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MATRIX ISOLATION OF BORON AND CARBON VAPOR. CONTROL OF CLUSTER FORMATION DURING PREPARATION AND ANNEALING

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Abstract

The formation and recombination of small boron/carbon clusters were studied by *quantitative* Fourier transform infrared (FTIR) spectroscopy. Samples were prepared by evaporation of powder mixtures from a resistively heated oven (3000 K) and isolated at 10 K in solid argon. C_3 and BC_2 disappeared entirely over the course of several annealings. Yields of all the larger clusters (B_JC_{n-J}, $n \geq 4$, $J = 0, 1, 2$) increased during annealing. Clusters with $n \geq 4$ are linear, with the boron atoms of the $J = 1$ and 2 clusters capping the ends of carbon chains; B_2C_{n-2} clusters are inert (do not react to form larger clusters w/in matrix). During annealing, C_n and BC_{n-1} clusters grow by adding a mobile atom, dimer, or trimer to the carbon end of the chain. Dramatic growth of B_2C_2 during the first annealing is consistent with the presence of B atoms and/or BC molecules in the initial matrices.

Introduction

Under the auspices of the U. S. Air Force High Energy Density Matter (HEDM) Program [1], we have pursued the goal of production of a cryogenic matrix with an atom density of ~ 1 x 10^{21} atoms cm^{-3}, which amounts to ~ 5 mole percent atoms in an inert solid, or an equivalent atom gas pressure of ~ 60 atm at 298 K. This and our companion paper [2] describe qualitative and quantitative analysis of B_JC_{n-J} clusters in prototypical HEDM. Previously, the first conclusive identifications of small boron clusters, BC_2, B_2C, BC_3, and B_2C_2 were reported [3-5]. Observed FTIR fundamentals and isotope shifts were matched with predictions of *ab-initio* theory in those studies.

Verhaegen, Stafford, and Drowart [6] published the first experimental evidence of B_JC_{n-J} 35-years ago. Mass spectrometry was used to measure boron and boron carbide vaporization from graphite Knudsen cells heated by electron bombardment to ~ 2500 K. The vapor pressure of boron at 2200 K was ~ 0.008 torr, 94% atoms, 5% BC_2, 1% B_2C, and 0.07% BC. At the same temperature, boron carbide had about one-half the vapor pressure with 96% atoms, 4% BC_2, 0.1% B_2C. Distributions of anions and cations of B_xC_y with up to 17-atoms have been measured in plumes of laser vaporized boron carbide targets by Becker and Dietze [7]. Their mass spectrometric analysis showed that B_2C^-, B_2C^+, BC_2^-, and BC_2^+ were major components of the plume. Matrix isolated BC_2 has been produced by oven and laser vaporization of carbon/boron mixtures and targets and measured by FTIR [3,8] and ESR [9,10] spectroscopy. Most recently, Wyss, Grutter and Maier [11] isolated BC_2^- and BC^- in neon matrices by sputtering a boron carbide target with Cs^+ and trapping the mass-selected anions in neon matrices. Neutrals were produced by electron photodetachment with uv radiation. Electronic transitions of BC_2 and BC and their anions were studied. The FTIR

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spectrum of the previously identified [3] $\nu_2(a_1)$ fundamental of BC_2 was also observed. The infrared spectrum of BC has never been measured, but a CCSD(T)/cc-pVTZ calculation with quartic force field predicted [12] its vibrational fundamental at 1148 cm^{-1} with intensity of 43 km mol^{-1}. Of the pure boron clusters, only B_3 has been experimentally observed. Li, Van Zee and Weltner [13] identified all four isotopomers of B_3 in argon matrices by FTIR spectroscopy and found that experimental frequencies matched *ab-initio* frequencies of its cyclic geometry. Although *ab-initio* studies of B_n, $n \geq 4$, have been carried out, only geometries and energies have been reported [14,15]. Unlike C_n, B_n for $n \geq 5$ are predicted to have stable 3-dimensional geometries.

Carbon clusters were recently reviewed by Van Orden and Saykally [16]. Cyclic C_6 [17, 18], cyclic C_8 [19, 20], linear C_{11} [21], have recently been identified by their FTIR isotopomer spectroscopy. Most recently, electronic spectra of linear C_{17}, C_{19}, and C_{21} [22] and cyclic C_{10} and cyclic C_{12} [23] isolated in neon matrices were reported, and Raman spectra of linear C_{16}, C_{18}, and C_{20} were reported [24].

Figure 1 shows a Pascal's triangle representation of the boron/carbon system. In the limit of statistical recombination of well mixed atoms, the relative yields of B_JC_{n-J} clusters of given *n* is given by

$$\rho(B_JC_{n-J})/\rho(C_n) = n!/J!(n-J)![B/C]^J, \qquad (1)$$

where [B/C] is the molar ratio of boron to carbon, and $\rho(i)$ is the column density of species *i*.

Experimental

Mixtures of boron and carbon powders were evaporated with a resistively heated oven, to temperatures ~ 3000 K, and vapors were co-condensed with ~ 1000:1 excess argon at 10 K to form ~ 60 μ thick matrices in about one-hour. Beer's Law enabled quantitative analysis of the various species, $\rho(i) = 2.303\, A_i(experiment)/I_i(theory)$, where $\rho(i)$ is the average column density, which is the average value of the product of the species density and matrix thickness. $A_i(experiment)$ is the integrated intensity of the infrared absorbance of species *i*, equal to $-\log_{10} \tau_i(\nu)$, where $\tau_i(\nu)$ is the transmittance at absorption frequency ν. $I_i(theory)$ is the infrared absorption intensity of species *i*, which by necessity must be obtained by *ab-initio* calculation because experimental values are not available at this time. Fig. 1 indicates values of $I_i(theory)$ calculated by DFT/cc-pVDZ [25-28].

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Results and Discussion

Annealing of pure carbon matrices led to disappearance of atoms, dimers and trimers from the initial deposits. The identified products of recombination included cyclic C_6 and cyclic C_8, and linear C_n molecules, $4 \leq n \leq 13$. After annealing to constant composition, the total measurable carbon was found to be as much as twice the initial measurable carbon, indicating that about 50 % of the initially deposited carbon was isolated as atoms and dimers. The cyclic molecules, the dominant condensation products, amounted to as much as ~ 60% of total carbon in the fully annealed matrices.

In matrices containing boron, linear C_3 and cyclic BC_2, B_2C, and B_3, constituted about 80% of the total observable boron and carbon in the initially deposited matrix. The observation of approximately statistical distributions [Equation (1)] in clusters with n = 3, 4, and 5 in the initially deposited matrices implies that these smaller clusters form by random condensation of well-mixed atoms, uninfluenced by their relative energies, the energies of their precursors, or preferential kinetics pathways that could otherwise distort the statistics.

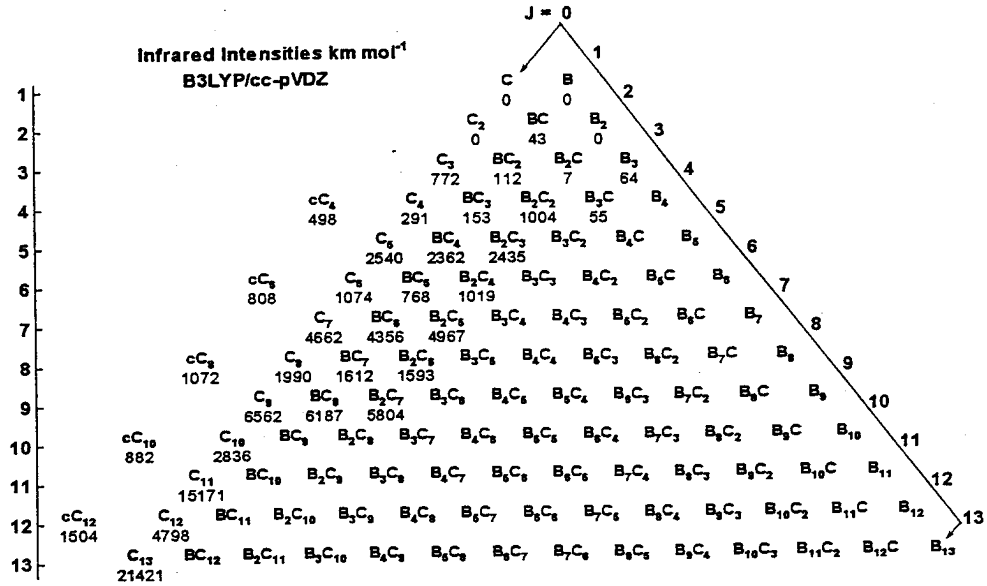

Figure 1. Representation of the B_JC_{n-J} (n = 1 - 13, J = 0 - n) system by Pascal's triangle. Numbers below molecular formulas denote the ab-initio intensities of the most intense infrared stretching fundamentals, Refs. [25] – [28]. Cyclic carbon clusters are removed from the triangle to the left.

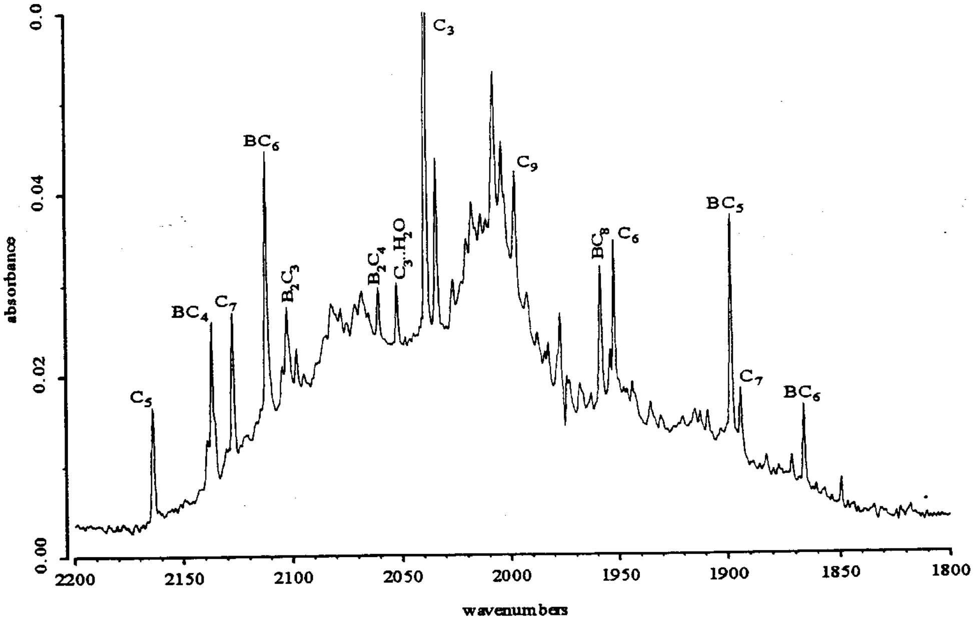

Figure 2. Survey spectrum of matrix containing carbon and boron at natural abundance with [B/C] ~ 1/3 after three annealings. All of the peaks indicated grow upon annealing except C_3. Fundamentals of BC_{n-1} for n = 5, 6, 7, and 9 are similarly red-shifted from fundamentals of linear C_n, and their experimental absorbances are all slightly greater in this matrix. Two fundamentals of BC_6 are observed at 2112 and 1866 cm^{-1}, red-shifted from the two fundamentals of linear C_7.

B_2C_{n-2} clusters, once formed, were inert to further condensation upon annealing. Thus, energy loss by recombination during preparation of high energy density matrices (HEDM) is minimized in matrices with large B/C ratios. For example, when B/C ~2, any recombination that does occur during co-deposition would tend to produce B_2C, a high-energy molecule that is inert in the cryogenic environment. In pure boron HEDM, the cyclic B_3 molecule may be similarly inert, which would suggest that energy loss by recombination will also stop at a B_3 "island of stability." Continuing experimental work to produce five-mole percent pure boron HEDM is concentrating on development of a resistively heated high-flux boron atom source, the "boron cannon", and production of higher density matrices.

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MATRIX ISOLATION OF BORON AND CARBON VAPOR.

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Abstract

This report supplements the companion paper published in this volume [1]. Details about the FTIR quantitative analysis of the disappearance and formation of clusters during annealing of solid argon matrices containing boron and carbon species are presented.

Introduction

The companion paper [1] summarized the literature of small boron clusters, about B_JC_{n-J} (n = 2 to 10, J = 0, 1, 2, 3) and described the formation of clusters during preparation and annealing of solid argon. This report presents additional details.

Experimental

A precision matched pair of matrices was prepared as described in Ref. [1] with two different boron isotopic compositions and natural abundance carbon. Matrix (a) contained natural abundance boron, $^{11}B/^{10}B = 4.0$, and matrix (b) contained boron with an inverted isotope ratio, $^{11}B/^{10}B = 0.37$. Each matrix had a [C/B] molar ratio of ~ 3.0, a thickness of ~ 60 m, and very similar absolute amounts of each element. Each matrix was annealed repeatedly according to the same annealing protocol given in the caption of Figure 1.

Results and Discussion

Figure 1 shows the annealing behaviors of the FTIR bands belonging to BC_2, BC_3 and B_2C_2 for each of the matrices. Cyclic BC_3 disappears entirely when one of its carbon atoms is attacked by a radical species. One of the B-C bonds is broken, and the BC_3 ring opens. The dramatic appearance of B_2C_2 during the first annealing is consistent a mechanism involving recombination of BC, whose density lies below the limit of detection, or condensation of B atoms with BC_2.

with

Figure 2 shows the annealing behaviors of the $^{11}B_J{}^{12}C^{n-1}$ clusters, n = 3 to 9 and J = 0, 1, 2 that were measured in matrix (a). Loss of clusters during the sixth annealing by matrix sublimation is generally greatest for C_n and smallest for B_2C_{n-2}, which is consistent with a stratified matrix with a higher [C/B] ratio near the subliming surface. Apparently, boron evaporates more rapidly than carbon during the early stages of oven evaporation, resulting in boron-rich layers near the substrate.

Column densities of the trimer clusters in the initially deposited matrices are in the ratio $\rho(C_3):\rho(BC_2):\rho(B_2C):\rho(B_3) \approx 1.0:1.5:0.5: < 0.05$, where only the upper limit for $\rho(B_3)$ may be determined because it was not observed. This is consistent with formation of the trimers by statistical condensation from a matrix with [B/C] ~ 1/3, which would produce a 1.0:1.0:0.33:0.05 distribution, $\rho(B_JC_{n-J})/\rho(C_n) = n!/J!(n-J)![B/C]^J$, Eq. (1), Ref. [1].

Agreement between distributions implies trimers form by random condensation of well-mixed atoms, uninfluenced by the relative energies of the trimers, the energies of their precursors, or preferential kinetics pathways that could otherwise distort the statistics. Linear C_3 and cyclic BC_2, disappeared entirely when the matrices were repeatedly annealed to

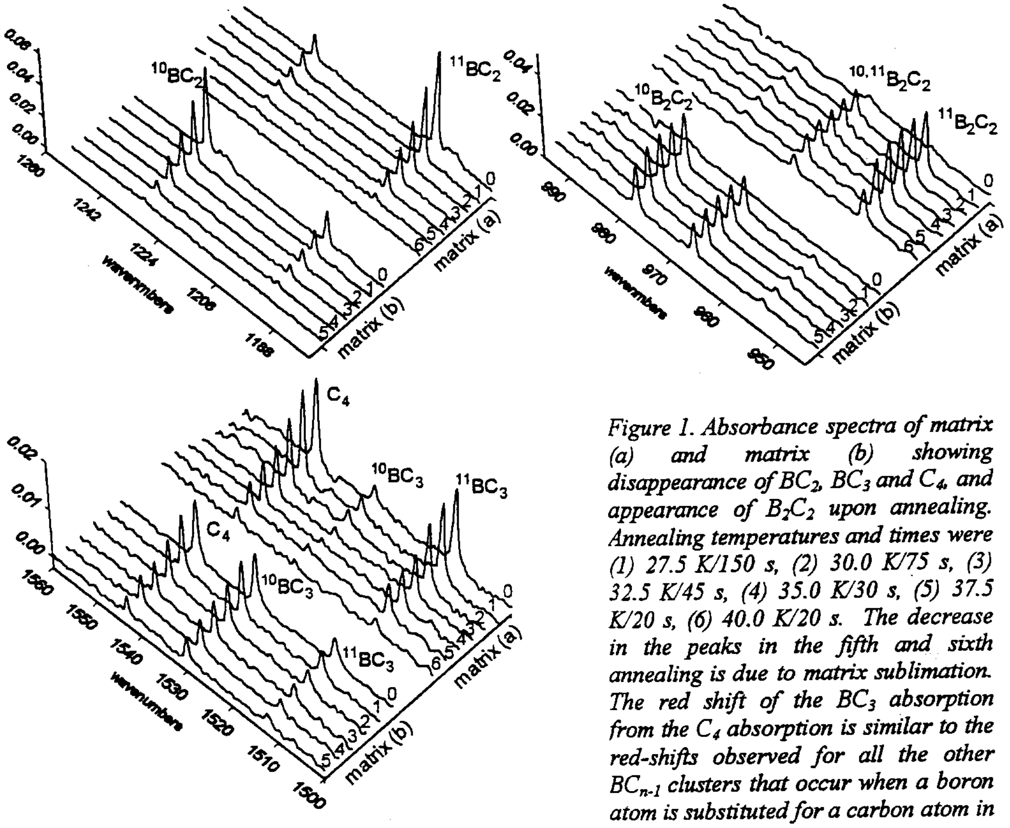

Figure 1. Absorbance spectra of matrix (a) and matrix (b) showing disappearance of BC_2, BC_3 and C_4, and appearance of B_2C_2 upon annealing. Annealing temperatures and times were (1) 27.5 K/150 s, (2) 30.0 K/75 s, (3) 32.5 K/45 s, (4) 35.0 K/30 s, (5) 37.5 K/20 s, (6) 40.0 K/20 s. The decrease in the peaks in the fifth and sixth annealing is due to matrix sublimation. The red shift of the BC_3 absorption from the C_4 absorption is similar to the red-shifts observed for all the other BC_{n-1} clusters that occur when a boron atom is substituted for a carbon atom in a C_n cluster.

temperatures between 25 K and 35 K, but cyclic B_2C was inert. Linear C_4 and BC_3 (BCCC) disappeared more slowly, and linear B_2C_2 (BCCB) grew to ~ 95% of its final value during the first annealing. Once formed, B_2C_2, like B_2C, was also inert to further reaction.

Figure 3 shows the absolute column densities of the analyzed clusters that was obtained by transformation of the Fig. 2 data with Beer's law and theoretical intensities shown in Fig. 1, Ref [1]. The BC molecule was not observed, but its upper limit column density was established to be somewhat larger than that of B_2C_2.

The sources of B_2C_2 are from condensation of atom plus trimer ($B + BC_2$ but not $C + B_2C$) or dimer + dimer ($BC + BC$ but not $B_2 + C_2$). Although BC was not observed, the upper limit of $\rho(BC)$ is larger than $\rho(B_2C_2)$ so that BC cannot be ruled out as a source of B_2C_2. The growth of B_2C_2 is consistent with of the presence of BC and/or B in the originally deposited matrix in an amount at least as great as the growth of B_2C_2.

Figures 1 and 2 show that C_4 and BC_3 do not change during the first annealing but begin to disappear in subsequent annealings. This indicates that a source for these tetramers, atom + trimer and/or dimer + dimer, operates during the first annealing .

Figure 2 shows that linear C_5, BC_4 (BCCCC) and B_2C_3 (BCCCB) and larger linear clusters all grew upon annealing. The sources of B_2C_3 are dimer + trimer ($BC + BC_2$ but not $B_2 + C_3$) and atom + tetramer ($B + BC_3$ but not $C + B_2C_2$). Since $\rho(BC_2) \sim 5\rho(BC_3)$ in the initially deposited matrix, the $BC + BC_2$ source is dominant. Growth of B_2C_3 is consistent with the presence of BC in the initially deposited matrix in an amount at least as great as the amount by which B_2C_3 grows.

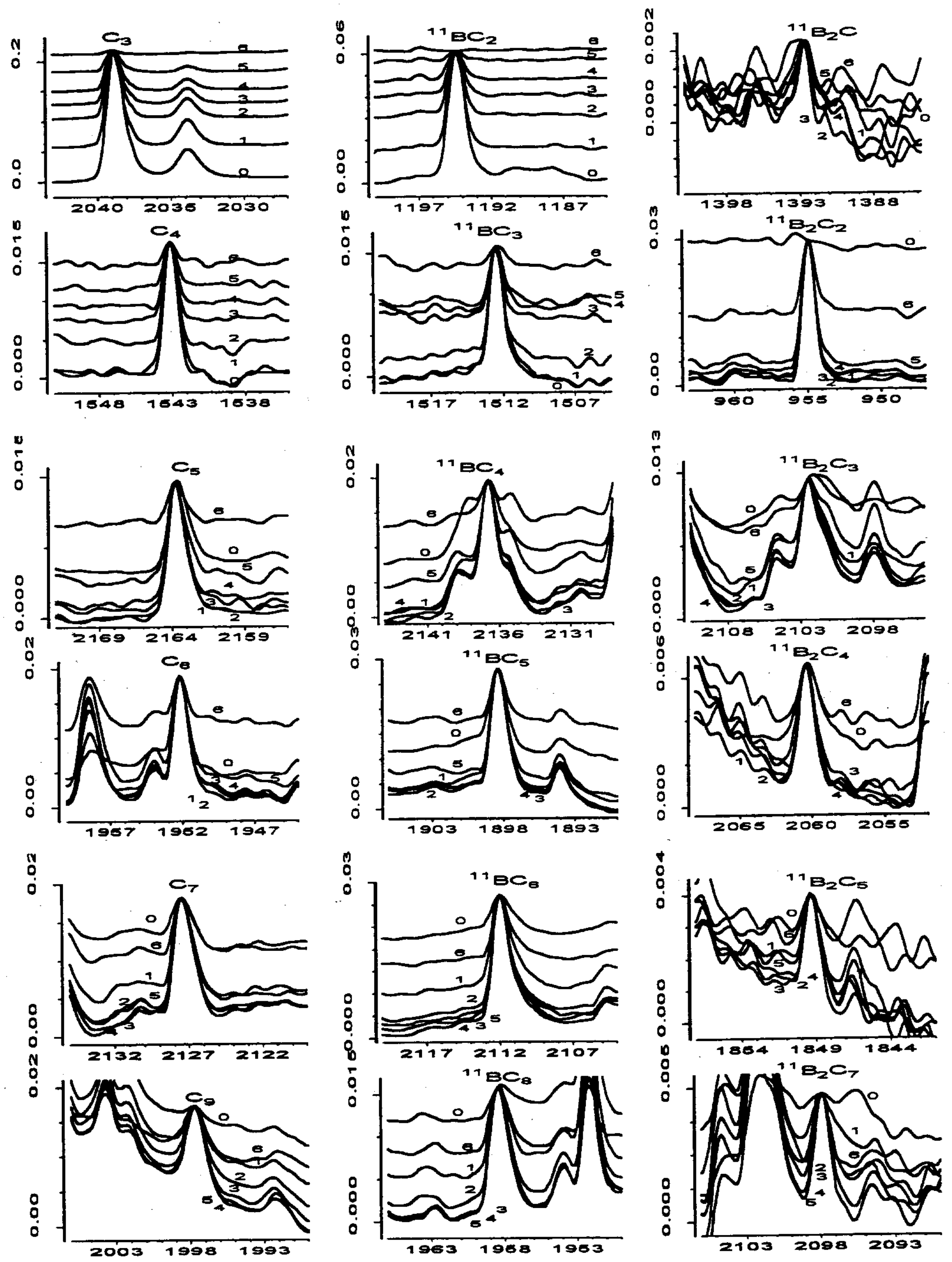

Figure 1. Annealing behaviors of $^{11}B_J{}^{12}C_{n-J}$ species in matrix (a), which contained natural abundance carbon and boron, $^{11}B/^{10}B=80/20$, $^{12}C/^{13}C=99/1$, with [C/B] ~ 3. Spectra labeled '0' were obtained from the originally deposited matrix, and spectra labeled '1' to '6' were obtained after successive annealings. During the 6th annealing (at 40 K for 20 seconds), almost half the matrix evaporates.

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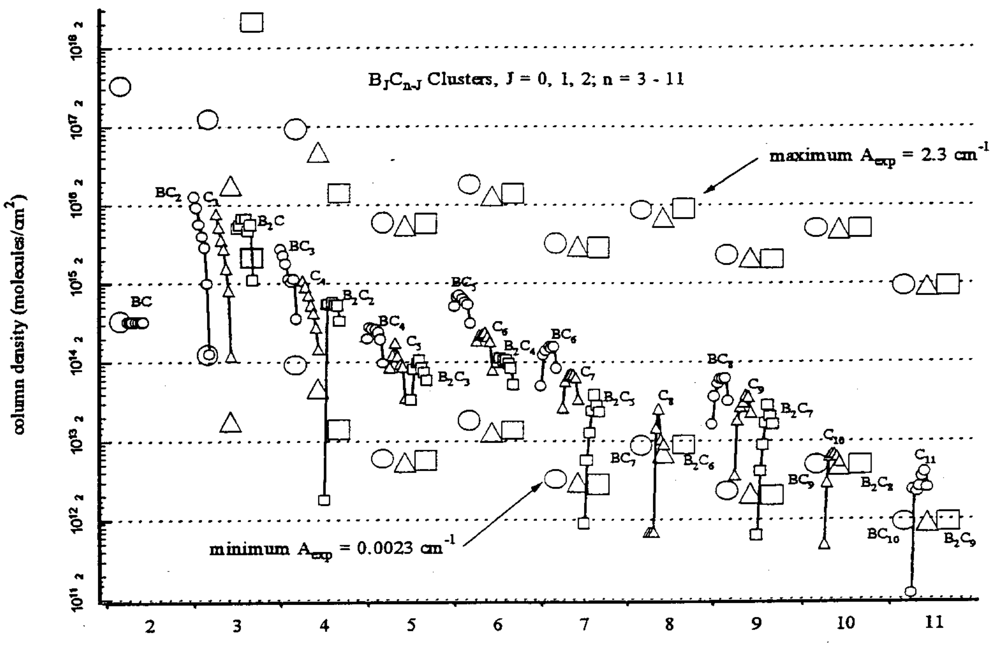

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Figure 2. Distributions of B_JC_{n-J} clusters, J = 0, 1, 2; n = 3 - 11. Circles, triangles and squares represent BC_{n-1}, C_n, and BC_{n-2} clusters, respectively. Large symbols denote upper and lower limits of measurement, based on a nominal minimum measurable absorbance of 0.0023 cm^{-1}, and a maximum absorbance for linearity of Beer's law of 2.3 cm^{-1} (1% transmittance). Small symbols denote measured quantities in the initial matrix, and in six annealed matrices. Some of the larger clusters (n = 8, 10, 11) have not been identified, BC_7, B_2C_6, BC_9, B_2C_8, BC_{10}, B_2C_9.

Growth of BC_4 occurs primarily by BC + C_3 rather than B + C_4 or C + BC_3 because $\rho(C_3) \sim 10\rho(C_4)$ and $\rho(C_3) \sim 2\rho(BC_3)$. Growth of C_5 occurs by C + C_4 and C_2 + C_3, which establishes the presence of C and/or C_2 in the original matrix in an amount at least as great as C_5 growth.

Conclusions

Disappearance of triangular BC_2 requires breaking of one of its B-C bonds when one of its carbon atoms is attacked. The major reorganization of electronic energy involved in opening the ring appears to occur with little (< ~3 kcal mol^{-1}) or no energy barrier, which makes this small molecule a candidate for an interesting *ab-initio* study of unusual reactivity at low temperature. Annealing kinetics of disappearance of C_3 and BC_2, and of appearance of B_2C, C_4, BC_3, B2C$_2$, C_5, BC_4, and B_2C_3 unequivocally establishes the presence of atoms and dimers in the originally deposited matrix. About 80% or more of the initially deposited HEDM existed as atoms, dimers and trimers. Molecules with two boron atoms are immune from radical attack and condensation during annealing.

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Reference

1. C. W. Larson, J. Harper, J. D. Presilla-Márquez, Poster Paper, This Volume.