



Experimental and theoretical determination of the magnetic dipole transition moment for the Br (4p 5)(2 P 1/2 \leftarrow 2 P 3/2) fine-structure transition and the quantum yield of Br (2 P 1/2) from the 193 nm photolysis of BrCN

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Experimental and theoretical determination of the magnetic dipole transition moment for the Br $(4p^5)({}^2P_{1/2}\leftarrow{}^2P_{3/2})$ fine-structure transition and the quantum yield of Br $({}^2P_{1/2})$ from the 193 nm photolysis of BrCN

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The integrated-absorption coefficients of several hyperfine lines of the magnetic dipole allowed transition of the bromine atom, Br, center at 3685.2 cm⁻¹ were measured, and a value for the square of the magnetic dipole transition moment of the Br atom was determined. A theoretical calculation for the magnetic dipole transition moment was also carried out using a relativistic *ab initio* atomic structure formulation. The theoretical value was in excellent agreement with the value predicted assuming pure LS coupling, and in reasonable agreement with experiment. The Br atom was generated in equal concentration with the cyano radical (CN) by the 193 nm photolysis of cyanogen bromine, BrCN. The CN radicals were titrated by the rapid reaction with C₃H₈ to generate HCN and a small amount of HNC. Both time-resolved and frequency-scanned infrared absorption spectroscopy were used to monitor the Br, HCN, and HNC species. The photolysis of BrCN at 193 nm produced both the ground state Br(${}^{2}P_{3/2}$) and the spin-orbit excited Br(${}^{2}P_{1/2}$) atoms, and the yield for the production of Br(${}^{2}P_{1/2}$) atoms was measured to be 0.31 ± 0.01 . The rate constants for the quenching of Br(${}^{2}P_{1/2}$) by BrCN and C₃H₈ at 293 K were also determined. [S0021-9606(99)01416-6]

I. INTRODUCTION

The UV laser photodissociation of R-X and/or related compounds, where R is an organic radical and X is a Br or I atom, is a convenient method for generating the radical R, without generating another reactive species. The radicals so generated can be used to study radical-radical kinetics; however, being second-order processes, it is necessary to know the radical's concentration in order to determine a rate constant. In some cases, the radical concentration can be inferred from the UV absorption cross section of the parent R-X molecule and the initial UV photolysis intensity; however, the photochemistry of R-X must be well-established for this to be a reliable technique. A more direct method of determining the initial concentration of the radical would be to determine the concentration of the corresponding atom X. This was the motivation of the present work, and the major effort devoted to providing an experimental measurement of the magnetic dipole transition moment between the two finestructure levels of the Br atom. Previously, Morter et al.¹ used the 193 nm photolysis of C₃H₃Br to study the recombination reaction of C₃H₃ radicals. These workers calculated the pure LS coupling value for the magnetic dipole transition moment to determine the peak absorption coefficient for the $Br(2 \leftarrow 3)$ atom hyperfine transition, and hence, deduced the initial C₃H₃ radical concentration. This procedure enabled a direct measurement of the important C_3H_3 selfrecombination rate constant.

The ground state electronic structure² of the halogen at-

oms, $X(np^5)$, gives rise to two low lying fine-structure levels, the ground state, ${}^2P_{3/2}$, and excited state, ${}^2P_{1/2}$, labeled X*. The energy separation between these fine-structure levels increases with atomic number of the halogen, and for Br it is 3685.2 cm⁻¹.³⁻⁶ Unfortunately, the radiative transition rates between the spin-orbit states are relatively slow because they are magnetic dipole-induced transitions.^{2,7} On the other hand, the long radiative lifetimes of Br* and I* make them excellent candidates for high power laser development,⁸ especially I*. Interest in Br* as a laser source⁹ has increased by the development of a photolytic repetitive energy transfer IR laser, based on efficient electronic-to-vibration, E–V, energy transfer processes.¹⁰ Detailed descriptions and laser development would benefit from an accurate determination of the magnetic dipole transition moment for the Br atom.

Recently, Ha *et al.*¹¹ studied the I* \leftarrow I transition to measure the magnetic dipole transition moment of the I atom. These workers applied high-resolution absorption spectroscopy to the hyperfine transitions in the I atom. The I atom was created in several different environments, i.e., using infrared multi-photon dissociation of various fluorocarboniodine compounds and the thermal dissociation of I₂ in a furnace. They also compared their measurements to *ab initio* atomic structure calculations for the magnetic dipole transition moment of the I atom.

In the present work, Br atoms were created by the 193 nm laser photolysis of BrCN in the presence of C_3H_8 in Ar. The CN radicals reacted rapidly with C_3H_8 to generate HCN and a small quantity of HNC. All three species, HCN, HNC, and Br, were monitored using infrared time-resolved and frequency-scanned absorption spectroscopy. The concentration of the Br atoms was equal to the measured concentra-

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tions of HCN and HNC, and the integrated-absorption coefficients of several hyperfine transitions of the Br atom were determined. These data were used to calculate the magnetic dipole transition moment of the Br atom. A theoretical calculation of the magnetic dipole transition moment using a relativistic formulation based on a Dirac–Fock–Breit (DFB) *ab initio* atomic structure calculation¹² was also carried out, and compared to the experimental measurement.

The photolysis of BrCN at 193 nm yielded a significant quantity of excited Br^{*} atoms, and the quantum yield for Br^{*} production determined by laser gain-vs-absorption spectroscopy described by Haugen *et al.*¹³ The quenching rate constants for Br^{*} with C_3H_8 and BrCN were also measured.

II. EXPERIMENT

The apparatus has been described¹⁴ in detail previously, but for completeness a brief description is given here. The transverse flow reactor (TFR) consists of a stainless steel chamber containing a TeflonTM box of dimensions 100 $\times 100 \times 5$ cm. The TFR is evacuated by a liquid-nitrogen trapped mechanical pump to a pressure of a few mTorr, and has a leak rate of less than 0.5 mTorr/min. The reactant gases continuously flow through the chamber, and their partial pressures determined from their known flow rates and total pressure.

The photolysis laser was either a Lumonics model 740 or a Lamda Physik model 203 Compex excimer laser, both operating in the power stabilization mode at a wavelength of 193 nm. The results were independent of the excimer laser parameters. Most of the data were collected at a nominal power density of $10-20 \text{ mJ cm}^{-2}$ and a repetition rate of 5 Hz.

The probe laser was a single-mode Burleigh model 20 FCL color center laser. This laser is continuously tunable from 2.6 to 3.4 microns with a bandwidth of \sim 2 MHz, which is much narrower than the 293 K thermal Doppler line widths of the probed species. All three species, Br, HNC, and HCN, can be monitored using this single laser source. The laser frequency was continuously monitored using the appropriate etalons, and the absolute wavelength determined by an evacuated Burleigh model 20IR wavemeter.

The infrared absorption path length was increased from the nominal photolysis length of 1 m to 14 m using a White cell to multi-pass the probe laser through the photolysis zone. Both the infrared and excimer laser radiation were overlapped using a UV-IR dichroic mirror mounted directly on the White cell optical axis.

Two types of absorption data were recorded, timeresolved and frequency-scanned. The time-resolved data were recorded using a LeCroy model 9410 digital oscilloscope. The passage of the excimer laser through the apparatus resulted in an undesirable background signal. To remove this interference, the following procedure was adapted. A signal-averaged trace was recorded with the infrared laser tuned to the peak of an absorption feature, and then, the laser was detuned several line widths and a signal-averaged background trace recorded. Both traces were transferred to a laboratory PC, and subtracted to obtain the unperturbed signal trace. The initial laser intensity, I_0 , was recorded by a boxcar signal averager, and was measured just before the excimer laser was fired. The frequency-scanned data were recorded using two boxcar signal averagers, one to record the absorption signal, $\Delta I = I_0 - I$, and the other to record I_0 . The gate of the boxcar recording the signal was delayed so that the probed species was monitored in a time regime where internal relaxation was complete and the loss by diffusion was minimal.

III. RESULTS

A. Integrated and peak absorption coefficients

Radiative transitions between the two fine-structure levels of the Br atom are dominated by the allowed-magnetic dipole transition moment. The allowed-electric quadrupole transition rate between these levels is three orders of magnitude smaller.¹⁵ Unfortunately, the hyperfine interactions complicate the situation. Bromine has two stable isotopes ⁷⁹Br and ⁸¹Br with natural abundances of 50.52% and 49.48%, respectively, and each isotope has a nuclear dipole moment, **I**, I=3/2. The total angular momentum, **F**, of the atom is given by $\mathbf{F}=\mathbf{I}+\mathbf{J}$, and the magnetic dipole selection rules are $\Delta F=0,\pm 1$ with parity conserved, resulting in six allowed-hyperfine transitions for each isotope.^{2,7}

Shortley¹⁶ has discussed magnetic dipole-allowed radiative transitions between fine-structure levels in the case of Russell–Sanders, LS, coupling, and gives the square of the magnetic dipole matrix element, $|\langle J' | \mu_m | J'' \rangle|$,² as

$$\frac{|J'|\mu_m|J''\rangle|^2}{4(J-S+L+1)(J+S-L+1)(J+S+L+2)(S+L-J)} \times \left(-\frac{eh}{4\pi m_e c}\right)^2,$$
(1)

where *h*, *c*, *e*, and *m_e* have their usual meaning, *S*, *L*, and *J* are the spin, orbital, and total angular momentum quantum numbers ($\mathbf{J}=\mathbf{S}+\mathbf{L}$), respectively. Note that for LS coupling, the evaluation of the magnetic dipole matrix element in Eq. (1) is independent of the radial portion of the electronic wave function, and is given by the Bohr magnetron, $\mu_B = eh/(4\pi m_e c)$. For the Br atom fine-structure transition, $|\langle J' | \mu_m | J'' \rangle|^2$ equals $4/3\mu_B^2$. In an absorption experiment, the magnetic dipole transition moment can be directly related to the observed attenuation of the probing radiation through the integrated-absorption coefficient, S(J', J'') given by¹⁷

$$S(J',J'') = \frac{8\pi^3}{3hc} \overline{\nu} \frac{|\langle J' | \mu_m | J'' \rangle|^2}{g_{J''}},$$
(2)

where $g_{J''}$ is the degeneracy of the lower fine-structure level, 2J'' + 1.

For the Br atom, the influence of hyperfine structure must be taken into account and Eq. (2) modified accordingly. Morter *et al.*¹ have described the evaluation of the integrated-absorption coefficients taking into account the hyperfine interaction using angular momentum algebra. The method used here was taken from Sobel'man,⁷ who provides a convenient table of normalized coefficients for the straightforward evaluation of the appropriate matrix elements. Zuev *et al.*¹⁸ have also summarized the evaluation of the hyperfine

TABLE I. Summary of the theoretical LS coupling integrated-absorption coefficients for the hyperfine lines of the Br atom. At 293 K and for $\overline{v_0}$ = 3685.2 cm⁻¹, the value of $g(v_0)$ is 185.9 (cm) so that the peak absorption coefficient can be calculated according to Eq. (4). The integrated-absorption coefficients for the hyperfine transitions in individual isotopes are obtained by multiplying the S(J'IF';J''IF'') by the relative isotopic abundance of ⁷⁹Br and ⁸¹Br.

Transition Br $(F' \leftarrow F'')$	$S(J'IF';J''IF'')$ $(10^{-21} \text{ cm}^1 \text{ molecule}^{-1})$ Br
2←3	19.24
2←2	6.87
$1 \leftarrow 2$	6.87
$2 \leftarrow 1$	1.37
$1 \leftarrow 1$	6.87
1 ← 0	2.75

matrix elements following the procedure outlined by Sobel'man. The integrated-absorption coefficient between hyperfine levels, $F' \leftarrow F''$, is given by

$$S(J'IF';J''IF'') = \frac{8\pi^3}{3hc}\overline{\nu}(2F+1) \left\{ \frac{J'FI}{F''J''1} \right\}^2 |\langle J'|\mu_m|J''\rangle|^2,$$
(3)

where S(J'IF';J''IF'') has units cm molecule⁻¹, the term in braces is the Wigner 6-*j* symbol, the degeneracy of the lower level (2F''+1) has been included, and the squared magnetic dipole matrix element is given by Eq. (1).

The integrated-absorption coefficient is related to the observed quantity, the absorption coefficient at a frequency v, $\sigma(v)$, through the normalized line shape function, g(v), according to

$$\sigma(v) = S(J'IF'; J''IF'')g(v), \tag{4}$$

where $\sigma(v)$ has units cm² molecule⁻¹. In the present experiments, g(v) is well-described by a thermal Doppler profile for $T=293\pm1$ K, and at line center, $v_0, g(v_0)$ is given by $\{\ln(2)/\pi\}^{1/2}/3.581\times10^{-7}\overline{v_0}(T/M)^{1/2}$, where $\overline{v_0}$ is the wave number at line center, *T* is the temperature, and *M* the mass of the absorbing species. For T=293 K, the calculated hyperfine integrated-absorption coefficients for the Br atom, based on pure LS coupling, are summarized in Table I.

In the present experiments, a nonequilibrium distribution of fine-structure states was initially created by the photolysis laser pulse so that stimulated emission from the excited spinorbit manifold must also be considered. This effect manifests itself as a correction to the population used to describe the time dependent absorption signal, with the population given by $N_{F''}-g_{F''}/g_{F'}N_{F'}$, where $N_{F''}$ and $N_{F'}$ are the populations in the corresponding hyperfine state of the lower and upper spin-orbit manifolds, respectively. The time dependent absorbance, $A(t) = \ln(I_0/I(t))$, is given by a modified Beer– Lambert Law as¹⁹

$$\ln(I_0/I(t)) = \sigma(v)l([N_{F''}(t)] - g_{F'}/g_{F''}[N_{F'}(t)]), \quad (5)$$

where *l* is the path length in cm, $g_{F''}$ and $g_{F'}$ are the degeneracies in the lower and upper levels, respectively, and the square brackets, [], indicate concentration units molecules cm⁻³. At long times or equilibrium Eq. (5) re-

duces to the normal Beer–Lambert Law expression. Furthermore, the energy separations among the hyperfine states within a spin-orbit manifold are very small compared to kT so that they can be considered to be nearly isoenergetic, and thus, populated according to their degeneracies. Hence, $[N_F]$, the concentration in a hyperfine level *F*, is given by $g_F[N]/\Sigma_F(2F+1)$, where [N] is the total concentration of the appropriate species in a spin-orbit manifold.

The integrated-absorption coefficient, $S(\nu'J';\nu''J'')$, for a fundamental rovibrational transition in a linear polyatomic molecule in a ${}^{1}\Sigma$ electronic state is given by 19,20

$$S(1,J';0J'') = \frac{8\pi^3}{3hc} \overline{v_{ji}} |\langle 1|\mu_1|0\rangle|^2 \quad \text{HW}$$
$$\times A_{ji} \frac{e^{-E_i/kT}}{Q_r Q_v} (1 - e^{h\nu/kT}) \text{FIA}, \tag{6}$$

where S(1J';0J'') has units cm molecule⁻¹, <u>j</u> is the upper state ($\nu = 1, J'$), and *i* the lower ($\nu = 0, J''$), ν_{ji} is the transition frequency in cm⁻¹, $|\langle 1|\mu_1|0\rangle|$ the vibrational transition dipole moment, HW, the Herman–Wallis factor, accounts for rotation-vibration interaction, A_{ji} the Honl– London factor, J+1 for an *R* branch and *J* for a *P* branch transition, E_i is the energy of the initial state, Q_r and Q_ν are the rotational and vibrational partition functions, respectively, and FIA is the fractional isotopic abundance of the absorbing species.

There have been several experimental determinations of the v_3 H–C stretch vibrational transition moment and the Herman–Wallis parameters for HCN.^{21–23} For the present experiments, these quantities were taken from Smith *et al.*²² For 293 K the H¹²C¹⁴N(000) *P*(8) transition, the peakabsorption coefficient was calculated to be 3.84 ×10⁻¹⁷ cm² molecule⁻¹. The fundamental vibrational transition moment of the v_1 H–N stretch vibration and an estimate of the first order Herman–Wallis parameter has recently been measured in this laboratory.²⁴ The peak-absorption coefficient for the H¹⁴N¹²C(000)*R*(9) transition was calculated to be 9.69×10⁻¹⁷ cm² molecule⁻¹ at *T*=293 K.

B. Determination of the Br atom magnetic dipole transition moment

The following series of reactions occur following the 193 nm photolysis of BrCN in a mixture of BrCN, C_3H_8 , and Ar:

$$BrCN \xrightarrow{193 \text{ nm}} Br(^2P_{3/2}) + CN, \qquad (7a)$$

$$BrCN \xrightarrow{193 \text{ nm}} Br({}^{2}P_{1/2}) + CN, \qquad (7b)$$

$$Br({}^{2}P_{1/2}) + C_{3}H_{8} \xrightarrow{\kappa_{8a}} Br({}^{2}P_{3/2}) + C_{3}H_{8},$$
 (8a)

$$\operatorname{Br}({}^{2}P_{1/2}) + \operatorname{BrCN} \xrightarrow{\kappa_{8b}} \operatorname{Br}({}^{2}P_{3/2}) + \operatorname{BrCN},$$
(8b)

$$CN+C_3H_8 \rightarrow HCN+C_3H_7, \tag{9}$$

$$CN+C_3H_8 \xrightarrow{k_{10}} HNC+C_3H_7,$$
 (10)

$$X + Y \xrightarrow{k_{11}} , \tag{11}$$

$$Z \xrightarrow{k_{\text{diff}}} , \qquad (12)$$

where reaction (11) stands for any removal process involving atoms and radicals, Br or C₃H₇, such as recombination, i.e., $-k_{11}[Y][X]$, and reaction (12) stands for the removal of all species by diffusion.

The concentration of Br atoms created in the initial photolysis of BrCN was small, $<3 \times 10^{12}$ atoms cm⁻³, and the only possible loss processes for Br atoms were recombination with Br or C₃H₇ and diffusion. At a maximum total pressure of 4 Torr, the self-recombination²⁵ of Br atoms occurs through a three body process with a rate constant estimated to be 3×10^{-34} cm⁶ molecules⁻² s⁻¹, resulting in a completely negligible first-order decay of $< 10^{-4} \text{ s}^{-1}$. The $Br+C_3H_7$ atom-radical recombination process has not been investigated experimentally, but the rate constant should be similar to that for I+C₃H₇, which has been measured²⁶ to be 5×10^{-11} cm³ molecule⁻¹ s⁻¹ at 298 K. Even if k_{11} were gas kinetic, the time scale for the recombination reaction would still be several orders of magnitude longer than the measurement time scale, i.e., the time scale for the relaxation of the excited $Br({}^{2}P_{1/2})$ spin-orbit state, and would be the same order of magnitude as the removal rate by diffusion (~150 s⁻¹).²⁷ Reaction (10) was included to account for the observed production of HNC.

As is evident from the above reaction sequence, all of the CN reacted with C₃H₈ to form HCN and HNC, and the only removal process for these molecules was by diffusion so that the total concentration of Br atoms is given by [Br]=[HCN]+[HNC]. Typical time-resolved absorption profiles for HCN, HNC, and Br are shown in Fig. 1. With C_3H_8 as the CN radical titrant, not only was reaction (9) rapid²⁸ ($k_9 = 2.6 \times 10^{-11} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ at 297 K), but the vibrational relaxation of all the vibrational modes of both HCN and HNC were also rapid and vibrational equilibration was complete in several hundred microseconds, as is evident by the nearly constant absorption region for HCN and HNC in Fig. 1. Some excited vibrational levels for both HCN and HNC were directly monitored, and observed to decay rapidly back to the baseline. Not shown is the decay of HCN or HNC on long time scales, but at 4 Torr total pressure these molecules were removed from the observation region by diffusion,²⁷ with the fast diffusion component having a rate constant of about 150 s⁻¹. Note that the decay of the Br atom, Fig. 1(c), appears slightly faster than either HCN or HNC. This was attributed to the atom-radical recombination process, reaction (11).

Figure 1(b) shows that HNC was produced directly by reaction (10); however, this reaction was not initiated by thermal CN radicals. Although the exothermicity of the $CN+C_3H_8$ reaction is sufficient to produce HNC, the yield of HNC decreased with the decreasing partial pressure of C_3H_8 , $P_{C_3H_8}$, indicating that the HNC product was not from the reaction of thermalized CN radicals. This is shown in Fig. 2 where the mole fraction of C_3H_8 is plotted against the yield of HNC at a total pressure of 4 Torr. The 193 nm photolysis



FIG. 1. (a) Typical time-resolved absorption profile for HCN(000) P(8). The initial negative signal indicates a degeneracy-weighted population inversion, Eq. (5). Vibrational relaxation was complete after 200 μ s. On this time scale, removal by diffusion is barely detectable. (b) Same as (a) except for HNC(000) R(9). (c) Same as (a) except for the Br(2 \leftarrow 3) hyperfine transition. The conditions of the experiment were $P_{\rm Ar}$ =3.66, $P_{\rm C_3H_8}$ =0.280 and $P_{\rm BrCN}$ =0.0795 Torr at 293 K.

of BrCN produces CN radicals that are highly rotationally excited, $^{29-32}$ with a rotational state distribution peaking near J=60.5 for CN($\nu=0$) and with considerable translational energy, $\langle E_T \rangle = 43$ kcal mole⁻¹. The rapid decrease in the yield of HNC with decreasing $P_{C_3H_8}$ suggests that the excess translational energy may be primarily responsible for generating the HNC channel. Generally, very high rotational states are difficult to relax in collisions with spherically symmetric collision partners.³³ As a further investigation into this effect, some experiments were carried out with (CN)₂ as a CN radical source because the CN radicals are produced with much less translational and rotational energy.³⁴ No HNC production was detected at all in these experiments indicating that k_{10} was small for thermal CN radicals.

It was not discovered until most of the data had been collected that HNC was produced in this system. Thus the total CN concentration was corrected for the small production of HNC using the linear relationship between the yield of HNC and the mole fraction of C_3H_8 shown in Fig. 2 in order to interpolate to other conditions.

As shown by Eq. (5), an absorption experiment monitors the degeneracy-weighted population difference between the two levels connected by the radiative transition. Thus the population in the upper level must be completely equilibrated in order to infer a total population. As will be dis-



FIG. 2. The yield of HNC from reaction of CN with C_3H_8 following the 193 nm photolysis of BrCN. The linear relationship between the yield of HNC and the C_3H_8 mole fraction, indicated by the least-squares fit solid line, was used to correct the results of experiments in which HNC was not monitored.

cussed in Sec. III D, the 193 nm photolysis of BrCN produced a significant population of excited $Br({}^{2}P_{1/2})$ atoms; however, the relaxation of the excited spin-orbit state, reactions (8a) and (8b), was fast, as evident by the rapid rise to the nearly constant absorbance region in Fig. 1(c). The kinetics of this relaxation process will be discussed further in Sec. III E.

The Br($2\leftarrow 3$) hyperfine transition is the most intense spectral feature of the six allowed transitions (see Table I); however, because the two Br atom isotopes have slightly different transition frequencies³⁻⁶ this transition consists of two lines separated by 154 MHz, almost the Br atom thermal FWHM (full width half maximum) Doppler width at 293 K. For accurate measurements, it was necessary to scan this absorption feature as a function of frequency in order to determine the actual line profile. Furthermore, a frequencyscanned absorption profile eliminates the uncertainty in manually tuning the probe laser frequency to the peak of an absorption line. Typical frequency-scanned absorption profiles for HCN, HNC, and Br are shown in Fig. 3 for the same experimental conditions as the time-resolved traces shown in Fig. 1. The frequency-scanned line profiles were recorded with the boxcar gate delayed to sample the absorption signal in the nearly constant absorbance region for the species being probed.

The peak absorbance for each species was determined by a nonlinear least-squares fit to the line profiles assuming a Gaussian line shape function. As is evident from Fig. 3, the line shapes were well-represented by a Gaussian functional



FIG. 3. (a) Frequency-scanned absorption profile for HCN(000) P(8) for the same experimental run as in Fig. 1. The absorption signal was taken from a boxcar gate delayed to sample in the constant absorbance region of Fig. 1(a). The solid line is a nonlinear least-squares fit to the experimental points, \bullet , and the difference between the experimental and calculated points, *x*. The FWHM of the Doppler profile has the expected value of 230 MHz. (b) Same as (a) except for HNC(000) R(9). (c) Same as (a) except for the Br(2 \leftarrow 3) hyperfine transition. The ⁷⁹Br and ⁸¹Br peaks were fit independently in the nonlinear least-squares analysis. The ⁸¹Br peak is at zero frequency.

form, and the FWHM were in agreement $(\pm 5\%)$ with the expected thermal Doppler widths at 293 K. Unfortunately, the scatter in the measurements of the line widths was large enough to prevent a determination of pressure broadening parameters. Over the 2-4 Torr pressure range of the experiment, pressure broadening effects are small, and for HCN, with Ar as the collision partner, can be calculated to decrease the peak absorption cross section from the pure Doppler broadened value by a factor of 0.97–0.94, respectively.³⁵ To a first-order approximation, pressure broadening is proportional to the collision frequency so that the effects of collision broadening on the Br atom transitions should be about 75% of those on HCN. Thus the effects of pressure broadening should be similar for each species and almost cancel out. As a result, no pressure broadening correction was applied to the data.

As is evident from Fig. 3(c), the Br $(2 \leftarrow 3)$ transition consists of two overlapping peaks both of which should have very nearly the same line width; however, to obtain a completely independent measurement of the maximum absorbance for the two Br isotopes, the absorbance traces for the Br $(2 \leftarrow 3)$ hyperfine transition were fit to two independent Gaussian functions. This introduced extra uncertainty into



FIG. 4. (a) Frequency-scanned absorption profile for HCN(000) P(8). Similar to Fig. 3(a) except $P_{Ar}=1.75$, and $P_{BrCN}=0.083$ Torr at 293 K. (b) Frequency-scanned absorption profile for the Br(2 \leftarrow 2) hyperfine transition.

the nonlinear least-squares determination of the fitted-peak height because of increased scatter in the determination of the Gaussian widths. To overcome this difficulty, another transition was also probed, the Br $(2\leftarrow 2)$ hyperfine transition. For this transition, the frequencies of the two isotopic species are well-separated, but the integrated-absorption coefficient is a factor of 2.8 less than for the Br $(2\leftarrow 3)$ transition, Table I. Typical frequency-scanned profiles for HCN(000) P(8) and Br $(2\leftarrow 2)$ are shown in Fig. 4. The fitted FWHM widths for the Br $(2\leftarrow 2)$ transition were welldescribed by the expected thermal Doppler width for Br atoms at T=293 K.

As noted, the concentration of Br atoms was equal to the concentration of HCN and HNC. This enabled the peakabsorption coefficient of the probed-hyperfine transition, $\sigma(v_0)$, to be evaluated according to Eq. (5), from which the integrated-absorption coefficient was calculated using Eq. (4). The measured $\sigma(v_0)$ depends only on the ratio of the absorbances for Br and HCN and is independent of path length. The results of these measurements are plotted in Fig. 5 and summarized in Table II. Figure 5 is shown to illustrate the scatter in the data; however, the [CN] is only a nominal concentration, calculated from the observed absorbances using a path length of 1400 cm.

The measurements provide several internal checks on their consistency. The first is provided by the relative isotopic abundance. The ratio of the cross sections for ${}^{81}\text{Br}/{}^{79}\text{Br}$ should be 0.9794; unfortunately, the experimental scatter, one standard deviation from the mean $(\pm 1\sigma)$, was up to 10% in some cases. Nevertheless, the ratio is 1.06 for the Br(2 \leftarrow 3) transition and 0.98 for the Br(2 \leftarrow 2) transition. The



FIG. 5. Results of the measurements of the integrated-absorption coefficients for hyperfine transitions of individual Br isotopes, open symbols ⁷⁹Br and closed symbols ⁸¹Br, as a function of the [CN]. The approximate total pressure is indicated by the shape of the symbol, \bigcirc (2 Torr), \triangle (3 Torr), and \Box (4 Torr). The lines indicate the average value for the indicated isotope. (a) For the Br(2 \leftarrow 3) hyperfine transition. (b) For the Br(2 \leftarrow 2) transition.

second is provided by the ratio of cross sections for the two hyperfine transitions for the same isotope. According to Eq. (3) and given in Table I, the ratio for LS coupling should be 2.800 and depends only on angular momenta coupling coefficients. The measurements give 2.68 and 2.92 for the ⁷⁹Br and ⁸¹Br isotopes, respectively, and an average of 2.80 if all the data are combined. The agreement between the expected value and the measurements is good, and indicates that random errors dominate the scatter in the measurements.

The theoretical integrated-absorption coefficients for pure LS coupling in the Br atom at 293 K have been summarized in Table I. A comparison with the experimental

TABLE II. Summary of the experimental data for the determination of the peak-absorption coefficient and integrated-absorption coefficients for the Br(2 \leftarrow 3) and Br(2 \leftarrow 2) hyperfine transitions. The measurements were made at total pressures of 2–4 Torr, with $P_{C_3H_8}$ ranging from 0.03 to 1.5 Torr, and P_{BrCN} from 0.03 to 0.08 Torr, at $T=293\pm1$ K.

Br	$\sigma(10^{-18} \mathrm{cm^2})$	$\frac{\sigma(v_0)}{(10^{-18} \mathrm{cm}^2 \mathrm{molecule}^{-1})}$		S(1/2,3/2,2;3/2,3/2,F'') (10 ⁻²¹ cm ¹ molecule ⁻¹)	
$(F' \leftarrow F'')$	⁷⁹ Br	⁸¹ Br	⁷⁹ Br	⁸¹ Br	
2←3	1.85 ± 0.16^{a} (18) ^b	1.97±0.20	9.95 ± 0.86	10.6±1.1	
2←2	0.691 ± 0.024 (9)	0.675 ± 0.048	3.72±0.13	3.63±0.26	

^aThe uncertainty is one standard deviation $(\pm 1\sigma)$ from the average of the indicated number of independent measurements.

^bNumber in parenthesis is the number of independent measurements.

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TABLE III. Results of the relativistic wave function calculations compared to the LS coupling and the experimental measurement of the present work for $A_{1/2 \ 3/2}$ and $|\langle 1/2 | \mu_m | 3/2 \rangle|^2$.

Method	Fine-structure splitting (cm ⁻¹)	$\begin{array}{c}A_{1/2\ 3/2}\\({\rm s}^{-1})\end{array}$	$ \langle 1/2 \mu_m 3/2 \rangle ^2$ (10 ⁻⁴⁰ erg ² /G ²)
DF	3758.3	0.953	1.145
DF+BQ	3682.2	0.897	1.146
LS	3685.2	0.899	1.147
Experiment (This work)	3685.2	0.96 ± 0.09^{a}	1.23 ± 0.11^{a}

^aThe uncertainty includes $\pm 1\sigma$ of 7% from the experimental scatter and an estimate of 2% in the HCN and HNC absorption coefficients.

integrated-absorption coefficients shows that the experimental measurements are 6.1% and 7.6% higher for the Br(2 \leftarrow 3) and Br(2 \leftarrow 2) transitions, respectively. This difference is within one standard deviation, $\sigma = \pm 7.4\%$, of the combined measurements. The absolute uncertainty is slightly larger than this because the uncertainty in the HCN and HNC infrared cross sections must be included, and was estimated to be about $\pm 2\%$. Thus the overall uncertainty in the experimental was estimated to be $\pm 9\%$.

The magnetic dipole transition moment defined by Eq. (1) was evaluated from the experimental measurement of the integrated-absorption coefficient and the numerical factors appearing in Eq. (3). The results are summarized in Table III and will be discussed in the next section.

C. Relativistic calculation of the magnetic dipole transition moment for Br

As noted in Sec. III A, in pure LS coupling $|\langle 1/2 | \mu_m | 3/2 \rangle|^2 = 4/3 \mu_B^2$ for the Br atom, and in this approximation, the matrix element is completely independent of the radial electronic wave functions in the two fine-structure levels. For the heavier I atom, Ha *et al.*¹¹ found that the experimentally determined $|\langle J' | \mu_m | J'' \rangle|^2$ was 13% smaller than the LS coupling prediction. They also evaluated this matrix element for several configuration interaction wave functions using *ab initio* atomic structure theory, and found close agreement with the LS coupling value. However, a relativistic calculation of the magnetic dipole transition matrix element gave a value that was substantially too low. In order to explore some of these effects, a relativistic calculation of the $|\langle J' | \mu_m | J'' \rangle|^2$ for the Br atom was carried out.

In light of the results of Ha *et al.*¹¹ and the fact that the Br atom ${}^{2}P_{1/2}$ and ${}^{2}P_{3/2}$ electronic wave functions must be quite similar, it was felt that the best procedure was to use a relativistic formulation using *jj* coupled four-component wave functions.¹² Equations for the matrix elements between states described by four-component wave functions arising in multipole transitions have been derived by Grant,^{12,36} Dyall *et al.*,³⁷ and Rosner and Bhalla.³⁸ The magnetic dipole matrix element can be written in terms of single-electron transition integrals as

where the orbitals are represented by the principle quantum number *n*, κ is the relativistic angular quantum number, $\kappa = \pm (j + 1/2)$ for $1 = j \pm 1/2$, and *a*,*b* represent the orbitals comprising a configuration. In atomic units, these matrix elements have the form

$$\langle n_b \kappa_b \| \mu_m \| n_a \kappa_a \rangle = \sqrt{\frac{(j_b + 1)\omega}{\pi c}} (-1)^{j_a - 1/2} \times \begin{pmatrix} j_a & 1 & j_b \\ 1/2 & 0 & -1/2 \end{pmatrix} \overline{M_{ab}},$$
 (14)

where the magnetic radiative transition integral, M_{ab} , is defined by

$$\overline{M_{ab}} = \frac{3}{\sqrt{2}} (\kappa_a + \kappa_b) I_1^+ \tag{15}$$

with

$$I_1^+ = \int_0^\infty (P_{n_a \kappa_a}(r) Q_{n_b \kappa_b}(r) + Q_{n_a \kappa_a}(r) P_{n_b \kappa_b}(r)) j_1(\omega r/c) dr.$$
(16)

The energy separation between the spin-orbit states is given by ω , *P*, and *Q* are the large and small component of the orbital wave function divided by *r* and *ir*, respectively, *r* is the radial distance of the electron, and $j_1(\omega r/c)$ is the firstorder spherical Bessel function of the first kind.

The necessary wave functions and matrix elements for the $Br({}^{2}P_{1/2})$ atom were evaluated using the GRASP program.³⁷ The calculation was at the averaged level (AL) type including only the configuration state functions (CSFs) corresponding to the $p_{1/2}^2 p_{3/2}^3$ and $p_{1/2}^1 p_{3/2}^4$ electron configurations. The influence of the Breit interaction was included perturbatively as was an approximate treatment of higherorder QED effects. The use of an AL wave function has the drawback that the same set of orbitals are used to describe both the ${}^{2}P_{1/2}$ and ${}^{2}P_{3/2}$ states. It has been found, however, that AL calculations give fine-structure splittings of similar quality to those derived using optimized level (OL) calculations where the orbitals used to describe each state are optimized separately.³⁹ To the authors' knowledge a similar comparison of magnetic dipole transition rates has not been made, but the accuracy of the AL method should be sufficient for the purposes of the present calculation. A second drawback of the method used is the neglect of electron correlation. This should not cause significant errors due to the similarity of the two fine-structure states causing correlation effects to be suppressed.⁴⁰ The fine-structure splitting and spontaneous emission rate constant were calculated using both the Dirac-Fock (DF) and Dirac-Fock+Breit and QED (DF+BQ) wave functions.

The magnetic dipole transition matrix element was used to calculate the spontaneous emission rate constant, $A_{J',j''}$, for the Br fine-structure transition¹⁶

$$\langle J' | \mu_m | J'' \rangle = \sum_{a,b} d_{a,b} \langle n_b \kappa_b \| \mu_m \| n_a \kappa_a \rangle, \qquad (13)$$

$$A_{J'J''} = \frac{64\pi^4}{3hc^3} \frac{\nu^3}{g_{J'}} |\langle J' | \mu_m | J'' \rangle|^2.$$
(17)

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The results of the calculation are summarized in Table III. Also included in Table III are the LS and experimental values for the $A_{(1/2)(3/2)}$ factor and squared magnetic dipole transition matrix elements. The spontaneous emission rate constant was calculated according to Eq. (17), using the appropriate $|\langle J' | \mu_m | J'' \rangle|^2$ matrix element. As is evident from Table III, the DF calculated fine-structure splitting is 2% larger than the observed value, and at the DF+BQ level it is, perhaps fortuitously, in excellent agreement. The calculated relativistic dipole matrix elements were both in excellent agreement with the pure LS value. Although the experimental value for $|\langle J' | \mu_m | J'' \rangle|^2$ is slightly larger than the theoretical predictions, the agreement is well within the estimated uncertainty (scatter and systematic error) of the measurement, and the best value to use may still be the theoretical LS prediction, Table III.

D. Yield of $Br({}^{2}P_{1/2})$ from the photolysis of BrCN

The bond dissociation $energy^{41}$ of BrCN is 86.9 kcal mole⁻¹ so that there is an excess energy of 61.3 kcal mole⁻¹ available to the products in the photolysis of BrCN at 193 nm. This is more than sufficient energy to produce excited Br atoms in the photolysis process. Furthermore, there has been much interest in elucidating the photodissociation dynamics of cyanogen halides, especially ICN, to which BrCN is closely related.

The use of time-resolved absorption spectroscopy to monitor the Br atom spin-orbit populations is particularly useful for this task because the degeneracy weighted difference in population is monitored directly [see Eq. (5)]. As long as the detection electronics is fast enough to resolve rapid changes in absorption that may occur due to relaxation processes, the absorption signal is internally calibrated from the initial difference created in the photodissociation step to the final equilibration stage, where the upper level has been removed by relaxation. Haugen *et al.*¹³ have used this elegant laser gain-vs-absorption technique to completely map out the yield of Br(${}^2P_{1/2}$) as a function of photolysis wavelength for Br₂ and IBr.

The yield of excited Br(${}^{2}P_{1/2}$), $\phi_{\text{Br}*}$, from the photodissociation of BrCN at 193 nm is defined by

$$\phi_{\rm Br*} = \frac{[{\rm Br}({}^{2}P_{1/2})]_{i}}{[{\rm Br}({}^{2}P_{1/2})]_{i} + [{\rm Br}({}^{2}P_{3/2})]_{i}},\tag{18}$$

where the $[Br({}^{2}P_{1/2}]_{i}$ is the initial concentration of the Br^{*}, and the total concentration of Br, [Br], created in the photolysis laser pulse is $[Br] = [Br({}^{2}P_{1/2})]_{i} + [Br({}^{2}P_{3/2})]_{i}$. At thermal equilibrium for 293 K, the $[Br({}^{2}P_{1/2})]$ is virtually zero, and the final absorbance, A_{f} , determines the total concentration of Br atoms created in the photolysis step provided no Br atoms are lost from the system. The determination of ϕ_{Br^*} was carried out in mixtures where either $P_{C_{3}H_{8}}$ was zero or small, $P_{C_{3}H_{8}} < 0.06$ Torr, so that the only significant loss process for Br atoms was diffusion, and this occurred on a time scale long compared to the time scale for relaxation, reaction (8): see Fig. 6(b).

At t=0, the initial absorbance, A_i , is proportional to the degeneracy weighted population difference between the two article is copyrighted as indicated in the article. Reuse of AIP content is



FIG. 6. Determination of the quantum yield of Br* from the 193 nm photolysis of BrCN. (a) The laser frequency was tuned near the peak of the Br(2 \leftarrow 3) transition. The insert shows the absorption of the final [Br] after complete quenching of Br*. (b) The very long time decay of the Br atom is shown. Diffusion was assumed to dominate, but reaction (11) may contribute. The conditions of the experiment were $P_{\rm Ar}$ =2.94 and $P_{\rm BrCN}$ =0.050 Torr at 293 K.

hyperfine levels, according to Eq. (5). The population in individual hyperfine levels, $[Br]_F$, has been discussed in Sec. III A, and the observed absorbance from a hyperfine transition can be expressed in terms of the total atom population in a spin-orbit manifold. The initial A_i measured at a particular frequency, v_i in terms of total populations is given by

$$A_{i} = l\sigma(v) \left([Br(^{2}P_{3/2})]_{i} - \left(\frac{g_{F''}}{g_{F'}}\right) [Br(^{2}P_{1/2})]_{i} \right), \quad (19a)$$

and the final absorbance is given by

$$A_f = l\sigma(v) \frac{g_{F''}}{16} [Br(^2 P_{3/2})]_f.$$
(19b)

An expression for the yield of Br^{*} can be obtained by dividing Eq. 19(a) by 19(b) and rearranging the terms. For the Br $(2 \leftarrow 3)$ hyperfine transition, the result is

$$\phi_{\rm Br*} = \frac{1}{3} \left\{ 1 - \frac{A_i}{A_f} \right\}.$$
(20)

It is important to note that $\phi_{\rm Br^*}$ does not depend explicitly on the probe laser frequency as long as thermalization of the translation motion of the Br atoms occurs more rapidly than spin-orbit relaxation. Similarly, as long as equilibration within a hyperfine manifold proceeds faster than spin-orbit

TABLE IV. Summary of measurement of $\phi_{\rm Br*}$ from the photolysis of BrCN at 193 nm.

P _{Ar} (Torr)	P _{C3H8} (Torr)	P _{BrCN} (Torr)	$\phi_{ m Br*}$
2.9-3.9	0.0	0.03-0.08	0.304 ± 0.0026 (4) ^a
2.9	0.015-0.06	0.045	0.308 ± 0.0047 (4)
		Summary	0.306 ± 0.0042

^aNumber of independent experiments.

relaxation, only a single hyperfine transition needs to be monitored. Both these conditions are satisfied in the present experiments.

Typical temporal absorption profiles for the Br atom, following photolysis of BrCN at 193 nm, are shown in Fig. 6. Figure 6(a) shows the initial time dependence, and Fig. 6(b) the long time dependence. It is clear from Fig. 6(b) that the loss of Br atoms occurs on a much longer time scale than that for the quenching of Br*, shown in the insert in Fig. 6(a). The A_i values were determined by simply extrapolating the early time dependence of the difference curve to the t =0 intercept, as indicated in Fig. 6(a). The frequency response of the detection electronics was better than 5 MHz, and at 4 Torr total pressure translational and hyperfine relaxation should be complete over a time scale of less than a microsecond. No evidence for any rapid transients was observed. The results of several experiments with and without C₃H₈ are given in Table IV. The average of the eight independent measurements gives $\phi_{Br*} = 0.306 \pm 0.0041$ so that a significant amount of the Br atoms are formed in the excited spin-orbit state in the 193 nm photolysis of BrCN.

E. Relaxation of Br* by BrCN and C₃H₈

As shown in the previous section, 30.6% of the Br atoms are initially formed in the excited spin-orbit state, and the increase in the Br atom absorbance, as illustrated in Figs. 1(c) and 6(b), is due to the removal of the Br^{*} atoms by C_3H_8 and BrCN, reactions 8(a) and 8(b), respectively. The exponential rate constant describing these relaxation processes is given by $k = k_{8a}[C_3H_8] + k_{8b}[BrCN]$, and can be determined by fitting the temporal absorbance profiles to a series of exponential terms, i.e., $A(t) = A_f \exp(-k_{\text{diff}}t)$ $-A_r \exp(-kt)$ using a nonlinear least-squares fitting procedure based on Marquardt's method.⁴² If the [BrCN] is kept constant and the $[C_3H_8]$ varied, then a plot of k against $[C_3H_8]$ gives a straight line with slope k_{8a} and intercept $k_{\rm 8b}$ [BrCN]. This procedure is valid as long as the contribution from the quenching of Br* by Ar is small, which is the case here as the rate constant for the removal of Br* by Ar has been measured⁴³ to be 2.5×10^{-16} cm³ molecule⁻¹ s⁻¹ at 295 K.

A plot of k as a function of $P_{C_3H_8}$ is shown in Fig. 7 for 293 K. A least-squares analysis gives k_{8a} to be $1.99 \pm 0.052 \times 10^{-11}$ cm³ molecules⁻¹ s⁻¹ and the intercept to be 3.85 $\pm 0.96 \times 10^4$ s⁻¹. In these experiments the intercept only provides a crude order of magnitude estimate of k_{8b} because of



FIG. 7. Determination of the quenching rate constant for $Br^*+C_3H_8 \rightarrow Br+C_3H_8$. A linear least-squares fit to $k=k_{8a}[C_3H_8]$ + $k_{8a}[BrCN]$ for fixed [BrCN] gives k_{8a} . As expected, the quenching rate constant was independent of which Br atom hyperfine level was monitored.

the large slope-to-intercept ratio (a factor of 20). A small change in slope results in a large change in the intercept; furthermore the $P_{\rm BrCN}$ was not completely constant but varied, with the average value being $P_{\rm BrCN}=0.06\pm0.02$ Torr. A better estimate of $k_{\rm 8b}$ was provided from an analysis of the experiments with $P_{\rm C_3H_8}=0.0$. The removal rate was a sensitive function to $P_{\rm BrCN}$, but no systematic variation in $P_{\rm BrCN}$ was possible. From these experiments, it was estimated that $k_{\rm 8b}$ was $4.1\pm3.0\times10^{-12}$ cm³ molecules⁻¹ s⁻¹.

IV. DISCUSSION

There have only been two reported measurements of the magnetic dipole transition moment for the Br atom.^{44,45} These have relied on using Br* laser radiation as a probe of Br atoms in photolyzed IBr samples or in thermal equilibrium with Br₂. The Br* laser operates only on the strongest hyperfine $Br(2 \leftarrow 3)$ transition, which has a complicated line shape [see Fig. 3(b)], making the precise lasing and hence absorption frequency uncertain. The interpretation of the data of Efimenko et al.45 used integrated-absorption coefficient data for the $I^*(4 \leftarrow 3)$ transition, and hence has extra uncertainty associated with it. The direct determination by Boriev et al.44 gives the square of the magnetic dipole transition moment for the Br atom that is a factor of 1.42 larger than the LS prediction of $4/3\mu_B^2$, with an uncertainty of $\pm 37\%$. Again, the LS coupling value is within the experimental scatter of the measurement although this measurement has considerably more uncertainty associated with it than the measurements of the present work.

Garstang¹⁵ carried out a large number of calculations on forbidden transitions in atomic spectra, and suggested that

the deviation between the LS coupling predictions and the actual magnetic dipole transition moments could differ by as much as 20%. The processes that are ignored in arriving at Eq. (1) are the neglect of intermediate coupling, configurational mixing, relativistic effects, and the contribution of the magnetic moment of the nucleus. Garstang⁴⁶ has recently addressed the effects of these contributions to the electronic wave function in discussing radiative hyperfine transitions, and concludes that they will contribute only a few percent from the pure LS coupling predictions for the lighter elements. Indeed, these conclusions are borne out for the I atom. Ha et al.¹¹ compared their experimental measurement for the magnetic dipole transition moment for the I atom using several different configurational atomic wave functions as well as a relativistic calculation. The configuration interaction calculations gave only a slight deviation from the LS value. This is to be expected because Lilenfeld et al.⁴⁷ have measured the Lande g value for the $I({}^{2}P_{1/2})$ atom, and found it to be within $\pm 0.2\%$ of the pure LS value. Ha *et al.*¹¹ found that the relativistic calculation improved the energy separation between the I atom fine-structure levels, but the calculated-magnetic dipole transition moment was in considerable disagreement with experiment. In comparison with the I atom, the lower atomic number Br atom, with even a smaller spin-orbit interaction and more energetic excited electronic configurations, should behave even more as a pure LS coupling case.

This expectation was borne out in the relativistic calculations of the Br atom magnetic dipole transition moment reported in Table III. The more refined relativistic calculation was in perfect agreement with the LS coupling value for $|\langle J' | \mu_m | J''^2 \rangle|$, and any variation in the radiative spontaneous emission rate constant arose from differences in the calculated fine-structure splitting. More accurate experiments, with less scatter, will be necessary in order to determine if there is a real difference between the LS predictions and experiments. It appears that the best values for the integrated-absorption cross sections for the hyperfine transitions in the Br atom are still based on the LS model, as listed in Table I.

The first absorption feature in the UV spectra of the cyanogen halides is the A band continuum absorption, and it is attributed to transitions to similar electronic states in ClCN, BrCN, and ICN.⁴¹ For various technical reasons, the photodissociation dynamics of ICN have played an important part in elucidating the interplay among the processes that can occur on excited state potential energy surfaces.⁴⁸ Among these are the nonadiabatic couplings on the excited potential energy surfaces that lead to the production of the excited atomic states. Hess and Leone⁴⁹ have studied the photodissociation of ICN, and measured the quantum yield of I* as a function of photolysis wavelength. They found that the peak wavelength for I* production was shifted to the red of the peak in the A band absorption for ICN. Their quantum yields were in good agreement with the those deduced from the rotational state distribution of the CN fragment.⁵⁰ Such measurements cannot be made for BrCN. The 193 nm photolysis of BrCN, produces a CN rotational distribution²⁹⁻³¹ that is a smooth function of J, and it is not possible to infer the quantum yield of Br^{*} from such measurements.

For BrCN, the 193 nm photolysis wavelength is slightly to the blue of the peak of the *A* continuum, and value of ϕ_{Br^*} was found to be $\phi_{Br^*} = 0.31$; Table IV. For ICN, the quantum yield of I* was found to be $\phi_{I^*} = 0.44$ near the peak in the *A* continuum.⁴⁹ Both quantum yields for the production of the corresponding spin-orbit states are substantial, and indicate that similar mechanisms for their production may be operative in both cases.

Wannenmacher *et al.*⁵¹ have investigated the photodissociation dynamics of BrCN as a function of wavelength to the red of the peak wavelength of the *A* band continuum, (202 nm).⁵² These workers used a detailed Doppler analysis of the rotational lines of the CN fragment to deduce ϕ_{Br^*} as a function of the both photolysis wavelength and CN(ν =0,*J*) rotational state. Near the peak of the BrCN *A* band continuum, they found that ϕ_{Br^*} =1 for *J*'s<50.5 and decreased with increasing *J*, resulting in a total ϕ_{Br^*} =0.87 for a photolysis wavelength of 209 nm. The results of this work, Table IV, indicate that the production of Br^{*} must decrease rapidly as the photolysis wavelength shifts to the blue of the peak *A* band absorption.

The electronic-to-vibrational (E–V) energy transfer processes represented by reactions 8(a) and 8(b) were found to be efficient, Fig. 7. Generally, an E–V transfer process is rapid if there is a near resonant vibrational energy level in the quenching molecule involving the transfer of a small number of vibrational quanta.^{9,10,43} For both C_3H_8 and BrCN, the energy transfer step must involve multi-quanta of vibrational energy; however, the measured rate constants are still large. Perhaps, the rather dense rotational state density of each molecule could act as another near-resonant energy reservoir not available to smaller and lighter quenching partners to enhance the collisional efficiency of the E–V process.

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