

Unexpectedly large $O^{37}ClO/O^{35}ClO$ intensity ratios of the fluorescence from the low-energy vibrational levels of $OCIO$ (\tilde{A}^2A_2)

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The fluorescence intensity ratios of $O^{37}ClO/O^{35}ClO$ excited to the \tilde{A}^2A_2 state have been found to be much larger than that expected from the $^{37}Cl/^{35}Cl$ natural abundance ratio for several low-energy vibrational levels. For instance, the $O^{37}ClO/O^{35}ClO$ ratios are 1.67 and >10 for the (0,0,0) and (1,1,0) bands, respectively, which are 5 and 30 times larger than those expected from the natural abundance ratio. These unusual isotope effects are observed in a narrow energy region within $\sim 1000\text{ cm}^{-1}$ above the electronic origin. It is likely that the isotopomer-selective, near-resonant spin-orbit coupling of the low-energy vibrational levels of the 2A_2 state with those of the 2A_1 state, which provides a decay channel for the 2A_2 state via spin-orbit coupling, is responsible for the unusual isotope effect. © 1999 American Institute of Physics. [S0021-9606(99)02126-1]

I. INTRODUCTION

Recently, numerous studies have focused attention on the spectroscopy, photochemistry, and photodissociation dynamics of $OCIO$. Vaida and co-workers have reported the detailed spectroscopic studies of the $\tilde{A}^2A_2 \leftarrow \tilde{X}^2B_1$ transition of $OCIO$ cooled in supersonic jets by using a Fourier-transformed ultraviolet (FTUV) spectrometer.¹⁻⁴ They also have detected the primary photodissociation fragments, ClO and Cl , by using resonantly enhanced multiphoton ionization-mass spectrometry (REMPI-MS).^{4,5} The vibrational energy distributions of the ClO fragments and the branching ratios of two competing $Cl+O_2$ and $O+ClO$ channels were measured for the photolysis wavelength range from 350 to 475 nm by Davis and Lee.^{6,7} While Gericke and co-workers measured the rotational and vibrational energy contents among the ClO fragments by using the two-photon laser-induced fluorescence technique,⁸ Huber's group focused their attention on the fragment translational energy release and recoil anisotropy, and vector correlations for the fragmentation process of the electronically excited $OCIO$ molecules.⁹ Stimulated by the experimental studies, Peterson and Werner have calculated the potential energy surfaces (PES) of the various excited electronic states of $OCIO$ and explored the possible intramolecular pathways to the $ClO+O$ and $Cl+O_2$ fragments.^{10,11}

In this communication, we report an experimental observation which may provide a clue to elucidate the predissociation mechanisms of the electronically excited $OCIO(^2A_2)$. It was observed that the $O^{37}ClO/O^{35}ClO$ intensity ratios of fluorescence are unexpectedly large for some low-energy vibrational levels in a small energy range near the origin band. Such isotopomer-specific phenomenon suggests that the initially prepared 2A_2 state interacts with a nearby electronic state which crosses near the origin of the 2A_2 state.

II. EXPERIMENT

The experimental setup for the generation and jet-cooled fluorescence excitation (FE) spectroscopy of $OCIO$ was reported previously.¹² In short, the $OCIO$ mixture in He, kept at the pressure of 1 atm, was expanded through a 0.5 mm-diameter nozzle, which was driven with a homemade driver. The visible wavelengths spanning 480 to 400 nm were directly generated with a pulsed dye laser pumped with a Q -switched Nd:YAG laser. The excitation laser beam was directed through the side arms, exciting the cooled $OCIO$ molecules in the jet expansions. The distance from the nozzle to the excitation laser beam was ~ 20 mm. Fluorescence from the excited $OCIO$ was collected with a quartz lens, filtered with various color filters depending upon the excitation wavelength, and then detected with a photomultiplier tube (PMT). The shot-to-shot fluctuation of the excitation laser pulses was normalized with a pyroelectric joulemeter.

The mass-selective photofragment excitation (PHOFEX) spectra of $OCIO$ were taken by measuring the ClO fragments formed from the photodissociation of $OCIO$ with a resonantly enhanced multiphoton ionization/time-of-flight mass spectrometer (REMPI/TOF-MS) detection system. The $OCIO$ sample was expanded through a pulsed valve with a nozzle diameter of 0.8 mm. At 30 mm from the nozzle, a 1.0 mm-diameter skimmer was placed, separating the source and ionization chambers. The $OCIO$ beam was then photolyzed in the ionization chamber with the output beam of the same dye laser used in the FE spectroscopy. After about 50 ns delay, the ionization laser pulse, which was generated by frequency doubling of a dye laser output, counterpropagated the photolysis laser beam. The ionization laser was focused into the ionization region with a 50 cm focal length quartz lens. The ClO^+ ions formed by the (2+1) REMPI process were extracted and accelerated to a microchannel plate detector. The detector signal was processed in the same way as in the FE spectroscopy.

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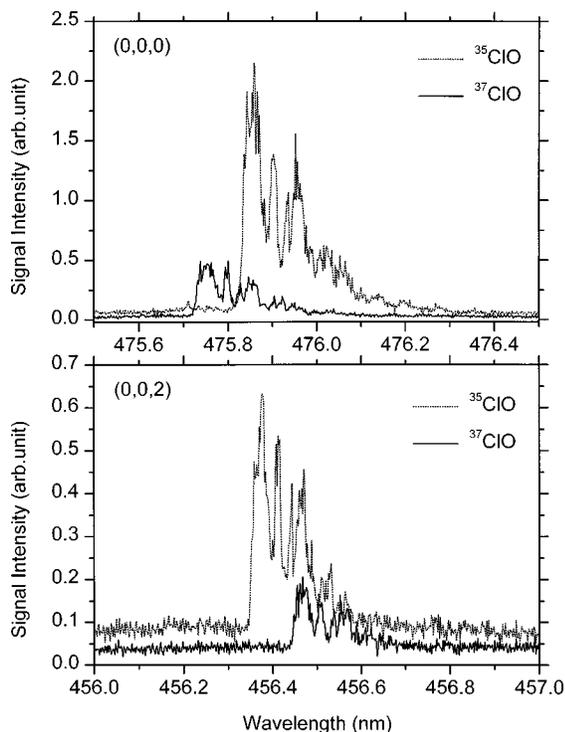


FIG. 1. The isotopomer-selective photofragment excitation (PHOFEX) spectra of the (0,0,0) and (0,0,2) bands of OCIO. The mass-resolved PHOFEX spectra provides the relative band positions of $O^{37}ClO$ and $O^{35}ClO$, which were used in the simulation. (See the text.) The spectra were obtained by measuring the mass-resolved REMPI signal while scanning the photolysis laser frequency with the ionization laser frequency fixed at the P -branch head of the (0-0) band of the $ClO \tilde{C}-\tilde{X}$ transition. The background level of the signal is due to the photolysis by the ionization laser pulse.

In order to obtain the isotope-selective PHOFEX spectra, the ionization laser frequency was fixed at the P -branch head of the (0-0) band of the $ClO \tilde{C}-\tilde{X}$ transition,¹³ and the photolysis laser was scanned while measuring the REMPI signal intensity. As shown in Fig. 1, the mass-resolved PHOFEX spectra unambiguously resolved two isotopomer bands. By comparing the PHOFEX and FE spectra, the $O^{37}ClO$ and $O^{35}ClO$ bands in the FE spectrum were identified and assigned.

III. RESULTS AND DISCUSSION

The fluorescence excitation spectrum of the (0,0,0) band is shown in Fig. 2. The band structure consists of the contributions from two isotopomers, $O^{37}ClO$ and $O^{35}ClO$, of which bands are represented with thin solid and dotted lines, respectively, in Fig. 2(b).

The most surprising observation in Fig. 2 is that the relative intensity of the $O^{37}ClO$ band is unexpectedly large compared to that of $O^{35}ClO$. Since the natural abundance of the ^{37}Cl isotope is about 1/4 of the total, the band intensity of $O^{37}ClO$ is expected to be 1/3 of that of $O^{35}ClO$. It can be noticed at a glance that the fluorescence intensity of $O^{37}ClO$ for this vibrational level, however, is much larger than the expectation. In order to obtain the quantitative intensity ratios, we analyzed the spectra with the following procedure.

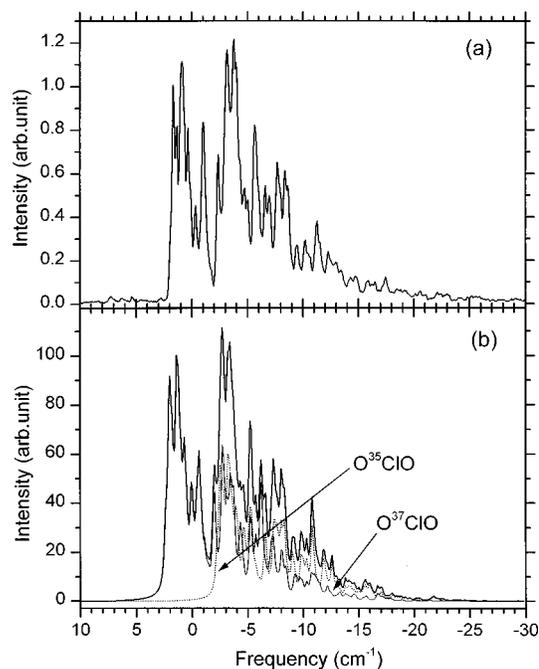


FIG. 2. The rotational structure of the (0,0,0) band of the $\tilde{A}^2A_2 \leftarrow \tilde{X}^2B_1$ transition of OCIO cooled in supersonic jets. (a) The fluorescence excitation spectrum. (b) The simulated spectrum. The thin solid and broken lines represent for the $O^{37}ClO$ and $O^{35}ClO$ bands, respectively, and the thick solid line represents the sum of both. Unexpectedly, the intensity of the $O^{37}ClO$ band is stronger than that of the $O^{35}ClO$. The abscissa is the frequency shift relative to the origin of the $O^{37}ClO$ band.

First of all, the rotational band structures of $O^{37}ClO$ and $O^{35}ClO$ are simulated by using a simulation program for the asymmetric rotors.^{14,15} In this procedure, the rotational constants of the ground and excited states of the OCIO molecules are taken from the high-resolution spectroscopic data¹⁶ and the rotational temperature is adjusted so that the simulated spectrum best matches a well-resolved and experimentally obtained spectrum. The best fit was accomplished with the rotational temperature of 15 K. By using the best-fit rotational temperature and the known rotational constants, we obtained the final simulation spectra of $O^{37}ClO$ and $O^{35}ClO$.¹⁷ Then, the two simulated spectra corresponding to $O^{37}ClO$ and $O^{35}ClO$ are combined to give the overlapped band structure. In this procedure, the corresponding $O^{37}ClO$ and $O^{35}ClO$ bands were shifted with respect to each other by the frequency difference of the $O^{37}ClO$ and $O^{35}ClO$ bands, which has been determined from the mass-resolved PHOFEX spectra, Fig. 1. The relative intensities of the $O^{37}ClO$ and $O^{35}ClO$ bands are varied until the simulated spectrum best reproduces the FE spectra. As a typical example, the analysis for the (0,0,0) band is shown in Fig. 2(b).

The fluorescence intensity ratios obtained for several vibrational levels are summarized in Table I along with the band assignments and positions. From the natural abundance ratio of ^{37}Cl and ^{35}Cl , the fluorescence intensity ratio of 0.324 is expected.¹⁸ However, it can be noticed that the (0,0,0), (0,1,0), (0,0,2), and (1,1,0) bands show the unusually large $O^{37}ClO/O^{35}ClO$ intensity ratios compared to the isotope abundance ratio. The (1,1,0) band, where the $O^{37}ClO$ band is hardly noticeable, shows the most dramatic ratio

TABLE I. The measured fluorescence intensity ratios of $O^{37}ClO/O^{35}ClO$ for the low vibrational levels of $OCIO(\bar{A}^2A_2)$.

Band assignment	Frequency of $^{35}ClO_2$ (cm^{-1})	Frequency of $^{37}ClO_2$ (cm^{-1})	$\Delta\nu$ (cm^{-1}) ($^{35}ClO_2 - ^{37}ClO_2$)	Intensity ratio ($^{37}ClO_2 / ^{35}ClO_2$)
(0,0,0)	21 015.73	21 021.33	-4.59	1.67
(0,1,0)	21 304.79	21 308.15	-3.36	1.10
(1,0,0)	21 723.64	21 722.32	1.32	0.30
(0,0,2)	21 912.72	21 908.30	4.42	0.75
(1,1,0)	22 010.34	22 008.01	2.33	>10
(2,0,0)	22 425.95	22 387.29	6.74	0.28
(1,0,2)	22 599.79	22 589.58	10.21	0.29
(2,1,0)	22 707.04	22 699.00	8.04	0.40
(1,1,2)	22 875.02	22 863.52	11.51	0.25
(3,0,0)	23 119.78	23 107.39	12.39	0.36

(>10). Although the other bands (except these four) give the slightly larger or smaller ratios, the intensity ratios of all other bands measured are close to the isotopic abundance ratio ($^{37}Cl/^{35}Cl$) of 0.324.¹⁸

It is also interesting to note that most of the vibronic levels showing the unusual isotopic intensity ratio are located in the low-energy region of the (\bar{A}^2A_2) state. At higher energies than the (1,1,0) band, the $O^{37}ClO$ and $O^{35}ClO$ bands are well separated due to the large isotope shift^{1-3,12} and the relative intensity measurement is trivial. But, no vibrational level shows the unusual isotopic effect at the higher energies than those covered in this work.¹²

Many examples of the isotope effect in the decay rates of the electronically excited states have been reported.¹⁹ Most of the cases are for the H/D isotopes and have been explained in terms of the more rapid tunneling of H atoms through the barrier than D atoms. Although recent experimental and theoretical studies have shown that the 2A_2 state PES of $OCIO$ is bound with a barrier of ca. 4000 cm^{-1} ,¹⁰ the isotope-dependent tunneling rate through the barrier cannot explain our observation, since the masses of ^{35}Cl and ^{37}Cl are only slightly different. Due to this potential energy barrier, the photodissociation of $OCIO$ at the low-energy region near the origin must be indirect and takes place only through the interactions with one or more low-lying electronic states.

McDonald and Innes,²⁰ and Michielsen *et al.*²¹ have concluded that the 2A_2 state decays via spin-orbit coupling with the nearby 2A_1 or 2B_2 states. They also reported that the measured linewidths of $OCIO$ are independent of the rotational levels, suggesting that the perturbing state has geometry similar to the 2A_2 state. The recent *ab initio* calculation by Peterson and Werner showed that the molecular structure in the 2A_2 state more resembles that of the 2A_1 state than that of the 2B_2 state:¹⁰ i.e., the PES of the 2B_2 state along the asymmetric stretch coordinate is nearly repulsive, whereas the 2A_2 and 2A_1 states are bound with a finite barrier. Additionally, their calculation predicts that the 2A_2 state couples with the 2B_2 state at relatively higher energies, while the 2A_1 PES crosses the 2A_2 state near its equilibrium potential minimum. By combining all this experimental and theoretical evidence, Peterson and Werner have thus concluded that the excited $OCIO$ molecules excited to the 2A_2 decay via spin-orbit coupling with the 2A_1 state.¹⁰

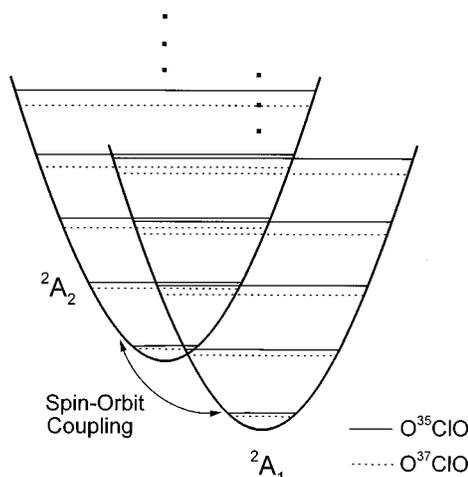


FIG. 3. A schematic vibrational level diagram of the 2A_2 and 2A_1 electronic states of $OCIO$, showing the accidental near-resonance coupling of the vibrational levels of the two states. The solid and broken lines represent the vibrational levels of the $O^{35}ClO$ and $O^{37}ClO$, respectively, and the vibrational frequencies of two electronic states are assumed to be identical. Since the 2A_1 state is located below the optically active 2A_2 state, the energy spacing between two near-resonance coupling levels is larger for $O^{37}ClO$ than for $O^{35}ClO$, giving the slower decay rate for $O^{37}ClO$ than for $O^{35}ClO$.

Based on the conclusion that the 2A_1 state is the perturber to the 2A_2 state, a possible vibrational level diagram of the 2A_2 and 2A_1 states, which is likely to account for the unusual isotope effect observed in this work, is proposed and shown in Fig. 3. According to this diagram, the vibrational levels of the 2A_2 state of $O^{35}ClO$ are near resonant with but located slightly above the levels of the lower 2A_1 state by chance, as shown in Fig. 3. If this is the case, the vibrational levels of $O^{37}ClO$ are more off-resonant than those of $O^{35}ClO$ because of the isotope shift. As a result, $O^{35}ClO$ decays faster than $O^{37}ClO$ since the 2A_2 state in $O^{35}ClO$ is more strongly coupled to the 2A_1 state than that of $O^{37}ClO$, in accordance with the experimental observation.

This model also provides an explanation for the observation that the (1,0,0) level does not show the unusual isotope effect. A possible explanation for this is that the fundamental frequencies of the symmetric vibration (ν_1) of the 2A_2 and 2A_1 states are significantly different. Hence, the (1,0,0) level of $O^{35}ClO$ will not be in near-resonance with a vibronic level of the 2A_1 state, and thus the decay rate of this level is not much enhanced compared to the $O^{37}ClO$. Indeed, the *ab initio* calculation¹⁰ demonstrated that the ν_1 frequency of the 2A_2 state is larger than that of the 2A_1 by at least 40 cm^{-1} depending on the levels of calculations, in accordance with our expectation.

An additional experimental observation, which has to be accounted for in terms of the accidental near-resonance mixing model of two close-lying electronic states, is that this unexpectedly large isotope effect disappears drastically in a narrow energy region between the (1,1,0) and (2,0,0) levels. Since the resonance is strongest for the (1,1,0) level, at least a few more levels above this level are expected to show a noticeable isotope effect because the fundamental frequencies are not very much different for two coupling states,¹⁰ in

contrast to our observation. This apparent contradiction can be successfully reconciled with our model.

The *ab initio* calculation¹⁰ indicated that there exists a barrier on the 2A_1 PES along the bending coordinate to the linear geometry, from which OCIO dissociates into $ClO+O$ with nearly no barrier. If the top of the barrier is located near the (1,1,0) level of the 2A_2 state, the vibronic levels of the 2A_1 state above this barrier must be significantly more broadened by rapid dissociation than the levels below. If this is the case, the decay rates of the 2A_2 vibrational levels above this barrier have to increase drastically and the isotope effect of the decay rates should be significantly alleviated even though not completely vanished. The recently reported FE spectrum¹² and the absorption cross-section measurement²² of OCIO provide strong evidence for existence of the barrier near the (1,1,0) level; i.e., the intensities of the ($n,0,0$) bands of the FE spectrum decrease with increasing the n value for $n \geq 2$, which is in sharp contrast to the drastic increase of the absorption cross sections for the transitions to the corresponding levels, while the (1,0,0) band is stronger than the (0,0,0) band as expected from the measured absorption cross sections.

In summary, we experimentally demonstrated that the fluorescence intensity ratios of $O^{37}ClO/O^{35}ClO$ excited to the $\tilde{A} {}^2A_2$ state are abnormally large compared with that of the ${}^{37}Cl/{}^{35}Cl$ natural abundance for the (0,0,0), (0,1,0), (0,0,2), and (1,1,0) levels. This unusual isotope effect of the fluorescence intensity is understood in terms of the accidental near-resonance spin-orbit coupling of the vibronic levels of the close-lying 2A_2 and 2A_1 states, of which coupling strengths are isotopomer dependent. Although our simple coupling model qualitatively explains most of the experimental observations, more quantitative interpretation of our results based on the accurate full-dimensional *ab initio* PESs of the electronic states involved in the OCIO photodissociation will help provide better understanding of the OCIO photochemistry.

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- ¹E. C. Richard, C. T. Wickham-Jones, and V. Vaida, *J. Phys. Chem.* **93**, 6346 (1989).
- ²E. C. Richard and V. Vaida, *J. Chem. Phys.* **94**, 153 (1991).
- ³E. C. Richard and V. Vaida, *J. Chem. Phys.* **94**, 163 (1991).
- ⁴V. Vaida, E. C. Richard, A. Jefferson, L. A. Cooper, R. Flesch, and E. Ruhl, *Ber. Bunsenges. Phys. Chem.* **96**, 391 (1992).
- ⁵E. Ruhl, A. Jefferson, and V. Vaida, *J. Phys. Chem.* **94**, 2990 (1990).
- ⁶H. F. Davis and Y. T. Lee, *J. Phys. Chem.* **96**, 5681 (1992).
- ⁷H. F. Davis and Y. T. Lee, *J. Chem. Phys.* **105**, 8142 (1996).
- ⁸R. F. Delmdahl, S. Baumgartel, and K.-H. Gericke, *J. Chem. Phys.* **104**, 2883 (1996).
- ⁹C. J. Kreher, R. T. Carter, and J. R. Huber, *Chem. Phys. Lett.* **286**, 389 (1998); A. Furlan, H. A. Scheld, and J. R. Huber, *J. Chem. Phys.* **106**, 6538 (1997).
- ¹⁰K. A. Peterson and H.-J. Werner, *J. Chem. Phys.* **96**, 8948 (1992).
- ¹¹K. A. Peterson and H.-J. Werner, *J. Chem. Phys.* **105**, 9823 (1996).
- ¹²S.-M. Lim, T.-S. Kim, G.-I. Lim, S. K. Kim, and Y. S. Choi, *J. Phys. Chem. A* **103**, 2097 (1999).
- ¹³J. A. Coxon, *Can. J. Phys.* **57**, 1538 (1979).
- ¹⁴F. W. Birss and D. A. Ramsay, *Comput. Phys. Commun.* **38**, 83 (1984).
- ¹⁵R. H. Judge, *Comput. Phys. Commun.* **47**, 361 (1987).
- ¹⁶Y. Hamada, A. J. Merer, S. Michelsen, and S. A. Rice, *J. Mol. Spectrosc.* **86**, 499 (1981).
- ¹⁷In the simulation, the spin-rotation splitting and centrifugal distortion were neglected as done in Ref. 5 since the rotational temperature was quite low.
- ¹⁸*CRC Hand Book of Chemistry and Physics*, edited by D. R. Lide (CRC Press, Boston, 1991), pp. 11–37.
- ¹⁹G. Herzberg, *Electronic Spectra of Polyatomic Molecules* (Van Nostrand, New York, 1966).
- ²⁰P. A. McDonald and K. K. Innes, *Chem. Phys. Lett.* **59**, 62 (1978).
- ²¹S. Michielsen, A. J. Merer, S. A. Rice, F. A. Novak, K. F. Freed, and Y. Hamada, *J. Chem. Phys.* **74**, 3089 (1981).
- ²²A. Wahner, G. S. Tyndall, and A. R. Ravishankara, *J. Phys. Chem.* **91**, 2734 (1987).