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MEASUREMENT OF LIFETIMES AND QUENCHING CROSS SECTIONS OF

THE B STATE OF I_2

Ara Chutjian, John K. Link and Leo Brewer

September, 1966

Measurement of Lifetimes and Quenching Cross Sections of

the B State of I_2

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ABSTRACT

The phase shift method was used to measure lifetimes of selected vibrational regions from $v' = 10$ to $v' \sim 100$, together with self-quenching collision cross sections, of the $B^3\Pi_{0_u^+}$ state of I_2.

The reliability of the method was confirmed by good agreement with other measurements for the lifetime of the mercury $^3P_1$ state. At high optical densities, the observed increase in lifetime was shown to be due to radiation entrapment.

Reasonable agreement was found between the lifetime values and absorption measurements, but, contrary to expectations, the self-quenching cross sections

varied only a factor of 1.3 with vibrational excitation whereas the lifetimes varied by as much as a factor of eight.

The substantial variation of lifetime with v', which can not be merely a wavelength effect, indicates either that spontaneous predissociation of the B state of I_2 is an important process which has a rate at least as great as that for radiative decay and which varies considerably with v' or that the transition moment is changing with vibrational stretching.

INTRODUCTION

The lifetime of any vibrational level of the B $^3\Pi_{0_u^+}$ state of I_2 may be measured by observing the decay of fluorescent intensity according to the simple first order process $dI/dt = -I/\tau$. Here τ is the lifetime of the emitting state and I the fluorescent intensity from that state. The present work extends the previous measurements[1] for $v' = 25$ by the phase shift method to a number of vibrational levels of the B state. The observed lifetimes vary with iodine pressure due to $I_2^*-I_2$ collisional quenching. By measuring τ, the reciprocal of the total decay rate, as a function of I_2 pressure, the unimolecular lifetime, τ_o, of the excited state is obtained, as well as the effective collision cross section for $I_2^*-I_2$ quenching. As an additional check on the reliability of the phase shift method, measurements also were made for mercury vapor.

EXPERIMENTAL METHOD

If a particular resonant transition is excited with intensity-modulated light, the fluorescent light will be modulated at the same frequency but shifted back in phase relative to the exciting light because of the finite lifetime of the emitting state. The phase shift, $\Delta\emptyset$, is related to the lifetime, τ, by the relation

$$\tan \Delta\emptyset = \omega\tau \qquad (1)$$

where ω is the radial modulation frequency.

The experimental procedures and precautions described by Link[2] were followed in this work. It was especially important to reproduce the

fluorescent geometry when determining the phase of the exciting light as the phase was found to vary over the cross section of the light beam by as much as 15°. These large variations were attributed to defects in the rulings on the wheel and in the wire grating which combined with pincushion and barrel distortions from the lenses to cause mismatch between the grating image and the wheel rulings.

PHASE SHIFT APPARATUS

Figure 1 gives a block diagram of the apparatus. It has been modified from that reported by Brewer et al.[3] The feed-back control of the motor speed gives a short term stability of ±3 cps out of 359 kc for several minutes but requires occasional adjustment to correct for long term drift. The modulation frequency is always 1 kc below that of the crystal oscillator. Thus changing the modulation frequency only involves providing a new oscillator and two new mixers. All work on mercury and iodine used 359 kc as a modulation frequency.[4]

A more compact optics (Ref. 3, Fig. 1) for the wheel modulator is shown in Figure 2. The grating G was made by wrapping No. 37 (0.114 mm) copper wire on an expandable aluminum frame with grooves cut 0.254 mm apart. After wrapping, the wire was epoxied to the frame and stretched. The new grating was equivalent to the celluloid film gratings previously used,[3] and had the advantage of transmission in the ultraviolet.

EXPERIMENTAL PROCEDURES AND RESULTS FOR THE $^3P_1$ STATE OF MERCURY

The resonant absorption cell was made of fused quartz with a Wood's horn to minimize scattering of the incident light. The cell was evacuated

to 2×10^{-5} torr for 24 hours, during which it was heated several times to 500-600°C. to facilitate outgassing. Triply distilled mercury was distilled into the cell and the cell sealed off at a residual gas pressure of 10^{-4} torr.

The light source was a General Electric germicidal lamp powered by a Burdick Diathermy Machine, and the 2537 Å line was filtered with a 5 cm path of 0.35M $CoSO_4$-2M $NiSO_4$ solution.[5] All light levels in these and subsequent iodine experiments were measured with Amperex 56 UVP phototubes having an S-11 spectral response.

The diathermy output was set to give a maximum fluorescent signal from the resonance cell. If too much power was coupled to the lamp, the exciting line became self-reversed, leaving less light to be absorbed by the mercury atoms in the cell with their narrower Doppler width. In the present experiments, 65% of the exciting line was absorbed by the mercury atoms at room temperature where the vapor pressure is 1.94×10^{-3} torr.

Vapor densities in the cell were varied by means of a cooling jacket around a 10 cm stem at the bottom of the resonance-cell. A Haake Type-F pump-thermal regulator was used to circulate cooled ethanol around the stem and to maintain stem temperatures to 0.05°C in the range from -30° to 0°C.

It was found that the measured fluorescent phase shift and fluorescent intensity were very slow in coming to a repeatable equilibrium as the stem temperature was varied. Thus the measured stem temperature could not be used to compute the vapor density in the cell unless several hours were allowed for attainment of equilibrium. In practice the measured lifetime, τ_m, was determined as a function of fluorescent intensity and the scattered

light corrections made according to the relation given by Brewer et al.[3]

$$\tau = \tau_m \cfrac{1}{1 - \cfrac{I_s}{(I_f + I_s)\cos \Delta\phi_m}} \qquad (2)$$

where I_s is the intensity of scattered exciting light, I_f the intensity of fluorescent light, and $\Delta\phi_m$ the measured phase difference between the exciting light and the sum of scattered and fluorescent signals.

The results are shown in Figure 3. The temperature scale was established by holding the stem of the cell at constant temperature until reproducible signals were obtained. The lifetime was obtained from the level region between $I_f/I_s = 3$ to 10, and was $(1.10\pm0.05) \times 10^{-7}$ sec. This is in good agreement with the value of Garrett and Webb[6] of $(1.08\pm0.01) \times 10^{-7}$ sec from modulated electron excitation and optical detection; with the absorption measurements of Kopfermann and Tietze[7,8] giving $(1.08\pm0.03) \times 10^{-7}$ sec; and with a recent value cited by Lurio[9] from zero-field crossing measurements of $(1.145\pm0.02) \times 10^{-7}$ sec.

The gradual sloping in Figure 3 is due to radiation entrapment of the emitted photons by, at first, the most abundant mercury isotope Hg^{202}. The fraction of the exciting line absorbed (Ref. 10, p. 118) was calculated using the method of Kopfermann and Wessel (Ref. 11, Eq. 8) with path length $L = 6$ cm, Doppler width ratio $\alpha/\beta = 0.866$, absorption oscillator strength $f_{abs} = 0.0263$ (corresponding to $\tau = 1.10 \times 10^{-7}$ sec); and with vapor pressures from Busey and Giauque.[12,13] The absorption is 10% at approximately 242°K. The deviation from the limiting linear curve of growth is 10% at approximately 246°K. These two temperatures correspond to

(I_f/I_s) of approximately 8 and 12, respectively. These calculations show that the lifetimes will be relatively unentrapped when (I_f/I_s) is below 10.

LIFETIMES AND COLLISION CROSS SECTIONS OF I_2

The same single-horned quartz cell used in the mercury lifetime measurements was used in the I_2 work. The temperature range covered was - 4°C to 24°C (0.0202 to 0.282 torr I_2 pressure) and the exciting light phase was measured with a dilute MgO scattering sol. The concentration of the sol was adjusted so that the scattered light amplitude was equal to the largest fluorescence amplitude from the iodine cell.

The empty quartz cell was evacuated to 1×10^{-5} torr, and heated to 600°C to drive off water and adsorbed gases from the cell walls. The system was then bled with helium, and the cell removed and filled with Baker reagent grade I_2 in a dry-box flushed with dry nitrogen, and containing $CaSO_4$ ("Drierite") and NaOH pellets as dessicants. The I_2 was introduced into the long stem only, and was distilled into the cell at a pressure of 8×10^{-5} torr. After 10-15 minutes, the cell was sealed off at approximately 10^{-4} torr.

Cell temperatures were controlled with the Haake Thermoregulator, and no difficulty was had in varying the I_2 pressure in the cell with changes in the finger temperature; and in reproducing data points by starting from low temperatures and heating to room temperature, and then reversing the process. No slow decrease in τ with time as mentioned by Berg (Ref. 14, p. 78) was observed, since his cell was sealed with a greased stopcock which leaked slowly.

LIGHT SOURCES AND FILTERS

Excitation of the I_2 fluorescence was accomplished with a variety of light sources which included Osram Lamps, a mercury 100 watt AH4 lamp, and a commercial 600 watt G.E. "Sun Gun" (used for floodlight illumination) which served as a continuum light source. The "Sun Gun" was operated on 60 cps AC, the Osram Lamps on 50-100 cps square wave, and the mercury lamp on DC.

Scattered light from the cell was reduced to a minimum by using Kodak Wratten filters (except for Na D line excitation where a Dydimium filter was used) to transmit only that portion of the fluorescent light which fell 200Å or more to the red of the exciting light. Several Wratten filters were tested at each wavelength, and the one giving the maximum (I_f/I_s) was used.

All of the exciting atomic lines and continua were isolated by Baird-Atomic interference filters. The full width at half and 10% maximum, and the peak wavelength of these filters are presented in Table I along with other light source data.

SCATTERED LIGHT CORRECTION

In measuring the ratio (I_f/I_s) at a particular temperature, it is necessary to know the fraction of scattered light that is transmitted by the filter. With the filter placed in front of the sample PMT, and the I_2 in the cell frozen out with liquid N_2, the sample PMT voltage was adjusted to give a 15 v p-p signal at 1 kc (the amplitude at which all phase readings were taken). The cell and filter were removed, and the sol positioned before the PMT. With the same PMT voltage, sufficient Kodak neutral density filters were used to attenuate the sol-scattered

Table I.

Light Sources and Filters Used in Iodine Excitation.

Peak Wavelength of Excitation Light Selection Filter (Å)	Full Width (Å) at Half Max.	Full Width (Å) at 10% Max.	Excitation Light Blocking Filter (Wratten No.)	Light Source	Mode of Operation
6040	87	153	33	Sun Gun	AC
5895	58	102	Dydimium Plate	Na Osram / Sun Gun	Square AC
5592	57	103	23A	Sun Gun	AC
5461	50	98	23A	Mercury AH4 / Sun Gun	DC / AC
5277	49	90	21	Sun Gun	AC
5168	48	86	21	Sun Gun	AC
5087	29	58	16	Cd Osram / Sun Gun	Square AC
5011	28	60	16	Sun Gun	AC

light to a 15 v p-p signal. When a fluorescent plus scattered light amplitude was measured at a temperature T, its amplitude was again matched by the sol-scattered light, now attenuated to the higher signal amplitude (lower PMT voltage) by neutral density filters. From these measurements, one can calculate (I_f/I_s). The maximum corrections[1] to the lifetime amounted to 15-20% for the lowest temperature points with 6040Å excitation while most other corrections varied from 0 to 5%.

STERN-VOLMER PLOTS

The Stern-Volmer equation[15]

$$\frac{1}{\tau} = \frac{1}{\tau_0} + (2.264 \times 10^5) \, \sigma^2 P \qquad (3)$$

with σ, the collision diameter of I_2, may be used to correct for collisional quenching.[1] A plot of $1/\tau$ against the iodine vapor pressure yields the unquenched unimolecular lifetime as the intercept, and the $I_2^*-I_2$ self-quenching collision cross section from the slope. Vapor pressures for I_2 were derived from a smooth curve drawn through the data of Shirley and Giauque[16] from 273 to 308°K. Pressures at temperatures below 273°K were interpolated from their $-(F° - H°)/T$ value of 52.759 cal/deg mole at 250°K for $I_2(g)$.

Two representative quenching plots are shown in Figures 4 and 5 for excitation with the Hg 5461Å line and with a continuum peaked at 5461Å, respectively. The results of all the measurements are summarized in Table II and Figure 6. The assignments of v' are based on the studies by Dymond[17,18] and recently by Brown and Klemperer[19] on resonant spectra excited by low to

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Table II.

Lifetimes and Cross Sections for Emission from

Various v' Regions of the B State of I_2.

Wavelength (Å)	v' Region	No. of Data Points	$\tau_o(10^{-7}\text{sec})$	$\sigma^2(\text{Å}^2)$
6040	10-14	63	6.79 ± 0.33	73.7 ± 5
5895 (Cont.)	13-16	42	11.4 ± 0.6	70.0 ± 4
5890 (NaD)	14-16	37	11.9 ± 0.7	69.4 ± 3
5592	20-24	61	6.89 ± 0.33	65.3 ± 4
5461 (Cont.)	25-27	44	7.69 ± 0.3	67.4 ± 4
5461 (Hg Green)	25, 26, 28	39	7.13 ± 0.25	63.0 ± 3
5277	34-36	56	9.66 ± 0.5	60.0 ± 4
5168	41-44	58	$24.1 {}^{+3.3}_{-2.6}$	72.7 ± 5
5087 (Cont.)	47-54	66	$42.2 {}^{+7}_{-5}$	65.8 ± 4
5086 (Cd Blue)	49-50	48	$53.2 {}^{+8}_{-6}$	78.7 ± 3
5011	~100	42	17.5 ± 1.5	67.8 ± 4

medium pressure light sources. For a narrow Hg 5461Å line, the excited level is v' = 25, J' = 34; for the NaD (reversed) lines, v' = 14, J' = 113 (10%), v' = 15, J' = 44 (50%) and J' = 37(25%), and v' = 16, J' = 106 (10%); and for the Cd 5086Å line, v' = 49, J' = 8 and v' = 50, J' = 43. The assignments of the other levels in Table II were made using the spectroscopic data for the ground state of I_2 given by Rank and Rao[20] and the data for the B state given by Steinfeld et al.[21] The regions of v' which were excited were determined using the Franck-Condon factors of Steinfeld[24] and represent v', J' levels which had populations greater than 10% of the sum of the populations in all the excited states. The absence of sufficient population in v' = 27, in the case of excitation with the Hg green line, is due to the fact that absorptions to 25', 26' and 28' originate from J" levels closer to the J" level with maximum population and are therefore much more intence.

From the new constants for the B state, Steinfeld et al found that they had to decrease the vibrational numbering of that state by one unit over the original assignment by Mecke and Loomis[22] in order to bring their calculated intensity distributions into agreement with known fluorescent intensities. This renumbering has been confirmed by Brown and James[23] through isotopic shifts and the new v' numbering has been used in Table II. The vibrational assignment for the 5011Å excitation region is only an estimate due to the fact that the vibrational energy levels can not be accurately assigned from existing spectroscopic constants so close to the dissociation limit of 4990 ± 5Å.

All results were obtained by a least-square fit to the 35-65 points taken at each wavelength. The runs at each wavelength were taken on separate days; and from lower to higher, and higher to lower temperatures. The maximum spread in lifetimes for the smallest phase shifts (20-22°C) was 10%, and no systematic trends either due to impurity gas quenching

or lack of equilibrium were seen. The assignment of errors was made by drawing high and low slope lines about the least square lines, taking into consideration the spread in values at each temperature, and are a measure of the random variation of the data in the present experiments. The errors in τ_o are greatest for small values of $1/\tau_o$ (large τ_o), since the usual uncertainty in the intercept (0.8×10^5 sec^{-1}) is a larger percentage of the smaller intercept values.

DISCUSSION

Radiation Entrapment

Several checks were made on the experimental data to ensure that the measured lifetimes and cross sections did not reflect the effects of radiation entrapment. In the case of excitation with a narrow Hg 5461Å line absorption occurs from $v'' = 0$, $J'' = 33$ going to $v' = 25$, $J' = 34$. Since the intensity of fluorescence was strongest for this excitation, and since very accurate Franck-Condon factors were known[24] for all the 25' - v'' transitions, this seemed the most likely excitation to check.

If the vapor density of I_2 is sufficiently high, any of the P and R doublets from the (25', 34') level which terminate in the $v'' = 0$, 1 and 2 levels correspond to emitted photons which may be reabsorbed to the (25', 34') level, then re-emitted to higher v'' levels. These latter photons would then be shifted in phase more than once and the lifetime of the emitting state would seem to increase.

However, the ratio of the radiative decay rate to the quenching rate at the highest pressure points in Figure 4 is $1.4/(5.0-1.4) = 0.38$, so that at most only 38% of the re-excited I_2 molecules would ever remain as I_2

long enough to re-emit. Of this 38%, the fraction which could emit photons in the observable wavelength region 5700Å (onset of transmission by the 23A filter) to 6500Å (photomultiplier cut-off) is 23%, as calculated from known emission frequencies and Franck-Condon factors. Thus, only 6.9%, or less if spontaneous dissociation occurs, of the reabsorbed 25'-0" line would ever be seen in re-emission by the photomultiplier.

One would expect that any entrapment effects would cause a lengthening of the room temperature lifetimes and a subsequent leveling-off of the Stern-Volmer plots. No such effect was observed in any of the plots. As a further check, a 14 cm. long cylindrical cell with a 3.5 cm diameter was built, and the I_2 fluorescence observed at three points along the cell: at the entrance window, 7 cm. from the entrance window, and at the rear exit window. If the effects of entrapment were present, there would be a gradual lengthening of τ towards the rear of the cell. The lifetime at each of these three positions was measured at I_2 pressures of 0.067 torr (8°C) and 0.238 torr (22°C) and no change in lifetime with position was observed.

SELF-QUENCHING CROSS SECTIONS

In view of the past speculations about the $I_2^*-I_2$ self-quenching mechanism we anticipated that the measured quenching cross sections would show effects of dissociative levels crossing the B state, especially at v' ~ 25, or v' = 22, 29, and 39 as seen by Turner[18,25] and Kondratjew and Polak.[26] The small variation of quenching cross section with v' shown in Table II and Figure 6 is less than estimated experimental error. This lack of variation would seem to indicate that the quenching process is not dependent on the presence of nearby repulsive states.

A comparison of the cross sections obtained by excitation with the Hg 5461Å and NaD wavelengths with those in the recent work of Brown and Klemperer[19] do not agree within stated experimental error. Since they used the lifetime of $(7.2\pm1) \times 10^{-7}$ sec obtained for $v' = 25$ by Brewer, et al[1] to obtain quenching cross sections from their Stern-Volmer quenching plots, their reported values should be multiplied by a factor of $7.2/7.13$ for the mercury line excitation, and $7.2/11.9$ for the NaD line excitation (see their Table VI). Their results after correction are $91.1\pm2.4\text{Å}^2$ and $78.7\pm5.3\text{Å}^2$, as compared with our values of $63.0\pm3\text{Å}^2$ and $69.4\pm3\text{Å}^2$ for the mercury and sodium wavelengths, respectively.

In order to investigate the cause of this disagreement, Brown and Klemperer's[19] work was repeated. Their method gives the product of the lifetime τ and the quenching cross section from the ratio of intercept to slope of a plot of $1/I_f$ against reciprocal I_2 pressure. The derivation of the necessary relations assumes that the intensity of light capable of exciting fluorescence, in front of the fluorescence viewing window, remains constant through the whole range of I_2 pressures involved with no attenuation due to I_2 absorption. For example, this assumption is badly violated between 5° and 22°C for 5461Å excitation with a fluorescent viewing window set even 3 cm in from the entrance window for the exciting light. The data of Brown and Klemperer[19] were taken between 0° and 22°C and so their cross sections are too large due to this exciting light attenuation effect. Use of their method for I_2 pressures between -12° and 2°C eliminated this effect and gave quenching cross sections of $61\pm6\text{Å}^2$ for 5461Å excitation and $60\pm6\text{Å}^2$ for NaD light excitation. These values agree within experimental error with the values derived from the measured lifetimes.

It should be noted that the work of Steinfeld[24,27] on I_2 self-quenching suffers from the same error.

Because the 359 kc modulation frequency used in our work was a factor of six greater than the 60 kc modulation frequency used by Brewer, Berg and Rosenblatt,[1] we were able to measure smaller quenched lifetimes, and to extend their quenching plot (Ref. 1, Fig. 6) by an order of magnitude in pressure. This then gave a cross section for the v' = 25 level of almost exactly one-half their 128Å^2 value, whereas the lifetimes agreed within experimental error.

RADIATIVE TRANSITION PROBABILITIES

From Table II or Figure 6 we see that no great differences in either cross section or lifetimes were observed when excitation was made with either an atomic line or a narrow spread of wavelengths peaked at the atomic line wavelength except for the Cd 5086Å excitation where the lifetime is changing abruptly. Since iodine has several v" or v' absorption transitions in the region of each excitation continuum, the results indicate that the lifetimes varies slowly with v' over a small interval ($\Delta v' \sim 3\text{-}5$) around v' = 15 and 26. In terms of the transition moment $R^{v'v'',J'}$ for fluorescence from a state of given v' and J' to states of any v" with J" = J' ± 1, the lifetime of state v' can be expressed[28] as

$$\frac{1}{\tau_{v'}} = \sum_{v''} A_{v'v''} = \frac{64\pi^4}{3h} \sum_{v'',J''} \lambda^{-3} |R^{v'v'',J'}|^2 \qquad (4)$$

with $A_{v',v''}$ the Einstein emission coefficient and λ in cm.

In terms of Franck-Condon overlap and the assumption of separability of electronic, vibrational, and rotational energies, one obtains

$$\sum_{v''} A_{v'v''} = \frac{64\pi^4}{3h} |R_e|^2 \sum_{v''} \lambda^{-3} q_{v'v''} \qquad (5)$$

where $q_{v'v''}$ is the Franck-Condon overlap factor between the levels v' and v'', and where R_e, the electronic contribution to the transition moment, is usually assumed to be independent of the vibrational transition.

The present results imply that the sum of Eq. (4) changes only slightly from $v' = 25$ (line excitation) to $v' = 25, 26, 27$ (continuum excitation). Polyanyi[30] notes that the doublet intensities of the series $25' - 0'', 1' \ldots$; $26' - 0'', 1'' \ldots$; $27' - 0'', 1'' \ldots$, are nearly the same. This indicates that changes in overlap are usually small between the adjacent vibrational levels.

Zare[31,32] used the Rydberg-Klein-Rees procedure[33-35] to calculate Franck-Condon factors for $v' = 15$, 16, and 26 to $v'' = 0$ to 69. Recalculations based on more accurate spectral data have been made[21,24] for $v' = 25$. Verma[36] used the same procedure to map the turning points of the X state from $v'' = 0$ to $v'' = 112$. Zare's compiled RKR program[31] can, in principle, be extended to calculate the Franck-Condon overlap integrals to v' up to around 100. On the basis of the Franck-Condon factors weighted by λ^{-3} as in Eq. (5), one predicts smooth changes in the sums of overlap factors with vibration and it is difficult to account for the lifetime peaks at $v' = 15$ and 50. Correction of the lifetimes of Figure 6 for the λ^{-3} factor has little effect upon their large variation with v'.

To account for the observed variation, there must be additional radiative or non-radiative processes that can preferentially depopulate different

vibrational levels of the B state of I_2 or one must abandon the assumption

of constancy of R_e in Eq. (5). Verma[36] and Mathesen and Rees[37] have

summarized the potential curves and data for the known and expected states

of I_2. The B $^3\Pi_{0_u^+}$ state of I_2 arises from $I(^2P_{3/2}) + I(^2P_{1/2})$. The B

state can radiate only to a state of gerade symmetry. No attractive

states of gerade symmetry are expected below the B state beside the

ground state. The only conceivable radiative processes that might compete

with the B to X fluorescence, which lies between 20,056 and 3273 cm^{-1},

would be transitions to the repulsive $^3\Pi_{1_g}$ or $^3\Pi_{0_g^+}$ states which correlate

to a pair of ground state iodine atoms. As the ground atoms lie 3273 cm^{-1}

below the $v = 0$ level of the B state and 7,603 cm^{-1} below the convergence

limit of the B state, these transitions must be at long wavelengths

and should contribute little to the lifetime except at very high v'.

It is possible that the abnormally low lifetime around $v' = 100$ might be

due in part to additional emission in the infra red beyond 1.3μ. For such

a transition at 2μ, for example, to compete with the B-X transition,

it must have an oscillator strength ten times greater, or around 3×10^{-2}.

Non-radiative perturbations of the B state can be brought about by

states of ungerade symmetry. The $^3\Pi_1$ and $^3\Pi_2$ sublevels corresponding to

the B $^3\Pi_{0+}$ level are expected[37] to be attractive states correlating to

ground atoms and thus should lie too low to perturb the B state. The

$^3\Pi_{0-}$ sublevel is also predicted[37] to be attractive, but other authors[38,43]

believe that it may be repulsive and approach the B level. Other repulsive

states correlating with the ground atoms, and thus possibly crossing the B

state, are $^1\Pi_{1_u}$ and $^3\Sigma_{0_u^+}^+$ with the $^1\Pi_1$ state predicted[37] to lie lower in

energy.

Magnetic quenching of the B state of I_2 in a field of 12,500 gauss to produce atomic iodine is well established.[18,25,39] Van Vleck[40] has given a detailed analysis of the symmetries of electronic states that may mix in the magnetic and collisional quenching cases. The magnetic quenching of the B state of I_2 is attributed[37,38] to the crossing of the B state by the $^3\Sigma^+_{0_u^-}$ repulsive state at around $v = 24$, where the quenching is greatest.

It has been reported[41] that the fluorescent spectrum of 0.3 torr I_2 with 11 torr Ar shows weakening of bands above $v' = 14$ and that 0.2 torr I_2 with O_2 between a few cm to 1 atm shows[42] enhanced absorption above $v' = 12$ with a peak at $v' = 25$. These effects are attributed to shortening of the lifetimes of levels around $v' = 25$ by a predissociative process. Our observation of little change of quenching cross section with v' contradicts these claims. Recent high dispersion measurements[43] confirm the same degree of broadening of all rotational levels from 5000Å to 6300Å when 1 atm Ar is added to iodine. Kondratjew and Polak[26] have reported three extinction maxima in the visible spectrum of I_2 with added gas which are assigned to crossovers of the B state to the $^1\Pi_{1_u}$, $^3\Pi_{1_u}$, and $^3\Pi_{0_g^+}$ states. Zener[44] has indicated that no special selection rules have to be obeyed in collision-induced predissociations which would allow a variety of possible perturbing states. Our results and those of Ogryzlo and Thomas[43] indicate that all of the reported effects are due to complete absorption at the centers of the strong rotational lines of iodine at low foreign gas pressures. The general pressure broadening of all of the rotational lines upon addition of foreign gas will cause apparent enhancements of the spectral regions where the strongest lines lie. There is no evidence that there is enhanced broadening due to shortening of the lifetimes by collision induced crossovers from the

B state to any repulsive states. If there is any such effect, it must occur uniformly for all vibrational levels. This might be possible if the $^3\Pi_{0_u^-}$ potential curve were to coincidentally parallel the B $^3\Pi_{0_u^+}$ potential curve.[43] There is no question that collisional quenching of the B state produces atoms but a process like $I_2^* + Ar = I + IAr$ may be responsible.[43]

There still remains the question of whether a crossing of the B state by a repulsive state could affect the lifetime under low-pressure-non-quenching conditions. Rabinowitch and Wood[45] measured the quantum yield for iodine atom formation upon photoexcitation of I_2 in the presence of 200-500 torr of He, Ne, Ar and N_2. They found the same quantum yield for excitation with light of wavelengths shorter than the convergence limit of the B-X transition as with wavelengths longer than the convergence limit. They concluded that all excited I_2 molecules dissociate into atoms at high pressures of quenching gas due to collisions of the B state with quenching molecules (which may be I_2). At low pressures, below .05 torr, they assert that the major process is the natural decay $I_2^* = I_2 + h\nu$. The quantum yield of atom production is given[46] as unity for wavelengths shorter than 4990A and zero at longer wavelengths, but no explicit data are given for quantum yields in the low pressure region.

More recently, Bowers, et al.[47] measured the paramagnetic absorption of I atoms produced by dissociation of I_2 vapor in a resonator cavity. They irradiated I_2 with wavelengths above and below the dissociation limit and reported no change in I atom concentration with changes in exciting wave-length, magnetic field, addition of air, and changes in I_2 pressure from 0.02 to 0.2 torr. Mayo[51] has confirmed some of these observations, but a clear wavelength dependence was demonstrated and a decrease in I atom

concentration with decreasing I_2 concentration was found for I_2 pressure below 0.07 torr as would be expected when the I atoms are removed by heterogeneous wall reaction rather than by homogeneous reaction with I_2. The assumption of a dissociative (spontaneous plus collisional) quantum yield of almost unity and recombination completely by the homogeneous reaction $I + I + I_2$ accounts for the constancy of the I atom concentration with variation of I_2 pressures above 0.07 torr. Mayo[51] has demonstrated that irradiation by wavelengths to the red of the dissociation limit of 5000A does result in extensive atom formation, but the I_2 pressure of these experiments is unspecified and probably was high enough to insure rather complete dissociative quenching.

There are thus no data which give a clear answer to the question of whether the variation of lifetime with v' could be due to spontaneous predissociation. Our observation of constancy of quenching cross section with v' indicates that crossing of the B state by specific repulsive states is not significant for the quenching process. If one assumes, in agreement with Rabinowitch and Wood[45,46] that predissociation of the B state by repulsive states does not compete with the fluorescent process under the non-quenching conditions of low pressure iodine vapor, the observed variations of lifetime with v' must be attributed to variations of the transition moment upon vibrational and rotational stretching.

COMPARISON OF LIFETIME AND ABSORPTION DATA

Absorption data[19,50] exist for single rotational lines which yield Einstein A and B coefficients for specific transitions. For a v"

to v' transition, these coefficients will be designated as $A_{v'v''}$ and $B_{v'v''}$. The lifetime measurements for a v' state give the sum over v'' of $A_{v'v''}$. The relative intensities $I(v',v'')$ of the fluorescent lines can be estimated from the λ^{-3} values and the Franck-Condon factors of Steinfeld[24] The equation

$$\tau_{v'} = \frac{I(v',v'')}{A(v',J'; v'',J'') \Sigma_{v''} I(v'v'')} \frac{(J' + J'' + 1)}{2(2J' + 1)} \tag{6}$$

relates the measured lifetime to the A value for a specific rotational line. If there is no spontaneous predissociation, the observation of variation of the lifetime with v' indicates a breakdown of the sum rule for summation of Franck-Condon overlap factors over v', but the reasonable check of measured fluorescent intensities with the calculations of Steinfeld[24] indicates that the sum rule is applicable for v''.

The absorption coefficients for the 14-3 P(114) and 15-3 P(45) rotational lines were determined by Brown and Klemperer,[19] but their calculation of A values are in error by a factor of ten.[53] Their data have been recalculated to obtain the A values listed in column two of Table III. Eq. (6) was used to convert these A values to the calculated lifetimes in column three for comparison with the directly measured lifetimes given in column four. Similar calculations have been carried out with the value given[50] for the 25-0 transition.

Rabinowitch and Wood[48] and Sulzer and Wieland[49] have taken total band absorption measurements using pressure broadening to minimize deviation from the linear curve of growth. Their data yield sums of $\Sigma_{v'} B_{v'v''}$ for v' = 0, 1, 2 and possibly several more low lying levels,

Table III.

Comparison of Lifetimes Calculated from Absorption Measurements

with Directly Observed Lifetimes

Line $v'-v''$	$A_{v'v''}$ 10^5/sec	Calculated $1/\sum_{v''} A_{v'v''}$ or $\tau_{v'}$ 10^{-6}sec	Observed $\tau_{v'}$ 10^{-6}sec
14-3 P(114)	0.36[a]	1.2	1.14
15-3 P(45)	0.10[a]	3.3	1.19
25-0 R(33)	0.6 [b]	1.	0.71
Broad Band Absorption		1.0-2.0[c]	0.68-5.3[d]

[a] Recalculated from the absorption data of Reference 19 taking into account the effect of nuclear spin and correcting for a decimal point error.

[b] Equivalent width measurement of Reference 50 was corrected for deviation from linear curve of growth.

[c] From Table X of Reference 31 and recalculation of results of Reference 50 to correspond to a mean fluorescent wavenumber of 11,500 to 12,000 cm^{-1}.

[d] Range of observed lifetimes between $v' = 10$ and 100.

each weighted by its Boltzmann factor. An accurate comparison between these data and either the lifetimes or the individual line absorptions is not possible because of breakdown of the vibration sum rule over values of v' as shown by the variation of lifetime with v'. However, it is worthwhile to make an approximate comparison on the only basis possible. This requires assumption of the sum rule for Franck-Condon overlap factors, $\sum_{v'} q_{v'v''} = 1$, which allows equating of $\sum_{v'} B_{v',0} = \sum_{v'} B_{v',1} = \sum_{v'} B_{v',2}$, etc.; so that the weighting by Boltzman factors can be neglected and the total absorption taken to correspond to $\sum_{v'} B_{v',0}$ value in as much as the average wavelengths for each term do not differ significantly.

From the value of $\sum_{v'} B_{v',0}$ one can calculate $|R_e|$, the electronic transition moment. The assumption of the sum rule for Franck-Condon overlap factors corresponds to assuming that $|R_e|$ is independent of v'. On the basis of this assumption one can then calculate fluorescent lifetimes for various v' from Eq. (5) using the mean cubed reciprocal fluorescent wavelength weighted by the overlap factor, e.g. 8350Å for $v' = 14$, 8380Å for $v'=15$, and 8760Å for $v'=25$. Zare[31] has calculated lifetimes of 1.5×10^{-6} and 1.8×10^{-6} on this basis from the data of Rabinowitch and Wood[48] and Sulzer and Wieland.[49] Stafford[50] has treated these same data as well as additional data. Recalculation of his results to correspond to a mean cubed fluorescent wavenumber of 11,500 to 12,000 cm^{-1} yields lifetimes from 1.0 to 2.0×10^{-6} sec.

Figure 6 provides a comparison between the measured lifetimes for different v' regions, the lifetimes derived from the rotational line absorption measurements by Brown and Klemperer[19] and by

Stafford,[50] and the range of values from broad band absorption measurements. In view of the unreliability of the assumptions that had to be made to obtain lifetimes from broad band absorption values, it is not clear whether the comparison is meaningful, but the values fall in the range of the measured lifetimes.

If $|R_e|$ were independent of v' and the vibrational sum rule held over v', all points should lie within the dashed lines. Although the lifetime values and the total absorption values are in reasonable agreement, the range of values outside the dashed lines indicate (if there is no appreciable spontaneous predissociation) that the vibrational sum rule does not hold and that the stretching of the molecule upon vibrational and rotational excitation must change the electronic wavefunctions of the states quite significantly and thus cause variation of $|R_e|^2$. Since the B-X transition is forbidden in the limit of separated atoms, one might expect that $|R_e|^2$ would decrease upon increase of internuclear distance. Mulliken and Rieke[52] report calculations of Sayvetz that indicate a large variation of $|R_e|^2$ with internuclear distance for chlorine and bromine. Figure 6 shows a general increase in lifetime and thus decrease in $|R_e|^2$ up to v' = 50. The v' = 100 lifetime is much lower but may be due to radiation to a repulsive curve as discussed earlier. If extensive non-quenching pre-dissociation which varied with v' were responsible for the observed variation in lifetimes, one might expect the lifetimes calculated from absorption measurements to be much longer than the measured values. The lifetime derived from Brown and Klemperer's A- values is three times longer than the measured lifetime for v' = 15, but the value for v' = 14 is close to the measured values

for the region around v' = 15. The closeness of the broad band absorption values to the measured lifetimes would indicate little dissociation, but as indicated above, the comparison may be questionable. A more explicit clarification of the quantum yield of dissociative photolysis to the atoms under non-quenching conditions is necessary before one can clearly establish how much of the lifetime trends can be definitely attributed to variation of $|R_e|^2$ with stretching. Such work is now in progress.

CONCLUSIONS

1. The lack of significant variation of iodine quenching cross section with variation of v' indicates that crossing of the B state by repulsive states at specific v' values does not play a role in the quenching mechanism. Thus the crossing repulsive state responsible for specific magnetic quenching around v' = 24 does not interact specifically in the collisional quenching process.

2. The substantial variation of lifetime with v' indicates that either the transition moment varies with vibrational excitation of the B-state or spontaneous pre-dissociation of the B-state is an important process which has a rate at least as great as that for radiative decay and which varies considerably with v'.

ACKNOWLEDGEMENT

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FIGURE CAPTIONS

Figure 1. Block diagram of the lifetime apparatus.

Figure 2. Light modulating optics

L_1 Collimating lens (fused quartz)

G Wire grating (100 strands/inch)

L_2 Lens for focusing grating image on wheel (fused quartz)

$S/S' = 5$

Figure 3. Lifetime of the mercury $^3P_1$ state vs fluorescence to scattered light intensity. Lifetime in the absence of entrapment $(I_f/I_s = 3$ to $10) = (1.10 \pm .05) \times 10^{-7}$ sec. Increase in lifetime with I_f/I_s is due to radiation entrapment.

Figure 4. Stern-Volmer plot for Hg 5461Å excitation of I_2 fluorescence.

Figure 5. I_2 Stern-Volmer plot for continuum excitation peaked at 5461Å.

Figure 6. Variation of I_2-I_2 self-quenching cross section (top scale) and unquenched radiative lifetime (bottom scale) with vibrational level of the B state of I_2.

(atomic line excitation), (continuum excitation) and

(average of the two excitations): directly determined lifetimes and cross sections with extent of experimental scatter indicated by height of bracketed line.

△ calculated from rotational line absorption data[19]

X calculated from rotational line absorption data[50]
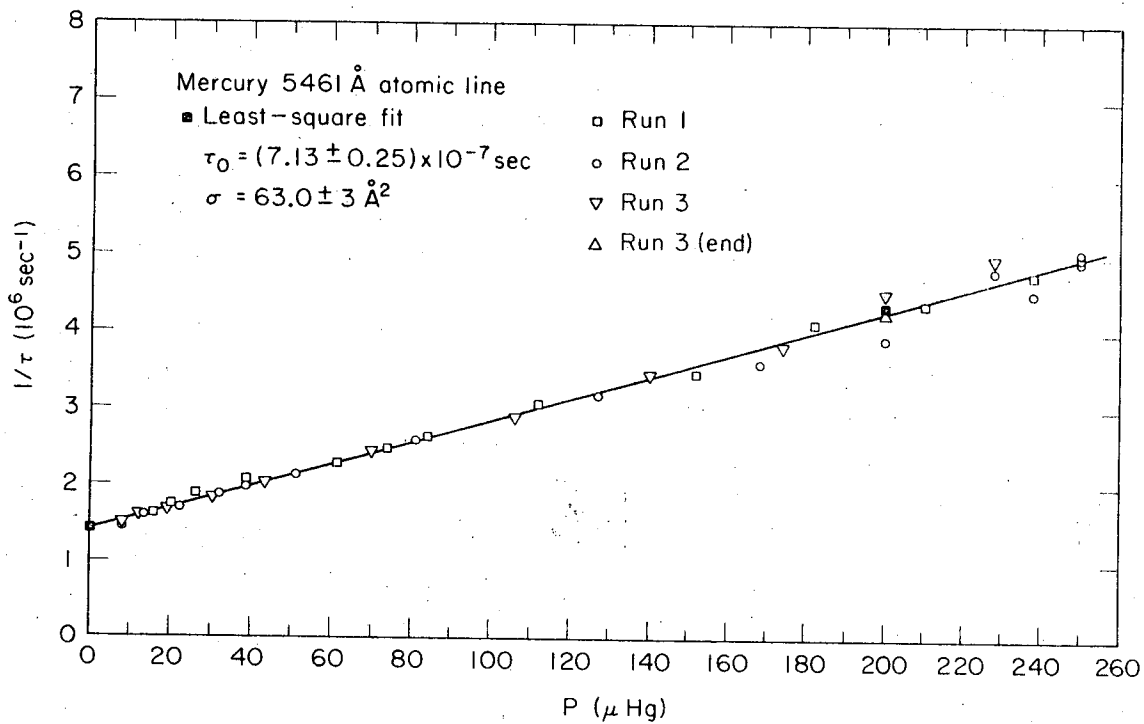
- - - range of calculations from broad band absorption[31,50]

Fig. 1

Light L_1 G L_2 Wheel
source

MU-36894

Mercury 5461 Å atomic line

- Least—square fit

$\tau_0 = (7.13 \pm 0.25) \times 10^{-7}$ sec

$\sigma = 63.0 \pm 3$ Å^2

□ Run 1
○ Run 2
▽ Run 3
△ Run 3 (end)

$1/\tau$ (10^6 sec^{-1})

P (μ Hg)

Continuum peaked at 5461 Å

■ Least-square fit   □ Run 4

$\tau_0 = (7.69 \pm 0.3) \times 10^{-7}$ sec   ○ Run 5

$\sigma = 70.0 \pm 4$ Å^2 △ Run 6

$1/\tau$ (10^6 sec^{-1})

P (μ Hg)

MU-36890-A