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

Goo-II Lim, Soon-Mi Lim, Sang Kyu Kim, and Young S. Choi

Department of Chemistry, Inha University, Incheon 402-751, Republic of Korea

(Received 5 March 1999; accepted 3 May 1999)

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 $>$10 for the (0,0,0) and (1,1,0) bands, respectively, which are 5 and 30 times larger than those expected from the natural abundance ratio. These unusual isotope effects are observed in a narrow energy region within ~1000 cm$^{-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 \(\tilde{A}\,^2A_2\) \(\rightarrow\) \(X\,^2B_1\) 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.
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 C–X transition, 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 O37 ClO and O35 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, O37ClO and O35ClO, 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 O37ClO band is unexpectedly large compared to that of O35ClO. Since the natural abundance of the 37Cl isotope is about 1/4 of the total, the band intensity of O37ClO is expected to be 1/3 of that of O35ClO. It can be noticed at a glance that the fluorescence intensity of O37ClO 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.

First of all, the rotational band structures of O37ClO and O35ClO are simulated by using a simulation program for the asymmetric rotors. In this procedure, the rotational constants of the ground and excited states of the OClO molecules are taken from the high-resolution spectroscopic data 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 O37ClO and O35ClO. Then, the two simulated spectra corresponding to O37ClO and O35ClO are combined to give the overlapped band structure. In this procedure, the corresponding O37ClO and O35ClO bands were shifted with respect to each other by the frequency difference of the O37ClO and O35ClO bands, which has been determined from the mass-resolved PHOFEX spectra, Fig. 1. The relative intensities of the O37ClO and O35ClO 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 37Cl and 35Cl, the fluorescence intensity ratio of 0.324 is expected. 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 O37ClO/O35ClO intensity ratios compared to the isotope abundance ratio. The (1,1,0) band, where the O35ClO band is hardly noticeable, shows the most dramatic ratio.
explain our observation, since the masses of $^{35}\text{Cl}$ and $^{37}\text{Cl}$ are isotope-dependent tunneling rate through the barrier cannot
asymmetric stretch coordinate is nearly repulsive, whereas
the $2\text{PES}$ of OClO is bound with a barrier of ca. 4000 cm$^{-1}$.

Many examples of the isotope effect in the decay rates of the electronically excited states have been reported. 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 $2\text{A}_1$ state PES of OCIO is bound with a barrier of ca. 4000 cm$^{-1}$, the isotope-dependent tunneling rate through the barrier cannot explain our observation, since the masses of $^{35}\text{Cl}$ and $^{37}\text{Cl}$ 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, and Michielsen et al. have concluded that the $2\text{A}_2$ state decays via spin-orbit coupling with the nearby $2\text{A}_1$ or $2\text{B}_2$ 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 $2\text{A}_2$ state. The recent ab initio calculation by Peterson and Werner showed that the molecular structure in the $2\text{A}_2$ state more resembles that of the $2\text{A}_1$ than that of the $2\text{B}_2$ state, i.e., the PES of the $2\text{B}_2$ state along the asymmetric stretch coordinate is nearly repulsive, whereas the $2\text{A}_2$ and $2\text{A}_1$ states are bound with a finite barrier. Additionally, their calculation predicts that the $2\text{A}_2$ state couples with the $2\text{B}_2$ state at relatively higher energies, while the $2\text{A}_1$ PES crosses the $2\text{A}_2$ 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 $2\text{A}_2$ decay via spin-orbit coupling with the $2\text{A}_1$ state.

Many bands are close to the isotopic abundance ratio ($^{37}\text{Cl}/^{35}\text{Cl}$) of 0.324. 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 ($\tilde{A}-\tilde{A}_2$) state. At higher energies than the (1,1,0) band, the $^{37}\text{Cl}$ and $^{35}\text{Cl}$ bands are well separated due to the large isotope shift 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.

Table I. The measured fluorescence intensity ratios of $^{37}\text{ClO}/^{35}\text{ClO}$ for the low vibrational levels of OCIO ($\tilde{A}-\tilde{A}_2$).

<table>
<thead>
<tr>
<th>Band assignment</th>
<th>Frequency of $^{35}\text{ClO}_2$ (cm$^{-1}$)</th>
<th>Frequency of $^{37}\text{ClO}_2$ (cm$^{-1}$)</th>
<th>$\Delta \rho$ (cm$^{-1}$)</th>
<th>Intensity ratio ($^{37}\text{ClO}_2/^{35}\text{ClO}_2$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>(0,0,0)</td>
<td>21 015.73</td>
<td>21 021.33</td>
<td>-4.59</td>
<td>1.67</td>
</tr>
<tr>
<td>(0,1,0)</td>
<td>21 304.79</td>
<td>21 308.15</td>
<td>-3.36</td>
<td>1.10</td>
</tr>
<tr>
<td>(1,0,0)</td>
<td>21 723.64</td>
<td>21 722.32</td>
<td>1.32</td>
<td>0.30</td>
</tr>
<tr>
<td>(0,0,2)</td>
<td>21 912.72</td>
<td>21 908.30</td>
<td>4.42</td>
<td>0.75</td>
</tr>
<tr>
<td>(1,1,0)</td>
<td>22 010.34</td>
<td>22 008.01</td>
<td>2.33</td>
<td>&gt;10</td>
</tr>
<tr>
<td>(2,0,0)</td>
<td>22 425.95</td>
<td>22 387.29</td>
<td>6.74</td>
<td>0.28</td>
</tr>
<tr>
<td>(1,0,2)</td>
<td>22 599.79</td>
<td>22 589.58</td>
<td>10.21</td>
<td>0.29</td>
</tr>
<tr>
<td>(2,1,0)</td>
<td>22 707.04</td>
<td>22 699.00</td>
<td>8.04</td>
<td>0.40</td>
</tr>
<tr>
<td>(1,1,2)</td>
<td>22 875.02</td>
<td>22 863.52</td>
<td>11.51</td>
<td>0.25</td>
</tr>
<tr>
<td>(3,0,0)</td>
<td>23 119.78</td>
<td>23 107.39</td>
<td>12.39</td>
<td>0.36</td>
</tr>
</tbody>
</table>

FIG. 3. A schematic vibrational level diagram of the $2\text{A}_2$ and $2\text{A}_1$ 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 $^{37}\text{Cl}$ and $^{35}\text{Cl}$, respectively, and the vibrational frequencies of two electronic states are assumed to be identical. Since the $2\text{A}_1$ state is located below the optically active $2\text{A}_2$ state, the energy spacing between two near-resonance coupling levels is larger for $^{37}\text{Cl}$ than for $^{35}\text{Cl}$, giving the slower decay rate for $^{37}\text{Cl}$ than for $^{35}\text{Cl}$.

Based on the conclusion that the $2\text{A}_1$ state is the perturber to the $2\text{A}_2$ state, a possible vibrational level diagram of the $2\text{A}_2$ and $2\text{A}_1$ 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 $2\text{A}_2$ state of $^{35}\text{Cl}$ are near resonant with but located slightly above the levels of the lower $2\text{A}_1$ state by chance, as shown in Fig. 3. If this is the case, the vibrational levels of $^{35}\text{Cl}$ are more off-resonant than those of $^{37}\text{Cl}$ because of the isotope shift. As a result, $^{35}\text{Cl}$ decays faster than $^{37}\text{Cl}$ since the $2\text{A}_2$ state in $^{35}\text{Cl}$ is more strongly coupled to the $2\text{A}_1$ state than that of $^{37}\text{Cl}$, 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 ($\nu_1$) of the $2\text{A}_2$ and $2\text{A}_1$ states are significantly different. Hence, the (1,0,0) level of $^{35}\text{Cl}$ will not be in near-resonance with a vibronic level of the $2\text{A}_1$ state, and thus the decay rate of this level is not much enhanced compared to the $^{37}\text{Cl}$. Indeed, the ab initio calculation demonstrated that the $\nu_1$ frequency of the $2\text{A}_2$ state is larger than that of the $2\text{A}_1$ 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.
Unexpectedly large $^{37}\text{ClO}/^{35}\text{ClO}$

**ACKNOWLEDGMENTS**

The Korean Science and Engineering Foundation (Project No. 981-0307-037-2) and the 1998 Inha University Research Fund supported this work.

17. In the simulation, the spin-rotation splitting and centrifugal distortion were neglected as done in Ref. 5 since the rotational temperature was quite low.