\psi^{*}(^{2}\Sigma^{*}) = b\Phi_{0}^{*} + a\Phi_{*1}^{*}$$
(2)

level where a and b are as before [their Eq. (3)]:

$$a = \left\{1 + \frac{1}{4}\left[5 - 6x + 9x^2 + 3(1 - 3x)(x^2 - \frac{2}{3}x + 1)^{1/2}\right]\right\}^{-1/2},$$

$$b = (1 - a^2)^{1/2}.$$
(3)

Here $x = \Delta/\zeta$, where ζ is the atomic spin-orbit coupling constant, and Δ is the energy difference between the lower ${}^{2}\Sigma$ state and the upper ${}^{2}\Pi$ state of the quenched atom produced by the (assumed) axial crystal field. The g components [in their Eq. (4)] now become:

$$g_{\parallel} = g_{e}(b^{2} - a^{2}) + 2a^{2} \cong g_{e}b^{2} , \qquad (4)$$

$$g_{1} = g_{e}(1 - a^{2}) + 2\sqrt{2} ab = g_{e}b^{2} + 2\sqrt{2} ab .$$
(5)

These have been plotted in Fig. 8 of AS as the dotted lines.

According to the g tensor components in Table II,

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TABLE III. Gas-phase hyperfine parameters (in MHz) for Br atoms.

	Atom (natural abundance)				
Magnetic parameter	⁷⁹ Br (50.57%)	⁸¹ Br (49.43%)			
A _{3/2}	884.09 ^a 884.810 ^b	953.04 ^a 953.768 ^b			
A _{1/2}	5336.3 ^a 5332.55°	5747.0 ^a 5748.15 ^c			
A 3/2, 1/2	$\sim 130^{d}$	$\sim 130^{d}$			
P_L	1713	1840			
P _s	2327	2519			
— к	0.0686	0.0754			

^aReference 23.

^bReference 25.

^cReference 24.

^dEstimated from theory, see text.

atoms are well quenched, i.e., both g components are approaching rather closely $g_e = 2.00$. The g components can be used with Eqs. (3) through (5) to evaluate a, b, and Δ . Because this can be done independently for g_{\parallel} and g_{\perp} , one can calculate two values of Δ , Δ_{\parallel} , and Δ_{\perp} : with $\zeta_{Br} = 2456 \text{ cm}^{-1}$,

$$a_{\mu} = 0.4745$$
, $\Delta_{\mu} = 705 \text{ cm}^{-1}$,
 $a_{\mu} = 0.3124$, $\Delta_{\mu} = 2320 \text{ cm}^{-1}$.

The perpendicular measurements are more reliable than the parallel so that Δ_{\perp} is the more accurate one within the framework of the crystal field model. However, if the g_{\parallel} values are correct, the discrepancy between Δ_{\parallel} and Δ_{\perp} indicates the inadequacy of that simple model.¹³ Because of the inaccuracy of the experimental data, it did not appear useful to pursue the theory beyond this crystal field model.

The hyperfine Hamiltonian is^{13,20}

$$\mathcal{H}_{\mathbf{hf}_{\mathbf{S}}} = P_{L} (\mathbf{L} \cdot \mathbf{I}) + P_{\mathbf{s}} \{ [\xi L (L+1) - \kappa] (\mathbf{S} \cdot \mathbf{I}) - \frac{2}{3} \xi [(\mathbf{L} \cdot \mathbf{S}) (\mathbf{L} \cdot \mathbf{I}) + (\mathbf{L} \cdot \mathbf{I}) (\mathbf{L} \cdot \mathbf{S})] \}$$
(6)

with $\xi = \frac{2}{5}$ for a single *p* electron, and²¹

$$P_{L} = g_{n}\beta_{n}g_{e}\beta_{e}\langle r_{l}^{-3}\rangle , \qquad (7)$$

$$P_{S} = g_{n}\beta_{n}g_{e}\beta_{e}\langle r_{sC}^{-3}\rangle , \qquad (8)$$

$$-P_{S}\kappa = g_{n}\beta_{n}g_{e}\beta_{e}\frac{8}{3}\pi |\psi(0)|^{2}.$$
⁽⁹⁾

Then the isotropic and anisotropic parts of the hyperfine tensor can be expressed [Eq. (7b) of AS] in terms of these hyperfine (hf) parameters and the g shifts:

$$A_{1so} = \frac{A_{\parallel} + 2A_{\perp}}{3}$$

= $\frac{2}{3}P_{L}(\Delta g_{\perp} - \frac{3}{2}\Delta g_{\parallel}) - P_{S}[\kappa(1 + \frac{2}{3}\Delta g_{\parallel}) - \frac{1}{3}\Delta g_{\parallel}],$ (10)

$$A_{dip} = \frac{A_{j_{1}} - A_{j_{1}}}{3}$$

= $-\frac{1}{3}P_{L} \cdot \Delta g_{1} + \frac{1}{3}P_{S}[\frac{6}{5} - \frac{9}{10}\Delta g_{1} + (\frac{7}{10} - \frac{1}{2}\kappa)\Delta g_{1}].$ (11)

Gas phase work can provide values of the hfs parameters $A_{3/2}$, $A_{1/2}$, and $A_{3/2,1/2}$ from which the radical parameters can be calculated from the following relations²²:

$$P_{L} = \frac{5}{6}A_{3/2} + \frac{1}{6}A_{1/2} + \frac{2}{3}A_{3/2,1/2} ,$$

$$P_{S} = -\frac{5}{9}A_{3/2} + \frac{5}{9}A_{1/2} - \frac{10}{9}A_{3/2,1/2} ,$$

$$-P_{SK} = \frac{10}{9}A_{3/2} - \frac{1}{9}A_{1/2} - \frac{16}{9}A_{3/2,1/2} .$$
(12)

Presently available gas-phase data on Br atoms²³⁻²⁵ and calculated values of P_L , P_S , and κ are given in Table III. $A_{3/2,1/2}$ is not available for Br, and it was necessary to estimate it using the value of $|\psi(0)|^2 = -0.053$ a.u. of

TABLE IV. Comparison of data and crystal field parameters for quenched Br and I atoms.²

Gas-phase parameters					Experimental matrix data ^a									
Atom	ζ (cm ⁻¹)	$\frac{P_L}{(10^{-4} \text{ cm}^{-1})}$	$\frac{P_{s}}{(10^{-4} \text{ cm}^{-1})}$	A (10-4	cm ⁻¹)	Matrix	gu	g_	$A_{\rm ii}$ (10 ⁻⁴ cm ⁻¹)	A_{\perp} (10 ⁻⁴ cm ⁻¹)	A_{iso} (10 ⁻⁴ cm ⁻¹)	Adlp (10 ⁻⁴ cm ⁻¹)		
^{79,81} Br	2456	(592) ^d	(807) ^d	(58.2) ^d		(58.2) ^d	(8.2) ^d Ar	Ar	1,55	5 2.646	141	645.7	478	- 168
¹²⁷ [*	5060	516	5.4 ^e	(80) ^e		Xe	1,400	2.532	2 297	535.3	455.7	-79.7		
					Static	crystal fi	eld para	meters	b					
			-	Atom	$\Delta_{\rm lf}$ (cm ⁻¹)	Δ_{\perp} (em ⁻¹)	A_{130}^{M} (10 ⁻⁴ cr	n ⁻¹) ($A_{dip}^{M} c$ 10 ⁻⁴ cm ⁻¹)					
			;	^{9,81} Br	710	2320	440		- 49					
			:	¹²⁷ I ^e	392	1076	375°	-	- 24 ^e					

²Experimental data for I atoms in solid xenon are from Iwasaki *et al.* (Ref. 11). Signs of A_{\parallel} and A_{\perp} in all cases were not experimentally determined.

^bUtilizing the theory of Ammeter and Schlosnagle (Ref. 13). Δ_{\parallel} and Δ_{\perp} are obtained from Δg_{\parallel} and Δg_{\perp} , respectively.

^cCalculated from Eqs. (10) and (11) [or Eq. (7b) of Ammeter and Schlosnagle (Ref. 13)] using gas-phase parameters and matrix Δg values.

^dSee Table III and text.

 $^{6}A_{0}$ was approximated as an average $[A_{130}(I)/A_{130}(X)] \cdot A_{0}(X)$ where X is either Br or Cl. The ratios in square brackets were obtained from Table I of Morton and Preston [J. Magn. Reson. 30, 577 (1978)] and $A_{0}(X)$ are the gas-phase values. A_{130}^{H} and A_{d1p}^{H} were calculated from Eq. (7b) of Ammeter and Schlosnagle (Ref. 13) assuming that either P_{L} or $P_{S} = 516.4 \times 10^{-4}$ cm⁻¹, $P_{S}/P_{L} = 1.25$, an average is taken in each case.

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Bagus *et al.*,²⁶ derived using spin-unrestricted Hartree Fock (SUHF) theory. Judging by a comparison of calculated and experimental results for Cl,²⁷ the theoretical value is probably in error by more than a factor of 2. $A_{3/2,1/2}$ is calculated to be 62 MHz, but we have used 130 MHz as a better estimate for Br atoms.

Since the ESR lines were too broad to distinguish the isotopes of a particular atom, a natural-abundance weighted average of the radical parameters given in the last three rows of Table III was used in Eqs. (10) and (11). Then one finds for Br atoms: $A_{iso} = 1320$, $A_{dip} = -148$ MHz to be compared with the matrix values (Table II) $A_{iso} = 1433$, $A_{dip} = -505$ MHz. There is some ambiguity in the experimental matrix isotropic and dipolar hf parameters because of the choice of signs for A_{\parallel} and A_{\perp} . Other than choosing both positive, a second possibility is A_{\perp} positive and A_{\parallel} negative. This choice gives much worse agreement with the gas-phase data for Br. One concludes from a comparison of matrix hf parameters and those derived from the gas-phase atomic data that there is reasonable agreement for the Br case.

V. CONCLUSION

Within the accuracy of the data, it appears that the axial crystal field model applied to trapped Br atoms formed in the H + Br2 reaction fits as well as can be expected. A crystal field parameter Δ of about 2000 cm⁻¹ will approximately account for the g tensor shifts, and the hyperfine splittings are also approximately reproduced using that model and gas phase hfs parameters. In view of the past failure to observe ${}^{2}P_{3/2}$ atoms in matrices when prepared from halogen molecules¹⁰ one can logically infer that here the site of the observed atom is unique and because of the reaction in which the Br atom is produced, that the site involves a neighboring HBr molecule. The ESR signals strongly favor an axial field, although there is a small possibility that the weak lines under the four strong perpendicular lines in Fig. 1 represent a third g component. Experimentally in the gas phase an unambiguous prediction of the geometry of the activated complex in the $H + Br_2$ reaction has not been obtained, but the preferred geometry for HF_2 and HCl_2 is linear and unsymmetrical. Early work on the $H + Br_2$ reaction indicated that H-Br-Br might be bent at an angle of 120°-140°. The matrix results clearly are not informative enough to indicate the relative positioning of HBr and atomic Br, but perhaps a critical point is the good agreement obtained between the isotropic hf constant A_{iso} in the matrix and the crystal field value derived from the gas parameters. Thus, although Br seems to be well quenched in an axial field, this agreement infers that the site is symmetrical in the matrix.¹³ since little sp hybridization is indicated. The HBr molecule might be separated from the Br atom by an argon atom so that its interaction is weakened, or possibly the HBr is rotating rapidly enough in its adjacent site to provide an axial but "neutral" field. There is evidence of rotation of *isolated* HBr in argon matrices.²⁸

Table IV gives a comparison of the quenched Br and I atom data with the crystal field analysis used here. Overall, their properties are quite similar. Iwasaki et al.¹¹ have indicated in their discussion of the iodine atom results that there is fair agreement between A_{iso} and A_{dip} measured in the matrix and those parameters derived from gas data using the simple crystal field model. From Table IV, one sees that our slightly different approach for iodine supports their conclusion, and the agreement is even more convincing for Br. This implies that each of these quenched atoms is not very sphybridized and that each lies in symmetric sites in the matrices.

The signals obtained in the $H + Cl_2$ spectrum are perplexing. Assignment of the three broad lines, with rapidly decreasing intensity toward lower fields, to perpendicular lines of quenched Cl atoms yields $g_1 \cong 2.49$, $A_1 \cong 1100$ MHz, $A_n \cong 100$ MHz. A fourth line, unobserved, is then calculated to lie at 2310 G if $g_n \cong 1.9$ is assumed. No parallel lines were positively identified. Although this suggested pattern is similar to that of a quenched atom, the rapid decrease in intensity is not reproduced by a computed simulated ESR spectrum for a ${}^2\Sigma$ molecule with the above parameters.

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