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Headline Articles

Photodissociation and Vibrational Dynamics of OCS in the VUV Region

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The photofragment excitation (PHOFEX) spectrum of jet-cooled OCS was remeasured for the 154.5 nm peak in the $^1\Sigma^+$–$^1\Sigma^+$ transition by scanning a tunable vacuum ultraviolet (VUV) laser wavelength in the deep VUV region and by probing the S(^{1}S) product with a second laser. Due to the efficient cooling of the sample in the free-jet expansion and the high-resolving power of the VUV laser, the homogeneous broadening of the dissociative state was derived directly from the observed PHOFEX spectrum. Based on the measured peak width, the lifetime (τ) of the dissociative state was determined to be $\tau\cong 0.14$ ps. The profile of the PHOFEX peak was found to be asymmetric and was fit to a Fano line profile to derive the value of the asymmetry parameter, $q=-3.5(9)$, which indicates a considerable mixing of the continuum and discrete states in that particular energy region. A Fourier-transform analysis was also performed for the whole distinct absorption feature in the 160—140 nm region measured by McCarthy and Vaida [*J. Phys. Chem.*, **92**, 5875 (1988)], and the period of the vibrational motion on the dissociative potential-energy surface was derived to be 41 fs. Using these pieces of experimental evidence, the dissociation dynamics on the repulsive $^1\Sigma^+$ surface in the 154.5 nm region was inferred.

When molecules absorb light in the vacuum ultraviolet (VUV) wavelength region, in most cases, a direct or indirect breaking of a chemical bond occurs, resulting in the production of reactive species, such as atoms or free radicals, which then induce chemical chain reactions. Therefore, an investigation of the photochemical processes initiated by the absorption of VUV photons should clarify the reaction mechanisms of the photochemistry in the atmosphere, especially in the stratosphere, where irradiation by short-wavelength light in the VUV region governs the photochemical processes.[1] An investigation of the photo-absorption of VUV light is also important for a fundamental understanding of the elementary processes of chemical reactions, since it directly excites molecules to their transition-state region for unimolecular decomposition reactions. It is therefore expected that the fast dissociation dynamics of polyatomic molecules in their transition state region can be extracted from an investigation of the photoabsorption processes.

For various molecules, the absorption spectra in the VUV wavelength region have been measured, and very broad absorption features and/or broad peaks embedded in a much broader background have been reported.[2] Usually, such an absorption spectrum is measured under bulb conditions at room temperature, it often suffers from a considerable overlap of vibrational hot-bands and a widely spread rotational structure. There are three kinds of contributions to form a broad feature in the absorption spectrum: (i) homogeneous broadening due to a fast dissociation process superimposed on the Franck–Condon projection of the initial vibrational wavefunction onto the excited potential-energy surface (PES), (ii) a congested overlap of vibrational and rotational hot-bands, and (iii) a limited instrumental spectral resolution. It is rather natural to think that among the above-mentioned contributions (i) is the dominant one, since a very fast dissociation process is expected in such a high-energy region. This may be the reason why so little effort has been paid to decrease the other two contributions ((ii) and (iii)) to the spectral line broadening. However, in order to extract dynamical information, such as the dissociation lifetime of a dissociative state, it is really necessary to know the

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absorption profile free from these two contributions.

Recent advances in molecular-beam technology have enabled spectroscopic investigations of ultra-cooled molecules. Indeed, for some molecules, the absorption spectra in the VUV region have been recorded under jet-cooled conditions. However, even when molecules are prepared in a free-jet expansion, it is rather difficult to record an absorption spectrum under the sufficiently cooled condition because the ultra-cooled region is limited to a small central region of the free jet expansion. Furthermore, if the absorption spectrum is measured using the dispersed emission from a discharge lamp, the resolution of the absorption spectrum has a practical limit of ca. 10 cm^{-1} at best. To overcome this difficulty in measuring the absorption of spectrum of ultra-cooled molecules with higher resolution in the VUV wavelength region, VUV PHOFEX laser spectroscopy of jet-cooled molecules is a most powerful and promising technique. In VUV PHOFEX spectroscopy, the VUV laser wavelength is scanned while the specific quantum state of product atoms or molecules is detected by another probe laser. Since the spectral resolution is limited only by the resolution of the VUV laser, a resolution better than 1 cm^{-1} can be easily achieved. Furthermore, the fluorescence emitted in the cold central region of the free-jet expansion is detected in the PHOFEX measurements, and, as a consequence, the PHOFEX spectrum, which has a close correspondence with the absorption spectrum, can be recorded under ultra-cold conditions (below ca. 5 K). Therefore, homogeneous spectral line broadening due to a fast dissociation reaction can be obtained directly from the peak width of the spectrum. We recently measured the PHOFEX spectrum of OCS, which was efficiently cooled in a supersonic jet expansion.(3) This measurement was the first experimental attack of photodissociation dynamics in the VUV wavelength region by PHOFEX spectroscopy, in which a novel light source, i.e. a tunable VUV laser, was used as a light source to initiate the photodissociation reaction.

The dynamics of small polyatomic molecules prepared in their transition-state region through absorption of a photon has sometimes been interpreted by the Fourier transform of an absorption feature covering a relatively wide energy region in the UV or VUV wavelength region.(4) Johnson and Kinsey(5) obtained a Fourier transform of the absorption spectrum of the Hartley band of ozone measured at 195 K by Freeman et al.,(6) and argued that peaks in the auto-correlation function can be related to unstable periodic orbits on the dissociative PES. However, in the case of ozone, such information (the periods of unstable periodic orbits) was derived from the Fourier transform of a very broad absorption feature, on top of which a small oscillatory structure is identified. Considering the possibility that the overlap of rotational and vibrational hot bands affects the small oscillatory structure in the absorption spectrum, an interpretation of the peaks appearing in the auto-correlation function would not be straightforward. In spite of this difficulty in discussing the autocorrelation function obtained from the Fourier transform of the absorption spectrum, such Fourier-transform analyses have also been applied to other simple polyatomic molecules(7—9) in order to extract their dynamics on a repulsive PES. It is interesting to note that some absorption bands of simple polyatomic molecules in the VUV region exhibit a relatively sharp progression in spite of the rapid dissociation processes which broaden absorption peaks.(2,10) In the case of OCS, the absorption spectrum in the 160—140 nm region shows a simple and characteristic vibrational structure, which has been ascribed to vibrational progressions in the symmetric and antisymmetric stretching vibrations of the excited $^1\Sigma^+$ state.(10,11)

In the present study, by combining state-specific information derived from the PHOFEX spectrum and global dynamical information via the auto-correlation function, obtained from a Fourier-transform analysis of the $^1\Sigma^+$–$^1\Sigma^+$ absorption band, we aimed to draw a consistent picture of the dissociation dynamics on the mostly repulsive $^1\Sigma^+$ potential. We first describe the experimental setup for the PHOFEX measurements in Section 1. Then, in Section 2 we present the PHOFEX spectrum of the vibronic peak at 154.5 nm in the $^1\Sigma^+$–$^1\Sigma^+$ band of jet-cooled OCS, and based on a least-square fitting to the Fano line profile, the homogeneous line broadening as well as a q-parameter in the Fano formula(12) were obtained. Furthermore, we performed a Fourier-transform analysis in order to derive an auto-correlation function for the whole $^1\Sigma^+$–$^1\Sigma^+$ band measured by McCarthy and Vaida(11) under jet-cooled conditions. From the auto-correlation function, we derived information concerning the period of vibrational motion, which may be regarded as being that of an unstable periodic orbit, on the PES near the transition-state region. Finally, in Section 3 we summarize with conclusions obtained by combining the results from the two kinds of spectroscopy, i.e. the PHOFEX spectroscopy and the absorption spectroscopy.

1. Experimental

We introduce here our experimental setup for the VUV PHOFEX measurements of jet-cooled OCS. Three dye lasers were simultaneously pumped by a XeCl excimer laser (Lambda Physik 205i). The laser beams of two tunable dye lasers (Lambda Physik FL3002E) (ω_1 and ω_2) were spatially merged through a dichroic half mirror, and were focused into a frequency-conversion cell filled with Xe gas with an acromat lens ($f=250$ nm). After passing through a LiF lens, coherent VUV light having a frequency of $\omega_{\mathrm{VUV}}=2\omega_1-\omega_2$, generated through a two-photon resonant four-wave difference frequency-mixing (2PR-4WDM) scheme in Xe, was introduced into the separator. At the separator, the VUV light beam was separated by a LiF prism from the two incident laser beams (ω_1 and ω_2). Only the VUV light beam proceeded into the main vacuum chamber and crossed the free jet of the OCS/Ar (ca. 7%) mixture gas expanded from a pulsed valve (General Valve 9-279-900). The orifice diameter of the pulsed valve was 0.8 mm, and the stagnation pressure was 1—3 atm. The frequency-doubled UV output of the third dye laser (Questeck 5200B), which was used to detect the $S(^1S)$ atom, was co-axially counter propagated with the photolysis laser light.

During the measurements, the VUV laser intensity and the UV laser intensity were simultaneously monitored, and the observed fluorescence intensity for the probe transition, $S(^3D)$–$S(^1S)$, was normalized by these laser intensities. It is known that the quantum yield of the $S(^1S)$ fragments exceeds 80% for the photolysis wavelength region of 160—140 nm,[13] and that the dominant open channel of photodissociation is $OCS \rightarrow CO + S(^1S)$. Therefore, in this case, the PHOFEX spectrum obtained by monitoring the $S(^1S)$ fragment is almost identical with the absorption spectrum. In the PHOFEX measurements, the photolysis wavelength was scanned around the 154.5 nm region by monitoring the $S(^1S)$ product by LIF according to the following scheme:

$$OCS + h\nu \text{ (ca. 154.5 nm)} \rightarrow CO(X^1\Sigma^+) + S(^1S) \quad (1)$$

$$S(^1S) + h\nu \text{ (219 nm)} \rightarrow S(^3D_1) \quad (2)$$

$$S(^3D_1) \rightarrow S(^3P) + h\nu \text{ (147 nm)}. \quad (3)$$

Before being mixed with a rare-gas carrier gas in a container, the sample gas of OCS (Matheson) was further purified by several freeze-and-pump cycles. The fluorescence emission from the excited $S(^1D)$ in the crossing region of the VUV and UV light beams and the expanded free jet, which was located ca. 18 mm downstream from the nozzle orifice, was detected by a solar-blind photomultiplier (Hamamatsu R1259) placed in a direction perpendicular to both of the laser beams and the jet. The fluorescence signals were amplified by a preamplifier and were averaged by a boxcar integrator (Stanford SR250) to record the PHOFEX spectra. The absolute wavelength in the measured spectra was calibrated with respect to the rotational transitions of the A–X(0,0) band of CO, whose origin is located at 64748.48 cm^{-1}.[14] In measurements of the PHOFEX spectrum, repetitive frequency scans were performed in order to confirm the reproducibility of the spectrum. During the experiment, the background pressure in the main vacuum chamber was kept at 1—5×10^{-4} Torr by pumping through a 6" (6 inches) oil diffusion pump backed up by a tandem series of a mechanical booster pump and a rotary pump. Further details concerning the experimental setup for the tunable VUV spectroscopy have been described in a recent review article.[15]

2. Results and Discussion

(i) Overall Feature of the $^1\Sigma^+$–$^1\Sigma^+$ Band. The absorption spectrum of OCS in the 160—140 nm region shows a simple and distinct progression of seven vibronic peaks with an interval of around 800 cm^{-1}. The absorption spectrum of the $^1\Sigma^+$–$^1\Sigma^+$ band recorded by McCarthy and Vaida under jet-cooled conditions[11] is shown in Fig. 1(a). The spectrum was retraced by reading points off of an enlarged copy of the published spectrum presented as Fig. 2 in Ref. 11, and presented in a linear scale of the wavenumber. The wavelength positions for these seven peaks were reported to be 156.1, 154.6, 152.5, 150.7, 149.0, 147.3, and 145.7 nm. An interesting feature of this distinct progression is the characteristic peak-to-peak fluctuation of the peak width. It is apparent that the lowest energy side peak, a peak at 156.1 nm, is very broad, and the next peak at 154.6 nm has the narrowest width among these seven peaks. It seems that the peak width (FWHM) becomes larger for the 152.5 nm peak, and is largest for the 150.7 nm peak. The peak width then begins to decrease again for the 147.3 and 145.7 nm peaks as the energy increases.

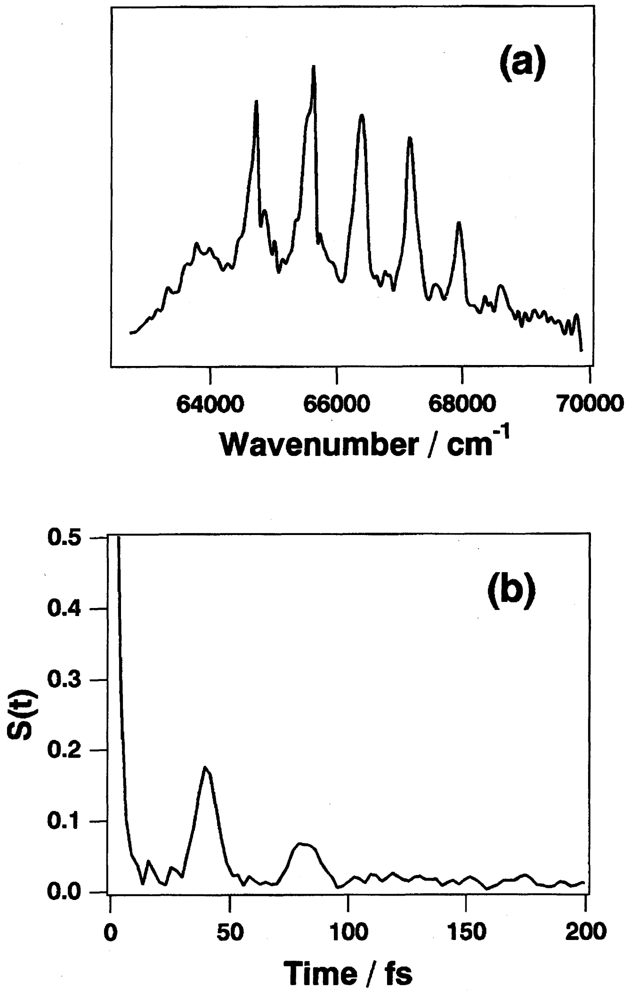

Fig. 1. (a) The retrace of the jet-cooled absorption spectrum measured by McCarthy and Vaida (Ref. 11) and (b) the autocorrelation function obtained from the Fourier transform of the $^1\Sigma^+$–$^1\Sigma^+$ band of OCS in the 159.3—143.1 nm region.

Though these peaks were classified as belonging to the $^1\Sigma^+$–$^1\Sigma^+$ electronic transition,[10] McCarthy and Vaida[11] claimed that the lowest energy peak, the peak appearing at 156.1 nm, may be assigned to the $^1\Pi$–$^1\Sigma^+$ transition. However, Houston and co-workers,[16,17] performing pump-and-probe photodissociation experiments at a photolysis wavelength of 157 nm, indicated

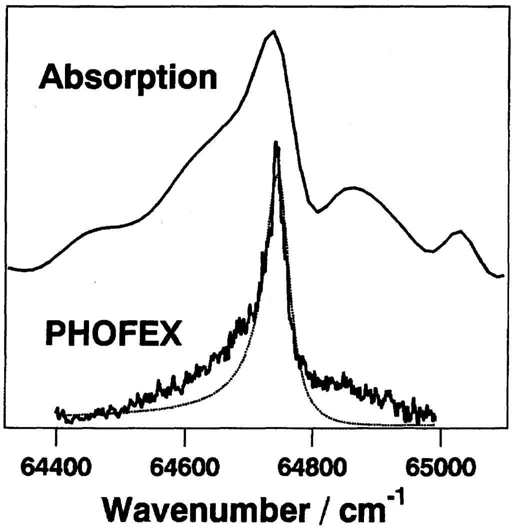

Fig. 2. The PHOFEX spectrum (lower trace; solid line) and the absorption spectrum (upper trace) (Ref. 11) of the 154.5 nm band of the $^1\Sigma^+$–$^1\Sigma^+$ band of jet-cooled OCS. The Fano line profile (lower trace; dotted line), which is fit to the observed PHOFEX spectrum, is also shown.

that the transition is assigned to the $^1\Sigma^+$–$^1\Sigma^+$ transition based on the recoil anisotropy parameter (β=1.8±0.2). Since no definite assignment of the electronic transition has been made for the lowest energy peak at 156.1 nm, the entire band system in the 160—140 nm region is referred to as the $^1\Sigma^+$–$^1\Sigma^+$ transition throughout this paper. In the future, a PHOFEX spectrum of the 156.1 nm peak measured under cold conditions could provide a key to definite assignments by disclosing a spectral feature buried under the rotational band structure.

The absorption spectrum in the 160—140 nm region was also measured under the bulb condition at room temperature by McCarthy and Vaida[11) as well as by Rabalais et al.[10) A comparison of the jet-cooled absorption spectrum and the room-temperature spectrum showed that the width of the vibronic peaks in the jet-cooled spectrum is somewhat narrower. This temperature dependence of the width of the absorption feature indicates a significant contribution from the rotational band width, as inferred by McCarthy and Vaida. However, as is clarified below in the present study, the observed absorption peaks measured under jet-cooled conditions still contain considerable contributions from the rotational band width.

(ii) PHOFEX Measurements of the 154.5 nm Band. In the present study the PHOFEX spectrum of jet-cooled OCS was measured for the absorption peak observed at 154.6 nm by McCarthy and Vaida.[11) Our PHOFEX measurements, in which the wavelength was calibrated with respect to the rotational transitions of the A–X(0,0) band of CO, show that the band center of the corresponding peak is located at 154.5 nm. Therefore, this second peak in the $^1\Sigma^+$–$^1\Sigma^+$ transition is called the 154.5 nm peak hereafter. The observed PHOFEX spectrum is shown in Fig. 2 together with the jet-cooled absorption spectrum.[11) In our previous report,[3) a small derivative-shaped profile was observed in the slightly lower energy region of the PHOFEX peak. It was found later that the generated VUV intensity, itself, has a small, but characteristic, shape at the same energy as the derivative shaped peak. Therefore, in the present measurements, the VUV intensity was simultaneously recorded when the PHOFEX spectrum was measured, and after the measurements the PHOFEX spectrum was normalized using the monitored VUV intensity. The background spectrum was also recorded with the probe laser off in order to confirm the zero-base line of the PHOFEX spectrum. This background spectrum exhibited a small contribution of the A–X(0,0) band of CO, which could be located on top of the PHOFEX peak. Therefore, the background spectrum was subtracted from the observed PHOFEX spectrum before intensity normalization. The wavenumber of the maximum position of our PHOFEX peak at 154.5 nm was determined to be 64 743.9(20) cm^{-1} using the A–X(0,0) transition of CO for wavelength calibration.

The peak width (FWHM) for this 154.5 nm peak measured in the present study is 41.8(2) cm^{-1}, which is somewhat larger than that previously reported,[3) mainly due to the fact that a zero-base line was established in the present study. The corresponding peak in the absorption spectrum measured under the jet-cooled condition by McCarthy and Vaida[11) is 156 cm^{-1}. In our measurements the rotational band width of the single vibronic transition was estimated to be at most 4.5 cm^{-1}, using the rotational constants of OCS (0.2029 cm^{-1}) and the rotational temperature (ca. 5K), which was determined by fitting the intensity pattern of the rotational structure of the A–X(0,0) transition of CO measured under the same expansion condition. Furthermore, the resolution of the PHOFEX spectrum is significantly high (0.4 cm^{-1}), which was confirmed by the peak width of the rotational structure of A–X(0, 0) transition of CO. Therefore, homogeneous broadening due to the dissociation reaction is only slightly smaller (by about 5 cm^{-1}) than the observed line broadening. This means that the homogeneous line width is ca. 37 cm^{-1}, and that the corresponding lifetime (τ) is $\tau \cong 1.4\times10^2$ fs. The reason why the same peak at 154.5 nm in the absorption spectrum is much broader than our PHOFEX spectrum could be due to the fact that only the coldest region of the jet-expansion is sampled in our PHOFEX measurements. If the spectral resolution of 16 cm^{-1} in the absorption measurements by McCarthy and Vaida[11) and the homogeneous broadening of 37 cm^{-1} derived above are subtracted from the observed width of 156 cm^{-1} in the absorption spectrum, a width of ca. 103 cm^{-1} is obtained as the contribution from the rotational band width.

The observed PHOFEX peak itself exhibits a clear and characteristic asymmetric line profile. This kinds of asymmetric line profile is known as a Fano line profile,[12) which has often been observed in the auto-ionization spectrum of atoms and molecules, as well as in the absorption spectrum of diatomic molecules in the highly excited region above the dissociation limit.[18) A similar asymmetric line shape was observed in the optical–optical double resonance (OODR) spectrum for the 7s Rydberg state of HgNe.[19) All of these asymmetric line profiles were observed when there were comparable transition probabilities to both of the discrete and continuum states, which interact with each other, from the lower electronic state. A Fano line profile is usually observed when a discrete state interacts with continuum states in a *different* electronic state. A Fano-type asymmetric line profile can also be observed when a resonant state is formed in a *single* adiabatic interatomic potential function, as observed for HgNe.[19)

In order to extract homogeneous broadening (Γ) caused by a fast dissociation reaction the PHOFEX spectrum was fitted by a Fano line profile written as

$$I(E) \propto \frac{(q+\varepsilon)^2}{1+\varepsilon^2}, \qquad (4)$$

where ε is defined as $\varepsilon=(E-E_r)/(\Gamma/2)$, with E_r and Γ representing the energy and the FWHM of the resonance state, respectively, and an asymmetric parameter (q), which reflects the interference between the discrete and dissociative states. This q-parameter can take either positive or negative values; as the absolute value of q increases, the absorption profile feature approaches a symmetrical Lorentzian line shape.

In Fig. 2, the results of the fitting of the Fano profile (lower trace; dotted line) to Eq. 4 and the observed PHOFEX profile (lower trace; solid line) are shown. In the fitting, a larger weight was placed on the peak region than on the tail region in order to reproduce the center region of the asymmetry line profile. As the optimized parameters, $\Gamma=41.6(2)$ cm^{-1} and $q=-3.5(9)$ were obtained. The width is consistent with that derived above ($\Gamma=41.8(2)$ cm^{-1}) as a simple FWHM of the observed peak. If the q-parameters are derived for the other six vibronic features in the 160—140 nm region, a comparison of these q-parameters could be useful in the characterization of the electronic structure responsible for the repulsive PES. The fitting shows that the Fano line profile does not well reproduce the shape of the tail region. It is possible that small absorption features for transitions to the bending excited states overlap in the tail region. In such a case an effect of overlapping resonances should be taken into account and a simple Fano formula of Eq. 4 becomes inappropriate to simulate the entire asymmetry profile of the 154.5 nm peak.

(iii) Fourier Transform of the $^1\Sigma^+$–$^1\Sigma^+$ Absorption Feature. In this sub-section, the Fourier-transform analysis is performed for the absorption feature of the whole system of the $^1\Sigma^+$–$^1\Sigma^+$ transition in the 159.3—143.1 nm region shown in Fig. 1(a), which was previously measured by McCarthy and Vaida,[11) in order to extract the vibrational dynamics near the transition-state region of the dissociative PES. As demonstrated by Heller,[4) the dynamical behavior of the system is reflected in the auto-correlation function, which is the Fourier transform of the light-absorption spectrum. Since a study of the photodissociation of O_3,[5) this procedure has been applied to a number of molecules and their dynamics after the photoabsorption of the UV and VUV light were discussed. For example, the absorption spectra of H_2O[7,8) and H_2S[7) and the SEP spectra of Na_3 and HCN[9) were analyzed in a similar manner. It has been also argued that the peak position in the autocorrelation function corresponds with the period of an unstable periodic orbit on the repulsive PES.

Considering that the progression of the absorption features in the $^1\Sigma^+$–$^1\Sigma^+$transition of OCS exhibits a well-separated sharp structure compared with the absorption spectra of O_3, H_2O, and H_2S, it is highly expected that some clear and distinct recurrences will appear in its autocorrelation function. The auto-correlation function for the jet-cooled absorption feature measured by McCarthy and Vaida[11) was obtained by an Fourier-transform analysis, as shown in Fig. 1(b). The auto-correlation function reveals the existence of at least one distinct vibrational period, which might be that of an unstable periodic orbit which starts near the transition-state region of the PES. Since the distinct progression with a ca. 800 cm^{-1} interval has been assigned to a symmetric stretching mode, this period, 41 fs, may be attributed to the symmetric stretching mode near the transition-state region. The other period of 84 fs may represent either the second recurrence of the symmetric stretching mode with a 41 fs period or another vibrational motion which has a substantial contribution from an anti-symmetric vibrational motion. It is interesting to note that the dissociation dynamics of CO_2, which is isovalence with OCS, on the corresponding PES has an unstable periodic orbit having a shortest period of 38 fs,[20) whose magnitude is comparable with that of OCS. The absorption spectrum suffers from considerable broadening due to the rotational band width, as discussed above. However, the period extracted from the spectrum, 41 fs, reflecting a spacing of ca. 800 cm^{-1} between the distinct peaks in the 160—140 nm region, would not be influenced so much by this rotational broadening. Indeed, the autocorrelation function derived from the absorption spectrum measured at room temperature by McCarthy and Vaida[11) and Rabalais et al.[10) also exhibits clear recurrences at ca. 41 and ca. 84 fs.

Combining the lifetime, 1.4×10^2 fs, for the dissociative state at 154.5 nm and the period, 41 fs, for the vibrational motion on the dissociative PES, it can be said that, after being excited to the 154.5 nm peak, OCS oscillates ca. 3 times along the particular vibrational mode within the dissociation lifetime. In other words, the wave packets as a whole evolves to the product valley as time elapses while a remnant of the wave packet oscillates along the symmetric stretching coordinate starting from the Franck-Condon point, as discussed by Schinke.$^{20)}$

3. Summary and Conclusion

A PHOFEX spectrum of one vibronic transition at 154.5 nm in the $^1\Sigma^+$–$^1\Sigma^+$ transition of OCS has been remeasured under jet-cooled conditions by scanning the wavelength of the tunable VUV laser and by monitoring the S(^{1}S) photofragment. Due to efficient cooling by the free-jet expansion, the PHOFEX spectrum, which corresponds to the absorption spectrum, exhibits significantly narrower features than do the previously recorded absorption spectra. This type of VUV-PHOFEX measurements should be helpful in gaining an understanding of the dissociation dynamics of small polyatomic molecules.

A Fourier-transform analysis has been performed for the absorption spectrum of jet-cooled OCS in the 160—140 nm region, covering the whole $^1\Sigma^+$–$^1\Sigma^+$ transition, measured previously by McCarthy and Vaida under jet-cooled conditions. In the auto-correlation function, a characteristic vibrational period of 41 fs, related to an unstable periodic orbit, has been identified. It can be said that this vibrational period carries information about the dissociative PES over a wide energy range near the transition-state region, while the spectral line broadening, obtained from the PHOFEX spectrum of the jet-cooled molecules, shows the rate of photodissociation at a particular peak in the absorption feature. The vibrational period may represents that of an unstable periodic orbit, which characterizes the transition state of an unimolecular dissociation of a small polyatomic molecule. By combining the results obtained from the Fourier transform of the whole absorption band and those from the high-resolution PHOFEX measurements, the fate of the photo-excited molecules in the transition state region could be inferred.

More about the dynamics of the dissociating OCS in the 160—140 nm region could be derived via measurements of the whole $^1\Sigma^+$–$^1\Sigma^+$ transition by high-resolution VUV PHOFEX spectroscopy. Recently, Yamashita$^{21)}$ calculated the ab initio PES for the electronically excited states of OCS and confirmed that the $^1\Sigma^+$–$^1\Sigma^+$ transition has a strong transition dipole moment, which is consistent with the experiments. The theoretically derived PES would also be very helpful for interpreting the experimental observations. The characteristic dissociation dynamics of OCS in the deep VUV region may be extracted more clearly in the near future through cooperative experimental and theoretical approaches.

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