Photodissociation of XeF$_2$ at 193 nm

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The absorption coefficient of XeF₂ has been measured at 193, 206, and 253 nm. The measurements have been compared with those of Black et al. and Jortner et al. The present measurements of XeF₂ absorption at 193 and 253 nm appear to resolve the discrepancy in those absorption measurements. Adjusting the data of the two previous investigations to match our values at these two wavelengths brings the two sets of measured absorption coefficients into agreement in the overlapping wavelength interval, 203 to 210 nm. We determined experimentally that one molecule of XeF₂ is dissociated for each photon absorbed at 193 nm.
CONTENTS

I. INTRODUCTION ........................................................... 5

II. EXPERIMENTAL MEASUREMENTS ........................................... 7

   A. ABSORPTION BY XeF₂ .................................................. 7

   B. OMA MEASUREMENTS OF XeF(B) EMISSION .......................... 15

III. DISCUSSION AND SUMMARY .............................................. 19

REFERENCES ..................................................................... 21
FIGURES

1. Schematic of measurement apparatus ........................................ 8
2. Plot of XeF₂ absorption versus XeF₂ pressure .......................... 10
3. Plot of XeF₂ absorption at 206 nm versus XeF₂ density ............ 12
4. Plot of XeF₂ absorption at 206 nm versus XeF₂ density ............ 13
5. Photolysis laser power measurement for quantum yield experiment .................................................. 14
6. Measured and calculated cell pressures versus time in quantum yield experiment .................................................. 16
7. XeF(B) emission spectrum from the photolysis of XeF₂ at 193 nm .................................................. 17
8. The XeF(B) emission spectrum of Fig. 7 with the underlying continuum subtracted .................................................. 18
I. INTRODUCTION

Interest in the spectroscopy of xenon difluoride (XeF\textsubscript{2}) has been stimulated by the xenon fluoride (XeF) laser, which operates on the B-X transitions at 351 and 353 nm and the C-A transitions at 483 nm. The vacuum ultraviolet (VUV) photolysis of XeF\textsubscript{2} can be used either to obtain laser action on these transitions or to produce the several electronic states of XeF for kinetic studies. The XeF\textsubscript{2} photodissociation laser has been pumped by UV sources, such as discharges initiated by exploding wires,\textsuperscript{1,2} UV radiation emitted by Xe\textsubscript{2} excited by an electron beam,\textsuperscript{3,4} and sliding surface discharges.\textsuperscript{5-7}

Modeling the performance of the XeF laser, whether the laser is E-beam pumped, electric-discharge pumped, or photolysis pumped, requires rate coefficients for the kinetic processes that produce and remove the vibronic levels of the upper electronic state (the B\textsuperscript{2}Σ\textsuperscript{+} state and the coupled C\textsuperscript{2}Π\textsuperscript{+} state) and the lower state (X\textsuperscript{2}Σ\textsuperscript{+},v\textsuperscript{\prime}). The UV photolysis of XeF\textsubscript{2} is a convenient method of producing both the B state and the X state of XeF for kinetics studies of the required rate coefficients. B-state kinetic studies have been reported by Eden and Waynant,\textsuperscript{8,9} Brashears et al.,\textsuperscript{10,11} Black et al.,\textsuperscript{12} and Helm et al.\textsuperscript{13}

The photolysis of XeF\textsubscript{2} with a 15-nsec ArF excimer laser pulse at 193 nm can produce electronically excited XeF(B), which decays with a 14-nsec lifetime\textsuperscript{8} to the ground electronic state, XeF(X,v). It can also produce XeF(X,v) directly. Photolysis of XeF\textsubscript{2} was used by both Fulghum et al.\textsuperscript{14,15} and Bott et al.\textsuperscript{16} in studies of the dissociation and vibrational relaxation of the ground electronic state of XeF. In designing such experiments, it is helpful to know both the absorption coefficient of XeF\textsubscript{2} and the quantum yield of the products.

Black et al.\textsuperscript{12} measured the absorption coefficient of XeF\textsubscript{2} between 145 and 210 nm and the quantum yield between 145 and 175 nm. Jortner et al.\textsuperscript{17} measured the absorption coefficient from 203 to 280 nm. The present study was directed to resolving the discrepancy in the previous two sets of
measurements in the overlapping region of 203 to 210 nm and to determining the absorption coefficient at 193 nm, the wavelength of the ArF laser used in several kinetic studies. The quantum yield for the dissociation $\text{XeF}_2$ was also measured at 193 nm.
II. EXPERIMENTAL MEASUREMENTS

A. ABSORPTION BY XeF₂

A schematic of the experimental apparatus is shown in Fig. 1. The main elements include a flow cell and gas handling system, a Lambda Physik excimer laser (ArF), a Bausch and Lomb 1/4-m monochromator, a photomultiplier, a Stanford Research Systems model SR 250 boxcar averager, and a DEC 11/23 computer for data acquisition and storage. The experimental apparatus are also described in Ref. 16.

Room temperature measurements were made in a 5-cm-diam flowtube of stainless steel and two sections of anodized aluminum. The flowtube is more accurately described as an absorption cell through which gas flows slowly to replenish the photolyzed XeF₂. Flow velocities of 2.5 to 5 cm/sec are controlled by a throttle valve just downstream of the flowtube and an upstream needle valve. The stainless steel was coated with Teflon to reduce the loss of XeF₂ to the walls. Suprasil windows mounted in aluminum and brass window holders define the length of the cell to be 75 cm. A stainless steel mixing vessel holds XeF₂ crystals at their vapor pressure, which is about 4.4 Torr at 298 K. Baratron gauges measure the pressures in the flowtube and in the XeF₂ reservoir, and thermocouples measure the temperature of the absorption cell.

A second flowtube designed for studies at elevated temperatures is a straight copper tube with window flanges on the ends and inlet and outlet ports for the gas flow. Thermocouples are located at the two ends and in the middle of the flowtube. The copper tube is wrapped with heating tape and insulation to permit elevated-temperature studies. The distance between the windows is 59.7 cm, although extensions to the tube permit heating outside the windows to ensure a uniform temperature in the flowtube.

The Lambda Physik excimer laser produces 15-nsec pulses with energies of about 100 mJ when lasing on ArF at 193 nm. However, atmospheric
Fig. 1. Schematic of measurement apparatus.
absorption and losses in the optical train attenuate the energy by about a factor of 2, even though the path is partially flushed with nitrogen. The beam is compressed by a factor of 2 with a telescope and turned 90° with a front-surface dielectric mirror. A 10-mm-diam aperture cuts off the edges of the 6- × 12-mm beam. An energy per pulse of about 40 mJ is delivered to the window of the flowtube for photolyzing XeF₂.

Experiments were performed to determine the spectral absorption coefficients of XeF₂ at 193 nm, the wavelength of the ArF laser, and at 253 nm. The ArF laser beam was apertured to 1 mm diam, attenuated a factor of 30° by neutral-density filters, and monitored with silicon photodiodes before and after passing through the absorption cell. Also, the telescope was removed from the optical train. Beam splitters reflected only a small fraction of the beam to the photodiodes to avoid saturating the photodiode signals. The photodiode signals were sent to separate channels of a Stanford Research Systems model SR 250 boxcar averager, whose outputs were recorded with the DEC 11/23 computer. The absorption in the cell could be calculated from changes in the ratio of the attenuated signal to the reference signal.

A collimated beam from a deuterium lamp was passed in the opposite direction, filtered with a Hg line UV interference filter, and monitored with an RCA 1P28 photomultiplier. The photomultiplier signal was amplified and recorded with the computer. The absorption at 253 nm could be recorded simultaneously with the absorption at 193 nm to improve the accuracy of the absorption coefficients relative to each other. Measurements were recorded for XeF₂ pressures between 0.143 and 1.24 Torr; the data are shown in Fig. 2. From these data and a cell length of 75 cm we calculated an absorption coefficient at 193 nm of 0.0262 (Torr-cm)^{-1} and an absorption cross section of 7.9 × 10^{-19} cm². We obtained a value of 8.0 × 10^{-20} cm² for the absorption cross section at 253 nm.

We measured the absorption coefficient of XeF₂ at 206 nm in a separate experiment in the 59.7-cm-long copper flowtube. The wavelength of 206 nm lies in the 203- to 210-nm spectral range for which both Black et al.¹² and
Fig. 2. Plot of XeF\(_2\) absorption [-\(\ln(\text{transmission})\)] versus XeF\(_2\) pressure.
Jortner et al.\textsuperscript{17} reported absorption coefficients. The emission from a deuterium lamp was filtered with a 206-nm interference filter and passed through the flowtube to a Bausch and Lomb 1/4-m monochromator and photomultiplier. For this measurement, a chopper was placed in front of the deuterium lamp, and the photomultiplier signal was amplified with a PAR lock-in amplifier. With the flowtube initially evacuated and the XeF\textsubscript{2} reservoir pumped down to its vapor pressure, a low-pressure flow through the flowtube was established. Both the pressure in the flowtube and the photomultiplier signal were recorded by the computer with a 12-bit A-to-D converter. Once the throttle valve was shut the pressure rose to 1.4 Torr in about 1 min. Figure 3 shows the natural logarithm of the transmission plotted versus the pressure, reduced to XeF\textsubscript{2} number density for the temperature of 21°C. From the slope of the data and the 59.7-cm length of the cell, we calculated an absorption coefficient of $2.56 \times 10^{-19}$ cm\textsuperscript{2}. These measurements were repeated with the flowtube heated to 81°C, and a somewhat larger value, $2.96 \times 10^{-19}$ cm\textsuperscript{2}, was obtained from the data of Fig. 4.

When XeF\textsubscript{2} was isolated in the copper flowtube for 8 min, the absorption decreased 5% or less. This extrapolates to an exponential decay time of 160 min for the XeF\textsubscript{2} density. In contrast, the XeF\textsubscript{2} had a lifetime of about 12 to 15 min in the Teflon-coated stainless steel and aluminum flowtube.

The absorption coefficient and the quantum yield of the photolysis products are of importance to the design of an experiment based on the photolysis of XeF\textsubscript{2}. We measured the quantum yield of dissociation products per absorbed photon in the following way. The copper flowtube was filled with XeF\textsubscript{2} to a pressure of 1.34 Torr and isolated with the valves. The ArF laser was used to photolyze the XeF\textsubscript{2}, and the pressure in the flowtube was monitored with the Baratron gauge. The energy of the photolysis pulses was monitored with a Laser Precision energy meter; it was calibrated in situ and recorded a measured fraction of the total pulse energy at the entrance to the cell. The energy per pulse is plotted versus time in Fig. 5 for two sequences. Note the break in the laser power at 700 sec and its slow
Fig. 3. Plot of XeF$_2$ absorption [-ln(transmission)] at 206 nm versus XeF$_2$ density.
\[ T = 81^\circ \text{C} \]
\[ \text{SLOPE} = 1.768 \times 10^{-17} \]

Fig. 4. Plot of XeF\(_2\) absorption [-ln(transmission)] at 206 nm versus XeF\(_2\) density.
Fig. 5. Photolysis laser power measurement for quantum yield experiment.
recovery. The fraction of the laser pulse absorbed by the XeF$_2$ depends on the partial pressure of XeF$_2$ and its cross section at 193 nm. We have modeled this photolysis sequence using our measured cross section of $7.9 \times 10^{-19}$ cm$^2$ and the assumption that the absorption of one photon results in the removal of one XeF$_2$ molecule, leading ultimately to the formation of one Xe and one F$_2$. The photolysis of XeF$_2$ can produce XeF in the B state as well as in the X state. However, radiative decay of the B state to the X state occurs in about 14 nsec. The X state of XeF dissociates to Xe + F in a few microseconds. The F atoms recombine on the walls to form F$_2$. The result of these processes is that two molecules are produced for each molecule dissociated, with an accompanying increase in pressure. Our calculated pressure profile for the laser sequence in Fig. 5 is shown in Fig. 6, along with the measured pressure history. The excellent agreement of the calculated and measured pressure histories justifies the assumption of the 100% yield of dissociated XeF$_2$ per photon absorbed.

B. OMA MEASUREMENTS OF XeF(B) EMISSION

We have recorded the B-state emission spectrum with an optical multi-channel analyzer (OMA). The spectrum obtained from low-pressure photodissociation of XeF$_2$ at 21°C is shown in Fig. 7. The spectrum exhibits banded structure on top of an underlying continuum. The continuum may result from transitions from the B state to unbound states above the dissociation limit of the ground state. Figure 8 shows the spectrum with the continuum subtracted, leaving only the banded emission features. Integrations of the banded spectrum and the underlying continuum indicate that 10% of the B-state emission goes to the bound vibrational levels of the ground electronic state and 90% goes to unbound levels. Therefore, the quantum yield of bound states of XeF(X,v) via the B state is rather small.
Fig. 6. Measured and calculated cell pressures versus time in quantum yield experiment.
Fig. 7. XeF(B) emission spectrum from the photolysis of XeF$_2$ at 193 nm.
Fig. 8. The XeF(B) emission spectrum of Fig. 7 with the underlying continuum subtracted.
III. DISCUSSION AND SUMMARY

In Ref. 12, Black et al. plot absorption coefficients of XeF$_2$ that they and two other groups measured between 142 and 280 nm. Measurements between 142 and 210 nm by Black et al. overlap measurements reported by Jortner et al. between 203 and 280 nm, but they disagree by a factor of 2.4 in the region of overlap. Our measurement of 0.0262 (Torr-cm)$^{-1}$ or $7.9 \times 10^{-19}$ cm$^2$ at 193 nm is approximately 32% larger than the value of $6.0 \times 10^{-19}$ cm$^2$ measured by Black et al. Likewise, our value of $2.56 \times 10^{-19}$ cm$^2$ at 206 nm is 34% larger than their value of $1.87 \times 10^{-19}$ cm$^2$. On the other hand, our value of $8.0 \times 10^{-20}$ cm$^2$ at 253 nm is less than the value of $1.6 \times 10^{-19}$ cm$^2$ reported by Jortner et al. When both sets of data in Ref. 12 are scaled to agree with our three data points they agree in the region of overlap. This agreement appears to suggest that the difficulty of measuring the partial pressure of XeF$_2$ accounts for the systematic source of the discrepancy in the previously reported data. It should be noted that the absorption coefficients of Jortner et al. plotted in Ref. 12 were recalculated by Black et al. on the basis of the vapor pressure data of Schreiner et al.

Our XeF$_2$ absorption coefficient measured at 206 nm had a value of $2.56 \times 10^{-19}$ cm$^2$ at 21°C and a 16% larger value of $2.96 \times 10^{-19}$ cm$^2$ at 81°C. This 16% increase with temperature may indicate the presence of hot band absorption by XeF$_2$; however, a more complete temperature study is required before conclusions can be drawn.

In the present studies we determined that the absorption of a 193-nm photon leads to the removal of one molecule of XeF$_2$. We cannot state, however, the fraction of XeF molecules produced in the B state or the X state. The energetic threshold for the production of the B state is 204 nm. Therefore, a photon at 193 nm has sufficient energy to produce XeF(B) with 2790 cm$^{-1}$ of vibrational/rotational energy, which corresponds to a vibrational level of about $v = 9$ in the B state. Black et al. reported the B-state quantum yield for the photolysis of XeF$_2$ to be
0.9 (+0.1,−0.2) between 146 and 172 nm. They estimate, however, that the quantum yield of the B state at 193 nm is less than 1%. Bibinov et al. have also reported a quantum yield of about 0.8% at 193 nm. Although their quantum yield measurements are significantly lower than those of Black et al. in the important range of 142 to 175 nm, both groups report low quantum yields of the B-state for 193-nm photolysis.

We recorded, with an optical multichannel analyzer, the emission from the B state following the photolysis of XeF₂ at 193 nm. The OMA measurements indicate that only 10% of the B state radiates to the bound vibrational levels of the ground state, and the other 90% radiates to unbounded levels above the dissociation limit. Therefore, even if the dissociation products of Xe and F atoms are not produced directly by the XeF₂ photolysis, they are produced subsequently by the radiative decay of the B state to the unbound states, which dissociate rapidly.

In summary, the present measurements of the XeF₂ absorption at 193 and 253 nm appear to resolve the discrepancy in the absorption measurements plotted in Fig. 1 of Ref. 12. Adjusting the data in that figure to match our values at these two wavelengths brings the two sets of measured absorption coefficients into agreement in their overlapping wavelength interval. We determined experimentally that the absorption of one photon at 193 nm leads to the dissociation of one XeF₂ molecule.
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