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**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

by

Stephen D. Rockwood and Sherman W. Rabideau

ABSTRACT

A 14% enrichment in the ratio of B^{10}/B^{11} has been achieved by selective excitation of $^{11}BCl_3$ (ν_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 comparison to other recent work in the field¹ 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 ν_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 ν_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 ν_3 mode using CO_2 laser powers readily obtainable with today's technology.

The relaxation of the ν_3 mode by vibration-vibration (V-V) transfer is known to be rapid and the equilibration of excitation energy between $^{11}\text{BCl}_3$ (ν_3) and $^{10}\text{BCl}_3$ (ν_3) proceeds with a rate of ⁴

$$\frac{1}{\text{pr}} = 2 \times 10^6 \text{ sec}^{-1} \text{ torr}^{-1} \quad (1)$$

To avoid scrambling of the selected isotopic state the vibrationally excited $^{11}\text{BCl}_3$ 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 available 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

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: $I/I_0 = \exp(-\epsilon p x)$, where ϵ is the extinction coefficient of BCl_3 , p is the pressure in torr, and x is the path length in cm, a value of $0.003\text{ cm}^{-1}\text{ torr}^{-1}$ is computed for ϵ at room temperature.

Using the measured width of the 207.6-nm absorption and a Morse potential ground state with constants appropriate to the ν_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/Å.

Using the measured absorption curve shown in Fig. 2 and assuming that all the energy of the ν_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 $213.0 \leq \lambda \leq 215.0\text{ nm}$ 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 ν_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

$$\phi \geq \left(\frac{RN}{\sigma} \right) \times 6 \text{ eV} = 1.9 \times 10^7 \text{ W/cm}^2/\text{torr BCl}_3 \quad (2)$$

where $\sigma = 1.0 \times 10^{-19} \text{ cm}^2$ is the uv absorption cross section, $R = 5.7 \times 10^{-11} \text{ cm}^3/\text{s}$ 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 ν_3 mode assuming conservation of energy. The relative amplitudes assume 50% of the $^{11}\text{BCl}_3$ has been promoted to $v=1$ of the ν_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	$\text{C}_2\text{H}_5\text{Cl}$	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	$(\text{BOCl})_3$ 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 photolysis 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 radiation providing a contrast ratio of about 10:1 between 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 reaction chamber is placed at one focus of a Raytheon model LHS ruby laser flash lamp cavity. A Xe, FX-5, flash lamp is placed at the other focus and discharges 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 efficient in initiating the photochemical reaction between 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 $\mu\text{s}/\text{div}$.

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 $(\text{BOCl})_3$. 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 $(\text{BOCl})_3$.

TABLE II

IR Absorption Spectrum of $(\text{BOCl})_3$

Absorption peak (present work)	Ref. 6
790 cm^{-1}	620
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 $(\text{BOCl})_3$ (g) using the spectrum of $(\text{BOCl})_3$ (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_2Cl^+ , BOCl_2^+ , and BO_2Cl_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 $(\text{BOCl})_3$ 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 $(\text{BOCl})_3$ 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 $(\text{BOCl})_3$ could be contained for periods of several days at room temperature without evidence of further decomposition. These facts suggest that the "instability" of $(\text{BOCl})_3$ is principally a manifestation of a very rapid reaction rate with H_2O 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 $(\text{BOCl})_3$ 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 Karlov² 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 $^{10}\text{BCl}_3$ (ν_3) to $^{11}\text{BCl}_3$ (ν_3). However, the discovery of the $(\text{BOCl})_3$ feature at 930 cm^{-1} complicated this measurement by adding an underlying background to the $^{11}\text{BCl}_3$ (ν_3) mode at 947 cm^{-1} . For this reason all isotopic analyses of the irradiated gases were performed with the Bendit 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	$^{10}\text{B}^+$	.019	.252 ± .002	.247
11.0	$^{11}\text{B}^+$	.077	1.000	1.000
17.5	$^{35}\text{Cl}^{++}$	.002	—	1.000
18.0	$^{10}\text{B}^{35}\text{Cl}^{++}$	—	—	1.000
18.5	$^{37}\text{Cl}^{++}$	9×10^{-4}	—	.320
19.0	$^{10}\text{B}^{37}\text{Cl}^{++}$	—	—	.320
29.0	$^{10}\text{BF}^+$	.012 (*)	.336 ± .003	.247
30.0	$^{11}\text{BF}^+$	.036	1.000	1.000
35.0	$^{35}\text{Cl}^+$	.223 *	1.000	1.000
36.0	BCl^+	.183	2.000	1.000
37.0	$^{37}\text{Cl}^+$	.067	.336 ± .010	.320
38.0	BCl^+	.052	.290 ± .012	.320
40.0	$^{10}\text{B}^{35}\text{Cl}^{35}\text{Cl}^{++}$	.010	—	.247
40.5	$^{11}\text{B}^{35}\text{Cl}^{35}\text{Cl}^{++}$	.034	—	1.000
41.0	$^{10}\text{B}^{35}\text{Cl}^{37}\text{Cl}^{++}$	.003	—	.159
41.5	$^{11}\text{B}^{35}\text{Cl}^{37}\text{Cl}^{++}$	.020	—	.610
45.0	$^{10}\text{B}^{35}\text{Cl}^+$	.030	.227 ± .010	.247
46.0	$^{11}\text{B}^{35}\text{Cl}^+$	.128	1.000	1.000
47.0	$^{10}\text{B}^{37}\text{Cl}^+$	.010	—	.079
48.0	$^{11}\text{B}^{37}\text{Cl}^+$	.054 (*)	(*)	.320
49.0	$^{10}\text{BF}_2^+$	—	—	—
49.0	$^{11}\text{BF}_2^+$	.075	—	1.000
54.0	$^{10}\text{B}^{35}\text{ClF}^+$	.035	.242 ± .003	.247
55.0	$^{11}\text{B}^{35}\text{ClF}^+$	.155	1.000	1.000
56.0	$^{10}\text{B}^{35}\text{ClF}_2^+$	.010	.082 ± .005	.079
57.0	$^{11}\text{B}^{37}\text{ClF}^+$	.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.

70.0	$^{35}\text{Cl}_2^+$	.015	1.000	1.000
72.0	$^{35}\text{Cl}^{37}\text{Cl}^+$	.007	.40 ± .10	.320
80.0	$^{10}\text{B}^{35}\text{Cl}_2^+$	.253	.253 ± .002	.247
81.0	$^{11}\text{B}^{35}\text{Cl}_2^+$	1.00	1.000	1.000
82.0	$^{10}\text{B}^{35}\text{Cl}^{37}\text{Cl}^+$	.159	.159 ± .003	.159
83.0	$^{11}\text{B}^{35}\text{Cl}^{37}\text{Cl}^+$	.624	.624 ± .004	.639
	$^{10}\text{B}^{35}\text{ClF}_2^+$	—	—	.247
64.0	$^{10}\text{B}^{37}\text{Cl}_2^+$	.056	.056 ± .007 [†]	.026
	$^{11}\text{B}^{35}\text{ClF}_2^+$	—	—	1.000
85.0	$^{11}\text{B}^{37}\text{Cl}_2^+$	.100	.100 ± .005 [†]	.102
	$^{10}\text{B}^{37}\text{ClF}_2^+$	—	—	.079
86.0	$^{11}\text{B}^{37}\text{ClF}_2^+$	.005 ^(*)	—	.320
99.0	$^{10}\text{B}^{35}\text{Cl}_2\text{F}^+$	.014	.267 ± .010	.247
100.0	$^{11}\text{B}^{35}\text{Cl}_2\text{F}^+$	.057	1.000	1.000
101.0	$^{10}\text{B}^{35}\text{Cl}^{37}\text{ClF}^+$	.008	.153 ± .010	.157
102.0	$^{11}\text{B}^{35}\text{Cl}^{37}\text{ClF}^+$	.033	.620 ± .007	.639
104.0	$^{11}\text{B}^{37}\text{Cl}_2\text{F}^+$	.003	—	.102
115.0	$^{10}\text{B}^{35}\text{Cl}_3^+$	.050	.244 ± .008	.247
116.0	$^{11}\text{B}^{35}\text{Cl}_3^+$	.398	1.000	1.000
117.0	$^{10}\text{B}^{35}\text{Cl}_2^{37}\text{Cl}^+$	.045	.227 ± .007	.238
118.0	$^{11}\text{B}^{35}\text{Cl}_2^{37}\text{Cl}^+$	.188	.952 ± .004	.957
119.0	$^{10}\text{B}^{37}\text{Cl}_2^{35}\text{Cl}^+$	.015	.054 ± .015	.074
120.0	$^{11}\text{B}^{37}\text{Cl}_2^{35}\text{Cl}^+$	.055	.266 ± .010	.306
121.0	$^{10}\text{B}^{37}\text{Cl}_3^+$	5×10^{-4}	—	.008
122.0	$^{11}\text{B}^{37}\text{Cl}_3^+$	.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 $^{10}\text{B}/^{11}\text{B}$ 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 $.253 \pm .002$ 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.

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 residual 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 $(\text{BOCl})_3$ product is formed. However, the greater effectiveness 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 separation since only the ir photons are isotopically selective.

For the results shown in Fig. 8b both isotopic 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 duration 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 maintained 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 analysis 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 spectrometer. The enrichment of the residual gas in ^{10}B increases to a value of 14% at an initial BCl_3 pressure 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.

Fig. 9. Ratio of $^{10}\text{B}/^{11}\text{B}$ 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 $^{11}\text{BCl}_3$ (ν_2) and $^{10}\text{BCl}_3$ (ν_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 $^{10}\text{B}/^{11}\text{B}$ 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 $^{10}\text{B}/^{11}\text{B}$ 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 $^{10}\text{BCl}_3$ (v_3) $\equiv X_{10}$, $^{11}\text{BCl}_3$ (v_3) $\equiv X_{11}$ and the products may be described by the following equations:

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

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

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

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

where N is the BCl_3 concentration and is assumed to be constant, P_{10} and P_{11} are the photodissociation fragments of $^{10}\text{BCl}_3$ and $^{11}\text{BCl}_3$, respectively, R is the V-V transfer rate used in Eq. (2), σ_{ir} and σ_{uv} are the ir and uv absorption cross sections and ϕ_{ir} and ϕ_{uv} are the ir and uv photon fluxes. With the assumptions that N , ϕ_{ir} , and ϕ_{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 $^{10}\text{BCl}_3/^{11}\text{BCl}_3$ in the residual gas:

$$\left(\frac{^{10}\text{BCl}_3}{^{11}\text{BCl}_3} \right)_{t_p} = \left(\frac{^{10}\text{BCl}_3}{^{11}\text{BCl}_3} \right)_{t=0} \times \left[1 + \left(\frac{\sigma_{uv} \phi_{uv}}{RN} \right) \left(\sigma_{ir} \phi_{ir} \right) t_p \right] \quad (7)$$

where $t_p \gg (RN + \sigma_{uv} \phi_{uv})^{-1}$ is the duration of the radiation pulse. Evaluating Eq. (7) with parameters $\sigma_{uv} = 1 \times 10^{-19} \text{ cm}^2$, $R = 5.7 \times 10^{-11} \text{ cm}^3/\text{s}$, $N(\text{cm}^{-3}) = 3.52 \times 10^{16} P_{\text{BCl}_3} (\text{torr})$, and $\sigma_{ir} \phi_{ir} t_p = 20$ gives the results parametric in ϕ_{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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