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Time-Resolved Observation of Vibrationally Excited 1,3-Butadiene in Laser Induced Photolysis of Bromocyclobutane and Cyclohexene

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The pulsed CO_2 laser induced SF_6 sensitized photodissociation of bromocyclobutane (BCB) and cyclohexene (CHN) is investigated. BCB has two dissociation channels from its ground electronic state, HBr elimination yielding 1,3-butadiene is the major channel (>90%) whereas, the ring cleavage producing vinyl bromide and ethylene is the minor one. The time-resolved formation of 1,3-butadiene is monitored by UV absorption from which unimolecular rate constants for BCB and CHN dissociation are found to be 8×10^5 s^{-1} and 1×10^6 s^{-1}, respectively. A red-shift of 38 nm and 50 nm observed in the UV spectra of butadiene produced respectively from BCB and CHN, suggests that vibrationally hot butadiene molecules are formed. The effects of laser fluence, pressure of SF_6 and the no. of laser pulses on dissociation yield and the branching ratio in BCB are also investigated.

The advent of infrared multiphoton dissociation (IRMPD) has opened a new area of research in photodissociation dynamics from the vibrationally excited ground electronic state. Investigations of the unimolecular processes, especially the mode of ring-opening, and energy dynamics in the ground electronic state of cyclic molecules are of current interest.$^{1)}$ The pulsed CO_2 laser induced photodissociation studies reveal that consequent on the ring opening an appreciable amount of excess energy is partitioned among vibrational modes of the product molecules, thereby, populating these nascent molecules in higher vibrational quantum states.$^{2,3)}$ The vibrationally excited molecules can be probed, and their energy dynamics studied by time-resolved UV absorption, IR emission and laser induced fluorescence or; more sophisticated Raman spectroscopic techniques. The time-resolved UV absorption technique can generate UV absorption spectra of vibrationally hot species.$^{2—6)}$ These species generally give red-shifted, broad and structureless spectra; the extent of these changes depend on the nature of the molecule and the vibrational temperature.$^{7)}$ The UV absorption spectra of vibrationally highly excited molecules often appear continuous. These spectra are either truly continuous or the overlapping of many hot bands results in highly congested spectra. The analysis of these hot UV absorption spectra is involved, and a theoretical simulation of these spectra as a function of excited state populations becomes very difficult. Therefore, experimental investigations of the hot UV absorption spectra become important, especially in understanding collisional energy transfer processes.

In the case of spirohexane$^{3)}$ (SHX), the photoproduct 1,3-butadiene is vibrationally excited, exhibiting a red-shift of 40 nm in its UV absorption spectrum. The excited butadiene molecules undergo collisional relaxation leading to the formation of vibrationally relaxed molecules, which give normal UV spectrum when observed in post-irradiated mixture. Bromocyclobutane (BCB) and cyclohexene (CHN), different sources of butadiene, were investigated to monitor nascent butadiene molecules and to have a comparative study of their UV spectra. Further, two competitive dissociation channels are observed in thermolysis of chlorocyclobutane, one to yield 1,3-butadiene and hydrogen chloride and the other to produce ethylene and vinyl chloride.$^{8,9)}$ However, in thermolysis of bromocyclobutane,$^{10)}$ exclusively one channel leading to formation of butadiene and HBr is reported upto 1200 K. The authors explained that the second channel, ring cleavage, is too slow to compete with HBr elemination. A pulsed CO_2 laser can pump very high energy in the molecules leading to high transient vibrational temperature, which can be sufficient to open a thermally non-competitive channel. Thus the other interest was to investigate the feasibility of ring-cleavage reaction channel in BCB under laser photolytic conditions.

Experimental

The sensitized dissociation of BCB and CHN was studied in a SS cell, 4.7 cm long with a total volume of 32 ml. The cell was fitted with two polished KCl windows. 0.8 Torr (1 Torr=133.322 Pa) of BCB or CHN was taken and different amount of SF_6 was added to find the optimum conditions for maximum dissociation yield. The mixture was irradiated for a total of 100 pulses at a fluence of 0.6 J cm^{-2}. For fluence dependence studies a 1 : 2 mixture of BCB : SF_6 was made in a stock bulb and known amounts of sample were transferred to the irradition cell through vacuum line. At each fluence the mixture was irradiated for 100 pulses. All sensitized experiments were carried out at 10P (20) line of CO_2 laser. Depletion of BCB, or CHN was monitored by Gas chromatography (home-made) and FT-IR spectrometry (Mattson, Cygnus 100). In GC analysis, the products were separated on a 6 feet column (1 feet=0.3048 m) of silicone grease and detected using flame ionization detector.

Time-resolved experiments were carried out in a specially designed SS cell (volume=263 ml) fitted with a pair of KCl windows orthogonal to another pair of quartz windows in

IR/UV crossed beam configuration. The laser beam was partially focused in the center of the cell by a BaF_2 lens ($f=25$ cm). A cw spectroscopic UV probe beam from a pulsed mode operated Xe lamp (150 W) with associated optics, monochromator ($f=3.5$), fast PMT (IP28) and signal processing system (Gould Biomation 4500, 10 ns resolution), as discussed in our earlier paper,[11)] was used for detection of transient/stable products in CO_2 laser irradiation. The CO_2 laser is triggered at a time when the pulsed lamp intensity reaches the maximum and remains steady over a period of 200 μs. The complete operation from firing of CO_2 laser to data collection is computer controlled. Signal was averaged for 16 shots and data were transferred to computer/plotter for further processing. The post irradiated sample was transferred to a quartz cell of 1 cm path length (vol. 15 ml) and analyzed on Hitachi 330 UV-vis spectrophotometer.

Results

CO_2 laser induced SF_6 sensitized dissociation of CHN leads to formation of 1,3-butadiene and ethylene, akin to numerous thermolytic and photolytic studies reported. There exists a rich and unambiguous literature on CHN dissociation[1,12—14)] and therefore, except for time-resolved studies, other details about the system are not probed. In the case of BCB, two dissociation channels were found to operate from its ground electronic state, the major one (reaction 1) yields 1,3-butadiene and HBr whereas, the minor one (reaction 2) gives vinyl bromide and ethylene.

$$C_4H_7Br \rightarrow C_4H_6 + HBr \quad (> 90\%) \tag{1}$$

$$\rightarrow C_2H_3Br + C_2H_4 \tag{2}$$

$$C_6H_{10} \rightarrow C_4H_6 + C_2H_4 \tag{3}$$

1 Effect of Laser Fluence. A mixture of 0.8 Torr of BCB and 1.6 Torr of SF_6 was photolyzed at different laser energy fluence (0.5—1.3 J cm^{-2}) for 100 pulses. The dissociation yield of BCB increased with increasing fluence (Fig. 1). It was observed that once laser fluence exceeds the dissociation threshold fluence (0.45 J cm^{-2}), dissociation increased rapidly with fluence and then, the increase gradually slowed down. The branching ratio (BR), k_1/k_2, as determined from the product yield was almost insensitive to the laser fluence.

2 Effect of Partial Pressure of SF_6 and No. of Laser Pulses. With increase in SF_6 partial pressure, the dissociation yield increased linearly (Fig. 2). However, there was no effect on BR, except at high SF_6 pressure of 5 : 1, where it was found to decrease from 14 to 8. When a mixture of BCB (0.8 Torr) and SF_6 (1.6 Torr) was irradiated at the fluence of 1.3 J cm^{-2} for varying no. of pulses (10—200), the dissociation yield was found to have a linear dependence on no. of laser pulses (Fig. 3). BR also remained unaffected by varying the no. of laser pulses.

3 Time-Resolved Studies. 1,3-Butadiene, produced in IR photolysis of BCB and CHN, was monitored by kinetic UV absorption spectrometry. The UV spectrum of nascent butadiene (Fig. 4) produced from BCB and taken at 5 μs delay is found to be structureless and red-shifted with λ_{max} at 248 nm, whereas that produced from CHN and taken at 4 μs delay is broader and more red-shifted with λ_{max} at 260 nm. The post-irradiated mixture was analyzed by UV spectrophotometer and vibrationally relaxed butadiene was observed with its characteristic structured spectrum in gas phase ($\lambda_{max}=210$ nm). In the post irradiated sample, no absorption was observed beyond 230 nm, where the vibrationally excited butadiene has an appreciable absorption. The temporal growth of butadiene generated from BCB and CHN was recorded at 248 nm and 260 nm, respectively (Fig. 5). The absorption signal gradually decays due to the combined effects of cooling

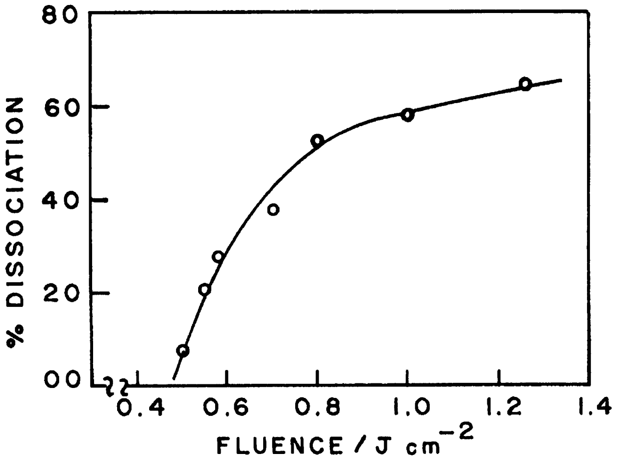

Fig. 1. Dependence of dissociation yield of BCB on laser fluence (0.5—1.3 J cm^{-2}) for 100 pulses.

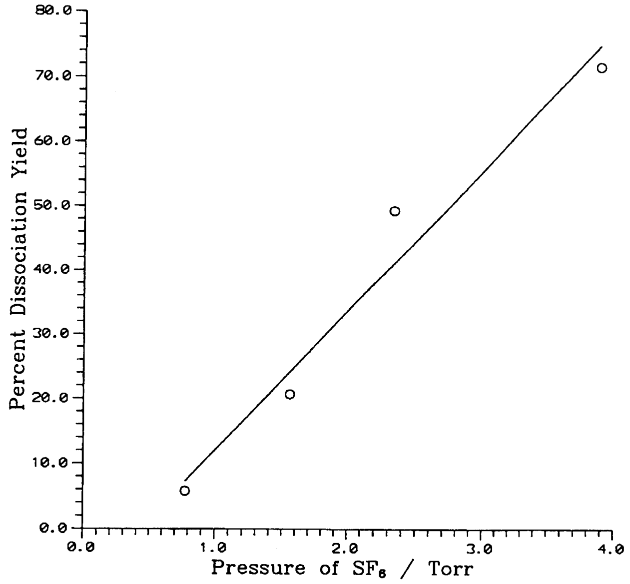

Fig. 2. Linear dependence of dissociation yield of BCB on partial SF_6 pressure at the laser fluence of 0.8 J cm^{-2}.

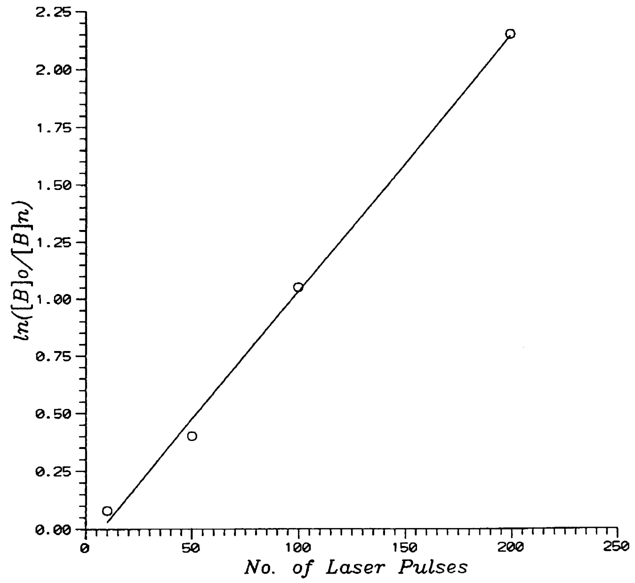

Fig. 3. Dissociation yield dependence of BCB on number of laser pulses at the fluence of 1.3 J cm^{-2}.

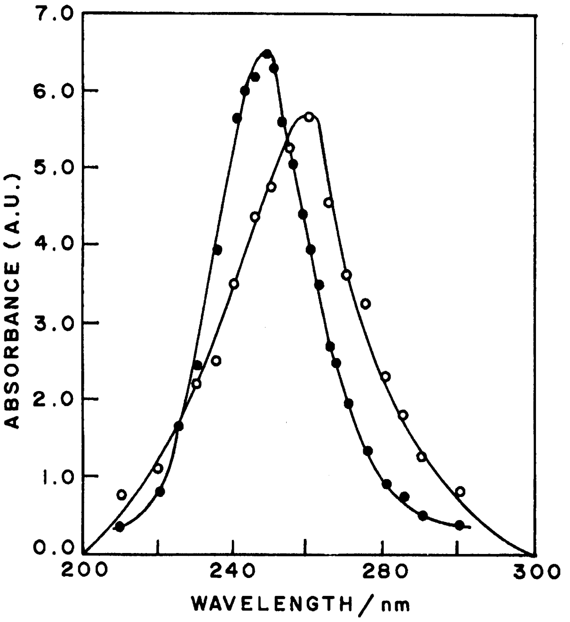

Fig. 4. UV spectra of nascent 1,3-butadiene, produced from IR laser induced dissociation of BCB (filled circles, taken at 5 µs) and CHN (empty circles, at 4 µs).

down of hot butadiene molecules and their diffusion out of the observation zone. These rise curves were fitted to a single exponential growth,

$$[\text{Butadiene}]_t = [\text{Butadiene}]_{\max}\{1-\exp(-kt)\}, \qquad (4)$$

and the unimolecular dissociation rate constants, k, for BCB and CHN were calculated to be 8×10^5 s^{-1} and 1×10^6 s^{-1}, respectively.

Discussion

1 Laser Parametric Studies. Although only one dissociation channel is reported in thermal dissociation of BCB up to 1200 K, an additional channel yielding ethylene and vinyl bromide is detected in pulsed CO_2 laser induced SF_6 sensitized photodissociation of BCB. The second channel is observed due to higher vibrational temperature of >1500 K (discussed in the end of this section) in our photolytic conditions. In such a case of dual dissociation channel, branching ratio (BR) is expected to depend on laser fluence and relative sensitizer pressure; which can alter the average energy content/vibrational temperature of the system. Depending on the Arrhenius kinetic parameters and the temperature dependence of frequency factor (A), BR can vary with temperature. Under our experimental conditions of photolysis, BR remained unaffected by laser fluence and relative sensitizer pressure. This suggests that probably the temperature change under our experimental conditions was insufficient for bringing about an observable change in BR. However, under both these conditions of increase in fluence and SF_6 pressure, the dissociation yield increases as a result of increase in average no. of photons absorbed per SF_6 molecule.

The dissociation yield dependence on no. of pulses can be described by a simple equation,

$$[B]_n = [B]_0 \exp(-n\alpha), \qquad (5)$$

where, $[B]_n$ and $[B]_0$ stand for the concentration of BCB after n pulses and that to start with, respectively. α represents the dissociation yield per pulse. Eq. 5 was plotted (Fig. 3) and α was obtained to be 1×10^{-2}. BR remains unaltered with no. of pulses, suggesting that both the photodissociation channels from BCB are primary ones.

For the observed overall dissociation rate constant of BCB to be 8×10^5 s^{-1} and BR (k_1/k_2) to be 13.0 — obtained from the dissociation yields of two channels — the temperature is calculated, using kinetic parameters from literature,[10] to be 1530 K.

2 Mechanistic Aspects. Thermolysis and IRMPD of CHN yield only 1,3-butadiene and C_2H_4 (reaction 3) by concerned mechanism of ring-opening. In BCB, the major channel (>90%) leads to the formation of 1,3-butadiene directly or via the precursor, cyclobutene. An unsuccessful attempt was made to stabilize cyclobutene (if at all, it's an intermediate) by Ar and N_2 (10 Torr). This result suggests that either cyclobutene is not an intermediate for butadiene or, the former isomerizes very fast to the latter. Therefore, the treatment of growth of butadiene by Eq. 4, for calculating k, remains valid.

3 Spectral Features and Energetics. The UV absorption spectra often show a pronounced temperature dependence. Internal energy of vibrationally

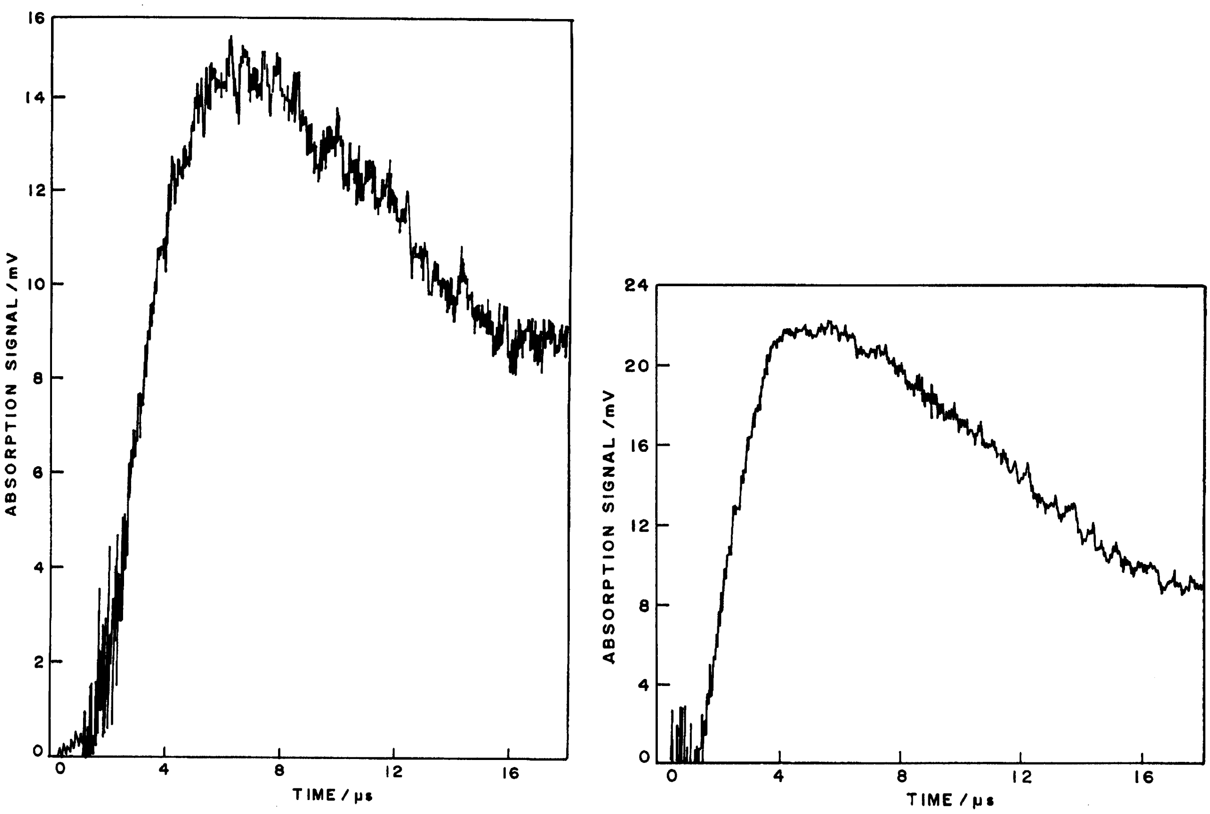

Fig. 5. Temporal growth of 1,3-butadiene, generated from BCB (at 248 nm, curve (a)) and CHN (at 260 nm, curve (b)).

highly excited molecules influence their electronic spectra which is often demonstrated by pronounced changes in the spectra. With increasing vibrational energy content line structures disappear, absorption continuum broadens and different electronic transitions may overlap.[7] The observed transient spectra can, in principle, be assigned to the vibrationally excited parent/product molecules, or to an intermediate involved in the photodissociation. BCB and CHN are not expected to absorb the UV radiation at such a high wavelength. Moreover, no UV absorption signal in this region was observed at fluences below the dissociation threshold value for BCB. This rules out the possibility of vibrationally hot parent molecule being responsible for the transient absorption. CHN is shown to dissociate from its ground electronic state in a concerted pathway without involving any intermediate.[1] Therefore, the UV spectra can not be assigned to any intermediate also. Furthermore, the post-irradiated mixture, in both the cases of BCB and CHN, yields the characteristic UV structured spectra of 1,3-butadiene. Hence, with confidence the transient UV spectra can be attributed to vibrationally hot butadiene product molecules. This conclusion is further supported by a comparable extinction coefficient of the vibrationally hot specie produced in BCB photolysis. It is estimated to be about 2×10^4 M^{-1} cm^{-1} at 248 nm from the observed dissociation yield per pulse and absorbance at this wavelength. Thus, the UV absorption spectra of transient butadiene, produced from BCB and CHN, show red-shift of 38 and 50 nm, respectively. The hot butadiene molecules, therefore, give structureless and broad UV spectra. The spectra from CHN are comparatively more red-shifted and broader, implying that vibrational energy content of butadiene, produced from CHN, is higher. However, butadiene generated from BCB, shows almost an identical spectrum as that from SHX (red-shift is 40 nm). These spectral features can be rationalized semi-quantitatively, by considering energetics of the photolytic reactions.

From the unimolecular dissociation rate constants (k) of BCB and CHN, the average internal energy contained (E) in the energized BCB and CHN molecules were calculated, using RRK expression

$$k(\mathrm{s}^{-1}) = A(1 - D/E)^{(s-1)}, \tag{6}$$

to be 303.1 and 425.0 kJ mol^{-1}, respectively. Here, A (4×10^{13} s^{-1}) and D (217.7 kJ mol^{-1}) are frequency factor and dissociation energy, respectively (taken from Ref. 10). Effective vibrational degrees of freedom (s) were taken to be 50% of the total vibrational modes of the parent molecule. An addition of the enthalpy of reaction (ΔH) to E, gives the total energy available for being distributed among various modes of product molecules. This value comes out to be 262.9 and 257.1 kJ mol^{-1} for BCB and CHN, respectively. Notwithstanding almost the same total internal energy content of BCB and CHN, butadiene produced from the

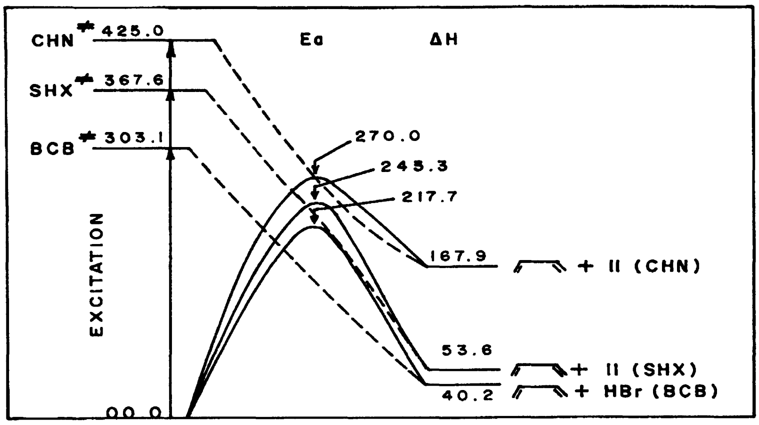

Fig. 6. Energy diagram of dissociation channels of CHN, BCB, and SHX with energies in kJ mol^{-1}. The values for transition states are activation energies.

latter has higher vibrational energy. This can be explained by considering energy disposal in the case of concerted reactions. In concerted dissociation of most midsized molecules in ground electronic state, translational energy release mainly correlates with the exit barrier along the reaction coordinate and it is less influenced by the excess energy when there is an appreciable exit barrier.[1,15] Moreover, a significant fraction of exit barrier (85% in CHN) is transferred as translational energy.[1] From energy diagram of dissociation channels (Fig. 6), it is obvious that exit barrier for reactions in BCB and CHN is 177.5 and 102.1 kJ mol^{-1}, respectively. Assuming concerted photodissociation reaction in BCB also, only the exit barrier will affect translational energy of products. Therefore, the excess energy (E_{ex}) of 85.4 kJ mol^{-1} in BCB and 155 kJ mol^{-1} in CHN is available mostly for internal modes of the products. Higher E_{ex} in the case of CHN implies a higher vibrational energy transfer to butadiene and hence, more red-shifted butadiene spectrum in this case. This rationalization of excess energy, E_{ex}, to be mainly responsible for excitation of internal modes of the products in a concerted reaction is further substantiated by transient UV spectrum of 1,3-butadiene produced from SHX. In the case of SHX, an E_{ex} of 124.3 kJ mol^{-1} is observed to bring about a red-shifted of 40 nm. The red shift is somewhat less than the expected value.

Conclusions

The pulsed CO_2 laser induced SF_6 sensitized photodissociation of BCB opens up two dissociation channels. The major channel (>90%) yields 1,3-butadiene and HBr whereas, the minor one gives vinyl bromide and ethylene. The branching ratio of two reactions in BCB is independent of laser fluence. CHN, under similar photolytic conditions, undergoes retro Diels–Alder reaction producing 1,3-butadiene and ethylene.

From the time-evolution of 1,3-butadiene, the unimolecular dissociation rate constants of BCB and CHN under sensitized condition are found to be 8×10^5 s^{-1} and 1×10^6 s^{-1}, respectively. The nascent 1,3-butadiene product molecules are formed in vibrationally excited states, exhibiting a red-shift of 38 nm and 50 nm in UV absorption spectra, when produced respectively from BCB and CHN. The red-shift in UV spectra of transient butadiene, obtained from three different sources (BCB, CHN, and SHX) can be qualitatively explained by excess energy in the energized parent molecule.

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