π bond. This assumption is consistent with a small ϵ value of **3** at 544 nm compared with those of **1** and **2** at 512 and 526 nm, respectively.

Registry No. $Mo_2O_3(Et_2NCS_2)_4$, 18539-11-2; $Mo_2O_3(Et_2NCSSe)_4$, 68539-98-0; $Mo_2O_3(Et_2NCSe_2)_4$, 68539-99-1.

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Resonance Raman Spectra of Tetrapyrrole Complexes of Oxomolybdenum(V)

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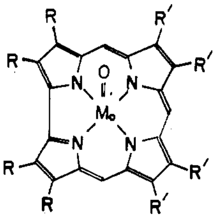
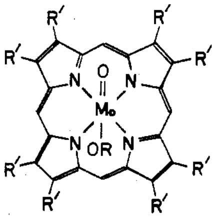
The resonance Raman spectra of MoO(MEC) and MoO(OEP)(OMe) have been measured in the solid state. Due to low symmetry of the tetrapyrrole core, the former exhibits about 2 times more bands than the latter in the 1650–400-cm^{-1} region. Excitation profile studies on MoO(MEC) show that some tetrapyrrole core vibrations give maxima at the α(0–0) band and that two bands at 950 cm^{-1} (Mo=O stretching) and 320 cm^{-1} are enhanced more than the core vibrations as the exciting frequency approaches the strong band at 455 nm. These results suggest that the 455-nm band is largely due to a ligand–metal charge-transfer transition and that the 320-cm^{-1} band is assignable to the Mo–N stretching vibration enhanced via such charge-transfer. The spectral change caused by laser irradiation of MoO(OEP)(OMe) in the solid state has been attributed to polymerization through the formation of the methoxy bridge between two metal atoms.

Recently, Murakami et al.[1] have prepared a novel molybdenum(V) complex with 2,3,17,18-tetramethyl-7,8,-12,13-tetraethylcorrole (abbreviated as MEC) and concluded from its ESR spectrum that the $MoON_4$ skeleton is close to a tetragonal pyramid. They also reported that MoO(OEP)(OMe) exists as a single monomeric species in dichloromethane or chloroform while more than one species is present in aromatic solvents.[2] The purpose of this paper is to report the resonance Raman spectra of MoO(MEC) and MoO(OEP)(OMe).



MoO(MEC)



MoO(OEP)OCH_3

(R=CH_3 , R'=C_2H_5)

Although resonance Raman spectra of many metalloporphyrins have been reported, most of these compounds contain porphin cores of D_{4h} symmetry which severely limits the number of core vibrations observed in Raman spectra. The MEC complex is unique in that all the core vibrations are nondegenerate and Raman active due to its low symmetry (C_s or C_1). Thus, it is interesting to compare the number of Raman-active core vibrations between MoO(MEC) and MoO(OEP)(OMe). Secondly, metalloporphyrins of W(V), Cr(III), Mn(III), Mo(V), Re(V), etc. belong to "d-type hyperporphyrins",[3] which exhibit strong bands near 450 nm in addition to the α, β, and Soret bands. In the case of manganese(III) etioporphyrin I complexes, these extra bands near 460 nm (band V) have been assigned to the charge-transfer (CT) transition from the ligand ($a_{1u}(\pi)$ or $a_{2u}(\pi)$ orbital) to the metal ($e_g(d\pi)$ orbital)[3,4] or the ligand π–π^* transition mixed with such a CT transition.[5] According to Gouterman,[3] the assignments of two bands at 500–440 nm (band V) and 350–340 nm (band VI) of the MoO(OEP)L type compounds depend upon the nature of L; when L is OCH_3, the stronger band (band V) at 443 nm is assigned to a Soret and a weaker band (band VI) at 342 nm is assigned to a CT transition. However, these assignments are reversed for L = Cl since band V at 500 nm is weaker than band VI at 350 nm. However, such an intensity criterion is by no means certain. Our excitation profile study may provide clues in elucidating the nature of these electronic bands.

Experimental Section

The compound MoO(MEC) was prepared by the method described previously.[1] The analogous MoO complex MoO(OEP)(OMe) was prepared by the literature method.[2] The resonance Raman spectra of these compounds were measured by using a Spex 1401 double monochromator. Detection was made with a cooled RCA C31034 photomultiplier tube and a Spex digital photometer. Excitation lines were provided by a Spectra-Physics Model 164 Ar-ion laser and a Spectra-Physics Model 375 CW dye laser (Rhodamine 6G) pumped by the Ar-ion laser. Calibration of frequency reading was made by using Ar-ion laser lines.

The resonance Raman spectra of MoO(MEC) (Figure 1) were measured in thin films cooled to 20 K using the apparatus described in our previous paper.[6] The excitation profile studies (Figure 4) were made in a K_2SO_4 pellet (2×10^{-3} molar ratio). The pellet was rotated during the measurement to avoid thermal decomposition. Using the 986-cm^{-1} band of K_2SO_4 as the internal standard, we estimated the relative intensity of the MoO(MEC) band from the band area or the peak height if the band is partially overlapped. The detector sensitivity and ν^4-law corrections were made on relative intensities thus obtained. The Raman spectrum of MoO(OEP)(OMe) was measured in a KBr pellet at room temperature. The electronic spectra of both compounds

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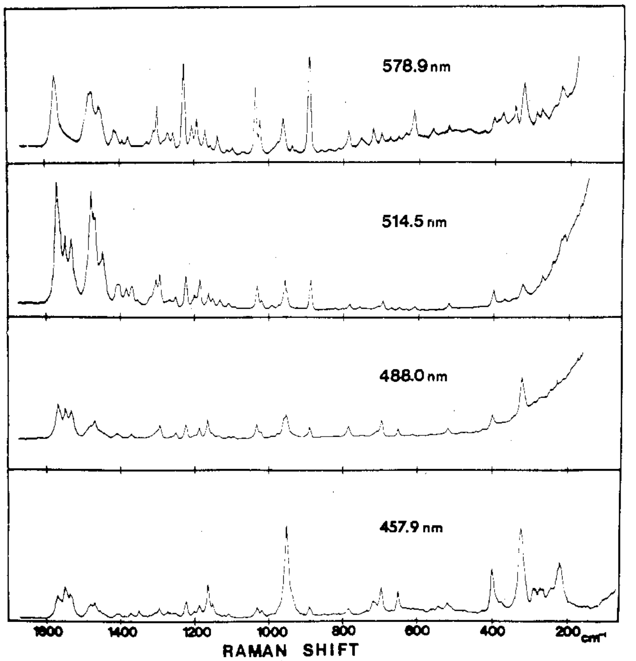


Figure 1. Resonance Raman spectra of MoO(MEC) in a thin film at 20 K.

Table I. Resonance Raman Spectra of MoO(MEC) and MoO(OEP)(OMe) (cm^{-1})

MoO(MEC)[a]	MoO(OEP)(OMe)[b]	approx description
1567, 1548, 1531	1625, 1569, 1547	$\nu(C\underset{..}{-}C)$[c]
1480, 1468, 1448, 1439, 1406	1471, 1404	$\nu(C\underset{..}{-}N)$[c]
1398, 1384, 1368, 1352	1376	$\nu(C\underset{..}{-}C)$[c]
1319, 1304, 1293, 1264, 1249, 1222	1317, 1260, 1210	$\nu(C\underset{..}{-}C) + \delta(CH)$[c]
1199, 1185, 1162, 1148, 1132, 1107, 1089, 1029, 1018, 991, 971, 955	1161, 1145, 1106, 1067, 1030, 974, 944	$\nu(C\underset{..}{-}C) + \nu(C\underset{..}{-}N) + \nu(C-C) + \nu(CH)$[d]
950	910	$\nu(Mo{=}O)$
886, 818	871, 811	$\delta(C-C) + \nu(C\underset{..}{-}C) + \delta(CCC) + (C\underset{..}{-}C)$[e]
782, 713, 693, 668, 647, 605, 516, 419, 368	766, 730, 675, 499, 443	$\delta(CCC) + \delta(CCN) + \delta(CNC) + \delta(C\underset{..}{-}C)$[e]
398, 320, 284, 268, 241, 224	333	$\nu(M-N) + \delta(CCC) + \delta(NMN) + \nu(C\underset{..}{-}C)$[e]

[a] Thin film at 20 K. [b] KBr pellet. The spectrum at the initial stage of laser irradiation. [c] Assignments given for octamethylporphyrin.[7,8] [d] Assignments given for zinc porphine.[9] [e] Assignments given for Ni(OEP).[10]

were measured at room temperature in the solid state using a Cary Model 14 spectrophotometer.

Results and Discussion

Figure 1 shows the resonance Raman spectra of MoO(MEC) obtained as a thin film at 20 K using four exciting lines. Table I compares these frequencies with those of MoO(OEP)(OMe) obtained in a KBr pellet. Assuming the ethyl group (R′) as a single atom, the total number of Raman-active modes under resonance condition is 43 for the porphine core ($C_{20}N_4H_4R'_8$) of D_{4h} symmetry ($9\ A_{1g} + 8\ A_{2g} + 9\ B_{1g} + 9\ B_{2g} + 8\ E_g$). For the MEC core ($C_{19}N_4H_3R_4R'_4$) of C_s or C_1 symmetry, this number becomes 96 since all the vibrations are nondegenerate and Raman active. It is clearly impossible to make rigorous comparisons of these predictions with the observed spectra unless complete band assignments are available for both compounds. Since this is not the case, we have made rough comparisons in the 1650–400-cm^{-1} region (Table I): MoO(OEP)(OMe) exhibits 24 whereas MoO(MEC) shows 41 bands. These large discrepancies between

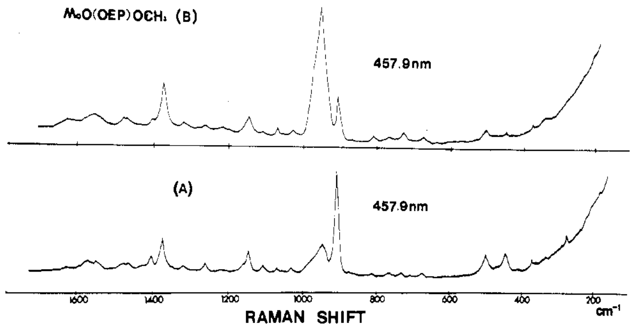
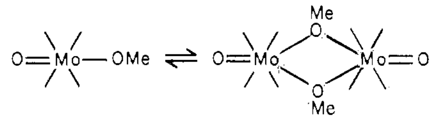


Figure 2. Resonance Raman spectra of MoO(OEP)(OMe) in a KBr pellet: (A) original spectrum, (B) spectrum obtained after 1 h of irradiation of 457.9-nm exciting line (~50 mW).

the calculated and observed numbers of Raman bands are due to several reasons. First, this region does not include the C–H stretching and low-frequency skeletal modes although it includes alkyl group and some metal–ligand vibrations. Second, out-of-plane vibrations may be too weak to be observed under the resonance condition. Finally and most importantly, there are many bands of similar frequencies which cannot be resolved. Such band overlappings are more serious in MoO(MEC) than in MoO(OEP)(OMe).

The last column of Table I gives approximate descriptions of vibrational modes based on the results of normal-coordinate analyses on similar systems.[7-10] It is rather difficult to give precise descriptions of these vibrations because of serious coupling among those represented by individual internal coordinates. Two bands of MoO(MEC) deserve special comments. It is well established[11] that the Mo=O stretching band appears strongly in the region from 980 to 910 cm^{-1} in the infrared spectrum. In fact, the infrared spectrum of MoO(MEC) exhibits a strong band at 948 cm^{-1}. In the resonance Raman spectra, both MoO(MEC) and MoO(OEP)(OMe) show relatively strong bands at 950 and 910 cm^{-1}, respectively, when excited by the 457.9-nm line. These bands can be assigned to the Mo=O stretching mode. As will be shown later, the bands at 950 and 320 cm^{-1} of MoO(MEC) are enhanced more than other bands as the exciting frequency approaches the strong electronic band at 455 nm. Since we associate the 455-nm band with a ligand–metal CT transition (vide infra), it is most reasonable to attribute the 320-cm^{-1} band to a mode containing the Mo–N stretching character. The corresponding infrared band is observed at 318 cm^{-1}.

Figure 2 shows the resonance Raman spectra of MoO(OEP)(OMe) in a KBr pellet obtained with the 457.9-nm excitation. The strong band at 910 cm^{-1} is assigned to the Mo=O stretching mode. After 1 h of laser irradiation (~50 mW), this band became weaker and a new band appeared strongly at 956 cm^{-1} (Figure 2). A similar change was also observed in CH_2Cl_2 solution: the strong band at 880 cm^{-1} became weaker and a new band grew at 942 cm^{-1} as the laser irradiation continued. Previously, Matsuda et al.[2] suggested from electronic and ESR studies that MoO(OEP)(OMe) is in a monomer–dimer equilibrium in benzene.



The fact that only the spectra in the Mo=O stretching region undergo marked changes by laser irradiation seems to suggest the occurrence of similar dimerization or polymerization in the solid state. The Mo=O stretching frequency of the monomer may be lower than that of the dimer because the trans influence of the methoxy group in the monomer may weaken the Mo=O bond. Thus, the strong bands at 910 cm^{-1} of Figure 2A and at 956 cm^{-1} of Figure 2B may be assigned

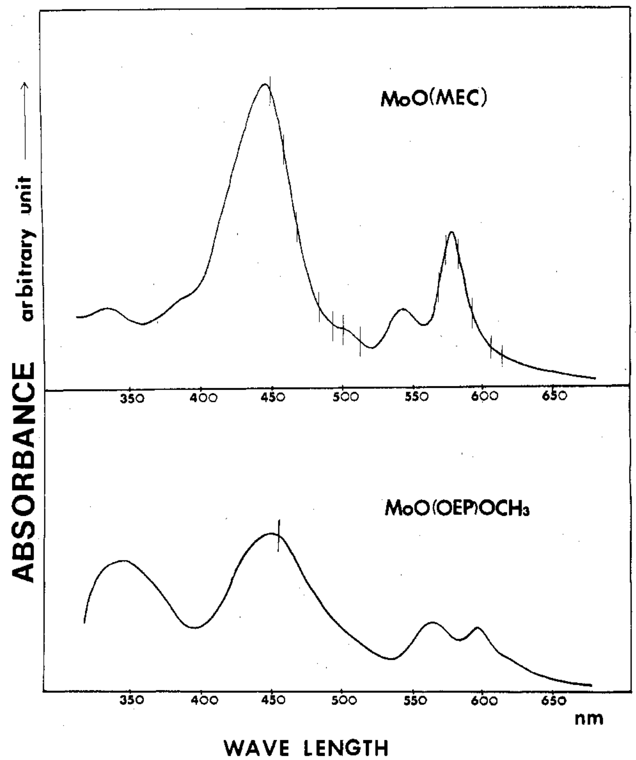


Figure 3. Electronic spectra of MoO(MEC) and MoO(OEP)(OMe) in the solid state. Vertical lines indicate the positions of the laser lines used.

to the Mo=O stretching vibrations of the monomer and dimer (or polymer), respectively. The broadness of the 956-cm^{-1} band in Figure 2B may indicate, however, that several species having different degrees of polymerization are mixed in the solid state. At present, it is not clear whether this irreversible reaction is thermal or photochemical, although the fact that other laser lines cause similar changes seems to preclude the latter.

Electronic Spectra and Excitation Profiles

Figure 3 shows the electronic spectra of MoO(OEP)(OMe) and MoO(MEC) in the solid state. The spectrum of the former is in good agreement with that obtained previously in CH_2Cl_2 solution.[2,12] According to Gouterman,[3] the bands at 595, 564, 450, and 343 nm of MoO(OEP)(OMe) are assigned to the α, β, Soret, and a CT band, respectively. On the other hand, the electronic spectrum of MoO(MEC) shows only one strong band (455 nm) below 500 nm. This absorption may be a CT or a Soret band or a band containing both characters or an overlap of these two bands.

Previously, Shelnutt et al.[5] assigned the electronic bands near 460 nm (band V) of manganese(III) etioporphyrin I complexes to a transition containing both CT and π–π^* characters and concluded that no selective enhancements of ligand–metal vibrations occur when the exciting frequency approaches band V. An opposite conclusion was drawn, however, by Asher and Sauer,[4] who attributed band V to a CT transition and assigned several low-frequency vibrational modes to ligand–metal vibrations.

In this paper, we have obtained the excitation profiles of MoO(MEC) to study the nature of its electronic band at 455 nm. As is seen in Figure 4, the tetrapyrrole core vibrations at 1567, 1548, 1468, 1293, 1222, 1162, 1029, and 886 cm^{-1} give maxima at the α band within experimental errors as previously observed for oxyhemoglobin.[13] When the exciting frequency approaches the strong band at 455 nm, the intensities of two bands at 950 and 320 cm^{-1} increase much more rapidly than those of the core vibrations. This result definitely rules out the possibility of assigning the 455-nm band to a pure π–π^* (Soret) transition. These results can only be accounted for if we assume some CT character for this electronic transition. A charge transfer from the highest occupied π orbital of the MEC core to the empty d_{xz} and d_{yz} orbitals of the Mo(V) atom causes the change in the Mo=O distance since these d orbitals are overlapped with the p_x and p_y orbitals of the oxygen atom. Thus, such a charge transfer may enhance the Mo=O as well as Mo—N stretching mode when the exciting frequency approaches the 455-nm band. Hence, it is reasonable to assign the 320-cm^{-1} band to a vibration largely due to the Mo–N stretching mode. Several other bands (398 and 224 cm^{-1}) show similar behavior although their enhancements are less dramatic. Presumably, all these low-frequency modes contain the Mo–N stretching character although the degree of coupling with other modes is different for each vibration. Previously, Asher and Sauer[4] assigned several bands at 375–260 cm^{-1} of manganese(III) etioporphyrin I halides to the modes containing the Mn–N stretching character. Our conclusion on MoO(MEC) is similar to that of these workers. Namely, an excitation profile study on a metal–ligand CT band provides a means of assigning metal–ligand vibrations of coordination compounds.

For MoO(OEP)(OMe), we could not carry out an excitation profile study since this compound undergoes spectral changes during the laser irradiation. It is possible, however, to minimize such changes if the spectra are measured with low laser power and short exposure time. Figure 2A shows the resonance Raman spectrum of MoO(OEP)(OMe) with the 457.9-nm line

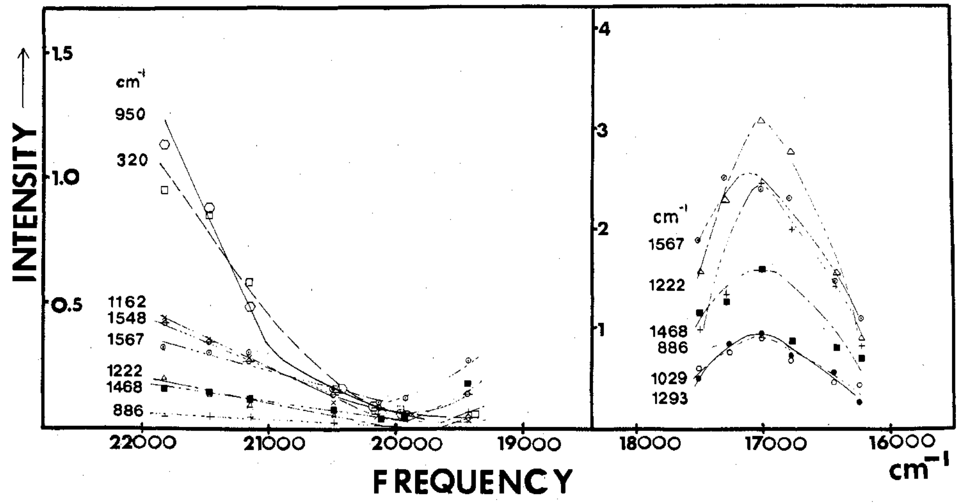


Figure 4. Excitation profiles of MoO(MEC) obtained in a K_2SO_4 matrix.

obtained under these conditions. As is seen in its electronic spectrum (Figure 3), the 457.9-nm line is almost at the center of the strong band V. Thus, this band is mainly responsible for the large enhancement of the Mo═O stretching mode at 910 cm^{-1} relative to other vibrations. As stated before, the peak position of band V in the MoO(OEP)L series is very sensitive to the nature of the axial ligand, L. These observations suggest that band V of MoO(OEP)(OMe) is mainly due to a CT transition.

In general, the total scattering intensity is proportional to the absorption intensity in a pure radiative process. Thus, we expect that the total scattering intensity of MoO(MEC) by the 457.9-nm excitation should be larger than that by the 587.0-nm excitation. Although we cannot estimate the Rayleigh scattering intensity, it is generally proportional to the total Raman intensity. We observed that the total Raman intensity by the 457.9-nm excitation is much less than that by the 587.0-nm excitation. This result may imply that the internal energy transfer from the CT excited state to the higher vibronic π^* states is occurring rapidly while the molecule is irradiated by the 457.9-nm line.[14]

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Registry No. MoO(MEC), 63621-40-9; MoO(OEP)(OMe), 39048-14-1.

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Low-Power CO_2 Laser Induced Chemistry of SF_6-Sensitized Diborane

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Inverse quantum yields for B_2H_6 conversion and H_2, B_5H_9 + B_5H_{11}, and $B_{10}H_{14}$ formation were measured as a function of B_2H_6 initial partial pressure for constant 5 Torr of SF_6 with the CO_2 CW laser operating on the P–16 (947.75 cm^{-1}) line at 6.1 W and at an intensity of 15.9 W/cm^2. Sensitization with SF_6 was found to increase laser-induced conversion and formation efficiencies by a factor of 2–3 relative to the neat B_2H_6 case. Percent yield by weight for $B_{10}H_{14}$ production was found to be as high as 23% of the B_2H_6 reacted. Power and intensity studies demonstrated measurable product yields at 3.5 W and 9 W/cm^2. Average initial inverse quantum yields were measured for B_2H_6 conversion and H_2, B_5H_9 + B_5H_{11}, and $B_{10}H_{14}$ formation and found to be 46, 49, 112 and 3100, respectively. B_2H_6 conversion and B_5H_9 + B_5H_{11} and $B_{10}H_{14}$ formation yields were measured as a function of wavelength for laser lines between P32 (933 cm^{-1}) to P12 (951.2 cm^{-1}) for 400 Torr of B_2H_6 and 5 Torr of SF_6 at a power of 6.1 W and 15.9 W/cm^2 intensity. "Red shifting" relative to the room-temperature absorption spectrum of the ν_3 band of SF_6 was noted. All "red shifting" was interpreted as resulting from laser heating of SF_6 and indicated temperatures of 500–550 K.

Introduction

Recently, considerable attention has been focused on the infrared laser induced chemistry of diborane.[2-4] This attention may be partially attributed to the interest in applying lasers to demonstrate vibrationally enhanced synthesis of boron hydride cages. Of general importance are the aspects of the work that elucidate the nature of low-power laser-induced processes in laser-enhanced synthetic chemistry at high reactant pressures. There is both supportive and nonsupportive evidence that under these experimental conditions vibrationally controlled processes, and not only thermolysis, may be encountered.[2,4-7]

Reasons for the present study are twofold. First, regardless of the nature of the processes, can we improve on the efficiency of product formation over that of the neat B_2H_6 laser experiments?[3] Second, the sensitized experiments should shed light upon the question of predominance of laser-induced vibrationally controlled processes vs. laser-induced thermolysis under low-intensity CW infrared laser illumination.

Experimental Section

Details regarding the laser cells, sample preparation, postirradiation analysis, the laser, and tuning have been outlined previously.[3] In all the CW experiments 5 Torr of SF_6 was used which was added to the measured diborane sample in the cell from a calibrated volume by condensation with liquid nitrogen in the side vial of the cell. The room-temperature infrared spectrum of SF_6 was obtained using a Digilab Model 20B Fourier transform spectrophotometer at 0.5 cm^{-1} resolution with 6-cm cells. Data reproducibility was dependent upon maintaining a homogeneous 7 mm diameter laser beam. This was aided by adjusting the laser to oscillate in the TEM 00 mode in all experiments. Beam diameter was controlled by a variable aperture and determined from the burn spot and the image on an Optical Engineering CO_2 laser thermal image plate, Model 22A, No. 4.

Results

B_5H_{11}, B_5H_9, $B_{10}B_{14}$, and $(BH)_n$ along with H_2 were found as products in all CW runs. Figures 1 and 2 show the inverse quantum yields (number of photons required per molecule) as a function of B_2H_6 partial pressure for H_2 and B_2H_6, B_5H_n (B_5H_9 + B_5H_{11}), and $B_{10}H_{14}$ using P-16 (947.75 cm^{-1}) illumination. Although smaller by a factor of 2–3, they follow the general trends as noted for the neat irradiations.[3] It should be pointed out that for a specific laser setting (power, frequency) energy is absorbed within the same volume at a given pressure of sensitizer, regardless of B_2H_6 partial pressures. Below approximately 200 Torr, for our cells, transmission occurred for the neat irradiations with the R-16 line and were corrected for proper ϕ^{-1}'s to be measured.[3] This was not necessary in the sensitized experiments since all energy is absorbed within a few tenths of a centimeter. Figure 3 depicts the percent yield by weight of $B_{10}H_{14}$ as a function of initial B_2H_6 partial pressure for the P-16 line. Taken throughout the entire pressure range, average yields for $B_{10}H_{14}$ were 2–3 times

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