# Emission spectroscopy of jet-cooled $\mathrm{CS}_{2}$ upon excitation of the ${ }^{1} \Sigma_{g}^{+} \rightarrow{ }^{1} B_{2}\left({ }^{1} \Sigma_{u}^{+}\right)$transition in the $48500-51000 \mathrm{~cm}^{-1}$ region 

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#### Abstract

The jet-cooled emission spectroscopy of gaseous carbon disulfide $\left(\mathrm{CS}_{2}\right)$ was performed in the $48500-51000 \mathrm{~cm}^{-1}$ region in order to investigate changes in the early time dynamics of $\mathrm{CS}_{2}$ in the predissociative ${ }^{1} B_{2}\left({ }^{1} \Sigma_{u}^{+}\right)$state. The spectra show emission into progressions of both the symmetric stretching ( $\nu_{1}$ ) and bending ( $\nu_{2}$ ) motions and combinations bands of these two motions. Analysis shows that the contribution of symmetric stretching and bending motion varies over the range of excitation wavelengths and the progression of $\nu_{2}$ decreases in intensity relative to the progression in $\nu_{1}$ as one scans through the energetic region near the barrier to linearity of this bent excited state molecule. We estimate the barrier height to be approximately $3400 \mathrm{~cm}^{-1}$ above the zero-point level of the ${ }^{1} B_{2}\left({ }^{1} \Sigma_{u}^{+}\right)$state. © 1998 American Institute of Physics. [S0021-9606(98)00542-X]


## I. INTRODUCTION

Carbon disulfide $\left(\mathrm{CS}_{2}\right)$ is a linear triatomic with a highly structured absorption in both the $290-330 \mathrm{~nm}^{1}$ ( $30000-$ $34000 \mathrm{~cm}^{-1}$ ) and $185-230 \mathrm{~nm}^{2-5}$ (43000-54 $000 \mathrm{~cm}^{-1}$ ) region. The transition is known to involve a prototypical ' $N-V$ ' ' type transition ${ }^{6}$ from a linear ground state configuration of ${ }^{1} \Sigma_{g}^{+}$in $D_{\infty h}$ symmetry to a predissociative bent excited state with electronic configuration of ${ }^{1} B_{2}$ in $C_{2 v}$ symmetry (one that correlates to configuration of ${ }^{1} \Sigma_{u}^{+}$in $D_{\infty h}$ symmetry). Analysis of the excited state rotational constants by Douglas and Zanon ${ }^{3}$ of the absorption bands in this wavelength region yielded the observation that the equilibrium $\mathrm{C}-\mathrm{S}$ bond lengths increase from $1.55 \AA$ to $1.66 \AA$, and the equilibrium $\mathrm{S}-\mathrm{C}-\mathrm{S}$ bond angle decreases from $180^{\circ}$ to $153^{\circ}$. These studies also confirmed the symmetry of the excited state to be ${ }^{1} B_{2}$, if the molecule is assumed to be well described in the $C_{2 v}$ symmetry point group. High resolution studies of the molecule showed the upper state to have a rather complicated and irregular vibrational structure, not easily explained with a single mode vibrational progression. Douglas and Zanon explain this complication in the upper state vibrational structure to be due to the near degeneracy of the excited state symmetric stretching and bending frequencies, both of which would be active modes of the molecule upon excitation. They also performed a temperature dependency study of the hot-band structure and concluded that the bending mode is the most active.

At excitation energies greater than $48500 \mathrm{~cm}^{-1}$, there is little detailed information concerning the exact nature of the spectrum of $\mathrm{CS}_{2}$ due to the increase in the rate of predissociation. ${ }^{7}$ Also, contributions from hot-band transitions in this energy region further complicate the already congested absorption spectrum, making the analysis of room temperature spectroscopic studies of this molecule prohibitively complicated.

Vaida and co-workers ${ }^{8,9}$ were the first to adapt the use of jet-cooling to the absorption spectrum of gaseous $\mathrm{CS}_{2}$. By
using this method of cooling a gaseous sample, they were able to reduce the complexity of the absorption spectrum by freezing out contributions due to hot-band transitions and thermal broadening of rotational levels. By analyzing the upper state $K$ structure of the excited state of $\mathrm{CS}_{2}$, Vaida and co-workers were able determine that the location of the bent to quasilinear transition in the ${ }^{1} B_{2}$ state (the height of the barrier between the two equivalent bent geometries) is $49000 \mathrm{~cm}^{-1}$ above the ground state minimum.

Many more studies of $\mathrm{CS}_{2}$ have been performed, including resonantly enhanced multiphoton ionization, ${ }^{10}$ excitation and dispersed fluorescence, ${ }^{11-13}$ resonance Raman, ${ }^{14-16}$ and molecular beam photofragment translational energy spectroscopies. ${ }^{17-19}$ The $(1+1)$ REMPI spectrum of Donaldson and co-workers ${ }^{10}$ determine the origin of the ${ }^{1} \Sigma_{g}^{+}$ $\rightarrow{ }^{1} B_{2}\left({ }^{1} \Sigma_{u}^{+}\right)$electronic transition to be at $46247 \mathrm{~cm}^{-1}$, while the $(2+2)$ REMPI spectrum led to the observation of the one-photon disallowed single quantum antisymmetric stretch at $1563 \mathrm{~cm}^{-1}$. Certain dispersed fluorescence spectroscopy ${ }^{11,12}$ experiments, while not performed at wavelengths corresponding to the excited state in question, but to the lower energy ${ }^{1} \Sigma_{g}^{+} \rightarrow{ }^{1} B_{2}\left({ }^{1} \Delta_{u}\right)$ transition, show activity in the symmetric stretching and bending modes. The dispersed fluorescence study at 210 nm , performed by Liou and co-workers, ${ }^{13}$ also show emission into symmetric stretching and bending modes as well. The resonance Raman spectroscopy ${ }^{14-16}$ of $\mathrm{CS}_{2}$ has been performed at various excitation wavelengths within the ${ }^{1} B_{2}$ excited state envelope and all show activity in the symmetric stretching and bending frequencies. Assignments have also been made for observed peaks corresponding to the antisymmetric stretching feature. Hyper-Raman studies ${ }^{20}$ of the $\mathrm{CS}_{2}$ molecule as well show activity in the antisymmetric stretch mode.

From the observed bandwidths in the absorption spectra, it is obvious that the peaks are broadened by the predissociative nature of the ${ }^{1} B_{2}$ excited state. The lifetime of the mol-
ecule in the ${ }^{1} B_{2}$ excited state has been experimentally determined using several methods. Hara and co-workers ${ }^{7}$ reported from a measurement of the fluorescence quantum yield, excited state lifetimes of between 1.2 and 9 ps in duration. Liou and co-workers ${ }^{13}$ used the transition linewidths from their dispersed fluorescence studies at 210 nm to calculate an excited state lifetime of 4.4 ps . Using the technique of resonance Raman depolarization measurements, Li and Myers ${ }^{15,16}$ measured a lifetime of 0.44 ps for excitation at 200 nm to 1.5 ps near 212 nm . Molecular beam studies ${ }^{17-19}$ of the angular product distribution at 193 nm excitation have led to a measurement of an upper limit of 1-2 ps for the excited state lifetimes. Hepburn and co-workers ${ }^{21,22}$ have shown for excitation energies below the barrier to linearity, the lifetime is roughly 1.5 ps . However, once above the barrier, in the higher energy bands of the ${ }^{1} B_{2}$ excited state, the lifetime decreases to roughly 0.4 ps . This energy dependency would suggest that at 193 nm the lifetime should be on the order of several tenths of picoseconds, much smaller than the upper limit reported in the literature for the other experiments performed at this wavelength.

In addition to the energy dependent lifetime of the ${ }^{1} B_{2}$ excited state, Hepburn's group ${ }^{21,22}$ has shown the rate constant for the dissociation leading to the production of different electronic states of sulfur photoproducts to be highly energy dependent as well. For excitation energies below the barrier to linearity, the rate constant for production of $S\left({ }^{1} D_{2}\right)$ and $S\left({ }^{3} P_{2}\right)$ is about one-half to one-third the rate of production of the same photofragments for an excitation energy above the barrier to linearity. These results imply that there is a greater amount of coupling between the initially prepared predissociative state and the dissociative exit channels when the molecule is above the barrier to linearity, thus leading to the increase in observed dissociation rate.

Very little theoretical work ${ }^{23-25}$ has been performed on the $\mathrm{CS}_{2}$ molecule in this absorption band. Earlier work ${ }^{23}$ on the ground and lower energy excited states of $\mathrm{CS}_{2}$ confirm that the equilibrium ground state configuration is ${ }^{1} \Sigma_{g}^{+}$in $D_{\infty h}$ symmetry. Vaccaro and co-workers ${ }^{24}$ observe for the lower energy transition, ${ }^{1} \Sigma_{g}^{+} \rightarrow{ }^{1} B_{2}\left({ }^{1} \Delta_{u}\right)$, the existence of a curve crossing between the ${ }^{1} \Delta_{u}$ and ${ }^{1} \Sigma_{u}^{-}$along the $\mathrm{C}-\mathrm{S}$ bond coordinate for linear $\mathrm{CS}_{2}$ and a second curve crossing along the SCS bend coordinate where the lower energy ${ }^{1} B_{2}$ RennerTeller doublet and higher energy ${ }^{1} A_{2}\left({ }^{1} \Sigma_{u}^{-}\right)$states cross. The ${ }^{1} B_{2}$ state is the lower energy Renner-Teller pair that correlates with the ${ }^{1} \Delta_{u}$ excited state in linear geometry. The ${ }^{1} A_{2}$ state correlates with the linear ${ }^{1} \Sigma_{u}^{-}$state which is lower in energy than the ${ }^{1} \Delta_{u}$ excited state.

Early $a b$ initio calculations on the higher energy ${ }^{1} B_{2}\left({ }^{1} \Sigma_{u}^{+}\right)$state, performed by Jego et al., ${ }^{26}$ show the state is bound and in the asymptotic limit yields $\operatorname{CS}\left(X^{1} \Sigma^{+}\right)$ $+\mathrm{S}\left({ }^{1} S\right)$ photoproducts. The ground ${ }^{1} \Sigma_{g}^{+}$and excited ${ }^{1} \Pi$ and ${ }^{1} \Delta$ states diabatically correlate to the $\operatorname{CS}\left(X^{1} \Sigma^{+}\right)$ $+\mathrm{S}\left({ }^{1} D_{2}\right)$ limit. In the potential well of the ${ }^{1} \Sigma_{u}^{+}$surface, they show that the state is crossed by the repulsive ${ }^{1} \Pi$ state. As the $\mathrm{CS}_{2}$ molecule bends, this ${ }^{1} \Pi$ state splits to yield ${ }^{1} B_{2}$ and ${ }^{1} A_{2}$ Renner-Teller pairs, just like the ${ }^{1} \Delta_{u}$ state in Vaccaro's study, with the lower energy Renner-Teller pair, ${ }^{1} A_{2}\left({ }^{1} \Delta_{u}\right)$, crossing with the ${ }^{1} B_{2}\left({ }^{1} \Sigma_{u}^{+}\right)$state. The general
agreement is that the triplet products are produced upon spinorbit coupling between the two possible triplet states $\left({ }^{3} \Sigma_{g}\right.$ and ${ }^{3} \Pi_{g}$ ) and one of the above singlet states. They also note for the bent geometry ${ }^{1} B_{2}$ state, the surface is unbound in the antisymmetric stretch coordinate.

Using the jet-cooled absorption spectrum of Vaida and co-workers ${ }^{8,9}$ to help tune into the vibrational features in the absorption spectrum, this work reveals the emission spectrum of gaseous $\mathrm{CS}_{2}$ cooled in a seeded pulsed molecular beam. We tune the excitation laser energy between 48500 and $51000 \mathrm{~cm}^{-1}$ to excite into the most intense 14 vibrational features in the absorption spectrum and dispersed the resulting emission from the predissociating $\mathrm{CS}_{2}$. In addition, two spectra are recorded at nonresonant wavelengths and compared with those tuned to resonances within the 48500 $51000 \mathrm{~cm}^{-1}$ region. We will use the results of our experiments to examine the early dynamics of this predissociative state of $\mathrm{CS}_{2}$, focusing on how the bent equilibrium structure of the excited state influences the emission spectrum and how the spectra probes the barrier between the two equivalent bent structures.

## II. EXPERIMENTAL METHOD

The KDP doubled output of a Quantel YG-581-C Nd:YAG laser pumps a Lambda Physik dye laser at 20 Hz with pulses of approximately 20 ns at $350 \mathrm{~mJ} /$ pulse. The dye laser is tuned between 592 and 614 nm within the lasing ranges of Rhodamine 590, Rhodamine 610, and Rhodamine 640 dyes; an intracavity etalon reduces the bandwidth from approximately $0.2 \mathrm{~cm}^{-1}$ to $0.05 \mathrm{~cm}^{-1}$. Two stage amplification within the dye laser increases the overall output to $30-35 \mathrm{~mJ} /$ pulse. Calibration of the dye laser was performed using a Fisher Scientific Mg/Ne optogalvanic hollow cathode lamp. The output of the dye laser is then doubled in frequency via second harmonic generation in a potassiumdihydrogen phosphate (KDP) crystal. After separating the visible and UV light via a dichroic beam splitter, the polarization of the visible light is rotated by a half-wave plate, recombined with the visible and is then passed through the BBO crystal which generates the $197-205 \mathrm{~nm}$ output beam via sum frequency mixing the fundamental visible light with the frequency doubled ultraviolet light. The conversion efficiency for each nonlinear crystal is on the order of $20 \%$ $25 \%$, thus giving us $196-205 \mathrm{~nm}$ light at approximately $100-150 \mu \mathrm{~J} /$ pulse from the initial dye laser fundamental pulse energy of approximately $30-35 \mathrm{~mJ} /$ pulse.

The frequency tripled output of the dye laser is first spatially separated from the residual visible and ultraviolet light by a Pellin-Broca prism and then passed through a stainless steel vacuum chamber where it photodissociates the molecules in the sample gas. The gaseous sample ( $20 \%$ partial pressure $\mathrm{CS}_{2}$ in helium buffer, total pressure 600 Torr) is introduced into the vacuum chamber by means of a General Valve IOTA-1 pulsed molecular beam valve with 0.5 mm orifice diameter. Ultimate background pressures within the chamber, pre-sample introduction, range between 1.5 $\times 10^{-6}$ and $5.0 \times 10^{-7}$ Torr. The pulsed molecular beam valve is triggered sufficiently prior to the Q -switch of the YAG laser so as to assure that the valve has reached its


FIG. 1. Emission spectrum of jet-cooled $\mathrm{CS}_{2}$ photoexcited at $48868 \mathrm{~cm}^{-1}$. Note the intensity of the $(1,0,0)$ peak in comparison to the $(0,2,0)$ peak. The $(0,2,0)$ peak is more intense, suggesting more bending than stretching motion.
maximum open position and to account for transit time to the interaction region approximately 1 cm from the valve tip. The pulsed valve is allowed to remain open for $200 \mu$ s assuring a well developed gas pulse, as well as, taking into consideration, the transit time of the gas pulse to the interaction region. Timing of gas pulse with the tripled laser light is monitored using a homemade photodiode and a Beam Dynamics FIG-1 fast ion gauge. The laser pulse intersects the gas pulse, about $100 \mu \mathrm{~s}$ after the leading edge of the $200 \mu \mathrm{~s}$ gas pulse. The emitted light is collected orthogonal to the direction of propagation of the excitation laser beam. The emitted light is then recollimated, passed through a depolarizing wedge optic and imaged onto the entrance slit ( 75 mm ) of a Spectra-Pro 0.275 m spectrometer. The light is then dispersed by a 1200 grooves $/ \mathrm{mm}$ Milton-Roy holographic grating onto an EG\&G 1455 B- 700 HQ Optical Multichannel Analyzer (OMA), which consists of a 18 mm photodiode array of 700 pixels, covering a 50 nm wide emission spectrum. The resolution of the OMA is limited by the grating, path length, and intensifier resolution ( 3 pixels) to $75 \mathrm{~cm}^{-1}$. The detector is thermoelectrically cooled to a temperature of


FIG. 2. Emission spectrum of jet-cooled $\mathrm{CS}_{2}$ photoexcited at $49270 \mathrm{~cm}^{-1}$.


FIG. 3. Emission spectrum of jet-cooled $\mathrm{CS}_{2}$ photoexcited at $49312 \mathrm{~cm}^{-1}$.
$-30^{\circ} \mathrm{C}$ and the intensifier is gated by an amplified TTL pulse that is synchronized to the laser with a set delay from the Nd:YAG Q-switch. The OMA intensifier is 'on'" for only 200 ns around each laser pulse, so as to reduce the background noise from dark counts in the photodiode array. The OMA is connected to an IBM-compatible computer which collects and displays the data. Each scan is collected for 100 s at 20 Hz , or approximately 2000 laser shots per scan. Each spectrum of carbon disulfide was collected over 10 scans, summing over a total of 20000 laser shots.

Liquid carbon disulfide ( $99.9 \%$ ) was obtained from Sigma-Aldrich Chemical Company and was not distilled prior to use. Samples were degased prior to introduction into the pulsed valve. Sample temperatures were held at $-10^{\circ} \mathrm{C}$ throughout the whole experiment via an Endocal RTE-110 constant temperature bath, yielding a partial pressure of $\mathrm{CS}_{2}$ of approximately 100 Torr. The equilibrium vapor pressure of $\mathrm{CS}_{2}$ at this temperature was then entrained in a flow of room temperature helium, bringing the total beam backing pressure to 600 Torr.


FIG. 4. Emission spectrum of jet-cooled $\mathrm{CS}_{2}$ photoexcited at $49662 \mathrm{~cm}^{-1}$. Note the intensity of the $(1,0,0)$ peak in comparison to the $(0,2,0)$ peak. The $(0,2,0)$ peak is reduced in intensity relative to the $(1,0,0)$ peak, suggesting less bending motion.


FIG. 5. Emission spectrum of jet-cooled $\mathrm{CS}_{2}$ photoexcited at $49697 \mathrm{~cm}^{-1}$.

## III. COMPUTATIONAL METHOD

In order to better interpret the results of our emission spectroscopy experiments, the GAUSSIAN $94^{27}$ set of ab initio electronic structure programs was used. The configuration interaction with singles excitations (CIS) method along with the second-order perturbative corrections (CIS-MP2) to the excited state energies of $\mathrm{CS}_{2}$ was performed. A $6-311+\mathrm{G}^{*}$ basis set was used in all cases and the calculations were performed on an SGI Power Challenge L computer with 4 CPUs running IRIX 6.2. The CIS and CIS-MP2 methods have been shown ${ }^{28-30}$ to work well in describing the excited electronic states of many molecules with both valence and Rydberg-type electronic states. Following the work of Zhang et al., ${ }^{24}$ only the valence shell electrons are included in the calculations involving the CIS-MP2 calculations on the excited state geometry. The $6-311+\mathrm{G}^{*}$ basis set was selected so as to minimize computational costs, while maximizing relative accuracy of the results.

## IV. RESULTS AND ANALYSIS

## A. Emission spectrum

Figures 1 through 16 present the emission spectra of gaseous $\mathrm{CS}_{2}$ upon excitation in the $48500-51000 \mathrm{~cm}^{-1}$ re-


FIG. 6. Emission spectrum of jet-cooled $\mathrm{CS}_{2}$ photoexcited at $49945 \mathrm{~cm}^{-1}$.


FIG. 7. Emission spectrum of jet-cooled $\mathrm{CS}_{2}$ photoexcited at $50055 \mathrm{~cm}^{-1}$.
gion. We assign the peaks in the emission spectrum according to the fundamental vibrational frequencies previously determined by Blanquet et al. ${ }^{31}$ in their study of gaseous $\mathrm{CS}_{2}$. In all cases, emission to the symmetric stretching $\left(\nu_{1}\right)$ and bending ( $\nu_{2}$ ) modes are observed. Much less emission intensity is observed in the antisymmetric stretching ( $\nu_{3}$ ) mode. Up to 5 quanta in the symmetric stretch $\left(\nu_{1}\right)$ and 10 quanta in the bend $\left(\nu_{2}\right)$ are observed in this excitation range. The extremely long progressions in the even quanta of the bending mode would be qualitatively expected as the molecule changes from linear to bent geometry upon excitation to the ${ }^{1} B_{2}$ excited state. The quanta in the symmetric stretch is further experimental evidence that the excited state geometry has extended $\mathrm{C}-\mathrm{S}$ bond lengths from those of the equilibrium ground state geometry.

We can understand the observed emission features in relation to the molecular orbital diagrams put forth by Walsh, ${ }^{2,32}$ Mulliken, ${ }^{6,33}$ Rabalais, ${ }^{4}$ and many others. The $\mathrm{CO}_{2}$ and $\mathrm{CS}_{2}$ molecules are isoelectronic and therefore have analogous electronic configurations. The ground state of $\mathrm{CS}_{2}$ has the electronic configuration $1 \sigma_{u}^{2} 1 \sigma_{g}^{2} 2 \sigma_{g}^{2} 2 \sigma_{u}^{2} 3 \sigma_{g}^{2} 3 \sigma_{u}^{2}$ $4 \sigma_{g}^{2} 1 \pi_{g}^{4} 1 \pi_{u}^{4} 5 \sigma_{g}^{2} 4 \sigma_{u}^{2} 6 \sigma_{g}^{2} 5 \sigma_{u}^{2} 2 \pi_{u}^{4} 2 \pi_{g}^{4} 3 \pi_{u}^{0}$. Excitation in the $185-215 \mathrm{~nm}$ wavelength region causes promotion of an electron from the bonding $2 \pi_{g}$ orbital into the antibonding $3 \pi_{u}$


FIG. 8. Emission spectrum of jet-cooled $\mathrm{CS}_{2}$ photoexcited at $50097 \mathrm{~cm}^{-1}$.


FIG. 9. Emission spectrum of jet-cooled $\mathrm{CS}_{2}$ photoexcited at $50333 \mathrm{~cm}^{-1}$.
orbital. According to the standard Walsh diagram for molecules of the form $A B_{2}$, upon bending, the $\pi_{g}$ orbital splits into an $a_{2}$ and a $b_{2}$ orbital and the $\pi_{u}$ orbital splits to give an $a_{1}$ and a $b_{1}$ orbital. For angles smaller than $180^{\circ}$, the ground $a_{1}$ and excited $b_{2}$ orbitals cross, with the excited $b_{2}$ orbital being lower in energy. It is for this reason that upon excitation, the equilibrium geometry of the excited state of the $\mathrm{CS}_{2}$ molecule is bent. The extended $\mathrm{C}-\mathrm{S}$ bond lengths are a result of the $2 \pi_{g}^{4} \rightarrow 2 \pi_{g}^{3} 3 \pi_{u}^{1}$ transition which implicitly involves an extension in these bonds due to the antibonding character of the excited state.

In addition to the pure symmetric stretching $\left(\nu_{1}\right)$ and bending ( $\nu_{2}$ ) modes observed, combination band of $\nu_{1}$ with $\nu_{2}$ are also observed, but with less intensity than the pure $\nu_{1}$ and $\nu_{2}$ modes. The assignments of bands with over 3000 $\mathrm{cm}^{-1}$ of vibrational energy becomes more difficult because of the higher density of vibrational states, so though we assign a few bands to states with one quantum in the antisymmetric stretching ( $\nu_{3}$ ) mode, we consider these assignments to be more speculative. We do, however, see emission to $2 \nu_{3}$ and various combinations of the $2 \nu_{3}$ mode with the other two modes.

As the excitation wavelength is changed from spectrum to spectrum, we observe dramatic and nonmonatonic


FIG. 10. Emission spectrum of jet-cooled $\mathrm{CS}_{2}$ photoexcited at $50397 \mathrm{~cm}^{-1}$.


FIG. 11. Emission spectrum of jet-cooled $\mathrm{CS}_{2}$ photoexcited at $50447 \mathrm{~cm}^{-1}$.
changes in the relative intensities of the $(1,0,0)$ peak with respect to the $(0,2,0)$ peak. Figure 17 is a graph of the ratio of the integrated intensity of emission into these bands, $2 \nu_{2} / \nu_{1}$, as a function of excitation energy and also as a function of the vibronic assignment, when available, given by Vaida and co-workers. ${ }^{8}$ For excitation energies greater than $49600 \mathrm{~cm}^{-1}$ we plot only intensity ratios from exciting in absorption bands assigned by Vaida and co-workers to the main symmetric stretching and bending progressions. Note that for the lowest three excitation energies the intensity of emission into the bending mode ( $2 \nu_{2}$ ) is greater that the emission into the symmetric stretching mode $\left(\nu_{1}\right)$. For all excitation energies greater than these the ratio drops dramatically, there is less emission into the bending mode than the stretching mode. Although calibrating the intensity of the emission features and weighing them with the absorption intensity is difficult to do reliably between each spectrum, it is clear from a rough analysis that the drop in the $2 \nu_{2} / \nu_{1}$ ratio is due to a decrease in the emission into $2 \nu_{2}$ rather than an increase in $\nu_{1}$. Note that the change in the intensity ratio does not follow the change in the number of quanta in the nominal $\nu_{2}^{\prime}$ vs $\nu_{1}^{\prime}$ modes in the excited state vibronic assignments. ${ }^{8}$ For example, in Fig. 17, there are three points labeled with vibronic assignment $(m+3, n, 0),(m+2, n$


FIG. 12. Emission spectrum of jet-cooled $\mathrm{CS}_{2}$ photoexcited at $50479 \mathrm{~cm}^{-1}$.


FIG. 13. Emission spectrum of jet-cooled $\mathrm{CS}_{2}$ photoexcited at $50518 \mathrm{~cm}^{-1}$.
$+1,0)$, and $(m+1, n+2,0)$, respectively. This assignment would naively suggest that we should observe increasing amounts of emission into $\nu_{2}$ as one excites at the energies at these points. However, as Fig. 17 shows, we do not see the expected increase in the ratio, $2 \nu_{2} / \nu_{1}$. In Sec. V we outline how the observed change in the $2 \nu_{2} / \nu_{1}$ ratio as a function of excitation energy rather results from accessing, at excitation energies greater than about $45500 \mathrm{~cm}^{-1}$, the region of the excited state above the barrier at linear geometry between the two bent equilibrium structures.

Let us now look at the resonant spectra, those in Figs. $1-14$. For the first three excitation energies ( $48868 \mathrm{~cm}^{-1}$, $49270 \mathrm{~cm}^{-1}$, and $49312 \mathrm{~cm}^{-1}$ ) greater intensity is observed in the bending feature $(0,2,0)$ than in the symmetric stretch feature ( $1,0,0$ ). The next two excitation energies (49 662 $\mathrm{cm}^{-1}$ and $49697 \mathrm{~cm}^{-1}$ ) yield spectra where the intensity distribution switches to greater intensity in the symmetric stretch than in the bend. As for the spectra from the remaining nine resonant excitation energies, six $\left(50055 \mathrm{~cm}^{-1}\right.$, $50097 \mathrm{~cm}^{-1}, 50447 \mathrm{~cm}^{-1}, 50479 \mathrm{~cm}^{-1}, 50518 \mathrm{~cm}^{-1}$, and $50555 \mathrm{~cm}^{-1}$ ) show more symmetric stretch than bend and only three ( $49945 \mathrm{~cm}^{-1}, 50333 \mathrm{~cm}^{-1}$, and $50379 \mathrm{~cm}^{-1}$ ) show more bend than stretch. It should be noted that these same three spectra ( $49945 \mathrm{~cm}^{-1}, 50333 \mathrm{~cm}^{-1}$, and 50378


FIG. 14. Emission spectrum of jet-cooled $\mathrm{CS}_{2}$ photoexcited at $50555 \mathrm{~cm}^{-1}$.


FIG. 15. Emission spectrum of jet-cooled $\mathrm{CS}_{2}$ photoexcited at $49849 \mathrm{~cm}^{-1}$ (nonresonant).
$\mathrm{cm}^{-1}$ ), as well as several others here, involve transitions that have not been assigned by Vaida and co-workers as main peaks in the vibronic band of interest, so these will have to be dealt with separately in our discussions. Analysis of the observed intensity change between the progressions in the symmetric stretch and bend mode as a function of excitation wavelength will be discussed in a later section.

## B. $A b$ initio results

Geometry optimization of the ground electronic state was performed using the HF and MP2 levels of theory. The results are listed in Table I. Both levels of theory simulate well the bond angle and bond length to within several percent error. HF level theory produces a bond length of 1.5433 $\AA$, while MP2 corrections yielded a bond length slightly longer at $1.5617 \AA$. This is in comparison to the experimentally determined $\mathrm{C}-\mathrm{S}$ bond length of $1.5562 \AA \AA^{33}$ The bond angle is assumed to be $180^{\circ}$. Changing the basis set from the selected $6-311+\mathrm{G}^{*}$ to an other higher order basis set proved to yield little to no worthy increase in accuracy. Configuration interaction with singles excitation (CIS) calculations were carried out prior to excited state geometry optimizations to see if the GAUSSIAN 94 set of $a b$ initio programs


FIG. 16. Emission spectrum of jet-cooled $\mathrm{CS}_{2}$ photoexcited at $50178 \mathrm{~cm}^{-1}$ (nonresonant).


FIG. 17. Graph of the ratio of emission intensity between $\nu_{2}$ and $\nu_{1}$ as a function of excitation energy and also as a function of vibronic assignment given in Vaida and co-workers' paper (Ref. 8). (Assignments for the first and third excitation energy bands plotted were not given in Ref. 8.) The data in Figs. 1-5, 7, 8, and 11-13 were used for the integrated intensities plotted.
could correctly find an excited state that corresponds to the state of interest in this experiment. The CIS calculations correctly find the electronic transition from a nonbonding $\pi$ orbital with most of the electron density located on each of the sulfur atoms to a $\pi^{*}$ antibonding MO which consists of nodes between each of the sulfur atoms and the central carbon atom. This state was then used to perform an optimization of the excited state molecular geometry. The standard HF geometry optimization technique gave a $\mathrm{C}-\mathrm{S}$ bond length of $1.6803 \AA$, compared to a slightly shorter experimental value of $1.66 \AA^{3}{ }^{3}$ The bond angle was found to be $143.9^{\circ}$ in comparison to the experimental value of $153^{\circ} .^{3}$ The CIS-MP2 geometry optimization yields a slightly shorter C-S bond length of $1.6401 \AA$ and a smaller SCS bond angle of $139.8^{\circ}$.

## V. DISCUSSION

The emission spectra exhibit a large difference in the relative intensity of progressions in the purely symmetric stretching and purely bending eigenstates in the final state.

TABLE I. Geometry optimization of the ground and excited states of $\mathrm{CS}_{2}$ using the GAUSSIAN 94 set of programs with a $6-311+\mathrm{G}^{*}$ basis set and the HF, MP2, CIS, and CIS-MP2 methods. Comparisons with experimentally determined values are made.

| Electronic state | Method | $\mathrm{C}-\mathrm{S}$ bond length | $\mathrm{S}-\mathrm{C}-\mathrm{S}$ bond angle |
| :--- | :--- | :---: | :---: |
| ${ }^{1} \Sigma_{g}^{+}$ | HF | $1.5433 \AA$ | $180.0^{\circ}$ |
| ground state | MP 2 | $1.5617 \AA$ | $180.0^{\circ}$ |
|  | Experiment $^{\mathrm{a}}$ | $1.5562 \AA$ | $180.0^{\circ}$ |
| ${ }^{1} B_{2}\left({ }^{1} \Sigma_{u}^{+}\right)$ | CIS-HF | $1.6803 \AA$ | $143.9^{\circ}$ |
| excited state | CIS-MP2 | $1.6401 \AA$ | $139.8^{\circ}$ |
|  | Experiment $^{\mathrm{b}}$ | $1.66 \AA$ | $153^{\circ}$ |

[^0]This results from a variation in the contribution of each of these motions to the overall vibronic characterization of each of the $\mathrm{CS}_{2}$ excited state resonances in the Franck-Condon region. The observed spectra with progressions in $\nu_{1}$ (symmetric stretch) and $\nu_{2}$ (bend) are generally consistent with a change in molecular geometry upon excitation from the ground to the ${ }^{1} B_{2}\left({ }^{1} \Sigma_{u}^{+}\right)$excited state. Our ab initio calculations of the molecular geometry in the ${ }^{1} B_{2}\left({ }^{1} \Sigma_{u}^{+}\right)$state confirm this conclusion. We now tune across the absorption band and observe the intensity in the emission to $n_{1} \nu_{1}$ and $n_{2} \nu_{2}$, which reveal dynamics relative to the barrier at quasilinear geometries.

Vaida and co-workers ${ }^{8,9}$ showed the peaks in the ultraviolet absorption spectrum could be easily accounted for by a progression in two fundamental frequencies, 392 and 426 $\mathrm{cm}^{-1}$. The $392 \mathrm{~cm}^{-1}$ mode (predominantly stretching) is seen to form the main progression of peaks, with shorter progressions in the $426 \mathrm{~cm}^{-1}$ mode (predominantly bending) in combination with the main $392 \mathrm{~cm}^{-1}$ band of peaks. Using a normal mode basis, they attribute a large amount of symmetric stretching character to this progression of peaks in the absorption spectrum. Rabalais and co-workers ${ }^{4}$ have shown the ${ }^{1} \Sigma_{g}^{+} \rightarrow{ }^{1} B_{2}\left({ }^{1} \Sigma_{u}^{+}\right)$transition is dipole allowed for bending levels above and below the barrier to linearity. A simple Franck-Condon analysis ${ }^{35}$ would then suggest that the most intense transitions from the linear ground state would be to bending levels in the upper state in the region of the linear-to-bent potential barrier. Since there were no observed irregularities in the main progression, they attribute the main band to progressions in mostly symmetric stretching motions. Thus the higher energy, $426 \mathrm{~cm}^{-1}$ bands are assigned to progressions in mostly bending motions. They stress, however, that the near degeneracy of the stretching and bending vibrations implies that each mode will contribute mutually to each of the progressions and that their relative contributions to each peak in the absorption spectrum will differ for transitions above and below the barrier to linearity.

We noted in the results section that our observed emission intensity into the symmetric stretching and bending modes as a function of excitation wavelength do not follow the increase in each of the nominal $\nu_{1}^{\prime}$ and $\nu_{2}^{\prime}$ modes as assigned by Vaida and co-workers in their analysis of the absorption spectrum of $\mathrm{CS}_{2}$. This is not unexpected considering the near degeneracy of the two modes would suggest that each peak in the absorption spectrum would be of mixed character.

We can, however, gain some information from the overall excitation energy dependence of the emission features. If one considers the intensity distributions that we observe as we tune through the major peaks in the $48500-51000 \mathrm{~cm}^{-1}$ band (defined as greater than $10 \%$ of the maximum line at $49697 \mathrm{~cm}^{-1}$ ), we see a propensity for emission into the bending progression for excitation below $49500 \mathrm{~cm}^{-1}$ over that into the symmetric stretching progression; for excitation energies above $49500 \mathrm{~cm}^{-1}$ the intensity of the emission into the bending progression decreases relative to the emission into the symmetric stretch bands (see Fig. 17). We attribute the change in the emission spectrum between 49312
and $49662 \mathrm{~cm}^{-1}$ as spectroscopic evidence of the energetic barrier between the completely bent and quasilinear excited $\mathrm{CS}_{2}$ molecule (see next paragraph). Thus the observed features at $49662 \mathrm{~cm}^{-1}$ is near the barrier at linear geometries, giving the barrier height measured relative to the zero point of the ${ }^{1} B_{2}$ state ${ }^{10}$ (not the minimum of the ${ }^{1} B_{2}$ state) of near $3415 \mathrm{~cm}^{-1}$. Vaida and co-workers, ${ }^{8,9}$ from the analysis of the $K$ structure of the upper state, were able to identify the barrier as being roughly in the $49000 \mathrm{~cm}^{-1}$ region (an energy from the zero-point level in the ground electronic state). They note the increase in the $A$ rotational constant of the $\mathrm{CS}_{2}$ molecule in the higher energy range as evidence for the wavelength position of the bent to quasilinear potential barrier.

Let's analyze how the changes in the relative intensities of the emission into stretching and bending progressions gives an indication of what energy accesses regions above and below the quasilinear potential barrier. Consider the Franck-Condon factors for transitions between the linear ground state and various vibrational wave functions in the excited state with a double minimum at bent geometries. We first assume that the oscillator strength of the ${ }^{1} \Sigma_{g}^{+}$ $\rightarrow{ }^{1} B_{2}\left({ }^{1} \Sigma_{u}^{+}\right)$electronic transition even at linear geometries dominates the absorption, so there is not a strong coordinate dependence of the electronic transition dipole moment. When the $\mathrm{CS}_{2}$ molecule is excited below the upper state barrier to linearity, the Franck-Condon factor, $\left|\left\langle\psi_{v^{\prime}} \mid \psi_{v^{\prime \prime}}\right\rangle\right|^{2}$, is a maximum near the outer turning points of each potential well. Since the turning points are all at bent geometries, there is considerable Franck-Condon overlap with a progression of eigenstates with increasing quanta in the bend in the ground state. Thus the emission spectrum from excitation energies below the barrier should show a strong progression in the bending mode [Note: In Figs. 1-3, intensity in the bend $(0,2,0)$ is comparable to or greater than symmetric stretch intensity $(1,0,0)$.] However, when the excitation energy reaches regions of the potential surface above the barrier to linearity, the excited state vibrational wavefunction in the bend coordinate has considerably more amplitude near linear geometries. Emission from such a wavefunction does not contribute as strongly to the bending progression and so we see the intensity of the progression in the bend decreases as one excites at energies near and above the barrier.

There are two emission spectra that were taken at wavelengths that are nonresonant with peaks in the absorption spectrum. The excitation wavelengths are above the barrier to quasilinear geometry and therefore we should expect much greater symmetric stretch motion than bend motion. In both cases, at 49849 and $50178 \mathrm{~cm}^{-1}$, the intensity of emission to symmetric stretch modes is greater than the emission to the bending modes.

The remaining three spectra taken at excitation wavelengths of 49945,50333 , and $50379 \mathrm{~cm}^{-1}$ are all resonant on very weak ( $<10 \%$ of most intense peak at $49697 \mathrm{~cm}^{-1}$ ) peaks in Vaida's absorption spectrum; they were not included in the data plotted in Fig. 17. These peaks, however, do not fit within the assignment scheme used by Vaida to explain the most intense peaks in their absorption spectrum. In their paper, Vaida and co-workers ${ }^{8}$ note that the weak
features become more numerous in the higher energy range and attribute their appearance to anharmonic coupling of the two nearly degenerate vibrational modes. This anharmonic coupling, or Fermi resonance, ${ }^{34}$ between the two modes serves to distribute the observed intensity within a cluster of vibrational states rather than to either of the pure vibrational modes. It is then not unexpected that the emission spectra from excitation in such weak features could evidence emission into modes with a different intensity pattern than emission from states that correspond to the strong features observed in Vaida and co-workers' absorption studies. Heller et al. ${ }^{36}$ have shown using time dependent semiclassical methods that anharmonic coupling is possible for FranckCondon transitions such as those observed in our experiments.

Preliminary ab initio calculations ${ }^{22,26}$ performed by Hepburn's group show that the ${ }^{1} B_{2}$ excited state is essentially flat in the antisymmetric stretch coordinate and so the two bound coordinates should dominate the spectrum in this energy region. As our results show, the emission from states in this energy region are to both the bound symmetric stretching and bending modes. They note that in order for $\mathrm{CS}_{2}$ to dissociate to give CS and S products, the predissociative ${ }^{1} B_{2}$ state must couple to other directly dissociative surfaces and this is mediated by antisymmetric stretching motion. In fact, in all of our emission spectra, we see low intensity emission into the antisymmetric stretching mode.

## VI. CONCLUSIONS

The emission spectrum of jet-cooled $\mathrm{CS}_{2}$ was recorded in the $48500-51000 \mathrm{~cm}^{-1}$ region in order to identify the character of the excited state or states that make up the electronic transition in this energy region. As our spectra show, Vaida's initial assignment of the absorption spectrum as a progression in the symmetric stretch and bend modes is essentially correct. We observed no evidence of other optically bright electronic states interacting with the initially prepared ${ }^{1} B_{2}$ state in the Franck-Condon region. Preferential emission to bending modes were observed for energies below the barrier to linearity, while preferential emission to symmetric stretch modes were observed near or above the barrier. In addition, we observe further spectroscopic evidence of the barrier between bent and quasilinear excited state geometries along the ${ }^{1} B_{2}$ excited state potential surface.

While important information has been obtained on the relevant motions $\mathrm{CS}_{2}$ experiences upon excitation to the ${ }^{1} B_{2}\left({ }^{1} \Sigma_{u}^{+}\right)$excited state, further work is needed. Especially helpful would be higher level ab initio calculations on the nature of the potential surface or surfaces involved in the photodissociation dynamics. Wavepacket propagation calculations performed upon these surfaces would then help in further explaining the observed emission spectra.

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[^0]:    ${ }^{\text {a/ }}$ Values taken from Ref. 33.
    ${ }^{\mathrm{b}}$ Values taken from Ref. 3.

