LA-5761-SR
Status Report

**c.3**

# The Status of Laser Separation of Boron Isotopes - June 1974

by

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# THE STATUS OF LASER SEPARATION OF BORON ISOTOPES–JUNE 1974

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## ABSTRACT

A 14% enrichment in the ratio of $B^{10}/B^{11}$ has been achieved by selective excitation by $^{11}BCl_3$ ($v_3$) with a $CO_2$ laser followed by preferential photodissociation of the excited state molecules. The subsequent photochemistry used $O_2$ as a scavenger.

## I. INTRODUCTION

At this time we can report a 14% isotopic enrichment of a 5-µg sample of $BCl_3$ obtained with 5 pulses of laser radiation using two photon induced photochemistry. This mass of material represents a relatively large sample in comparision to other recent work in the field [1] and, furthermore, the present results indicate that both the enrichment and the yield can be greatly improved by the development of a brighter uv source.

As stated we have employed selective two photon dissociation of $BCl_3$ in the presence of chemical scavengers. The first step is the selective excitation of $^{11}BCl_3$ in the $v_3$ mode using the P(20) line of a $CO_2$ laser. This is immediately followed by photodissociation of the excited state molecules yielding fragments containing an enhanced fraction of $^{11}B/^{10}B$. The fragments of the photodissociation are then consumed by a chemical scavenger. In the present case $O_2$ has been used as the principal scavenger leading to a product which has a much lower vapor pressure than the $BCl_3$. Physical separation of the two isotopes is thus accomplished by trapping of the product gas onto a cold surface while leaving the $^{10}B$ enriched $BCl_3$ in the gas phase. Subsequent portions of this report will examine in some detail the necessary physical properties of $BCl_3$ which allow the present process to work and conclude by presenting the isotopic enrichment obtained to date

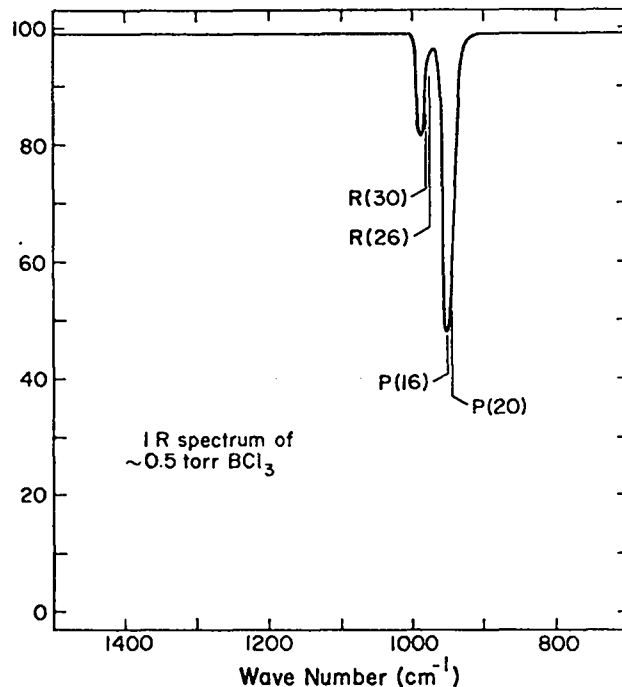along with projected future experiments.

## II. INFRARED REQUIREMENTS



Fig. 1. ir absorption spectrum of $BCl_3$ to the $v_3$ mode showing the isotope shift between $^{10}BCl_3$ and $^{11}BCl_3$. Path length was 10.2 cm. Pressure was not measured precisely.

Figure 1 displays the absorption spectrum of $BCl_3$ in the vicinity of 1000 $cm^{-1}$ along with the location of many $CO_2$ laser lines as presented in Refs. (2-4). The attenuation coefficients and saturation flux for many of these lines are given in Ref. 3. From these data it is readily observed that quantities of $BCl_3$ on the order of 10 - 100 torr can be promoted to the $\nu_3$ mode using $CO_2$ laser powers readily obtainable with today's technology.

The relaxation of the $\nu_3$ mode by vibration-vibration (V-V) transfer is known to be rapid and the equilibration of excitation energy between $^{11}BCl_3$ $(\nu_3)$ and $^{10}BCl_3$ $(\nu_3)$ proceeds with a rate of [4]

$$\frac{1}{p\tau} = 2 \times 10^6 \ sec^{-1} \ torr^{-1} \ . \qquad (1)$$

To avoid scrambling of the selected isotopic state the vibrationally excited $^{11}BCl_3$ must be dissociated on a time scale short compare to this V-V transfer rate. This rapid dissociation rate requires in turn a large uv photon flux as discussed in the following section.

III. ULTRAVIOLET REQUIREMENTS

Figure 2 displays the measured uv absorption of $BCl_3$ containing a natural abundance of both B and Cl isotopes. The absorption spectrum was measured on a Cary Model 14 spectrophotometer with a 10-cm quartz absorption cell at room temperature. A hydrogen lamp was used for the light source. A $BCl_3$ pressure equal to its vapor pressure at the temperature of solid $CO_2$ was used to record spectrum A of Fig. 2. This pressure is approximately 4.0 torr. Spectrum B was run at a pressure of 2.1 torr.

The peak at 207.6 nm was recorded at 0.05 nm/s. At 210 nm the dispersion of the Cary is 0.29 nm when using a slit of 0.22 nm. No evidence of structure is observed in the 207.6-nm peak at either pressure. Since matched sample cells were not avail-able it is necessary to subtract the background spectrum C of sample cell with vacuum from the results A and B. To obtain greater precision in the measurement of the extinction coefficient of $BCl_3$ in the ultraviolet, a slidewire was used which expanded the optical density scale tenfold. An optical density of 0.046 was recorded with this
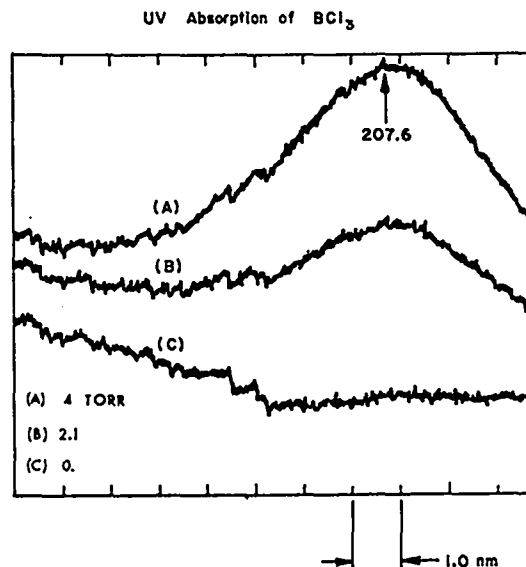


UV Absorption of $BCl_3$

207.6

(A)

(B)

(C)

(A) 4 TORR

(B) 2.1

(C) 0.

1.0 nm

Fig. 2. uv absorption of $BCl_3$ near 207.6 nm parametric in pressure.

slidewire with 4 torr of $BCl_3$ in a 10-cm cell. Defining the extinction coefficient of $BCl_3$ by the expression: $I/I_0 = exp \ (-\varepsilon px)$, where $\varepsilon$ is the extinction coefficient of $BCl_3$, p is the pressure in torr, and x is the path length in cm, a value of 0.003 $cm^{-1} \ torr^{-1}$ is computed for $\varepsilon$ at room temperature.

Using the measured width of the 207.6-nm absorption and a Morse potential ground state with constants appropriate to the $\nu_3$ mode one can construct the potential curves shown in Fig. 3 using the theory of Winans and Stueckelberg.[5] The calculated slope of the upper state of the 207.6-nm transition is -1.6 ev/A.

Using the measured absorption curve shown in Fig. 2 and assuming that all the energy of the $\nu_3$ mode is available for dissociation one can construct the excited state absorption curve displayed in Fig. 4. This curve does not account for possible Frank-Condon shifts of the dissociation energy indicated in Fig. 3. From these data we conclude that uv radiation in the wavelength range $213.0 \le \lambda \le 215.0$ nm is desirable to obtain at least a 10:1 enhancement in absorption from the excited state over absorption in the wings of the ground state.
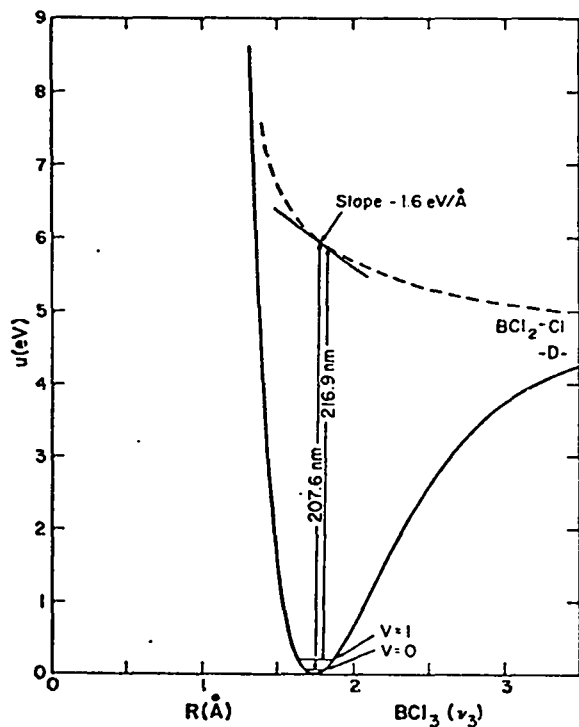
Fig. 3. Morse potential curve for the $\nu_3$ mode of $BCl_3$ plus estimated excited state from uv absorption. Indicated wavelengths are for transitions from the probability maxima regions of the ground and first excited states.

From the measured uv absorption coefficient and the known V-V relaxation time, Eq. (1), one can compute the required uv flux for efficient enrichment as

$$\phi \geq \left(\frac{RN}{\sigma}\right) \times 6 \text{ ev} = 1.9 \times 10^{7} \text{W/cm}^{2}/\text{torr } BCl_3 \qquad (2)$$

where $\sigma = 1.0 \times 10^{-19}$ cm$^2$ is the uv absorption cross section, $R = 5.7 \times 10^{-11}$ cm$^3$/s is the V-V transfer rate from Eq. (1) and N is the $BCl_3$ number density. Flux densities of this magnitude in the desired 2.0-nm bandwidth almost certainly require a uv laser. However, no lasers at the appropriate wavelength are currently available and development of these sources must receive attention in the immediate future.

IV. PHOTOCHEMISTRY

To assess the results of absorption of uv light by $BCl_3$ in the absence of other gases a sample cell containing 4.0 torr of pure $BCl_3$ was placed in front of a 1-kW deuterium discharge lamp for 1 h. No evidence of solid formation or alteration in the uv or ir absorption spectra of the gas was observed.
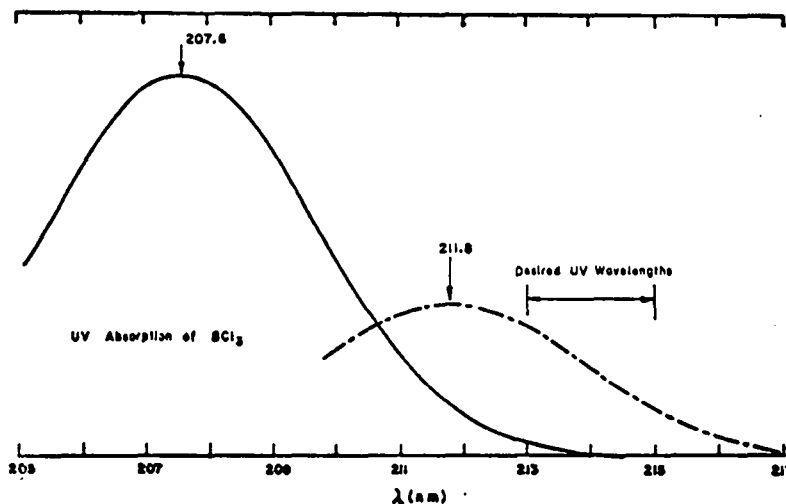


Fig. 4. Smooth curve fit to uv absorption from ground state at p=4 torr plus absorption from the first vibrational level of the $\nu_3$ mode assuming conservation of energy. The relative amplitudes assume 50% of the $^{11}BCl_3$ has been promoted to v=1 of the $\nu_3$ mode.

However there was evidence that a radical species had been formed because of a markedly improved transmission of the empty sample cell. The radical species was most likely Cl which rapidly recombined with $BCl_2$ to reinstate the $BCl_3$ population.

A second photolysis experiment was then performed to examine the scavenging action of an olefin for the radiation fragments of $BCl_3$. The system consisted of 23 torr of research grade (Phillips Petroleum, 99.7 mol% purity) ethylene and 40 torr of $BCl_3$ in a 10-cm quartz cell. There was no apparent reaction at room temperature in the absence of radiation. A mass spectrographic analysis of the product formed after 2 h of radiation with the continuum from a 1-kW deuterium lamp indicated that approximately 1% of the product was ethyl chloride. The kinetic aspects of the effective addition of HCl to $C_2H_4$ were not examined further. Unreacted $BCl_3$ and $C_2H_4$ were also present.

From the results of these experiments it was clear that absorption of uv light by $BCl_3$ could be used to initiate photochemical reactions and it appeared feasible to separate boron isotopes by the process described in the introduction if the appropriate scavenger could be selected. The scavenger must be nonreactive with $BCl_3$ at moderate pressures, exhibit no uv or ir absorption at the wavelengths of interest, and produce a simple chemistry with little or no scrambling of isotopic information.

A summary of the scavengers which have been studied to date is given in Table I.

All of the present experimental attempts to achieve isotopic enrichment have used $O_2$ as a scavenger and will be described in the following sections. This does not imply that $O_2$ is the best scavenger but of the present list it was the most convenient experimentally.

## V. EXPERIMENTAL APPARATUS

It was noted in Section II that the uv requirements demand light of laser intensities at frequencies at which lasers are not currently available. As an alternative we have used $BCl_3$ to filter a Xe flash lamp in the configuration displayed in Fig. 5.

The reaction chamber shown in Fig. 5a is constructed of quartz with KCl windows mounted at 45° on either end. The $CO_2$ laser pulse is provided by a 1-m helical pin laser and is propagated axially through the 3-mm capillary tube. The $CO_2$ laser provides 150 mJ on the P(20) line with a temporal FWHM of 1.5 µs as measured with a Au-Ge detector into a 50-Ω load. The 3-mm capillary is centered at the intensity maximum of the unfocused $CO_2$ laser beam and a nominal energy of 11 mJ is transmitted through the evacuated capillary tube. Burn patterns indicate that this energy is uniformly distributed across the 3-mm diameter of the capillary tube. The peak $CO_2$ power as determined from oscilloscope tracings and the known geometry was about $10^5$ W/cm$^2$.

TABLE I

PHOTOCHEMISTRY OF $BCl_3$, SCAVENGER MIXTURES

| Scavenger | Light Source | Product | Comments |
|---|---|---|---|
| $C_2H_4$ | CW $D_2$ lamp, and 206.1-nm line of CW $I_2$ lamp | $C_2H_5Cl$ | Ethylene absorbs 10.6 µ light |
| $C_2H_2$ | — | White volatile solid. Condensation of product in liquid $N_2$ gave rise to a transient pink colored solid. | Reacts spontaneously with $BCl_3$ at 40 torr pressure |
| cis-butene-2 | uv lamps also $CO_2$ laser only | Dark brown, sticky liquid | Note that $CO_2$ laser alone produces a reaction |
| $O_2$ | $D_2$, $I_2$ CW, and Xe flash lamp | $(BOCl)_3$ plus white solid | Product is only tentatively identified based upon work of Refs. 6,7. See present ir spectrum in Fig. 7. $CO_2$ laser alone would not induce a reaction. |
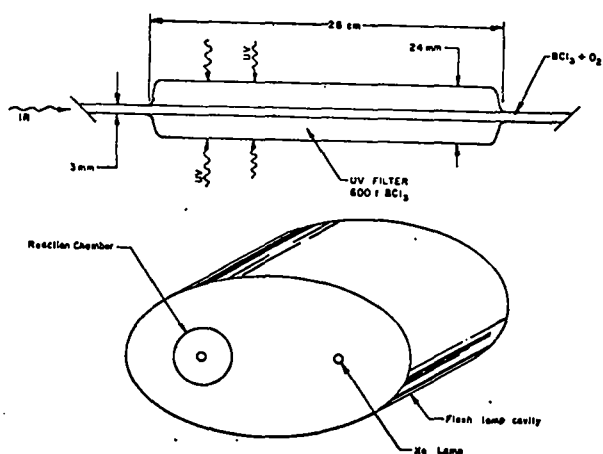
Fig. 5. Experimental configuration of the photoly-
sis chamber.

The reaction chamber is surrounded by a coaxial
jacket of quartz containing pure $BCl_3$ at pressures
of 600-700 torr. This acts as a filter for radia-
tion providing a contrast ratio of about 10:1 be-
tween 215.0 nm and 207.6 nm light as shown in Fig.
6a.

Since pure $BCl_3$ did not suffer photodecomposition
as noted in Section III the filter showed very little
aging on a span of 20 to 30 shots. The entire re-
action chamber is placed at one focus of a Raytheon
model LH5 ruby laser flash lamp cavity. A Xe, FX-5,
flash lamp is placed at the other focus and dis-
charges 840 J of electrical energy in 250 μs
with the pulse shape shown by the lower trace of
Fig. 6b. The $CO_2$ laser was triggered at the peak
of the uv pulse as shown in Fig. 6b.

The output spectrum of the Xe lamp was not
measured; thus it is difficult to state accurately
the energy contained in the desired uv bandwidth.
However it was noted that this lamp was very effi-
cient in initiating the photochemical reaction be-
tween $BCl_3$ and $O_2$. Six torr of $BCl_3$ in an excess of
$O_2$ could be completely reacted using 15 shots of the
uv lamp alone when no filter gas was employed. From
the known $BCl_3$ pressure and volume one can then infer
a uv output of $\sim$ .1 J/shot in the bandwidth of the
207.6-nm absorption feature. This assumes no chain
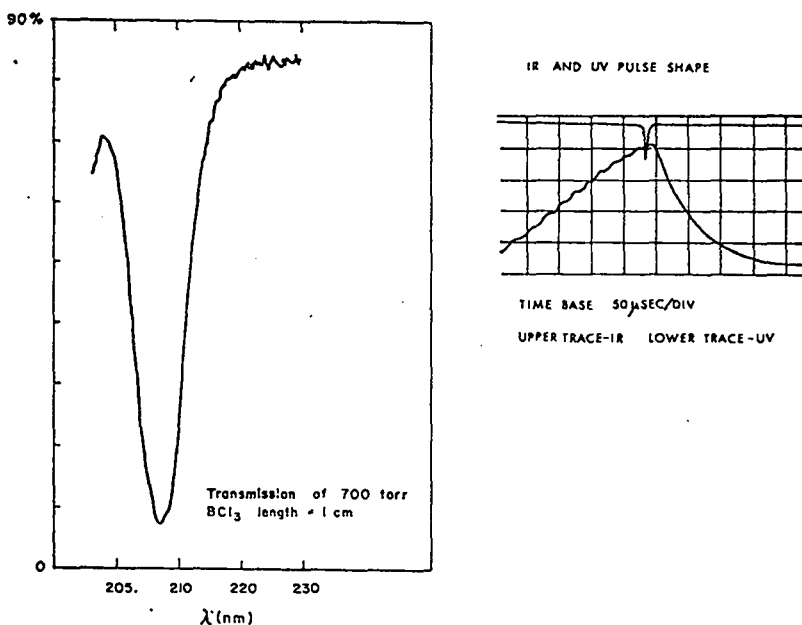reactions were occurring which is consistent with



Fig. 6. (a) Spectral response of uv filter. The cutoff
below 205 nm is due to the quartz glass.

(b) Oscilloscope tracing showing timing of uv and
ir radiation pulses. Sweep speed is 50 μs/div,

the fact that the irradiation could be stopped after a smaller number of uv shots and the remaining (BCl$_3$, O$_2$) mixture would show no further reaction for time scales on the order of at least 24 h.

## VI. RESULTS AND FUTURE WORK

The first experiments with the flash lamp system were designed to verify the (BCl$_3$,O$_2$) photochemistry described in Ref.6. Figure 7 displays the ir spectrum of the residual gas resulting from the irradiation of 3 torr BCl$_3$ and 6 torr O$_2$ by three shots of the unfiltered Xe lamp. Three distinguishable species are present in this sample: the BCl$_3$, a solid product which is deposited on the windows, and a gaseous product showing peaks attributed in Ref. 6 to (BOCl)$_3$. In addition to the peaks observed in Ref. 6 we observe 4 additional absorption peaks lying between 800 cm$^{-1}$ and 950 cm$^{-1}$ which are attributed to the same species giving rise to the strong 1370 cm$^{-1}$ absorption feature.
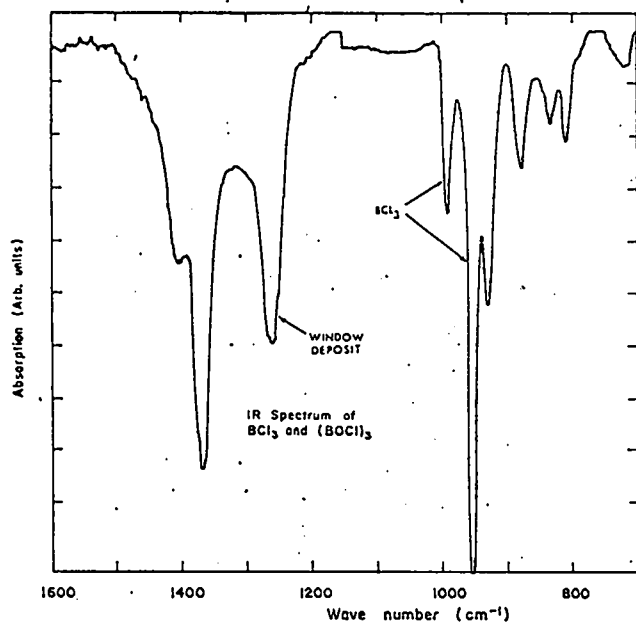


Fig. 7. ir absorption spectrum of residual gas following irradiation of 3 torr of BCl$_3$ and 6 torr of O$_2$ by three flashes from the unfiltered Xe lamp. Absorption features, except as noted, are assigned to (BOCl)$_3$.

TABLE II

IR Absorption Spectrum of (BOCl)$_3$

| Absorption peak (present work) | Ref. 6 |
|---|---|
|  | 620 |
| 790 cm$^{-1}$ |  |
| 810 |  |
| 835 (shoulder at 845) |  |
| 880 (structure) |  |
| 930 |  |
| 1210 | 1210 |
| 1370 | 1385 |
| 1405 | 1430 |
| 1450-1600 (much structure) | 1470 |

The peaks identified with the gas phase product in the present work are compared with those of Ref. 6 in Table II. Some of the new absorption features can be assigned to modes of (BOCl)$_3$ (g) using the spectrum of (BOCl)$_3$ (s) given in Ref. 7 however, we have not yet attempted a detailed classification of the product and its spectrum.

Attempts were made to determine the identity of the product by analysis in a Bendix MA3-A time-of-flight mass spectrometer. Mass peaks which were not observed in scans of pure BCl$_3$ could be attributed to BO$^+$, BO$_2$Cl$^+$, BOCl$_2$$^+$, and BO$_2$Cl$_2$$^+$. However, from these results we could not identify a parent molecule. For the remainder of this report we will identify the gaseous product as (BOCl)$_3$ on the basis of its ir spectrum however this identification is tentative and subject to further investigation.

In Ref. 6 it was stated that the gaseous (BOCl)$_3$ was unstable with respect to decomposition into the solid phase product. We found this to be the case only in sample cells which had recently been exposed to room air. The ir sample cells used in this investigation were made of brass and used KCl windows. Once the solid phase product was present, as demonstrated by its ir absorption feature, the (BOCl)$_3$ could be contained for periods of several days at room temperature without evidence of further decomposition. These facts suggest that the "instability" of (BOCl)$_3$ is principally a manifestation of a very rapid reaction rate with H$_2$O adsorbed onto

the surface of the sample cells and that the solid product, which appears to passivate the surface, may be the result of reactions between $(BOCl)_3$ and $H_2O$.

No reaction between $BCl_3$ and $O_2$ could be induced by the $CO_2$ laser alone at the power densities employed in this investigation. Also, in contrast to the work of Karlov[2] where much higher power $CO_2$ laser pulses were used, we observed no visible fluorescence from the irradiated $BCl_3$. No attempts were made to monitor the ir fluorescence of the $BCl_3$ gas.

We had initially intended to measure isotopic enrichment by changes in the ratio of the area of the ir absorption of $^{10}BCl_3$ ($\nu_3$) to $^{11}BCl_3$ ($\nu_3$). However, the discovery of the $(BOCl)_3$ feature at 930 cm$^{-1}$ complicated this measurement by adding an underlying background to the $^{11}BCl_3$ ($\nu_3$) mode at 947 cm$^{-1}$. For this reason all isotopic analyses of the irradiated gases were performed with the Bendix time-of-flight mass spectrometer.

TABLE III.
MASS SPECTROMETER ANALYSIS
OF $BCl_3$

| Mass | Species | Relative Intensity | Experimental Isotopic Ratio | Theoretical Isotopic Ratio Based on Natural Abundance[#] |
|---|---|---|---|---|
| 10.0 | $^{10}B^+$ | .019 | .252 ± .002 | .247 |
| 11.0 | $^{11}B^+$ | .077 | 1.000 | 1.000 |
| 17.5 | $^{35}Cl^{++}$ | .002 | — | 1.000 |
| 18.0 | $B^{35}Cl^{++}$ | — | — | 1.000 |
| 18.5 | $^{37}Cl^{++}$ | $7\times10^{-4}$ | — | .320 |
| 19.0 | $B^{37}Cl^{++}$ | — | — | .320 |
| 29.0 | $^{10}BF^+$ | .012(#) | .336 ± .003 | .247 |
| 30.0 | $^{11}BF^+$ | .036 | 1.000 | 1.000 |
| 35.0 | $^{35}Cl^+$ | .223 | 1.000 | 1.000 |
| 36.0 | $BCl^+$ | .183 | 1.000 | 1.000 |
| 37.0 | $^{37}Cl^+$ | .067 | .336 ± .010 | .320 |
| 38.0 | $BCl^+$ | .052 | .299 ± .012 | .320 |
| 40.0 | $^{10}B^{35}Cl^{35}Cl^{++}$ | .010 | — | .247 |
| 40.5 | $^{11}B^{35}Cl^{35}Cl^{++}$ | .034 | — | 1.000 |
| 41.0 | $^{10}B^{35}Cl^{37}Cl^{++}$ | .003 | — | 159 |
| 41.5 | $^{11}B^{35}Cl^{37}Cl^{++}$ | .020 | — | .639 |
| 45.0 | $^{10}B^{35}Cl^+$ | .030 | .227 ± .010 | .247 |
| 46.0 | $^{11}B^{35}Cl^+$ | .128 | 1.000 | 1.000 |
| 47.0 | $^{10}B^{37}Cl^+$ | .010 | — | 079 |
| 48.0 | $^{11}B^{37}Cl^+$ $^{10}BF_2^+$ | .054(†) | (†) | .320 |
| 49.0 | $^{11}BF_2^+$ | .075 | — | 1.000 |
| 64.0 | $^{10}B^{35}ClF^+$ | .035 | .242 ± .003 | .247 |
| 65.0 | $^{11}B^{35}ClF^+$ | .155 | 1.000 | 1.000 |
| 66.0 | $^{10}B^{35}ClF^+$ | .010 | .082 + .005 | .079 |
| 67.0 | $^{11}B^{37}ClF^+$ | .045 | .297 ± .003 | .320 |

[#] Indicated numbers for F containing species are typical but actual values varied with history of the mass spectrometer.

Table III cont.

| Mass | Species | Relative Intensity | Experimental Isotopic Ratio | Theoretical Isotopic Ratio |
|---|---|---|---|---|
| 70.0 | $^{35}Cl_2^+$ | .015 | 1.000 | 1.000 |
| 72.0 | $^{35}Cl^{37}Cl^+$ | .007 | .40 ± .10 | .320 |
| 80.0 | $^{10}B^{35}Cl_2^+$ | .253 | .253 ± .002 | .247 |
| 81.0 | $^{11}B^{35}Cl_2^+$ | 1.00 | 1.000 | 1.000 |
| 82.0 | $^{10}B^{35}Cl^{37}Cl^+$ | .159 | .159 ±.003 | .159 |
| 83.0 | $^{11}B^{35}Cl^{37}Cl^+$ $^{10}B^{35}ClF_2^+$ | .624 | .624 ± .004 | ..639 / .247 |
| 84.0 | $^{10}B^{37}Cl_2^+$ $^{11}B^{35}ClF_2^+$ | .056 | .056 ± .007† / — | .026 / 1.000 |
| 85.0 | $^{11}B^{37}Cl_2^+$ $^{10}B^{37}ClF_2^+$ | .100 | .100 ± .005† / — | .102 / .079 |
| 8.60 | $^{11}B^{37}ClF_2^+$ | .005(#) | — | .320 |
| 99.0 | $^{10}B^{35}Cl_2F^+$ | .014 | .267 ±.010 | .247 |
| 100.0 | $^{11}B^{35}Cl_2F^+$ | .057 | 1.000 | 1.000 |
| 101.0 | $^{10}B^{35}Cl^{37}ClF^+$ | .008 | .153 ±.010 | .157 |
| 102.0 | $^{11}B^{35}Cl^{37}ClF^+$ | .033 | .620 ±.007 | .639 |
| 104.0 | $^{11}B^{37}Cl_2F^+$ | .003 | — | .102 |
| 115.0 | $^{10}B^{35}Cl_3^+$ | .050 | .244 ± .008 | .247 |
| 116.0 | $^{11}B^{35}Cl_3^+$ | .198 | 1.000 | 1.000 |
| 117.0 | $^{10}B^{35}Cl_2^{37}Cl^+$ | .045 | .227 ± .007 | .238 |
| 118.0 | $^{11}B^{35}Cl_2^{37}Cl^+$ | .188 | .952 ± .004 | .957 |
| 119.0 | $^{10}B^{37}Cl_2^{35}Cl^+$ | .013 | .064 ± .015 | .074 |
| 120.0 | $^{11}B^{37}Cl_2^{35}Cl^+$ | .055 | .266 +.010 | .306 |
| 121.0 | $^{10}B^{37}Cl_3^+$ | $5\times10^{-4}$ | — | .008 |
| 122.0 | $^{11}B^{37}Cl_3^+$ | .003 | — | .032 |

Table III presents the results of mass spectral analyses of 10 separate samples of pure $BCl_3$ as supplied by Matheson Co. A CRS-160 Infotronics digital read out and a MDS P-20 printer was used for data acquisition. The results of these analyses were used to establish the cracking pattern of $BCl_3$ in our mass spectrometer and also to establish a baseline for the ratio of $^{10}B/^{11}B$ in the gas received from Matheson. The dominant ion in the fragmentation of $BCl_3$ is $BCl_2^+$. For the two $^{35}Cl$ isotopes the boron peaks occur at masses 80 and 81. We found the ratio of mass 80 to 81 in our sample of $BCl_3$ to be .253 ± .002 and free from interference with mass peaks of the product. The ratio of mass 80 to 81 was thus used for all subsequent analysis of the boron 10 to 11 ratio in $BCl_3$.

* Varied depending on history of the mass spectrometer. Hydrogen compounds appear to come from a reaction between $BCl_3$ and $H_2O$ adsorbed in the mass spectrometer vacuum lines.

† Varied depending on history of the mass spectrometer. The primary source of F was the mass spectrometer which had been used previously to examine fluorine compounds.
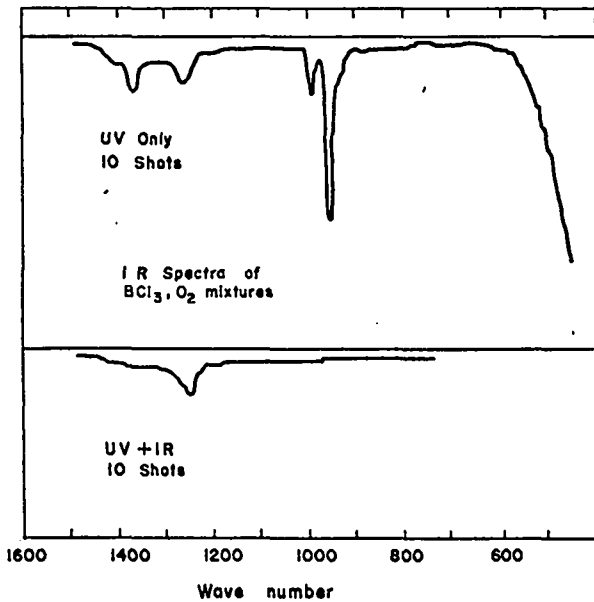
4 Torr BCl₃    16 Torr O₂



UV Only
10 Shots

I R Spectra of
BCl₃, O₂ mixtures

UV + IR
10 Shots

1600    1400    1200    1000    800    600

Wave number

Fig. 8.    (a) ir spectrum of residual gas following
irradiation of 4 torr $BCl_3$ plus 16 torr $O_2$
by 10 shots of filtered uv radiation.

(b) ir spectrum of residual gas following
irradiation of $(BCl_3, O_2)$ mixture as in (a)
by 10 shots of filtered uv plus ir laser
radiation.

Figure 8 compares the ir spectrum of the re-
sidual gas following irradiation of 6 torr of $BCl_3$
in 12 torr of $O_2$ by 10 shots using in (a), filtered
uv light only and, (b) filtered uv light plus ir
radiation. The filter consisted of 600 torr of
pure $BCl_3$ in the coaxial jacket as described above.
Notice that there appears to have been some leakage
of light through the filter because some $(BOCl)_3$
product is formed. However, the greater effective-
ness of the filtered uv-ir combination in inducing
the photochemical reaction is clearly demonstrated
by the destruction of all the $BCl_3$ in case b. This
result is a necessary condition for isotope separa-
tion since only the ir photons are isotopically
selective.

For the results shown in Fig. 8b both iso-
topic species were reacted because the ir laser
pulse was triggered 200 μs before the peak of the
uv pulse. Since the $BCl_3$ pressure was 6 torr the
timing delay allowed complete V–V equilibration of

the ir energy between both isotopes during the dura-
tion of the uv pulse and no isotopic selective could
be expected.

At this point conditions were defined for a
series of experiments to attempt to show isotopic
enrichment. All of the experiments used 5 shots of
the filtered uv plus ir laser combination with the
timing shown in Fig. 6.    The filter was 600 torr
of $BCl_3$ in all cases. The oxygen pressure was main-
tained at 20 torr and the $BCl_3$ pressure varied. The
ratio of mass 80 to 81 was used as the principal
diagnostic for the $^{10}B$ to $^{11}B$ ratio.

Figure 9 displays the results of this anal-
ysis as a function of the original $BCl_3$ pressure in
the reaction chamber. The error bars on the data
points are pessimistic in that they display the full
range of values for the ratio of 80:81 obtained in
from 3 to 10 scans of the sample by the mass spectro-
meter. The enrichment of the residual gas in $^{10}B$
increases to a value of 14% at an initial $BCl_3$ pres-
sure of 0.8 torr which is consistent with a uv flux
limited process as indicated by the dashed lines.
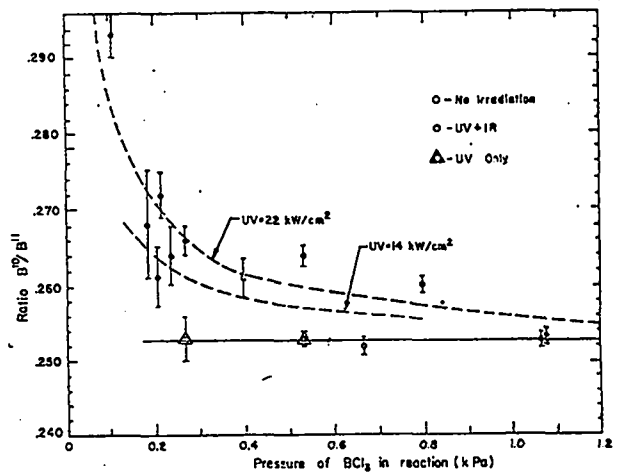This model will be discussed below.



.290

.280

.270

.260

.250

.240

    0    0.2    0.4    0.6    0.8    1.0    1.2

Ratio B¹⁰/B¹¹

Pressure of BCl₃ in reaction (kPa)

O – No Irradiation
O – UV+IR
Δ – UV Only

UV·22 kW/cm²

UV·14 kW/cm²

Fig. 9.    Ratio of $^{10}B/^{11}B$ as determined by mass
spectrum analyses of residual gas following
irradiation by 5 flashes of filtered uv
plus ir laser radiation as a function of
initial $BCl_3$ pressure. Error bars display
the full range of observed data. Dashed
lines indicate expected results based upon
rapid V–V transfer between $^{11}BCl_3$ ($\nu_3$) and
$^{10}BCl_3$ ($\nu_3$). Note 1 kPa = 7.502 torr.

The data indicated by the open circles and triangles represent null experiments where all steps were repeated just as before with the exception of triggering the $CO_2$ laser. These null experiments give a $^{10}B/^{11}B$ ratio in good agreement with the value of 0.253 obtained previously in analysis of pure $BCl_3$. Also from the null experiments no pressure dependence is observed in the measured $^{10}B/^{11}B$ ratio which tends to rule out the possibility of a systematic error in the mass spectrometer yielding an apparent enrichment with decreasing $BCl_3$ partial pressure.

For weak irradiation the time rate of change of the concentrations of $^{10}BCl_3$ $(\nu_3) \equiv X_{10}$, $^{11}BCl_3$ $(\nu_3)$ $\equiv X_{11}$ and the products may be described by the following equations:

$$\frac{d}{dt} X_{11} = \sigma_{ir} \phi_{ir} N - (RN + \sigma_{uv}\phi_{uv}) X_{11} \quad (3)$$

$$\frac{d X}{dt} 10 = RNX_{11} - \sigma_{uv} \phi_{uv} X_{10} \quad (4)$$

$$\frac{d P}{dt} 11 = \sigma_{uv} \phi_{uv} X_{11} \quad (5)$$

$$\frac{d P}{dt} 10 = \sigma_{uv} \phi_{uv} X_{10} \quad (6)$$

where N is the $BCl_3$ concentration and is assumed to be constant, $P_{10}$ and $P_{11}$ are the photodissociation fragments of $^{10}BCl_3$ and $^{11}BCl_3$, respectively, R is the V-V transfer rate used in Eq. (2), $\sigma_{ir}$ and $\sigma_{uv}$ are the ir and uv absorption cross sections and $\phi_{ir}$ and $\phi_{uv}$ are the ir and uv photon fluxes. With the assumptions that N, $\phi_{ir}$, and $\phi_{uv}$ are independent of time Eqs. (3-6) are readily integrated. From the resulting solutions and consistent with assumptions of Eqs. (3-6) that the product produced is small compared with the initial $BCl_3$ concentration one obtains for the ratio of $^{10}BCl_3/^{11}BCl_3$ in the residual gas:

$$\left(\frac{^{10}BCl_3}{^{11}BCl_3}\right)_{t_p} = \left(\frac{^{10}BCl_3}{^{11}BCl_3}\right)_{t=o} \times \left[1 + \left(\frac{\sigma_{uv} \phi_{uv}}{RN}\right)\left(\sigma_{ir} \phi_{ir}\right) t_p\right] \quad (7)$$

where $t_p \gg (RN + \sigma_{uv} \phi_{uv})^{-1}$ is the duration of the radiation pulse. Evaluating Eq. (7) with parameters $\sigma_{uv} = 1 \times 10^{-19}$ cm$^2$, R = 5.7 $\times 10^{-11}$ cm$^3$/s, N(cm$^{-3}$) = 3.52 $\times 10^{16}$ $P_{BCl_3}$ (torr), and $\sigma_{ir} \phi_{ir} t_p = 20$ gives the results parametric in $\phi_{uv}$ indicated by the dashed lines in Fig. 9.

These simple analytic results appear to be in good agreement with the experimental data when values for the uv flux appropriate to experimental conditions are assumed. One thus infers that the present experiment was severely deficient in uv power and considerable scrambling of ir excitation was induced by V-V transfer. The most immediate modification of the experimental apparatus will be the construction of a faster flash lamp to provide a higher peak power. Preliminary results also indicate that a $D_2$ filled lamp will provide more radiation in the desired bandwidth. On a longer time scale we will attempt to obtain laser radiation at the required wavelength using harmonic generation in ADP crystals as described by Massey. [8]

Other experiments currently in progress involve attempts to obtain isotopic enrichment by $CO_2$ laser induced chemistry between $BCl_3$ and numerous olefins. Should these experiments prove successful it would be possible to eliminate the need to develop a hard uv source. However, one step laser induced chemistry is severely limited in its approach to isotope separation since it requires the reaction time to be short compared to the V-V exchange time while at the same time keeping the V-T deactivation of the selected state by the reagent long compared to the chemical reaction time. It may prove very difficult to find a reagent which will meet all these requirements.

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