Fluorescence Excitation Spectrum of OClO ($\tilde{A}^2A_2$)

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The fluorescence excitation (FE) spectrum for the $\tilde{A}^2A_2 \leftrightarrow \tilde{X}^2B_1$ transition of OClO cooled in supersonic jet expansions has been obtained for the first time from the origin band at 476 nm up to 355 nm. Despite rapid predissociation of the excited OClO molecules, the fluorescence emission is strong enough to give the FE spectrum with a high signal-to-noise ratio. The present FE spectrum shows the much lower rotational temperature and hence better state resolution than seen in previously reported spectra, demonstrating that it can be used as a convenient spectroscopic tool for the state and mode selection in the photodissociation dynamics studies. The FE spectroscopy can be also applied for the high-resolution spectroscopy and various kinetic studies on the OClO molecules.

1. Introduction

The potential role of OClO in the stratospheric ozone depletion cycle has stimulated both intensive and extensive studies on its photodissociation processes in the near-ultraviolet (UV) region.[1,2] While some of those studies have been carried out for the OClO samples at room temperature,[3−7] recent state-resolved studies[8−19] have been mostly performed for the cold samples prepared in supersonic jet expansions. For the state-to-state dynamics investigation, a well-resolved absorption spectrum of OClO, which is taken at the identical experimental conditions as used in the photodissociation studies, is ideal for the interpretation of experimental results. Recently, Vaida and co-workers[15−18] have reported the absorption spectra of the $\tilde{A}-\tilde{X}$ transition for the OClO sample cooled in supersonic jet expansions, using a Fourier transform absorption spectrometer. They obtained the absorption spectrum of OClO at the rotational temperature as low as 30 K, which is fairly close to the temperature at which most of photodissociation studies in jet expansions are performed. Although the OClO spectrum obtained at the low rotational temperature is available, the room-temperature spectra have been mostly used as a guideline for the interpretation in many photodissociation studies carried out in jets.[9−11,13,14] This has been mainly because the cold absorption spectra could not be obtained at the same experimental conditions as those used in dynamical studies.

Generally, if a molecule has a nonnegligible quantum yield of fluorescence, the fluorescence excitation (FE) spectrum can be easily obtained, and a minor modification of the setup would be necessary for the further dynamics study. Then, the characters of the initial quantum states, from which the dissociation occurs, can be obtained from the FE spectrum. Fluorescence emission from the $\tilde{A}$ state of OClO was first observed by Sakurai et al. in 1971.[20] Later, Curl et al. reported the more extensive analysis by using an Ar^+ laser as the excitation source.[21] Interestingly, however, the FE spectrum of the $\tilde{A}^2A_2 \leftarrow \tilde{X}^2B_1$ transition has never been reported before neither at room temperature nor in supersonic jet expansions. In this article, we report for the first time the FE spectrum for the $\tilde{A}^2A_2 \leftarrow \tilde{X}^2B_1$ transition of OClO cooled in supersonic jet expansions. It is found that the fluorescence from the OClO molecules excited to the $\tilde{A}$ state is strong enough to give its spectrum from the origin band up to 355 nm, where the fluorescence quantum yield becomes negligible due to the rapid predissociation. We demonstrate that the FE spectroscopy is a simple and sensitive tool to obtain a spectrum due to the $\tilde{A}^2A_2 \leftarrow \tilde{X}^2B_1$ transition of OClO, which is required for the state selection in the photodissociation dynamics studies.

2. Experimental Section

OClO was generated by passing the 5% gas mixture of Cl_2 in He through a tube containing the $NaClO_2$ powder.[22] Although it is well-known that H_2O catalyzes this reaction,[10] water was not added because the water is found to generate some corrosive species. Instead, the $NaClO_2$ powder was replaced every 20 h, and no sign of signal change was observed during this period.

The generated OClO mixture in He was expanded into the vacuum chamber through a 0.5 mm diameter nozzle with a backing pressure of 1 atm. The laser pulse covering the visible range (480−380 nm) was directly generated with a pulsed dye laser (Lambda Physik SCANmate 2E) pumped with the third harmonic output of a Q-switched Nd:YAG laser (Spectra-Physics GCR-150). For the wavelength shorter than 380 nm, the output from the dye laser was frequency-doubled in a KD^*P crystal. The phase-matching angle of the crystal was maintained by an autotracker (Inrad I) controlled by a personal computer. The second harmonic output was separated from the fundamental through reflections by three dichroic mirrors. The laser beam was directed through the sidearms to excite the cooled OClO molecules in the jet expansions. The distance from the nozzle to the interaction zone with the laser beam was set to be 25 mm. Fluorescence from the excited OClO was collected with a 2 in. diameter *f*/2 quartz lens, filtered with adequate color filters selected for the particular excitation wavelength and detected with a PMT (Hamamatsu H1161). The shot-to-shot intensity fluctuation of the excitation laser pulses was monitored with a pyroelectric joulemeter (Molectron P5-01) to be normalized later. The energy of the excitation pulse was maintained at ~1 mJ/pulse and the laser beam was mildly collimated with a 1 m focal length quartz lens to the size of 1.0 mm diameter

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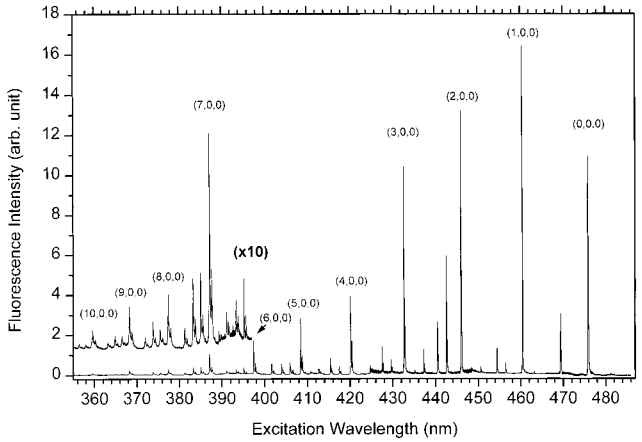

Figure 1. The fluorescence excitation spectrum for the $\tilde{A}^2A_2 \leftrightarrow \tilde{X}^2B_1$ transition of OClO cooled in supersonic jet. The long progression of ν_1 is assigned. Despite the rapid predissociation, the spectrum persists up to 355 nm, where the peak broadening is significant.

at the interaction region. The optogalvanic spectrum of a Ne hollow cathode lamp provided a frequency calibration for the dye laser with an accuracy of ± 0.2 cm^{-1}.

3. Results and Discussions

Figure 1 shows the fluorescence excitation spectrum for the $\tilde{A}^2A_2 \leftarrow \tilde{X}^2B_1$ transition of OClO cooled in supersonic jet expansions. The fluorescence intensities decrease gradually as the energy increases and almost fade away at near 350 nm. The increase of the predissociation rate with increasing the energy seems to be responsible for this intensity variation on the excitation energy.[3,4] As expected from the reported line widths,[3,4] the fluorescence lifetime is too short to be measured with our fluorescence detection system, of which the response time is about 6 ns. From the line width of 0.06 cm^{-1} and the radiative lifetime of 140 ns, which is estimated by integration of the absorption spectrum and the frequency distribution of the dispersed fluorescence spectrum,[21] the fluorescence quantum yield is estimated[23] to be less than 0.1% for the origin band. And the fluorescence quantum yields of higher vibronic levels must be smaller than this value.

Although the fluorescence quantum yield is quite low in the entire energy region studied in this work, the *S*/*N* ratio of the FE spectrum is fairly good, demonstrating the high sensitivity of the FE spectroscopy. It is mainly due to the fact that the $\tilde{A}^2A_2 \leftrightarrow \tilde{X}^2B_1$ system of OClO is a strong allowed transition. The efficient rotational cooling in the jet also helps the further increase of the peak intensity and gives the better state resolution as shown in Figure 2. As a natural result of the higher sensitivity and better resolution, several weak bands, which have not been reported previously in the direct absorption[24] and Fourier transform absorption spectra,[17,18] are noticeable in Figure 2. For example, the (2,2,0) band is observed at 22 983.8 cm^{-1} and the (1,1,2) band of the O^{37}ClO molecule at 22 860.0 cm^{-1}. The frequencies of those newly observed bands as well as the strong ones are summarized in Table 1 with their assignments. The observed transition frequencies of O^{35}ClO were fit to the following equation:

$$\nu_{\text{obs}} = \nu_{00} + \sum_i \omega_i^0 \nu_i + \sum_i \sum_{k \geq i} \chi_{ik}^0 \nu_i \nu_k \qquad (1)$$

where $\omega_i^0 = \omega_i + \chi_{ii} + {}^1/_2 \sum_{i \neq k} \chi_{ik}$ and $\chi_{ik} = \chi_{ik}^0$ in the second-order approximation.[25] The assignments for the strong bands,

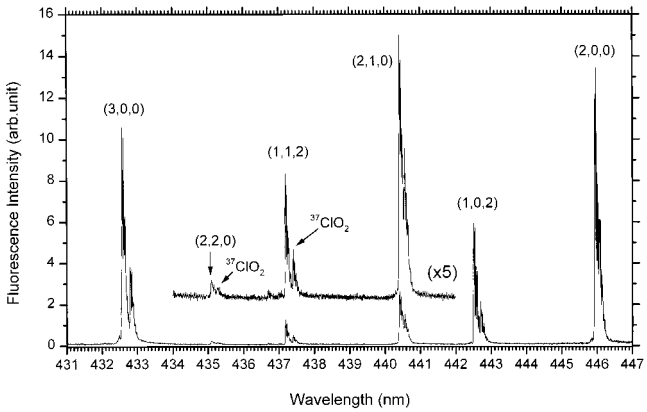

Figure 2. An expanded view of the 431 nm − 447 nm region of the OClO FE spectrum. The (2,2,0) bands of O^{35}ClO and O^{37}ClO and the (1,1,2) band of O^{37}ClO, which were not previously reported, are clearly discernible.

TABLE 1. Observed O^{35}ClO and O^{37}ClO Transition Frequencies and Their Assignments

assignment $\nu_1\ \nu_2\ \nu_3$	O^{37}ClO	O^{35}ClO	ν_{fit} for O^{35}ClO	$\nu_{\text{fit}} - \nu_{\text{obs}}$ for O^{35}ClO
0 0 0		21014.8	21018.7	3.9
0 1 0		21304.5	21308.5	4.0
0 2 0		21590.6	21596.7	6.1
1 0 0		21722.8	21722.8	0.0
0 0 2		21907.2	21903.8	−3.4
1 1 0		22005.6	22008.4	2.8
0 1 2		22192.6	22185.3	−7.3
1 2 0		22298.9	22292.3	−6.6
2 0 0	22416.3	22423.0	22421.4	−1.6
1 0 2	22587.9	22598.1	22595.5	−2.6
2 1 0	22698.1	22705.9	22702.8	−3.1
1 1 2	22860.0	22873.4	22872.8	−0.6
2 2 0	22975.0	22983.8	22982.5	−1.3
3 0 0	23103.5	23117.4	23114.7	−2.7
2 0 2	23265.0	23280.7	23281.9	1.2
3 1 0	23379.0	23393.7	23391.8	−1.9
2 1 2		23551.3	23554.9	3.6
3 2 0	23652.7	23668.1	23667.2	−0.9
4 0 0	23786.9	23804.4	23802.5	−1.9
3 0 2	23937.8	23959.0	23962.8	3.8
4 1 0	24058.1	24076.7	24075.4	−1.3
3 1 2	24203.7	24226.6	24231.5	4.9
2 0 4	24213.1	24238.9	24238.0	−0.9
4 2 0		24346.3	24346.5	0.2
5 0 0	24462.4	24485.8	24484.9	−0.9
4 0 2	24607.5	24634.2	24638.2	4.0
5 1 0	24728.6	24752.8	24753.5	0.7
4 1 2	24868.2	24896.9	24902.8	5.9
3 0 4	24875.9	24905.6	24906.5	0.9
5 2 0		25019.9	25020.4	0.5
6 0 0	25133.5	25162.2	25161.9	−0.3
5 0 2	24275.2	25307.2	25308.3	1.1
6 1 0	25397.5	25427.8	25426.2	−1.6
5 1 2	25537.6	25570.2	25566.6	−1.6
6 2 0	25659.5	25689.1	25688.9	−0.2
7 0 0	25799.8	25834.1	25833.4	−0.7
6 0 2	25936.0	25971.7	25972.9	1.2
7 1 0	26059.7	26094.7	26093.5	−1.2
6 1 2	26193.4	26230.5	26228.9	−1.6
7 2 0		26349.8	26352.0	2.2
8 0 0	26459.6	26499.5	26499.5	0.0
7 0 2	26591.5	26632.6	26632.1	−0.5
8 1 0	26714.0	26754.4	26755.4	1.0
7 1 2	26844.2	26886.4	26883.9	−2.5
9 0 0	27115.7	27157.7	27160.2	2.5
8 0 2	27239.8	27287.4	27285.8	−1.6
9 1 0	27366.5	27412.3	27411.8	−0.5
8 1 2		27534.2	27533.4	−0.8
10 0 0	27764.3	27813.7	27815.5	1.8
9 0 2		27937.3	27934.2	−3.1
10 1 0		28061.9	28062.9	1.0

vibrational frequencies, and anharmonicity constants (Table 2) are in a good agreement with those reported by Richard and Vaida.[17]

TABLE 2: Harmonic Frequencies and Anharmonicity Constants (cm^{-1}) from Fit to Eq 1

$\nu_{00} = 21\,018.7$		
$\omega_1{}^0 = 706.8$	$\chi_{11} = -2.71$	$\chi_{12} = -4.24$
$\omega_2{}^0 = 290.7$	$\chi_{22} = -0.85$	$\chi_{13} = -6.18$
$2\omega_3{}^0 = 837.3$	$\chi_{33} = 11.96$	$\chi_{23} = -4.17$

The use of the FE spectroscopy for OClO is expected to facilitate the state-selective studies on the photodissociation dynamics and high-resolution spectroscopy of OClO, since the FE spectroscopy has several advantages over other spectroscopic methods. First of all, it can be applied to the low-density sample at the low rotational temperature in supersonic jet expansions, where it is possible to resolve the otherwise overlapped bands. Since the dynamics of the OClO photodissociation are known to be state and mode specific, a clean excitation to a single and unambiguously assigned quantum state must be crucial to understand the nature of the chemical bond dissociation. Second, as mentioned in the Introduction, the FE spectrum can be obtained at the same experimental conditions as those used in the photodissociation dynamics studies. In other words, the FE spectrum is taken at the same interaction region where photodissociation takes place and more importantly can it be done without or with only a little modification of the experimental setup for the photodissociation dynamics studies. Hence, the possible complications, which are anticipated for the cases using two separate setups for the spectroscopy and the photodissociation studies, can be avoided.

In addition to the application to photodissociation dynamics studies, FE spectroscopy opens up the possibility of high-resolution spectroscopy for the $\tilde{A}-\tilde{X}$ transition of the OClO molecules cooled in supersonic jets. Up to now, high-resolution spectra of this system have been taken with a direct absorption method using photographic plates.[26] Since FE spectroscopy is a much more sensitive method than the previous direct absorption measurements, higher resolution spectroscopy would be possible, especially for the dilute samples cooled in supersonic jet expansions. Such high-resolution spectra will provide more accurate molecular parameters of OClO.

The third possible application of the FE spectroscopy is the monitoring of the OClO concentration in the atmosphere and reaction systems for kinetic studies. Since OClO is known to take part in the stratosphere ozone depletion,[1,2] a sensitive and selective monitoring technique of OClO would be of great importance. In addition, the FE method can also be employed to measure the rate constants of reactions in which the OClO molecules are involved. Its higher sensitivity and selectivity than the direct UV absorption measurement will significantly alleviate the experimental complications expected otherwise.

4. Summary

Here, we obtained the laser-induced fluorescence excitation spectrum of OClO ($\tilde{A}^2A_2 \leftrightarrow \tilde{X}^2B_1$) in the supersonic jet. The present FE spectrum provides a cooler and better resolved spectrum of the excited state than previously reported spectra. The FE spectroscopy is found to be an extremely useful tool for the state selection in photodissociation dynamics studies. It is also suggested that the FE spectroscopy may be a useful tool for high-resolution spectroscopy and kinetic studies on OClO molecules.

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