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ROTATIONAL DISTRIBUTIONS OF CO FROM THE 193 nm PHOTODISSOCIATION OF BH_3CO USING NONRESONANT FOUR-WAVE MIXING FOR VUV GENERATION

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BH_3CO is photolyzed using an excimer laser operating at 193 nm and the nascent rotational energy distributions in CO $v''=0$ and $v''=1$ are measured by using laser-induced fluorescence of the fourth positive system of CO near 140 nm. The rotational energy distributions in the two manifolds can be characterized by temperatures of 362 ± 22 and 175 ± 8 K, respectively. The tunable VUV is generated using a nonresonant four-wave mixing process in Hg vapor. This technique has enabled us to extend the range of laser-induced fluorescence measurements in the vacuum ultraviolet using a single dye laser.

1. Introduction

Photodissociation of BH_3CO using an ArF excimer laser has recently been used to produce BH_3 [1] and, more surprisingly, BH [2]. Fluence measurements [2], as well as the fact that both BH and BH_2 have been observed in the flash photolysis of BH_3CO [3–5], indicate that the formation of BH results from single-photon absorption. Since the dissociation of BH_3CO to form BH_3 and CO requires only 20.7 kcal/mol [6,7], the fragments likely contain a significant amount of both internal and translational energy. The photon energy at 193 nm is 147.7 kcal/mol and, if a substantial fraction of the 127 kcal/mol excess energy is partitioned into internal degrees of freedom, the BH_3 fragment could unimolecularly decompose to BH and H_2. In order to determine the fragmentation dynamics of this system, a series of experiments aimed at measuring the energy distributions of the fragments was undertaken.

The amount of energy deposited in the BH_3 photofragment is crucial to our understanding of the dissociation process. However, this quantity is difficult to determine experimentally since only transitions from the ground vibrational state have been identified [1]. Weiner and Pasternack [8] have monitored the BH_3 fragment in the $v''=0$ level using a tunable diode laser and have found that the nascent population is small but increases in time over the first 60 µs at 0.5 Torr total pressure with N_2 buffer gas. The rise time decreases to < 5 µs at 2.5 Torr total pressure. This finding supports the assumption that a large fraction of the excess energy is partitioned into internal degrees of freedom in the BH_3 fragment. Additionally, Rice et al. have measured the vibrational and rotational distributions of the BH fragment [2]. They compare their experimental results with prior distribution calculations for both two-fragment (BH_3+CO) and three-fragment ($BH+H_2+CO$) channels. They find that the rotational energy distributions of the BH fragment are nonstatistical for $v''=0$, 1, and 2. The vibrational energy distribution can be fit assuming a two-fragment prior distribution if the energy of the BH_3 fragment is 16 kcal/mol greater than the energy required to dissociate BH_3 to $BH+H_2$ with 28 kcal/mol remaining in translational energy or in CO internal energy. Since there have been no previous studies on the translational energy of the fragments or on the internal energy distribution of the CO fragment, the energy available to the BH_3 or $BH+H_2$ fragments is difficult to determine.

In this paper, we report the nascent rotational energy distribution in CO $v''=0$ and $v''=1$ using laser-

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induced fluorescence (LIF) on the fourth positive system of CO near 140 nm as a probe. In contrast to other studies using LIF to observe CO, we generate tunable VUV using a nonresonant four-wave mixing process in Hg vapor. A brief description of the technique and its advantages will also be given.

2. Experimental

The basic apparatus has been described previously [9,10]. A rare gas halide laser Lambda-Physik EMG 101 MSC) operating on ArF at 193 nm with 30 mJ/cm^2 fluence is used as the photolysis source. A Nd:YAG-pumped dye laser (Quantel Datachrome 5000) with frequency doubling provides both the fundamental and doubled outputs used in the four-wave mixing process. Using rhodamine 6G and DCM dyes, tunable VUV at 139–143 and 154–160 nm can be generated by nonresonant four-wave mixing in Hg vapor via the process $\omega_{UV}+2\omega_L=\omega_{VUV}$, where ω_L is the fundamental dye frequency, ω_{UV} is the frequency of the doubled output, and ω_{VUV} is the VUV output frequency [11]. Both the (collinear) fundamental and doubled output from the dye laser are focused with a lens (300 mm focal length) into the central region of a heated glass cell similar in design to that described by Hilbig and Wallenstein [12]. The central region of the cell is wrapped with heating tape and provides a reasonably uniform concentration of Hg over a 2 cm length. Water-cooled side arms are used to condense the Hg vapor and return it to the central portion of the cell as well as provide inputs for the rare gas necessary for attaining the proper phase matching conditions. Depending upon the wavelength to be generated, typical conditions for optimizing the power of the VUV beam are a partial pressure of Hg of approximately 30 Torr and a partial pressure of Ne of 60–120 Torr. The exact pressure of Ne is determined empirically, using the work of Hilbig et al. [11] as a guideline. At a given pressure of Hg and Ne only a particular VUV wavelength is properly phase matched. This is due to the small but nonnegligible wavelength dependence of the dispersion of Hg in the VUV. However, it is found experimentally that this phase mismatch does not vary appreciably over the gain curve of any one dye and consequently does not adversely affect the conversion efficiency. Typical conversion efficiencies, measured by a solar blind photomultiplier at the exit of a VUV monochromator, are approximately 10^{-5}, corresponding to about 10^{12} VUV photons per pulse. This intensity is sufficient to perform LIF experiments. This technique has the advantage of ease of operation due to the fact that only a single laser is needed to generate the VUV, unlike the more commonly used resonance-enhanced four-wave mixing processes.

After generation of the VUV, all frequencies (ω_L, ω_{UV}, ω_{VUV}, and also difference frequencies generated in the Hg vapor) are transmitted through a MgF$_2$ window attached to the molecular beam chamber. These beams are collinearly counter-propagated with the ArF photolysis beam in the chamber. BH$_3$CO enters the chamber through a commercial pulsed supersonic nozzle (Laser Technics, 1 mm nozzle diameter). The free jet is operated over a variety of conditions with mixtures of from 1% to 5% BH$_3$CO in both He and CO at backing pressures of 1 to 3 atm.

The lasers intersect the free jet at a distance of 17 nozzle diameters. The timing of both lasers and the pulsed valve is controlled by pulse generators. Fluorescence is collected at right angles to the laser beams using a solar blind PMT (EMI G26E314LF) and bandpass filters to discriminate against the doubled dye laser and the ArF laser. A gated integrator (Stanford Research Systems, model 250) is used to process the PMT output and the signal is sent to an IBM PC-AT for averaging, storage and analysis.

BH$_3$CO is synthesized following the method of Burg and Schlesinger [13,14]. A cylinder containing B$_2$H$_6$ at 3000 Torr and CO at 10000 Torr is heated to 100°C for several hours. BH$_3$CO is collected at liquid nitrogen temperature, separated from any remaining B$_2$H$_6$ at −160°C, and stored at 77 K. In CO, BH$_3$CO lasts several days, but in He it decomposes on the stainless steel tubing and pulsed nozzle within a few hours.

3. Results

We monitor the CO A $^1\Pi$–X $^1\Sigma^+$ (4, 0) band at 141.9 nm and (5, 0) band at 139.1 nm. Due to the decomposition of BH$_3$CO, CO in its ground vibrational state is always present in our experiments.

However, only low rotational levels are populated in the beam. When the excimer laser photolyzes the BH_3CO, CO in high rotational levels is produced. A semilog plot of the intensity of the higher rotational lines ($J \geqslant 9$) as a function of rotational energy for the (4, 0) band is shown in fig. 1. For $J \geqslant 9$, the intensity of the CO from photolysis is much greater than the intensity of the background CO. The intensities of the P, Q and R lines are measured and corrected for the Hönl–London factors, S_J. Since the probe laser is fired 90 ns after the photolyzing laser, this distribution represents the nascent population in CO ground state. It can be characterized by a temperature of 362 ± 22 K ($\pm 2\sigma$). Perturbations in the A $^1\Pi$ $v = 4$ level have been observed only in rotational levels higher than those measured in this study and therefore are not expected to significantly affect our results.

We also measure the CO A $^1\Pi$–X $^1\Sigma^+$ (6, 1) band at 140.9 nm. A typical spectrum taken 70 ns after the photolyzing laser is shown in fig. 2. A Boltzmann plot of the nascent CO rotational distribution is shown in fig. 3. It can be characterized by a temperature of 175 ± 8 K ($\pm 2\sigma$). Although the A $^1\Pi$ $v = 6$ level is perturbed [15], only a few rotational lines in the region we measure ($J = 1$–16) have been observed to be affected by perturbations. We see no systematic error in the rotational distribution introduced by these perturbed levels. We are unable to observe any transitions of CO from vibrational levels higher than $v'' = 1$ in these experiments.

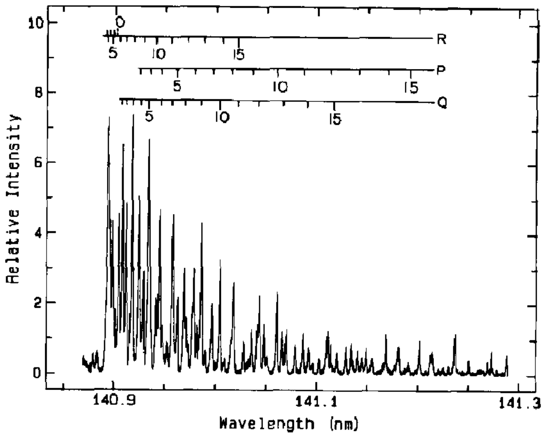

Fig. 2. Spectrum of the CO A $^1\Pi$–X $^1\Sigma^+$ (6, 1) band measured 70 ns following 193 nm photolysis of BH_3CO.

We also observe several bands which we cannot identify. At short delay time (70 ns), there is considerable structure underlying the higher rotational lines of the (6, 1) fourth positive band as can be seen in fig. 2. The intensity of these lines is 5–15% of the largest fourth positive lines. We are unable to spectroscopically identify all these lines, although several

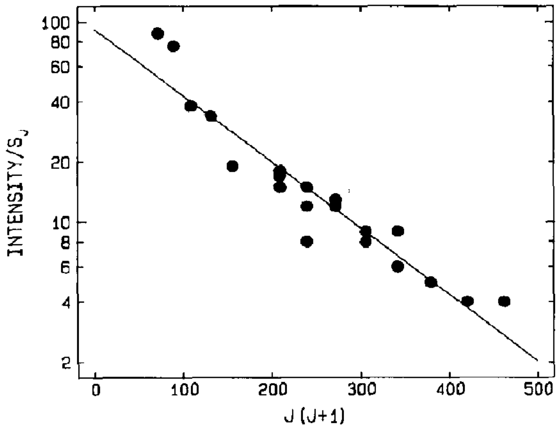

Fig. 1. Semilog plot of the intensity of the CO $v'' = 0$ rotational lines corrected for the Hönl–London factors, S_J, measured 90 ns following 193 nm photolysis of BH_3CO. The solid line is a linear least-squares fit to the data and corresponds to a Boltzmann temperature of 362 ± 22 K.

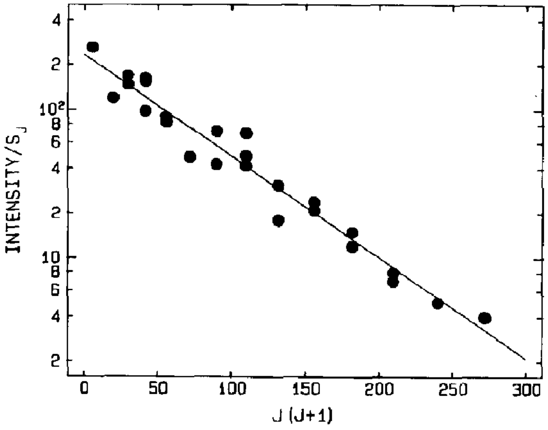

Fig. 3. Semilog plot of the intensity of the CO $v'' = 1$ rotational lines corrected for the Hönl–London factors, S_J, measured 70 ns following 193 nm photolysis of BH_3CO. The solid line is a linear least-squares fit to the data and corresponds to a Boltzmann temperature of 175 ± 8 K.

of them may be the extra lines in the A $^1\Pi$ $v=6$ level which have previously been observed [15] and identified as due to perturbations. They are too intense to be due to the isotopic ^{13}CO (6, 1) fourth positive band. They are produced by the photolysis laser and are only observed at short times (<2 μs) after the photolysis laser so they cannot be due to a forbidden transition from ground state CO. Several other unidentified bands exhibit different temporal behavior than the CO and they are optimized using different operating conditions of the Hg vapor cell. These other bands occur near 140.7 and 157.0 nm. They are observed immediately following the photolysis pulse. At short times (<1 μs) the 140.7 nm band is of greater intensity than the CO (6, 1) band of the fourth positive system. However, at longer times, the CO lines are more intense. We have been able to rule out ground state CO, HCO, H_2CO or BH as the origin of these bands. We attempted to determine if they were due to BH_3. We photolyzed B_2H_6 at 193 nm which has a quantum yield of 2.0±0.25 to form BH_3. We were unable to observe any of the unidentified lines.

Under our experimental conditions using a metal vapor to produce tunable vacuum UV light, we not only generate the fourth harmonic of the dye laser, but under different conditions we have observed laser-induced fluorescence in CO due to absorption of the fifth harmonic. It is also possible to generate the third harmonic. As note above, we do not separate these wavelengths, so the unassigned lines which we observe may be due to any of these frequencies. Further experiments using nonresonant frequency tripling, where no such ambiguity exists, are planned to resolve this problem.

4. Discussion

Photolysis of BH_3CO at 193 nm forms BH_3+CO with 127 kcal/mol excess energy. This is the predominant photolysis channel [#1]. The maximum energy available to the products of the photolysis depends on the electronic state in which the products are formed. The nascent electronic state for the BH_3 fragment is unknown since there exists no definitive spectroscopic information on excited electronic states of BH_3, although recently Harrison et al. [17] have tentatively assigned two BH_3 electronic states. The CO appears to be formed solely in its ground electronic singlet state. We do not observe any CO in triplet states. We do observe chemiluminescence from the photolysis, most likely due to electronically excited BH which energetically requires the absorption of two photons of 193 nm radiation. It is not known if BH is formed from excited BH_3 or if it is a direct product of the photodissociation [2].

We do not observe CO vibrational excitation into levels higher than $v''=1$. This may be due to discrimination of the band pass filters. From these experiments, it is not possible to determine the relative populations of $v''=0$ and $v''=1$ levels of CO since the $v''=0$ level is always present due to decomposition of BH_3CO. If we assume that the full photolysis exoergicity is available to be statistically partitioned among the products, excitation into higher vibrational levels would be expected [18]. However, since in BH_3CO the bond length of CO is very similar to that in free CO, a Franck–Condon model [19,20] for determining the vibrational energy distribution predicts a very low ratio of population in $v''=1/v''=0$. Using this model, $v''=1$ would be unobservable under our experimental conditions. Experiments are currently in progress in our laboratory to better characterize the energy disposal in the BH_3CO photolysis.

From the experiments reported in this paper, it can be seen that there is little rotational excitation in the CO fragment. In CO $v''=0$ rotational excitation accounts for less than 1 kcal/mol of the available energy and in CO $v''=1$ it accounts for less than 0.5 kcal/mol. Statistical theories would predict much greater rotational excitation [18]. The observation of different rotational distributions in the two vibrational levels is surprising. If a single photodissociative state is accessed, one would expect identical rotational distributions determined solely by the kinematics involved in the photodissociation process. Multiple photodissociation channels, contributions from two-photon dissociation, and curve crossing are all possibilities for this observation. Further theoretical and experimental work is required in order to determine the source of this difference.

[#1] In ref. [16] it is shown that $\phi_{BH_3}>0.7$ for the 193 nm photolysis of BH_3CO.

The experiments reported in this paper represent the first application of the nonresonant sum-frequency mixing technique for generating tunable VUV radiation. This technique has enabled us to extend the range of laser-induced fluorescence measurements. Using this process, the region from 130 to 180 nm is easily accessible with intensities of $\approx 10^{12}$ photons/pulse. Because of the ease with which these wavelengths can be generated and the broad tunability, this is an attractive technique for spectroscopy and photofragment studies.

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