

ArF laser photolysis of OCSe. II. Effect of vibrational excitation on Se(¹S) quantum yields

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The dependence of Se(¹S) production on the vibrational excitation of the parent molecule OCSe by a CO₂ laser operating at 10.6 μm has been examined for a photolysis wavelength of 193 nm produced by an ArF laser. Measurements of the absorption cross section for several CO₂ laser lines as well as a determination of the infrared energy deposition for the P(34) and P(44) transitions have been made. A vibrationally induced enhancement of 25% in the Se(¹S) concentration has been observed and is interpreted as resulting from a vibrationally induced increase in the UV absorption coefficient.

INTRODUCTION

It is now clearly established¹ that photolytically produced electronically excited fragments such as group VI atoms (in the ¹S electronic state) are attractive candidates for a laser fusion source. For example, lasing has recently been demonstrated on the electric dipole forbidden transitions (¹S → ¹D) and (¹S → ³P) in atomic selenium.² Implementation of such a system requires optimization of the production of these metastable atoms. In particular, it might be desirable to shift the peak of the quantum yield curve to longer wavelengths where the constraints arising from photolytic sources and optical materials are considerably relaxed.

One problem confronting the photolysis system described in Ref. 1 is that the photolytic light source, in addition to generating the ¹S state, may also remove it by photoionization. Further, the electrons produced by this mechanism have been shown to efficiently quench the ¹S state.³ These effects arise when the photolysis wavelength is below the ionization threshold for the ¹S atom [131.5, 162.9, and 177.8 nm for O(¹S), S(¹S), and Se(¹S), respectively]. An obvious solution to the photoionization problem is to use a photolysis wavelength longer than the photoionization threshold. Moving to longer wavelengths may also allow the use of the efficient rare gas halide lasers for photolysis. Unfortunately, this generally results in a low photodissociation quantum yield—in the case of 193 nm (ArF laser) photolysis of OCSe, the Se(¹S) quantum yield⁴ is ~30%. Therefore, in this paper, we examine mechanisms which are able to modify the UV absorption/dissociation process, possibly leading to higher quantum yields at larger wavelengths. One method of accomplishing this is to mode selectively vibrationally excite the ground electronic state of the donor molecule.

Vibrational excitation of ground state molecules has been shown to be effective in modifying their visible and ultraviolet electronic absorption profiles.⁵⁻⁷ The factors that can contribute to this modification are illustrated in Fig. 1 and are described as follows.

(1) The addition of the infrared excitation quantum allows a small red shift in the UV quantum (δ in Fig. 1).

(2) The position of the vibrating molecule on the electronic energy surface is shifted from the ground position, resulting in altered Franck-Condon factors (Δ' in Fig. 1).

(3) Bending vibrations can lower the symmetry of a polyatomic molecule; thus, transitions that are symmetry forbidden in the ground configuration are allowed in the distorted molecule. (The strong 2600 Å absorption in benzene is a good example of this phenomenon.⁸) Moreover, energy surfaces that cross adiabatically at the higher symmetry may avoid crossing when the symmetry is lowered; the avoided crossing can then give rise to changes in the photolytic yield of a desired fragment (Δ in Fig. 1).

These mechanisms could allow the efficient operation of a photodissociation laser system at longer photolysis wavelengths.

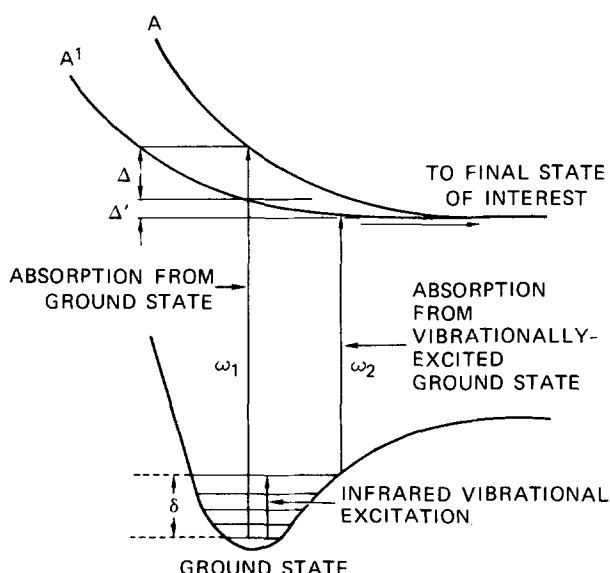


FIG. 1. Schematic diagram of the effects of vibrational excitation on the UV absorption process. State A is the state involved in the symmetry allowed transition from the ground state while A' is the state involved in the vibrationally induced transition.

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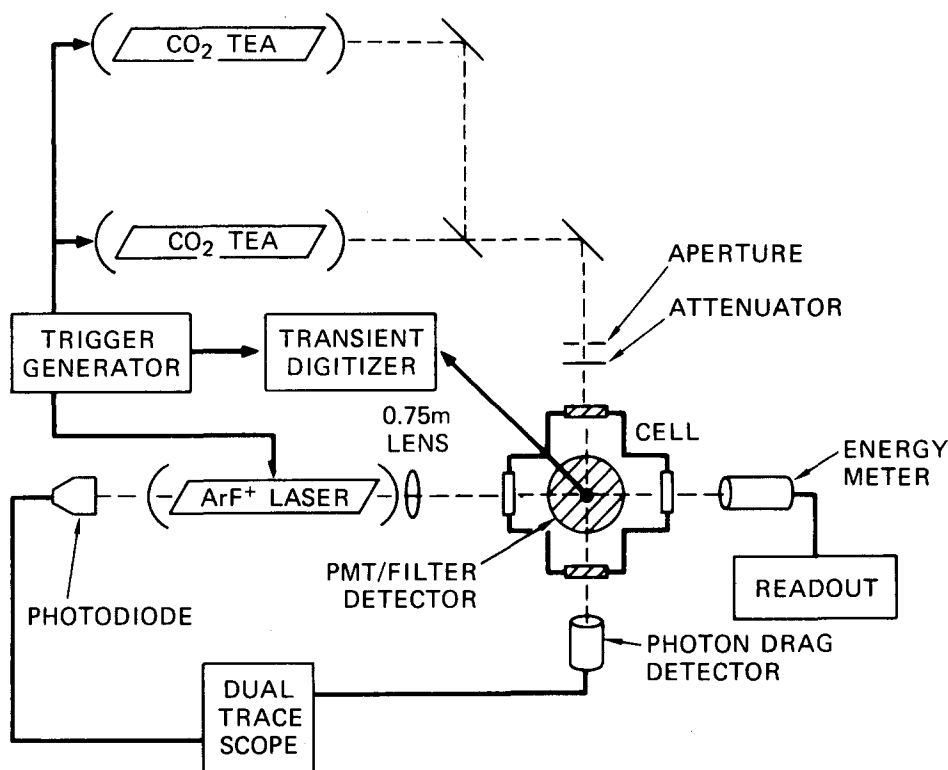


FIG. 2. Apparatus for the detection of vibrationally enhanced quantum yields in OCS_e.

The photolysis of OCS_e at 193 nm by the ArF laser was the subject of the preceding paper.⁹ In this paper, we extend that work to describe the effect of vibrational excitation of the ν_2 mode of OCS_e on the quantum yields of Se(¹S).

EXPERIMENT

The experimental arrangement was similar to the one used previously to study the effect of vibrational excitation on S(¹S) production from OCS⁷ and is shown in Fig. 2. A transverse-electric-discharge-pumped ArF laser (Lambda Physik) was focussed by a 3/4 m lens into a six-port experimental cell. Typically, laser energies between 1–30 mJ in a 15 nsec pulse were incident in the cell. The cell was fitted with reentrant windows to allow the possibility of examining the effect of bleaching at 193 nm. Due to the weak focussing, the beam area in the observation volume was approximately 0.2 cm². A series of attenuators could be inserted in the ArF beam before the cell and the intensity was monitored using a CaF₂ beam splitter and a Laser Precision energy meter.

The fluorescence detection apparatus is comprised of a RCA C31034A photomultiplier/filter system and is similar to the one described in the preceding paper. One modification which has been made is to use a slot aperture to limit the viewing region to a volume which is homogeneously excited by the ArF laser. Although this reduced the fluorescence signal intensities by a factor of 50 from those reported in the preceding paper, signal/noise ratios were still greater than 10:1 for the data reported here.

The two CO₂ lasers used in the experiments were grating-tuned Lumonics 103 TEA lasers. The experi-

ments described here were performed at typical laser energies of 350 mJ (0.5 cm²) in a long 1 μ sec pulse with a 150 nsec dump spike. The two CO₂ beams with perpendicular polarizations were combined in a ZnSe Brewster angle beam combiner, passed through a variable aperture, and entered the cell through a ZnSe window at right angles to both the ArF laser beam and the detector optics. The lasers were triggered by pulses from a four-channel variable delay generator (California Avionics), which also triggered the detection apparatus. The timing of the lasers was monitored by simultaneously displaying the outputs of a photon drag detector for the IR beams and a Hamamatsu R617U photodiode for the UV laser on an oscilloscope (Tektronix 7844). This apparatus allowed us to vary the synchronization of the laser beams in steps of \sim 100 nsec (the timing jitter of ArF laser).

The infrared spectrum of OCS_e has not been studied in detail. Low resolution IR spectra have been taken by Bavia *et al.*¹⁰ which indicate that the 0–2 ν_2 overtone band, analogous to that observed in OCS,¹¹ occurs at 927.1 cm⁻¹. The ground state rotational constants ($B = 0.134$ cm⁻¹) have been derived from the microwave absorption data of Strandberg *et al.*¹² From these data, we can qualitatively predict which vibrational levels in OCS_e will be populated by the CO₂ laser at 10.6 μ m. These levels are indicated in Fig. 3. Clearly, there is a need for a high resolution study of the vibrational bands of OCS_e.

In order to predict the amount of vibrational excitation obtainable under excitation by a pulsed CO₂ TEA laser, we measured the absorption coefficient for several cw CO₂ laser lines near 927 cm⁻¹. These data are shown

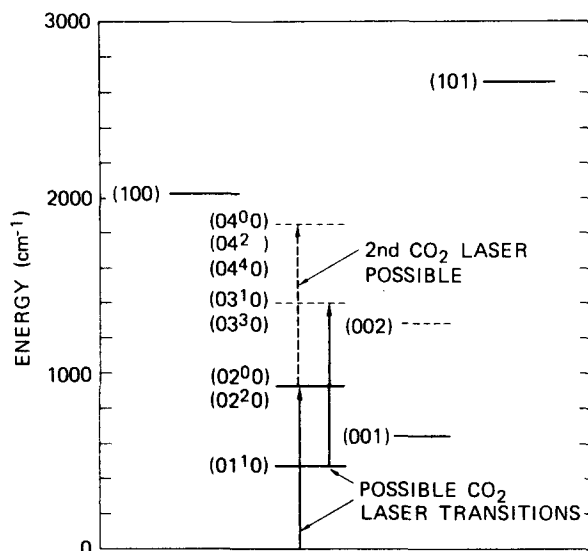


FIG. 3. Vibrational levels in OCSe below 3000 cm^{-1} . The black lines are the observed level positions from Ref. 10. The dotted lines are the approximate positions of vibrational levels whose position could be determined using the methods of Ref. 11.

in Fig. 4. Note that the band origin occurs at 927 cm^{-1} with both *P* and *R* branches as expected. Maximum absorption was observed on the *P*(34) and *P*(44) $10.6 \mu\text{m}$ CO_2 lines. Using the ground state rotational constant of $B = 0.134 \text{ cm}^{-1}$, we estimate that the *P*(34) absorption corresponds to a ground state rotational quantum number of $J \approx 14$ whereas the *P*(44) would correspond to $J \approx 23$. We can estimate the absorption cross section (σ) from¹³

$$\sigma = \ln\left(\frac{I}{I_0}\right) / -N_0 f_J L, \quad (1)$$

where f_J is the fraction of the population *NO* in the level *J* and is equal to $f_J \approx (\hbar B/kT) (2J+1) \exp[-\hbar B J(J+1)/kT]$, *L* is the absorption length, and I/I_0 is the ratio of the transmitted to incident laser intensity. For the above rotational line and the parameter given in Fig. 4, we find that $\sigma(P34) \sim 7 \times 10^{-18} \text{ cm}^2$ and $\sigma(P44) \sim 4 \times 10^{-18} \text{ cm}^2$. From these cross sections, we can estimate a laser intensity necessary to saturate the transition of $I_0 \sim 10^4 \text{ W/cm}^2$, a value consistent with unfocussed CO_2 TEA lasers. The *P*(34) and the *P*(44) CO_2 laser lines were used in the subsequent experiments.

Since the number of vibrationally excited molecules is of primary importance in the interpretation of the combined UV/IR experiment, we have made energy deposition measurements for different OCSe/rare gas mixtures at the high CO_2 TEA laser intensities used in the combined beams experiments. These experiments were done in a 2.8 m absorption cell using a Laser Precision energy meter/ratio-meter to measure the fraction of the light absorbed in the gas. With this apparatus, we measured an energy deposition of $0.5 \pm 0.25 \text{ CO}_2$ quanta/molecule and 0.30 ± 0.15 quanta/molecule for the *P*(44) and *P*(34) lines, respectively. These measurements were taken at an OCSe pressure of 0.5 Torr and a peak CO_2 laser intensity of 2 MW/cm^2 . The addition

of 250 torr Xe buffer gas did not change this value by more than 10%.

In the final stage of these experiments, the ArF and CO_2 lasers irradiated the OCS sample synchronously, allowing us to study the effect of OCS(ν_2) vibrational excitation on $\text{Se}^{\text{I}}\text{S}$ production and fluorescence. One of the CO_2 lasers was tuned to the $10.6 \mu\text{m}$ *P*(34) line, and the other to $10.6 \mu\text{m}$ *P*(44), which excited the OCS vibrational transitions described. The CO_2 lasers could be fired simultaneously or individually and their timing with respect to the ArF* laser was varied from 20 μsec before to 20 μsec after the ArF* laser pulse. In these experiments, data were taken at OCSe pressures of 0.5 and 1.0 torr and Xe pressures of 100 and 200 torr. This limited pressure range was necessary to insure that the fluorescence intensity from the collision-induced $\text{Se}^{\text{I}}\text{S} - ^1\text{D}$ transition was at least ten times greater than the background Se_2^* fluorescence intensity.

A sample plot of the dependence of the ratio of the enhancement of the $\text{Se}^{\text{I}}\text{S}$ fluorescence on the timing difference between the CO_2 [*P*(44, 400 mJ/cm²)] and ArF lasers for an OCSe pressure of 0.5 and 1 torr and a Xe pressure of 200 torr is given in Fig. 5. The enhancement ratio was determined by recording the observed peak of the XeSe* fluorescence at 780 nm (scaled to constant UV laser intensity) with and without CO_2 laser excitation and taking the ratio. This plot shows that, when the infrared (vibrational) excitation occurs before the ultraviolet (photolytic) excitation ($\tau > 0$), the fluorescence yield increases dramatically. This plot is similar to the ones given in Ref. 6 for OCS photolysis. As a check on the enhancement ratios, no increase in the yield was observed when the CO_2 laser was triggered after the UV laser. As can be seen from the plot, a peak enhancement ratio of 25% was observed when approximately half the OCSe molecules are excited to the $\nu_2 = 2$ vibrational level. An analysis of the fluores-

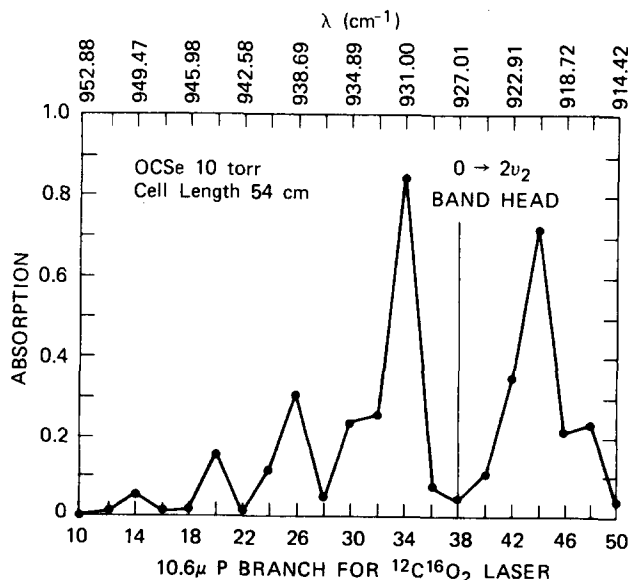


FIG. 4. IR absorption data for OCSe for various CO_2 laser lines in the $10.6 \mu\text{m}$ *P* branch.

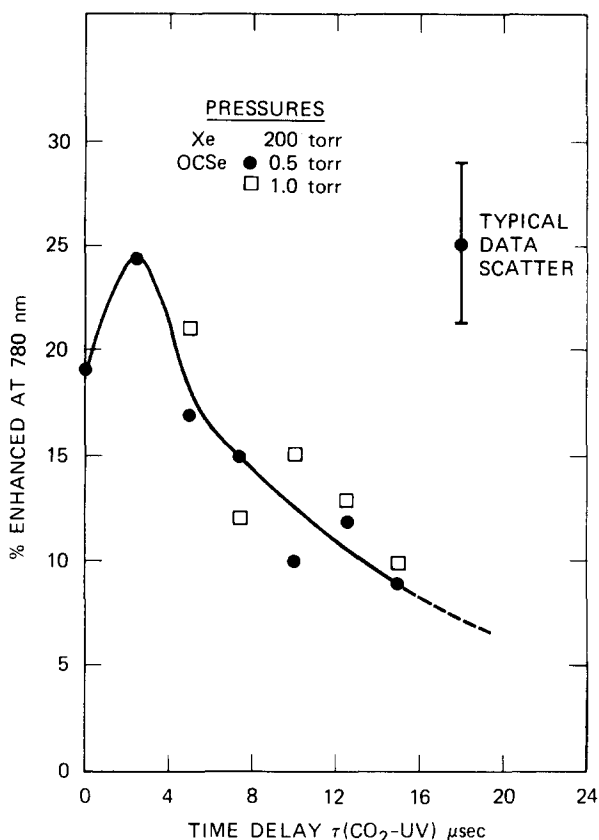


FIG. 5. Vibrationally induced enhancement of the collision-induced $\text{Se}(^1\text{S} \rightarrow ^1\text{D})$ fluorescence at 780 nm as a function of the time delay (τ) between the CO_2 and ArF lasers.

cence decay rates with and without vibrational excitation indicated that the increased collisional quenching of the ^1S state by vibrationally excited molecules observed in Ref. 7 for OCS was not present in this case. This can be qualitatively understood from the fact that OCSe already has such a large quenching rate^{4,9} ($k_q = 1.6 \times 10^{-10} \text{ cm}^3/\text{sec}$), a rate which approaches gas kinetic rates, that the increase $\Delta k_q \sim 2 \times 10^{-12} \text{ cm}^3/\text{sec}$ observed in Ref. 6 would not be detectable under these circumstances.

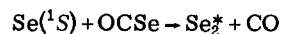
A number of observations were obtained from these data:

(1) the observed signal enhancement for excitation with the $P(34)$ CO_2 laser line was similar to that given in Fig. 5 with the peak enhancement ratio reduced from 25% to 20%. This is consistent with the measured IR energy deposition.

(2) The enhancement ratio was approximately constant for CO_2 energy densities between 200–500 mJ/cm^2 , consistent with the $0 \rightarrow 2\nu_2$ vibrational transition being saturated.

(3) Use of two CO_2 lasers [$P(34)$ and $P(44)$] at the same total energy as the single laser data of Fig. 5 did not increase the enhancement ratio.

(4) The enhancement ratio at 480 nm [$\text{Se}(^1\text{S} \rightarrow ^3\text{P})$] had similar values and time dependences to that shown in Fig. 5. The $\text{Se}_2^+(B \rightarrow X)$ emission formed by the reaction



also shows a similar enhancement due to vibrational excitation. All of these observations conclusively show that the $\text{Se}(^1\text{S})$ population has increased by approximately 25%.

DISCUSSION

As discussed in the Introduction, an increase in $\text{Se}(^1\text{S})$ population produced by vibrationally exciting OCSe before photolysis at 193 nm can arise from at least two mechanisms:

(1) a vibrationally induced increase in absorption coefficients at 193 nm (without a change in the photofragment distribution), or

(2) a vibrationally induced increase in the branching ratio into the $\text{Se}(^1\text{S})$ photodissociation channel.

Clearly, both mechanisms could combine to give the observed effect. In order to isolate an increase in $\text{Se}(^1\text{S})$ quantum yield [mechanism (2)], one could measure the number of ArF laser photons absorbed with and without vibrational excitation.¹⁴ Since this would require a substantial modification of our experimental cell, we chose the alternate technique of increasing the ArF energy density to the point where all the OCSe had been photolyzed. A simple bleaching analysis indicates that an energy density of $E(\text{J}/\text{cm}^2) = \hbar\omega/\sigma$ (where σ is the OCSe absorption cross section at 193 nm) is necessary to completely photolyze the OCSe. For an absorption cross section⁴ of $\sigma \sim 10^{-17} \text{ cm}^2$, we find that $E \geq 100 \text{ mJ}/\text{cm}^2$. Under these conditions, any change in the absorption cross section would not be observed and any increase in fluorescence intensity could be directly attributable to an increase in the quantum yield for $\text{Se}(^1\text{S})$ production.

A plot of the $\text{Se}(^1\text{S})$ fluorescence versus laser energy flux is given in Fig. 6. In this experiment, the viewing region was restricted using apertures to a volume where the laser flux was approximately constant. Although the relative laser fluxes shown in Fig. 6 are accurate to less than 5%, the absolute value has an error of $\pm 25\%$ due to the fact that Se_2 is deposited on the cell window, thus altering the window transmission during the course of the experiment. As can be seen from Fig. 6, the $\text{Se}(^1\text{S})$ fluorescence intensity without CO_2 excitation (dots) depends linearly on the ArF laser energy up to a flux of 70 mJ/cm^2 , where the plot starts to show bleaching effects. The fluorescence intensity with CO_2 excitation (squares) shows that, in the unbleached region, the increase is approximately 25%, whereas under bleached conditions ($E > 120 \text{ mJ}/\text{cm}^2$), there is no measurable increase. These data clearly indicate that the quantum yield for $\text{Se}(^1\text{S})$ production has not significantly changed and the effect must be attributed to an alternate mechanism, such as an increase in the absorption coefficient.

These results are in contrast to the recent data of Black and Sharpless¹⁴ taken by measuring the temperature dependence of the $\text{S}(^1\text{S})$ quantum yield produced by photolysis of OCS. In these experiments, an increase

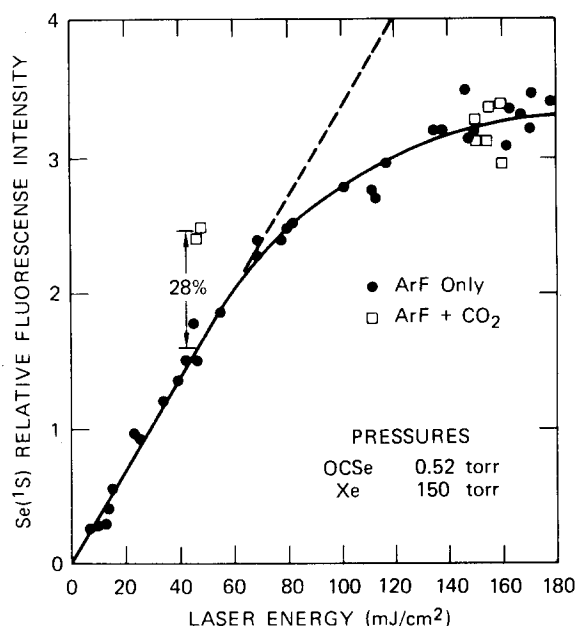


FIG. 6. Dependence of the $\text{Se}(^1\text{S})$ fluorescence intensity on the ArF laser energy flux with (squares) and without (dots) CO_2 laser excitation. The deviation from a linear increase at 70 mJ/cm^2 indicated that the ArF laser is bleaching the OCSe. Note that the 28% increase observable at low laser energy fluxes is not observable under bleached conditions.

in the $\text{S}(^1\text{S})$ quantum yield was observed at elevated temperatures and has been interpreted to be the result of a vibrationally induced increase in the quantum yield. The difference in the results of these two experiments could be explained from the fact that the photolysis wavelength used in our experiments is twice as far from the peak of quantum yield curve for ^1S production as was used in Ref. 14. Certainly, experiments should be done over the whole photolysis spectrum (172–193 nm) to determine the effect of the mode specific vibrational excitation.

CONCLUSIONS

In conclusion, we have demonstrated that vibrational excitation can significantly affect the UV absorption process in OCSe. In these experiments, the $\text{Se}(^1\text{S})$ photofragment density produced by absorption at 193 nm was monitored by observing emission on the collision-induced $^1\text{S}-^1\text{D}$ transition at 780 nm. Our observations indicate that the observed increase in the $\text{Se}(^1\text{S})$ fluores-

cence cannot be attributed to a vibrationally induced change in the quantum yield, but rather is interpreted as a vibrationally induced change in the absorption coefficient. In principle, experiments such as these should be also to determine specific parameters concerning the potential surfaces of triatomic molecules. Studies of the absorption spectrum of molecules with state specific vibrational excitation have generated much interest in the past few years and will undoubtedly be developed into a useful tool to diagnose the electronic structure of polyatomic molecules.

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